

**THE OXIDATION BY PEROXIDES
OF CYANIDES, CYANIDE COMPLEXES
AND RELATED SPECIES.**

A Thesis presented by
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In partial fulfilment of the requirements
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Abstract

The work described in this thesis is concerned with the study of the oxidation of free and complexed cyanides by H_2O_2 and a variety of other peroxy species in aqueous solution.

The kinetics of oxidation of free cyanide were measured between pH 9 and 10 using a cyanide ion selective electrode. Intermediates such as cyanate, and the products of the reaction, carbonate or bicarbonate and ammonia were identified by chemical methods and using infra-red, Raman and ^{13}C NMR spectroscopy. Factors affecting the rate of oxidation were studied. These included the effects of pH, ionic strength, UV light, radical traps and of carrying out the reaction in a variety of buffers. We investigated the catalytic effects of a variety of transition metal species including salts of Cu(I), Cu(II), Ni(II), Fe(II) and Zr(IV), and the tungstate, molybdate and orthovanadate ions. Qualitative observations were made on the oxidation of free cyanide by persulphate and the oxidation and hydrolysis of free cyanate in the presence and absence of oxidants.

Spectroscopic observations were made on the oxidation of the complexes $[\text{Zn}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ by H_2O_2 and caroate, $[\text{HSO}_5]^-$. The kinetics of oxidation of these complexes by H_2O_2 were found to be complicated, although simple kinetics were observed for the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ using triple salt ($\text{K}_2\text{SO}_4 \cdot \text{KHSO}_4 \cdot 2\text{KHSO}_5$) and potassium caroate ($\text{KHSO}_5 \cdot \text{H}_2\text{O}$). The reactions of these oxidants with a variety of other cyanide complexes, including $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{Cu}(\text{CN})_3]^{2-}$ have been investigated using electronic spectroscopy and High Pressure Ion Chromatography.

A wide variety of pseudohalide complexes were prepared and characterised using infra-red and Raman spectroscopy, and FAB mass spectrometry. These included cyanato complexes and isomeric forms of thiocyanato species. Work was carried out on the adsorption of cyanide complexes and copper species on inert supports in attempts to develop a heterogeneous catalyst for the oxidation of cyanides.

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List of Abbreviations.

A.A.	Atomic absorption Spectrophotometry.
AsPh ₃	Triphenyl arsine.
AU	Absorbance units.
Bipy	2,2-Dipyridyl
Caroate	[HSO ₅] ⁻ .
cm ⁻¹	Wavenumber.
Curox	Triple salt, as supplied by Interlox.
Dequest 2060	Diethylenetriamine-NNN'N"N"-pentamethylene-phosphonic acid.
Dionex HPIC	High performance (or pressure) ion chromatography.
DMSO	Dimethylsulphoxide, (CH ₃) ₂ SO.
EDTA	Ethylenediaminetetraacetic acid.
f. a. b.	Fast atom bombardment.
FTIR	Fourier transform infra-red.
IETS	Inelastic electron tunnelling spectroscopy.
IRRAS	Infra-red reflective absorption spectroscopy.
m/z	Mass: charge ratio.
nm	Nanometers.
NMR	Nuclear magnetic resonance.
Oxone	Triple salt as supplied by Dupont or BDH Ltd.
Phen	1,10-phenanthroline
ppm	parts per million
R	Raman.
RT	Retention time.
Trien	Triethylenetetramine, H ₂ NC ₂ H ₄ NHC ₂ H ₄ NHC ₂ H ₄ NH ₂ .
Triple salt	K ₂ SO ₄ .KHSO ₄ .2KHSO ₅ .
TsPc	Tetrasulphonatophthalocyanine, tetrasodium salt.

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C.D.L.1990.

"Science in the modern world has many uses;
its chief use, however, is to provide long words..."

G.K.Chesterton

To my parents,
without whom none of this would have been possible,
and to Sarah,
for being there and putting up with me throughout.

Aims of this work

The principal theme of this thesis is the use of peroxy species to oxidise (and thus detoxify) free and complex cyanides. The first chapter covers work carried out to study the peroxidic oxidation of free cyanide and free cyanate, the latter being the initial product of the oxidation of cyanide .

In chapter 2, we consider the oxidation of cyano complexes by peroxidic oxidants while chapter 3 concerns the other main theme of this thesis, the preparation and vibrational spectra of pseudohalide complexes, those containing CN^- , NCO^- and NCS^- .

Chapter 1.

The Oxidation of Free Cyanide and Cyanate Ions by Peroxo Species.

Introduction.

Cyanide is a versatile material and is widely used in many varied industrial processes. It is important for electroplating and in galvanising baths, in the manufacture of many dyes and pharmaceuticals, photographic development and in the extraction of metals from their ores. It is also produced as an effluent in blast furnaces, smelters and in coking processes.¹ Obviously, the well documented toxicity of cyanide renders it necessary that all wastes containing cyanide must be detoxified prior to their release into the environment.^{2,3}

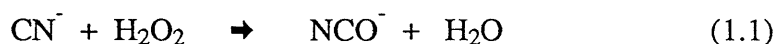
We start this chapter with a brief account of the main methods which have been used to effect such detoxification, placing emphasis on the methods using peroxides such as H_2O_2 , $[\text{S}_2\text{O}_8]^{2-}$ and $[\text{HSO}_5]^-$, but also including other reported industrial oxidative procedures. In the following section we summarise the analytical procedures suited for the determination of free and coordinated cyanide and in section 1.3 we deal with the oxidation of free cyanide by H_2O_2 and other peroxidic oxidants. In section 1.4 the reactions involving the oxidation of free CN^- by persulphate are studied and section 1.5 concerns the oxidation and hydrolysis of free NCO^- , cyanate being an initial product of the oxidation of cyanides.

1.1 Review of Methods of Treatment of Cyanide Wastes.

Methods for the detoxification of cyanide in effluents and wastewaters encompass a multitude of principles. The following review briefly encompasses some of the industrial procedures developed to overcome this potential problem and the academic research in this area.

1.1.1. Methods involving hydrogen peroxide.

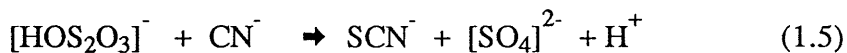
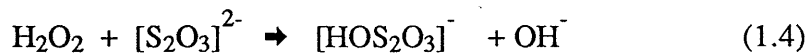
As early as 1907 Masson had discovered that aqueous solutions of KCN could be oxidised by H_2O_2 .⁴ He concluded that the main products of the exothermic reaction were KNCO and $\text{K}(\text{NH}_4)\text{CO}_3$, the latter formed by hydrolysis of the cyanate which could be removed from the solution after the reaction. About one fifth of the cyanide was converted by hydrolysis into HCO_2K and NH_3 and this reaction was catalysed by the presence of peroxide. Thus the overall reactions are as follows:



The kinetics of the oxidation were found to be first order with respect to the concentrations of both the peroxide and the cyanide, and addition of either KOH or H_2SO_4 lead to retardation of the reaction. Since this early discovery attempts have been made to study and improve the efficiency and speed of the reaction using a variety of catalysts and conditions.

More recently an alternative route for this oxidation was discovered via a thiocyanate intermediate, formed when thiosulphate was added to a reaction mixture of CN^- and H_2O_2 .⁵ It was thought that in this reaction H_2O_2 reacted with $[\text{S}_2\text{O}_3]^{2-}$ to form $[\text{HOS}_2\text{O}_3]^-$ which normally decomposed into two molecules of $[\text{SO}_4]^{2-}$ as shown

in reaction 1.6. However, in the presence of free CN^- , SCN^- and one molecule of $[\text{SO}_4]^{2-}$ were formed as follows.



Reviews of industrial processes have cited the optimum conditions for uncatalysed oxidations of CN^- by H_2O_2 to be at pH 9 to 11⁶ (or 4 or 5⁷), temperature 283-353K (or >313K⁷) and using a H_2O_2 : CN^- ratio of 0.7-2 (or 2-3⁷). However the addition of a catalyst can considerably reduce reaction times and alter the optimum conditions.⁸ The favoured catalyst is a copper(II) salt added as CuSO_4 , CuCl_2 or $\text{Cu}(\text{OAc})_2$ at a concentration of 10^{-2} - 10^{-4} M although Cu_2Cl_2 has also been used. In comparative studies copper(II) salts were found to be more effective catalysts than NiSO_4 , and additions of CrCl_3 , SnCl_2 , CoCl_2 , FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$, HgCl_2 , MnSO_4 and $\text{Pt}(\text{OAc})_2$ were found to have hardly any catalytic activity.⁹ Another catalyst involved a combination of iodide ions (10^{-4} - 10^{-6} M) with a soluble silver salt (AgNO_3 > 10^{-4} M) used at pH 10 to 10.5, and temperatures of around 50°C. This was found to be more efficient than the use of copper(II) salts but oxidation was achieved more slowly.¹⁰ On completion of the oxidation AgI was precipitated out, the silver could thus be recovered and the reaction could be followed potentiometrically.¹¹ Other potential catalysts proposed were soluble salts of Ag(I), W(VI) and V(V) (10^{-2} - 10^{-5} M) in a pH range 8.5 to 10.5 using a H_2O_2 : CN^- ratio of 0.8.¹² Successful oxidation has also been achieved using $[\text{S}_2\text{O}_3]^{2-}$ with rhodanine (cyanide sulphurtransferase) as a catalyst to form SCN^- and this reaction has been studied with respect to its biological significance.^{13,14}

Various attempts have been made to develop a heterogeneous catalyst. One claimed that the ions of silver(I), copper(II) or nickel(II) adsorbed on a high surface area ($10 \text{ m}^2 \text{ g}^{-1}$) metal oxide base such as Al_2O_3 , SiO_2 or aluminosilicates gave unexpectedly efficient catalytic results over the range of pH 4 to 12 although the reasons

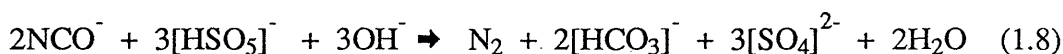
for this were not discussed.¹⁵ A more sophisticated system used a resin loaded with Cu(II) species in conjunction with a second resin exchanger to remove from solution any copper(II) species that dissolved from the first bed during oxidation.¹⁶ Gierzatowicz investigated the catalytic capacity of various insoluble transition metals compounds and also metal salts deposited onto alumina and montmorillonite.¹⁷ No catalytic activity was found and although an aqueous solution of CuSO₄ was readily adsorbed onto montmorillonite the catalysis of oxidations was attributed to copper(II) species being leached. The addition of SiO₂ to reaction solutions has been patented as a method of stabilizing the H₂O₂ in the belief that foaming observed in reactions was due to the decomposition of H₂O₂ and that this unnecessarily increased the H₂O₂:CN⁻ ratio required.¹⁸ The basis for the ability of SiO₂ to act as a stabilizer was not explained.

Serpone *et al.* discovered that UV irradiation of solutions containing cyanide and H₂O₂ increased the rate of oxidation tenfold at pH 9 to 10.¹⁹ A radical pathway for this reaction was proposed involving OH[·], which is more reactive to CN⁻ than HO₂⁻ which is thought to be the reactive species in the uncatalysed oxidation at alkaline pH. Intermediate NCO⁻ was detected, and the final products were NH₃ and CO₂. In another study Imamura concluded that metal complexes containing Mn(II), Ti(II), Ce(IV), [VO₄]³⁻ and Cu(II) interfered with the UV irradiated oxidation of CN⁻ by peroxide.²⁰ Addition of H₂O₂ to solutions of cyanide complexes whilst they were being irradiated did not accelerate the oxidation because the H₂O₂ was decomposed before all the metal-cyanide bonds were broken.

1.1.II. Other peroxy species.

There has been relatively little study of the use of other peroxy species as oxidants for free CN⁻. Persulphate, Caro's acid and potassium caroate (KHSO₅) have all been proposed as alternative oxidants to H₂O₂.^{7,9} Caro's acid will not oxidise organic nitriles but is effective for the oxidation of inorganic cyanide complexes at [HSO₅]⁻:CN⁻

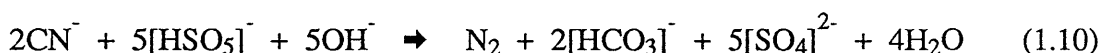
ratios of 1.5-1.8 and has been used to oxidise free cyanide at pH 5 and between pH 9 and 12 industrially.^{21,22} The complex triple salt ($K_2SO_4.KHSO_4.2KHSO_5$), known industrially as Oxone (Du Pont) or Curox (Interox), has also been used at pH 9 to oxidise strong solutions of CN^- within 15 minutes.²³ The stoichiometry required 15g. of triple salt for each g. of CN^- (caroate: $CN^- = 1.2$).⁷ The oxidation with peroxymonosulphate (caroate) is thought to proceed via the following equations:



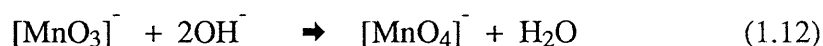
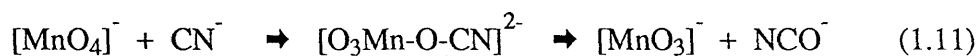
If a caroate: CN^- ratio of 1.5-1.8 is used the overall reaction is;



If a higher ratio of 2.5 or greater is used complete oxidation is achieved.



Persulphate was only efficient as an oxidant for concentrated cyanide solutions but was slow and did not to produce a cyanate intermediate.^{9,24,25} A study of the reaction catalysed by Ag(I) claimed that the final products were CO_2 and $[NO_3]^-$.²⁶ The oxidation of CN^- using permanganate has also been studied.²⁷ The oxidation was thought to proceed via an activated complex as below:



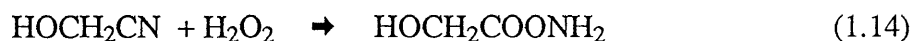
The reaction rate increased with pH and the kinetics were complicated in the range pH 6 to 9. Using ^{18}O labelling it was calculated that 70-80% of the oxygen on the NCO^- came from the oxidant.

A desirable aspect for any oxidative process is to have a system that can be continuously monitored. One solution to this problem was to measure the redox potential of the effluent with a silver, gold or an ion sensitive electrode.^{24,28,29} This followed the decomposition of a *measuring* oxidising agent, one which reacted more rapidly than H_2O_2 under comparable conditions (such as caroate, permanganate or

ozone) and it was this which governed the addition of proportional quantities of H_2O_2 to continue the oxidation. One advantage of using peroxy species is that they have greater potential for use in continuous monitoring systems.

1.1.III. The Kastone process.

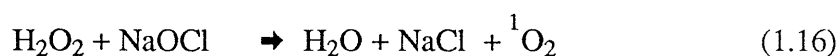
This has been used as an industrial treatment for over forty years.³⁰ It involves the use of peroxides in conjunction with formaldehyde to oxidise cyanide to glyconitrile and then form glycolic acid amide. This then undergoes hydrolysis to glycolic acid and ammonium hydroxide.



A competing reaction is the direct oxidation of the cyanide to cyanate which accounts for about 30% of the CN^- .³¹ This process has been used to oxidise CN^- in the presence of SCN^- using a $[\text{Cu}(\text{CN})_2]^-$ catalyst.³² If zinc ions are present, as is the case in electroplating baths, then magnesium(II) salts added as MgCl_2 , MgCO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Mg}(\text{OAc})_2$ or MgO will aid the process but the role they play was not discussed. An elevated temperature of above 50°C is advocated to reduce the reaction times.³³

1.1.IV. Singlet oxygen.

This is formed when H_2O_2 is added to NaOCl .³⁴



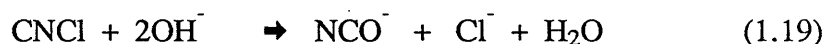
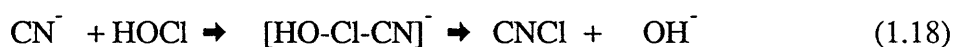
The kinetics of the above reaction have been measured.³⁵ Singlet oxygen can also be obtained by the action of Cl_2 or Br_2 on H_2O_2 or by spectrophotometric processes.^{36,37}

Cyanide is oxidised to cyanate and it is claimed that all complexes except

hexacyanoferrates can be destroyed . A peroxide: CN^- ratio of 1-1.3 at pH 9 to 9.5 will oxidise CN^- in solution.

1.1.V. Oxidation with hypochlorite.

This is the traditional method of detoxification of cyanide containing wastes. The most recent kinetic study³⁸ of the reaction concluded that both OCl^- and HOCl react with CN^- , but HOCl was nearly 4×10^6 times more reactive than OCl^- because of the very fast proton transfer reaction between HOCl and OH^- and the logical pathway of the reaction as shown below.



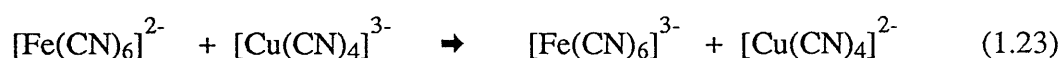
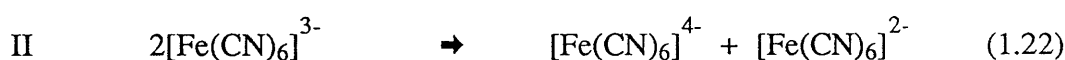
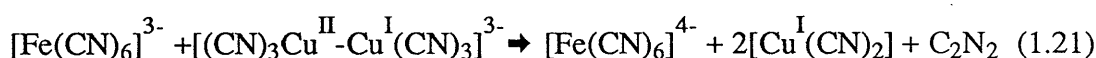
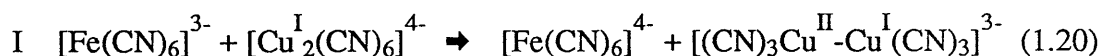
Older studies³⁹⁻⁴¹ proposed that between pH 9-10 there was a three step pathway involving the direct formation of cyanate but it appears that even at high pH cyanogen chloride is the initial product of oxidation, but the hydrolysis of this species to NCO^- is very rapid.

Below pH 9 the hydrolysis of CNCl to NCO^- is slow, an undesirable feature due to the toxicity of CNCl .⁴¹ The second step of the reaction, the oxidation of cyanate, has also been studied but this aspect is discussed elsewhere (see section 1.5). Hypobromite is a similarly effective oxidant for both CN^- and NCO^- .⁴²

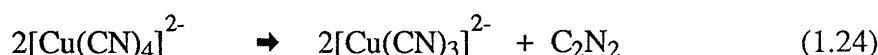
1.1.VI. Oxidations with $[\text{Fe}(\text{CN})_6]^{3-}$.

It has long been known that free CN^- can be oxidised to NCO^- by $[\text{Fe}(\text{CN})_6]^{3-}$. The kinetics of this reaction were studied and found to be complex, but it was concluded that the rate was independent of pH in the range 9 to 11, had a proportional

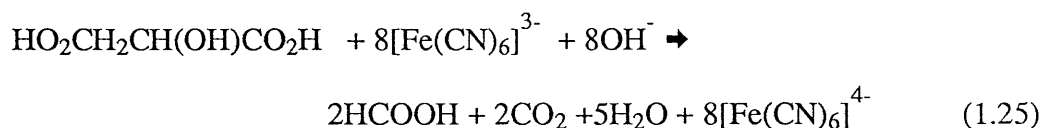
relationship with ionic strength and involved a C_2N_2 intermediate.⁴³ A more recent study showed that the reaction is very strongly catalysed by the presence of copper(II) ions.⁴⁴ Kinetic measurements showed a first order dependence on the copper(II), an inverse first order dependence with respect to $[Fe(CN)_6]^{4-}$ and that the reaction was independent of the concentrations of CN^- and OH^- . Two mechanisms were proposed to explain these observations. The first proceeded via a postulated $Cu^{II}-Cu^I$ dimer whilst the other required a hitherto unknown disproportionation of $[Fe(CN)_6]^{3-}$.



In each case it was the copper that acted as the oxidant in the following reaction.⁴⁵

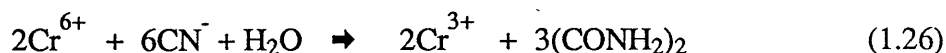


There are no other data to support either of these, fanciful mechanisms. However in the copper catalysed oxidation of malic acid by $[Fe(CN)_6]^{3-}$ the proposed mechanism proceeded via a copper(II) complex which was then thought to be oxidised to a copper(III) malate.⁴⁶ This dissociated oxidatively to give two molecules of formate, two molecules of CO_2 and left $Cu(I)$. It is possible that this is the principle of the oxidation of CN^- by $[Fe(CN)_6]^{3-}$. The overall equation for the reaction was as follows.



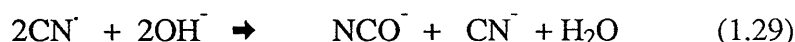
Another oxidant used in similar reactions is $Cr(VI)$ which has been used in conjunction with $Cu(II)$ to remove CN^- from wastes at pH 5.⁴⁷ The main product is oxamide but some CO_2 and C_2N_2 have been detected. The optimum reaction ratio was $CN^- : Cr(VI) = 3$ but with excess $Cr(VI)$, kinetic measurements showed that the reaction was sixth order in CN^- and independent of the concentration of $Cr(VI)$. The

reaction was catalysed via a $[\text{Cu}(\text{CN})_2]^-$ species and was thought to involve the overall schematic reaction;

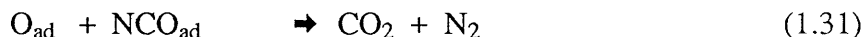
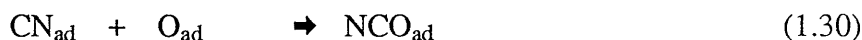


1.1.VII. Electrochemical oxidations.

There has been wide interest in electrochemical oxidation of free CN^- and cyanide complexes.⁴⁸ It has been generally accepted that free CN^- ions are electrochemically oxidised at the anode by the formation of $\text{CN}^\cdot$ radicals which decompose to C_2N_2 in acidic solution and NCO^- at higher pH.⁴⁹

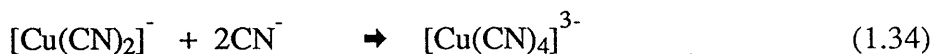
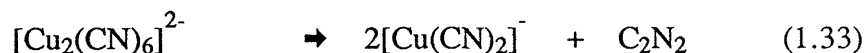


One study demonstrated the formation of NCO^- at a Pt electrode by infrared reflective absorption spectroscopy (IRRAS).⁵⁰ Free NCO^- has an IR peak at 2170 cm^{-1} corresponding to ν_{CN} and other peaks forming later were assigned to adsorbed CO_2 ($\nu_{\text{CO}} = 2342 \text{ cm}^{-1}$) and terminal surface-coordinated OCN^- species ($\nu_{\text{CN}} = 2260 \text{ cm}^{-1}$). The oxygen was supplied by dissociated OH^- or H_2O molecules which reacted as surface adsorbed O atoms thus:



There was a pH effect in which the rate of oxidation decreased as the pH rose.⁵¹ A study involving metal oxide electrodes recommended the use of a $\text{RuO}_2/\text{TiO}_2$ mixed electrode as the most effective in wastewater treatment of CN^- and SCN^- ;⁵² platinum electrodes tended to dissolve with time and $\text{Co(II) oxide}/\text{TiO}_2$ electrodes were less efficient. Addition of Cu(II) salts increased the rate of the oxidation reaction and it was concluded that the catalysis occurred by formation of the unstable $[\text{Cu}(\text{CN})_4]^{2-}$

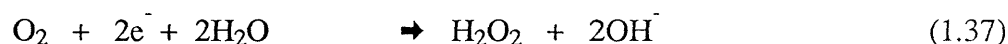
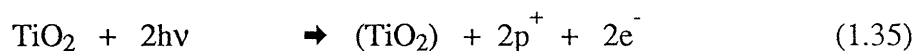
which formed a dimeric $[\text{Cu}_2(\text{CN})_6]^{2-}$ species prior to decomposition into $[\text{Cu}(\text{CN})_2]^-$ and C_2N_2 .⁵³



Research into the direct electrooxidation of $[\text{Cu}(\text{CN})_4]^{3-}$ and other complexes is discussed in the next chapter (see section 2.1).

1.1.IX. Oxidations by UV light.

UV light catalyses the oxidation of free CN^- by H_2O_2 as discussed earlier¹⁹ (section 1.1.I). It can also be responsible for the direct oxidation of CN^- over semiconductor powders such as TiO_2 , ZnO and CdS .^{54,55} It was found when using TiO_2 that the rate of oxidation was independent of CN^- concentration in the range 0.1-0.001M but there was a dependence at lower concentrations. The quantum efficiency of this reaction was calculated as 0.06 and it was shown that at least 90% of the CN^- formed NCO^- . The mechanism for this is thought to be the creation of holes (p^+) in the valence band of the TiO_2 by the UV excitation of electrons into the conduction band. The proposed equations are shown below.



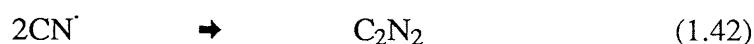
Platinisation of the TiO_2 increased the activity because the platinum increased the rate of O_2 reduction.⁵⁶ On the basis of the above equation it would be expected that the rate of formation of H_2O_2 would be increased, thus increasing the rate of oxidation of CN^- . Above pH 11 the rate of oxidation decreases.⁵⁷

Of the other semiconductor powders used Fe_2O_3 and WO_3 were inactive as catalysts but ZnO gave increased activity relative to TiO_2 . CdS was less active than TiO_2 but when loaded with rhodium the oxidation proceeded more swiftly ($Q > 0.25$) and probably involved the formation of thiocyanate.⁵⁸



1.1.X. Ozonolysis.

This is another oxidative reaction for the detoxification of cyanide containing wastes. General aspects of the reaction have been reviewed.⁵⁹ Kinetics of the oxidation of CN^- by O_3 in the pH range 2.5-12 were determined using stopped flow methods⁶⁰ and showed a first order dependence with respect to the concentration of O_3 . At neutral pH the reaction was also first order with respect to CN^- but this order decreased as the pH rose such that at pH 11.2 the order with respect to CN^- was 0.55. It was suggested that the reaction is not a simple bimolecular elementary reaction of O_3 but that there is a significant dependence on free radical reactions. The following mechanistic steps have been postulated to account for this.



A further study in the presence of copper and iron at high pH found that the copper catalysed the reaction by entering into a redox reaction in which Cu(I) was oxidised to Cu(II) by O_3 in a fast electron transfer which was more rapid than the oxidation of CN^- by O_3 .⁶¹ The Cu(II) then oxidised CN^- to cyanogen as it was reduced

to a cyanocuprate(I) species to provide an overall catalysis. It was found that iron hindered the oxidation due to the formation of stable hexacyanoferrate species. There was no build up of NCO^- in solution and this observation has been superficially explained by there being an oxidation of NCO^- by a hydroxyl radical. The solution to this problem involves irradiation of the solution followed by ozonation at pH 5-9. Plant details have been suggested to ensure that maximum decomplexation occurs in the wastestream before the ozone is added.⁶²

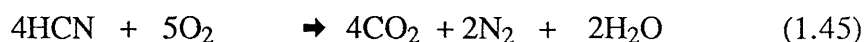
1.1.XI. Other methods.

The INCO process uses SO_2 and air at elevated temperature or at room temperature in the presence of a dissolved copper catalyst to oxidise free CN^- to NCO^- .⁶³

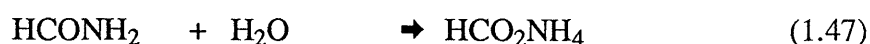


The process is suitable for free and complex cyanides except those of iron and cobalt. It also preferentially oxidises cyanide in the presence of thiocyanate.⁶⁴ Stable complexes are removed by precipitation with copper(II), nickel(II) or preferably zinc(II) salts and additions of iron(III) can be made to maximise the cyanide removal by formation of $[\text{Fe}(\text{CN})_6]^{3-}$.

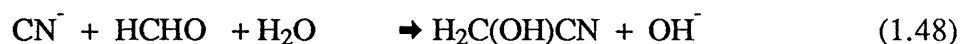
In the CYAN CAT process HCN is liberated from wastewater by the addition of H_2SO_4 and decomposition is carried out by catalytic combustion in air.⁶⁵



The catalyst for the reaction is an unidentified metal and the process is carried out at 350-400°C.⁶⁶ Other thermal treatment of solutions can be carried out at 180°C to form formamide and ultimately ammonium formate.



Another proposed treatment involves the use of air as the oxidant in conjunction with a catalyst of Cu(II) adsorbed on activated carbon.⁶⁷ Conversion with aldehydes and ketones is suitable over all pH for the removal of CN⁻ and moderately strong complexes. As in the peroxide assisted process a cyanohydrin is formed. Elevated temperature and pH 11 to 12 are required for complex cyanides.



Other processes involve the use of ionizing gamma radiation⁶⁸, biological treatment⁶⁹ and precipitation⁷⁰ of cyanide wastewaters but these are not discussed in this thesis.

1.2. Review of the Analytical Procedures used in the Determination of Free and Complexed Cyanide.

Accurate, reliable methods for the determination of both free and complexed cyanide species in solution are a prerequisite for the study of the reactions between such species and peroxides. Often it is sufficient to determine only the ionizable or *available* cyanide. This is defined⁷¹ as those species which can be directly oxidised by chlorine and includes simple cyanides and weak complexes with overall stability constants up to $\beta_n \sim 30$. However the total cyanide content, including that bound in strong complexes such as $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Co}(\text{CN})_6]^{3-}$ is more difficult to determine and what follows is a review of various published methods with critical assessment of their accuracy and facility.

1.2.I. Distillation methods.

The traditional method⁷² for the determination of total cyanide is to distill off HCN from an acidified sample of the salt or complex in the presence of a decomplexing agent (CuCl_2 or HgCl_2). The HCN is then absorbed into strong NaOH solution and the concentration determined titrimetrically or colorimetrically. The principal method used is Liebig's method⁷³ in which the cyanide is reacted with chloramine-T to form CNCl ; this reacts with pyridine-pyrazolone to form a blue complex. A variation of this is Aldridge's method⁷⁴ in which CNBr is formed by reaction with excess Br_2 and the cyanogen bromide determined colorimetrically by reaction with a pyridine-benzidine reagent. A titrimetric determination involves AgNO_3 using p-dimethylaminobenzylidinerhodanine as an indicator. Other titrimetric determinations are reviewed by Bark and Higson.⁷⁵

One problem of the distillation method is that interfering species such as sulphide and thiocyanate can be distilled over with the HCN. To overcome this sulphide can be

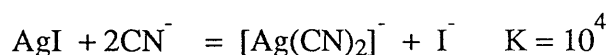
preprecipitated by adding aqueous solutions of $\text{Cd}(\text{NO}_3)_2$, PbCO_3 ⁷¹ or $\text{Bi}(\text{NO}_3)_2$ ⁷⁶ and filtered or reduced with NaHSO_3 . Thiocyanates can also decompose into sulphide and it is necessary to use MgCl_2 as the decomplexing agent to suppress this.

There are various procedures suggested to standardise the distillation and ensure that all complexes are completely decomposed. The use of $\text{Zn}(\text{OAc})_2$ is not totally efficient⁷⁷ but ligand exchange involving 1,2-hydroxy-3,5-benzenedisulphonic acid (Tiron) and tetraethylenepentamine (TEP)⁷⁸ in HCl is effective for all complexes except $[\text{Co}(\text{CN})_6]^{3-}$. The use of EDTA in phosphoric acid has also been advocated⁷⁹ to recover free CN^- even from ferricyanides and cobalticyanides.

Another method of decomplexation is irradiation of an acidic sample by UV light. This is rapid, accurate and will break down even strong complexes. It has been used successfully as part of an automated process^{80,81}

1.2.II. Electrode techniques.

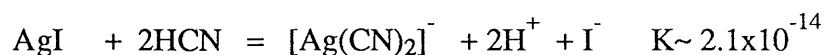
The cyanide selective electrode uses a silver iodide (or $\text{AgI}/\text{Ag}_2\text{S}$) membrane surface. When in contact with CN^- ions the following reaction occurs:⁸²



Thus the electrode responds to CN^- ion⁸³ in a Nernstian manner following the equation.

$$E = E_x + S \cdot \log[\text{CN}^-]$$

where S is the slope of a plot of E against $\ln[\text{CN}^-]$ and is equal to approximately 59mV for a ten fold increase in CN^- concentration over the concentration range 10^{-1} - 10^{-5} M ⁸³. Considering the above equation alone assumes that the electrode is only responsive to ionic CN^- (at $\text{pH} > 11$) but Mascini showed that responses at pH as low as 7 were due to the reaction.⁸²



At $\text{pH} 11$ the electrode will measure total CN^- in the presence of excess $\text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$ ions. The stability constants of these species lie below those of $[\text{Ag}(\text{CN})_2]^-$

($\beta_2=20.9^{84}$) $[\text{Zn}(\text{CN})_4]^{2-}$ ($\beta_4 = 19.62^{85}$), $[\text{Cd}(\text{CN})_4]^{2-}$ ($\beta_4 = 19.2^{86}$). In the presence of low concentrations of Cu(I) species the electrode will measure total CN^- but this response falls off at high concentrations due to the formation of $[\text{Cu}(\text{CN})_2]^-$, $[\text{Cu}(\text{CN})_3]^{2-}$ and $[\text{Cu}(\text{CN})_4]^{3-}$.⁸⁷ At lower pH (6 to 8) an AgBr electrode is said to give a better response to the above species but for metal ions forming complexes more stable than $[\text{Ag}(\text{CN})_2]^-$ pretreatment is required to decomplex metals in order to determine the total CN^- concentration.⁸⁸ This pretreatment can be carried out by heating in the presence of EDTA to form a metal - EDTA complex or else by UV irradiation.

The presence of other ions in solution can affect the electrode response. Selectivity constants⁸⁹ indicate that the AgI electrode has the highest selectivity for CN^- in the presence of Cl^- (10^6), Br^- (5×10^3), I^- (0.1), $[\text{NH}_4]^+$ and $[\text{SO}_4]^{2-}$ (figures in brackets indicate the maximum ratio of the ions $\text{X} : \text{CN}^-$ in mols dm^{-3}). Sulphide must be absent from the solution as must any other ions which would form a highly insoluble complex with silver.⁹⁰

Low concentrations of CN^- can be measured accurately using an Ag_2S electrode as an indicator electrode in a known addition method.⁹¹ In this a known volume of sample is taken and the electrode potential plotted using a Gran's plot as successive known additions of CN^- are made. This gives accurate response ($\pm 2.5\%$) even at 10^{-6}M and in the presence of 10^{-4}M metal ions which have been pretreated with EDTA. This indicator method has been used⁸³ in conjunction with EDTA pretreatment as the basis for a continuous flow monitor for cyanide in wastewaters. A $[\text{Zn}(\text{CN})_4]^{2-}$ selective electrode has been reported⁹² based on a membrane of di-butylphthalate. This works at pH 8.5 to 10 for a concentration range of 10^{-1} - 10^{-4}M $[\text{Zn}(\text{CN})_4]^{2-}$. Another electrode selective for $[\text{Co}(\text{CN})_6]^{3-}$ uses Na_2S to mask the effects of $[\text{Ag}(\text{CN})_2]^-$ at a membrane which involves a $(\text{R}_4\text{P})_3[\text{Co}(\text{CN})_6]$ complex ($\text{R}=\text{decyl}$).⁹³ It has also been suggested that the two abrupt potential changes associated with the formation of $[\text{Cu}(\text{CN})_3]^{2-}$ and $[\text{Cu}(\text{CN})_2]^-$ can be used as the basis of a method for determining both CN^- and Cu(II) species in aqueous solution.⁹⁴

1.2.III. Chromatographic methods.

Gas chromatography has been used⁹⁵ for the determination of HCN in the presence of O₂, N₂, CH₄, and CO by passing through a column of celite impregnated with polyoxyethylene-glycol at 100°C. Determination of the complexes [Fe(CN)₆]³⁻, [Fe(CN)₆]⁴⁻ and [Co(CN)₆]³⁻ has been achieved by initial UV irradiation to break them down, followed by reaction of the released CN⁻ with Br₂ to form CNBr which can then be separated at 100-140°C.⁹⁶ Ionic cyanides can also be separated using the same principle by conversion to CNCl with hypochlorite.

Ion chromatographic determinations have been made⁹⁷ for CN⁻ as ICN (made by reaction of CN⁻ with I₂) and this can also be carried out in the presence of sulphide using electrochemical determination. Using a silver working electrode⁹⁸ accuracy can be maintained down to parts per billion levels CN⁻ (10⁻⁹M) in the presence of interfering species, but the only complexes which have been determined quantitatively by this method are [Cd(CN)₄]²⁻ and [Zn(CN)₄]²⁻. Partial determination is possible for [Cu(CN)₃]²⁻ and [Ni(CN)₄]²⁻ whilst [Au(CN)₂]⁻, [Fe(CN)₆]³⁻ and [Co(CN)₆]³⁻ are not detected.⁹⁹ Direct determination of complexes is discussed in the next chapter (see 2.2.III).

Another method to distinguish *available* and total cyanide involves running the sample down a fast run ion exchange column before and after UV irradiation.^{69,100} The difference in area of the peaks corresponding to CN⁻ measured potentiometrically arises from that strongly bound cyanide which is not detected in the first run. Irradiation takes about six minutes which is considerably quicker than for distillation procedures and gives accurate results even for the strongly bound complexes.

1.2.IV. Other methods.

Polarographic procedures have been used to analyse CN⁻ down to 1.5 mg dm⁻³

(10^{-7} M). Using AC polarography in conjunction with complex-forming electrodes many cyanide complexes can be determined in clear water, but accuracy is severely impaired in sewage and turbid effluents.^{77,101}

There are various indirect methods of determination involving the use of atomic absorption spectrometry. These can involve the formation of an insoluble precipitate which can then be redissolved to determine the metal concentration. In the determination of hexacyanoferrates¹⁰² the complexes are precipitated with copper and interfering species removed by washing with HCl. The precipitate is then resolubilised by addition of NH_3 and the resulting solution analysed directly by atomic absorption spectrophotometry (A.A.). Another method is to form a stoichiometric complex of CN^- and analyse this by A.A. The most suitable metals to form this stoichiometric complex are copper (as a copper(I) cyanide bed¹⁰³) which forms $[\text{Cu}(\text{CN})_3]^{2-}$ and silver (as Ag wool¹⁰⁴) which would form $[\text{Ag}(\text{CN})_2]^-$. Neither seems to be suitable for the analysis of complex cyanides and no mention is made of the possibility of formation of the complexes $[\text{Cu}(\text{CN})_4]^{3-}$ and $[\text{Ag}(\text{CN})_3]^{2-}$ which would affect the accuracy of determination.

Spectrophotometric determination of CN^- can be carried out by bubbling cyanide distillate into ammoniacal NiCl_2 solution to form the complex $[\text{Ni}(\text{CN})_4]^{2-}$ and analysing the characteristic UV absorption at 268 nm.¹⁰⁵ This is accurate to at least 10^{-4} M complex but can be subject to interference by any species which also absorbs UV in this region. The formation of the $[\text{Ni}(\text{CN})_4]^{2-}$ complex has been used as the basis of a method to distinguish CN^- from SCN^- in a stopped-flow spectrophotometric method.¹⁰⁶

1.3. Studies of the Oxidation of Free Cyanide by Hydrogen Peroxide.

In this section we present results of our work on the oxidation of free CN^- by H_2O_2 . The following aspects in particular have been studied:

- i. Products of the reaction.
- ii. Kinetic data measured for the oxidation at pH 9 - 9.5.
- iii. The effect of pH on the reaction and of carrying out the oxidation in specific buffers.
- iv. The effects of ionic strength, sequestering agents and of carrying out the reaction in the presence or absence of UV light.
- v. The addition of copper(I) and copper(II) salts and their catalytic effects and observations on the addition of other possible catalysts in the reaction.
- vi. The oxidation of free CN^- by H_2O_2 in the presence of thiosulphate, $[\text{S}_2\text{O}_3]^{2-}$.

1.3.I. Products of the Reaction.

In virtually all the published reports¹⁻²⁷ concerning the oxidation of CN^- by H_2O_2 it is stated that NCO^- is the initial product of the reaction and that this is then destroyed either by hydrolysis to form ammonia and carbonate salts, or by oxidation to produce N_2 and carbonate (or bicarbonate). The formation of formate at low pH has also been reported.⁴ However, only one report gives accurate details of how the products are analysed, and in that study H_2O_2 and Au(III) interfered with the accepted chemical method for the determination of NCO^- , the formation of a blue Cu(II) pyridine complex with NCO^- .¹⁹ Thus it seems that the formation of NCO^- has become a well known yet unsubstantiated fact. We have shown by using a number of chemical and spectroscopic techniques that the cyanate and bicarbonate / carbonate species are indeed formed as products in the oxidation.

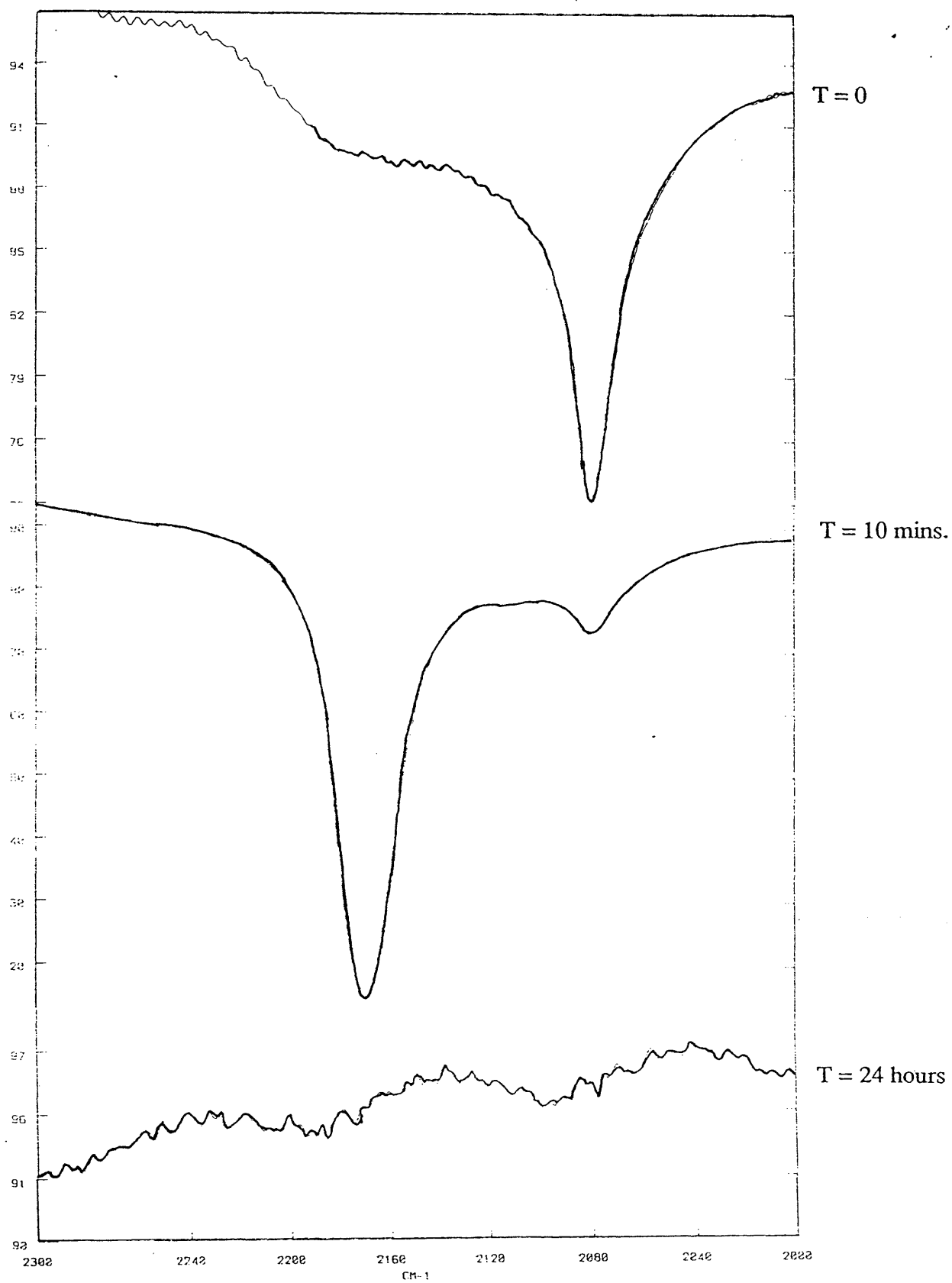
a. Detection of cyanate using FTIR spectroscopy.

We have used FTIR to measure the spectra of solutions of CN^- (0.05 -1M) in H_2O_2 (0.05 -1M) in the region 2000 to 2300 cm^{-1} at pH above 9 in order to assess the decrease in intensity of the peak at 2079 cm^{-1} which is due to the stretching vibration (ν_{CN}) of free CN^- ¹⁰⁷, and to observe the formation of NCO^- by detection of the ν_{CN} vibration of this species which occurs at 2169 cm^{-1} .¹⁰⁸ Initially only one peak at 2079 cm^{-1} was visible but after a matter of minutes a second stronger peak became apparent at 2169 cm^{-1} , which can be attributed to free NCO^- . The intensity of the ν_{CN} band of NCO^- ($\epsilon = 1330 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) was much stronger than that of ν_{CN} in CN^- ($\epsilon = 19 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) and soon this former peak obscured the latter despite the greater concentration of CN^- . After continued oxidation in excess H_2O_2 for over two hours the intensity of this second peak began to decrease indicating the conversion of the NCO^- to other products and thus confirming that it is indeed only an intermediate in the overall reaction. Unfortunately it was not possible to identify any further products using aqueous solution FTIR as the CaF_2 plates used are opaque to IR radiation below 1100 cm^{-1} . These results are shown by the spectra in fig 1.3.i. overleaf.

b. Detection of other reaction products using Raman spectroscopy.

Raman spectroscopy has been used in the same way as FTIR to follow the progress of the reaction. This technique is particularly useful for the study of this system and other reactions in aqueous solution because the quartz or glass solution cells used do not interfere and the Raman active vibrations of water are only very weak; thus spectra of aqueous solutions can be measured in the range 100 to 3000 cm^{-1} . The spectra in fig 1.3.ii overleaf clearly show how the composition of a solution of CN^- (0.1M) changed with time as the oxidation progressed after successive additions of H_2O_2 (0.05M) at pH above 10.

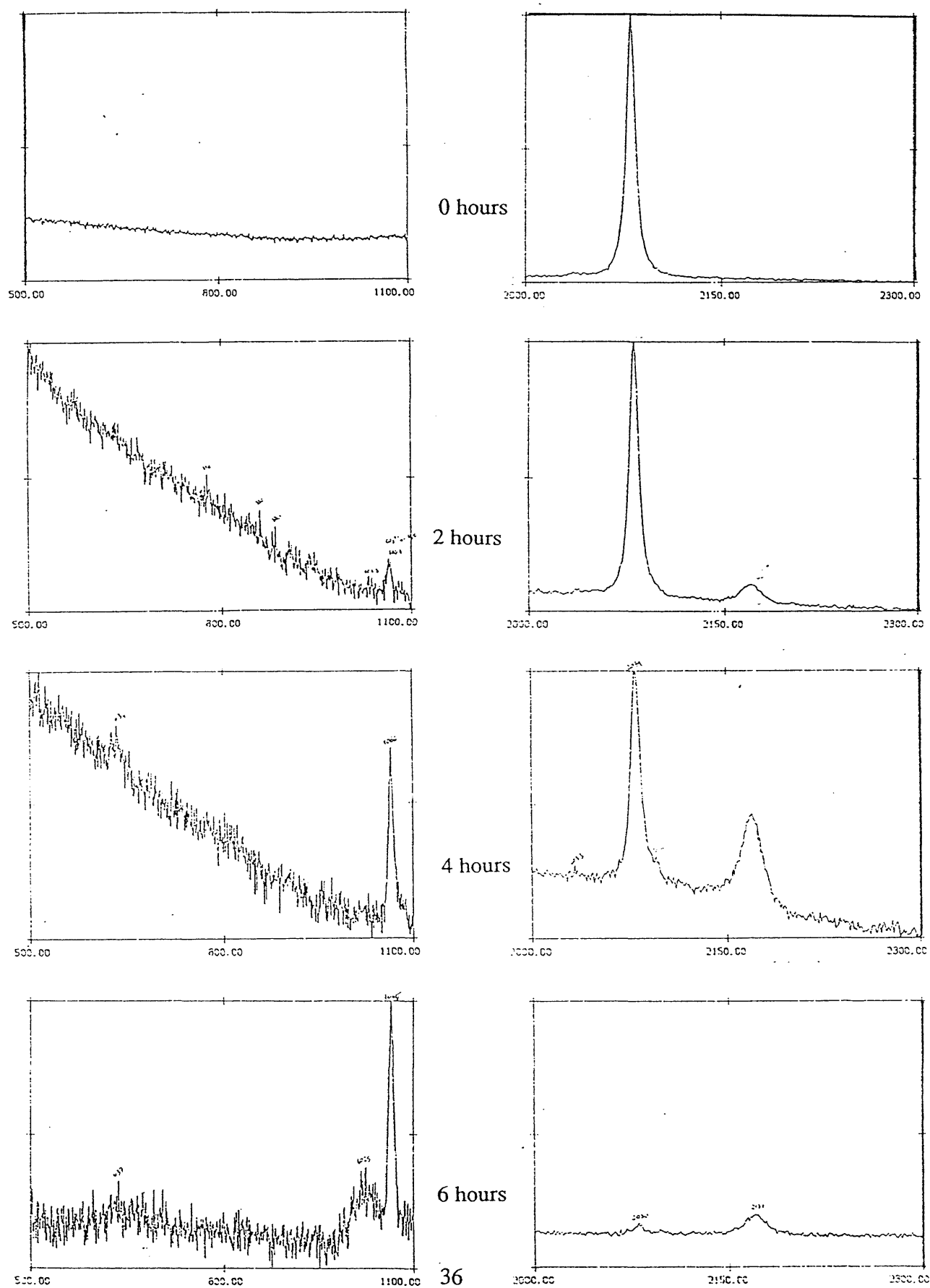
Fig 1.3.i. FTIR spectra showing the oxidation of CN^- (0.5M) to NCO^- by H_2O_2 (0.5M).



In the initial solution the only peak observed in the scan ranges of 500 - 1100 cm^{-1} and 2000-2300 cm^{-1} was at 2080 cm^{-1} , and this was clearly due to the ν_{CN} of free CN^- . After two hours a small peak at 2170 cm^{-1} due to the ν_{CN} of NCO^- was observed and in the lower scan group it was possible to make out one band at 1067 cm^{-1} which we assigned as ν_{CO} of $[\text{CO}_3]^{2-}$. After four hours had elapsed the peak at 2079 cm^{-1} had decreased in size and those at 2179 and 1067 cm^{-1} increased. After six hours reaction in the presence of a large excess of H_2O_2 almost all of the CN^- had been oxidised and the peak at 2080 cm^{-1} was barely distinguishable from the baseline. Similarly the NCO^- peak at 2179 cm^{-1} had also decreased in size indicating that this species had largely decomposed, either by oxidation or hydrolysis (see section 1.5). The $[\text{CO}_3]^{2-}$ peak at 1067 cm^{-1} continued to grow in size and there was a weaker peak at 1025 cm^{-1} which can be assigned to $[\text{HCO}_3]^-$. A standard of $[\text{HCO}_3]^-$ (0.5M) had a weak, broad band at around 1020 cm^{-1} .

No peaks assignable to formate, $[\text{HCOO}]^-$ were observed which Masson⁴ reported was formed at low pH by the hydrolysis of NCO^- . Bands due to nitrate $[\text{NO}_3]^-$ were also sought as this was reported as a product of the oxidation of free SCN^- by H_2O_2 ¹⁰⁹ but the strongest Raman band for $[\text{NO}_3]^-$, the symmetric stretch, ν_{NO} at 1049 cm^{-1} lies very close to the symmetric stretch, ν_{CO} of $[\text{CO}_3]^{2-}$ at 1067 cm^{-1} . Although the solution was acidified to remove the carbonate the Raman spectrum failed to show a peak that might be due to nitrate, even though this method proved successful with standard solutions containing both K_2CO_3 (1M) and KNO_3 (1M). It therefore seems unlikely that nitrate is formed in substantial quantities under these conditions.

Fig. 1.3.ii. Raman spectra showing the progression of the reaction between CN^- (0.1M) and successive additions of H_2O_2 (0.05M) at $\text{pH} > 10$.



c. Use of ^{13}C nmr spectroscopy to study reaction solutions.

Although ^{13}C ($S = 1/2$)¹¹⁰ has a natural abundance of only 1.1%, NMR spectra of strong concentrations (at least 0.1M) have been recorded which give further data supporting the above results. These data and the conditions of the reactions are recorded below in table 1.3.i. The ^{13}C shift due to free CN^- occurred at $\delta = 166.7$ ppm (relative to $(\text{CH}_3)_4\text{Si}$)¹¹¹, and was clearly observed in our solutions before oxidation. This peak was joined within one hour by a peak at $\delta = 129$ ppm which could be assigned to NCO^- ¹¹² although this actually appeared as a 1:2:1 triplet. There is no obvious reason why this should be and we are unable to offer an explanation for this observation. There is no evidence for ^{14}N - ^{13}C coupling, which should also be observed in the CN^- peak, and the NCO^- is uncoordinated, but we found that a saturated solution of KNCO in water also gave a triplet at $\delta = 128.8$ ppm. with a separation of 22 Hz. This shift was in agreement with the value reported in the literature but we could find no mention of the splitting.¹¹²

After one hour a third resonance was observed in the region $\delta = 165$ to 173 ppm which we attributed to the pH dependent $[\text{CO}_3]^{2-}/[\text{HCO}_3]^-$ species. The position of the ^{13}C resonance in $[\text{CO}_3]^{2-}/[\text{HCO}_3]^-$ solutions depends on the pH since the proton exchange between $[\text{CO}_3]^{2-}$ and $[\text{HCO}_3]^-$ is rapid on the NMR timescale; the position of the peak in our solutions was in agreement with published work¹¹³ and also ^{13}C NMR studies carried out previously in these laboratories.¹¹⁴ A further peak occurring at $\delta = 164$ ppm. whose shift was also dependent upon the pH was observed in a number of spectra recorded after at least two hours of reaction. It is not clear to what this was due but we have tentatively assigned it to the exchanging peroxocarbonate $[\text{HCO}_4]^- / [\text{CO}_4]^{2-}$ species which are known to be formed by the interaction of $[\text{CO}_3]^{2-}$ and H_2O_2 . However this assignment is by no means certain as the equilibrium of this system has been studied in some detail in these laboratories over the pH range 7 to 10, above which no evidence for the existence of peroxocarbonate was found.¹¹⁴ The peak at $\delta = 164$

ppm. for which we are making this assignment, was observed in our studies at pH 11.5 and since the concentration of $[\text{CO}_3]^{2-}$ would be far short of 0.1M, the initial concentration of CN^- in the reaction, it would seem that the probability of peroxocarbonate being formed in sufficient concentration to render it visible by ^{13}C NMR is low. However, in the absence of further data we conclude that there is still a possibility that this peak is due to a peroxocarbonate species.

Fig 1.3.iii. A ^{13}C NMR spectrum of a solution of KCN (5.3M) with H_2O_2 (0.1M) after one hour of reaction at pH 12.5.

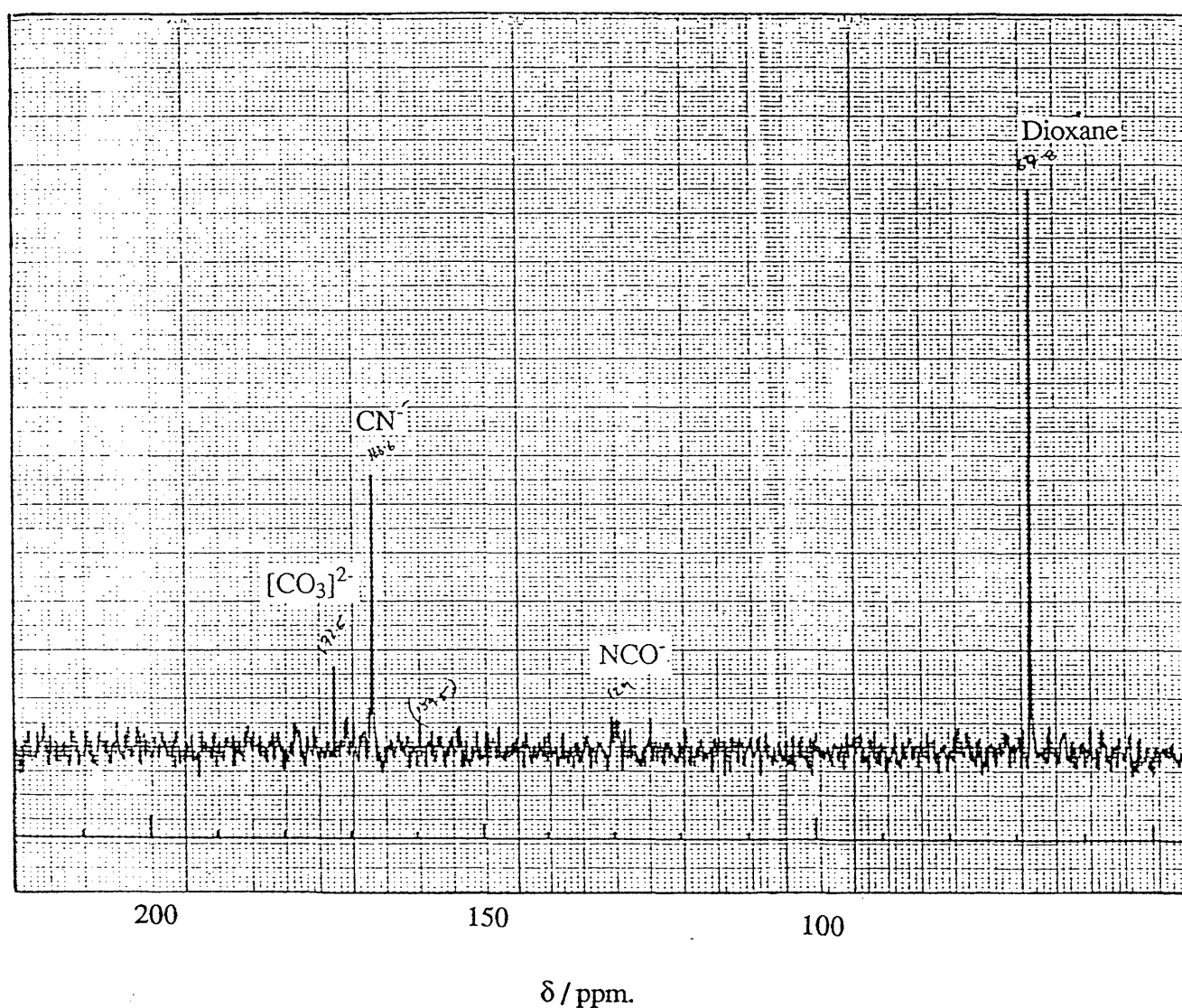


Table 1.3.i. Resonances observed in the ^{13}C NMR spectra of reaction solutions containing CN^- and H_2O_2 . Shifts relative to δ of $\text{Me}_4\text{Si} = 0$ ppm.

$[\text{CN}^-] / \text{M}$	$[\text{H}_2\text{O}_2] / \text{M}$	pH	Reaction Time	δ / ppm	Assignment
1.5	1.5	12.1	1 hour	129	NCO^-
				166	CN^-
				172.5	$[\text{HCO}_3]^- / [\text{CO}_3]^{2-}$
5.3	0.1	12.5	1 hour	129	NCO^-
				166.6	CN^-
				171	$[\text{HCO}_3]^- / [\text{CO}_3]^{2-}$
1.5	1.5	11.3	1 hour	129.9	NCO^-
				164	$[\text{HCO}_4]^- / [\text{CO}_4]^{2-}?$
				167	CN^-
				172.5	$[\text{HCO}_3]^- / [\text{CO}_3]^{2-}$
1.5	1.5	11.5	1 day	129	NCO^-
				164	$[\text{HCO}_4]^- / [\text{CO}_4]^{2-}?$
				166.7	CN^-
				171.5	$[\text{HCO}_3]^- / [\text{CO}_3]^{2-}$

d. Isolation of solid species present in the $\text{CN}^-/\text{H}_2\text{O}_2$ reaction.

FTIR spectra were taken of solids obtained from evaporation of the reaction solutions and of precipitates formed when the reaction was carried out in mixtures of ethanol and water. In these spectra we observed weak bands due to KNCO at 2175, 1208 and 631 cm^{-1} . Bands at 1439(s), 1061(m) and $885(\text{m})\text{ cm}^{-1}$ were assignable to K_2CO_3 and those at 1401(s), 1007(s), 832(s), 702(s) and $663(\text{m})\text{ cm}^{-1}$ could be attributed to KHCO_3 . The assignments for all the above bands were determined by comparison with the spectra of the pure compounds. No peaks were observed which could definitely be assigned to vibrations of the nitrate anion, which has been proposed as a possible product of the oxidation of NCO^- .^{9,109} Nor were any peaks observed which we could attribute to the presence of formate which is thought to be a minor product of the oxidation when carried out below pH 7.⁴

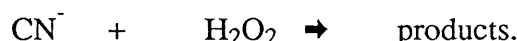
One reaction, carried out in a mixture of H_2O and ethanol separated into two layers after a week and the lower layer turned blue. Colourless crystals isolated from the lower layer of this solution were found by elemental analysis to be KHCO_3 .

e. Conclusions.

Using Raman, FTIR, ^{13}C NMR spectroscopy and chemical procedures we have shown that NCO^- is an intermediate in the reaction between CN^- and H_2O_2 at pH above 8 and that, depending upon the pH, $[\text{HCO}_3]^-$ or $[\text{CO}_3]^{2-}$ is the ultimate carbon containing product. The fate of the nitrogen is not entirely clear although we have shown that approximately 75% of the NCO^- formed is transformed to NH_3 above pH 8 (see section 1.5.II). On the basis of our studies we discount the possibility of $[\text{NO}_3]^-$ being formed in any substantial quantity and it seems likely that the remainder of the nitrogen is evolved as N_2 as proposed in the literature.^{4,19}

1.3.II. Kinetics of the Oxidation.

Although there are a number of studies concerning the kinetics of oxidations using H_2O_2 ,^{35,115,116} and the oxidation of CN^- using other oxidants, notably hypochlorite^{38,39}, we can find only three studies that are relevant to the oxidation of CN^- using H_2O_2 . Masson⁴ studied the kinetics of the reaction between equimolar concentrations of H_2O_2 and CN^- at high pH (>10). Serpone *et al*¹⁹ measured some rate constants for the reaction but their main study was on the effects of UV light. Data measured by Schiller⁵ were fitted to a complex third order polynomial equation for the reaction of H_2O_2 and CN^- in the presence of $[\text{S}_2\text{O}_3]^{2-}$ at pH 7 to 9. Bearing in mind the factors discussed in the sections below, all of which have some effect on the rate and reproducibility of reactions we have confined ourselves to a simple study of the uncatalysed reaction using a large excess of H_2O_2 , so that the concentration of the latter effectively remains unchanged during the reaction, and measuring the decrease in concentration of the CN^- as the reaction progresses using the cyanide selective electrode. Under these pseudo first order conditions the rate equation for the reaction can be written in simple terms as follows.



$$\text{Rate} = \frac{-d[\text{CN}^-]}{dt} = k[\text{CN}^-].[\text{H}_2\text{O}_2]$$

Using Ostwald's dilution method¹¹⁷, if a large excess of H_2O_2 is used, then the concentration of this reagent will not alter significantly during the course of the reaction and can be taken as a constant so simplifying the rate expression.

$$\frac{-d[\text{CN}^-]}{dt} = k_{\text{obs}}[\text{CN}^-]$$

where $k_{\text{obs}} = k.[\text{H}_2\text{O}_2]_0$. The integrated form of this expression is thus:

$$\frac{\ln.[\text{CN}^-]_t}{\ln.[\text{CN}^-]_0} = \ln.[\text{CN}^-]_t - \ln.[\text{CN}^-]_0 = -k_{\text{obs}}.t$$

where a plot of $\ln.[\text{CN}^-]_t$ against t should be a straight line of gradient $-k_{\text{obs}}$.

We have used this treatment of our results and as can be seen from graph 1.3.i below, the data conform to a straight line. In table 1.3.ii we list values measured for k_{obs} with calculated errors (for details of the calculation of these errors see experimental section 1.5). These k_{obs} values are in relatively close agreement with those measured by Serpone *et al.*¹⁹ for the H_2O_2 - CN^- reaction carried out in the dark under similar conditions. However, in our study changing the concentration of H_2O_2 from 0.014M to 0.029M nearly doubled k_{obs} , (from $1.40 \times 10^{-5} \text{ s}^{-1}$ to $2.4 \times 10^{-5} \text{ s}^{-1}$) whilst the results of Serpone indicate that a twelve fold increase of k_{obs} was observed from quadrupling the H_2O_2 concentration.

Graph 1.3.i. First order plot for the oxidation of free CN^- ($1.1 \times 10^{-3} \text{ M}$) by H_2O_2 (0.16M) with $k_{\text{obs}} = 2.93 \times 10^{-4} \text{ s}^{-1}$.

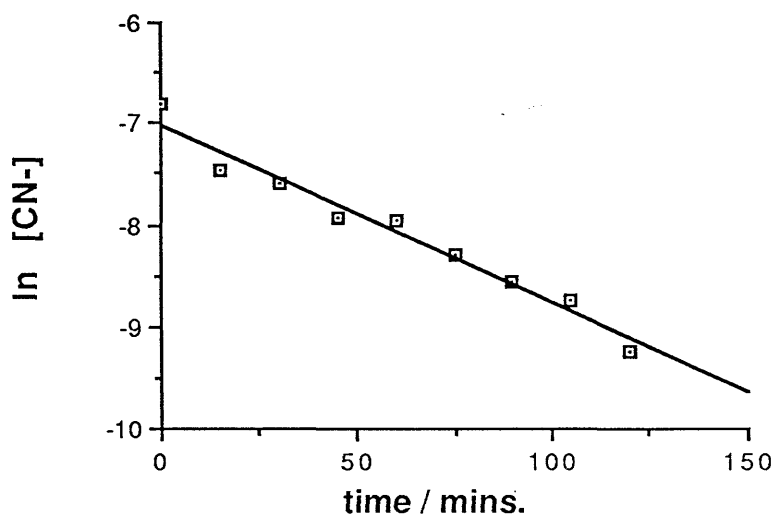
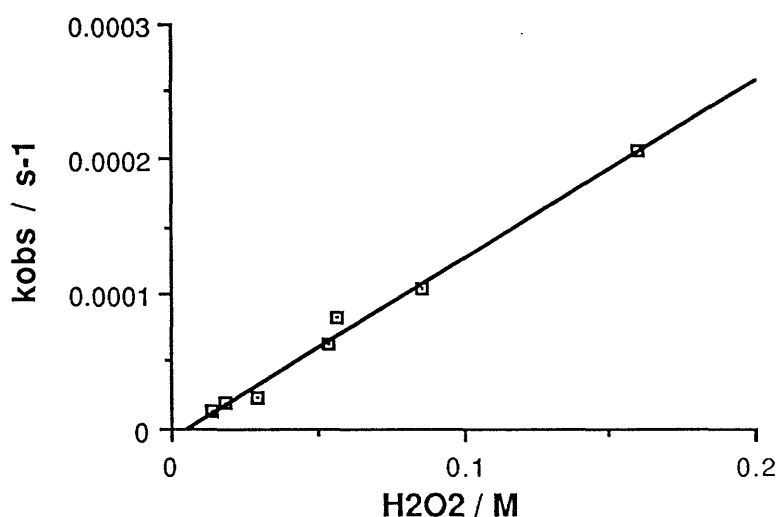


Table 1.3.ii Rate constants determined for the oxidation of free CN^- by H_2O_2 at pH 9.0, 23°C using the cyanide electrode.

$10^3 [\text{CN}^-] / \text{M}$	$\text{H}_2\text{O}_2 / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$
1.0	0.054	6.53×10^{-5}
1.0	0.054	5.83×10^{-5}
1.0	0.054	6.36×10^{-5}
1.0	0.054	6.61×10^{-5}
(Average = $6.30 (\pm 0.14) \times 10^{-5}$)		
1.0	0.014	1.40×10^{-5}
1.0	0.018	1.89×10^{-5}
1.0	0.029	2.40×10^{-5}
1.0	0.057	8.30×10^{-5}
1.0	0.086	1.04×10^{-4}
1.0	0.160	2.05×10^{-4}
1.0	0.500	4.03×10^{-4}
10	0.018	3.82×10^{-5}
10	0.018	4.06×10^{-5}
10	0.018	3.89×10^{-5}
(Average = $3.92 (\pm 0.14) \times 10^{-5}$)		
10	0.036	9.80×10^{-5}
1.1	0.16	2.92×10^{-4}
2.9	0.16	2.32×10^{-4}
4.6	0.16	2.57×10^{-4}

The dependence of k_{obs} on the concentration of H_2O_2 found in our work is plotted in graph 1.3.ii below and this follows a straight line indicating that the reaction is first order with respect to the concentrations of both the CN^- and the H_2O_2 . These results are in agreement with those of Masson⁴ who found the overall reaction to be second order, (first order in each reactant) when using concentrations of about 0.5M of both H_2O_2 and CN^- at pH about 11. Under the conditions of our study, we found that increasing the CN^- concentration ten fold only doubled the rate and there was no linear relationship between our values of k_{obs} and the concentration of CN^- . This observation is also in broad agreement with the work of Serpone *et al.*¹⁹

Graph 1.3.ii. Plot of k_{obs} against concentration of H_2O_2 for the oxidation of CN^- 10^{-3} M at pH 9. Data is from table 1.3.ii above.



1.3.III. The effect of pH on the rate of reaction and the use of buffers.

a. Reactions in unbuffered solution.

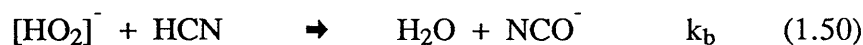
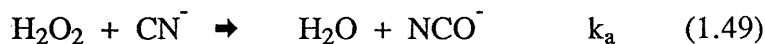
Much of our earlier work carried out to measure the kinetics of the oxidation of CN^- with H_2O_2 was hampered by irreproducible results. Some anomalous results were obtained where first order kinetics were not observed, but these were usually found to be due to the presence of impurities in the solutions and once strict cleaning procedures (described in detail in the experimental section) were carried out to ensure that as far as possible, all impurities were eliminated the occurrences of these rogue results were reduced to a minimum. However some anomalous data were obtained in which first order kinetics were observed but for which the k_{obs} values differed widely, and it was apparent that some other parameter was affecting the rate of the reaction.

Most of the kinetic data discussed in section 1.3.II were collected using unbuffered solutions due to the problems encountered in finding a suitable buffer solution that did not itself affect the rate of reaction (see later in this section) and we found that the anomalous results occurred when the pH of the reaction was not exactly 9. An investigation into the effect of altering the pH over a wide range in the oxidation of CN^- (10^{-3}M) by H_2O_2 (0.054M) showed that the maximum rate of reaction was observed at pH 9.2 ($k_{\text{obs}} = 2.4 \times 10^{-5} \text{ s}^{-1}$), and the k_{obs} values for the reaction decreased rapidly as the pH was shifted away from this value.

Qualitatively, these results were in agreement with those published by Masson⁴ in which he found that the rate of reaction was greatest when pure KCN (0.24M) and H_2O_2 (0.24M) were mixed, for which we measure the pH to be 10.6. He found that the rate was reduced if KOH (0.12- 0.24M) were added (pH > 13.0), or if the pH was reduced to below 1 by addition of H_2SO_4 (0.12-0.24M).

The profile of k_{obs} as the pH was altered in our study is shown in graph 1.3.iii together with the theoretical curve calculated from the following expressions for either of the two following reactions, which are kinetically indistinguishable (these have been

taken from the analogous equations in a kinetic study of the reaction between H₂O₂ and hypochlorite.³⁵

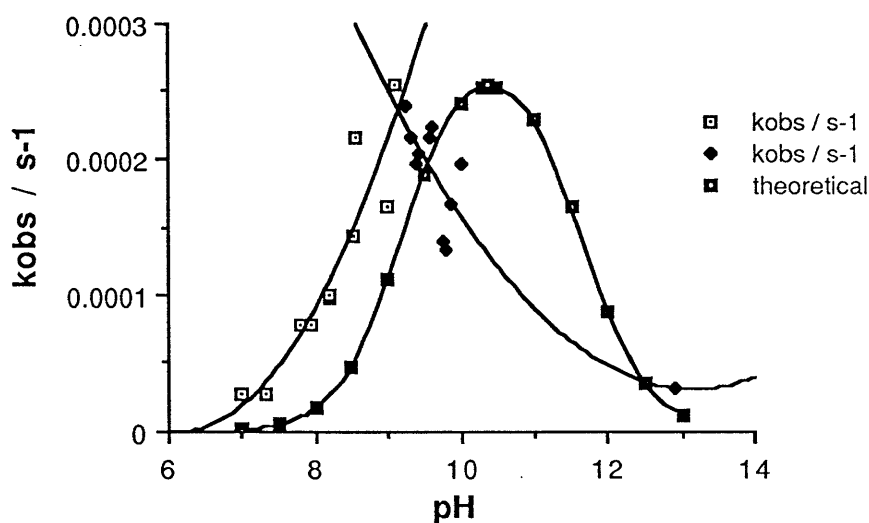


$$\text{For reaction 1.49, } k_{\text{obs}} = \frac{k_a}{1 + \frac{[\text{H}^+]}{K_1} 1 + \frac{K_2}{[\text{H}^+]}}$$

$$\text{For reaction 1.50, } k_{\text{obs}} = \frac{k_b}{1 + \frac{K_1}{[\text{H}^+]} 1 + \frac{[\text{H}^+]}{K_2}}$$

where K_1 is the acid dissociation constant for HCN ($6.31 \times 10^{-10} \text{ M}$)¹¹⁸ and K_2 is the acid dissociation constant for H₂O₂ ($2.2 \times 10^{-12} \text{ M}$).³⁵

Graph 1.3.iii The effect of pH on the rate of oxidation of free CN⁻ (10^{-3} M) by H₂O₂ (0.054M) with theoretical plot normalised to the maximum observed value of k_{obs} .



The maximum value for k_{obs} in our investigations was obtained at pH 9.2 which is equal to the pK_a of HCN at 25°C ¹¹⁸, although this appears to be coincidental.

At this pH the concentration of HCN is equal to the concentration of the ion CN^- ; at higher pH values the latter is the principle species and below pH 9.2 the HCN molecule predominates. If either of these species reacts more readily with H_2O_2 then it would be expected that the rate would increase with the concentration of this moiety, rather than achieve a maximum at the pH where the two species have equal concentrations. The pK_a of H_2O_2 lies at pH 11.65 (20°C)³⁵, above which the predominant species is the ion $[\text{HO}_2]^-$. Considering these factors we can suggest no convincing explanation for the pH profile we have observed.

From the theoretical curve on graph 3.1.iii. it is clear that the rate should be greatest at pH 10.4, whereas our data indicate that this occurs at pH 9.2. The difference in these values is quite large and the shapes of the curves are different. Assuming that our data are accurate it would suggest that there are competitive side reactions, possibly catalysed by transition metals or following free radical pathways which are responsible for the deviation of our data from the theoretical curve. It is unlikely that the other two possible reactions (equations 1.51 and 1.52 below) are contributing to this effect in the pH range 9 to 10, as the values of k_{obs} we have measured for these reactions were very much lower than those measured within our chosen pH window. At pH 2.3 we measured k_{obs} to be $1.6 \times 10^{-5} \text{ s}^{-1}$, and at pH 13.0, $3.1 \times 10^{-5} \text{ s}^{-1}$.



In the kinetic study of the reaction between HOCl and H_2O_2 to form singlet O_2 , the authors³⁵ concluded that although they were not the predominant species in solution, the mechanism proceeded via nucleophilic attack of $[\text{HO}_2]^-$ (which is more nucleophilic than H_2O_2) upon HOCl at the electrophilic chlorine atom. If this logic is correct and can be used with regard to the oxidation of cyanide by hydrogen peroxide, then the reactive species are $[\text{HO}_2]^-$ and HCN (i.e equation 1.50), and the attack must take place at the carbon atom to form a cyanate (NCO^-) rather than a fulminate (CNO^-).

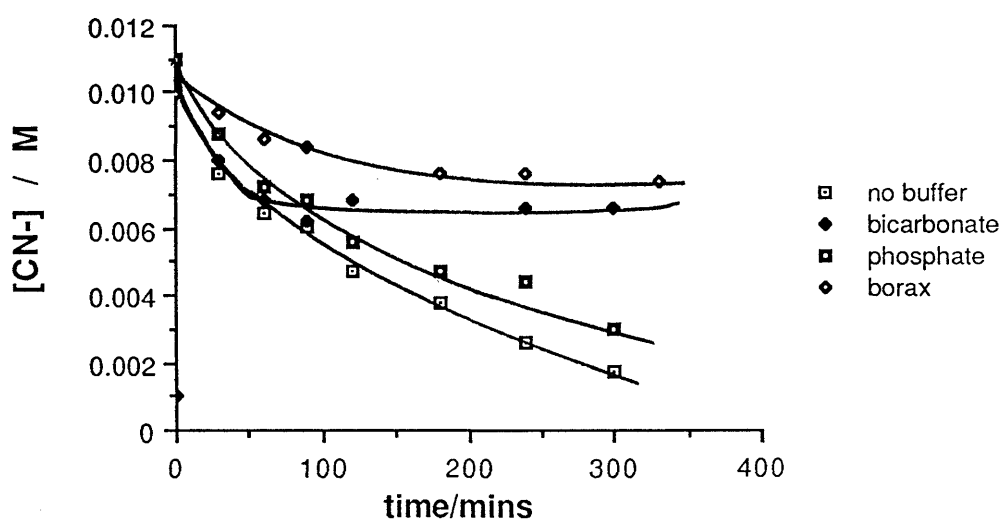
b. The effect of buffers on the rates of oxidation of free CN^- by H_2O_2 .

The pH of reaction solutions was often observed to fall by up to one pH unit as the oxidation progressed. This was largely due to the slight acidity of H_2O_2 but as we have discussed above the rate of reaction was very sensitive to the pH in the range in which we have carried out most of our reactions. To ensure that this was not greatly affecting the conditions and thus the overall rate of oxidation, reactions between H_2O_2 and CN^- were carried out in a number of buffers prepared by standard methods.¹¹⁹ This served to prevent or at least reduce the changes in pH but we discovered that in some cases the buffers themselves had an effect on the rates. The graph (1.3.iv) overleaf summarises the results of oxidations carried out between pH 9 and 10 in buffers made up from phosphate, bicarbonate and borax. We found that in general oxidations carried out in phosphate buffer followed the rates of oxidation in unbuffered solution most closely but of the buffers used it was least effective in maintaining pH. In oxidations carried out in buffers made from borax and bicarbonate the pH dropped a maximum of 0.2 pH units (e.g. in the oxidation of CN^- (10^{-2}M) by H_2O_2 (0.03M) in borax the pH dropped from 10.02 to 9.88 in five hours), in a similar oxidation in phosphate buffer the pH dropped from 10.22 to 9.55 in only two hours. By comparison, when the oxidation was carried out in unbuffered solution the pH had dropped from 10.22 to 9.67 after five hours reaction. It is likely that the similar drop in pH was the reason that those oxidations carried out in the phosphate buffer most closely resembled reactions carried out in unbuffered solution.

Oxidations carried out in borax buffer were found to proceed more slowly than those in unbuffered solution, although the pH control using this buffer was very efficient. We conclude that this reduction in rate was due to the formation of peroxyborate species in solution which are less reactive towards free CN^- than is free H_2O_2 . At pH 9 to 10 the principle peroxyborate species in solution are thought to be $[\text{B}(\text{OOH})(\text{OH})_3]^-$ and $[(\text{OH})_3\text{B}(\text{OO})\text{B}(\text{OH})_3]^{2-}$.¹²⁰ In studies of the oxidation of $[\text{Zn}(\text{CN})_4]^{2-}$ by H_2O_2 carried out in borax buffer we observed an opposite effect in

which the rates of oxidation in the buffer were greater than those in unbuffered solutions (See section 2.3.I). The only explanation we can offer for these observations is that H_2O_2 and the peroxyborate species formed have different reactivities towards free CN^- and $[\text{Zn}(\text{CN})_4]^{2-}$. After one day, oxidations carried out in all the above buffers and in unbuffered solutions proceeded almost to completion ($>99\%$ CN^- removed) as measured using the cyanide electrode. However as can be seen from the graphs the reaction profile over the first four hours of reaction was different according to the buffer used.

Graph 1.3.iv. Oxidations of $\text{CN}^- (10^{-2} \text{M})$ by $\text{H}_2\text{O}_2 (6.0 \times 10^{-2} \text{M})$ carried out in unbuffered solution, phosphate, bicarbonate and borax buffers. (For details of buffers see experimental section 1.6).



Oxidations of CN^- carried out in bicarbonate buffer (pH 9 to 10), showed the most pronounced buffer effect on the rates of reaction. In all cases the initial rate of oxidation was approximately the same as in unbuffered solution but after about one hour this rate decreased and the oxidation was completely halted within three hours,

leaving 60-70% of the CN^- unaffected. When the H_2O_2 and $[\text{HCO}_3]^-$ were premixed and the CN^- added after one hour only 7% of this was oxidised in total, indicating that the $[\text{HCO}_3]^-$ was reacting with the H_2O_2 in some way. The logical explanation for this is the formation of a peroxocarbonate species¹¹⁴, which we think may be responsible for the extra peak sometimes observed in ^{13}C NMR spectra of reaction solutions (see section 1.3.I.c). In this case, the $[\text{HCO}_3]^-$ was in excess (0.5M) and the pH was within the range in which these species are formed (pH 7 -10) and so this explanation seems most likely to account for the effects described. It would seem that peroxocarbonate is less effective as an oxidant than H_2O_2 for the oxidation of free CN^- and $[\text{Zn}(\text{CN})_4]^{2-}$ (see section 2.3.I).

In all our work involving the above buffers we could not achieve sufficient reproducibility to merit their use in the measurement of the kinetics of the oxidation of free CN^- by H_2O_2 . Some kinetic data were collected from oxidations carried out in a buffer comprising ammonia and ammonium chloride as we found that reactions carried out in this buffer occurred at the same rates as those in unbuffered solutions to which NaOH was added during the reaction to maintain the pH. This buffer was effective in controlling the pH during the reaction. In retrospect, our original decision to carry out oxidations between pH 9 and 10 was unfortunate as this coincided with the pH range over which there was the greatest change in the rate of oxidation

1.3.IV. The effects of ionic strength, UV light, sequestrants and radical traps.

In a practical sense the use of peroxidic oxidants especially at elevated pH is fraught with potential hazards. Much of our early work was hampered because the H_2O_2 decomposed at a disproportionately high rate relative to the oxidation of CN^- . Obviously reproducible data are essential in any study and the factors mentioned in this section were all investigated for their potential to alter the course of the reaction.

a. Ionic strength.

Reaction rates can be dependent upon the ionic strength especially when the concentrations of the reactants are low. This is known as the kinetic salt effect and the effect on the rate can be summarised by the equation below.¹²¹

$$\log k_{\text{obs}} = \log k_{\text{obs}}^{\circ} + 2Az_{\text{A}}z_{\text{B}}(I)^{0.5}$$

where k_{obs} is the observed rate constant

k_{obs}° is the rate coefficient when all activity coefficients are unity

A is the Debye Constant in Debyes (D).

$z_{\text{A}}z_{\text{B}}$ are the charges on the reactants

I is the ionic strength of the solution in mol kg^{-1} .

In simple terms, if the reactants are ions of the same charge, as would be the case at high pH where the reactants are CN^- and $[\text{HO}_2]^-$, increasing the ionic strength should increase the rate as the activated complex formed when the ions collide would interact favourably with the denser ionic atmosphere of the solution. However in the pH range in which we have carried out our studies (approximately 8 to 10), the reactants would be mostly H_2O_2 and CN^- above pH 9.2, (the pK_{a} of CN^- ¹¹⁸), and below this value a larger proportion of the cyanide would be present as HCN . If the reaction pathway proceeds via these uncharged species, then the rate of oxidation should be independent of the ionic strength but if the rate determining step in the mechanistic route involves the

interaction of two charged particles then there should be some dependence upon this parameter.

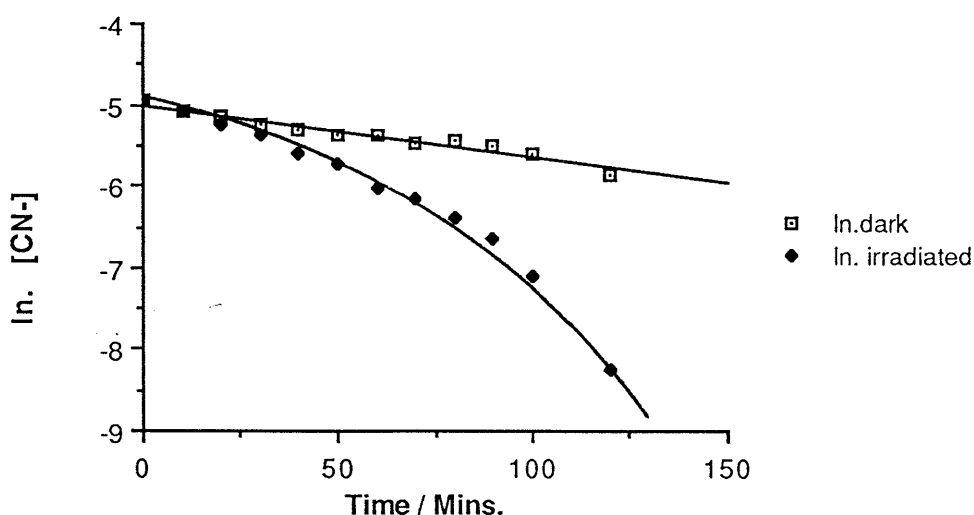
Our observations of reactions in buffer solutions suggested that, even with the phosphate and ammonia buffers where there are no peroxy complexes formed the rates of oxidations were not identical to those in unbuffered solutions (see graph 1.3.iv), and it is possible that this difference was due to the increased ionic strength of the buffered solution. To investigate this further oxidations were carried out in excess KCl or NaClO₄, which are commonly used to increase the ionic strength in kinetic studies. Oxidations carried out in excess KCl proceeded at an almost identical rate to those in unbuffered reactions, whilst for those carried out in the presence of excess NaClO₄ there was only a very slight retardation of rate which we attribute more to the drop in pH accompanying these reactions than to any kinetic salt effect. Thus it would appear that in the conditions in which we have studied the oxidation of free CN⁻ by H₂O₂, these being a pH range of 8 to 10 and using a large excess of H₂O₂, the ionic strength of the solutions does not have a measurable effect on the rate of the reaction.

b. UV light.

In his early study of the reaction between H₂O₂ and CN⁻ Masson⁴ concluded that there was some acceleration due to light. Serpone *et al*¹⁹ studied this effect in detail when investigating the photochemical reduction of Au(III) in cyanide solutions containing H₂O₂ and concluded that the observed rate constants for the irradiated oxidations of CN⁻ were about ten times greater than for the dark process. In our studies we carried out oxidations in brown flasks, thus excluding light altogether; in UV screened Pyrex flasks; and in open vessels under a UV lamp. We found that for oxidations in the dark and in UV screened flasks there was little difference in the rates compared with similar reactions in which the effect of light was not considered. It is probable that this was because Pyrex strongly absorbs UV radiation below ca. 320 nm and so "normal" oxidations in Pyrex volumetric flasks and beakers were effectively

screened from short wavelength UV light. When directly irradiated by UV light, oxidations were observed to proceed more quickly than those carried out under normal conditions and pseudo first order kinetics were not followed, i.e. a plot of $\ln.[\text{CN}^-]$ against time was not a straight line as is shown in graph 1.3.v below. The increase in rate was not as great as that observed by Serpone although the power of the lamp that we used was less, (440 W) compared to that in the published study (1000 W).¹⁹ Solutions of free CN^- irradiated by UV light did not appear to decompose to a measurable extent over three hours indicating that the catalysis of the reaction in this case was due to the photochemically-induced decomposition of the H_2O_2 . However it is known that cyanide and cyanide complexes will decompose slowly under UV irradiation and this is used to lower the concentration of cyanide waste in areas in which there is strong sunlight.¹²²

Graph 1.3.vi. First order plot for the oxidation of CN^- ($2 \times 10^{-3} \text{ M}$) by H_2O_2 ($6 \times 10^{-2} \text{ M}$) carried out in the dark ($k_{\text{obs}} = 6.36 \times 10^{-3} \text{ s}^{-1}$) and irradiated by UV light.



c. Sequestrants.

Another factor that can affect the stability of H_2O_2 is the presence in solution of transition metal cations. A number of oxidations were carried out in solutions to which had been added Dequest 2060 (diethylenetriamine-NNN'N"N"-pentamethylene-phosphonic acid)¹²³, a metal sequestering agent, to assess the possible effect of any metal ions present. Initially the oxidations were completely halted by these additions but it was found that the pH had dropped to 3 due to the acidity of the Dequest. When the pH was corrected oxidations proceeded at the same rate but the decomposition curves had lower errors and were more reproducible. However, Dequest was found to attack the surface of the cyanide selective electrode, thus interfering with the analysis of CN^- . It is likely that the presence of impurities in the solutions is a major cause of irreproducibility in this type of reaction and so practices were devised to ensure that all reactions were as clean as possible (see experimental section 1.6).

d. Radical traps.

There is a possibility that the oxidation of free CN^- proceeds by a free radical pathway, and this is supported by the observation that irradiation of reaction solutions increases the rate of oxidation and similar observations for other reactions involving H_2O_2 .^{19,35} To test this possibility we carried out a number of oxidations of CN^- (10^{-3}M) by H_2O_2 (0.054M) in the presence of added ethanol and methanol (5% v/v). We saw no evidence of retardation of these reactions but we were unable to conclude that there was no radical pathway for the reaction, only that any radical species formed were not trapped by ethanol or methanol. A more complete study would be required to conclusively determine whether or not the reaction proceeds via radical pathways.

1.3.V. Catalysts for the reaction between CN^- and H_2O_2 .

Many metal ions are reported to have catalytic properties for this reaction (see section 1.1). We have investigated the propensity of a number of these ions to increase the rate of oxidation. They can roughly be split into two groups: (a). copper species which are known to be particularly active as catalysts for the CN^- : H_2O_2 reaction, and (b). other metal ions, some of which have been shown to form peroxo complexes in solution with H_2O_2 . However it must be noted that the studies were not all carried out using the same conditions and so not all the data are directly comparable.

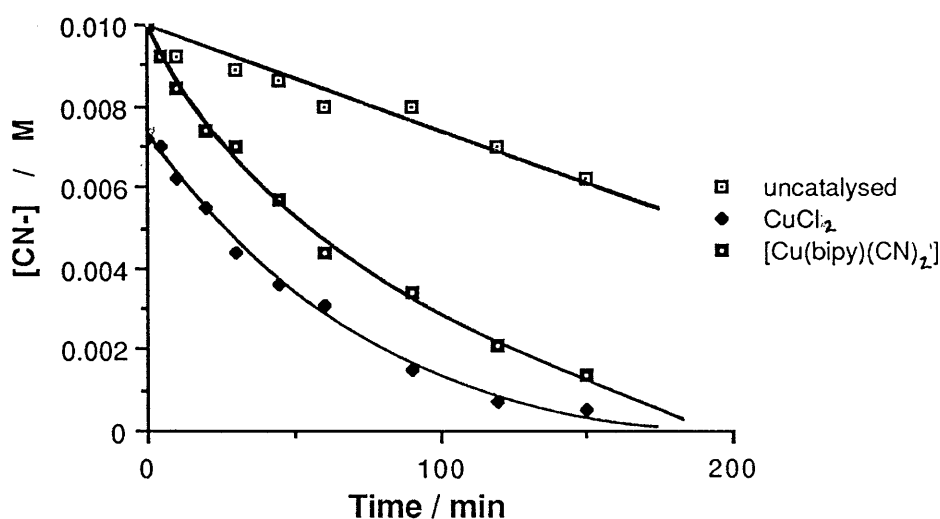
a. Catalysis by copper(I) and copper(II) species.

Of all the metal ions reported to have catalytic properties for the oxidation of CN^- by H_2O_2 salts of Cu(I) and Cu(II) have been used most frequently. We have used a number of different species to investigate catalysis using copper salts. The results are summarised in graphs 1.3.vi and 1.3.vii below.

In the reaction with added copper(II) chloride the catalytic effect was clearly demonstrated although pseudo first order kinetics were not observed. The CN^- concentration of the solution was measured using the cyanide selective electrode to be 10^{-2} M prior to the addition of the CuCl_2 (10^{-3} M) but this fell to only 7.0×10^{-3} M when the catalyst was added and before the addition of the H_2O_2 . The solution turned yellow after one hour of reaction (although this colour change has been observed within twenty minutes in other, similar reactions), and a fine brown precipitate was observed at the end of the oxidation, which had no IR peaks attributable to cyanide or cyanate in the ν_{CN} region ($2000\text{--}2300\text{ cm}^{-1}$). The other curve on graph 1.3.vi shows the progress of an oxidation of free CN^- carried out in the presence of $[\text{Cu}(\text{bipy})(\text{CN})_2]$, one of the first Cu(II) cyanide complexes to be prepared.¹²⁴ The rate of oxidation was slightly less with this purple complex than in the oxidation carried out with added copper(II) chloride and there was no apparent decrease in the CN^- concentration when the catalyst

was first added. During the oxidation the catalyst changed colour to light brown and the IR peaks in the ν_{CN} region of the spectrum of $[\text{Cu}(\text{bipy})(\text{CN})_2]$ which occurred at 2120 and 2100 cm^{-1} were replaced by new bands at 2220, 2170 and 2108 cm^{-1} in the IR of the solid after the oxidation. These bands indicate that some of the cyanide in the original complex had been oxidised to cyanate but the product was not $[\text{Cu}(\text{bipy})(\text{NCO})_2]$, which might have been expected, as this is a blue complex with a single strong IR band at 2200 cm^{-1} (see section 3.3). From these observations we conclude that the $[\text{Cu}(\text{bipy})(\text{CN})_2]$ was partially destroyed by the H_2O_2 in the reaction, thus releasing $\text{Cu}(\text{II})$ into the solution which acted as the catalyst.

Graph 1.3.vi. The oxidation of free CN^- (10^{-2} M) by H_2O_2 (0.09 M) in the absence of catalyst, and in the presence of added CuCl_2 (10^{-3} M), and $[\text{Cu}(\text{bipy})(\text{CN})_2]$ (10^{-3} M).

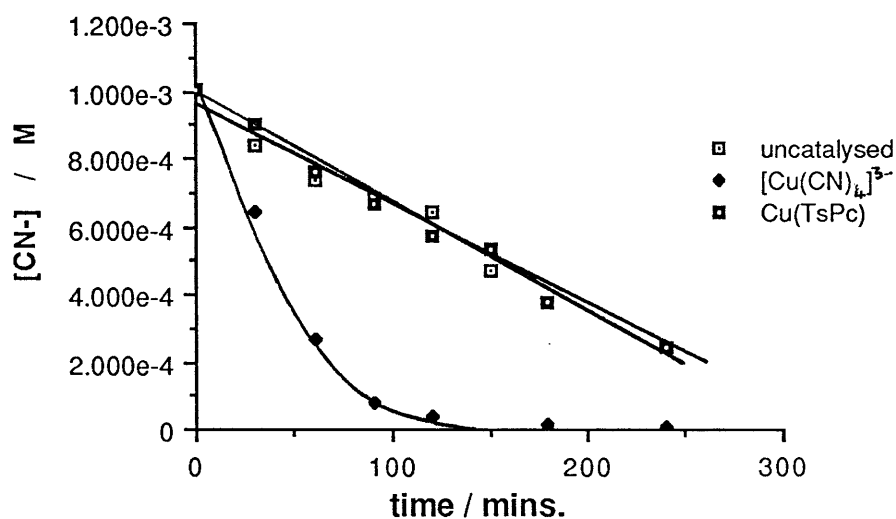


We found that $[\text{Cu}(\text{CN})_4]^{3-}$ had approximately the same catalytic activity as aqueous solutions of copper(II) chloride and sulphate although the concentration of CN^- as measured using the cyanide selective electrode did not fall when the $[\text{Cu}(\text{CN})_4]^{3-}$ was added, and in some experiments, occasionally increased. As in the oxidations

catalysed by Cu(II) salts, a yellow colouration was seen in the solution at times after 20 minutes although under the conditions of the experiment shown in graph 1.3.vii this was not observed until 90 minutes after the addition of the H_2O_2 .

There was no catalysis observed when copper phthalocyanine tetrasulphonic acid $[\text{Cu}(\text{TsPc})]$ was added to reaction solutions. The characteristic electronic spectrum (absorbance maxima at 328, 608 and 694 nm.) of this intense blue species was unchanged after the oxidation of free CN^- was complete indicating that it was unaffected by H_2O_2 . It is reasonable to conclude that the very strong planar, phthalocyanine ligand prevents the formation of catalytic intermediates at the metal centre.

Graph 1.3.vii. The catalytic effects of $[\text{Cu}(\text{CN})_4]^{3-}$ (10^{-5}M) and $\text{Cu}(\text{TsPc})$ (10^{-5}M) in the oxidation of free CN^- (10^{-3}M) by H_2O_2 (0.048M).

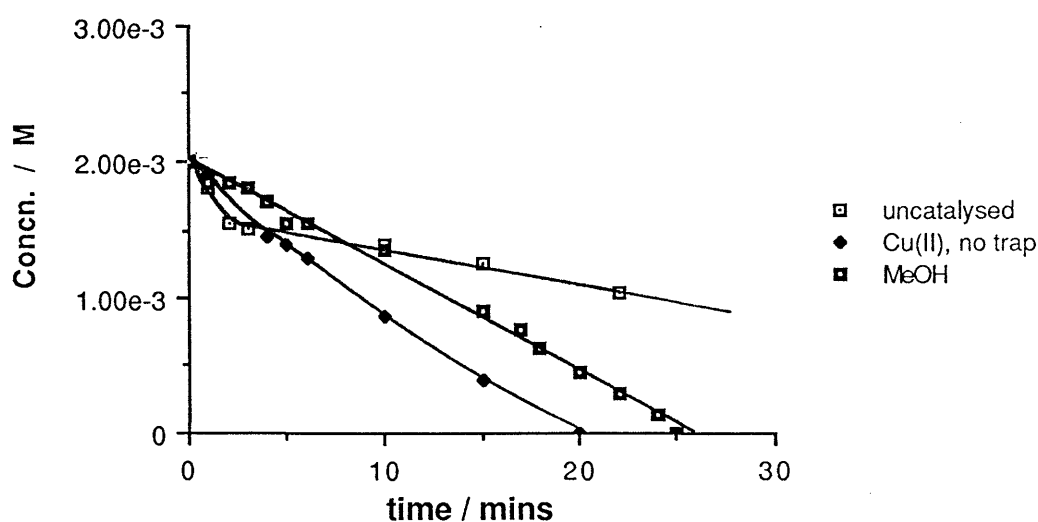


In copper catalysed oxidations of free CN^- ($2 \times 10^{-3}\text{M}$) by H_2O_2 (0.18M) in the presence of added radical traps (5% v/v), we observed a slight retardation of the catalysed reaction, although the rate was still much faster than an uncatalysed reaction. This observation suggests that one possible role that the copper could play in catalysing the oxidation of free CN^- is the promotion of the formation of radical species, probably

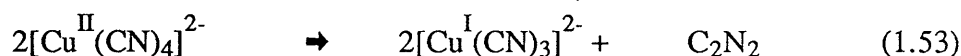
OH from the H_2O_2 .¹²⁵ This retardation was observed using ethanol, methanol and DMSO, although the effect was greatest with added methanol, which is shown in graph 1.3.viii. below.

In addition to the above homogeneous studies, we attempted to use $[\text{Cu}(\text{CN})_3]^{2-}$ adsorbed on basic alumina as a heterogeneous catalyst for the oxidation of free CN^- by H_2O_2 . Some $\text{Cu}(\text{II})$ species adsorbed on alumina have been used industrially.^{15,17} (For full details of the preparation of this and a more comprehensive discussion see section 3.1.II). Unfortunately we found that some of the adsorbed complex was dissolving into the reaction solutions and thus we could never be sure of the concentration of the catalyst in solution. This made it impossible to assess the extent of heterogeneous catalysis and so only qualitative observations were made. In the oxidation of CN^- ($2 \times 10^{-3} \text{ M}$) by H_2O_2 (0.16M) catalysis by $[\text{Cu}(\text{CN})_3]^{2-}$ adsorbed on basic alumina was the same as that catalysed by an equivalent concentration of copper(II) chloride dissolved in the solution.

Graph 1.3.viii. Oxidation of free CN^- ($2 \times 10^{-3} \text{ M}$) by H_2O_2 (0.18M) in the presence of CuSO_4 ($4 \times 10^{-5} \text{ M}$), and with added methanol (5% v/v).



A possible explanation for these observations is as follows: In solution copper(I) ions will form complexes with CN^- ions, these being $[\text{Cu}(\text{CN})_2]^-$, $[\text{Cu}(\text{CN})_3]^{2-}$ and $[\text{Cu}(\text{CN})_4]^{3-}$ and their respective concentrations will vary according to the ratio of $\text{Cu(I)} : \text{CN}^-$ present in solution as studied by Griffiths *et al.*¹²² If Cu(II) ions are added to a solution of CN^- at $\text{pH} > 7$, a transient wine red intermediate is formed (below this pH the colouration is green) which has been studied at low temperature using electronic spectroscopy¹²⁶ and ESR.¹²⁷ The species is thought to be $[\text{Cu}(\text{CN})_4]^{2-}$ which rapidly decomposes according to the equation .



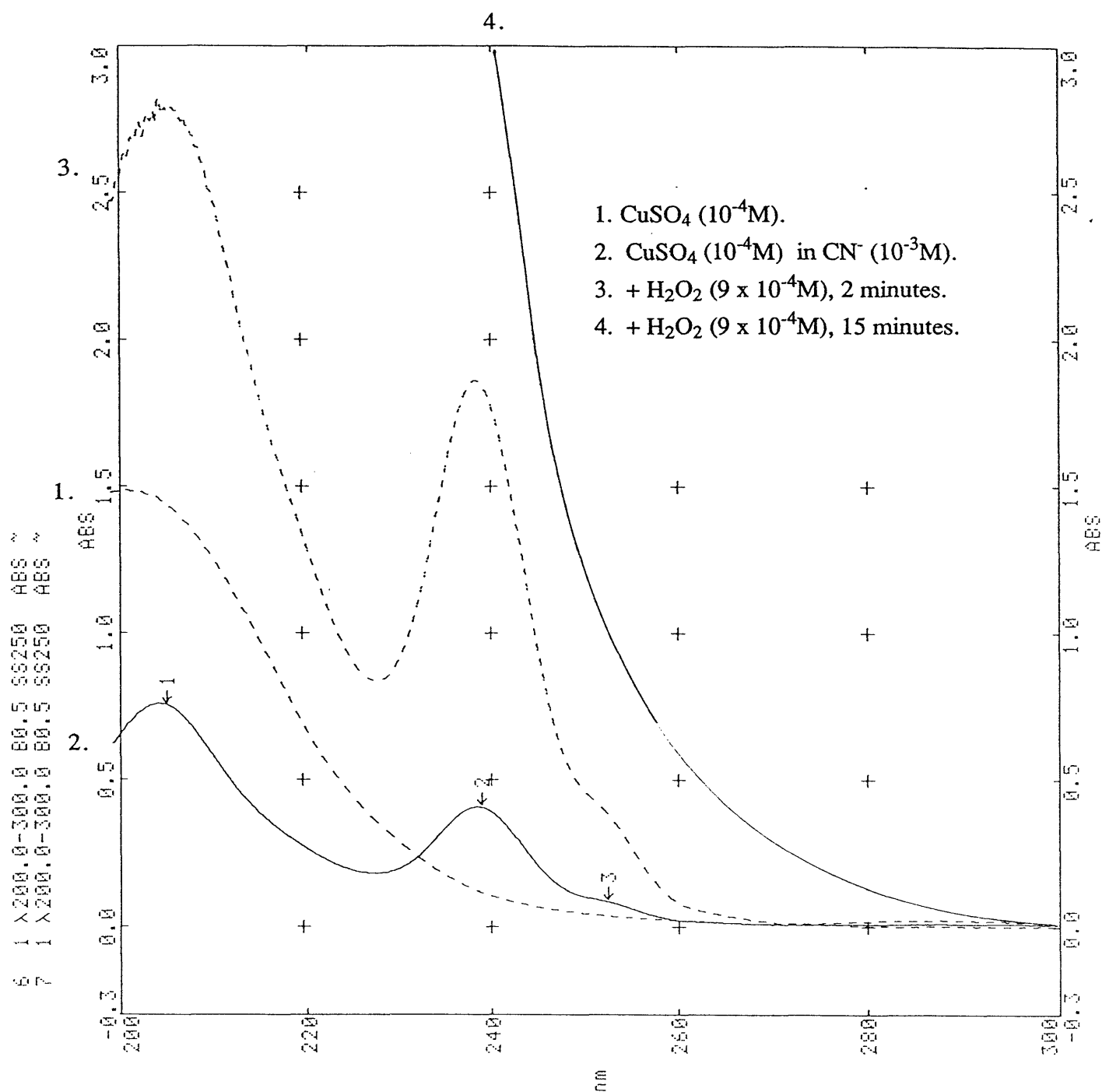
At room temperature, we found that absorption maxima at 205, 238 and 252 nm. due to $[\text{Cu}(\text{CN})_4]^{3-}$ were formed as soon as a solution of CN^- ($2 \times 10^{-3} \text{ M}$) was added to an aqueous solution of CuSO_4 ($3 \times 10^{-4} \text{ M}$).

This reduction reaction would account for the apparent decrease in the concentration of free CN^- , as measured using the cyanide selective electrode, when Cu(II) salts were added to reaction solutions. That cyanide which was present as $[\text{Cu}(\text{CN})_3]^{2-}$ would not be detected by the electrode since the overall stability of this complex ($\beta_3 = 29.2^{84}$) is greater than that of $[\text{Ag}(\text{CN})_2]^-$ ($\beta_2 = 20.4^{84}$), (see section 1.2).⁸⁷ This was not of major importance in most of our reactions because the catalyst was generally present very low concentrations relative to the concentration of free CN^- and so only a small proportion of the CN^- was destroyed by the above reaction.

The yellow colouration observed in the oxidations catalysed by Cu(I) and Cu(II) species was almost certainly due to the intermediate which is formed in the copper catalysed decomposition of H_2O_2 to H_2O and O_2 at pH above 8. This has been studied in some detail using electronic spectroscopy^{128,129} and ESR¹³⁰ at pH between 11 and 12 and is thought to be $[(\text{HO})_2\text{Cu}(\text{OOH})]^-$ which decomposes to a brown precipitate. Unfortunately this has no characteristic absorption maxima in the electronic spectrum which we could have used to detect its formation before the yellow colour

appeared in the solution. The published study¹²⁸ followed the decomposition of the species using the absorption at 345nm ($\epsilon = 1600 \text{ M}^{-1} \text{ cm}^{-1}$) but the conditions were not the same as in our investigations. We found that the intensity of the absorption maximum at 237 nm due to $[\text{Cu}(\text{CN})_4]^{3-}$ in a solution of CuSO_4 (10^{-4} M) dissolved in free CN^- (10^{-3} M) at pH 9.7 increased upon the addition of H_2O_2 ($9 \times 10^{-4} \text{ M}$). After 15 minutes the solution turned yellow and in the electronic spectrum there was only one very intense absorption maximum at ca. 240 nm. The spectra are reproduced below in fig 1.3.iv. The UV bands of $[\text{Cu}(\text{CN})_3]^{2-}$ and $[\text{Cu}(\text{CN})_4]^{3-}$ lie very close to the more intense maxima of H_2O_2 and $[(\text{HO})_2\text{Cu}(\text{OOH})]^-$, which both occur at ca. 240 nm so we were unable to follow the oxidation of the cyano species and could not conclusively show which of the above moieties was a catalytic intermediate.

Fig.1.3.iv. Electronic spectra showing the changes that occur when H_2O_2 ($9 \times 10^{-4} \text{ M}$) was added to a solution of CuSO_4 (10^{-4} M) dissolved in CN^- (10^{-3} M).



b. Catalysis by other metal complexes.

Although salts of Cu(I) and Cu(II) are reported to be the most effective catalysts for the oxidation of free CN^- by H_2O_2 , a number of other metal species have some catalytic effect in the reaction.⁹ The following table 1.3.iii briefly summarises some of the results obtained using a variety of other metal complexes as catalysts for the reaction.

Table 1.3.iii Use of metal complexes in the oxidation of CN^- by H_2O_2 (0.16M) as measured using the cyanide selective electrode.

Metal species	conc. (M)	pH	initial $[\text{CN}^-]$ (M)	% CN^- removed in one hour
-	-	9.5	5×10^{-3}	48
FeSO_4	2×10^{-5}	9.5	5×10^{-3}	54
CoCl_2	2×10^{-5}	9.44	5×10^{-3}	50
CrCl_3	2×10^{-5}	9.49	5×10^{-3}	50
-	-	9.5	1.8×10^{-3}	22
$\text{Ni}(\text{NO}_3)_2$	1×10^{-5}	9.35	1.8×10^{-3}	68
$\text{Ni}(\text{TsPc})$	1×10^{-5}	9.45	1.8×10^{-3}	67
$\text{Zr}(\text{NO}_3)_4$	1×10^{-5}	9.0	1.8×10^{-3}	50

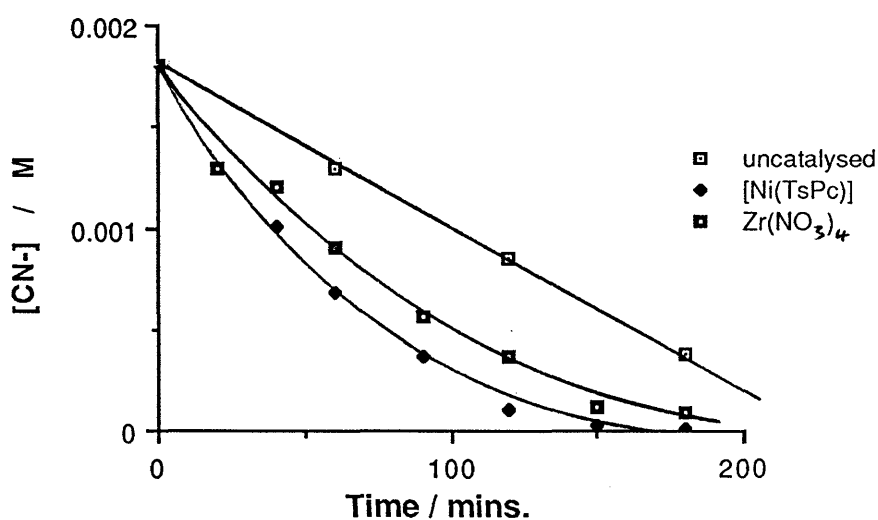
From the above table it can be seen that there was very little catalytic effect due to FeCl_3 , CoCl_2 and CrCl_3 . These results are in agreement with the literature.^{9,17}

When used as catalysts in aqueous solution both nickel(II) nitrate and $[\text{Ni}(\text{TsPc})]$ were found to have almost identical catalytic effects, which were less than those found with an equivalent concentration of a Cu(II) salt. However, the electronic spectrum of the green $[\text{Ni}(\text{TsPc})]$ changed during the course of the reaction and it is reasonable to assume that it was reacting with H_2O_2 , unlike $[\text{Cu}(\text{TsPc})]$ which we

found was unaffected by H_2O_2 . (A solution of $[\text{Ni}(\text{TsPc})]$ (10^{-5}M) in H_2O_2 (0.16M) was decolourised when left for one week). Taking into account the absence of any effect of H_2O_2 on $[\text{Cu}(\text{TsPc})]$ and the lack of catalysis of oxidation of CN^- by this complex we can suggest the following explanation for our observations. In $[\text{Cu}(\text{TsPc})]$ there is planar coordination of the phthalocyanine ligands around the metal centre. If there is axial coordination of H_2O_2 molecules this is likely to be fairly weak owing to Jahn-Teller distortion effects. In $[\text{Ni}(\text{TsPc})]$ in aqueous solution, it is quite possible that $\text{trans-}[\text{Ni}(\text{H}_2\text{O}_2)_2(\text{TsPc})]$ is present, since octahedral Ni(II) is relatively common. There is no evidence indicating that the catalytic intermediate involves a Ni(II) cyanide species as there was no change in the electronic spectrum when $[\text{Ni}(\text{TsPc})]$ and CN^- were mixed and furthermore $[\text{Ni}(\text{CN})_4]^{2-}$, which would be formed when an aqueous solution of nickel(II) nitrate was added to excess CN^- , is a moderately stable complex which is not easily oxidised by H_2O_2 . This reaction is discussed in detail in chapter 2. These results are in agreement with those reported by Gierzatowicz, who observed a greater catalytic effect using Ni(II) than with other transition metals.¹⁷ The graph below (1.3.ix) shows how the oxidations of CN^- by H_2O_2 progress in the presence of aqueous solutions of $[\text{Ni}(\text{TsPc})]$ and $\text{Zr}(\text{NO}_3)_4$.

Our work using buffer solutions indicated that different peroxy species had different reactivities towards free and complexed cyanides (see sections 1.3.III and 2.3.I). One possible reason that Cu(I) and Cu(II) salts are such effective catalysts for the oxidation of free CN^- by H_2O_2 is the formation of the peroxy complex $[(\text{HO})_2\text{Cu}(\text{OOH})]^-$ that we have discussed above. Graph 1.3.ix below shows that an aqueous solution of $\text{Zr}(\text{NO}_3)_4$ (10^{-5}M) had a slight catalytic effect on the oxidation reaction. The Raman spectrum of a solution containing zirconium(IV) nitrate (1g, 2.95×10^{-3} mols) and H_2O_2 (0.0108 mols) in H_2O (10 cm^3) had two peaks at 857 and 845 cm^{-1} which we attribute to the formation of a Zr(IV) peroxy complex¹³¹, this presumably being the reason for the catalytic activity shown by solutions of $\text{Zr}(\text{NO}_3)_4$ in the oxidation of free CN^- .

Graph 1.3.ix. The oxidation of free CN^- ($1.8 \times 10^{-3} \text{M}$) by H_2O_2 (0.16M) ($k_{\text{obs}} = 2.05 \times 10^{-4} \text{s}^{-1}$), and in the presence of $[\text{Ni}(\text{TsPc})]$ (10^{-5}M) and $\text{Zr}(\text{NO}_3)_4$ (10^{-5}M).



The complex ions $[\text{WO}_4]^{2-}$, $[\text{MoO}_4]^{2-}$ and $[\text{VO}_4]^{3-}$ all form coloured peroxy complexes which have been characterised in solution and have been used as cocatalysts in other peroxidic oxidations.¹³² The results obtained when they are added to oxidation mixtures at pH 10 to 11 are summarised in table 1.3.iv. below.

Table 1.3.iv. Oxidation of CN^- (0.1M) by H_2O_2 (0.1M) with added ions at pH 10 to 11.

Ion	Conc. / M.	% oxidation after 16 hours.
-	-	90
$[\text{MoO}_4]^{2-}$	0.08	72
$[\text{WO}_4]^{2-}$	0.006	99
$[\text{VO}_4]^{3-}$	0.05	-

The red colour which formed on addition of $[\text{MoO}_4]^{2-}$ to oxidation solutions at pH 11 arises from the $[\text{Mo}(\text{O}_2)_4]^{2-}$ species.¹³² This colour faded during the reaction time indicating that the Mo(VI) peroxo complex was being decomposed but nevertheless the overall proportion of CN^- oxidised was less than in a solution to which only H_2O_2 had been added. This contrasted with the degree of oxidation achieved by the yellow $[\text{W}(\text{O}_2)_4]^{2-}$, formed from $[\text{WO}_4]^{2-}$ and H_2O_2 . In this reaction nearly all of the CN^- was oxidised, more than was oxidised in the uncatalysed reaction. At pH 10 the ion $[\text{VO}_4]^{3-}$ reacted with H_2O_2 to form $[\text{VO}_2(\text{O}_2)_2]^{3-}$, a yellow orange species¹³³ which retained this colour even after one day, indicating it was a more stable complex; no CN^- was oxidised in this reaction.

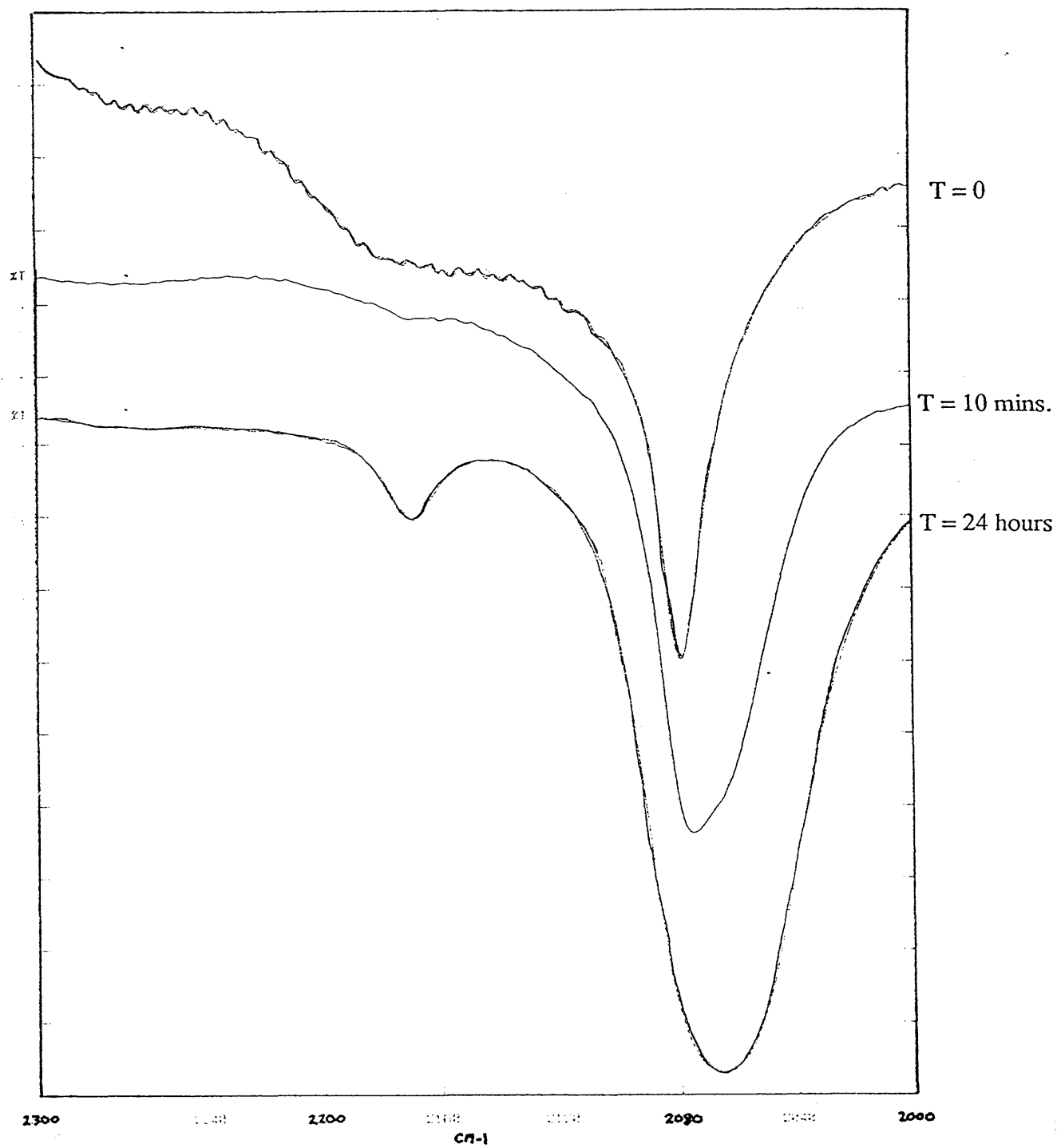
1.3.VI. The oxidation of free CN^- by H_2O_2 in the presence of thiosulphate ions.

It has long been known that elemental sulphur will react with CN^- in aqueous solution to produce SCN^- ¹³⁴, and CdS has been used in conjunction with H_2S and visible light to achieve the same reaction.⁵⁸ More recently a new reaction was reported in which the oxidation of cyanide by H_2O_2 at pH 7 to 9 was carried out in the presence of $[\text{S}_2\text{O}_3]^{2-}$ ions and SCN^- was produced rather than NCO^- .⁵ The reactions describing the mechanism of the reaction are given in section 1.1.I (equations 1.4 to 1.6) but to summarise, the oxidising species was thought to be $[\text{HOS}_2\text{O}_3]^-$, formed from the reaction between $[\text{S}_2\text{O}_3]^{2-}$ and H_2O_2 . The kinetics of the interaction between these species in the presence and absence of free CN^- were measured and the data computer fitted to a third order polynomial expression. We have studied this reaction using the spectroscopic techniques described in section 1.3.I and our results are discussed below.

a. Following the oxidation reaction by FTIR.

When a solution of CN^- (0.1M) in $[\text{S}_2\text{O}_3]^{2-}$ (0.1M) was oxidised by H_2O_2 (1M) the peak due to the ν_{CN} of free CN^- at 2080 cm^{-1} was swiftly replaced within five minutes by a new, stronger peak at 2060 cm^{-1} which can be attributed to the ν_{CN} of free SCN^- which is reported to occur at 2065 cm^{-1} .¹³⁵ We have measured the extinction coefficient of this peak to be $\epsilon = 456\text{ mol}^{-1}\text{ cm}^{-1}\text{ dm}^3$ which was stronger than the ν_{CN} of free CN^- ($\epsilon = 19\text{ mol}^{-1}\text{ cm}^{-1}\text{ dm}^3$) but not as strong as the equivalent peak in free NCO^- ($\epsilon = 1330\text{ mol}^{-1}\text{ cm}^{-1}\text{ dm}^3$). When excess H_2O_2 was added the SCN^- peak began to decrease in intensity and was replaced by another peak at 2170 cm^{-1} , due to free NCO^- . The spectra showing this are reproduced below in fig 1.3.v.

Fig.1.3.v. FTIR spectrum showing the oxidation of CN^- (0.1M) by H_2O_2 (1M) in the presence of added $[\text{S}_2\text{O}_3]^{2-}$ (0.1M).

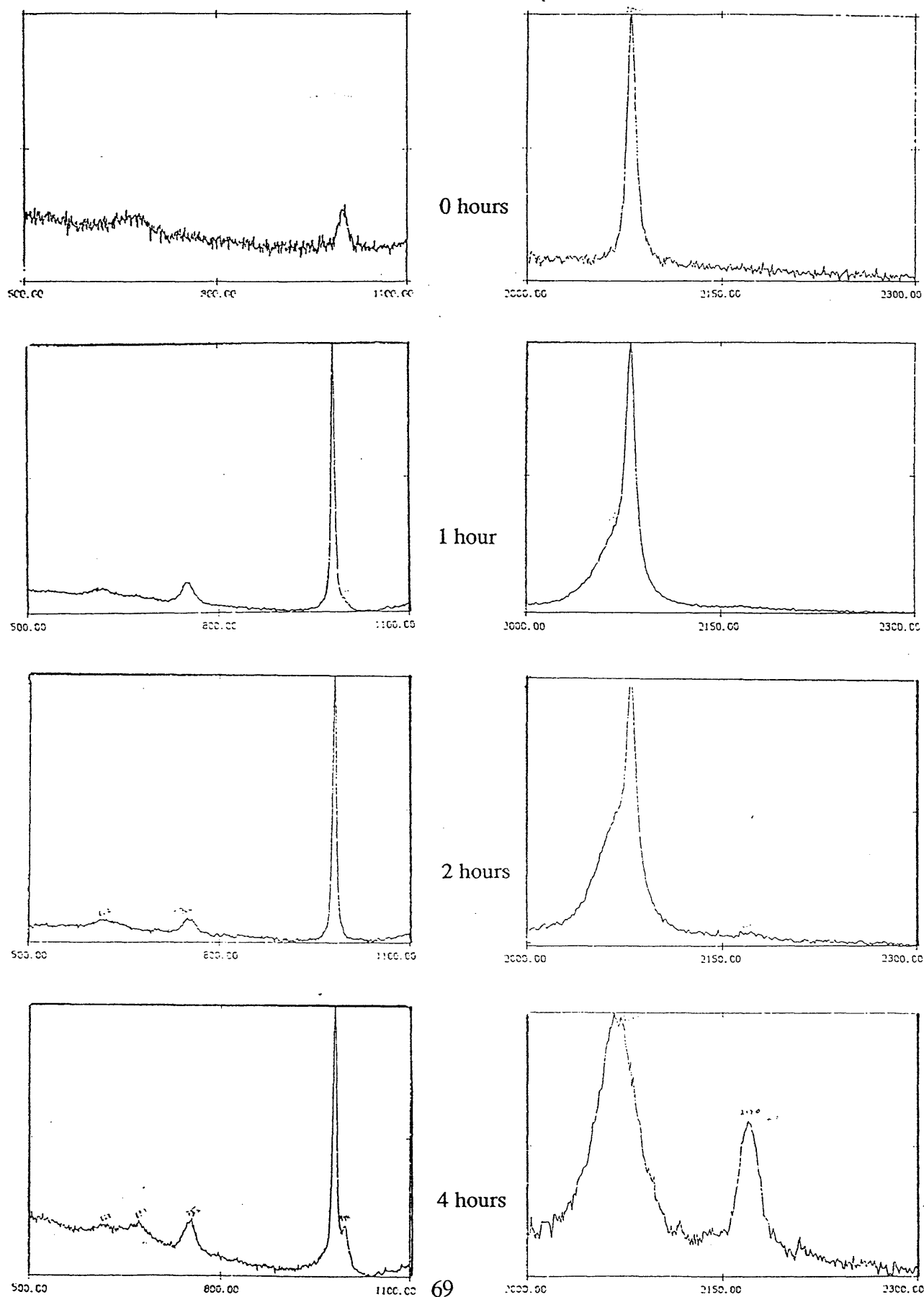


b. Raman spectroscopic study of the reaction.

The reaction between CN^- (1.5M), $[\text{S}_2\text{O}_3]^{2-}$ (1.5M) and H_2O_2 (portions of 0.5M) was followed at intervals for four hours using Raman spectroscopy in order to detect other intermediates and products in the reaction. Initially the only peaks observed in the spectrum, run from $500\text{-}1100\text{cm}^{-1}$ and $2000\text{-}2300\text{cm}^{-1}$ occurred at 2020cm^{-1} , due to ν_{CN} of free CN^- and at 670 and 1002cm^{-1} due to $[\text{S}_2\text{O}_3]^{2-}$. After one hour of reaction a shoulder had appeared at around 2060cm^{-1} which we attribute to the ν_{CN} of free SCN^- .¹³⁵ In the lower scan group a peak appeared at 755cm^{-1} which was most probably the δ_{NCS} of free SCN^- and a strong peak at 981cm^{-1} , which coincided with ν_{SO} for $[\text{SO}_4]^{2-}$ and a weaker band at 622cm^{-1} which was assigned to δ_{SO} .¹³⁶ The peak that can be seen in the spectra below in fig 1.3.vi. at 998cm^{-1} was due to unreacted $[\text{S}_2\text{O}_3]^{2-}$ in the solution.

After two hours reaction the shoulder at 2060cm^{-1} was more pronounced as more SCN^- was formed in the reaction. The vibrations due to $[\text{SO}_4]^{2-}$ at 982 and 619cm^{-1} had increased in intensity and the only other peak was at 749cm^{-1} (δ_{NCS} of free SCN^-). After four hours and when excess H_2O_2 had been added to the reaction the CN^- peak at 2080cm^{-1} had disappeared to leave the residual SCN^- visible as a peak at 2066cm^{-1} and a new peak appeared at 2170cm^{-1} which indicated that the SCN^- was being oxidised to NCO^- . The peaks visible in the lower scan group were the same as discussed above at 981 and 612cm^{-1} due to $[\text{SO}_4]^{2-}$ and 744cm^{-1} (NCS^-). The spectra recorded in this study are reproduced overleaf in figure 1.3.vi.

Fig.1.3.vi. Raman study of the reaction between CN^- (1.5M), $[\text{S}_2\text{O}_3]^{2-}$ (1.5M) and H_2O_2 (portions of 0.5M).



c. Study of the reaction by ^{13}C NMR.

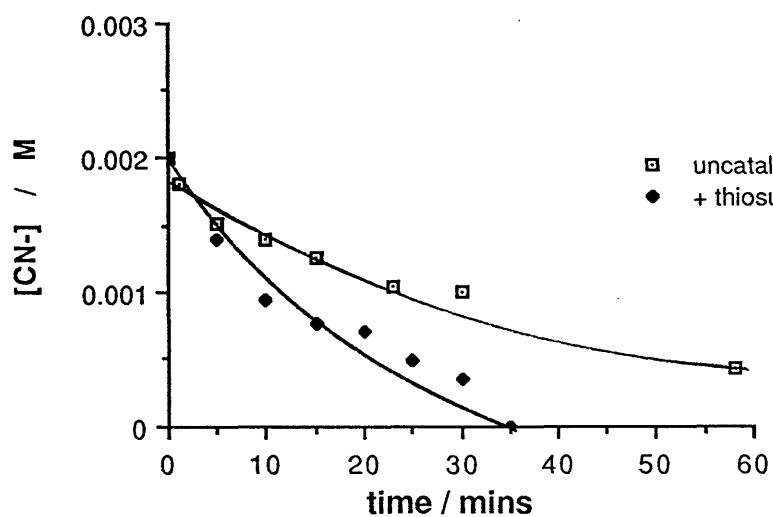
When the ^{13}C NMR spectrum was measured of a solution of CN^- (5M) and $[\text{S}_2\text{O}_3]^{2-}$ (5M) in H_2O_2 (1.5M) after thirty minutes of reaction, the following shifts (relative to Me_4Si) were observed. At 166.5 ppm lay a shift due to free CN^- , and at 134.5 ppm a second resonance that we attribute to free SCN^- in accordance with the literature.¹¹² No shifts attributable to NCO^- or carbonate were observed.

d. Conclusions.

We have confirmed that SCN^- is the initial product of the oxidation of free CN^- by H_2O_2 in the presence of $[\text{S}_2\text{O}_3]^{2-}$, and have shown that this intermediate will be further transformed into NCO^- , if H_2O_2 is in excess, and finally to ammonia and carbonate as discussed in section 1.3.1. If the $[\text{S}_2\text{O}_3]^{2-}$ is in excess the final product is SCN^- .

In a direct comparison of the oxidation of CN^- ($2 \times 10^{-3}\text{M}$) by H_2O_2 (0.18M) with a similar reaction containing $[\text{S}_2\text{O}_3]^{2-}$ ($5 \times 10^{-3}\text{M}$), we observed that the rate of oxidation of cyanide was greater if $[\text{S}_2\text{O}_3]^{2-}$ was present (see graph 1.3.x below) but first order kinetics were not followed and the H_2O_2 was used up more rapidly. These observations are in agreement with the published study in which kinetic data were fitted to a third order polynomial and the rate of decomposition of H_2O_2 by $[\text{S}_2\text{O}_3]^{2-}$ was also measured.⁵ It is worth noting that in our study no consideration was made of the competing reactions between H_2O_2 and CN^- , and also H_2O_2 and SCN^- , which might have some influence on the complexity of the data measured. There are separate studies on the latter reaction which are discussed in more detail in section 1.5 as the conditions were not comparable to those in our investigation.^{109,137,138}

Graph 1.3.x. The oxidation of free CN^- ($2 \times 10^{-3} \text{ M}$) by H_2O_2 (0.18M) at pH 9.3 and in the presence of $[\text{S}_2\text{O}_3]^{2-}$ ($5 \times 10^{-3} \text{ M}$).



1.4. Oxidations of Free CN^- using Persulphate.

The only published references to the oxidation of free CN^- mention that $[\text{S}_2\text{O}_8]^{2-}$ is effective only in strong solutions.^{9,23,24,26} It is also reported that cyanogen (C_2N_2) and not NCO^- is formed as an intermediate which then decomposes to form nitrate and CO_2 .

We carried out a short study of the oxidation of free CN^- by persulphate in buffer solutions using the cyanide selective electrode. At low concentrations of CN^- (10^{-3}M), with an excess of $[\text{S}_2\text{O}_8]^{2-}$ ($5 \times 10^{-2}\text{M}$) the following results in table 1.4.i were obtained.

Table 1.4.i. The oxidation of CN^- (10^{-3}M) with $[\text{S}_2\text{O}_8]^{2-}$ ($5 \times 10^{-2}\text{M}$).

Buffer (0.1M)	pH	% Oxidation.	
		5 hours, uncatalysed.	2 hours, CuSO_4 (10^{-5}M)
-	8.25-8.48	23	59
phosphate	8.01-8.90	30	90
borax	8.57-8.64	26	100
bicarbonate	8.64-8.93	-	35

It is clear from these figures that the degree of uncatalysed oxidation was approximately the same in borax and phosphate buffers as it was in unbuffered solution but that in carbonate buffer no oxidation occurred without a catalyst being present.

At high concentrations (CN^- and $[\text{S}_2\text{O}_8]^{2-}$ both 0.1M), no peak attributable to NCO^- was observed in the IR spectrum even when CuSO_4 ($4 \times 10^{-3}\text{M}$) was added. Both oxidation mixtures turned yellow in colour and a brown precipitate was formed. The elemental analysis showed %C, 27.61; %H, 2.74 and %N, 30.86 which corresponds to that of oxamide $(\text{CONH}_2)_2$, an intermediate in the hydrolysis of cyanogen¹³⁹ (requires C, 27.27; H, 4.54, N, 31.81%). The IR of the brown solid had

a band at 2162 cm^{-1} , indicating that some cyanide, or cyanogen was also being trapped in the lattice.

The Raman spectrum of an aqueous solution of $[\text{S}_2\text{O}_8]^{2-}$ (0.1M) at pH 9 had two strong peaks at 836 cm^{-1} ($\nu_{\text{O-O}}$) and 1076 cm^{-1} (ν_{SO}).¹⁴⁰ This spectrum changed little within one day even at pH 12, indicating that the $[\text{S}_2\text{O}_8]^{2-}$ species is relatively stable in solution at high pH, although after three days there were peaks due to the formation of $[\text{SO}_4]^{2-}$ indicating that decomposition was occurring slowly (see section 2.4.IV). When CN^- (0.1M) was oxidised by $[\text{S}_2\text{O}_8]^{2-}$ (0.5M) with added copper(II) sulphate (10^{-3} M), a third peak at 982 cm^{-1} rapidly appeared which could be assigned to the ν_{sym} of $[\text{SO}_4]^{2-}$.¹³⁶ No peak attributable to NCO^- was observed.

The data collected show that oxidations of free CN^- by $[\text{S}_2\text{O}_8]^{2-}$ proceed slowly unless a catalyst is present and confirm that NCO^- is not a reaction intermediate.

1.5. Studies of the Oxidation of Free Cyanate by Hydrogen Peroxide and Peroxy Salts.

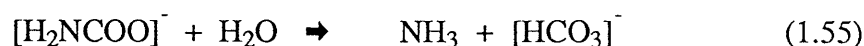
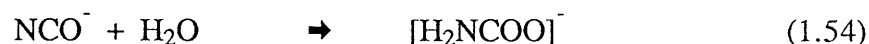
In this section we consider our studies on the reactions of free NCO^- in the systems that we have used to investigate the oxidation of free and complex cyanides. We start by summarising the published literature concerned with this subject, and in the second part of this section we discuss our own studies under the following headings.

- a. Spectroscopic and chemical investigations to determine the extent to which NCO^- is oxidised and/or hydrolysed by H_2O_2 .
- b. Quantitative studies of the reactions of NCO^- with H_2O_2 in the presence and absence of catalysts such as Cu(II) salts using both quantitative FTIR spectroscopy and Dionex HPIC.

The final part of this section concerns our observations on the effect of other oxidants, notably OCl^- , triple salt and $[\text{S}_2\text{O}_8]^{2-}$ on solutions containing NCO^- .

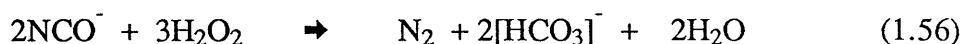
1.5.I. Review of the published work concerning the reactions of free NCO^- in aqueous solution.

There is apparently no published study of the oxidation of free NCO^- by H_2O_2 . However, a number of observations have been made with respect to the fate of NCO^- in the oxidation of free CN^- by H_2O_2 .^{4,19} Of the NCO^- formed in this reaction, it is reported that 60-80% is hydrolysed to form ammonia and bicarbonate via the carbamate ion as shown in the equations below.

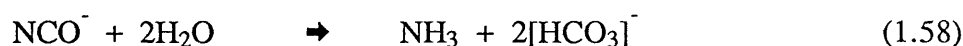
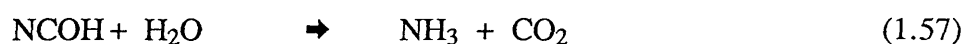


Oxidation of NCO^- is thought to account for the remaining 20-40% but there is no agreement as to the final products of this reaction.^{4,19,109} Both N_2 and nitrogen oxides have been proposed as the final form of the nitrogen although no contributory evidence

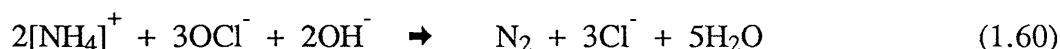
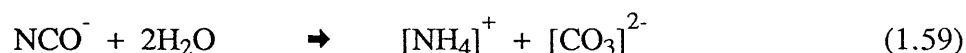
was supplied. A study of the oxidation of free SCN^- by H_2O_2 in alkaline solution showed that the initial product was NCO^- and the formation of $[\text{NO}_3]^-$ was also reported, although again there was no explanation of how this was detected.¹⁰⁹ The following equation would account for the formation of N_2 but not the nitrogen oxides mentioned above.



The hydrolysis of NCO^- has been studied in the pH range 0 to 7 and also in strong base.¹⁴¹ The rate constant for the first equation below was measured to be 0.047 min^{-1} at 18°C . Rate constants were also determined for the second reaction which predominates in alkaline solution but only at high temperatures, i.e. $70\text{-}94^\circ\text{C}$.



The oxidation of free NCO^- by hypochlorite has been the subject of a number of studies at different pH. At high pH (>11), the rate of reaction at room temperature was negligible even in the presence of excess OCl^- .¹⁴² At pH < 9.5 the following series of reactions were proposed.¹⁴³



The first of these reactions was catalysed by the presence of excess hypochlorite. The overall reaction was second order (first order with respect to each reactant) and at pH 9 to 10, and at 18°C , the k_{obs} was measured to be $0.13 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which decreased to $0.03 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at pH 7.1-7.5.^{39,40}

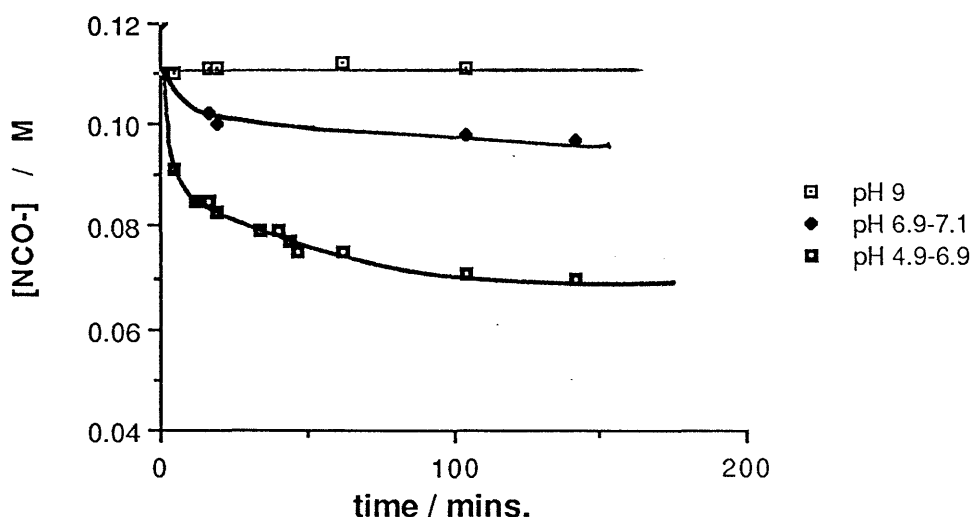
Anodic oxidation of NCO^- at a Pt electrode has been studied using Infra-Red Reflective Absorption Spectroscopy (IRRAS).⁵⁰ A band due to free NCO^- at 2170 cm^{-1} decreased in intensity and gave way to two new peaks, a strong band at 2342 cm^{-1} which was attributed to CO_2 and a second weaker band at 2260 cm^{-1} which was assigned as HOCN coordinated to the electrode via the nitrogen atom.

1.5.II. Studies of the oxidation and hydrolysis of free NCO^- with H_2O_2 .

a. Chemical and spectroscopic studies.

When a solution of NCO^- (0.1M) was oxidised by H_2O_2 (1M), the FTIR peak at 2170 cm^{-1} disappeared very quickly within one hour. The formation of $[\text{HCO}_3]^-$ and $[\text{CO}_3]^{2-}$ has been shown by both Raman and ^{13}C NMR spectroscopy and is discussed in section 1.3.I. At pH 12, NCO^- (0.1M) is fairly stable in solution and by using quantitative analysis of the peak at 2170 cm^{-1} (see the experimental section 1.6 for details of this method), the concentration of the solution was observed to decrease only to 0.098M in twenty four hours. This diminution of the NCO^- concentration continued slowly and after three days the concentration was 0.096M and 0.095M after three weeks. That the hydrolysis reaction becomes faster as the pH is lowered can be seen from graph 1.5.i.below.

Graph 1.5.i. The hydrolysis of NCO^- (0.1M) in aqueous solution at different pH using quantitative FTIR analysis of the intensity of the peak at 2170 cm^{-1} .



In the two solutions at lower pH there was a rise in the pH from 4.9 to 6.9 and 6.9 to 7.1 over the course of the reaction, which is presumably due to the formation of

$[\text{HCO}_3]^-$. In order to measure the proportion of NCO^- which was decomposed with formation of NH_3 oxidations of KNCO (0.5g) were carried out at pH 10.97 using excess H_2O_2 in a flask through which argon was passed into H_2SO_4 (1M) to collect any NH_3 evolved. After the reaction had been stirred overnight, and the FTIR spectrum run to ensure that there was no NCO^- remaining in the solution the concentration of NH_3 was determined by titration of the H_2SO_4 with NaOH . The results are summarised in table (1.5.i) below together with values measured for solutions in which KNCO was added directly to H_2SO_4 to ensure that all decomposition was via hydrolysis as a check that this titration method was accurate. The average value of 76.5% of the nitrogen in the NCO^- converted to NH_3 agrees well with literature values^{4,19} and indicates that the hydrolysis of NCO^- is indeed catalysed by the presence of H_2O_2 at high pH.

Table 1.5.i. Percentage of KNCO (0.5g , 6.17×10^{-3} mols) which decomposes with the formation of NH_3 when reacted with excess H_2O_2 (0.045 mols) at pH 11 as calculated by titration.

Run	% of KNCO forming NH_3
1	70
2	77
3	82
4	77
	Av = 76.5
Blank	100
Blank	99

b. Quantitative studies of the decomposition of NCO^- .

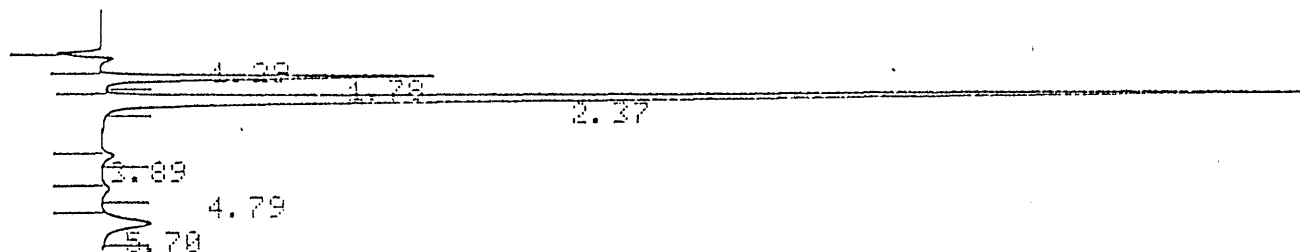
We have used two methods for the quantitative analysis of NCO^- . The first of these involved the quantitation of the peak area or peak height at 2170 cm^{-1} in the FTIR

spectrum. This was carried out using the quantitation method on the Perkin Elmer 1310 spectrometer and is discussed in the experimental section 1.6. It was possible to use this method because the peak at 2170 cm^{-1} is very strong and so analyses could be made of solutions containing as little as 10^{-3} M NCO^- .

The second method of analysis was by Dionex High Performance Ion Chromatography (HPIC) and was suitable for solutions of NCO^- having concentrations in the range 10^{-3} - 10^{-6} M . The principle of the Dionex technique is discussed in detail in section 2.2.III with regard to the analysis of cyanide complexes using spectrophotometric detection, although in this study a different anion column was used and the detection was conductometric. Full experimental details of the method are given in the experimental section at the end of this chapter. The complexity of the technique and the time required to run samples, which had to be free of all organic and metallic species to protect the anion column rendered this unsuitable for routine work and it was only used in conjunction with FTIR to check the relative accuracy of the two methods. Results indicated agreement between the two approaches of $\pm 5\%$; this relatively small difference could easily be accounted for by the dilution required for samples run on the Dionex. The Dionex trace in fig 1.5.i below shows that a solution containing NCO^- (retention time = 2.37 min) also contained other anionic species in the reaction solution. By running standards it was possible to determine that F^- (RT = 1.29 min), Cl^- (RT = 1.78 min) and $[\text{SO}_4]^{2-}$ (RT = 5.70 min) were present but we cannot conclusively identify $[\text{NO}_3]^-$ (RT = 3.79 min) although this ion is probably responsible for the peak at RT = 3.89 min.

Fig.1.5.i. Dionex trace showing the peaks due to anionic species in solution during the oxidation of NCO^- ($2.5 \times 10^{-4} \text{ M}$) by H_2O_2 ($2.5 \times 10^{-3} \text{ M}$).

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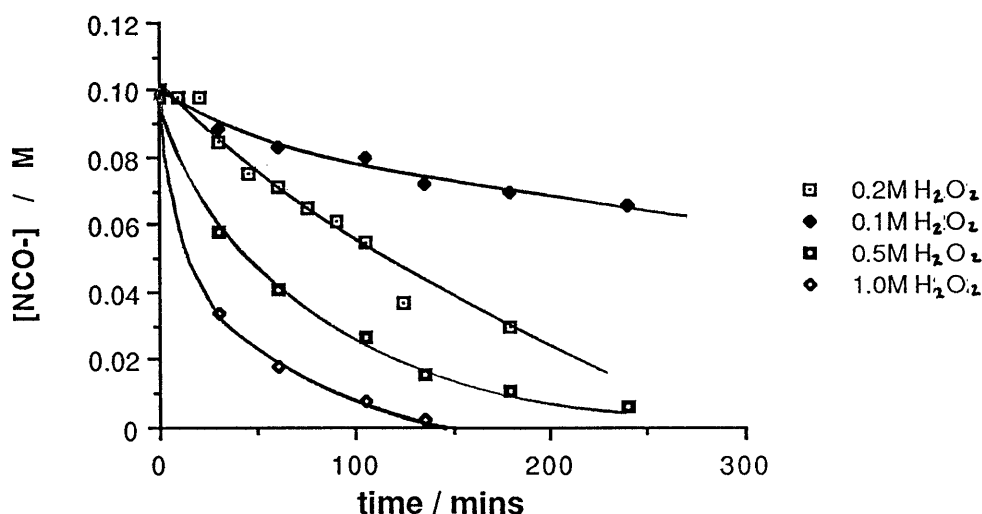
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PEAK#	AREA%	RT	AREA	BC	
1	5.309	1.29	1120593	02	F^-
2	16.466	1.78	3506362	03	Cl^-
3	71.015	2.37	15122072	01	NCO^-
4	0.734	3.89	156358	01	$[\text{NO}_3]^-$???
5	0.62	4.79	132115	01	
6	5.854	5.7	1246593	01	$[\text{SO}_4]^{2-}$
TOTAL	100.		21294093		

Using FTIR analysis reactions of NCO^- (0.1M) with different concentrations of H_2O_2 were carried out and the results are summarised on the graph (1.5.ii) below. In table 1.5.ii we list the concentration of NCO^- remaining and the stoichiometry of H_2O_2 consumed per mole NCO^- at different time intervals during the oxidation reactions. There seems little pattern in the stoichiometric figures, but by looking at the concentration data it is clear that the rate has some dependence upon the concentration of H_2O_2 used.

Graph 1.5.ii. Curves showing the decomposition of $[\text{NCO}^-]$ (0.1M) in reaction with H_2O_2 at pH 9.25 to 9.8.



Plots of the above data for first and second order kinetics with respect to both H_2O_2 and NCO^- did not give straight lines although the difference in the theoretical (as predicted from equation 1.56 above) and measured stoichiometries (see table 1.5.ii) indicate that the overall kinetics are likely to be the result of the competing oxidation and hydrolysis reactions. This is also possible because of the catalytic effect that H_2O_2 appears to have on the hydrolysis reaction. The results were further complicated by the experimental problems we encountered due to the decomposition of H_2O_2 , which

should be stable in aqueous solution at pH 9 to 10. Additions of Dequest (1%) were made to some solutions to ensure that transition metal impurities were eliminated but the decomposition of the oxidant continued to be erratic. The decomposition of H_2O_2 in solutions containing $[\text{HCO}_3]^-$ and $[\text{CO}_3]^{2-}$ has been studied.^{144,145}

Table 1.5.ii. Progress of reactions between NCO^- (0.1M) and H_2O_2 at pH 9.5.

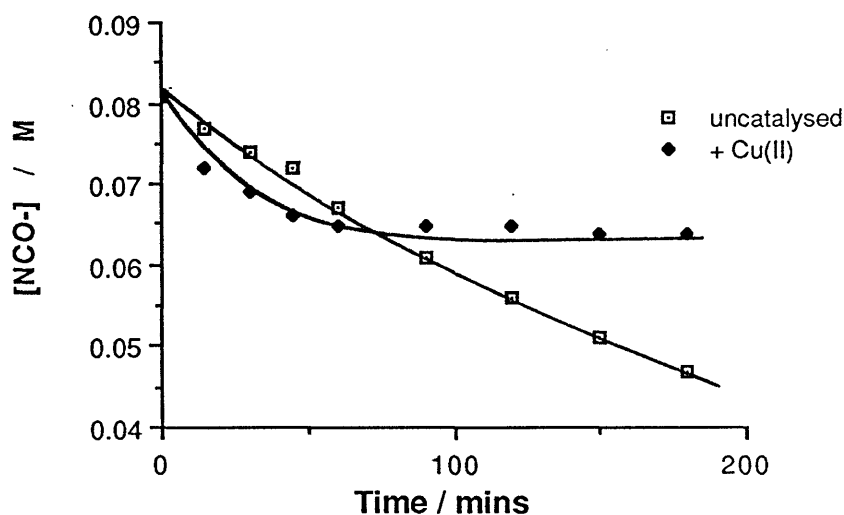
T=0		T= 1 hour		T= 2 hours		T= 3 hours	
$[\text{H}_2\text{O}_2] / \text{M}$	pH	$[\text{NCO}^-] / \text{M}$	stoich	$[\text{NCO}^-] / \text{M}$	stoich	$[\text{NCO}^-] / \text{M}$	stoich
0.1	9.4-9.6	0.083	4.0	0.078	1.1	0.066	1.6
0.2	9.7-9.8	0.071	2.5	0.037	1.76	-	-
0.5	9.35-9.6	0.041	1.2	0.019	2.0	0.009	4.6
1.0	9.25-9.5	0.018	1.95	0.004	8.75	0.000	-

stoich = Ratio of H_2O_2 : NCO^- in the period of the reaction elapsed since previous reading.

The addition of an aqueous solution of copper(II) chloride (10^{-3}M) to a solution containing NCO^- (0.8M) and H_2O_2 (0.8M) lead to an overall decrease in the amount of NCO^- removed from solution in two hours of reaction. Graph 1.5.iii below shows that the initial decrease in NCO^- concentration was actually faster than in reactions where no Cu(II) had been added, but this rate of decrease in NCO^- was short lived and after two hours reaction (in which 33% NCO^- disappeared compared to 50% in other reactions) no further removal occurred. This was probably because of the complete decomposition of H_2O_2 , presumably catalysed by the presence of Cu(II) although we did not observe the yellow colouration characteristic of the formation of the $[(\text{HO})_2\text{Cu}(\text{OOH})]^-$ species (see section 1.3.v). At the end of this reaction the concentration of Cu(II) ions in solution was approximately the same as at the beginning as measured using semi-quantitative colourimetric Cu(II) test strips. In some reactions to which copper(II)

chloride had been added, the final solution had a blue hue to probably arising from the formation of Cu(II) ammine species or possibly to a Cu(II) cyanato species, $[\text{Cu}(\text{NCO})_4]^{2-}$ or $[\text{Cu}(\text{NCO})_3]^-$ (see section 3.1.II).

Graph 1.5.iii. Oxidation of free NCO^- (0.8M) by H_2O_2 (0.8M) in the presence of an aqueous solution of CuCl_2 (10^{-3} M).



In conclusion, the reaction of H_2O_2 and NCO^- at $\text{pH} > 9$ appears to involve both oxidation and hydrolysis. Approximately 75% of the NCO^- undergoes hydrolysis to NH_3 and $[\text{HCO}_3]^-$ in a reaction that is catalysed by H_2O_2 , and 25% is oxidised by the H_2O_2 to products, the nature of which we have not been able to determine. The kinetics of the overall removal of NCO^- are complicated and the addition of Cu(II) salts catalyses the decomposition of H_2O_2 , thus reducing the proportion of NCO^- destroyed.

1.5.III. The reactions of NCO^- with triple salt, persulphate and hypochlorite.

a. Oxidations with triple salt.

Our studies using FTIR analysis indicate that NCO^- (0.1M) was completely destroyed by triple salt ($\text{K}_2\text{SO}_4 \cdot \text{KHSO}_4 \cdot 2\text{KHSO}_5$, 0.09M = 0.18M $[\text{HSO}_5]^-$) within sixty minutes. More significantly, 60% of the NCO^- was removed before ten minutes had elapsed but whether this was due to oxidation of NCO^- by $[\text{HSO}_5]^-$, or to hydrolysis by the H^+ associated with the triple salt was not clear. Despite strong buffering using phosphate (0.2M) or borax (0.2M) buffers, the pH always dropped from 8.5 to around 7 during the reaction which prevented us from measuring accurate kinetic data and this fall in pH would have promoted the hydrolysis reaction. When the reaction was carried out in NaOH (0.6M) to ensure that the pH remained above 10 the triple salt decomposed so rapidly that only 22% of the NCO^- was destroyed after one hour and no further reaction occurred. The decomposition of $[\text{HSO}_5]^-$ at pH >8 was rapid even if Dequest was added to remove transition metals from the solution, and this decomposition is discussed in more detail in section 2.4.IV. However, the decomposition was observed to occur more quickly in solutions which contained NCO^- indicating that the latter species was somehow accelerating the demise of $[\text{HSO}_5]^-$.

The removal of some NCO^- , even when the reaction was carried out at high pH using triple salt, indicates that there is certainly some reaction between $[\text{HSO}_5]^-$ and NCO^- , although at lower pH the destruction of the NCO^- was probably almost all due to hydrolysis.

b. Oxidations with persulphate.

When equimolar concentrations of NCO^- and $[\text{S}_2\text{O}_8]^{2-}$ (0.1M) were mixed in the pH range 8.5 to 10.5 there was no apparent reaction as assessed by using FTIR spectroscopy. When an aqueous solution of copper(II) sulphate (10^{-3}M) was added the

solution turned yellow-green and a black precipitate was formed. The IR of this solid had bands at 1295, 1114 and 1064 cm^{-1} , indicating that $[\text{S}_2\text{O}_8]^{2-}$ was present, possibly as CuS_2O_8 . In the reaction the pH dropped from 9 to 7 and after two hours the concentration of NCO^- had dropped from 0.1 to 0.079M, although it was not clear whether this was due to oxidation by the $[\text{S}_2\text{O}_8]^{2-}$ or hydrolysis because the pH had dropped. In borax buffer at pH 9.5 with an aqueous solution of copper(II) sulphate ($4 \times 10^{-3}\text{M}$), only 5-10% oxidation occurred in six hours and the concentration of $[\text{S}_2\text{O}_8]^{2-}$ after this reaction time was measured by titration with $[\text{MnO}_4]^-$ to be 0.093M. No precipitate was observed. From these observations we conclude that if NCO^- is oxidised by $[\text{S}_2\text{O}_8]^{2-}$ then the reaction is very slow under the conditions of our study.

c. Oxidations with hypochlorite.

Our observations using FTIR as the method of analysis merely confirm the published work.^{39,143} At high pH (>11), then oxidation of NCO^- (0.1M) by OCl^- (1M) was slow but after four hours 30% of the NCO^- was removed. When the same reaction was carried out at pH 9 then the rate increased such that 65% was destroyed in two hours. Qualitative comparison with the reaction of NCO^- with H_2O_2 showed that the removal from solution of NCO^- occurred much more rapidly if OCl^- was used as the oxidant.

1.6. Experimental.

Section 1.3. General spectroscopy.

IR spectra were run on a Perkin-Elmer 1720 Fourier Transform spectrometer. All FTIR spectra of aqueous solutions were run using CaF_2 plates with Teflon spacers of thickness 0.05 mm. (see section 2.5 for details of the method by which this thickness was determined). Spectra of solid samples were run using KBr discs or as nujol mulls between KBr plates.

Raman spectra were run using exciting lines at 488 and 514.5 nm. from an Innova 70 CRL Ar^+ laser, and at 647 nm. on a 90 CRL Kr^+ laser, with a Spex Ramalog 5 instrument and Spex Datamate acquisition unit. Solid samples were run pressed onto KBr discs or on a custom built BGSC Raman microscope.¹⁴⁶ Solutions were run in sealed glass capillaries or in spinning quartz solution cells.

^{13}C NMR spectra were run on a Jeol FX 90Q Fourier transform spectrometer and a Bruker WM250 Fourier transform spectrometer. We used 10 mm NMR tubes with an internal reference of 1,4 dioxane ($\delta = 67.8 \text{ ppm}^{147}$) in D_2O to act as a lock.

^{11}B NMR spectra were run on the above instruments using 10 mm NMR tubes with an internal reference of $\text{Na}[\text{BO}_2\text{H}]_4$ ($\delta = 1.3 \text{ ppm}^{12c}$) in D_2O to act as a lock.

^{31}P NMR spectra were run on the Jeol FX 90Q Fourier transform spectrometer in D_2O to act as a lock by Miss Julia Poat.

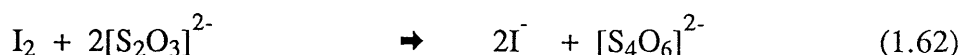
Section 1.3. Quantitative studies of the oxidation of free CN^- by H_2O_2 .

Free CN^- was analysed using an EDT ISE304 cyanide selective electrode in conjunction with a standard single junction reference electrode filled with saturated KCl. Both electrodes were connected to an EDT ECM202 pH/ion meter. The cyanide

electrode was calibrated with known concentrations of free CN^- in NaOH (0.1M) and a calibration curve drawn on logarithmic graph paper. The calibration was repeated after each kinetic experiment.

Solutions were made up in millipore water (triply distilled and deionised) using Analar reagents wherever possible. The oxidations were carried out in glassware that had been pickled in conc. HNO_3 , rinsed with millipore water and Decon solution (a surface active cleaning agent 5%) to ensure that as far as possible there were no contaminants. The reaction flasks were stirred in a constant temperature thermostatic bath and aliquots removed at intervals. For CN^- analysis, the aliquots were mixed with their volume of NaOH (0.2M) to raise the pH of the solution and MnO_2 (ca. 5mg) added to destroy the H_2O_2 before the electrode was used.

Analysis of H_2O_2 was carried out qualitatively using colourimetric test strips supplied by Merck, and quantitatively using iodometric titration as described below. The aliquot was added to a flask containing iced H_2SO_4 (2M, 100 cm^3) and to this was added KI solution (5%, 10 cm^3), and a few drops of saturated ammonium tungstate solution. The flask was then left in the dark for five minutes for the colour to develop. Once the orange-brown colour had fully appeared, the solution was titrated against 0.1M Convolve $\text{Na}_2[\text{S}_2\text{O}_3]$ solution, using starch indicator once the solution was straw coloured. The relevant equations for this titration are as follows.



Buffer solutions.

These were prepared using published methods¹¹⁹ and as follows.

Borax buffer was prepared from $\text{Na}[\text{B}(\text{OH})_4]$ (0.125M, 100 cm^3) and NaOH (1.43M, 1.4 cm^3) made up to 250 cm^3 with water for a pH of 9.50.

Bicarbonate buffer was prepared from $[\text{HCO}_3]^-$ (0.5M, 200 cm^3) and NaOH (1.43M, 17.5 cm^3) made up to 250 cm^3 . (pH = 9.50).

Phosphate buffer was prepared with $\text{K}_2[\text{HPO}_4]$ (10.5g in 250 cm^3) and NaOH (1.43M, 0.2 cm^3). (pH = 9.00)

Ammonium chloride buffer was prepared from NH_4Cl (2.61g) and NH_3 (0.88 s.g., 1 cm^3) made up to 100 cm^3 . (pH = 9.00).

Different volumes of NaOH were added for different pH buffers.

Ionic strength, UV light, radical trap and catalytic experiments.

In reactions investigating the effect of ionic strength we used Analar KCl and NaClO_4 (1M) in oxidations of free CN^- (10^{-2} M) by H_2O_2 (0.16M).

In investigations into the effect of UV light solutions were irradiated using a Blak-Ray 440W UV lamp.

Radical traps were ethanol, methanol and DMSO, added to the reaction solutions to 5% v/v. Catalysts and $\text{Na}_2\text{S}_2\text{O}_3$ were added as described in the text.

Section 1.4 Oxidations with persulphate.

Raman and FTIR spectroscopic studies were carried out as described above. Determination of CN^- was made using the cyanide selective electrode. $\text{Na}_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{S}_2\text{O}_8$ were Analar grade and supplied by BDH Ltd.

Section 1.5. Oxidations of free cyanate.

Chemical and spectroscopic studies.

FTIR studies were carried out as described above.

Determinations of the proportion of NCO^- that decomposed via NH_3 were carried out using the published procedure.¹⁹ The oxidation of a solution of KNCO (0.5g in 10 cm^3 0.05M NaOH) by H_2O_2 (30%, 5 cm^3) was carried out overnight in a flask with an argon bubbler and an exit tube into H_2SO_4 (1M, 20 cm^3). After checking to ensure that

no NCO^- remained, the H_2SO_4 was titrated against NaOH (0.18M) to determine the concentration of $(\text{NH}_4)_2\text{SO}_4$ and thus the amount of NH_3 formed.

Quantitative studies.

We determined the concentration of free NCO^- in solution by two methods; A quantitative FTIR method was available on the Perkin-Elmer 1310 FT spectrometer, which could be calibrated over the range $0.2\text{-}10^{-3}\text{ M NCO}^-$ using suitable standards. This was quick and convenient and so the majority of determinations were carried out by this method. Aliquots were removed from solution and injected into the FTIR cell without additions of MnO_2 to destroy the H_2O_2 .

Dionex HPIC analysis of NCO^- was carried out using a AS4 anion column with AG4 guard. The eluent was NaHCO_3 (0.005M) and Na_2CO_3 (0.0025M) with a regenerant of H_2SO_4 (0.0025N).

An aliquot was removed from the reaction solution, and MnO_2 added to destroy any remaining H_2O_2 . All solid matter was filtered off and the aliquot injected through a $0.45\text{ }\mu\text{m}$ disposable filter into the Dionex. Detection was conductometric and data were recorded on a Dionex 2470 integrator.

Chapter 2.

The Oxidation of Cyanide Complexes by Peroxidic Species.

Introduction.

Cyanide in industrial effluent streams is often present in the form of metal cyanide complexes. The stability of these complexes varies according to the nature of the metal ion involved and the complexes have a different reactivity towards the oxidants discussed in the first chapter. This second chapter includes the studies carried out on a selection of metal cyanide complexes using the oxidants H_2O_2 and $[\text{HSO}_5]^-$.

The first section provides a brief overview of the published values of the stability constants for a number of cyanide complexes and the effectiveness of methods currently used to detoxify solutions containing these moieties. In section 2.2 we discuss the techniques we have used for the direct determination and quantitative analysis of cyanide complexes and in the final sections 2.3 and 2.4 we deal with our own studies on oxidations of such complexes.

2.1. Review of Stability Constants and Current Methods Used in the Treatment of Cyanide Complexes.

2.1.I. Stabilities of cyanide complexes.

The effectiveness towards cyanide complexes of many of the published methods for the detoxification of cyanides (see section 1.1), is largely dependent upon the thermodynamic stability of the complex concerned. Weak complexes, generally regarded as those having overall stability constants of up to $\beta_n \sim 20$, will react as though the cyanide present is completely dissociated to free CN^- . Moderately strong complexes ($\beta_n \sim 20 - 30$) are generally only partly affected and those complexes with $\beta_n > 30$ are regarded as strong and are unaffected by normal treatments.⁶⁶ This classification is only general and in specific cases, for example in reactions of peroxides with copper(I) cyano species, different reactivities occur. Table 2.1.i below lists published values for the stabilities of a number of complex cyanides relevant to this work. Stability constants of several other cyanide complexes have been reviewed in a recent critical survey of the methods used to determine them.¹⁴⁸

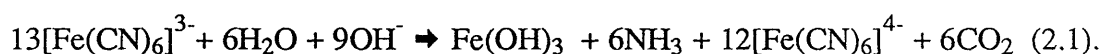
The toxicity of aqueous solutions of cyanide complexes is believed to be dependent upon the amount of free CN^- present and thus has a direct relationship to the stability constants of the complexes. There are published values for the toxicities of a number of complexes towards animals¹⁴⁹ and aquatic organisms.¹⁵⁰

Table 2.1.i. Values of total stability constants (β_n) for cyanide complexes.

Complex Ion	β_n / M^{-n}	Reference.
$[\text{Fe}(\text{CN})_6]^{3-}$	35.4	151
$[\text{Fe}(\text{CN})_6]^{4-}$	43.6	151
$[\text{Cr}(\text{CN})_6]^{3-}$	~35	152
$[\text{Cr}(\text{CN})_6]^{4-}$	~21	153
$[\text{Co}(\text{CN})_6]^{3-}$	~50	154
$[\text{Ni}(\text{CN})_4]^{2-}$	30.3	155
$[\text{Pt}(\text{CN})_4]^{2-}$	~40	156
$[\text{Pd}(\text{CN})_4]^{2-}$	42	157
$[\text{Zn}(\text{CN})_4]^{2-}$	19.62	85
$[\text{Cd}(\text{CN})_4]^{2-}$	19.2	86
$[\text{Hg}(\text{CN})_4]^{2-}$	38.97	158
$[\text{Cu}(\text{CN})_4]^{3-}$	30.7	84
$[\text{Cu}(\text{CN})_3]^{2-}$	29.2	84
$[\text{Cu}(\text{CN})_2]^-$	23.9	84
$[\text{Ag}(\text{CN})_2]^-$	20.4	84
$[\text{Au}(\text{CN})_2]^-$	37	84

2.1.II. Chemical oxidation of cyanide complexes.

Hydrogen peroxide will oxidise weak cyanide complexes in an apparently similar way to CN^- but there has been little work assessing these reactions quantitatively. As early as 1913 Grusse discovered that treatment of $[\text{Fe}(\text{CN})_6]^{3-}$ with H_2O_2 at high pH produces only $[\text{Fe}(\text{CN})_6]^{4-}$, a reduction, and at low pH the reverse reaction occurs. He also observed some dissociation of $[\text{Fe}(\text{CN})_6]^{3-}$ and postulated the overall equation below.¹⁵⁹



At pH 5, oxidation by H_2O_2 , PbO_2 or Ce(IV) of $[\text{Ru}^{\text{III}}(\text{CN})_6]^{3-}$ produced an absorption in the electronic spectrum at 1094 nm. and this was attributed to the presence of a cyanide bridged dimer $[(\text{CN})_5\text{Ru}^{\text{II}}-\text{CN}-\text{Ru}^{\text{III}}(\text{CN})_5]^{6-}$.¹⁶⁰ Some aquation of the complex and the formation in solution of free NCO^- was observed. In a comparable study at pH 6 using Ce(IV) as the oxidant, $[\text{Ru}(\text{CN})_6]^{4-}$ produced only $[\text{Ru}(\text{CN})_6]^{3-}$ which aquated and apparently dimerised to the above species. Direct reaction of $[\text{Ru}(\text{CN})_6]^{3-}$ with H_2O_2 was said to produce the complex $[\text{Ru}(\text{CN})_5(\text{CNO})]^{4-}$ as an intermediate but in this process the H_2O_2 acted only as a catalyst and decomposed after the intermediate was formed. Although written as a fulminate, CNO^- , it is not known if the ligand was this or a cyanate NCO^- , nor is it clear which atom was bonded to the ruthenium atom.¹⁶¹

A study of the reaction between $[\text{Cr}(\text{CN})_6]^{4-}$ and H_2O_2 in alkaline cyanide solution showed that it followed pseudo first order kinetics and a mechanism was proposed which involved the formation of the species $[\text{Cr}(\text{CN})_5\text{H}_2\text{O}]^{3-}$. No mention was made of further stepwise removal of CN^- , or of the effect of the oxidant upon the free CN^- in solution.¹⁶²

The catalytic activity of copper(II) species in the reaction between H_2O_2 and cyanide species has been discussed (see section 1.1). This makes it a relatively straightforward process to detoxify mining wastes containing high concentrations of

$[\text{Cu}(\text{CN})_4]^{3-}$ (12.9ppm), $[\text{Cu}(\text{CN})_3]^{2-}$ (67.2ppm) and $[\text{Cu}(\text{CN})_2]^{-}$ (0.9ppm). In these cases the concentration of total cyanide in the wastewater was reduced from 300ppm to 10ppm by direct dosage with H_2O_2 .¹²²

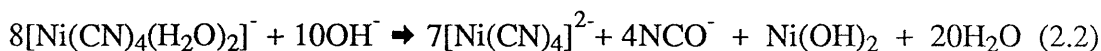
UV irradiation has been proposed as a method of decomposing stable cyanide complexes prior to oxidation with H_2O_2 .¹⁶³ Stepwise aquation of the complex $[\text{Co}(\text{CN})_6]^{3-}$ to yield free CN^{-} can be promoted using UV light and the kinetics of this dissociation have been measured,¹⁶⁴ with similar results obtained for $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$.¹⁶⁵ A kinetic study of the photochemically induced decomposition of alkaline solutions of both $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ concluded that the reaction rate was independent of the concentration of cyanide complex, but that this rate could be varied by both the pH and the intensity of irradiation. Both complexes dissociated via the complex $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$ and eventually produced CN^{-} and $\text{Fe}(\text{OH})_3$ which could be removed from wastewaters by circulation through a manganese zeolite absorption column.¹⁶⁶ This was an important observation since many complexes are resistant to direct attack by H_2O_2 and so must undergo a prior dissociation to ensure complete oxidation. The addition of EDTA or a similar chelating agent to solutions of cyanide complexes, particularly containing $[\text{Ni}(\text{CN})_4]^{2-}$, has been used as these chelates bind preferentially to the metal and thus decomplex the cyanide.¹⁶⁷ A number of kinetic studies have been carried out to measure rates of dissociation of $[\text{Ni}(\text{CN})_4]^{2-}$ using different competing scavengers such as I^{-} ¹⁶⁸ and triethylene-tetramine;^{169,170} such studies were also carried out in different pH ranges.^{171,172,173}

Another strategy is to oxidise catalytically a substantial proportion of the cyanide complex in solution with H_2O_2 and Cu(II) salts and then precipitate out those complexes (particularly $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, and $[\text{Fe}(\text{CN})_6]^{3-}$) which are not destroyed in the first part of the reaction with the remaining copper(II) species.¹⁷⁴ Any metal species in solution after the reaction can themselves be precipitated by trimercaptotriazene which has low toxicity and forms complexes of low solubility with nickel(II), copper(II) and mercury(II). An alternative precipitation agent is stearyl

dimethyl-benzyl-ammonium chloride which can be used in conjunction with ferric sulphate and an anionic polyacrylamide to coagulate the ferrocyanide precipitate and hasten its separation from solution.¹⁷⁵

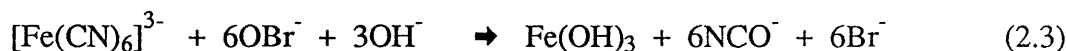
Caro's acid (H_2SO_5) has been used to oxidise the complexes $[\text{Zn}(\text{CN})_4]^{2-}$, $[\text{Cd}(\text{CN})_4]^{2-}$, $[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Ag}(\text{CN})_2]^-$, and $[\text{Ni}(\text{CN})_4]^{2-}$ using a three fold excess of oxidant for each molecule of cyanide; no details were given as to conditions and reaction times but the method was said to bring the level of cyanide down to $0.1 \text{ mg CN}^- \text{ dm}^{-3}$.²⁵ Using $[\text{S}_2\text{O}_8]^{2-}$ as the oxidant $[\text{Fe}(\text{CN})_6]^{4-}$ was oxidised to $[\text{Fe}(\text{CN})_6]^{3-}$ in a second order reaction¹⁷⁶, and in concentrated aqueous salt solution $[\text{Mo}(\text{CN})_8]^{4-}$ formed $[\text{Mo}(\text{CN})_8]^{3-}$. There was however, no suggestion that free CN^- was present in the solutions, so it is likely that an outer sphere oxidation occurred in these cases.¹⁷⁷ However, a study of the oxidation of $[\text{Mn}(\text{CN})_6]^{3-}$ to $[\text{Mn}(\text{CN})_6]^{2-}$ using persulphate in excess cyanide suggested that a radical $[\text{SO}_4]^\cdot$ species was formed which oxidised the free CN^- to cyanogen.¹⁷⁸ This radical has also been proposed as an intermediate in the Cu(II) catalysed decomposition of $[\text{S}_2\text{O}_8]^{2-}$.¹⁷⁹

Oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ with HOCl , triple salt ($\text{K}_2\text{SO}_4 \cdot \text{KHSO}_4 \cdot 2\text{KHSO}_5$), PbO_2 or by electrochemical methods produces $[\text{Ni}^{\text{III}}(\text{CN})_4(\text{H}_2\text{O})_2]^-$ in which the trans- H_2O molecules are readily replaceable.¹⁸⁰ This Ni(III) complex has been characterised by EPR, electronic spectroscopy¹⁸¹ and the kinetics of its formation using HOCl , Cl_2 , and Cl_2O have been measured.¹⁸² It is most stable in acid solution ($t_{1/2} = 28$ minutes at pH 1 to 3 and at 25°C), and it decomposes according to the following overall reaction.



Hypochlorite is said to be effective in oxidising all cyanide complexes including $[\text{Fe}(\text{CN})_6]^{4-}$ ³⁴ ($\beta_6 = 43.6$ ¹⁵¹) although some studies report that the hexacyanoferrates $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ are in fact not oxidised.¹⁸³ This oxidant has been used to measure the overall stability constants of the complexes $[\text{Zn}(\text{CN})_4]^{2-}$, $[\text{Cd}(\text{CN})_4]^{2-}$, $[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Ag}(\text{CN})_2]^-$, and $[\text{Ni}(\text{CN})_4]^{2-}$; ¹⁸⁴ the complexes were oxidised with a known excess of NaOCl which was then back titrated with As_2O_3 to give an indication

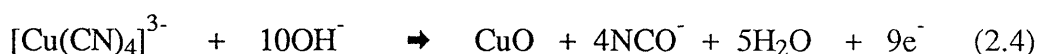
of the stabilities of the complexes. The time taken to oxidise $[\text{Cd}(\text{CN})_4]^{2-}$, and $[\text{Zn}(\text{CN})_4]^{2-}$ was less than five minutes whilst a reaction time of fifty minutes was necessary for $[\text{Ni}(\text{CN})_4]^{2-}$. Another method for the oxidation is to bubble Cl_2 gas through the solution at 70°C ⁷ or to use the hypobromite ion, in a reaction which was first reported in 1909.⁴² This oxidises $[\text{Fe}(\text{CN})_6]^{4-}$ to $[\text{Fe}(\text{CN})_6]^{3-}$ and then destroys the latter complex, yielding NCO^- . More recent studies have found that at 75°C in OH^- (0.05 -0.5M), the overall reaction is as follows.



If the concentration of OH^- is raised to above 1M then reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ occurs. It is stressed that OCl^- will not oxidise $[\text{Fe}(\text{CN})_6]^{3-}$ under these conditions.^{185,186}

2.1.III. Electrochemical oxidations.

Electrooxidation of wastewaters containing cyano complexes of copper(II), zinc(II) and cadmium(II) has been studied.¹⁸⁷ The rates of decomposition were measured and there was found to be an inverse pH effect. The products included $(\text{NH}_4)_2\text{CO}_3$, NCO^- and urea. In strongly alkaline solution ($\text{pH} > 12$) $[\text{Cu}(\text{CN})_4]^{3-}$ was directly oxidised to NCO^- and CuO was precipitated. The overall reaction was.¹⁸⁸



In solutions of pH 7 to 11 the $[\text{Cu}(\text{CN})_4]^{3-}$ dissociated and it was the CN^- that was electroxidised to NCO^- and brown azulmin polymer $(\text{HCN})_x$. It was suggested that this occurred via the formation of cyanogen.



In another study a transient purple colour attributed to $[\text{Cu}(\text{CN})_4]^{2-}$ was observed and $\text{Cu}(\text{CN})_2$ was deposited at the anode.¹⁸⁹ The above studies on copper cyanide complexes aside, there is little literature on the oxidation of cyanide complexes of other

transition metals. The electrooxidation of $[\text{Ru}(\text{CN})_6]^{3-}$ forms the dimeric $[(\text{CN})_5\text{Ru}-\text{CN}-\text{Ru}(\text{CN})_5]^{6-}$ ¹⁶⁰ and $[\text{Ni}(\text{CN})_4]^{2-}$ forms a nickel (III) species $[\text{Ni}(\text{CN})_4(\text{H}_2\text{O})_2]^{-}$ ¹⁸⁰ as discussed above.

2.1.III. Precipitation and thermal oxidations.

Precipitation of the cyano complexes of zinc, cadmium and copper onto basic anion exchange resins has been studied.^{70,190} The tetrahedral complexes $[\text{Zn}(\text{CN})_4]^{2-}$ and $[\text{Cd}(\text{CN})_4]^{2-}$ were absorbed on the resin at concentrations of 13.1 -13.5 g metal dm^{-3} . With copper complexes it was exclusively $[\text{Cu}(\text{CN})_2]^{-}$ that was adsorbed on the column (up to 17.2g copper dm^{-3}) despite the presence of $[\text{Cu}(\text{CN})_3]^{2-}$ and $[\text{Cu}(\text{CN})_4]^{3-}$ in the solution. It was thought that this preferential adsorption was due to the linear structure of $[\text{Cu}(\text{CN})_2]^{-}$ enabling it to lie very close to the resin sites. About 61-85% regeneration of the columns was achieved using NaSCN as a regenerant. In a similar study using $[\text{Co}(\text{CN})_6]^{3-}$, a number of isomers of this complex and related aquated species such as $[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$ were found to poison the resin.¹⁹¹

The thermal oxidation in air of cyano complexes of zinc(II), cadmium(II) and copper(II) has been achieved using an activated carbon catalyst and Cu(II) salts to initiate the reaction.^{67,192} Thermal analysis of the decomposition of strong cyano complexes found that NCO^{-} was produced and that CO_2 was evolved as the temperature was increased.¹⁹³ The INCO process involving SO_2 and air at high temperatures is also effective in the removal of all complexes except those of iron and cobalt.⁶³ Similarly conversion with aldehydes and ketones is suitable at all pH for the removal of both free CN^{-} and moderately strong complexes; see section 1.1.

2.2 Methods for the Direct Analysis of Cyanide Complexes.

Almost all of the analytical techniques discussed in section 1.2 require that the cyanide be present as CN^- , and so for the quantitative analysis of cyanide complexes the cyanide must first be decomplexed either by a traditional distillation from an acidic solution⁷² or by irradiation of the complex with an intense UV light source.⁸⁰ As these processes can be lengthy and complicated to carry out, we have investigated a number of techniques with which we can detect and analyse cyanide complexes directly.

2.2.I. FTIR of aqueous solutions.

Measuring the FTIR of aqueous solutions is potentially a very useful technique for detecting the presence and form of cyanide complexes as the infrared active stretches of the cyanide ligands, ν_{CN} lie in the region $2000 - 2300 \text{ cm}^{-1}$, an area free from virtually all other bands which could interfere with the spectra. We have measured the positions of the bands and their extinction coefficients using the Beer- Lambert law for a number of cyanide complexes and the results are given in the table 2.2.i below.

For those complexes where the extinction coefficient is above about $1000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ it was possible to detect the presence of species down to concentrations of 10^{-3} M provided there was no interference. For free CN^- and those complexes where the extinction coefficient is low, qualitative detection only was possible at concentrations below 10^{-2} M . However, the use of FTIR in following oxidation reactions of cyanide complexes is restricted because the product of the oxidation of cyanide is NCO^- ; the ν_{CN} of this species lies at 2169 cm^{-1} ¹⁰⁸ (see also section 3.I) and this peak has a high extinction coefficient ($1330 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$), and so soon obscured the peak of the cyanide complex, thus rendering the analysis inaccurate.

Table 2.2.i. FTIR data measured for cyanide complexes in aqueous solution using matched CaF₂ plates (cell path 5.2 x 10⁻³ cm.). Literature values are in brackets.

Species	$\nu_{\text{CN}} / \text{cm}^{-1}$	$\epsilon / \text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$
CN ⁻	2079	19 (29 ¹⁹⁴)
NCO ⁻	2170	1330
SCN ⁻	2066	456
[Ag(CN) ₂] ⁻	2135	- (264 ¹⁰⁷)
[Ag(CN) ₃] ²⁻	2105	- (379 ¹⁰⁷)
[Ag(CN) ₄] ³⁻	2092	- (556 ¹⁰⁷)
[Ni(CN) ₄] ²⁻	2124	937 (1070 ¹⁹⁵)
[Co(CN) ₆] ³⁻	2127	1941 (1748 ¹⁹⁵)
[Fe(CN) ₆] ³⁻	2115	1164 (1180 ¹⁹⁵)
[Cu(CN) ₂] ⁻	2125	- (165 ¹⁹⁴)
[Cu(CN) ₃] ²⁻	2094	1100 (1090 ¹⁹⁴)
[Cu(CN) ₄] ³⁻	2076	- (1657 ¹⁹⁴)
[Zn(CN) ₄] ²⁻	2149	88 (113 ¹⁹⁶)
[Cd(CN) ₄] ²⁻	2140	- (75 ¹⁹⁶)
[Au(CN) ₂] ⁻	2146	540

2.2.II. Electronic spectroscopy of cyanide complexes.

The cyanide ion lies at the end of the spectrochemical series and in complexes, d-d transitions can occur in the ultra-violet and visible regions (190 - 450nm.). The assignment of these transitions is regarded as difficult in comparison with those for complexes containing other ligands because there is often dispute as to the exact nature of the species in solution¹⁹⁷, but as they give rise to intense spectral bands which obey the Beer-Lambert law, they can be used to analyse for the complexes at concentrations as low as 10^{-5} M. We have measured the position and intensities of the principal absorption maxima for a number of cyanide complexes and the results are tabulated below. Published values are included in brackets where available.

The use of the absorption at 268 nm of $[\text{Ni}(\text{CN})_4]^{2-}$ has been proposed as a method for determining the concentration of free CN^- by distillation of the cyanide solution into an excess solution of aqueous ammoniacal NiCl_2 .¹⁰⁵ However, the accuracy of any technique of this nature is dependent upon the presence or absence in solution of other species which also absorb in the same region. Although we have used this method successfully, particularly for the quantitative analysis of $[\text{Ni}(\text{CN})_4]^{2-}$ during oxidations by triple salt and KHSO_5 , we found that other oxidants such as H_2O_2 and $[\text{S}_2\text{O}_8]^{2-}$ absorb strongly in this region and thus obscure the absorptions due to the complex under study. To overcome this we have had to add MnO_2 or Catalase (see experimental section) to destroy the H_2O_2 prior to analysis, or alternatively use the Dionex HPIC procedure (see section 2.2.III below) to separate the various species in the solution so that the concentration of the complex under study could be determined accurately.

Table 2.2.ii. Electronic spectra of cyano complexes. Literature values are in brackets.

Complex	Absorption Maxima / nm.	Extinction Coefficient $\epsilon / \text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$
$[\text{Fe}(\text{CN})_6]^{3-}$	261	1185 (1157 ¹⁹⁸)
	285(sh)	1137
	304	1529 (1338 ¹⁹⁸)
	322	1057
	420	897 (493 ¹⁹⁸)
$[\text{Fe}(\text{CN})_6]^{4-}$	267(sh)	2100
$[\text{Co}(\text{CN})_6]^{3-}$	215	2550
	239(aged solution)	245
	258(fresh solution)	170
	312	230
$[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$	215	21500
	239	7350
	386 (380 ¹⁹⁹)	210 (226 ¹⁹⁹)
$[\text{Ni}(\text{CN})_4]^{2-}$	268	11315 (16150 ²⁰⁰)
	286	4725 (4820 ²⁰⁰)
	310	810 (770 ²⁰⁰)
$[\text{Pd}(\text{CN})_4]^{2-}$	205	8750
	212	7250 (9000 ²⁰⁰)
	221	5800 (7200 ²⁰⁰)
	240	1100 (1200 ²⁰⁰)
$[\text{Cu}(\text{CN})_2]^-$	223	9000
$[\text{Cu}(\text{CN})_3]^{2-}$	205	21000 (21000 ²⁰¹)
	223	9000 (11000 ²⁰¹)
	234	10600 (11500 ²⁰¹)
$[\text{Cu}(\text{CN})_4]^{3-}$	238	11000
	252(sh)	3550

2.2.III. Dionex high pressure ion chromatography.

Since this method has been used in much of work involving the study of oxidations of complexes a relatively detailed description of it is given here. The principle of the technique used here is the separation of cyanide complexes from each other and also from other species present in reaction solutions by injection of a sample through a pellicular ion exchange column at high pressure so that each complex can be quantitatively determined.

Using a different anion exchange column from that in this study, separation and simultaneous analysis of mixtures of cyanide complexes has been achieved with both spectrophotometric⁸¹ and conductometric detection.⁶⁹ Separation of the complexes $[\text{Cu}(\text{CN})_3]^{2-}$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Au}(\text{CN})_2]^-$, $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{CN})_6]^{3-}$ was carried out using an eluent made up of 28% w/w acetonitrile, $t\text{Bu}_4\text{NOH}$ (2×10^{-3} M) and 22% w/w NaHCO_3 in H_2O which gave the best separation and most efficient recovery from the column. Other published chromatographic methods⁹⁵⁻¹⁰⁰ are discussed in section 1.2.III. We have also used Dionex HPIC for the analysis of NCO^- but this work is discussed in section 1.5.II.

The column used in this study was comprised of a resin base of polystyrene/divinyl benzene beads coated with sulphonic acid groups which bound the anion exchange material to ensure a high surface coverage.²⁰² Separation of species in the sample was achieved by competition between the mobile phase anions for the cationic sites on the resin, and the subsequent elution occurred due to the presence of a mobile phase counterion which was in equilibrium with the resin as an ion pair. In this study an optimised isocratic eluent comprising NaClO_4 (0.12M), NaOH (0.01M) and NaCN (0.005M) was used. The NaCN was present to maintain the integrity of the complexes as they passed through the column, preventing their dissociation to complexes of a different size and charge which would have different elution times, and preventing the formation of hydroxide complexes which might have bound irreversibly

to the cationic sites on the resin, hence reducing the efficiency of separation and damaging the column.

The NaOH is a standard component in anion exchange eluents. It ensured that species under analysis were present as anions and would thus be separated in passing through the column. In this analysis it was also vital to maintain the cyanide in solution as CN^- and prevent the formation of HCN for safety reasons. The function of NaClO_4 was to elute the cyanide complexes from the column by replacing them at the cationic sites on the resin. It is reported²⁰³ that, by using a gradient of increasing concentration of perchlorate, better separation can be obtained but for our purposes, in the absence of an ion gradient pump an optimised continuous concentration of all the above eluent components was used. Detection was spectrophotometric and could be set at a variety of wavelengths in the UV and visible regions, according to the electronic spectra of the complexes studied. This method would detect most cyanide complexes when set at 215 nm. A full discussion of the practical details involved in the optimisation of the eluent and detection is included in the experimental section.

The following table lists the retention times of a series of cyanide complexes injected through the column in the optimum eluent at different flow rates with the detector set at 215 nm. The retention times were not fixed and could vary according to the operating pressure of the machine and the composition of the solution but the approximate timescale and order of elution is correct.

Table 2.2.iii Retention times for cyanide complexes at three flow rates in the optimised eluent. (see also fig.2.2.ii. for Dionex trace).

Complex	β_n^a	Retention Time (minutes)		
		*FR=0.5	FR=1.0	FR=1.5
$[\text{Ag}(\text{CN})_2]^-$	20.4	-	1.83	-
$[\text{Cu}(\text{CN})_4]^{3-}$	30.7	4.99	2.65	1.83
$[\text{Cu}(\text{CN})_3]^{2-}$	29.2	4.99	2.65	1.83
$[\text{Ni}(\text{CN})_4]^{2-}$	30.3	7.11	3.77	2.48
$[\text{Au}(\text{CN})_2]^-$	37	-	3.0	-
$[\text{Pd}(\text{CN})_4]^{2-}$	42	-	5.2	-
$[\text{Fe}(\text{CN})_6]^{3-}$	35.4	8.44	4.41	3.16
$[\text{Fe}(\text{CN})_6]^{4-}$	43.6	8.44	4.41	3.16
$[\text{Co}(\text{CN})_6]^{3-}$	50	15.53	8.15	5.17
(aged)		6.13	3.24	2.22

* FR = flow rate in $\text{cm}^3 \text{min}^{-1}$

a = Refs as for table 2.1.i

Eluent = NaClO_4 (0.12M), NaOH (0.01M), NaCN (0.005M).

It is clear that the complexes eluted in an order of ascending stability constant but the following observations need to be noted.

a). The complexes $[\text{Cu}(\text{CN})_4]^{3-}$ and $[\text{Cu}(\text{CN})_3]^{2-}$ eluted as one species with a retention time of approximately 2.6 min. (FR= $1 \text{cm}^3 \text{min}^{-1}$). It is reasonable to assume that they both eluted as the $[\text{Cu}(\text{CN})_4]^{3-}$ complex since the excess CN^- in the eluent would have converted the $[\text{Cu}(\text{CN})_3]^{2-}$ species to $[\text{Cu}(\text{CN})_4]^{3-}$.

b). The complexes $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ also eluted at the same rate (4.4 min, FR= $1 \text{cm}^3 \text{min}^{-1}$). It has been suggested²⁰³ that this was due to the reduction of

$[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ but this does not occur naturally in alkaline solution and there is no reason for it to occur whilst passing through the column. Residual $[\text{Fe}(\text{CN})_6]^{4-}$, observable as a tail on the $[\text{Fe}(\text{CN})_6]^{3-}$ peak was not observed and we concluded that the sites on the column have the same attraction for both complexes, hence their elution times were the same.

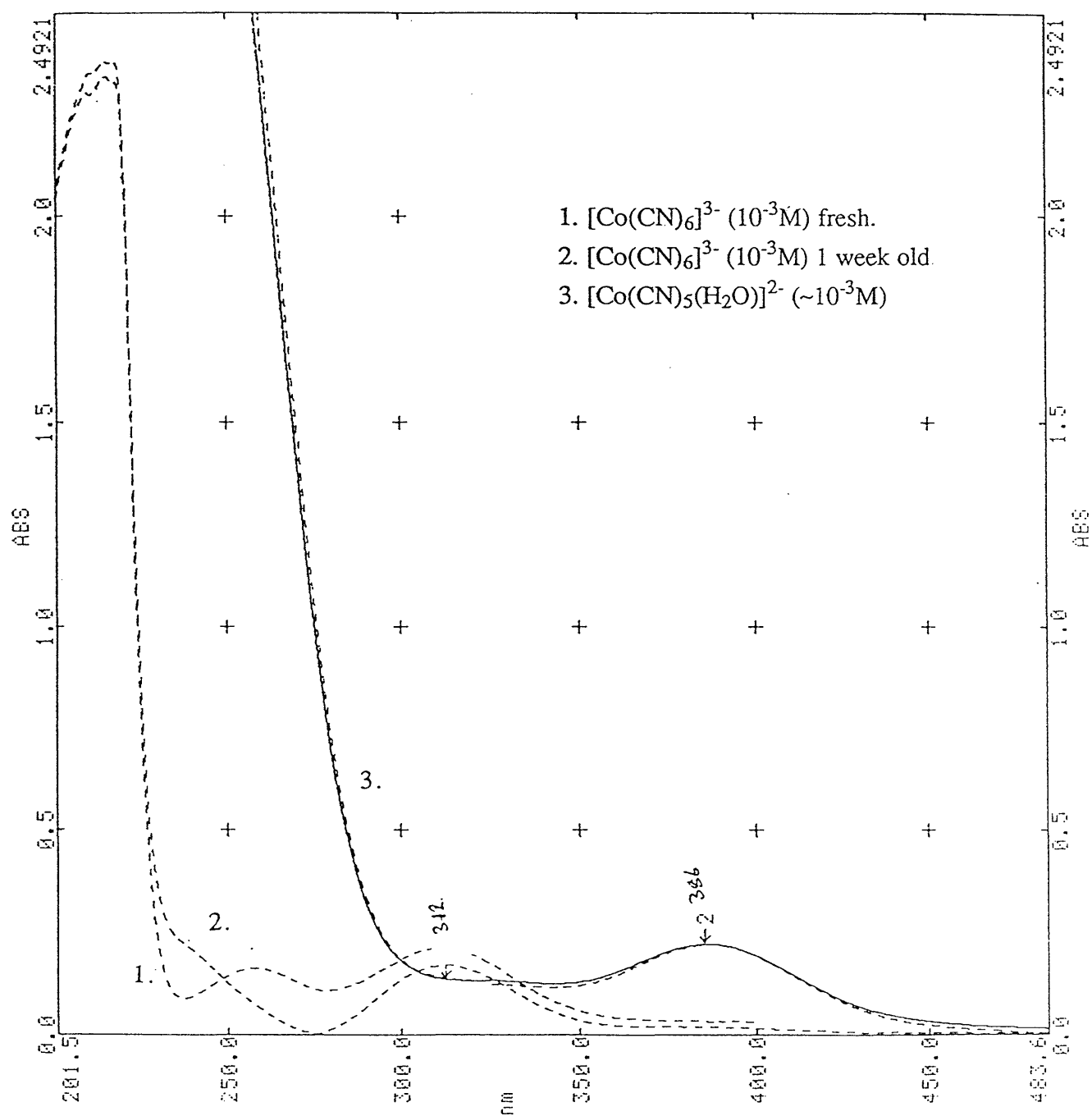
c). No peaks due to the complexes $[\text{Cd}(\text{CN})_4]^{2-}$ and $[\text{Zn}(\text{CN})_4]^{2-}$ were seen. This was because they have no absorption maxima in the UV region and so cannot be detected by this method, although they would be separated from other species on passage through the column.

d). Freshly prepared solutions of $[\text{Co}(\text{CN})_6]^{3-}$ eluted as one peak at 8.15 min. However when the same solution was injected after 24 hours two peaks were observed at 8.15 and 3.24 mins. This second peak is likely to be due to the natural aquation of $[\text{Co}(\text{CN})_6]^{3-}$ as follows.

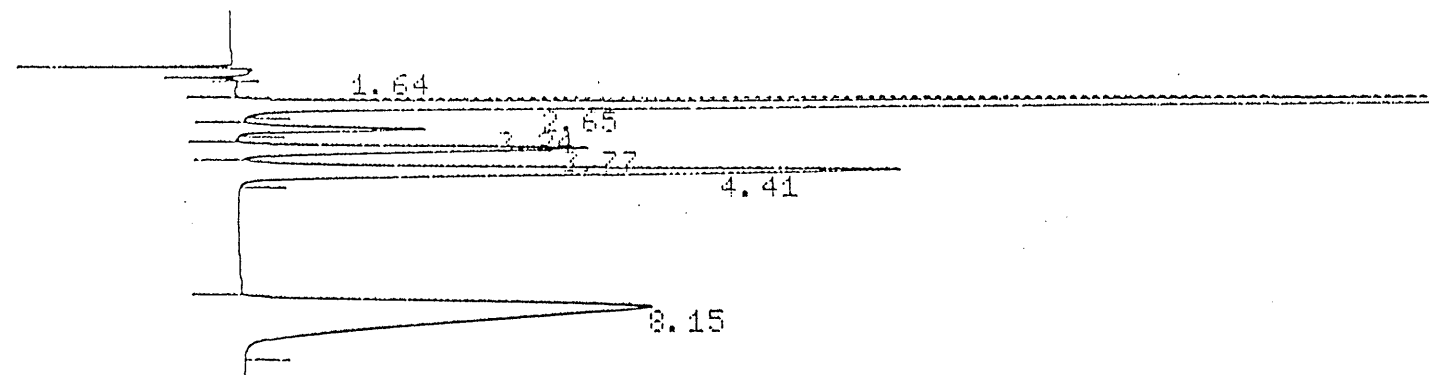


The two species have also been observed by Pohlandt using different columns and detection.^{69,81} The electronic spectrum of $[\text{Co}(\text{CN})_6]^{3-}$ changed as the solution aged and this can be seen in Figure 2.2.i below. Fresh $[\text{Co}(\text{CN})_6]^{3-}$ had absorption maxima at 215, 258 and 312 nm. As the complex aquated the 258nm absorption shifted to become a shoulder at 239nm. The spectrum of a solution containing a much higher concentration of $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$, prepared by irradiating $[\text{Co}(\text{CN})_6]^{3-}$ with UV light, had maxima at 386 nm and approximately 215 nm.¹⁹⁹ The latter absorption had a much larger extinction coefficient ($\epsilon = 21500 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) compared with that of fresh $[\text{Co}(\text{CN})_6]^{3-}$ ($\epsilon = 2550 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). This accounted for the peak at 2.6 min having an appreciable intensity even though only a small proportion of the $[\text{Co}(\text{CN})_6]^{3-}$ had undergone aquation. When the detector was set to 330 nm only one peak due to $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ at 2.48 min was observed since $[\text{Co}(\text{CN})_6]^{3-}$ does not absorb at this wavelength.

Fig 2.2.i. Electronic spectrum showing how the absorption maxima of $[\text{Co}(\text{CN})_6]^{3-}$ change as the complex aquates to $[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$.



CHANNEL A INJECT 28/10/88 12:21:46



INPUT OVERRANGE AT RT= 2.66

28/10/88 12:21:46 CH= "A" PS= 1.

FILE	1.	METHOD	0.	RUN	6	INDEX	6
PEAK#	AREA%	RT	AREA	BC			
1	2.89	1.64	1951172	03	-		
2	35.089	2.65	23685991	01	[Cu(CN) ₃] ²⁻ (2.5 x 10 ⁻⁴ M)		
3	3.259	3.24	2200177	01	[Co(CN) ₅ (H ₂ O)] ²⁻		
4	8.811	3.77	5947538	02	[Ni(CN) ₄] ²⁻ (2.5 x 10 ⁻⁴ M)		
5	18.979	4.41	12811672	03	[Fe(CN) ₆] ³⁻ (10 ⁻⁵ M)		
6	30.971	8.15	20906382	01	[Co(CN) ₆] ³⁻ (2.5 x 10 ⁻⁴ M)		
TOTAL	100.		67502932				

Fig 2.2.ii. Dionex trace (FR = 1 cm³ min⁻¹) showing peaks due to complex cyanides.

2.3. Studies on the Oxidation of Cyano Complexes using H₂O₂.

In this section we present the results and observations of our work on the oxidation of cyano complexes using H₂O₂. The work will be discussed in the following subsections:

- i. A comparison of the reaction of H₂O₂ with the complexes [Zn(CN)₄]²⁻ and [Ni(CN)₄]²⁻ using FTIR, Raman and ¹³C NMR spectroscopy, including studies on the precipitates formed in the above reactions.
- ii. A discussion of the kinetic data measured for the oxidations of [Zn(CN)₄]²⁻ and [Ni(CN)₄]²⁻ with H₂O₂.
- iii. Observations on the effect of H₂O₂ upon other complexes and mixtures of cyano complexes.

2.3.I. Oxidations of [Zn(CN)₄]²⁻ and [Ni(CN)₄]²⁻ with H₂O₂.

It is apparent from section 2.1.II that there has been very little work published concerning the destructive oxidation of cyano complexes, despite the industrial relevance of this topic. Thus there is no clear rationale which can be used to predict the efficiency with which H₂O₂ can be used for treatment of solutions of cyanide complexes, or the kinetics and mechanistic routes by which the oxidation of complexes can be achieved. We have concentrated much of our effort on the study of the oxidation of [Zn(CN)₄]²⁻ and [Ni(CN)₄]²⁻ which are suited to comparison with each other because they are both four coordinate, although the former is tetrahedral and is regarded as being a weak complex, ($\beta_4 = 19.62$ ⁸⁵) whilst [Ni(CN)₄]²⁻ is square planar and moderately strong, ($\beta_4 = 30.3$ ¹⁵⁵).

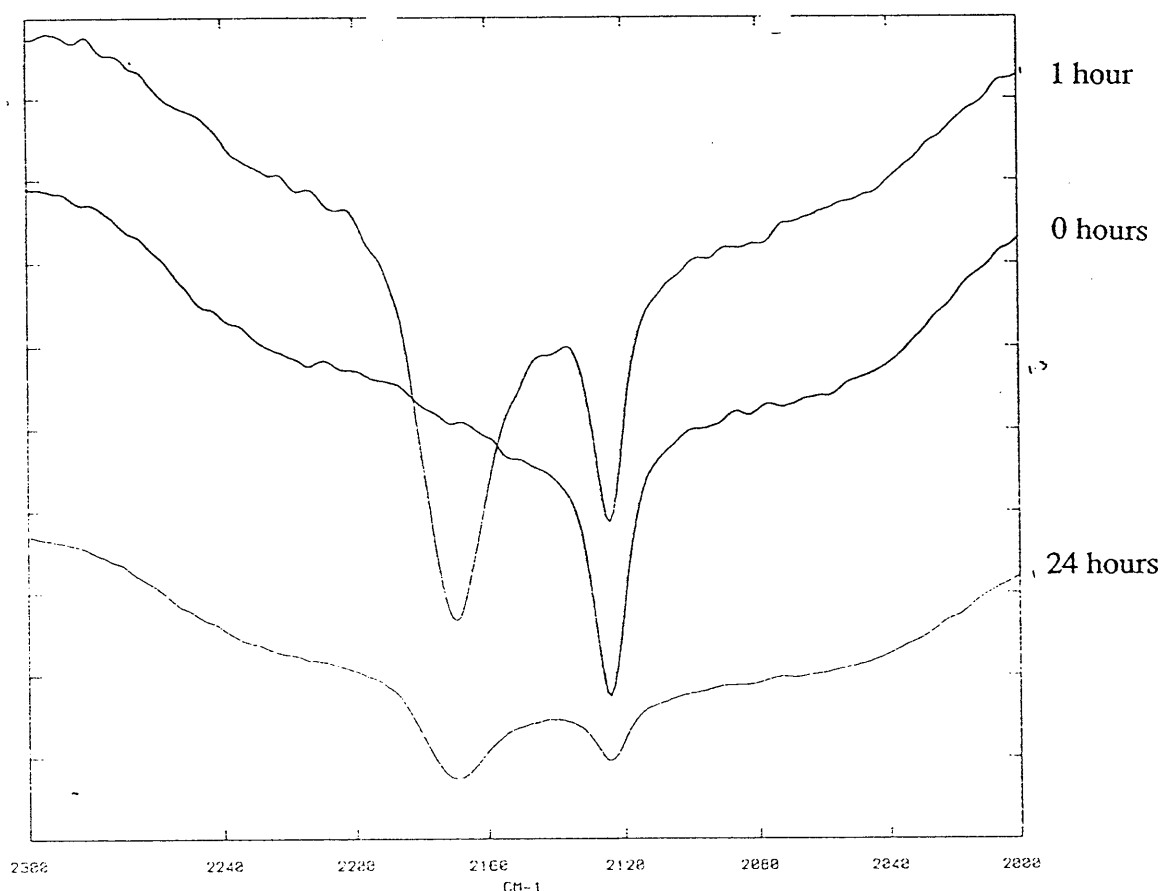
a. Spectroscopic studies of the oxidation of $[\text{Zn}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ by H_2O_2 .

The FTIR spectrum of an aqueous solution of $[\text{Zn}(\text{CN})_4]^{2-}$ (1M) at pH 11 had a single peak at 2151 cm^{-1} in the region $2000 - 2300\text{ cm}^{-1}$ which is known to be due to the asymmetric cyanide stretch (ν_{CN}) of the molecule.²⁰⁴ Upon the addition of H_2O_2 (1.6 M) this peak was rapidly obscured by a broad peak at 2170 cm^{-1} due to the formation of free NCO^- . Because of the proximity of these peaks and the strength of the NCO^- peak, it was not possible to follow the rate of disappearance of the $[\text{Zn}(\text{CN})_4]^{2-}$ by FTIR. The peak at 2170 cm^{-1} remained after one day and was accompanied by a weaker, broad absorption centred at about 2220 cm^{-1} which we tentatively assigned to the presence in solution of coordinated NCO^- , probably as $[\text{Zn}(\text{NCO})_4]^{2-}$. The FTIR spectrum of an aqueous solution of $[\text{Ni}(\text{CN})_4]^{2-}$ (0.1M) has a ν_{CN} band at 2124 cm^{-1} ; known to be due to the asymmetric cyanide stretch.²⁰⁵ H_2O_2 (1M) was added to this solution the band at 2124 cm^{-1} was joined by a band at 2170 cm^{-1} due to ν_{CN} of free NCO^- , although this peak was never broad enough to completely obscure the cyanide peak. Both of these peaks persisted for 24 hours and there was no evidence of a further peak which could be assigned to a coordinated cyanato species (see fig 2.3.i). Comparison of the spectra indicated that less $[\text{Ni}(\text{CN})_4]^{2-}$ was oxidised and thus that less NCO^- was formed overall than was the case with $[\text{Zn}(\text{CN})_4]^{2-}$.

In the Raman spectrum of an aqueous solution of $[\text{Zn}(\text{CN})_4]^{2-}$ (0.25M) at pH 10, there was one peak at 2151 cm^{-1} assigned to the symmetric stretch (ν_{CN}).²⁰⁴ Two hours after the addition of H_2O_2 (1M) this peak was still apparent and no peak due to the formation of NCO^- was observed, although the ν_{CN} vibration of NCO^- is less intense in the Raman than that of CN^- , (see section 1.3.I). However, a peak did appear at 1070 cm^{-1} which we assigned to the symmetric CO stretch of $[\text{CO}_3]^{2-}$, one product of the decomposition of NCO^- . A peak due to H_2O_2 at 874 cm^{-1} was also observed. A similar study of the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ (0.1M) by H_2O_2 (3M) at pH 8 was hampered by the appearance in solution of a blue precipitate (see below). The peaks due

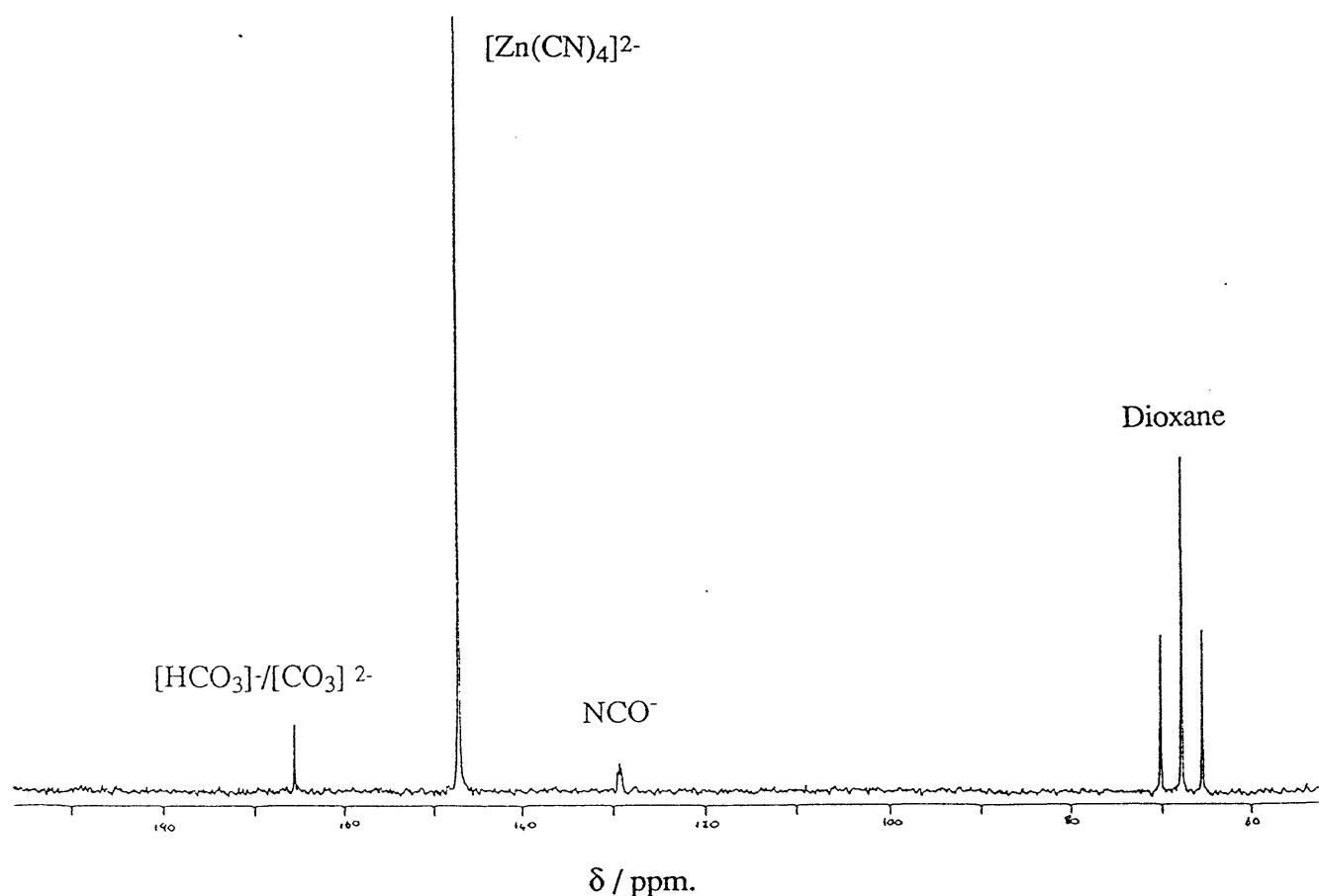
to the ν_{CN} of $[\text{Ni}(\text{CN})_4]^{2-}$ at 2136 and 2145 cm^{-1} gradually decreased in size but we observed no band due to NCO^- and only a very weak band at approximately 1065 cm^{-1} which we attributed to the formation of $[\text{CO}_3]^{2-}$. We saw no band at 1025 cm^{-1} due to $[\text{HCO}_3]^-$, which would also have been formed at this pH although the spectrum was rather noisy in this region.

Fig. 2.3.i. FTIR spectrum showing the incomplete oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ (0.1M) by H_2O_2 (1M).



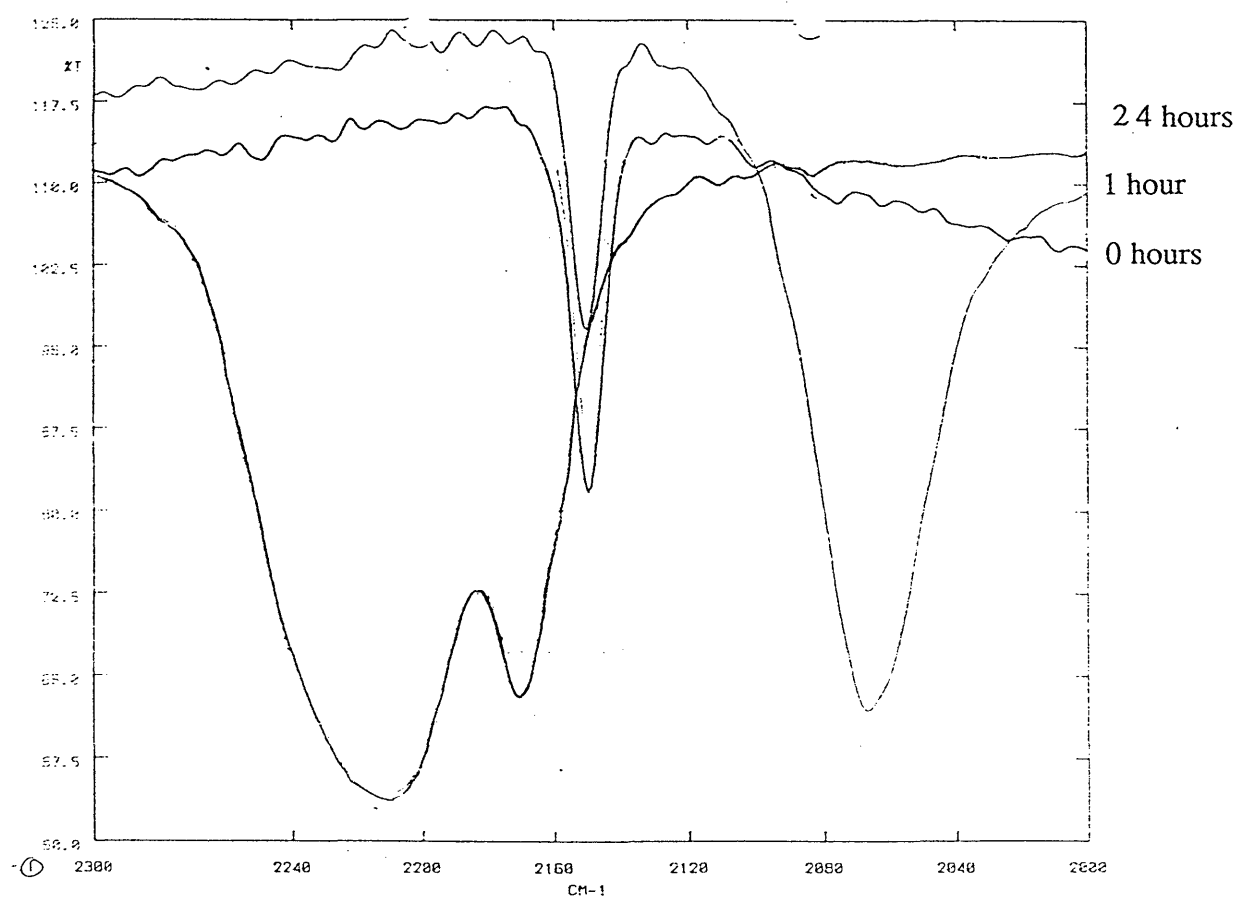
The ^{13}C NMR shift of an aqueous solution of $[\text{Zn}(\text{CN})_4]^{2-}$ (1.2M) occurred at $\delta=147$ ppm (relative to Me_4Si). Within one hour of the addition of H_2O_2 (1.5M), there appeared shifts due to NCO^- ($\delta = 129$ ppm), and $[\text{HCO}_3^-]/[\text{CO}_3]^{2-}$. Those due to these latter species were pH dependent and gave shifts at $\delta = 165.5$ ppm (see fig 2.3.ii) at pH 9.8 and $\delta = 169$ ppm at pH 10.5. In a spectrum run after three hours of reaction (pH = 10.5) there was an additional shift at $\delta = 162$ ppm which we assign as being due possibly to the species $[\text{HCO}_4^-]/[\text{CO}_4]^{2-}$ in accordance with the discussion in section 1.3.I.

Fig.2.3.ii. ^{13}C NMR spectrum of the oxidation of $[\text{Zn}(\text{CN})_4]^{2-}$ (1.2M) by H_2O_2 (1.5M) at pH 9.8 after one hour.



When the oxidation of an aqueous solution of $[\text{Zn}(\text{CN})_4]^{2-}$ (0.35M) or $[\text{Ni}(\text{CN})_4]^{2-}$ (0.1M) by H_2O_2 (0.35M) was carried out in the presence of $[\text{S}_2\text{O}_3]^{2-}$ (0.1M) at $\text{pH} > 10$, the formation of SCN^- was observed by its characteristic ν_{CN} peak at 2066 cm^{-1} in the FTIR. As in the oxidation of free CN^- (see section 1.3.VI), free SCN^- was oxidised by excess H_2O_2 to NCO^- (2170 cm^{-1}).¹⁰⁹ After one day, a broad band at 2212 cm^{-1} was observed in the solution of $[\text{Zn}(\text{CN})_4]^{2-}$ only which we attribute to the presence of coordinated NCO^- (see fig.2.3.iii below).

Fig.2.3.iii. FTIR spectra showing the progress of the oxidation of $[\text{Zn}(\text{CN})_4]^{2-}$ (0.35M) by H_2O_2 (0.35M) in the presence of $[\text{S}_2\text{O}_3]^{2-}$ (0.1M).



b. Precipitates formed in the oxidations of $[\text{Zn}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$.

When the above solution of $[\text{Zn}(\text{CN})_4]^{2-}$ (0.35M), H_2O_2 (0.35M) and $[\text{S}_2\text{O}_3]^{2-}$ (0.1M) after one day of reaction was poured into ethanol, a white precipitate was formed which, after filtration and drying, had infrared peaks at 2219 and 462 cm^{-1} which we attribute to $\text{Zn}(\text{CN})_2$. There was also a weak peak at 2080 cm^{-1} which could have been due to KCN, indicating that some dissociation of $[\text{Zn}(\text{CN})_4]^{2-}$ had taken place.²⁰⁶ There was a further peak at 2290 cm^{-1} which was in the region expected for a coordinated cyanate species, or possibly a polymeric cyanide. However, confirmation of the presence of a coordinated cyanate complex was not possible as the broad peaks due to $[\text{SO}_4]^{2-}$ at 1180 and 619 cm^{-1} would have obscured any other cyanate bands, which occur in the region around 1300 cm^{-1} (ν_{CO}), and between 600 and 700 cm^{-1} (δ_{NCO}).²⁰⁷ The presence of $[\text{SO}_4]^{2-}$ also meant that elemental analysis did not give useful data and so on the basis of the IR evidence we conclude that the precipitate contained principally $\text{Zn}(\text{CN})_2$ with a cyanate species and $[\text{SO}_4]^{2-}$ trapped in the lattice. A white precipitate was also formed from the aqueous $[\text{Ni}(\text{CN})_4]^{2-}$ solution which had bands at 2169 and 448 cm^{-1} characteristic of $\text{Ni}(\text{CN})_2$, and also strong bands at 1176 , 1128 and 619 cm^{-1} , possibly due to K_2SO_4 . There were no bands attributable to any form of cyanate species although the pH of this solution had dropped to 5.7, and so it is likely that any NCO^- would have been swiftly hydrolysed.

In a number of oxidations of $[\text{Zn}(\text{CN})_4]^{2-}$ by H_2O_2 a white precipitate was observed in the solution. The IR spectrum of one such solid after filtration and drying showed strong peaks at 2217 and 464 cm^{-1} . These peaks were assigned as ν_{CN} and δ_{ZnCN} of $\text{Zn}(\text{CN})_2$ and this assignment was confirmed by comparison with the spectrum of a sample of the authentic compound prepared from aqueous $\text{Zn}(\text{NO}_3)_2$ and KCN. Similarly a blue precipitate was also seen to form in the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ by H_2O_2 . The IR of this solid had a peak at 2172 cm^{-1} and 462 cm^{-1} which is in agreement with published values for $\text{Ni}(\text{CN})_2$ ²⁰⁸; we also observed these peaks in the spectrum of a prepared sample of $\text{Ni}(\text{CN})_2$. However, this species was observed less

frequently than was the $\text{Zn}(\text{CN})_2$, presumably because the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ takes place to a lesser extent under the conditions used in our experiments. The exact conditions that favour the formation of these precipitates have not been identified although it seems likely that incomplete oxidation occurs if a low excess of oxidant, or an excess of the complex is used. These precipitates were often observed in oxidations to which $\text{Cu}(\text{II})$ salts had been added as catalysts. As the presence of $\text{Cu}(\text{II})$ would catalyse the decomposition of the H_2O_2 hence lowering the excess of oxidant used this would be expected to favour the formation of such precipitates. (See section 2.3.III for a discussion of other precipitates formed in oxidations of cyanide complexes catalysed by $\text{Cu}(\text{II})$ salts).

c. Conclusions.

In conclusion, these observations show that the behaviour of the complexes $[\text{Zn}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ with H_2O_2 at $\text{pH} > 9$ is broadly similar and follows approximately the same course as the uncatalysed and catalysed reaction with of CN^- and H_2O_2 . However, even from these qualitative data it is apparent that $[\text{Zn}(\text{CN})_4]^{2-}$ undergoes oxidation more easily than does $[\text{Ni}(\text{CN})_4]^{2-}$. Incomplete oxidation of both complexes can occur, especially if the oxidations involve a high concentration of the complex or the reactions are catalysed by $\text{Cu}(\text{II})$, since this results in precipitates of white $\text{Zn}(\text{CN})_2$ and blue $\text{Ni}(\text{CN})_2$. There is evidence for the formation in solution of a $\text{Zn}(\text{II})$ cyanato species but we can find no sign of an analogous $\text{Ni}(\text{II})$ cyanato species.

2.3.II. Kinetic data for the oxidation by H_2O_2 of $[\text{Zn}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$.

Because of the problems that we have had both in the measurement and interpretation of the data we have generated for these systems this section is split into two parts. In the first part we discuss the observations made when oxidations of $[\text{Zn}(\text{CN})_4]^{2-}$ were carried out in buffers and the second part involves a discussion of possible mechanistic routes drawn from both the literature and our own work.

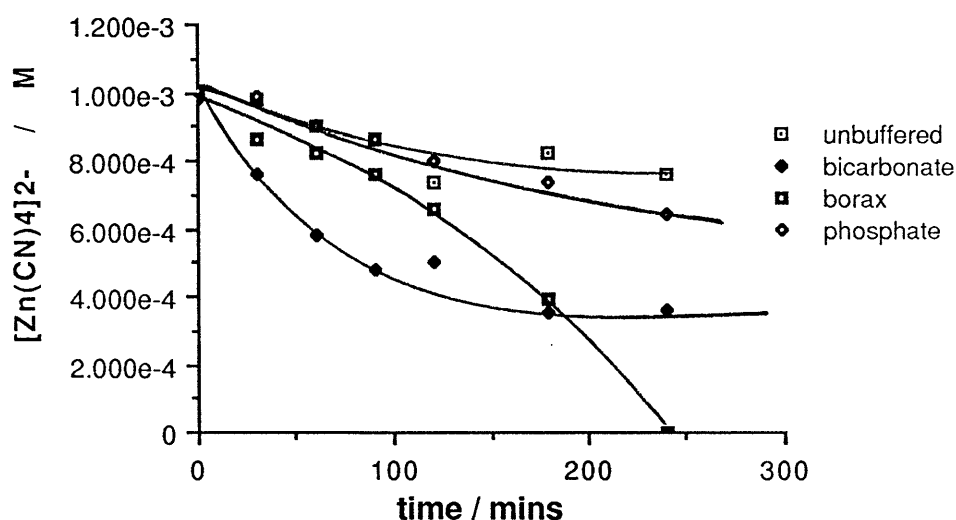
a. Oxidations of $[\text{Zn}(\text{CN})_4]^{2-}$ by H_2O_2 carried out in buffers.

Some work was carried out to investigate the effect of maintaining the pH of oxidations of $[\text{Zn}(\text{CN})_4]^{2-}$ by using a variety of different buffers. These buffers were the same as those used in similar work studying the oxidation of free CN^- (see section 1.3.III) although with these complexes the results were different.

In all the oxidations of $[\text{Zn}(\text{CN})_4]^{2-}$ (10^{-3}M) by H_2O_2 (0.18M) carried out in borax, bicarbonate or phosphate buffer solutions ($\text{pH} = 9.5$) the oxidation occurred at a faster rate than was observed for analogous oxidations in unbuffered solutions, as is clearly shown in graph 2.3.i. below. The rates of oxidations carried out in the phosphate buffer, which is known not to react with H_2O_2 under these conditions were closest to those carried out in unbuffered solutions but 10-20% more of the $[\text{Zn}(\text{CN})_4]^{2-}$ was oxidised in this buffer over five hours. In the bicarbonate buffer, about 65% of the complex was oxidised within 2 to 3 hours but after this no further oxidation took place despite the continued presence of H_2O_2 in the solution. This latter observation is similar to that made for oxidations of free CN^- in this buffer, and which we tentatively suggested was due to the formation of peroxycarbonate ($[\text{HCO}_4]^- / [\text{CO}_4]^{--}$) species in the solution which curtailed the reaction (see section 1.3.III). As can be seen from graph 2.3.i, oxidations of $[\text{Zn}(\text{CN})_4]^{2-}$ carried out in borax buffer at pH 9.5 proceeded at a much faster rate than those in other buffers and in unbuffered solutions, such that

all of the complex as measured using the cyanide electrode was destroyed within two to four hours. In some oxidations in borax buffer the solution turned cloudy just before all the cyanide was removed from solution. This turbidity was probably due to the formation of $\text{Zn}(\text{CN})_2$ and its formation is discussed in section 2.3.I. above. The reason that the oxidation proceeded more rapidly in a borax buffer is not immediately apparent. The ^{11}B NMR of a solution of borax (0.125M), H_2O_2 (0.74M) and $[\text{Zn}(\text{CN})_4]^{2-}$ at pH 9.88 after two hours of reaction had two shifts at $\delta = 3.27$ and $\delta = 3.6$ ppm relative to $\text{Et}_2\text{O} \cdot \text{BF}_3$ ($\delta = 0$ ppm). These have been assigned to the species $[\text{B}(\text{OOH})(\text{OH})_3]^-$ and $[(\text{HO})_3\text{BOOB}(\text{OH})_3]^{2-}$ respectively and their ^{11}B shifts lay at the same positions as reported by Powell *et al.*²⁰⁹ for a solution of $[\text{B}(\text{OH})_4]^-$ (0.5M) at pH 9.9. This would suggest that the $[\text{B}(\text{OH})_4]^- - \text{H}_2\text{O}_2$ equilibrium is not greatly shifted by the presence of $[\text{Zn}(\text{CN})_4]^{2-}$, and it must be assumed that either $[\text{B}(\text{OOH})(\text{OH})_3]^-$ or $[(\text{HO})_3\text{BOOB}(\text{OH})_3]^{2-}$ has greater reactivity towards $[\text{Zn}(\text{CN})_4]^{2-}$ than towards free CN^- .

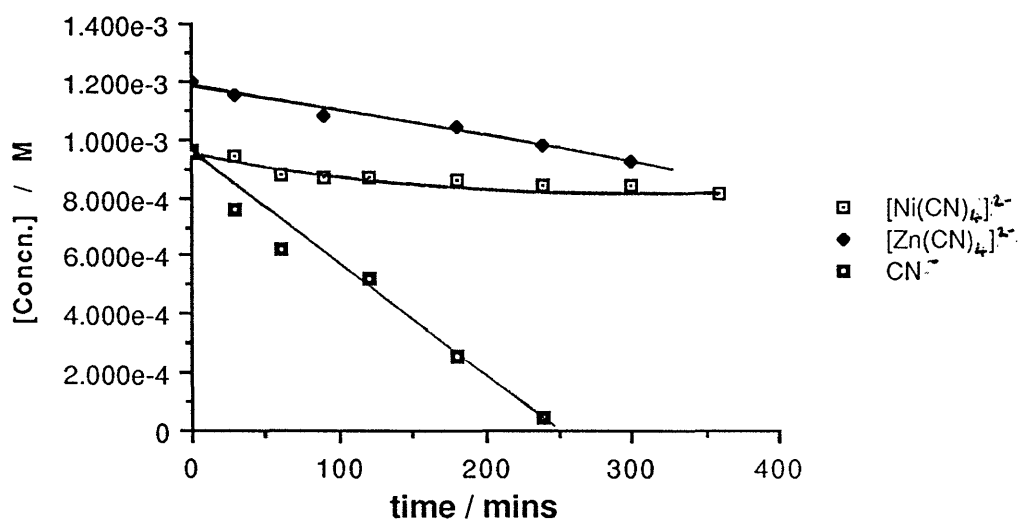
Graph 2.3.i. The oxidation of $[\text{Zn}(\text{CN})_4]^{2-}$ (10^{-3}M) by H_2O_2 (0.18M) at pH 9.5, and in bicarbonate, borax and phosphate buffers. (For details of buffers see section 1.6)



b. Discussion of the data collected regarding the oxidations by H_2O_2 of $[\text{Zn}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$.

Comparison of the data collected using the cyanide electrode for analysis of $[\text{Zn}(\text{CN})_4]^{2-}$ and electronic spectroscopy to analyse for $[\text{Ni}(\text{CN})_4]^{2-}$ confirm the qualitative observations discussed in section 2.3.I above, that $[\text{Zn}(\text{CN})_4]^{2-}$ is oxidised more rapidly by H_2O_2 than is $[\text{Ni}(\text{CN})_4]^{2-}$. The graph (2.3.ii) below shows the decomposition curves of free CN^- , $[\text{Zn}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ (10^{-3}M) in the oxidation reactions of each with excess H_2O_2 (0.16M). However, although the conditions of the oxidations of the complexes were similar to those used for free CN^- , we have been unable to fit the data to simple straight line plots using the theory outlined in section 1.3. for first order reactions, or for second order plots for which a straight line should be obtained when $1/[\text{conc}]$ is plotted against time.

Graph 2.3.ii. The oxidation of CN^- , $[\text{Zn}(\text{CN})_4]^{2-}$, and $[\text{Ni}(\text{CN})_4]^{2-}$ ($\sim 10^{-3}\text{M}$) by H_2O_2 (0.09M) at pH 9.



In the oxidation of these species, we encountered great problems in obtaining reproducible data, and the concentration of the H_2O_2 was observed to drop much more

quickly than was the case for the oxidation of free CN^- , as can be seen from the reaction stoichiometries listed in table 2.3.i. Obviously the lack of comparative k_{obs} values precludes a full discussion of kinetic data but consideration of the available literature concerning the relevant chemistry of these complexes is helpful in explaining some of the observations and in suggesting mechanistic routes for the oxidation.

The stoichiometries listed below were calculated using the ratio of the concentration of H_2O_2 consumed to total cyanide concentration (as CN^-) oxidised. The most likely reason for the wide variation in the stoichiometry of the reaction is the presence of species in solution that catalysed the decomposition of the H_2O_2 . Precautions carried out to ensure that solutions were as clean as possible are described in the experimental section of the first chapter (section 1.6). It was not possible to add Dequest to sequester metal species as this interfered with the analyses.

Table 2.3.i. Conditions and stoichiometries of some oxidations of $[\text{Zn}(\text{CN})_4]^{2-}$ (electrode analysis) and $[\text{Ni}(\text{CN})_4]^{2-}$ (UV analysis unless stated) by H_2O_2 .

Complex	Conc./M	$\text{H}_2\text{O}_2/\text{M}$	pH	$\text{H}_2\text{O}_2:\text{CN}^-$
$[\text{Zn}(\text{CN})_4]^{2-}$	$1 \times 10^{-3} \Delta$	0.045	9.5-8.3	10
$[\text{Zn}(\text{CN})_4]^{2-}$	$1 \times 10^{-3} \Delta$	0.090	9.5-8.5	25
$[\text{Zn}(\text{CN})_4]^{2-}$	$1 \times 10^{-3} \Delta$	0.19	9.5-8.0	6
$[\text{Zn}(\text{CN})_4]^{2-}$	$1 \times 10^{-3} \Delta$	0.27	9.5-8.2	7
$[\text{Ni}(\text{CN})_4]^{2-}$	2×10^{-4}	0.16	10.0-8.7	130
$[\text{Ni}(\text{CN})_4]^{2-}$	2×10^{-4}	0.16	12.2-11.4	750
$[\text{Ni}(\text{CN})_4]^{2-}$	2×10^{-4}	0.16	9.1-9.6	290
$[\text{Ni}(\text{CN})_4]^{2-}$	2×10^{-4}	0.16	9.4-8.1	34
$[\text{Ni}(\text{CN})_4]^{2-}$	5×10^{-4}	0.08	9.4-9.9	8
$[\text{Ni}(\text{CN})_4]^{2-}$	5×10^{-4}	0.16	9.3-9.4	160
$[\text{Ni}(\text{CN})_4]^{2-}$	5×10^{-4}	0.32	9.2-10.2	720
$[\text{Ni}(\text{CN})_4]^{2-}$	5×10^{-4}	0.48	9.2-10.8	440
$[\text{Ni}(\text{CN})_4]^{2-}$	5×10^{-4}	0.08	7.8-8.9	3
$[\text{Ni}(\text{CN})_4]^{2-}$	5×10^{-4}	0.16	7.7-8.6	11
$[\text{Ni}(\text{CN})_4]^{2-}$	5×10^{-4}	0.32	6.8-7.9	106
$[\text{Ni}(\text{CN})_4]^{2-}$	5×10^{-4}	0.48	7.3-8.1	330
$[\text{Ni}(\text{CN})_4]^{2-}$	$1 \times 10^{-3} *$	0.32	9.1-9.2	327
$[\text{Ni}(\text{CN})_4]^{2-}$	$1 \times 10^{-3} *$	0.32	9.1-9.2	540
$[\text{Ni}(\text{CN})_4]^{2-}$	$1 \times 10^{-3} *$	1.5	9.1-9.2	750
$[\text{Ni}(\text{CN})_4]^{2-}$	1×10^{-3}	0.09	7.1-8.3	69
$[\text{Ni}(\text{CN})_4]^{2-}$	1×10^{-3}	0.45	7.1-8.9	132

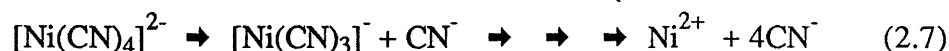
* Dionex analysis Δ in $[\text{ClO}_4]^-$ (10^{-2}M).

The oxidation of cyanide complexes could proceed by two routes; (a), a direct oxidation of the cyanide whilst it is still coordinated to the metal or (b), oxidation of free CN^- following its initial dissociation from the complex.

The principal problem with the first of these mechanisms is that it would require a change of coordination in the complex from a M-CN to a M-NCO moiety, i.e. a metal carbon bond would have to be broken and a metal nitrogen bond formed. We have observed evidence from FTIR spectra for the formation of $[\text{Zn}(\text{NCO})_4]^{2-}$ (see section 2.3.I.a) which we feel is responsible for the broad peak at 2216 cm^{-1} , sometimes observed after the complete oxidation by H_2O_2 of $[\text{Zn}(\text{CN})_4]^{2-}$. We have also isolated what we believe to be $[\text{Cu}(\text{NCO})_3]^-$ on alumina, observed as a blue colour after the oxidation of $[\text{Cu}(\text{CN})_3]^{2-}$ adsorbed on alumina and which has a peak in the IR at 2245 cm^{-1} (for details of this see section 3.1.II). However, we have observed no evidence for the formation of other metal cyanato species (such as $[\text{Ni}(\text{NCO})_4]^{2-}$) in reaction solutions, although the preparation of such complexes is not always possible in aqueous solution as they tend to dissociate or form polymeric precipitates (see section 3.3). Neither of the above observations conclusively proves that the attack by the oxidant occurs at the complex, as both of the above cyanato complexes can be formed from the metal ion and free NCO^- in solution.

In consideration of the second possible mechanism (the oxidation of free CN^- following its dissociation from the complex) it is useful to refer to those published studies that concern the dissociation of cyanide complexes, particularly $[\text{Ni}(\text{CN})_4]^{2-}$.¹⁶⁸⁻¹⁷³ These studies have mainly been carried out at pH below 8 and involve complex mechanisms to explain the kinetics, which are thought to be fifth order, (i.e. first order with respect to the $[\text{Ni}^{2+}]$ and fourth order with respect to $[\text{CN}^-]$).¹⁶⁹ As the conditions were different to those used in this present study (pH 8 to 10), the data cannot be compared directly although some inferences can be drawn from the proposed mechanisms given in the literature. The degree of dissociation of $[\text{Ni}(\text{CN})_4]^{2-}$ at equilibrium increases as the pH is lowered^{154,173}, and at pH >7 the

equilibrium is shifted almost completely to the left hand side of equation 2.7 below which is given by Persson as:¹⁷³



At higher pH the rate of formation of $[\text{Ni}(\text{CN})_4]^{2-}$ is considered to be too fast to be measured easily and any aquation of the complex would also be very fast. The aquation of other cyanide complexes has been shown to be fast on an NMR timescale since scrambling of labelled CN^- occurs but cannot be measured by ^{13}C NMR.¹¹¹ Our own measurements using the cyanide electrode have shown that in a solution of $[\text{Ni}(\text{CN})_4]^{2-}$ (10^{-2}M) at $\text{pH} > 10$, the concentration of free CN^- detected by the electrode is only $2.5 \times 10^{-4}\text{M}$.

A different published study¹⁶⁸ used I_2 as a scavenger for dissociated CN^- to measure the dissociation of cyanide complexes from pH 3 to 8. The observed first order rate constant for the dissociation of $[\text{Ni}(\text{CN})_4]^{2-}$ was found to be $4.8 \times 10^{-4} \text{ s}^{-1}$, which is of the same order of magnitude as we have observed for the oxidation of this complex by H_2O_2 . The observed first order rate constant for the dissociation of $[\text{Cd}(\text{CN})_4]^{2-}$ at pH 10.19 was also measured to be $>10^3 \text{ s}^{-1}$, indicating that dissociation would occur so quickly that this complex would be oxidised as free CN^- and this should thus be the rate determining step for the reaction, rather than the dissociation of the complex. Our studies have been on $[\text{Zn}(\text{CN})_4]^{2-}$, which has a similar overall stability constant ($\beta_4 = 19.62^{85}$) to $[\text{Cd}(\text{CN})_4]^{2-}$ ($\beta_4 = 19.2^{86}$), and it would be reasonable to assume that the dissociation of $[\text{Zn}(\text{CN})_4]^{2-}$ is of the same order as that of $[\text{Cd}(\text{CN})_4]^{2-}$. However the data that we have measured has not reflected this as we have been unable to calculate first order rate constants for this oxidation, which would be expected if the oxidation were solely of free CN^- . In the published study¹⁶⁸, data for the dissociation of $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{Pd}(\text{CN})_4]^{2-}$ indicate that the k_{obs} values are in the region $10^{-5} - 10^{-7} \text{ s}^{-1}$ which is much slower than the rates that we have measured for the oxidation of free CN^- and thus provides an explanation for their

stability to oxidation by H_2O_2 .

There are other possibilities in these reactions, one being the oxidation of Ni(II) to Ni(III) by the H_2O_2 , which has been shown to occur in other complexes such as $[\text{Fe}(\text{CN})_6]^{4-}$ ¹⁵⁹ and $[\text{Cr}(\text{CN})_6]^{4-}$ ¹⁶² using H_2O_2 , and also to $[\text{Mn}(\text{CN})_6]^{3-}$ ¹⁷⁸ and $[\text{Mo}(\text{CN})_8]^{4-}$ ¹⁷⁷ using $[\text{S}_2\text{O}_8]^{2-}$ as the oxidant (see section 2.1.II). If triple salt is used then Ni(III) species can be formed from $[\text{Ni}(\text{CN})_4]^{2-}$ ¹⁸⁰ (see section 2.4.II.), but there is no possibility of this occurring to $[\text{Zn}(\text{CN})_4]^{2-}$ and so the mechanism of the oxidation of this latter complex would have to be different.

2.3.III. The oxidation of other cyanide complexes using H_2O_2 .

We have investigated the effects of H_2O_2 on other cyanide complexes using FTIR and Raman spectroscopy for single complexes and Dionex HPIC to follow the oxidation of mixtures of complexes. FTIR is the most suitable method for observing qualitatively the oxidation of such cyanide complexes because the high extinction coefficient that we have measured for free NCO^- ($\epsilon = 1330 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) means that its formation should be observed even if only a small proportion of the complex, whose concentration is of the order of 0.1M, is oxidised. The table below (2.3.ii) summarises the results obtained based upon the observation of free NCO^- at 2170 cm^{-1} in the FTIR spectra of solutions of cyanide complexes (0.1M) before and after the addition of H_2O_2 (0.3-0.6M).

In the FTIR spectrum of an aqueous solution of $[\text{Cd}(\text{CN})_4]^{2-}$ (0.1M) there were peaks at 2140 and 2148 cm^{-1} , indicating that some dissociation of the complex had occurred to $[\text{Cd}(\text{CN})_3]^-$.¹⁹⁶ Upon addition of H_2O_2 (0.1M), both of these peaks were rapidly obscured as formation of free NCO^- gave rise to a peak at 2170 cm^{-1} . Similarly the complex $[\text{Mn}(\text{CN})_6]^{3-}$ (0.1M), which had an asymmetric stretch at 2112 cm^{-1} also had a peak due to free CN^- at 2068 cm^{-1} indicating hydrolysis had occurred according

to the following equation.



Upon the addition of H_2O_2 (0.6M) there was immediate effervescence and a brown precipitate of $\text{Mn}(\text{OH})_3$ appeared. The oxidant was destroyed within five minutes and very little (<5%) of the CN^- was oxidised, although NCO^- was observed in the FTIR. This was due to the catalytic decomposition of the H_2O_2 by the released metal.²¹⁰

Table 2.3.ii Observations made in the FTIR spectra of cyanide complexes (0.1M) oxidised by H_2O_2 over 24 hours.

Complex	H_2O_2 /M	Oxidation observed
$[\text{Cd}(\text{CN})_4]^{2-}$	0.1	yes
$[\text{Mn}(\text{CN})_6]^{3-}$	0.6	yes
$[\text{Ag}(\text{CN})_2]^-$	0.5	yes
$[\text{Cu}(\text{CN})_4]^{3-}$	0.064-0.64	yes
$[\text{Fe}(\text{CN})_6]^{3-}$	0.32	no
$[\text{Fe}(\text{CN})_6]^{4-}$	0.32	no
$[\text{Co}(\text{CN})_6]^{3-}$	0.8	no

When solutions of $[\text{Cu}(\text{CN})_4]^{3-}$ (0.1M) were oxidised the initial peak at 2076 cm^{-1} was replaced by one at 2093 cm^{-1} , due to $[\text{Cu}(\text{CN})_3]^{2-}$ and sometimes a weak third peak at 2125 cm^{-1} due to $[\text{Cu}(\text{CN})_2]^-$ could also be seen. The band due to free NCO^- usually obscured this latter peak and so it was not always observed. This complex was oxidised very swiftly, which was surprising in view of its overall stability constant ($\beta_4 = 30.7^{84}$). Possible reasons for the facility of this oxidation, which renders copper species useful as catalysts are discussed in section 1.3.V.

When H_2O_2 (0.32M) was added to an aqueous solution of $[\text{Fe}(\text{CN})_6]^{3-}$ (0.1M) at pH 9 a peak at 2044 cm^{-1} appeared, indicating the formation of $[\text{Fe}(\text{CN})_6]^{4-}$. This

reaction, which was first reported by Grusse¹⁵⁹ in 1913, can be reversed to reform the $[\text{Fe}(\text{CN})_6]^{3-}$ if carried out at low pH. It will occur naturally at pH 7 to 10 but the process is relatively slow and it is obvious from the FTIR that the reaction was speeded up in the presence of H_2O_2 . Using FTIR, we found no evidence for the formation of NCO^- , nor did we observe any evidence for the presence of SCN^- when the reaction was carried out in the presence of an excess of $[\text{S}_2\text{O}_3]^{2-}$. Similarly, we were unable to detect the presence of any oxidation products when $[\text{Co}(\text{CN})_6]^{3-}$ (0.1M) and H_2O_2 (0.8M) were mixed at pH 12. This conclusion is reached despite the fact that $[\text{Co}(\text{CN})_6]^{3-}$ is known to aquate in solution to give $[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$ as shown in equation 2.9 below (see section 2.2.III).



This aquation, which releases free CN^- is presumably responsible for the results that we measured using the cyanide electrode in solutions of $[\text{Co}(\text{CN})_6]^{3-}$ (below 10^{-2}M). During calibration of such solutions we measured a potential corresponding to a small concentration of free CN^- . (At a concentration of 10^{-2}M complex this potential corresponded to approximately $4 \times 10^{-5}\text{M}$ free CN^-). This potential dropped rapidly on addition of H_2O_2 (0.09M), indicating that the CN^- was being oxidised, but over a period of one day following the addition, the concentration of CN^- appeared to rise again to its original value. A possible explanation is that, in solution, $[\text{Co}(\text{CN})_6]^{3-}$ aquates according to the equilibrium above. Upon addition of H_2O_2 , the free CN^- is oxidised and excess oxidant decomposes, whereupon the equilibrium is restored and the concentration of free CN^- increases again.

b. The formation of precipitates in oxidations catalysed by CuCl_2 .

When an aqueous solution of copper(II) chloride (10^{-2}M) was added to $[\text{Fe}(\text{CN})_6]^{3-}$ (0.1M) and H_2O_2 (0.18M) a red-purple precipitate was formed. The IR spectrum of this precipitate had a peak at 2089 cm^{-1} , indicating that cyanide was

present, presumably as a ferricyanide or ferrocyanide but the precise form was not clear. Similar precipitates were observed in other reaction solutions where Cu(II) salts were added at a relatively high concentration. The following table summarises the IR data in the ν_{CN} and ν_{MC} regions of these solids.

Table 2.3.iii IR data (in cm^{-1}) for precipitates formed from reaction solutions with an aqueous solution of copper(II) chloride (10^{-2}M).

Species in solution with CuCl_2	Precipitate		
	colour	ν_{CN}	ν_{MC}
$[\text{Ni}(\text{CN})_4]^{2-}$ (10^{-2}M) + H_2O_2 (0.16M).	grey	2185	463
$[\text{Zn}(\text{CN})_4]^{2-}$ (0.1M) + H_2O_2 (1.6M).	white	2217, 2157, 2136	465
$[\text{Zn}(\text{CN})_4]^{2-}$ (0.1M)	white	2138	478
$[\text{Co}(\text{CN})_6]^{3-}$ (10^{-3}M) + H_2O_2 (0.09M).	blue	2188, 2128	467, 417
$[\text{Fe}(\text{CN})_6]^{3-}$ (10^{-3}M) + H_2O_2 (0.09M).	red	2099, 2080	489
$[\text{Fe}(\text{CN})_4]^{4-}$ (10^{-3}M) + H_2O_2 (0.09M).	red-black	2079	475

Analyses of these precipitates did not agree with values calculated for the direct combination of the complexes with Cu(II) or for double salts such as $\text{KCu}[\text{Fe}(\text{CN})_6]$ proposed in the literature.²¹¹ The precipitation with Cu(II) of those cyanide complexes which are stable to copper catalysed oxidation with H_2O_2 has been proposed as a method of completely removing cyanide from effluent solutions.¹⁷⁴

2.3.IV. The oxidation of mixtures of cyanide complexes.

We have carried out a number of oxidations using H_2O_2 of solutions containing mixtures of cyanide complexes to assess whether the order in which the complexes are oxidised is related to their overall stability constants. The analysis of these solutions involved both separation of the complexes and their detection, so we used the Dionex HPIC method which is ideally suited to analyses of this type. All other published methods are useful only to analyse for available or total cyanide and the spectroscopic methods used herein are unsuitable as the absorbance maxima measured in the electronic spectra, and the peaks measured by FTIR and Raman spectroscopy are too close to each other to enable quantitative data to be gained.

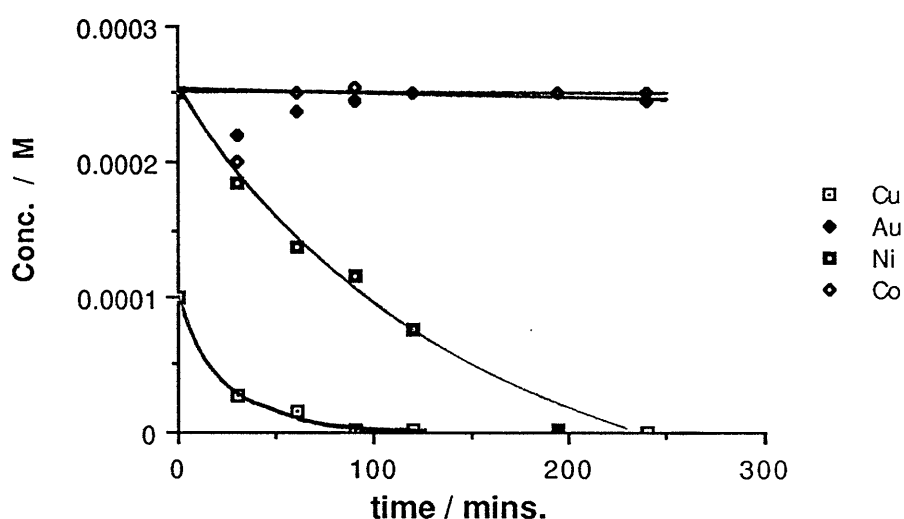
The following graphs show how the concentration of each species in the mixtures changed during the oxidation.

a. Mixture one.

The oxidation of mixture one proceeded in order of increasing overall stability of the constituent cyanide complexes. The peak at retention time (RT) of 2.3 minutes due to $[\text{Cu}(\text{CN})_3]^{2-}$ ($\beta_3 = 29.2^{84}$), which would elute as $[\text{Cu}(\text{CN})_4]^{3-}$ ($\beta_4 = 30.7^{84}$) because of the excess free CN^- in the eluent, disappeared within two hours of the addition of H_2O_2 . The $[\text{Ni}(\text{CN})_4]^{2-}$ (RT = 3.3 min, $\beta_4 = 30.3^{155}$) was steadily oxidised from the time of addition of the oxidant and the peak had disappeared after four hours. Meanwhile the two complexes with high stability constants, $[\text{Co}(\text{CN})_6]^{3-}$ (RT = 5.1 min, $\beta_6 = 50^{154}$) and $[\text{Au}(\text{CN})_2]^-$ (RT = 3.0 min, $\beta_2 = 37^{84}$) were unaffected by the H_2O_2 , even after four hours. However, after only half an hour of reaction the apparent concentration of the $[\text{Co}(\text{CN})_6]^{3-}$ had fallen from $2.5 \times 10^{-4}\text{M}$ to $2 \times 10^{-4}\text{M}$, and that of the $[\text{Au}(\text{CN})_2]^-$ to $2.25 \times 10^{-4}\text{M}$ after which the peaks corresponding to both complexes regained their initial heights. The reason for this apparent drop in the concentrations was not clear although it might have been due to a change in the

conditions of the Dionex, such as a drop in the working pressure and thus casts doubt upon the apparent concentrations of the other two complexes at these times. A peak at $RT = 2.6$ min which we have shown to be due to the formation of $[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$ was observed in the solution after 60 minutes. There was no indication that this species was oxidised.

Graph 2.3.iii The oxidation by H_2O_2 (0.16M) of mixture 1, comprising $[\text{Cu}(\text{CN})_3]^{2-}$ ($1.0 \times 10^{-4}\text{M}$), $[\text{Ni}(\text{CN})_4]^{2-}$ ($2.5 \times 10^{-4}\text{M}$), $[\text{Au}(\text{CN})_2]^-$ ($2.5 \times 10^{-4}\text{M}$), $[\text{Co}(\text{CN})_6]^{3-}$ ($2.5 \times 10^{-4}\text{M}$).

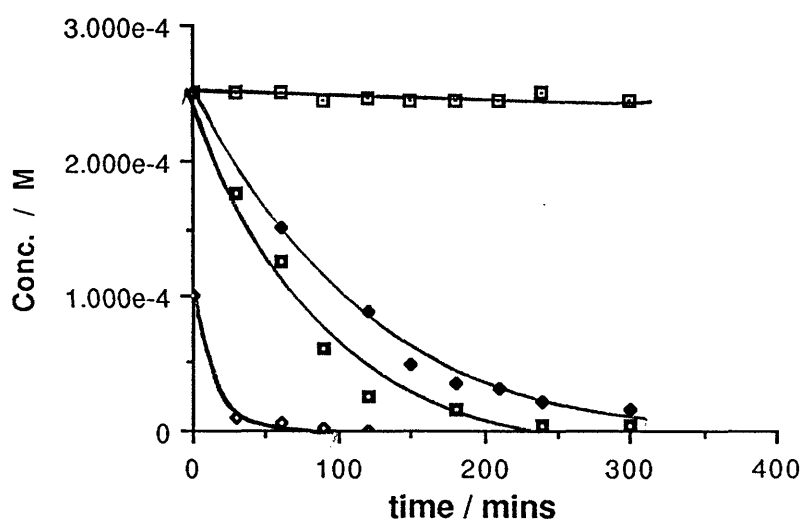


b. Mixture two.

When no $[\text{Cu}(\text{CN})_3]^{2-}$ was present, the second mixture was unaffected after two hours of oxidation by H_2O_2 (0.16M), indicating that $[\text{Ag}(\text{CN})_2]^-$ does not act as a catalyst despite its similarities with $[\text{Cu}(\text{CN})_3]^{2-}$, being below copper in the Periodic table and having the ability to coordinate two, three or four molecules of CN^- . This indicates that the important catalytic property in this reaction would seem to be the ability of copper salts to change their oxidation state between Cu(II) and Cu(I), which is

not a general property of silver salts. Upon the addition of $[\text{Cu}(\text{CN})_3]^{2-}$ ($1 \times 10^{-4}\text{M}$), oxidation did occur but the order was not according to the overall stabilities of the complexes. From graph 2.3.iv it can be seen that the $[\text{Ni}(\text{CN})_4]^{2-}$ ($\text{RT} = 3.3 \text{ min}$, $\beta_4 = 30.3^{155}$), was oxidised more quickly than the $[\text{Ag}(\text{CN})_2]^-$ ($\text{RT} = 1.82$, $\beta_2 = 20.4^{84}$), whilst the $[\text{Pd}(\text{CN})_4]^{2-}$ ($\text{RT} = 5.2 \text{ min}$, $\beta_4 = 42^{157}$) was unaffected even after five hours of reaction. The reason for this apparently anomalous sequence of oxidations is not known.

Graph 2.3.iv. The oxidation by H_2O_2 (0.16M) of mixture 2, comprising $[\text{Ag}(\text{CN})_2]^-$ ($2.5 \times 10^{-4}\text{M}$), $[\text{Ni}(\text{CN})_4]^{2-}$ ($2.5 \times 10^{-4}\text{M}$), $[\text{Pd}(\text{CN})_4]^{2-}$ ($2.5 \times 10^{-4}\text{M}$) and $[\text{Cu}(\text{CN})_3]^{2-}$ ($1 \times 10^{-4}\text{M}$).

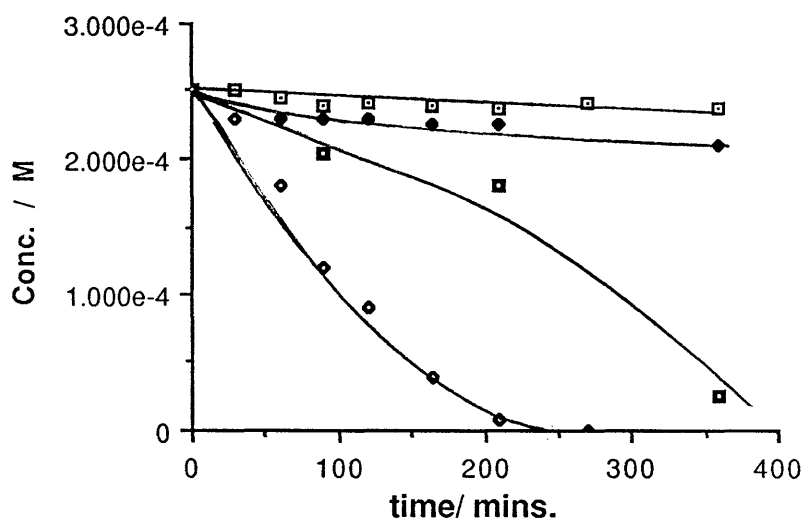


c. Mixture three.

In the uncatalysed oxidation of mixture three this anomalous result was again observed. The $[\text{Ni}(\text{CN})_4]^{2-}$ was oxidised first, (>90% within four hours), followed by $[\text{Ag}(\text{CN})_2]^-$ (> 90% in six hours) whilst $[\text{Au}(\text{CN})_2]^-$ (10%) and $[\text{Pd}(\text{CN})_4]^{2-}$

(<5%) were almost unaffected. When an aqueous solution of copper(II) sulphate (10^{-5} M) was added as a catalyst, the order of the oxidation was the same but the times by which $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ag}(\text{CN})_2]^-$ were completely oxidised were halved. Both $[\text{Au}(\text{CN})_2]^-$ (30%) and $[\text{Pd}(\text{CN})_4]^{2-}$ (10%) were oxidised to a greater degree in three hours when the copper(II) sulphate was present. When an aqueous solution of iron(II) sulphate (10^{-5} M) was added there was no noticeable catalytic effect. However, when an aqueous solution of $[\text{WO}_4]^{2-}$ (10^{-4} M) was added the $[\text{Ag}(\text{CN})_2]^-$ disappeared much more quickly than any other complex (>90% within ninety minutes). The only explanation that we can offer for this surprising result is that the complex formed by $[\text{WO}_4]^{2-}$ and H_2O_2 , $[\text{W}(\text{O}_2)_4]^{2-}$ (see section 1.3.V.b), has some specificity for $[\text{Ag}(\text{CN})_2]^-$ and thus this oxidation occurs more quickly.

Graph 2.3.v The oxidation by H_2O_2 (0.16M) of mixture 3, comprising $[\text{Ag}(\text{CN})_2]^-$ (2.5×10^{-4} M), $[\text{Ni}(\text{CN})_4]^{2-}$ (2.5×10^{-4} M), $[\text{Pd}(\text{CN})_4]^{2-}$ (2.5×10^{-4} M), $[\text{Au}(\text{CN})_2]^-$ (2.5×10^{-4} M).



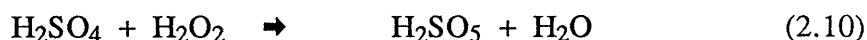
Conclusions.

From the data collected in both the preceeding sections it seems that the effectiveness of H_2O_2 as an oxidant for cyanide complexes decreases as the overall stabilities of the complexes increase. The principal exceptions to this are the complexes $[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Cu}(\text{CN})_3]^{2-}$ and $[\text{Cu}(\text{CN})_2]^-$ which are oxidised at a faster rate than is free CN^- . Possible reasons for the catalytic effect of copper salts are discussed in section 1.3.V.

2.4. Oxidations using Triple Salt and Potassium Caroate.

The practical problems associated with the use of H_2O_2 are great and we have encountered difficulty in measuring reproducible data when using this oxidant due to catalysed decomposition by trace impurities. As we have discussed in the preceeding section, H_2O_2 is not a sufficiently powerful or effective reagent to oxidise to any great extent those cyano complexes of higher overall stabilities than $[\text{Cu}(\text{CN})_4]^{3-}$ ($\beta_4 = 30.7$)⁸⁴, although we have observed some evidence for the copper catalysed oxidation by H_2O_2 of $[\text{Au}(\text{CN})_2]^-$ and $[\text{Pd}(\text{CN})_4]^{2-}$ in mixtures of complexes.

A more powerful peroxidic oxidant is the caroate ion $[\text{HSO}_5]^-$ which can be formed by the careful addition of H_2O_2 to H_2SO_4 at low temperature to make Caro's acid.²¹²



If this is then carefully neutralised with K_2CO_3 , the salt KHSO_5 can be precipitated.



This can be recrystallised to yield the monohydrate, $\text{KHSO}_5 \cdot \text{H}_2\text{O}$. A simpler alternative method of obtaining a solid sample is to pour the neutralised solution into excess ethanol whereby "triple salt", $\text{K}_2\text{SO}_4 \cdot \text{KHSO}_4 \cdot 2\text{KHSO}_5$ precipitates out. This is available commercially as Curox (Interox) and Oxone (Dupont). The advantage of both of these solids is that they can be weighed out and added to reaction solutions with comparative ease. Full details of the preparation of these compounds are given in the experimental section, 2.5. For the purposes of this thesis, triple salt and $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ will be used to describe the specific forms of the oxidant and caroate will refer to the ion, regardless of the form in which it was used.

In this section we first discuss the observations made on the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ using both of the above forms of the caroate ion, and then the kinetic data recorded for these oxidations, followed by observations made on the oxidation of other

complexes in section 2.4.III. In the final subsection we discuss the studies made into the form and decomposition products of the caroate ion.

2.4.I. Oxidations of $[\text{Ni}(\text{CN})_4]^{2-}$ using caroate.

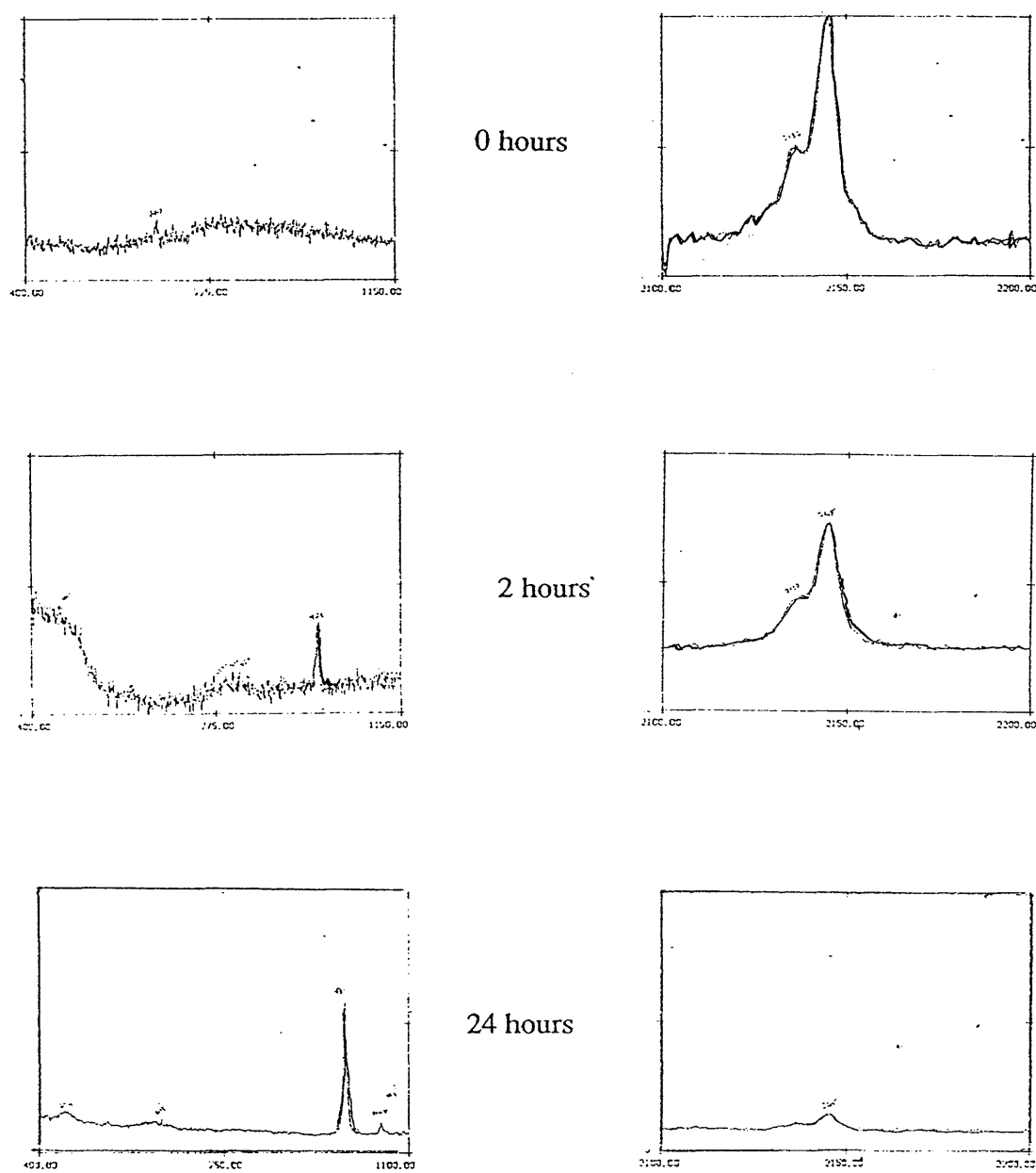
a. Studies of the reaction solutions.

A study of the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ using both triple salt and $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ has been carried out. This reaction proceeded visibly more quickly than did the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ by H_2O_2 under equivalent conditions. In the FTIR spectrum of a solution of $[\text{Ni}(\text{CN})_4]^{2-}$ (0.1M) and triple salt (0.2M) at pH 10 the peak at 2124 cm^{-1} due to the ν_{CN} of the cyano complex was rapidly obscured by a broad band at 2170 cm^{-1} due to the formation of free NCO^- . The appearance of this peak occurred within five minutes, much more rapidly than was observed in the reaction of $[\text{Ni}(\text{CN})_4]^{2-}$ with H_2O_2 . However, the NCO^- peak disappeared within two hours, demonstrating the equally swift removal of this species by hydrolysis in the acid environment created by the addition of triple salt.

The Raman spectrum of aqueous $[\text{Ni}(\text{CN})_4]^{2-}$ (0.1M) had two peaks due to ν_{CN} at 2136 and 2145 cm^{-1} .²⁰⁵ The intensity of these peaks decreased after the addition of triple salt (0.32M) but no peak due to NCO^- was observed probably due to the rapid hydrolysis of this species when the pH dropped from 10 to 2. In the other region scanned ($500 - 1100 \text{ cm}^{-1}$) the most intense peak occurred at 982 cm^{-1} , which was due to the symmetric stretch ν_{SO} of the $[\text{SO}_4]^{2-}$, present in the triple salt, and also the final product of the decomposition of the $[\text{HSO}_5]^-$. The only other peak visible after one day of reaction was at 1048 cm^{-1} and we concluded by comparison with a standard spectrum that it was due to $[\text{HSO}_4]^-$. There were no peaks which could be attributed to either $[\text{HCO}_3]^-$ or $[\text{CO}_3]^{2-}$, presumably because the drop in pH to around 2 that occurred when the triple salt was added caused CO_2 to be evolved and thus removed from the solution (see fig 2.4.i below). However when the above reaction was carried

out with additions of NaOH made after each addition of triple salt to correct the pH to between 8 and 10 the main peaks are as listed above with additional peaks due to $[\text{HCO}_3]^-$ at 1034 cm^{-1} , $[\text{CO}_3]^-$ (1063 cm^{-1}), and $[\text{SO}_4]^{2-}$ (835 , 1077 and 1125 cm^{-1}).

Fig. 2.4.i. Raman spectra showing the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ (0.1M) by triple salt (additions of 0.32M) at pH 2.



It was possible to follow the course of the oxidations using the characteristic absorption maxima of the $[\text{Ni}(\text{CN})_4]^{2-}$ at 268 and 286 nm in the electronic spectrum. We could find no evidence in the such spectra of an absorption at 255 nm, reported by Li Wang *et al.*¹⁸⁰ and attributed to the formation of $[\text{Ni}^{\text{III}}(\text{CN})_4(\text{H}_2\text{O})_2]^-$, although in correspondence with the principal author of this paper²¹³, we were informed that the formation of this rather transient species is only observed when excess triple salt is used and if the pH is kept below 3 to slow down the rate of decomposition of the $[\text{Ni}^{\text{III}}(\text{CN})_4(\text{H}_2\text{O})_2]^-$ complex. We did however observe the absorption maximum at 255 nm. using NaOCl as the oxidant at pH 3.

b. Precipitates formed during the reactions.

The nature of the nickel containing species after oxidation appeared to differ according to the concentrations of the reactants. If the ratio of $[\text{HSO}_5]^- : \text{CN}^-$ was small (<5) or if a high concentration of both reactants (>0.5M) was used, then a blue precipitate was observed. If the reaction was carried out at a low pH (<5) then this precipitate would dissolve in excess H_2O and was probably due to the formation of nickel(II) sulphate species. The IR spectrum of this blue solid had strong peaks at 1119 and 617 cm^{-1} and, upon addition of BaCl_2 solution to a solution of this solid, a white precipitate was formed which was insoluble in H_2SO_4 , suggesting both chemically and spectroscopically the presence of $[\text{SO}_4]^{2-}$. The Raman of this solid had no peaks due to cyanide in the region $2000\text{--}2300\text{ cm}^{-1}$, and the principal peaks occurred at 897, 982 and 1060 cm^{-1} from which we conclude the composition to be a mixture of nickel(II) sulphate and bisulphate. If the pH of the reaction was above 8, the caroate decomposed and incomplete oxidation occurred, resulting in a blue precipitate which would not redissolve. The IR of this solid had a strong band at 2172 cm^{-1} which coincided with ν_{CN} of $\text{Ni}(\text{CN})_2$. There were also bands at 1119 and 619 cm^{-1} which indicated that sulphate was present but elemental analysis of the blue precipitate showed the composition to be C (15.32%), H (2.56%) and N (17.82%). These values were

aproximately equivalent to a composition of $\text{Ni}(\text{CN})_2 \cdot 2\text{H}_2\text{O}$ (requires 16.35% C, 2.72% H and 19.09% N). If a large excess of triple salt was used then no such precipitate was observed although slow evaporation of strong solutions yielded crystals of nickel(II) sulphate. The solutions were generally green in colour after all oxidation was complete, indicating the presence of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.

In studies to determine the kinetics of oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ carried out at low concentration ($\approx 10^{-4}\text{M}$), using triple salt ($> 10^{-3}\text{M}$), pH stat equipment was used to maintain the pH. This used a pH electrode connected to a pump which added acid or alkali to the reaction solution when the pH of the solution drifted beyond preset levels. During these kinetic oxidations a fine black precipitate was sometimes observed, and this was particularly noticeable around the NaOH inlet of the pH stat. When the oxidation was carried out in an aqueous solution of NaOH (0.2M), the black precipitate was seen in the solution after ten minutes of reaction. The solid turned green after collection by centrifugation and oven drying at 80°C . Its IR spectrum showed peaks at 2129 and 2172 cm^{-1} indicating the presence of cyano groups but elemental analysis indicated only traces of C and N. It is likely that this black precipitate was a nickel hydroxy species contaminated with some cyanide or possibly cyanate.²¹⁴

c. Conclusions.

To summarise these observations, complete oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ by triple salt or $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ produces NCO^- which will rapidly be removed by hydrolysis if the reaction is carried out at low pH. If the oxidation is incomplete, blue $\text{Ni}(\text{CN})_2$ is precipitated out or it is possible to form a black solid of indeterminate structure if the reaction is carried out at high pH (>11).

2.4.II. Kinetics of the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ using caroate.

The salt $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ is the most suitable form of caroate for kinetic measurements as it is less acidic than triple salt. However we encountered problems of irreproducibility due to the instability of the caroate ion at elevated pH (>7) using both $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ and triple salt. In this section the kinetic data we measured using $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ and triple salt are discussed separately. The concentration of the $[\text{Ni}(\text{CN})_4]^{2-}$ was measured using the peak at 268 nm in the electronic spectrum, which was not obscured by absorption due to the oxidant (with H_2O_2 this method was not possible unless the oxidant, which absorbs strongly in the UV was first removed using MnO_2 or Catalase). The peroxide concentration was measured by iodometric titration with $[\text{S}_2\text{O}_3]^{2-}$ (see experimental section 1.6).

a. Kinetic data measured with $\text{KHSO}_5 \cdot \text{H}_2\text{O}$.

A number of oxidations were carried out in unbuffered solution using the pH stat to maintain the pH at 8 for reactions between $[\text{Ni}(\text{CN})_4]^{2-}$ (2×10^{-4} M) and at least a ten fold excess of $\text{KHSO}_5 \cdot \text{H}_2\text{O}$. The data listed in table 2.4.i were obtained using electronic spectrophotometry. In addition to these results there were other oxidations for which first order kinetics were not observed. The reasons why only some reactions appeared to follow these kinetics are not clear although the problems associated with the use of both triple salt and $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ are discussed below. The results suggest that there is no simple first order relationship with respect to the concentration of oxidant when measured in unbuffered solution. However the wide variation in stoichiometries calculated for these reactions, and the problems encountered in some oxidations for which straight line plots could not be drawn prompted an investigation into the use of buffers.

Table 2.4.i Kinetic data measured for unbuffered oxidations of $[\text{Ni}(\text{CN})_4]^{2-}$ ($2 \times 10^{-4}\text{M}$) by $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ at pH 8.

$[\text{HSO}_5]^- / \times 10^3 \text{ M}$	$k_{\text{obs}} / \times 10^5 \text{ s}^{-1}$	$[\text{O}_2]^{2-} : [\text{CN}]^-$
1.9	2.78	19.8
3.9	7.64	23.7
5.5	7.96	8.06
8.0	9.66	13.6

We used phosphate buffer (0.075-0.1M) for the majority of our studies of the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ by KHSO_5 . The ^{31}P NMR shift of $[\text{PO}_4]^{3-}$ (0.5M) at pH 8.1 had one resonance at $\delta = 5$ ppm, which was neither shifted nor split when an aqueous solution of $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ (0.25M) was added, indicating that no peroxophosphate species was formed in the solution. Both the chemical shift of the $[\text{PO}_4]^{3-}$ and the absence of splitting upon addition of the peroxide are in agreement with the published results for the $[\text{PO}_4]^{3-} / \text{H}_2\text{O}_2$ system which show that there is essentially no chemical reaction between phosphate and H_2O_2 in the pH range to 12, on the basis of ^{31}P NMR studies.¹⁴⁸ In this buffer some oxidations were carried out in a quartz UV cell, thermostatted at 23°C whilst in the spectrophotometer, thus removing possible errors which could have arisen from taking aliquots from the reaction and transferring them to the cell.

The following table (2.4.ii) summarises the conditions of some of the reactions carried out in this study. From the table it can be seen that there are a number of incongruous results but the overall trend is an increase in rate approximating to the best fit line on graph 2.4.i below and a reaction stoichiometry, $[\text{HSO}_5]^- : [\text{CN}]^-$ of between 10 and 27. This is far in excess of the four mols $[\text{HSO}_5]^-$ required per $[\text{Ni}(\text{CN})_4]^{2-}$ by the overall stoichiometric equation.

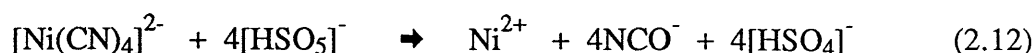
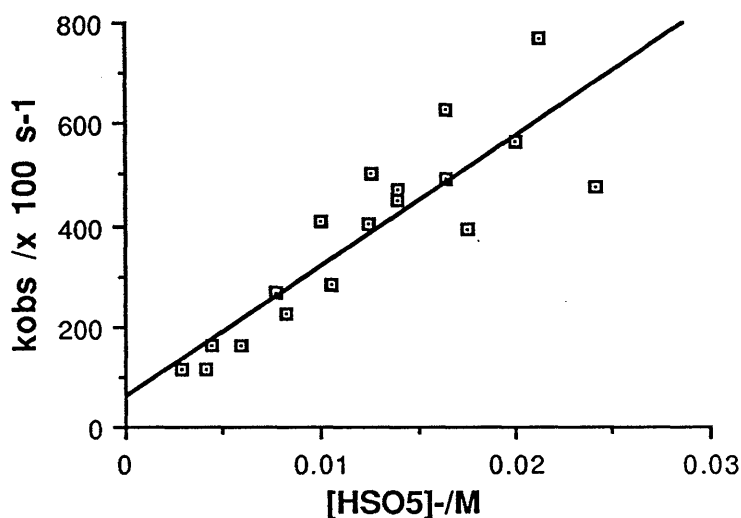


Table 2.4.ii. Data recorded for the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ ($2 \times 10^{-4}\text{M}$) using $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ in phosphate buffer (0.1M).

$[\text{HSO}_5]^- / \times 10^3 \text{M}$	pH	temp / $^\circ\text{C}$	$k_{\text{obs}} / \times 10^4 \text{s}^{-1}$	$[\text{HSO}_5]^- : [\text{CN}]^-$
2.9	8.00-7.95	22.5	1.16	-
4.12	7.91	24.7	1.14	0.31
4.41	8.01-7.93	23	1.6	-
5.88	7.91-7.85	23.8	1.63	20.3
7.65	8.01-7.84	23	2.68	-
8.23	7.91-7.64	23	2.26	5.8
10.0	8.00	22.5	4.07	-
10.6	7.91	24.0	2.83	-
12.4	7.91	23.0	4.02	-
12.6	8.0	22.5	5.04	-
14.0	8.08	23.3	4.5	14.0
14.0	8.1-7.6	22.7	4.69	10.75
16.5	7.91-7.49	23.7	4.90	25.0
16.5	8.0	22.5	6.25	-
17.6	8.07	23.8	3.92	26.9
20.0	8.0-7.75	23.0	5.67	26.3
21.2	8.0	22.5	7.67	-
24.1	8.07-7.55	24.0	4.75	23.8

Graph 2.4.i Plot of k_{obs} against concentration of $[\text{HSO}_5]^-$ for the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ ($2 \times 10^{-4}\text{M}$) in phosphate buffer at pH 8.



The best fit line on graph 2.4.i above is consistent with kinetics that are first order with respect to the $\text{KHSO}_5 \cdot \text{H}_2\text{O}$, although the scatter is rather wide. One reason for this might be due to photocatalysis caused by the UV lamp, which irradiated the reaction solution throughout as the cell was left in the spectrophotometer. However, no apparent effect was observed in oxidations carried out with the cell removed from the light beam for a period during the reaction. Nevertheless, photochemical reaction pathways involving the $[\text{HSO}_5]^-$ radical are known²¹⁵ and we have shown that oxidations of $[\text{Ni}(\text{CN})_4]^{2-}$ by triple salt are slowed down by the addition of radical traps (see next section). The most likely reason for the wide variation in the observed stoichiometries is catalysis caused by transition metal species in solution. Measures taken to ensure that these impurities were kept to a minimum are described in section 1.6.

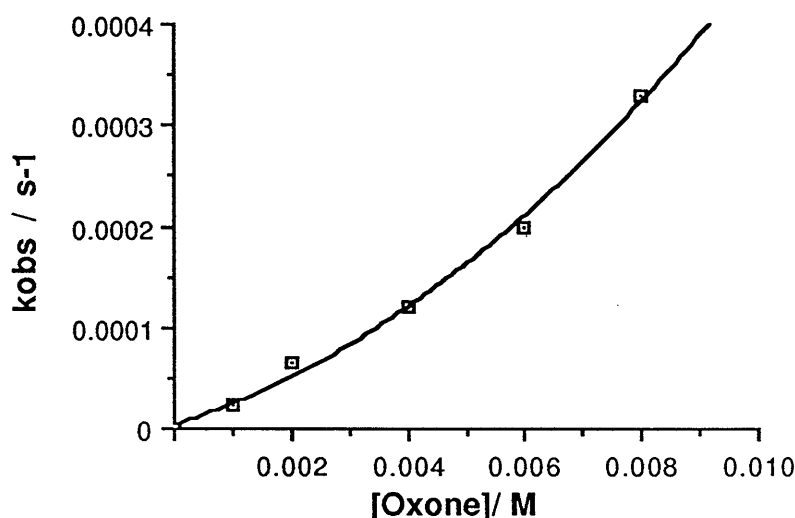
Some oxidations were carried out in buffers made up from borax (0.1M) and carbonate (0.1M) but none of the data from these oxidations would fit first or second order plots. The reasons for this are not clear although it is likely that the formation of

peroxy species in solution plays some role in the oxidation, as we have observed in the oxidation of CN^- with H_2O_2 in these buffers (see section 1.3.III).

b. Kinetics measured using triple salt.

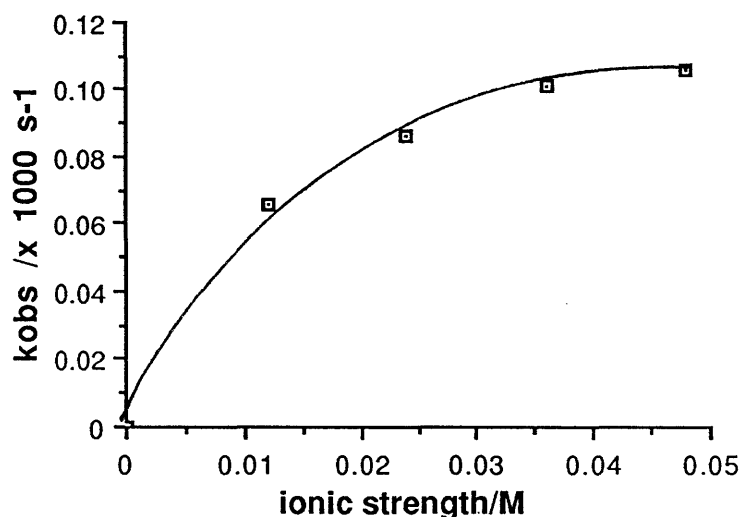
Initial work to measure the kinetics of the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ by caroate was carried out using triple salt, $(\text{K}_2\text{SO}_4.\text{KHSO}_4.2\text{KHSO}_5)$ as the oxidant. Triple salt is very acidic due to the presence of KHSO_4 and so reactions were carried out using pH stat equipment which automatically added NaOH when the pH dropped below a preset level. Using initial concentrations of $[\text{Ni}(\text{CN})_4]^{2-}$ ($2 \times 10^{-4}\text{M}$) and triple salt ($2 \times 10^{-3}\text{M} = [\text{HSO}_5]^- 4 \times 10^{-3}\text{M}$) at pH 8.3, a plot of $\ln.[\text{Ni}(\text{CN})_4]^{2-}$ against time was a straight line indicating that the reaction was first order with respect to the $[\text{Ni}(\text{CN})_4]^{2-}$. The gradient of the straight line was $1.23 \times 10^{-4} \text{ s}^{-1}$ which we took to be k_{obs} . Comparison of the values of k_{obs} measured using $\text{KHSO}_5.\text{H}_2\text{O}$ (see table 2.4.ii above) and triple salt indicated that at low concentrations of $[\text{HSO}_5]^-$ ($< 4 \times 10^{-3}\text{M}$) the rates of oxidation were essentially the same, but as the concentration of the oxidant was increased, then the oxidations by triple salt proceeded more quickly than those with $\text{KHSO}_5.\text{H}_2\text{O}$. Kinetics with respect to the $[\text{Ni}(\text{CN})_4]^{2-}$ were first order using both oxidants but the data were only poorly reproducible (see graph 2.4.i above). As the concentration of triple salt was increased the values of k_{obs} increased in a curve, rather than a straight line (see graph 2.4.ii below). This indicates that either the reaction was not first order with respect to the triple salt, or that some other effect was causing the slight deviation from the expected kinetics.

Graph 2.4.ii. Plot of k_{obs} against concentration of triple salt ($\text{Oxone} = 2[\text{HSO}_5]^-$) for the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ ($2 \times 10^{-4} \text{ M}$) at pH 8.3.



Using the equation in section 1.3.IV governing the effect of the ionic strength on the rate of reaction it can be deduced that for two reaction species of a similar charge, namely $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{HSO}_5]^-$, an increase in the ionic strength should result in an increase in the observed rate, which is in agreement with our data. This is because the activated complex formed when these species combine would be more stable in an environment of higher overall charge.¹²¹ In these oxidations the increase in the ionic strength comes about from the dissociation of the K_2SO_4 and KHSO_4 in the triple salt. To test this theory, oxidations of $[\text{Ni}(\text{CN})_4]^{2-}$ ($2 \times 10^{-4} \text{ M}$) using triple salt ($2 \times 10^{-3} \text{ M}$) were carried out in solutions containing different concentrations of K_2SO_4 , added to alter the ionic strength. In these oxidations the k_{obs} values increased with ionic strength but the data did not show a quantitative trend. This is illustrated in graph 2.4.iii below.

Graph 2.4.iii. Plot of k_{obs} against ionic strength for the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ ($2 \times 10^{-4} \text{ M}$) by triple salt ($2 \times 10^{-3} \text{ M}$) at pH 8.6 with added K_2SO_4 .

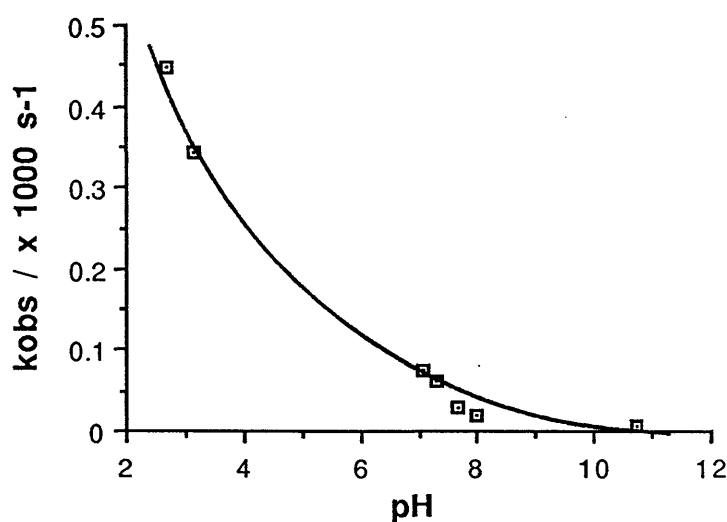


Another possible explanation for the irreproducible data and the deviations from first order kinetics could be the inability of the pH stat to maintain the pH. As the concentration of the triple salt was increased, then so did the concentration of KHSO_4 and the total volume of NaOH (0.02 M) required to maintain the pH of the reaction was larger, thus introducing an increasing systematic error into the analysis. To overcome this, the concentration of the NaOH was raised (up to a maximum of 0.2 M) but even small incremental additions of this stronger alkali caused the pH to rise above 9 whereupon there was visible decomposition of the triple salt, seen as effervescence in the solution, and in some solutions a black precipitate was observed as discussed in section 2.4.I.b above. A third possibility is the presence in solution of impurities that could cause the decomposition of the $[\text{HSO}_5]^-$. During all our work we took precautions to ensure that the solutions were as clean as possible but the addition of the sequestrant Dequest was not possible as it interfered with the analysis of the $[\text{Ni}(\text{CN})_4]^{2-}$. The measures that we used are described in section 1.5.

A short pH study of the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ by triple salt showed that the

rate of oxidation increased dramatically as the pH was lowered below 9 (see graph 1.4.iv) which stressed the need for the pH control to be absolute.

Graph 2.4.iv. The effect of pH on the rate of oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ ($2 \times 10^{-4}\text{M}$) by triple salt ($2 \times 10^{-3}\text{M}$).

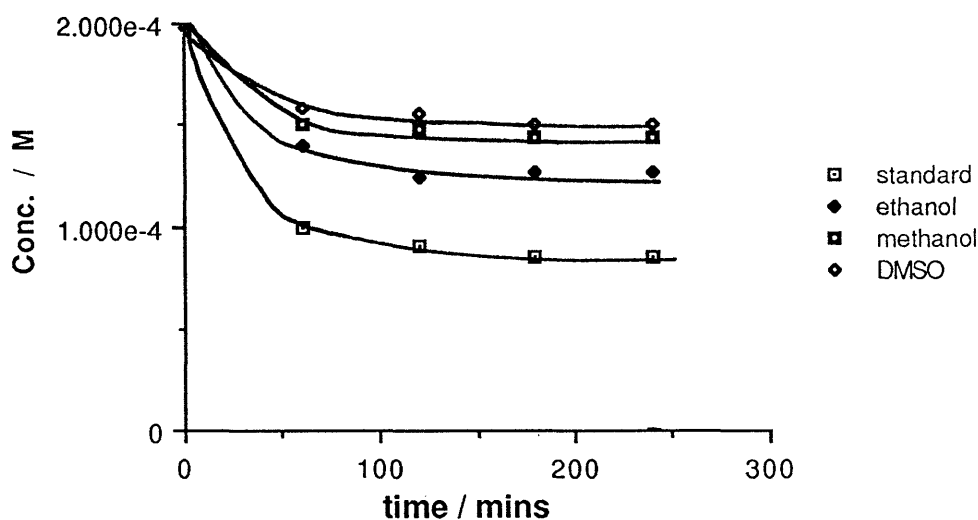


The reasons for this pH effect are probably twofold. The first is the increased stability of the caroate at pH below 8 which results in less oxidant being consumed by decomposition, and the second is the increasing rate of dissociation of $[\text{Ni}(\text{CN})_4]^{2-}$ as the pH is lowered, (for a discussion of published data pertaining to this effect see section 2.2.II). In an attempt to overcome this problem oxidations were carried out in buffers, which would act not only to maintain the pH but also ensure that the reactions took place in an environment of a high, effectively constant ionic strength. The buffers used were made up of borax, bicarbonate and phosphate, and these were as used in section 1.3.III. Despite the excess concentration of buffer over the concentration of reactants the pH control in the region 8 to 8.5 was poor and, as with the oxidations carried out with $\text{KHSO}_5 \cdot \text{H}_2\text{O}$, those oxidations of $[\text{Ni}(\text{CN})_4]^{2-}$ carried out in the borax and bicarbonate buffers did not follow first order kinetics, i.e. plots of $\ln.[\text{Ni}(\text{CN})_4]^{2-}$

against time were not straight lines. It was not clear whether the reason for this was due to the variable pH or because peroxy species were being formed in the same way as between H_2O_2 and bicarbonate or borax.

There are a number of mechanisms for the decomposition of $[\text{HSO}_5]^-$ involving free radicals such as $[\text{SO}_4]^\cdot$ and $[\text{OOSO}_3]^\cdot$ ²¹⁵, and it is possible that the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ proceeds via a free radical pathway. To investigate this we carried out a series of oxidations at high pH with additions of ethanol, methanol and DMSO (4% v/v). The results are summarised in graph 2.4.v. below. We found that over four hours all the triple salt had decomposed and 60% of the $[\text{Ni}(\text{CN})_4]^{2-}$ was oxidised in the standard, whereas in the oxidations carried out in the presence of the radical traps, all oxidation had ceased after three hours and the amount of $[\text{Ni}(\text{CN})_4]^{2-}$ oxidised was less overall in ethanol (35%), methanol (27%) and DMSO (22%).

Graph 2.4.v. Oxidations of $[\text{Ni}(\text{CN})_4]^{2-}$ ($2 \times 10^{-4}\text{M}$) by triple salt ($2 \times 10^{-3}\text{M} = 4 \times 10^{-3}\text{M}$ $[\text{HSO}_5]^-$) at pH 11.5 to 12 with additions of ethanol, methanol and DMSO (4%).



Similar reactions carried out at pH 8 to 9 using additions of ethanol were also decelerated indicating that there is some radical pathway by which the oxidation

occurs, but it is unlikely to be the only mechanistic route.

We carried out no detailed study of the effect of adding Cu(II) salts to oxidations of $[\text{Ni}(\text{CN})_4]^{2-}$ with triple salt. However, qualitative observations indicated that the oxidation of $[\text{Ni}(\text{CN})_4]^{2-}$ proceeded more rapidly when aqueous solutions of both copper(II) chloride and sulphate were added and the solution turned green in most cases. This colour was also observed if aqueous copper(II) chloride (0.1M) was added to a solution of triple salt (0.5M) at pH 7 and it is possible that this is due to the formation of an intermediate similar to that formed when Cu(II) salts are added to solutions of H_2O_2 (see section 1.3.V).^{129,130}

c. Conclusions.

In conclusion, oxidations of $[\text{Ni}(\text{CN})_4]^{2-}$ carried out using both triple salt and $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ appeared to follow first order kinetics with respect to the concentration of both $[\text{Ni}(\text{CN})_4]^{2-}$ and that of the oxidant but our data were poorly reproducible due to the effects of a variety of other parameters, including the pH and ionic strength of the solution, which affected the rate of reaction, and the presence in solution of species catalysing the decomposition of the $[\text{HSO}_5]^-$ ion. The mechanisms of this oxidation almost certainly involve some sort of free radical species and could well follow similar pathways to those discussed in section 2.3.II for the oxidation of cyanide complexes by H_2O_2 . It is likely that there are competitive reactions involving oxidation of complexed cyanide and free CN^- which has dissociated from the complex. In the specific case involving $[\text{Ni}(\text{CN})_4]^{2-}$ and triple salt, a published study has identified a Ni(III) species $[\text{Ni}(\text{CN})_4(\text{H}_2\text{O})_2]^-$, which has been characterised by electronic spectroscopy and ESR.^{180,181} According to the stoichiometry of the reaction this decomposes as shown in the following overall reaction to produce free NCO^- .



It is not clear whether this is only formed at pH <3 or if the lifetime of this species is too short to be measured by ESR at elevated pH. However, this oxidation of

the metal provides a potentially viable alternative route for the oxidation and the stoichiometry of the above equation would partially explain the high stoichiometries of the reaction which we have measured and are listed in table 2.4.ii above. However, there was no consideration given to the oxidation of free CN^- by triple salt in the published study¹⁸⁰ and it is possible that the NCO^- observed in this reaction is due to this latter reaction rather than the decomposition of the $[\text{Ni}(\text{CN})_4(\text{H}_2\text{O})_2]^-$ complex.

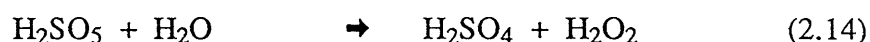
2.4.III. Observations on the effect of caroate on other cyanide complexes.

Using electronic spectroscopy, we found that solutions of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{CN})_6]^{3-}$ (both 10^{-3}M) were unchanged one day after treatment with a solution of triple salt (10^{-2}M) at both high (>10) and low (<2) pH. In those reactions carried out at low pH, the concentration of the triple salt was unchanged after twenty four hours, but all the oxidant had decomposed in those solutions of high pH. No oxidation was observed when an aqueous solution of CuCl_2 (10^{-4}M) was added to the above reactions and stirred for four hours.

We concluded that these complexes, which have very high overall stability constants, were resistant to oxidation by triple salt and at high pH the decomposition of the triple salt was so fast that the natural conversion of $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ was not catalysed by the triple salt, unlike the observation that H_2O_2 will catalyse this process at high pH (see section 2.1.II).¹⁵⁹

2.4.IV. The form of caroate in aqueous solution and its decomposition at high pH.

In this section we report the Raman studies that we have carried out to investigate the decomposition of caroate at high pH. It is reasonable to assume that at low pH and high concentration, caroate is largely present as Caro's acid H_2SO_5 , which is known to dissociate into H_2O_2 and H_2SO_4 when the concentration is reduced as shown by the equation below.²²⁰



However, this simple dissociation does not account for the increased reactivity that caroate exhibits towards cyanide complexes. We have measured the Raman spectra of aqueous solutions of caroate, Caro's acid, persulphate and sulphate at a variety of pH values to try to elucidate the nature of the sulphur containing species in solution and identify the active form of the caroate ion. Table 2.4.iii overleaf lists the bands observed in these spectra, and their assignments. The crystal structures have been determined for both triple salt²¹⁶ and $\text{KHSO}_5 \cdot \text{H}_2\text{O}$ ²¹⁷ (see fig. 2.4.ii) and thorough investigations of their vibrational spectra have also been published.^{218,219}

Fig. 2.4.ii. The structure of the $[\text{HSO}_5]^-$ ion.²¹⁷

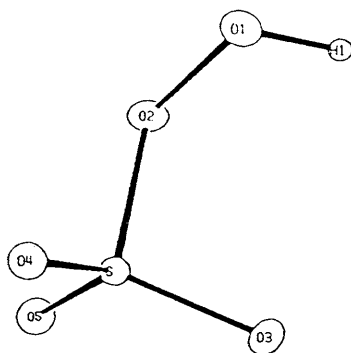


Table 2.4.iii. Bands observed in Raman spectra (400 - 1150 cm⁻¹) of solutions of [HSO₅]⁻ and associated species.

Species	pH	δ_{SO}	δSO_3	δ_{OSO}	$\nu\text{SO}_2\text{H}$	ν_{OO}	ν_{OO}	ν_{SO}	$\nu_{\text{S=O}}$	$\nu\text{SO}_3\text{H}$
H ₂ O ₂	10	-	-	-	-	-	877(10)	-	-	-
[SO ₄] ²⁻	10	-	450(2)	-	610(1)	-	-	982(10)	-	-
[HSO ₄] ⁻	3	430(1)	-	553(5)	595(1)	-	-	982(10)	1053(8)	-
[S ₂ O ₈] ²⁻	8	-	-	560(2)	628(1)	-	806(3)	837(7)	-	982(1) 1054(1) 1078(10)
	13	-	457(2)	558(1)	620(1)	-	802(3)	836(6)	-	981(10) 1060(2) 1079(7)
(lit ¹⁴⁰)		418	-	564	-	-	835	-	-	1084)
[HSO ₅] ⁻	1	-	450(3)	-	590(2)	-	-	878(8)	981(3)	1060(10) -
	9.5	-	450(5)	-	-	-	-	880(7)	982(10)	- -
	10.4	-	450(2)	-	-	-	-	880(1)	982(10)	- -
	13	-	451(2)	-	610(1)	800(2)	-	-	982(10)	- -
(lit ²¹⁸)		416	-	568	607	-	-	878	-	1057 -)
H ₂ SO ₅	0.5	424(4)	-	-	592(4)	771(1)	-	-	880(5)	983(6) 1056(10) -
(lit ²¹⁹)		428	-	-	580	774	-	-	886	960 - -)
Triple salt	1	423(2)	-	-	610(1)	770(1)	-	838(1)	883(5)	982(8) 1063(10) 1077(1)
	3	423(4)	440(2)	563(1)	609(1)	768(3)	-	836(1)	883(5)	981(8) 1060(10) 1077(1)
	8.5	-	453(2)	-	613(1)	-	-	-	875(8)	980(10) 1062(2) 1080(2)
	12	-	452(2)	-	609(1)	-	-	836(2)	-	981(10) 1053(1) 1077(3)

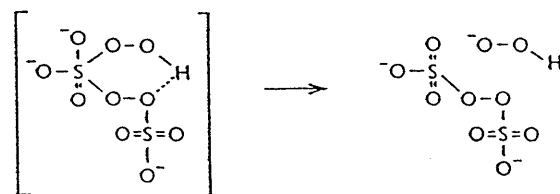
From the spectra there are no additional bands which might suggest the formation of some intermediate species which would account for the reactivity of the $[\text{HSO}_5]^-$ ion. However, the spectra do show how the bands due to this ion rapidly decreased in intensity and eventually disappeared as the $[\text{HSO}_5]^-$ decomposed to $[\text{SO}_4]^{2-}$ when the pH was raised.

Even at pH 1 the bands at 450 cm^{-1} and 981 cm^{-1} provide evidence for the presence of $[\text{SO}_4]^{2-}$ in the solution of $[\text{HSO}_5]^-$, although it is likely that this was due more to impurity in the original sample rather than decomposition of the caroate at this pH. The two strongest bands at 1060 cm^{-1} assigned as $\nu_{\text{S=O}}$ and 878 cm^{-1} ($\nu_{\text{O-O}}$) agreed well with the published study of $[\text{HSO}_5]^-$.²¹⁸ When the pH was raised carefully to 9.5, the strongest band was at 982 cm^{-1} , and the characteristic $[\text{HSO}_5]^-$ peak at 1060 cm^{-1} disappeared, although the O-O band at 880 cm^{-1} remained, albeit weaker. This latter peak was barely visible when the pH was raised to 10.4 and had disappeared completely at pH 13, clearly showing the rapid decomposition of the caroate.

A similar pattern was observed in the spectra of solutions of triple salt as the pH was raised, although the $[\text{SO}_4]^{2-}$ and $[\text{HSO}_4]^-$ present made these spectra much more complicated. At pH 1 and pH 3 the most intense band was at 1063 cm^{-1} due to ν_{SO} of the caroate. This band had almost disappeared when the pH was raised to 8.5, and the most intense band was due to $[\text{SO}_4]^{2-}$ at 982 cm^{-1} . The ν_{OO} occurred at 836 cm^{-1} ¹⁴⁰ and was visible up to pH 8.5 but had disappeared in the spectrum run at pH 12.

The existence of a small proportion of persulphate (~8%) in samples of triple salt was reported by Thompson²²¹, and this was also detected in the uncatalysed decomposition of $[\text{HSO}_5]^-$.²²² This was explained by the formation and subsequent decomposition of the intermediate pictured below in fig.2.4.ii., although it could also have occurred by the combination of $[\text{SO}_4]^\cdot$ radicals which can be formed in such reactions.^{215,221}

Fig.2.4.ii. The uncatalysed decomposition of $[\text{HSO}_5]^-$ to form $[\text{S}_2\text{O}_8]^{2-}$.²²²



In our studies we observed bands at 836 cm^{-1} in the spectra of triple salt at all pH except 8.5, and a weak band at 800 cm^{-1} was seen in the spectrum of $[\text{HSO}_5]^-$ at pH 13 which is similar to a band at 802 cm^{-1} in the spectrum of $[\text{S}_2\text{O}_8]^{2-}$ at this pH. The Raman spectrum of H_2SO_5 had bands in agreement with the published study.²¹⁹

2.5.Experimental Section.

Section 2.2.I. Quantitative FTIR spectroscopic measurements.

All measurements were carried out on a Perkin Elmer 1310 FTIR spectrometer.

a. Calculation of the path length of CaF₂ cells.

This was carried out using the published method.²²³ In brief, the IR spectrum was taken of the empty cells fitted with Teflon spacers of thickness 0.05mm. The actual pathlength was calculated from the fringes observed in the IR spectrum using the following equation.

$$t = n / 2 \times \Delta V$$

where, t = pathlength in cm.

n = no of fringes

ΔV = difference in cm^{-1} between first and last fringe.

We measured the pathlength of the cells to be 0.052 cm. and this value was used in all quantitations carried out on the FTIR machine.

b. Calculation of absorption coefficients for cyanide complexes.

These were calculated from the Beer-Lambert Law which states the following.

$$\text{Absorbance} = \epsilon \times c \times l$$

where ϵ = molar absorption coefficient in $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$.

c = concentration in $\text{mol}^{-1} \text{dm}^3$.

l = pathlength of cell in cm. (taken as 0.052 cm as from above).

The values of absorbance were measured using the callibration program for quantitative analyses on the Perkin Elmer 1310 FTIR spectrometer.

N.B. This method was also used to calculate the molar absorption coefficients of free CN^- , NCO^- and NCS^- as quoted in the text.

Section 2.2.II. Electronic spectroscopy.

Spectra were run on a Philips PU8740 UV/Vis single beam spectrophotometer using a 1 cm quartz cell. Molar extinction coefficients were calculated using the Beer-Lambert law (see above). Temperature controlled reactions were carried out in the Philips thermostatic cell holder connected to a thermostatic pump. For experimental details regarding the pretreatment of reaction solutions, see section 2.3 below.

Section 2.2.III. Dionex HPIC.

For details of the analysis of free NCO^- using the Dionex, see section 1.6.

Cyanide complexes were analysed on a Dionex 2010i machine using an AS5 HPIC column with an AG5 guard as specified in the literature.²⁰³ All solutions were made up in millipore water which had been triply distilled and passed through millipore deionisation columns. The conductivity of this water was 18 $\text{M}\Omega \text{ cm}$.

a. Optimisation of the eluent.

As discussed in the text (section 2.2.III) a positive concentration gradient of perchlorate was recommended to achieve maximum separation and elution of cyanide complexes from the column. An alternative to this was to use a fixed concentration optimised to give the best peak separation for the complexes being studied. Experiments to ascertain the effect of changing the relative concentrations of each of the components showed the following:

Decreasing the concentration of NaCN resulted in shorter elution times without affecting the separation. From a safety aspect it was desirable to keep the concentration of NaCN as low as possible whilst maintaining an excess of cyanide to ensure the integrity of the complexes being studied. Increasing the concentration of NaOH lead to considerably faster elution, but the separation of the complexes was reduced and so a

relatively low concentration of this component was used although this had to be held sufficiently high to ensure that the pH of the eluent did not drop. The concentration of NaClO_4 was kept high throughout these experiments because maximum elution of the complexes from the column was required to prevent a build up of material retained on the column.

From the above results the optimum eluent for the complexes listed below was made up of NaClO_4 (0.12M), NaOH (0.01M) and NaCN (0.005M). This eluent was pumped directly into NaOCl solution to destroy all cyanide present from both the eluent and samples. Flow rates were altered as required but since this tended to change the shape of the peaks all quantitative data were recorded using a flow rate of $1 \text{ cm}^3 \text{ min}^{-1}$, which was found to give the optimum separation. At this flow rate the working pressure of the instrument was between 400 and 440 psi.

b. Detection of cyanide complexes

This was carried out using a spectrophotometric cell with a UV detector set at 215 nm. The data were recorded on a 2470 integrator set up as follows; attenuation + 1024mv, chart speed 0.5 cm min^{-1} , peak threshold = 8000. Samples were injected through disposable millipore filters ($0.5\mu\text{m}$) or through Whatman cellulose nitrate filters ($0.45\mu\text{m}$) fitted in a syringe type stainless steel filter holder to ensure no that particulate matter entered the system. Lowest detection limits using the above conditions and the detector set at 0.2 absorbance units (AU) were 10^{-3}M for all complexes except $[\text{Fe}(\text{CN})_6]^{3-}$ which could be detected at 10^{-4}M . The 0.02AU setting on the detector could be used if the machine had been running for 2 to 3 hours but with this the baseline tended to drift and so frequent recalibrations were required.

c. Common impurities.

All samples gave extra peaks due to impurities in the solutions which absorb in the UV region and could be detected even at very low concentrations. This was

particularly pronounced in samples of solutions from oxidation reactions but fortunately the impurities present were not retained on the column and were the first species to elute. Running standards of the following likely impurities confirmed that they were detected and eluted at the following times.

HCO_3^-	1.1 min
NCO^-	1.1 min
NO_3^-	1.16 min
NO_2^-	1.79 min

Despite efforts to calibrate the large peak at 1.1 min for NCO^- and HCO_3^- the intensity of this peak was consistently much greater than would be expected for the concentrations of these species present in oxidation samples. It was concluded that other unidentified impurities also elute at this time, possibly including small concentrations of unreacted oxidant (H_2O_2), and so unfortunately this method was not suitable for the simultaneous analysis of NCO^- and cyanide complexes.

d. Procedure used for the regeneration of the column.

This was carried out when results indicated that material retained on the column was affecting data collected from the Dionex. The column was flushed with millipore H_2O (10 minutes at $1 \text{ cm}^3 \text{ min}^{-1}$). The guard was placed after the separator column in the system and the whole apparatus flushed with aqueous Na_2CO_3 (0.1M) for 30 minutes ($1 \text{ cm}^3 \text{ min}^{-1}$), and then overnight with HCl (1M) which was pumped straight into a solution of strong alkali to prevent any cyanide being evolved as HCN . The acid was washed out of the system using millipore H_2O (10 minutes) and then aqueous Na_2CO_3 (0.1M for 10 mins) and H_2O was pumped through for 10 minutes again. Finally the guard was replaced in front of the separator and the whole system flushed with eluent for 30 mins.

Section 2.3 Oxidations of Cyanide complexes with H₂O₂.

a. Observations using FTIR, Raman and ¹³C NMR spectroscopy.

These were carried out using the same procedures as outlined in section 1.6, for the oxidation of free CN⁻ by H₂O₂.

b. Analysis of [Ni(CN)₄]²⁻ and [Zn(CN)₄]²⁻ in studies of the kinetics of oxidation by H₂O₂.

We were forced to use different methods of analysis to measure the concentrations of [Ni(CN)₄]²⁻ and [Zn(CN)₄]²⁻ in oxidations of these complexes. The overall stability constant (β₄) of [Zn(CN)₄]²⁻ is 19.62⁸⁵ which is less than that of [Ag(CN)₂]⁻ (β₂ = 20.4⁸⁴), the complex which is formed at the surface of the cyanide electrode. Thus the cyanide in this complex should be detected as free CN⁻ by the electrode. Published results^{88,89} concerning the addition of Zn(II) ions to solutions of free CN⁻ indicate that excess Zn(II) can be added without affecting the calibration curve of the electrode. In our own electrode calibrations of solutions of [Zn(CN)₄]²⁻ we found that at low concentrations of the complex (< 2 × 10⁻⁴ M), the potential difference measured by the electrode corresponded to a free CN⁻ concentration of four times the concentration of [Zn(CN)₄]²⁻; i.e. all the cyanide in the complex was detected as free CN⁻. Above about 2 × 10⁻⁴ M the amount of cyanide detected by the electrode dropped to approximately three times the concentration of [Zn(CN)₄]²⁻, implying that the Zn(II) was affecting the electrode. However a calibration for [Zn(CN)₄]²⁻ gave a straight line over the range 10⁻⁵-10⁻³ M of the complex which enabled us to use the electrode for the analysis of [Zn(CN)₄]²⁻ in oxidations with H₂O₂.

It was not possible to use the electrode to analyse for [Ni(CN)₄]²⁻ since the overall stability of this complex (β₄ = 30.3¹⁵⁵) is higher than that of [Ag(CN)₂]⁻ and at the working pH of the electrode (>12), dissociation of free CN⁻ from the complex was

only of the order of 2.5%; i.e. in a solution of $[\text{Ni}(\text{CN})_4]^{2-}$ ($1 \times 10^{-2}\text{M}$) the potential measured by the electrode corresponded to a free CN^- concentration of only $2.5 \times 10^{-4}\text{M}$. However the characteristic absorbance maximum at 268 nm in the electronic spectrum was ideal for the analysis of $[\text{Ni}(\text{CN})_4]^{2-}$ at concentrations below $2 \times 10^{-4}\text{M}$, provided H_2O_2 , which absorbs strongly in the UV up to around 300 nm, was removed from reaction solutions prior to analysis using MnO_2 as discussed in section 1.6. Some data were also collected using the Dionex HPIC method which separated the $[\text{Ni}(\text{CN})_4]^{2-}$ from other species likely to interfere, but MnO_2 was still added to these solutions to remove H_2O_2 and thus prevent its decomposition with the possible formation of O_2 bubbles whilst in the column.

b. Oxidation of other complexes.

The procedure for carrying out the oxidations of all complexes was the same. An aliquot (5cm^3) was removed from the reaction and diluted with NaOH (0.2M , 5cm^3) to quench the reaction and raise the pH to >12 . A small quantity (ca. 5-10 mg) of MnO_2 was added to destroy the H_2O_2 . Suitable aliquots were also removed from the reaction for analysis for H_2O_2 , carried out by iodometric titration with $[\text{S}_2\text{O}_3]^{2-}$ (details given in section 1.6.). Precipitates formed were generally removed by centrifuging the solution, washed at least twice with water and oven dried at 80°C . Analyses were carried out using electronic spectroscopy for single complexes, on the Dionex for mixtures, or using FTIR for semi-quantitative data.

Section 2.4. Oxidations using triple salt and $\text{KHSO}_5 \cdot \text{H}_2\text{O}$.

a. Observations using FTIR and Raman spectroscopy.

These were carried out using the same procedures as outlined in section 1.6 for the oxidation of free CN^- by H_2O_2 . Triple salt $\text{K}_2\text{SO}_4 \cdot \text{KHSO}_4 \cdot 2\text{KHSO}_5$ was supplied as Oxone (BDH chemicals), or Curox (Interox). Potassium caroate monohydrate,

KHSO₅.H₂O was prepared as outlined below.

b. Analysis of [Ni(CN)₄]²⁻ in studies of the kinetics of oxidation by caroate.

All analysis of [Ni(CN)₄]²⁻ was carried out using the peak at 268 nm. ($\epsilon = 11315 \text{ mol}^{-1} \text{ dm}^{-3} \text{ cm}^{-1}$) in the electronic spectrum of this complex.

For unbuffered reactions carried out using the pH stat to maintain the pH by addition of NaOH (0.02-0.2M) a suitable aliquot was removed from solution and transferred directly to a quartz UV cell. There was no interference due to absorption by the [HSO₅]⁻ and so addition of MnO₂ was not required to quench the reaction. For reactions carried out at low pH (<5), where the rate of reaction was significantly faster, Catalase (~10mg) was added to remove the oxidant as MnO₂ dissolved in the solution at low pH. Catalase was supplied by Sigma.

For buffered reactions, (see section 1.6 for details of buffers), the reaction was carried out in the UV cell and the concentration of [Ni(CN)₄]²⁻ determined automatically by the UV machine every ten minutes.

Radical traps CH₃OH, C₂H₅OH and DMSO were added to reactions at concentrations up to 4% v/v.

The concentration of [HSO₅]⁻ was determined by iodometric titration as detailed in section 1.6. We found that there was no need to add ammonium molybdate solution to catalyse the release of I₂ as this occurred very rapidly upon the addition of the [HSO₅]⁻.

Section 2.4. Preparation of KHSO₅.H₂O and Raman studies of this salt in aqueous solution.

a. Preparation of KHSO₅.H₂O.

Hydrogen peroxide, H₂O₂ (86% 28cm³) was slowly added to H₂SO₄ (98% 70cm³) whilst stirring in an ice-salt bath. The temperature was kept below 10°C

throughout. On completion of the addition the solution was stirred for 10 minutes prior to analysis by ceric sulphate titration to determine the concentration of free H_2O_2 (4.62%), and by $\text{KI}/[\text{S}_2\text{O}_3]^{2-}$ titration to determine the concentration of H_2SO_5 (52.05%).

To the solution of Caro's acid was added, carefully to maintain the temperature below 5°C and whilst stirring with an overhead stirrer²²⁰, a 50% w/w solution of K_2CO_3 (30g in 30cm^3 H_2O). Following this addition the reaction mixture was stirred for 45mins at 0°C and then filtered. The filter cake was washed with ethanol ($2 \times 50\text{cm}^3$) and dried overnight under vacuum. (Yield = 11g, 15% calculated from concentration of H_2SO_5 , Literature²²⁰ claims that a yield of 60% is possible). A portion was recrystallised from warm H_2O_2 (60%) to yield the monohydrate.

The final product was analysed as follows:

Titration with CeSO_4 (0.1N) for % free H_2O_2	Found 0.00.	(calculated 0.00%)
Titration with $\text{KI}/[\text{S}_2\text{O}_3]^{2-}$ (0.1N) for % $[\text{O}_2]^{2-}$	Found 20.00	(18.82%)
Potassium analysis	%K	Found 18.91 (22.94%)

A second portion was precipitated from the solution on addition of ethanol. The analyses were found to correspond to those of triple salt. i.e. free H_2O_2 , 0.00 (0.00%), $[\text{O}_2]^{2-}$, 10.05 (10.42%).

b. Studies of this salt by Raman spectroscopy.

These were carried out in quartz spinning solution cells using the same general procedures as outlined for Raman spectroscopy in section 1.5.

Chapter 3.

The Preparation and Spectral Characterisation of Pseudohalide Complexes.

Introduction.

The term 'pseudohalogen' was introduced by Birckenbach in 1925²²⁴ and its derivative term, pseudohalide refers to those species containing one or more of those groups which can exhibit halide-like properties. The pseudohalide ions studied herein are cyanide (CN^-), thiocyanate (NCS^-), and cyanate (NCO^-). The group also includes azides (N_3^-), fulminates (CNO^-), selenocyanates (SeCN^-) and dicyanamides ($\text{N}(\text{CN})_2^-$). Cyanides were the first pseudohalides described in the literature; as early as 1704 Prussian blue was prepared by Diesbach and KCN made by Scheele in 1782²²⁵, whilst alkali metal salts of cyanates and thiocyanates were first obtained in the early nineteenth century.²²⁶ Since then they have been the subject of much investigation and are regarded as negative, polyatomic monoanions within which there is substantial delocalization of the ionic charge and also high symmetry. The chemistry of transition metal cyanides¹⁵³ and all the pseudohalides has been reviewed.¹³⁹

The first section of this chapter deals with our studies on those cyano species which we have prepared and used in the work discussed in the second chapter of this thesis. This includes work investigating the adsorption of these complexes on alumina and other solid supports. In section 3.2 we consider the work carried out on thiocyanato complexes. We have prepared a number of homoleptic and mixed complexes, using vibrational spectroscopy to determine the mode of bonding. The final part of this chapter concerns our investigations into cyanato species.

3.1. Studies on Cyanide Complexes.

In this section we describe the preparation and spectral characterisation of a number of cyanide complexes, with particular attention to those of Cu(I) and Cu(II). The various aspects of this work will be discussed in the following subsections.

- i. Notes on the preparation of the complexes and tables of spectral data recorded from the IR and Raman spectra of the solid species, and the FTIR, Raman and ^{13}C NMR spectra of these complexes in aqueous solution.
- ii. The adsorption of a number of cyanide complexes on alumina and other supports and observations made on reactions of these adsorbed species with H_2O_2 .
- iii. Mass spectral data for a number of cyanide complexes.

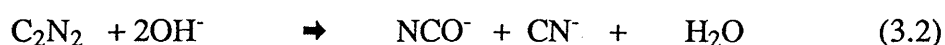
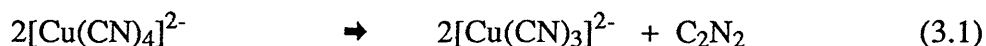
3.1.I. Preparation and spectral characterisation of cyanide complexes.

In this section we present the spectroscopic data measured for a number of cyanide complexes prepared during our period of study. We begin with spectral data we have measured for a number of cyanide complexes of Cu(I) and Cu(II) and then discuss the preparation and characterisation of a number of other cyanide complexes.

a. Complexes of Cu(I) and Cu(II).

Because of the catalytic properties of copper species in the oxidation of free and complexed cyanide, particular attention was paid to the preparation and characterisation of the cyano complexes of Cu(I) and Cu(II). A full discussion of the reaction between Cu(II) salts and free CN^- is presented in section 1.3.V. and the formation of the transient $[\text{Cu}^{\text{II}}(\text{CN})_4]^{2-}$ intermediate has been studied in the literature.¹²⁸⁻¹³⁰ We were unable to prepare pure samples of Cu(I) cyano complexes from Cu(II) salts, and when a solution of concentrated KCN was added dropwise to a cold aqueous solution of CuCl_2 (1.5 M) at pH 7.5 the light brown precipitate that formed upon the first addition

of CN^- rapidly redissolved to give a deep red solution when the $\text{CN}^- : \text{Cu}$ ratio was equal to four. These observations were in agreement with an early study of the reaction by Glasner and Asher.²²⁷ The FTIR spectrum of this solution had a peak at 2076 cm^{-1} , which could be assigned to $[\text{Cu}(\text{CN})_4]^{3-}$, and also a band at 2169 cm^{-1} which we attributed to the formation of free NCO^- from the hydrolysis of C_2N_2 as shown in equation 3.1 below.



Although the red colour faded within five minutes to leave a yellow solution the relative intensities of the two FTIR peaks barely changed over the following two hours. The spectral data for the complexes we have prepared are presented below in table 1.3.i. We have only measured the bands in the ν_{CN} region as full spectroscopic studies have already been published.²²⁸⁻²³³

We have also prepared some mixed cyanide complexes of $\text{Cu}(\text{II})$, which occur infrequently in the literature.¹²⁴ These were prepared to investigate whether or not they had the same catalytic activity as other $\text{Cu}(\text{II})$ salts in the oxidation of free and complexed cyanides but unfortunately proved prone to attack by H_2O_2 (see section 1.3.VI). The following table lists the complexes prepared and the spectroscopic data recorded for them. Unfortunately we were unable to measure the Raman spectra of these species as they were either too dark or decomposed in the laser beam when the Raman microscope was used.

Table 1.3.i. Data measured in the ν_{CN} region of the IR and Raman spectra of Cu(I) cyano complexes together with ^{13}C NMR shifts (relative to $\delta \text{ Me}_4\text{Si} = 0$) for these species in aqueous solution.

Complex	IR (cm^{-1})		Raman (cm^{-1})		δ (ppm)
	Solid	Solution	Solid	Solution	Solution
CuCN	2171 (2172 ²²⁸)	2171 (2170 ²²⁸)	-	-	-
K[Cu(CN) ₂]	-	2125 (2125 ²²⁸)	2127	-	154
	2110 (2109.5 ²²⁹)	-	2112 (2112 ²³⁰)	2112 (2113 ^{230,231})	
	2090 (2088 ²²⁹)	-	2090 (2091 ²²⁹)	- (2106 ²³²)	
K ₂ [Cu(CN) ₃]	2110 (2117 ²³³)	-	2111	2109 (2109.5 ²³⁰)	156
	2089 (2097 ²³³)	2093 (2094 ²²⁸)	2089	2096 (2096 ²³⁰)	
K ₃ [Cu(CN) ₄]	2093 (2094 ²³⁰)	-	2093 (2093 ²³¹)	2096 (2094 ³⁷⁷⁻⁹)	162
	2081 (2081 ²³³)	2076 (2076 ²²⁸)	2080 (2081 ²³⁰)	2080 (2079 ²³¹)	(162.2 ¹¹¹)
	2040 (2042 ²³⁰)		-	2038	

Table 1.3.ii. IR data measured for substituted Cu(II) cyano complexes in the solid state. Literature values are in brackets.¹²⁴

Complex	Colour	ν_{CN} (cm^{-1})	δ_{MCN} (cm^{-1})
[Cu(phen)(CN)]NO ₃ .H ₂ O	turquoise	2136,2083 (2136)	373,364
[Cu(phen) ₂ (CN)]-	green	2141,2100,2083	359
-[Cu(phen)(CN) ₂].6H ₂ O		(2140,2100,2082)	
[Cu(bipy)(CN) ₂]	purple	2120,2100	371,359
[Cu(bipy)(CN)]NO ₃ .H ₂ O	brown	2148,2131,2098	368,360

b. Other cyanide complexes.

The preparations of these complexes were carried out using published methods²³⁴⁻²³⁶, or modifications of these methods except with $K_2[Zn(CN)_4]$, for which a new preparation was developed using ZnO as a starting material. Full details of all the preparations and the elemental analyses carried out are given in the experimental section of this chapter. Table 3.1.iii below lists the principal bands measured in the IR and Raman spectra of these complexes with comparative literature values. The data that we have measured are incomplete but full vibrational assignments have been published for all the complexes.^{204,205,237}

Table 3.1.iii. Spectroscopic data for cyano complexes in (cm⁻¹)with literature values in brackets.

Complex		ν_{CN}		δ_{CN}	
K ₂ [Ni(CN) ₄]	IR	2121,2127	(2127 ²⁰⁵)	415	(405 ²⁰⁵)
	IRaq.	2124	(2123 ²⁰⁵)	-	
	Raq.	2145,2136	(2143 ³⁷¹)	453	(451 ²⁰⁵)
K ₂ [Pd(CN) ₄]	IR	2137	(2134 ²⁰⁵)	470	(485 ²⁰⁵)
K ₂ [Pt(CN) ₄]	IR	2136,2122,2095	(2134,2123 ²⁰⁵)	406	(406 ²⁰⁵)
K[Ag(CN) ₂]	IR	2140,2096	(2140 ²³⁷)	391	
	IRaq.	2135	[2135 ²³⁷)	-	
	Raq.	2143,2108,2097	(2145 ²³⁷)		
K ₂ [Zn(CN) ₄]	IR	2154,2107	(2152 ²⁰⁴)	357	(355 ²⁰⁴)
	IRaq.	2150	(2149 ²⁰⁴)	-	
	Raq.	2154	(2152 ²⁰⁴)		
K ₂ [Cd(CN) ₄]	IR	2146,2100	(2146 ²⁰⁴)	-	(315 ²⁰⁴)

Key. IRaq.- IR of aqueous solution.

Raq. - Raman of aqueous solution.

3.1.II. Adsorption of cyanide complexes on alumina and other supports.

We have investigated the capacity of a number of cyanide complexes to adsorb on alumina and other supports such as montmorillonite, bentonite and ion-exchange resins. This was carried out in connection with the work reported in section 1.3.V. with a view to develop a heterogeneous catalyst system for the oxidation of cyanide. Similar studies have been reported in the literature.^{15,17} In this study we have used IR spectroscopy to determine the position of the ν_{CN} vibrations of species which were adsorbed on these supports. Unfortunately we were unable to measure the Raman spectra of the adsorbed species even with the aid of a Raman microscope because of fluorescence by the supports.

a. Adsorption onto alumina.

Some work was carried out using the literature preparative methods²³⁸ (crystallisation on to the alumina by evaporation to dryness of a solution of the relevant complex), but it was more useful to determine which complexes would adsorb on to alumina from solution. (i.e slurrying a dilute solution with alumina and filtering; see the experimental section (3.4) for details of the method). All the complexes were mixed with different types of alumina and after filtration, washing and drying the IR spectra were run to establish whether any of the complex had been adsorbed. The results are summarized in table 3.1.iv. below which shows the IR peaks measured in the ν_{CN} region .

Table 1.3.iv..IR bands observed (cm^{-1}) in the ν_{CN} region of cyano complexes when adsorbed on different types of alumina and for their aqueous solutions.

Species	Basic	Neutral	Acidic	Solution
$[\text{Cu}(\text{CN})_3]^{2-}$	2090	-	2090w	2094
$[\text{Cu}(\text{CN})_4]^{3-}$	2077	-	-	2076
	2091	-	-	-
$[\text{Ag}(\text{CN})_2]^-$	2090	-	-	2092
	2125sh	-	-	2125
	2140	-	-	2140
	2161	-	-	-
$[\text{Au}(\text{CN})_2]^-$	2104	-	-	-
	-		2143	2140
$[\text{Ni}(\text{CN})_4]^{2-}$	-	2121	2122	2124
	-	2127	-	-
$[\text{Pd}(\text{CN})_4]^{2-}$	2108	-	2109	-
	2117	-	2126	2134
$[\text{Co}(\text{CN})_6]^{3-}$	-	-	2126	2127
$[\text{Fe}(\text{CN})_6]^{3-}$	-	-	2026	-
	-	-	2050	2044
	-	-	2115	2118
$[\text{Fe}(\text{CN})_6]^{4-}$	-	2026	2027	-
	-	2044	2044	2044
	-	2114w	2115	2118
CN^-	-	-	-	2065
NCO^-	-	2170	2170w	2170
	-	2245	2250w	-
NCS^-	2063	2068	2065	2065
	2120	-	2114	-

The cyano complexes of zinc, cadmium and mercury all appeared to decompose when stirred with alumina. The $[\text{Zn}(\text{CN})_4]^{2-}$ solution went grey and $[\text{Cd}(\text{CN})_4]^{2-}$ brown. A solution of $[\text{Pd}(\text{SCN})_4]^{2-}$ adsorbed on basic alumina gave IR peaks at 2111 and 2067cm^{-1} . Comparison of the ν_{CN} bands observed for the solutions of the complexes and those measured for the adsorbed species suggest that in most cases the solution species remains unchanged upon adsorption.

The form of $\text{Na}_2[\text{Cu}(\text{CN})_3]$ supported on basic alumina at various loadings was investigated using IR spectroscopy, f.a.b. mass spectrometry and scanning electron microscopy by Duke *et al.*²³⁸ They concluded that at high loadings (2 mmol g^{-1}) $\text{Na}[\text{Cu}(\text{CN})_3]$ is present as discrete crystals on the surface of the alumina and the IR of this adsorbed species has peaks at 2110 and 2090 cm^{-1} . At lower loadings it is dispersed over the surface with the IR spectrum in the ν_{CN} region of the adsorbed species closely resembling that of aqueous $[\text{Cu}(\text{CN})_3]^{2-}$ (2090cm^{-1}). Our results support the above conclusion for lower loadings, but the presence of a second peak at 2077 cm^{-1} in the IR of $[\text{Cu}(\text{CN})_4]^{3-}$ adsorbed onto basic alumina suggests that some of this species was adsorbed as $[\text{Cu}(\text{CN})_3]^{2-}$. The three peaks observed in the IR of a solution of $[\text{Ag}(\text{CN})_2]^-$ suggested that the three species $[\text{Ag}(\text{CN})_2]^-$, $[\text{Ag}(\text{CN})_3]^{2-}$ and $[\text{Ag}(\text{CN})_4]^{3-}$ were present and that all these were adsorbed onto basic alumina. The fourth peak at 2161 cm^{-1} in the IR of the adsorbed material might have been due to AgCN precipitating onto the support.

The adsorption of complexes of higher stability occurred on neutral or acidic alumina, rather than on the basic form. The reason for this is not clear as there is no obvious link between the stability of a complex and the form of alumina to which it will be adsorbed. When $[\text{Ni}(\text{CN})_4]^{2-}$ was adsorbed on neutral alumina, the IR spectrum showed two peaks at 2121 and 2127 cm^{-1} which were in agreement with our observations (see table 3.1.iii) and the literature for the solid compound.²⁰⁵ In solution, $[\text{Ni}(\text{CN})_4]^{2-}$ has one IR active band at 2134 cm^{-1} but when it was adsorbed on acidic alumina two bands appeared at 2126 and 2109 cm^{-1} , while on basic alumina

these lay at 2117 and 2108 cm^{-1} . The complex did not adsorb onto neutral alumina. When $[\text{Fe}(\text{CN})_6]^{3-}$ was adsorbed on acidic alumina or when $[\text{Fe}(\text{CN})_6]^{4-}$ adhered to neutral and basic alumina the peaks at 2115 cm^{-1} and at 2050 and 2026 cm^{-1} in the IR spectra indicated that both species were adsorbed. However these observations for $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ were at variance with a study by inelastic electron tunnelling spectroscopy (IETS) which concluded that ferric cyano complexes were uniformly reduced to ferrous complexes at the surface.²³⁹ A different study by IR spectroscopy published results that were broadly similar to ours for the adsorption of a number of cyano complexes on acid modified alumina.²⁴⁰

The adsorption of free pseudohalides has also been investigated using IETS and the results confirm our observations for these ions.²⁴¹ The SCN^- ion adsorbs as Al-NCS giving an IR peak at 2065 cm^{-1} and at concentrations of around 10^{-5}M SCN^- , it will also bind as Al-SCN. This probably explains why we observed two peaks in the IR spectrum of SCN^- adsorbed on both basic and acidic alumina. Similarly the two peaks that we observed upon the adsorption of NCO^- can be explained by Al-OCN bonding giving rise to the peak at 2145 cm^{-1} and Al-NCO, that at 2250 cm^{-1} . No evidence was found to indicate that CN^- was adsorbed in the pH range 7 to 12²⁴¹, which is in agreement with our results.

We attempted to use electronic spectroscopy to quantitate the adsorption of complexes onto alumina but we were only able to assess approximately the loading because equilibration of the various species in the solution introduced inaccuracies into the analysis. This was estimated to be $1.4\text{--}2.1 \times 10^{-3}$ mols $[\text{Cu}(\text{CN})_2]^{3-}$ g^{-1} basic alumina and $1.8\text{--}2.2 \times 10^{-3}$ mols $[\text{Fe}(\text{CN})_6]^{3-}$ g^{-1} acidic alumina. All the adsorbed complexes were leached from the alumina if stirred in aqueous solutions, and this also prevented accurate assessment of the loading.

b. Reactions of adsorbed complexes with H₂O₂.

In all cases where the cyano complexes appeared to be adsorbing onto the alumina, we investigated the reactivity of the adsorbates towards H₂O₂. With adsorbed [Ni(CN)₄]²⁻, NCO⁻ and SCN⁻ the IR spectra of the alumina after reaction with H₂O₂ (0.16M) had no peaks in the ν_{CN} region, indicating that the complex was leaching back into the solution or oxidation had occurred. When [Pd(CN)₄]²⁻ adsorbed on alumina was stirred in a solution of H₂O₂ (0.16M), the only peak that persisted after the reaction was at 2108 cm⁻¹. The spectra of [Fe(CN)₆]³⁻ and [Fe(CN)₆]⁴⁻ adsorbed on alumina indicated that although further equilibration had occurred during the reaction with H₂O₂ there was no evidence for any destructive oxidation.

When a solution of H₂O₂ (0.16M) was slurried with [Cu(CN)₃]²⁻ adsorbed on alumina the solid turned blue within ten minutes and the H₂O₂ decomposed rapidly accompanied by vigorous effervescence, and the solution turned brown. The IR of the blue solid had a single broad peak at 2245 cm⁻¹ and we conclude that this was due to the formation of a cyanate species, [Cu^{II}(NCO)_x]^{2-x}. A similar peak was observed when a solution of blue [Cu(NCO)₃]⁻ was adsorbed on basic alumina and it seems likely that this was the adsorbed species in both cases. Repeated treatment of the product with H₂O₂ lead to decolourisation and the IR of the final white solid had no peaks in the ν_{CN} region. These observations could be explained by two mechanisms.

In the first, the adsorbed [Cu(CN)₃]²⁻ dissociates from the alumina and is oxidised as discussed in section 2.3.III. The Cu(II) species thus produced then form a complex with the NCO⁻ and are readsorbed as [Cu(NCO)₃]⁻. Although this mechanism is reasonable the distinctive colour change suggests that the whole oxidative process might occur without desorption of the [Cu(CN)₃]²⁻. Thus adsorbed [Cu(CN)₃]²⁻ could be oxidised by H₂O₂ to form adsorbed [Cu^{II}(NCO)₃]⁻, and the Cu(II) species could then be desorbed by further oxidation and hydrolysis of the NCO⁻ groups.

This second possible mechanism, which we prefer, is supported by two observations. In the oxidation of [Cu(CN)₃]²⁻ by H₂O₂ at any concentration we have

observed no blue colouration in solution which could be due to the formation of $[\text{Cu}(\text{NCO})_3]^-$ and when alumina was added to the reaction solution there was no adsorption of either $[\text{Cu}(\text{CN})_3]^{2-}$ or $[\text{Cu}(\text{NCO})_3]^-$. Secondly, the adsorbed $[\text{Cu}(\text{CN})_3]^{2-}$ decomposed over one to two weeks and turned green-blue in colour. The IR spectrum of this degraded material had peaks at 2259 and 2170 cm^{-1} , probably due to cyanate as well as those due to cyanide at 2113 and 2094 cm^{-1} indicating that aerial oxidation of adsorbed species may have occurred. This was also observed by Duke *et al.*²³⁸ Although these observations provide the most convincing evidence that complex cyanate species can be formed in the oxidation of $[\text{Cu}(\text{CN})_3]^{2-}$ by H_2O_2 we have not conclusively proved that this occurs unless the $[\text{Cu}(\text{CN})_3]^{2-}$ is adsorbed, so we cannot be sure whether the alumina is changing the mechanism or just trapping the intermediate cyanato complex. Our study of the reaction was made more complicated by the leaching of adsorbed species from the alumina as we could not be certain of the exact effect that this had on our observations.

c. Adsorption of cyano complexes onto other supports.

A little work was carried out using bentonite, montmorillonite and silica as supports for cyanide complexes. None of these appeared to adsorb $[\text{Cu}(\text{CN})_3]^{2-}$ sufficiently to give IR peaks. Montmorillonite was turned light blue by adsorption of $[\text{Fe}(\text{CN})_6]^{3-}$ at an estimated loading of 10^{-4} mol $[\text{Fe}(\text{CN})_6]^{3-}$ g^{-1} . The IR spectrum of the adsorbed complex in the ν_{CN} region had a single peak at 2083 cm^{-1} which does not correspond to either $[\text{Fe}(\text{CN})_6]^{3-}$ or $[\text{Fe}(\text{CN})_6]^{4-}$, and this was contrary to the report in the literature²⁴² of a peak at 2140 cm^{-1} which was assigned to $\text{Ca}_3[\text{Fe}(\text{CN})_6]_2$. Bentonite was turned khaki green by $[\text{Fe}(\text{CN})_6]^{3-}$ ($\sim 5 \times 10^{-5}$ mols g^{-1}) and the IR spectrum of the adsorbed complex had peaks at 2120, 2080, 2060 and 2025 cm^{-1} indicating the presence of both $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$. We were unable to measure the Raman spectra of either of the above as the supports both fluoresced. Silica did not adsorb $[\text{Fe}(\text{CN})_6]^{3-}$.

Two ion exchange resins were also examined for their ability to adsorb $[\text{Cu}(\text{CN})_3]^{2-}$ and aqueous solutions of copper(II) sulphate. It is reported that the resin CR-20 has high specificity for copper²⁴³, although the reference does not state the form of the copper. It has also been used to adsorb molybdenum peroxo species to form a heterogeneous catalyst for use in conjunction with H_2O_2 .²⁴⁴ When stirred in a concentrated solution of copper(II) sulphate the resin turned blue and the adsorption was measured by electronic spectroscopy to be in the range $0.5 - 1.0 \times 10^{-3}$ mols $\text{Cu}(\text{II}) \text{ g}^{-1}$. This colour change was also observed in a solution of $[\text{Cu}(\text{CN})_4]^{3-}$ (0.5M) and the IR of the solid after washing and drying had one weak IR band in the ν_{CN} region at 2090 cm^{-1} . This suggested that some adsorption of $[\text{Cu}(\text{CN})_4]^{3-}$ had occurred but it appeared that most of the adsorption was by $\text{Cu}(\text{II})$ species. When the loaded resin was stirred in a solution of H_2O_2 (0.16M) it turned green, the IR peak at 2090 cm^{-1} disappeared and the solution turned yellow as the oxidant decomposed. The final concentration of $\text{Cu}(\text{II})$ species in the solution was measured using test papers and found to be $3.2 \times 10^{-3} \text{ M}$ indicating that the metal was leaching from the resin. When the process was repeated, $3.2 \times 10^{-4} \text{ M}$ $\text{Cu}(\text{II})$ species were leached and the resin was only faintly coloured which indicated that nearly all of the adsorbed species had been leached away.

Amberlite IRC-60 cationic resin became green when stirred in a solution of aqueous copper(II) sulphate (0.1M). Uptake was estimated to be 2.5×10^{-3} mols $\text{Cu}(\text{II}) \text{ g}^{-1}$ resin. When stirred in H_2O_2 solution (0.1M) there was no decomposition of the H_2O_2 within one day despite approximately $1.5 - 3.0 \times 10^{-4} \text{ M}$ $\text{Cu}(\text{II})$ being leached off as measured using copper ion test papers. If stirred in CN^- solution (0.1M) the resin turned white and approximately 80% of the CN^- was removed from the solution. The IR spectrum of the resin had peaks in the ν_{CN} region at 2128 and 2087 cm^{-1} indicating that some of the CN^- was adsorbed onto the support as $[\text{Cu}(\text{CN})_2]^-$ and $[\text{Cu}(\text{CN})_4]^{3-}$. However, the solution contained $5.0 \times 10^{-4} \text{ M}$ $\text{Cu}(\text{II})$ after this which showed that some leaching had occurred

On the basis of results from all our experiments no solid support was found to which Cu(II) ions would adsorb irreversibly under the conditions that we used, such being the crucial property for a heterogeneous catalyst.^{1,15,17} However, in industrial situations the concentrations of reactants, particularly that of the H₂O₂, would usually be much lower and so it is possible that desorption of the catalyst would be less of a problem.

3.1.III. Mass spectrometry of cyanide complexes.

A recent publication²⁴⁵ showed that fast atom bombardment (f.a.b.) mass spectra of cyanide complexes showed considerable fragmentation. The spectra revealed the existence of several families of ions from each complex, each family giving sequences of peaks corresponding to the sequential loss of neutral CN and (CN)₂ fragments. According to the report, the complexes studied included those of Fe, Cr, Mn, Ni, Mo and W in various oxidation states. We examined the f.a.b. mass spectra of some of the complexes used in the course of our work to determine whether they too gave useful data. The following tables give data measures from the negative f.a.b. mass spectra of complex cyanides.

Table 3.i.v Masses and percentage relative abundances (normalised to the base peak) in the negative f.a.b. mass spectra of complex cyanides.

Mass (% Base)		Assignment.
K[Ag(CN)₂]		
359	(26)	[KAg ₂ (CN) ₄] ⁻
294	(31)	[Ag ₂ (CN) ₃] ⁻
159	(100)	[Ag(CN) ₂] ⁻
K₂[Cu(CN)₃]		
245	(2)	[K ₂ Cu(CN) ₄] ⁻
206	(8)	[KCu(CN) ₄] ⁻
180	(15)	[KCu(CN) ₃] ⁻
156	(7)	[KCu(CN) ₂] ⁻
141	(5)	[Cu(CN) ₃] ⁻
115	(100)	[Cu(CN) ₂] ⁻
K[Au(CN)₂]		
249	(100)	[Au(CN) ₂] ⁻
K₃[Co(CN)₆]		

The negative f.a.b. mass spectrum of this complex was very complicated, with peaks corresponding to the three ions below and the successive loss of CN (26) and KCN (65) fragments from each. This is similar to that observed by Jennings *et al.*²⁴⁵ for other cyanide complexes. The spectrum is reproduced in fig.3.1.i. overleaf.

Mass (% Base).		Assignment
755	(1)	[K ₇ Co ₂ (CN) ₁₄] ⁻
332	(9)	[K ₃ Co(CN) ₆] ⁻
137	(100)	[Co(CN) ₃] ⁻

Fig.1.3.i. Negative f.a.b. mass spectrum of $K_3[Co(CN)_6]$.

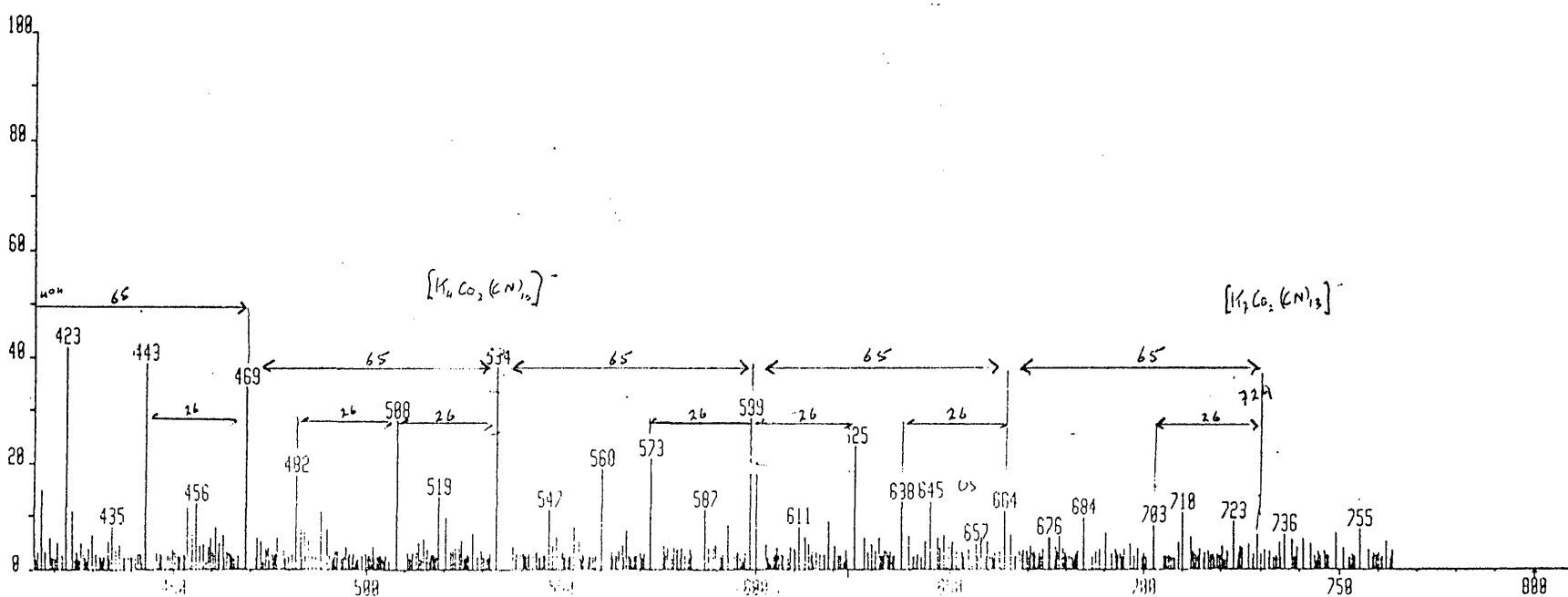
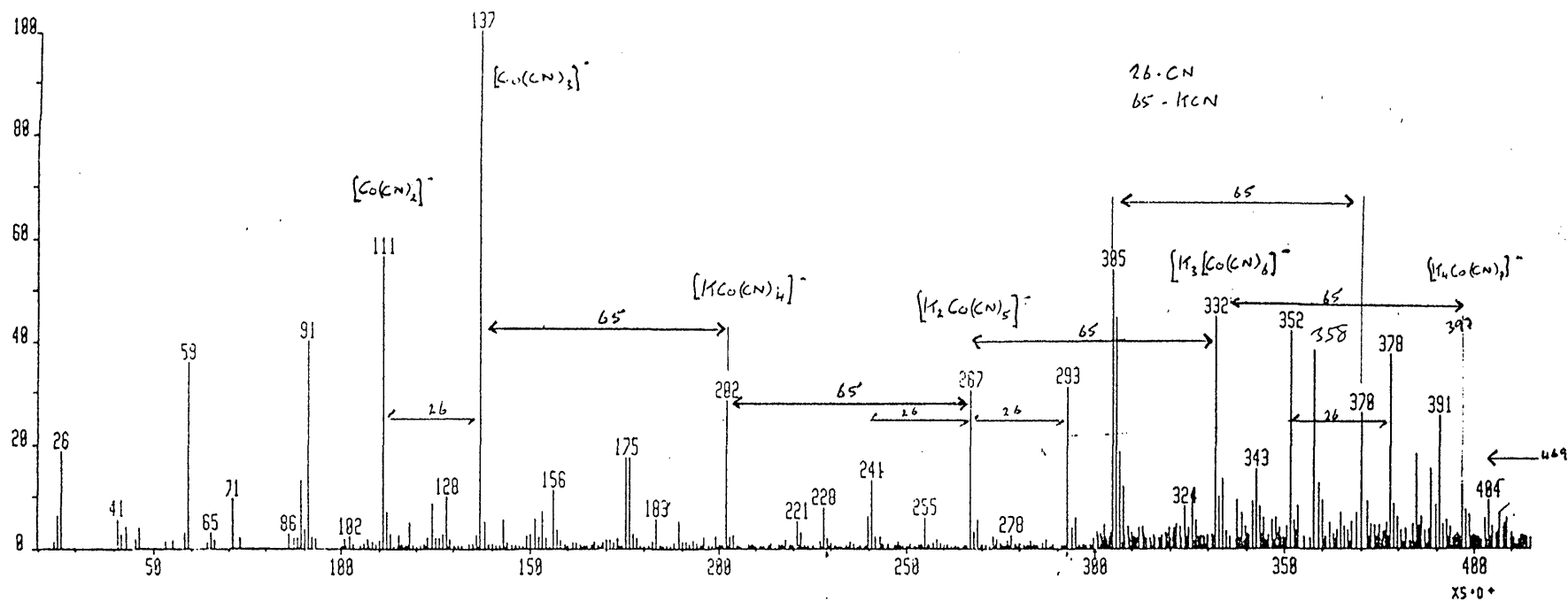


Table 3.i.vi. Masses and percentage relative abundances (normalised to base peak) observed in the negative f.a.b. mass spectrum of $\text{K}_2[\text{Ni}(\text{CN})_4]$.

Mass (% Base)		Assignment.
443	(10)	$[\text{K}_3\text{Ni}_2(\text{CN})_8]^-$
415	(5)	$[\text{K}_3\text{Ni}_2(\text{CN})_7]^-$
391	(3)	$[\text{K}_3\text{Ni}_2(\text{CN})_6]^-$
378	(10)	$[\text{K}_2\text{Ni}_2(\text{CN})_7]^-$
352	(13)	$[\text{K}_2\text{Ni}_2(\text{CN})_6]^-$
350	(6)	$[\text{K}_2\text{Ni}_2(\text{CN})_6]^-$
324	(7)	$[\text{K}_2\text{Ni}_2(\text{CN})_5]^-$
285	(3)	$[\text{KNi}_2(\text{CN})_5]^-$
259	(4)	$[\text{KNi}_2(\text{CN})_4]^-$
220	(2)	$[\text{Ni}_2(\text{CN})_4]^-$
194	(9)	$[\text{Ni}_2(\text{CN})_3]^-$
142	(2)	$[\text{Ni}_2(\text{CN})]^-$
333	(4)	$[\text{K}_3\text{Ni}(\text{CN})_6]^-$
293	(4)	$[\text{K}_2\text{Ni}(\text{CN})_6]^-$
267	(8)	$[\text{K}_2\text{Ni}(\text{CN})_5]^-$
240	(6)	$[\text{K}_2\text{Ni}(\text{CN})_4]^-$
214	(1)	$[\text{K}_2\text{Ni}(\text{CN})_3]^-$
201	(35)	$[\text{KNi}(\text{CN})_4]^-$
175	(15)	$[\text{KNi}(\text{CN})_3]^-$
163	(2)	$[\text{K}_2\text{Ni}(\text{CN})]^-$
136	(58)	$[\text{Ni}(\text{CN})_3]^-$
110	(100)	$[\text{Ni}(\text{CN})_2]^-$

Conclusions.

It is evident that with the exception of the $\text{K}[\text{Au}(\text{CN})_2]$ complex, these cyanide complexes all give good negative f.a.b. mass spectra which exhibit the successive fragmentation of CN and KCN species from the parent ions. This is in agreement with the published study.²⁴⁵ However, this study did not discuss the peaks due to combination of fragments to form higher order species which then gave similar fragmentation patterns. In the spectrum of $\text{K}[\text{Au}(\text{CN})_2]$ there was only one peak, that of the $[\text{Au}(\text{CN})_2]^-$ ion at m/z 249 and no fragmentation or combination peaks were observed.

It was planned to extend this study to include some of the cyanide complexes adsorbed on alumina as has been reported by *Duke et al.*²³⁸ However, we had not received the results of these studies at the time of press.

3.2. Preparation and Characterisation of Thiocyanate Complexes.

The thiocyanate ligand is ambidentate; i.e. can bind through the S atom forming thiocyanato species or the N atom to produce *isothiocyanato* complexes. (The nomenclature used in this thesis is according to convention whereby the term thiocyanate refers to the ligand, irrespective of the mode of bonding. Thiocyanato and *isothiocyanato* will be used in reference to species in which the bonding has been determined). Although infra-red spectroscopy²⁴⁶ has been used to distinguish between these modes of bonding there are few analogous data on Raman spectra of such complexes. The only detailed studies of the mode of bonding by Raman spectroscopy are those by Preetz and co-workers on $[\text{Os}(\text{SCN})_6]^{3-}$ ²⁴⁷, $[\text{Os}(\text{SCN})_6]^{2-}$ ²⁴⁸, $[\text{Ir}(\text{SCN})_6]^{3-}$ ²⁴⁹, $[\text{Rh}(\text{SCN})_6]^{3-}$ ²⁵⁰, and $[\text{Ru}(\text{SCN})_6]^{3-}$ ²⁵¹. In this section the Raman and IR spectra are reported of a number of typical thiocyanato species for which the mode of bonding has been determined by X-ray crystallography, ¹⁴N NMR, ¹³C NMR or other techniques. Our measurements have been made on the solids and their solutions in order to establish the effectiveness of Raman spectroscopy in the determination of the bonding mode.

We begin this section with a discussion of the symmetry of the complexes, the published literature concerning this subject and the factors affecting the mode of bonding in thiocyanate complexes. In the second subsection we present our own results and discuss them with respect to the literature.

3.1.I. Symmetry and bonding in thiocyanate complexes.

a. Symmetry of thiocyanate complexes.

First it is useful to consider the numbers of bands expected in these complexes using group theory for the appropriate point groups. In N-bonded *isothiocyanato* complexes there is a linear MNCS unit. Thus $[\text{M}(\text{NCS})_6]^{n-}$ complexes have octahedral

O_h symmetry as shown by the X-ray structure of $(Et_4N)_3[Fe(NCS)_6]$ ²⁵², and tetrahedral $[M(NCS)_4]^{n-}$ complexes have T_d symmetry as in $K_2[Co(NCS)_4].3H_2O$ (fig 3.2.ii).²⁵³ The seven coordinate complex $K_3[UO_2(NCS)_5]$ has pentagonal bipyramidal D_{5h} symmetry.²⁵⁴ In the S-bonded thiocyanato analogues the MSCN unit is bent to an angle of around 100° due to the lone pair on the sulphur atom.²⁵⁵ For octahedral thiocyanato complexes, $[M(SCN)_6]^{n-}$ the point group will be distorted octahedral, D_{3d} symmetry, shown by the X-ray crystal structure of $K_3[Rh(SCN)_6]$ (fig.3.2.i.).²⁵⁶ For square planar thiocyanato $[M(SCN)_4]^{n-}$ the symmetry is D_{4h} as for example in $K_2[Pd(SCN)_4]$, (fig 3.2.iii) .²⁵⁷

b. Spectral characteristics of thiocyanate complexes.

The linear triatomic ion SCN^- ($C_{\infty v}$) has $[(3N-5) = 4]$ four normal vibrations, two stretches (ν_{CN} and ν_{CS}) and a doubly degenerate deformation (δ_{NCS}). All are IR active and the fundamentals as measured for $NaSCN$ ²⁵⁸ are listed below in table 3.2.i. On coordination all of these and additional modes should be found in the spectra of thiocyanate complexes. In this work we consider these main four 'fingerprint' modes which shift on coordination, and the shifts can be considered as characteristic of the mode of bonding. The ranges of frequencies found (in cm^{-1}) are as follows:

Table 3.2.i. Frequency ranges for the fingerprint modes of thiocyanate complexes.

	ν_{CN}	ν_{CS}	δ_{NCS}	$\nu_{MN/S}$
$NaSCN$ ³⁰⁷	2053	748	486, 471	-
N-bonded	2120-1950	880-760	490-450	270-260
S-bonded	2130-2080	720-690	440-400	320-290

Although there is overlap between these ranges the mode of coordination, whether the complex is N bonded or S bonded can usually be deduced using the

relative values of ν_{CS} and δ_{NCS} . Another factor, the intensity of the CN stretching vibration, has also been used²⁵⁹ as a criterion for the bonding mode. This uses the observation that the integrated absorption intensities for N bonded species are larger than for the equivalent concentration of free SCN^- anion whilst the integrated absorptions for S bonded species are lower. This has been used successfully for solutions of complexes²⁶⁰ and also qualitatively to distinguish N and S bonded complexes in the solid state.²⁴⁰ Bands below about 260 cm^{-1} have been tentatively assigned to δ_{MN} and δ_{MS} modes in accordance the work of Preetz.²⁴⁷⁻²⁵¹

Jones¹³⁵ concluded from analysis of the force constants in free SCN^- in aqueous solution that both bonds have multiple bond character and this is evident from X-ray data.²⁶¹ On coordination, the bond order between the C and the coordinating atom (N or S) would be expected to decrease and consequently that in the other bond should increase with a resulting effect on the intensity of the vibrational frequencies. Thus in an N bonded complex the intensity of the ν_{CS} band increases relative to the intensity of the ν_{CS} band of free SCN^- at the same concentration whilst the relative intensity of ν_{CN} in the complex decreases. This was true for solutions of $[Zn(NCS)_4]^{2-}$ as measured by Raman spectroscopy²⁶² and with $[Hg(SCN)_4]^{2-}$ the reverse occurred; the intensities of ν_{CN} increased and those of ν_{CS} decreased relative to those for SCN^- . This was thought to be due to the greater covalency in the M-SCN bond favoured by the Hg(II) ion as compared with the more ionic M-NCS bond preferred by the Zn(II).²⁶³

c. Factors affecting the mode of bonding

Transition metals can be broadly classified into hard (class a) and soft (class b) acceptors²⁶⁴, based on the stability constants of their complex halo-anions in solution. For hard metals the order of the strength of their attachment is $F^- \gg Cl^- > Br^- > I^-$, and this order is reversed for soft acceptors. This approach indicates that hard metals such as first row transition metals prefer the hard N end of the thiocyanate ligand whereas

soft polarisable metals, those in the latter half of the second and third transition series, are bonded via the S atom; however it must be stressed that the distinction is by no means clear cut.

Inversion of one or more of the thiocyanate groups can occur in metals which are borderline in this classification. This intermediate character has been shown for $[\text{Cd}(\text{SCN})_4]^{2-}$ ²⁶² and $[\text{Os}(\text{SCN})_6]^{2-}$ amongst others.²⁴⁸ Some typical group b metals such as Pd(II) and Pt(II), also exhibit this tendency and can have thiocyanato and *isothiocyanato* isomers in mixed complexes where the other ligands are good π -acceptors.^{265,266} This can be explained as follows: In a normal M-SCN bond the S atom has two empty antibonding π -molecular orbitals which can act as good π -acceptors for electrons from the filled nonbonding p molecular orbitals on the metal to stabilise the M-S σ bond. If other ligands on the metal are good π -acceptors (e.g. PPh_3 , AsPh_3 , bipy, phen) then these will destabilise the metal-sulphur backbonding and the energetics of the system could thus favour a metal-nitrogen bond. When these ligands are also bulky (e.g. PPh_3) then steric factors are also important, for the M-NCS unit is linear whereas the M-S-CN is bent to around 100° , so making the latter less favoured.²⁶⁴

Another factor affecting the mode of coordination of species in solution is the nature of the solvent. Burmeister²⁶⁷ classified these into three groups. Class I solvents have high dipole moments, high dielectric constants and are good coordinating solvents. They promote covalent interactions and so favour the formation of S bonded thiocyanates. Examples of such solvents are N,N dimethyl formamide, DMSO, acetone, acetonitrile and benzonitrile. Solvents such as benzene, carbon tetrachloride, dichloromethane and nitrobenzene are classified as class II and have low dielectric constants. They favour ionic bonding such that S bonded complexes tend to isomerise to the N bonded forms and naturally N bonded species retain their configuration. A third group (class III) includes methanol and ethanol which do not give characteristic effects. This is thought to be because of the time delay occurring due to the hydrogen

bond cleavage required before any isomerisation can occur. Isomerisation of S bonded species to their N bonded counterparts can also be effected by heating the solid compounds at temperatures in excess of 120° for a short period.²⁶⁵

3.2.II. Results and discussion of our studies on thiocyanate complexes.

a. Homoleptic thiocyanate complexes.

We have prepared a number of homonuclear thiocyanate complexes and measured their IR and Raman spectra to confirm the mode of bonding. The results for six coordinate complexes are summarised in table 3.2.ii below. In table 3.2.iii we present the IR and Raman data measured for four coordinate species and table 3.2.iv concerns spectral data for other homoleptic thiocyanate compounds that we have prepared.

i. Six coordinate complexes.

Of those complexes studied X-ray crystal structures have been determined for $K_3[Fe(NCS)_6]$ ²⁵² and $K_3[Rh(SCN)_6]$ ²⁵⁶ (see fig 3.2.i) which confirm the mode of bonding and the symmetry assumed in table 3.2.i. For the N bonded complexes we would expect one IR active (T_{1u}) and two Raman active ν_{CN} (A_{1g} , polarised and E_g , depolarised) modes and an equivalent number of ν_{CS} and ν_{MN} modes. In the δ_{NCS} region one IR (T_{1u}) and one Raman (T_{2g}) active band should be observed.

Table 3.2.ii Vibrational spectra for six coordinate thiocyanato and isothiocyanato complexes.

Complex		$\nu_{\text{CN}} (\text{cm}^{-1})$	$\nu_{\text{CS}} (\text{cm}^{-1})$	$\delta_{\text{NCS}} (\text{cm}^{-1})$	$\nu_{\text{M-X}} (\text{cm}^{-1})$	$\delta_{\text{M-X}} (\text{cm}^{-1})$
$(\text{Et}_4\text{N})_3[\text{Cr}(\text{NCS})_6]$	IR	2082vs	830vw	484s	364s	
	IR ²⁴⁶	2078	-	483	364	
	R	2125(8),2084(10),2077(8)	840(3)	486(1)	264(1)	239(3)
	R†	2120(4),2074(10)	-	488(1)	257(1)	233(4)
$(\text{Et}_4\text{N})_3[\text{Fe}(\text{NCS})_6]$	IR	2057vs	-	481m	353vw,348vw,281w,273w	
	IR ²⁶⁸	2098,2052	822	479	-	
	R	2110(7),2049(10)	-	-	-	256(3)
	R*	-	830(6)	493(5)	326(1),283(7)	255(3),230(3)
$\text{K}_4[\text{Ni}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$	IR	2117vs,2100sh	765s,748m	486w,470m	-	
	IR ²⁶³	2123,2101	766	469	-	
	R	2139(9),2122(10),2053(5)	776(4),750(1)	467(2)	-	219(10)
$(\text{Et}_4\text{N})_4[\text{Ni}(\text{NCS})_6]$	IR	2100sb	779s,722m	472m	-	
	IR ²⁴⁶	2112,2103	828	470	240	
	R	2124(9),2104(9),2098(10)	778(10)	472(4)	-	
	R*	2098(1)	a	474(1)	-	
$\text{K}_3[\text{Rh}(\text{SCN})_6]$	IR	2102s,2084s,2050s	748m,710w	486m,471w,453w,443m	283m	
	IR ²⁴⁶	2110,2098,2084	705,695	471,452,438	-	
	R	2114(5)	750(1),709(3)	-	281(10),262(7)	
	R ²⁵⁰	2098	700	460	283,267	
	R*	2120(10)	707(1)	467(2)	308(6)p,275(10)p,261(9)dp	

Key: R*- solution in acetone
R†- solution in acetonitrile
a - obscured by solvent band.

(Et₄N)₃[Cr(NCS)₆]

In the IR spectrum of the solid purple salt (Et₄N)₃[Cr(NCS)₆] we saw one band in each of the four fingerprint regions as predicted in the theory. In the Raman spectrum of the solid we observed three bands in the ν_{CN} region, but the third peak which occurred at 2084 cm⁻¹ did not appear in the Raman spectrum of a solution of the complex in acetone, indicating it was probably due to solid state splitting. Although two bands are predicted in each of the other two stretching regions ν_{CS} and ν_{MN} only one rather weak peak was observed for each vibration and the one at 840 cm⁻¹ did not appear in the Raman spectrum of the solution. The second predicted vibrations (E_g) were probably too weak to be observed. One band was seen in the Raman spectra of both the solid (486 cm⁻¹) and its solution (488 cm⁻¹) corresponding to the δ_{NCS} vibration.

(Et₄N)₃[Fe(NCS)₆]

Similar characteristics were observed in the spectra of the red salt (Et₄N)₃[Fe(NCS)₆]. In the ν_{CN} region we saw a single strong peak at 2087 cm⁻¹ in the IR and two bands at 2110 and 2049 cm⁻¹ in the Raman spectrum of the solid, although curiously the latter were not observed in the Raman spectrum of the solution. The only vibrational band which we could assign to the ν_{CS} vibration occurred at 830 cm⁻¹ in the Raman spectrum of the solution. Four very weak peaks were seen in the IR in the region where we expected ν_{MN} vibrations to occur but in the Raman only one peak was observed at 256 cm⁻¹ and as this fell outside the frequency range for a metal-N stretch as listed in table 3.2.ii. we have tentatively assigned it to a Fe-N (δ_{MN}) deformation mode using the example of Butje and Preetz who assigned a band at 246 cm⁻¹ to a δ_{OSN} mode.²⁴⁸ In the same region of the Raman spectrum of a solution of the complex in acetone there were four bands, two at 326 and 283 cm⁻¹ which we attribute to ν_{MN} vibrations and two at 255 and 230 cm⁻¹ to δ_{MN} . In the δ_{NCS} region we saw one IR band at 481 cm⁻¹ and one Raman band only was observed at 493 cm⁻¹ in the

spectrum of the solution in acetone in this region.

(Et₄N)₄[Ni(NCS)₆] and K₄[Ni(NCS)₆].

Direct comparison of the IR spectra of the solid blue complexes (Et₄N)₄[Ni(NCS)₆] and K₄[Ni(NCS)₆] showed them to be very similar although more bands were observed in the ν_{CN} region than are predicted. For the potassium salt there were two IR bands and three Raman bands (one more than predicted in each case) and the tetraethylammonium salt gave a single broad IR band and three Raman bands. In the Raman spectrum of the [Ni(NCS)₆]⁴⁻ ion in acetone there was only a single weak band at 2098 cm⁻¹ in the ν_{CN} region.

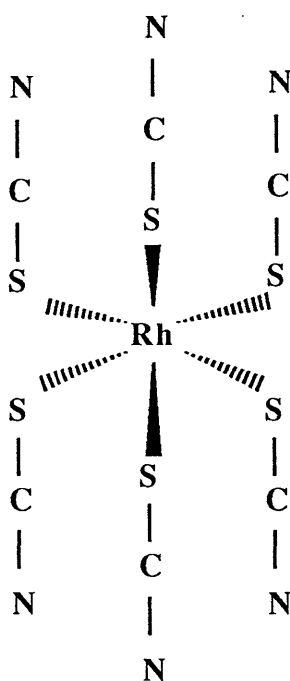
There were two IR bands in the ν_{MN} region of both salts but they occurred at surprisingly low frequencies for an N bonded complex (<780 cm⁻¹). However, as the positions of these bands in the complexes were in close agreement to each other and the bands in other regions occurred at frequencies expected for an N bonded species it is likely that the literature value of 825 cm⁻¹²⁴⁶ was a misassignment although it was in the region expected for the δ_{NCS} vibration of an N bonded thiocyanate. We observed no spectral features in the ν_{MN} region of either complex and the literature value of 240 cm⁻¹²⁴⁶ is more likely to be due to a δ_{MN} deformation mode. In the δ_{NCS} region of the spectra we observed bands which were as predicted plus one extra weak IR peak at 486 cm⁻¹ in the potassium salt.

K₃[Rh(SCN)₆].

As mentioned earlier the X-Ray crystal structure of K₃[Rh(SCN)₆], shown in fig. 3.2.i below has been determined and the D_{3d} symmetry confirmed.²⁵⁶ The group theory predicts two IR and two Raman bands for all the stretching modes and also for the δ_{NCS} deformation. In the IR spectrum of the solid we observed one extra ν_{CN} band at 2050 cm⁻¹, and two additional peaks in the δ_{NCS} region at 486 and 471 cm⁻¹ which could have been due to free SCN⁻ trapped in the lattice (see table 3.2.ii),

although the elemental analyses of this complex were good (see experimental section 3.4). In the Raman spectrum of the red solid we observed only one ν_{CN} band at 2114 cm^{-1} , one ν_{CS} band at 709 cm^{-1} and no discernible δ_{NCS} bands although this vibration generally appears to be weak in the Raman. The Raman spectrum of a solution of this complex in acetone yielded one each of the ν_{CN} , ν_{CS} and δ_{NCS} modes and three strong bands in the ν_{MN} region at 308 , 275 and 261 cm^{-1} , one more than observed by Fricke and Preetz²⁵⁰ for the isomeric system $[\text{Rh}(\text{NCS})_n(\text{SCN})_{6-n}]^{3-}$. However, in his study a peak at 306 cm^{-1} was seen in the IR of $(\text{Bu}_4\text{N})_3[\text{Rh}(\text{NCS})_2(\text{SCN})_4]$ and assigned to a δ_{NCS} vibration. If this is a correct assignment then the complex that we prepared was actually a mixed species in solution, (this band was not seen in the Raman spectrum of the solid) despite the fact that the acetone solvent is in class I and should thus have been expected to stabilise the Rh-SCN conformation (see section 3.2.I.c).²⁶⁷

Fig.3.2.i. The structure of the $[\text{Rh}(\text{SCN})_6]^{3-}$ anion.²⁵⁶



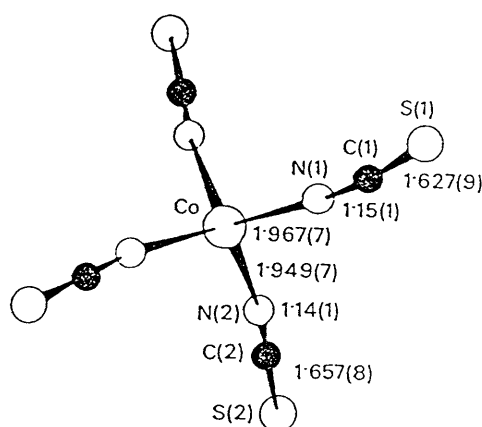
ii. Four coordinate complexes.

Crystal structures have been obtained for all the four coordinate complexes studied herein. The anions in N bonded isothiocyanato species, $K_2[Co(NCS)_4] \cdot 3H_2O$ ²⁵⁸ and $K_2[Zn(NCS)_4]$ ²⁶⁹ are tetrahedral with linear M-NCS units whilst a square planar configuration is found for the anions in the thiocyanato complexes $K_2[Pt(SCN)_4]$ ²⁷⁰ and $K_2[Pd(SCN)_4]$, (see fig.3.2.ii).²⁵⁷ The vibrational data are listed in table 3.2.iii.

$K_2[Co(NCS)_4]$ and $(Et_4N)_2[Co(NCS)_4]$.

For these N bonded tetrahedral species group theory predicts one coincident IR and depolarised Raman active (T_2) band for each of the modes ν_{CN} , ν_{CS} , δ_{NCS} and ν_{MN} plus one extra Raman active mode (A_1 for the stretching vibrations and E for the δ_{NCS} mode).

Fig.3.2.ii. The structure of the $[Co(NCS)_4]^{2-}$ anion.²⁵³



In the ν_{CN} region of the blue solid $K_2[Co(NCS)_4]$ two coincident bands were seen at 2090 and 2071 cm^{-1} in both the IR and Raman spectra; it was possible that solid state splitting made the A_1 mode IR active in this region. The tetraethylammonium salt was also deep blue but had only one peak in the ν_{CN} region of the IR spectrum at 2063 cm^{-1} which was not coincident with any of the three Raman peaks observed.

However, the Raman spectrum of a solution of the $[\text{Co}(\text{NCS})_4]^{2-}$ ion in acetone had peaks which confirmed the predictions of the group theory, the polarised A_1 mode occurring at 2103 cm^{-1} and the depolarised T_2 vibration at 2079 cm^{-1} .

In the ν_{CS} region solid $\text{K}_2[\text{Co}(\text{NCS})_4]$ again had two IR peaks, one of which lay at 819 cm^{-1} , very close to the Raman band at 816 cm^{-1} . The spectra of the solid tetraethylammonium salt had only one weak IR peak at 842 cm^{-1} and two strong Raman bands at 838 and 834 cm^{-1} . The Raman spectrum of the solution species in this region had only one polarised band at 826 cm^{-1} ; the depolarised band was presumably too weak to be observed in the Raman. In the other stretching region ν_{MN} , the expected behaviour was followed more closely. Solid $\text{K}_2[\text{Co}(\text{NCS})_4]$ had one IR (at 292 cm^{-1}) and two Raman bands (296 and 287 cm^{-1}) whilst solid $(\text{Et}_4\text{N})_2[\text{Co}(\text{NCS})_4]$ had a single strong IR band at 307 cm^{-1} , but no peaks were observed in the Raman. In the Raman spectrum of the solution the depolarised T_2 vibration was observed at 295 cm^{-1} and the polarised A_1 mode at 287 cm^{-1} .

Three weak bands were observed in the δ_{NCS} region of the IR spectrum of solid $\text{K}_2[\text{Co}(\text{NCS})_4]$, but only one weak peak was seen at 497 cm^{-1} in the Raman which did not coincide with any of the IR bands, but was very close to the band observed at 496 cm^{-1} in the Raman spectrum of the solution. It can be seen from table 3.2.iii that the IR bands that we observed for the above complexes were in close agreement with the literature values²⁴⁶ but few of these values agreed with the bands observed in the Raman spectra of the solid complexes or the $[\text{Co}(\text{NCS})_4]^{2-}$ ion in solution indicating the effect that solid state splittings have on the vibrational spectra of the solid complexes.

$(\text{Et}_4\text{N})_2[\text{Zn}(\text{NCS})_4]$

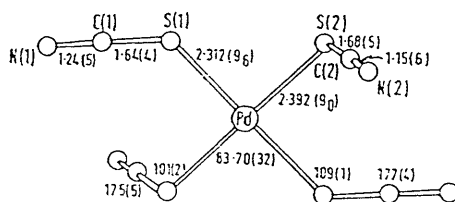
This white complex had very simple vibrational spectra. The IR spectrum of the solid had a single band in each of the fingerprint regions, all of which were in close agreement with the literature values.²⁴⁶ In the Raman spectrum of the solid there were

two strong bands in the ν_{CN} region. The lower of these lay at 2069 cm^{-1} and was close to the IR band at 2073 cm^{-1} ; we thus assigned it to the T_2 mode. In the ν_{CS} region there was one moderately strong Raman band which was also probably due to a T_2 mode due to its proximity to the IR band at 833 cm^{-1} . In the δ_{NCS} region we saw one weak band in the Raman coincident with the IR band at 483 cm^{-1} , and thus also assigned as T_2 . There was no Raman band in the ν_{MN} region and the peak at 284 cm^{-1} in the IR was very weak. In the Raman spectrum of a solution of salt in water we saw a single depolarised band at 2110 cm^{-1} in the ν_{CN} region and one very weak peak at 831 cm^{-1} in the ν_{CS} area. No other bands were observed.

$K_2[\text{Pd}(\text{SCN})_4]$ and $(\text{Et}_4\text{N})_2[\text{Pd}(\text{SCN})_4]$.

For these square planar thiocyanato complexes we expect two Raman (A_{1g} , polarised and B_{1g} , depolarised) and one IR active (E_u) band for each stretching mode.

Fig.3.2.iii. The structure of the $[\text{Pd}(\text{SCN})_4]^{2-}$ anion.²⁵⁷



In the ν_{CN} region of solid $\text{K}_2[\text{Pd}(\text{SCN})_4]$ we saw two strong IR bands at 2125 and 2093 cm^{-1} and three Raman bands whilst there was only one band in both the IR (at 2108 cm^{-1}) and Raman spectra (at 2110 cm^{-1}) of the tetraethylammonium analogue. We observed one IR and two Raman bands in accordance with the theory in the ν_{CS} region of solid $\text{K}_2[\text{Pd}(\text{SCN})_4]$, but there were two bands in both the IR and Raman spectra of $(\text{Et}_4\text{N})_2[\text{Pd}(\text{SCN})_4]$. The two IR bands at 302 and 206 cm^{-1} in the ν_{MS} region of the spectrum of the solid potassium salt agreed with the literature²⁴⁶ but no

bands were observed in the Raman spectrum of this salt. However, in $(\text{Et}_4\text{N})_2[\text{Pd}(\text{SCN})_4]$ we saw one IR band at 294 cm^{-1} and two peaks in the Raman at 275 and 260 cm^{-1} .

In the region of the bending modes we observed four IR bands in the spectrum of $\text{K}_2[\text{Pd}(\text{SCN})_4]$ all of which agreed with those reported in the literature²⁴⁶, but no Raman bands. There were two IR peaks at 431 and 418 cm^{-1} and one Raman band (at 498 cm^{-1}) in this region of the spectra of the tetraethylammonium analogue. The Raman spectrum of the $[\text{Pd}(\text{SCN})_4]^{2-}$ ion in acetone had one ν_{CN} band (at 2110 cm^{-1}), one ν_{CS} band (705 cm^{-1}) and one δ_{NCS} band (466 cm^{-1}), none of which was strong enough to enable us to carry out polarisation studies, but the two peaks in the ν_{MN} area were more intense and we ascertained that the band at 281 cm^{-1} was polarised and thus $\text{A}_{1\text{g}}$ whilst the other band, at 263 cm^{-1} we attributed to the depolarised $\text{B}_{2\text{g}}$ mode.

$\text{K}_2[\text{Pt}(\text{SCN})_4]$:

The spectra for this complex were very similar to the $\text{Pd}(\text{II})$ analogue. In the ν_{CN} region there were two IR bands and two Raman bands in the spectra of the solid, but only one strong band at 2123 cm^{-1} in the spectrum of the solution in acetone. In the ν_{CS} region we saw one band only at 698 cm^{-1} in the IR, at 701 cm^{-1} in the Raman of the solid complex and at 703 cm^{-1} in the spectrum of the solution. The ν_{MS} region of the spectra was different from that in other complexes; we saw no IR bands, two weak Raman bands were observed in the spectrum of the solid and three Raman bands at 312 , 302 and 278 cm^{-1} in the spectrum of the solution. The first two of these were both polarised and the latter depolarised.

There were three peaks in the δ_{NCO} region of the IR spectrum occurring at 478 , 438 and 428 cm^{-1} which agreed with the literature²⁴⁶ although we did not observe the fourth reported value at 472 cm^{-1} . Only one very weak band was seen at 466 cm^{-1} in the Raman spectrum of the solid and this was not strong enough for us to observe it in the spectrum of the solution.

Table 3.2.iii Vibrational spectra for four coordinate thiocyanato and isothiocyanato complexes.

Complex		$\nu_{\text{CN}} (\text{cm}^{-1})$	$\nu_{\text{CS}} (\text{cm}^{-1})$	$\delta_{\text{NCS}} (\text{cm}^{-1})$	$\nu_{\text{M-X}} (\text{cm}^{-1})$	$\delta_{\text{M-X}} (\text{cm}^{-1})$
$\text{K}_2[\text{Co}(\text{NCS})_4] \cdot 2\text{H}_2\text{O}$	IR	2090s, 2071s	836w, 819w	477w, 470w, 454w	292m	
	IR ²⁴⁶	2085, 2067	820	478	286	
	R	2090(10), 2071(9)	824(3), 816(6)	497(1)	296(1), 287(1)	237(1), 221(10)
$(\text{Et}_4\text{N})_2[\text{Co}(\text{NCS})_4]$	IR	2063s	842w	482m	307s	
	IR ²⁴⁶	2065	844, 838	481	311	
	R	2091(8), 2053(10), 2044(9)	838(9), 834(8)	-	-	
	R*	2103(5)p, 2079(6)dp	826(10)p	496(2)	295(5)dp, 287(4)p	
$(\text{Et}_4\text{N})_2[\text{Zn}(\text{NCS})_4]$	IR	2073vs	833w	483m	284w	
	IR ²⁴⁶	2072	837	482	287	
	R	2102(8), 2069(10)	840(6)	484(1)	-	
	R*	2110(8)dp	831(1)	-	-	
$\text{K}_2[\text{Pd}(\text{SCN})_4]$	IR	2125s, 2093s	704m	474m, 468m, 442s, 432s	302m, 286s	
	IR ²⁴⁶	2122, 2093	709, 703, 697	474, 468, 442, 432	300, 286	
	R	2130(2), 2125(10), 2101(8)	707(5), 699(1)	-	-	
	R*	2116(5)	705(3)	466(1)	281(10)p, 263(3)dp	
$(\text{Et}_4\text{N})_2[\text{Pd}(\text{SCN})_4]$	IR	2108vs	699m, 667m	431m, 418w	294m	
	IR ²⁴⁶	2112, 2109	698, 694	465, 433, 429, 418	294	
	R	2110	697, 668	498	275, 260	
$\text{K}_2[\text{Pt}(\text{SCN})_4]$	IR	2127s, 2097s	698w	478w, 438m, 428m	-	
	IR ²⁴⁶	2130, 2100, 2052	697	478, 472, 438, 427	293, 283	
	R	2129(10), 2103(9)	701(3)	466(1)	292(1), 257(1)	
	R*	2123(10)	703(2)	-	312(5)p, 302(3)p, 278(8)dp	

Key: R*- Raman solution in acetone
 Raq- Raman solution in water

iii. Other homoleptic thiocyanate complexes.

The data for these complexes are presented in table 3.2.iv. overleaf.

K₃[UO₂(NCS)₅].

The X-ray crystal structure of the caesium salt of this complex has been determined²⁵⁴ and confirms that the symmetry of the anion is pentagonal bipyramidal. On the basis of this symmetry, group theory predicts that there will be one IR band (E₁') and two Raman bands (A₁', polarised and E₂', depolarised) in each of the stretching regions ν_{CN} , ν_{CS} and ν_{MN} .

In the IR spectrum of the solid K₃[UO₂(NCS)₅] we observed three IR bands in both the ν_{CN} and ν_{CS} regions but none in the ν_{MN} region. The Raman spectrum of the solid was more complex with four bands in both the ν_{CN} and ν_{CS} regions and two in the ν_{MN} . The Raman spectrum of a solution of the complex in acetone had three bands in the ν_{CN} region although it was possible that one of these, at 2055 cm⁻¹ was due to free SCN⁻. In both the ν_{CS} and ν_{MN} regions we saw two bands in agreement with the predictions of group theory but these peaks were not strong enough to enable us to carry out polarisation studies. There were four bands in the IR spectrum of solid K₃[UO₂(NCS)₅] which we could assign to δ_{NCS} vibrations although three of these were weak. No bands were seen in the Raman spectra of either the solid or solution in acetone which we could attribute to the δ_{NCS} vibration.

K[Cu(NCS)₃] and Pd(SCN)₂.

It is likely that both of these species are polymeric or at least contain bridging thiocyanate groups as reflected by the high frequencies (above 2140 cm⁻¹) of the ν_{CN} bands.¹³⁹ The structure of K[Cu(NCS)₃] might be similar to that of K[Cu(NCO)₃] in which there is a pseudo-tetrahedral arrangement of ligands around each metal atom (see section 3.3.II). Unfortunately the dark green colour of the complex prevented us measuring the Raman spectrum but in the IR of the solid two bands occurred in each of

the fingerprint regions except the ν_{CN} region in which the single band at 2148 cm^{-1} was very broad. All the bands occurred at frequencies consistent with the anion containing N bonded *isothiocyanato* ligands.

In the spectra of $\text{Pd}(\text{SCN})_2$ there were coincident Raman and IR bands at 2158, 772 and 474 cm^{-1} . A second IR band was also observed in the ν_{CN} (at 2123 cm^{-1}), ν_{CS} (at 714 cm^{-1}) and δ_{NCS} (424 cm^{-1}) regions but no peaks were observed that could be attributed to ν_{MS} . In the Raman spectrum of this yellow solid there were, in addition to the coincident bands mentioned above, bands at 430, 284 and 233 cm^{-1} which we attributed to the vibrations δ_{NCS} , ν_{MS} and δ_{MS} respectively.

Table 3.2.iv. Vibrational spectra for miscellaneous thiocyanato and isothiocyanato complexes.

Complex		$\nu_{\text{CN}} \text{ (cm}^{-1}\text{)}$	$\nu_{\text{CS}} \text{ (cm}^{-1}\text{)}$	$\delta_{\text{NCS}} \text{ (cm}^{-1}\text{)}$	$\nu_{\text{M-X}} \text{ (cm}^{-1}\text{)}$	$\delta_{\text{M-X}} \text{ (cm}^{-1}\text{)}$
$\text{K}_3[\text{UO}_2(\text{NCS})_5]$	IR	2090m, 2057s, 2032w	828m, 805w, 770w	484s, 476w, 470w, 403w	-	
	IR ²⁷¹	2090, 2055	813, 802	482, 408	-	
	R	2089(5), 2061(5), 2047(5), 2028(7)	837(10), 820(4), 812(4), 805(3)	-	268(2), 231(1)	214(1), 193(1)
	R*	2099(1), 2055(2), 2046(1)	848(6), 813(1)	-	281(3), 272(1)	227(10)
$\text{K}[\text{Cu}(\text{NCS})_3]$	I.R	2148s, br	798m, 746w	469s, 440s	343vs, 256m	
$\text{Pd}(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$	IR	2158s, 2123sh	772w, 714w	474w, 424w	-	
	R	2175(1), 2162(2)	772(1)	475(1), 430(1)	284(3)	233(1)

Key: R*- Raman solution in acetone.

b. Mixed thiocyanate complexes.

We have prepared a variety of substituted thiocyanate complexes of palladium(II), platinum(II) and copper(II). Where possible both isomers were prepared to compare the differences in their vibrational spectra. The results for the Pd(II) complexes are summarised below in table 3.2.v. while table 3.2.vi. concerns the complexes of Pt(II) and Cu(II).

The symmetry of these species is much lower than for the homoleptic complexes above and so treatment of the group theory is not included. However, it is reported¹³⁹ that for complexes of the type $[ML_2(NCS)_2]$ based on a square planar structure like $K_2[Pt(SCN)_4]$ the skeletal point groups are C_{2v} for *cis* complexes and D_{2h} for their *trans* analogues. Using these point groups, we predict for *cis* complexes A_{1g} and B_1 modes which are each both Raman and IR active for each of the modes in the stretching regions (ν_{CN} , ν_{CS} and ν_{MN}). For centrosymmetric *trans* complexes we should find A_g (Raman polarised, infrared inactive) and B_{2u} (IR active only) for each of the ν_{CN} , ν_{CS} and ν_{MN} modes. The only X-ray crystal structures determined which clarify the bonding of the mixed species studied here are that of *trans*- $[Pt(py)_2(SCN)_2]$ (see fig.2.3.iv).²⁷² which is square planar and $[Cu(py)_2(NCS)_2]$ which is reported to have a tetragonal bipyramidal structure and must therefore contain bridging thiocyanate groups.²⁷³

$[Pd(phen)(SCN)_2]$.

Because of the bidentate nature of the phenanthroline ligand this complex is obviously *cis* and this was demonstrated by the observation of coincident bands in the IR and Raman spectra at 2106 and 2090 cm^{-1} in the ν_{CN} region and at 460 and 416 cm^{-1} in the δ_{NCS} region. All the bands seen in both the IR and Raman spectra occurred in the frequency ranges expected for an S-bonded thiocyanato complex although we did not see bands that agreed with those reported in the literature in either the ν_{CS} or ν_{MS} regions.²⁷⁴ The formation of an S-bonded thiocyanato species was expected from the

preparation carried out at low temperature ($>60^{\circ}\text{C}$) but the complex turned brown and decomposed when heated at 150°C and no isomerisation took place unlike as reported in the literature.

[Pd(bipy)(SCN)₂] and [Pd(bipy)(NCS)₂].

Both these isomers were prepared; the brown isothiocyanato complex was obtained by heating the yellow thiocyanato complex at 150°C for thirty minutes. In the ν_{CN} region the only differences that occurred in the vibrational spectra upon isomerisation were the loss of the peaks at 2072 cm^{-1} in the IR and 2078 cm^{-1} in the Raman spectra of $[\text{Pd}(\text{bipy})(\text{SCN})_2]$ and the appearance of a peak at 2101 cm^{-1} in the Raman spectrum of $[\text{Pd}(\text{bipy})(\text{NCS})_2]$. In the ν_{CS} region the IR bands at 706 , 644 and 647 cm^{-1} in the spectrum of $[\text{Pd}(\text{bipy})(\text{SCN})_2]$ were replaced by two at 850 and 843 cm^{-1} , changes which clearly showed the change in the mode of bonding. In the ν_{CN} region, one of the two IR peaks and one Raman peak at 322 cm^{-1} disappeared and were replaced by new peaks at 291 and 256 cm^{-1} in the IR spectrum and 282 and 274 cm^{-1} in the Raman. However, the presence of a strong band at 270 cm^{-1} , (a frequency indicating N-bonding) in the Raman spectrum of $[\text{Pd}(\text{bipy})(\text{SCN})_2]$ and IR bands at 431 and 417 cm^{-1} which were indicative of an S-bonded species in the spectrum of $[\text{Pd}(\text{bipy})(\text{NCS})_2]$ suggested that despite the low temperature preparative method used to favour the initial formation of the thiocyanato complex and the colour change accompanying the isomerisation, both the complexes were mixed to some degree. An initial attempt at the preparation of the S-bonded species resulted in the formation of the pink complex $[\text{Pd}(\text{bipy})_2][\text{Pd}(\text{SCN})_4]$ which demonstrated the variety of possible species that could be prepared by the same general method.²⁶⁵

Table 3.2.v. Vibrational spectra for substituted thiocyanato and isothiocyanato complexes of palladium(II).

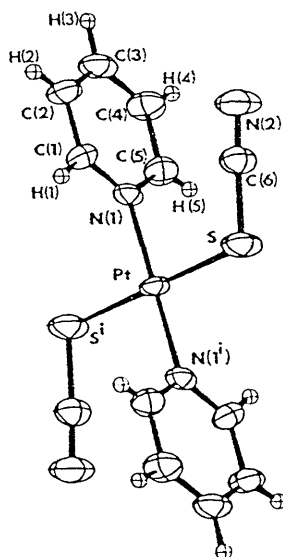
Complex		$\nu_{\text{CN}} \text{ (cm}^{-1}\text{)}$	$\nu_{\text{CS}} \text{ (cm}^{-1}\text{)}$	$\delta_{\text{NCS}} \text{ (cm}^{-1}\text{)}$	$\nu_{\text{M-X}} \text{ (cm}^{-1}\text{)}$	$\delta_{\text{M-X}} \text{ (cm}^{-1}\text{)}$
[Pd(phen)(SCN) ₂]	IR	2115m,2106m,2088s	716s	460w,431m,416w	327m,302w	
	IR ²⁷⁴	2116	695	418	319	
	R	2107(8),2092(6)	718(2),708(2),702(2)	460(1),416(3),399(1)	279(10),263(2)	231(1)
[Pd(bipy)(SCN) ₂]	IR	2123s,2104s,2072m	706w,664m,647m	430w,425w,414m	327w,278w	
	IR ²⁷⁵	2117	700	-	319	
	R	2121(3),2078(1)	-	-	322(8),270(10)	234(2),207(5)
[Pd(bipy)(NCS) ₂]	IR	2125s,2101s	850w,843m	448w,431m,417m	291m,256vw	
	IR ²⁷⁴	2115,2100	865	458	261	
	R	2125(4),2101(5)	844(1)	466(2)	282(9),274(10)	234(8)
[Pd(py) ₂ (SCN) ₂]	IR	2116s,2104s	a	432m	304w,291w,269w	
	IR ²⁷⁴	2112	-	436,424	-	
	R	2118(3),2104(1)	-	-	276(1),270(10)	207(3)
[Pd(AsPh ₃) ₂ (SCN) ₂]	IR	2119m,2072mbr	a	414vw	326w,311m,300w	
	IR ²⁷⁵	2119	-	418	311	
	R	2121(10),2097(3)	-	-	340(2),328(5),279(8)	
[Pd(AsPh ₃) ₂ (NCS) ₂]	IR	2090s	854s,848m	a	337m,329m,315w	
	IR ²⁷⁴	2085	854	-	265	
	R	2101(1),2094(1)	-	-	337(1),269(3)	232(1)

Key: a - Band obscured by organic ligands

$[Pd(py)_2(SCN)_2]$.

It is reasonable to assume that the structure of this complex is the same as for the Pt(II) analogue, which we did not prepare. The structure of the latter complex is shown below in fig.3.2.iv.

Fig.3.2.iv. The structure of $[Pt(py)_2(SCN)_2]$.²⁷²



The spectra of $[Pd(py)_2(SCN)_2]$ agreed well with each other and also with those reported in the literature.²⁷⁴ The δ_{NCS} band at 432 cm^{-1} in the IR was the best confirmation that the complex was S-bonded and coincident IR and Raman bands at 216 and 2104 cm^{-1} suggested that this complex adopts a *cis* conformation. Unfortunately the presence of ligand vibrations obscured any bands in the ν_{CS} region but in the ν_{MS} region we saw three bands in the IR and two bands in the Raman, one at 270 cm^{-1} coinciding with an IR band at 269 cm^{-1} . The complex decomposed on heating and so no isomer was prepared.

$[Pd(AsPh_3)_2(SCN)_2]$ and $[Pd(AsPh_3)_2(NCS)_2]$.

Both $[Pd(AsPh_3)_2(SCN)_2]$ and $[Pd(AsPh_3)_2(NCS)_2]$ were prepared; the

isothiocyanate isomer was formed by heating the S-bonded analogue at 150°C for thirty minutes. In the IR spectrum of $[\text{Pd}(\text{AsPh}_3)_2(\text{SCN})_2]$ the ν_{CN} bands at 2119 and 2072 cm^{-1} disappeared and a single strong peak at 2090 cm^{-1} was observed in the IR of $[\text{Pd}(\text{AsPh}_3)_2(\text{NCS})_2]$. In the Raman spectra of the S-bonded thiocyanato complex there were two bands at 2121 and 2097 cm^{-1} which were replaced by weak bands at 2101 and 2094 cm^{-1} in the spectrum of $[\text{Pd}(\text{AsPh}_3)_2(\text{NCS})_2]$. No vibrational modes were observed in the ν_{CS} region of the S-bonded species as there were strong organic ligand vibrations in this region but in the IR of $[\text{Pd}(\text{AsPh}_3)_2(\text{NCS})_2]$ there were two peaks at 854 and 848 cm^{-1} which were a good indication that isomerisation had occurred. Similarly, the IR band at 414 cm^{-1} in the spectrum of $[\text{Pd}(\text{AsPh}_3)_2(\text{SCN})_2]$ disappeared when the complex was heated, but any new bands would have been obscured by ligand vibrations in this region of the spectrum.

There were three bands in the IR spectra of both isomers but although these bands were at different positions there was no apparent shift to frequencies indicative of N-bonded species in the complex after heating. The lack of coincident IR and Raman bands lead us to believe that the complex adopts a *trans* conformation like the Pt(II) analogue (see below), and this appears likely from consideration of the relative size of the AsPh_3 ligand compared with that of pyridine which we concluded has a *cis* structure (see above).

$[\text{Pt}(\text{bipy})(\text{NCS})_2]$.

This orange complex was prepared at room temperature and the IR bands observed occurred at frequencies expected for an N-bonded species. The band at 2116 cm^{-1} was different from that reported in the literature at 2095 cm^{-1} ²⁶⁷, and we saw no band at 844 cm^{-1} in the ν_{CS} region as reported, but the peaks that we observed at 854 and 758 cm^{-1} were at frequencies expected for an isothiocyanato complex. This disparity suggests that the complex we prepared differed from that reported in the literature, although there were insufficient data to determine which of the complexes

was a mixed species. A single peak was observed in each of the other two fingerprint regions, occurring at 469 cm^{-1} (δ_{NCS}) and 324 cm^{-1} (ν_{MN}). Unfortunately this complex fluoresced and so we were unable to measure the Raman spectrum of the solid.

[Pt(AsPh₃)₂(SCN)₂] and [Pt(AsPh₃)₂(NCS)₂].

It was not possible to determine the structures of these complexes as there were insufficient bands in the vibrational spectra to demonstrate whether a *cis* or *trans* structure was adopted. The IR spectrum of the solid complex [Pt(AsPh₃)₂(SCN)₂] had two bands in the ν_{CN} region, and one of these, at 2126 cm^{-1} , lay very close to the only Raman band observed in this region at 2124 cm^{-1} . We saw only one IR band in the ν_{CS} region at 862 cm^{-1} , which was in agreement with the literature value²⁶⁵ although this occurred at a frequency expected for N-bonded complexes, but any bands at lower frequencies would have been obscured by the AsPh₃ bands at 735 and 695 cm^{-1} . There was one band at 874 cm^{-1} in the Raman spectrum of the S bonded species which we could attribute to a ν_{CS} vibration. It is likely that this complex was actually a mixed species with some N-bonds. In the ν_{MS} region there were three IR bands and two non coincident Raman bands. No bands attributable to δ_{NCS} vibrations were observed as strong ligand bands at 475 and 468 cm^{-1} occurred in this region.

There was little change in the vibrational spectra upon isomerisation although there was a clear colour change from bright yellow to a much lighter hue when the S-bonded complex was heated at 150°C to form [Pt(AsPh₃)₂(NCS)₂]. In the ν_{CN} region the two IR peaks and one Raman band observed for [Pt(AsPh₃)₂(SCN)₂] became a single strong IR band at 2107 cm^{-1} and two moderately strong Raman bands at 2122 and 2110 cm^{-1} in the spectra of the N-bonded isomer. The ν_{CS} band at 861 cm^{-1} in the IR was unaltered from that observed in the spectra of [Pt(AsPh₃)₂(SCN)₂] although the Raman band at 874 cm^{-1} was not observed in the spectrum of the isothiocyanato complex. One non-coincident band attributable to ν_{MN} was observed in both the IR and Raman spectra of [Pt(AsPh₃)₂(NCS)₂].

Table 3.2.vi. Vibrational spectra for substituted thiocyanato and isothiocyanato complexes of platinum(II) and copper (II).

Complex		$\nu_{\text{CN}} \text{ (cm}^{-1}\text{)}$	$\nu_{\text{CS}} \text{ (cm}^{-1}\text{)}$	$\delta_{\text{NCS}} \text{ (cm}^{-1}\text{)}$	$\nu_{\text{M-X}} \text{ (cm}^{-1}\text{)}$	$\delta_{\text{M-X}} \text{ (cm}^{-1}\text{)}$
[Pt(bipy)(NCS) ₂]	IR	2116s	854w,758m	469mbr	324s	
	IR ²⁶⁷	2095	844			
	R	FLUORESCES.				
[Pt(AsPh ₃) ₂ (SCN) ₂]	IR	2126m,2090s	862w,a	a	369m,342w,323w	
	IR ²⁶⁵	2090	861			
	R	2124(2)	874(1)	-	318(2),291(4)	235(3)
[Pt(AsPh ₃) ₂ (NCS) ₂]	IR	2107s	861m	a	339m	
	R	2122(8),2110(5)	-	-	347(1)	242(1),232(10)
[Cu(bipy)(NCS) ₂]	I.R	2093s,2078s,2043s	820w,814w	468m,420m	291w	
	R	2092(2),2050(2)	814(3),769(10),738(1)	478(1),435(9)	254(2)	230(3)
[Cu(py) ₂ (NCS) ₂]	IR	2155m,2092sbr	825m,692s	477m,468m,434s	319s	
	R	2099(1),2093(3)	863(1),822(1)	478(10)	288(2),245(8)	

a- bands obscured by organic ligand bands.

[Cu(bipy)(NCS)₂] and [Cu(py)₂(NCS)₂].

Both these complexes were prepared at room temperature and as Cu(II) is regarded as a hard metal centre it is to be expected that they would be N-bonded species. The blue solid [Cu(bipy)(NCS)₂] had vibrational bands characteristic of an isothiocyanato complex. In the ν_{CN} region we saw three strong IR bands and two weak Raman bands, one of which was coincident with the IR band at 2093 cm⁻¹. A coincident IR and Raman band also occurred in the ν_{CS} region at 814 cm⁻¹ and there was one extra peak at 820 cm⁻¹ in the IR spectrum, and two in the Raman at 769 and 738 cm⁻¹. We observed single peaks in the IR (at 291 cm⁻¹) and Raman (254 cm⁻¹) spectra attributable to ν_{MN} and a further peak at 230 cm⁻¹ in the Raman spectrum which was possibly due to a δ_{MN} deformation.

The complex [Cu(py)₂(NCS)₂] was also blue but had bands indicating that there were bridging and S-bonded thiocyanate groups. One of the two IR bands in the ν_{CN} region occurred at 2155 cm⁻¹, which indicated that the solid contains bridged thiocyanate groups¹³⁹ and in the ν_{CS} region the two IR peaks lay at 825 cm⁻¹, as expected for an isothiocyanato species and also 692 cm⁻¹, a frequency associated with an S-bonded complex (see table 3.2.i). In the Raman spectrum of this compound there were two weak bands in each of the above regions, one of which was coincident with an IR band at 2092 cm⁻¹ in the ν_{CN} region and also at 822 cm⁻¹ (ν_{CS}). The presence of these bands suggested that the complex adopted a *cis* configuration as coincident bands were observed in these regions for other complexes with *cis* structures such as [Pd(phen)(SCN)₂] and [Pd(bipy)(NCS)₂]. In the ν_{MN} region we observed one strong band at 319 cm⁻¹ in the IR spectrum and two bands at 288 and 245 cm⁻¹ in the Raman spectrum.

3.2.III. Conclusions.

We have measured vibrational spectroscopic data for a number of thiocyanate complexes and our results, particularly the new Raman data we have recorded confirm the conclusions regarding the modes of bonding reported in published work.^{265,274,275} We set out to assess the suitability of Raman spectroscopy as a technique to help indicate the mode of bonding in these complexes but have found that the bands in the fingerprint regions (ν_{CN} , ν_{CS} and δ_{NCS}) are all rather weak in the Raman and so we conclude that IR spectroscopy is better suited to this task. The ν_{MN} bands are often strong in the Raman and if the frequency of these bands is considered then this is a useful technique for their determination. However, there could be some confusion in distinguishing ν_{MN} stretches from δ_{MN} deformations which occur at lower frequencies. In our work we have assigned all vibrations below about 240 cm^{-1} as δ_{MN} modes in accordance with Preetz and coworkers in their studies of thiocyanate complexes of Ru(III)²⁵¹ and Os(III).²⁴⁸

Of the four fingerprint vibrations we consider the ν_{CS} mode to be the best to use in determination of the mode of bonding in thiocyanate complexes as the frequency ranges expected for N and S bonded species lie furthest apart. All of the N-bonded isothiocyanato complexes had ν_{CS} vibrations above 770 cm^{-1} and all the S-bonded thiocyanates had most bands below 720 cm^{-1} . The major exceptions to this are the salts of $[\text{Ni}(\text{NCS})_6]^{4-}$ for which we observed a band as low as 722 cm^{-1} in the IR spectrum of the solid complex $(\text{Et}_4\text{N})_2[\text{Ni}(\text{NCS})_6]$. We saw a band at 748 cm^{-1} in the IR and 750 cm^{-1} in the Raman spectrum of solid $\text{K}_3[\text{Rh}(\text{SCN})_6]$, although we have discussed the possibility of there being some isomeric N-bonded species in this complex taking into consideration the work of Fricke and Preetz.²⁵⁰ There is too great an overlap between the expected frequency ranges of the S and N-bonded species in the other fingerprint regions for determination of the mode of bonding to be conclusive, although the different numbers of bands, arising from the different symmetries of the

complexes, can provide valuable evidence which can aid this determination.

Our studies on the mixed complexes of Pd(II) and Pt(II) have shown that both S and N-bonded isomers can be prepared but the vibrational spectra often suggested that there was a mixture of both bonding modes in the prepared samples.

3.3 Studies on Cyanate Complexes.

In this section we present our results concerning the preparation and spectral characterisation of a number of cyanate complexes. These complexes were of particular interest to us because of their possible role in the oxidation of cyanide complexes by H_2O_2 and other proxy species. Our results on this topic are presented after a short introduction in which we outline the spectral and bonding characteristics of the cyanate ligand.

3.3.I Symmetry and bonding in cyanate complexes.

In principle the cyanate ligand is ambidentate like the thiocyanate ligand but in practice only a few examples of O-bonded cyanates with very hard, highly charged metal centres have been reported on the basis of evidence from their IR spectra²⁷⁶ including the complexes $[\text{Re}(\text{OCN})_6]^{2-}$ and $[\text{Mo}(\text{OCN})_6]^{3-}$.²⁷⁷ The overwhelming propensity for the formation of N-bonded species in preference to the O-bonded analogues probably arises because both sites on the cyanato ligand are hard and, unlike the sulphur atom on the thiocyanato ligand, there are no low lying vacant d orbitals on the oxygen. Vacant π^* orbitals lie on the nitrogen atom thus rendering it the preferred end for coordination²⁷⁸ and the nitrogen is less electronegative than the oxygen so it might be expected that the σ -donor orbital on the former will provide better overlap with the metal acceptor orbital than that on the oxygen. Those species which do form O-bonded cyanate species have vacant or partially filled d orbitals with the appropriate symmetry to interact with filled π -bonding orbitals on the cyanate, e.g. $[\text{Zr}(\text{OCN})_4]^{2-}$.²⁷⁸

The symmetry factors determining the number of spectroscopically active vibrational modes have been discussed above in section 3.2.I with respect to thiocyanate complexes. The linear free cyanate ion is characterised by three

fundamental vibrations; ν_{CN} at 2165cm^{-1} , ν_{CO} at 1203 cm^{-1} and the doubly degenerate δ_{NCO} at 628 and 635 cm^{-1} . The ν_{CO} is shifted from the calculated value of 1254 cm^{-1} due to Fermi resonance with the first overtone $2\delta_{\text{NCO}}$ which is also expected in this area.¹⁰³

In transition metal complexes all these vibrations shift to higher wavenumbers. The ν_{CN} band is generally found above 2200 cm^{-1} , ν_{CO} around 1330 cm^{-1} and the δ_{NCO} above 650 cm^{-1} . Metal nitrogen stretches (ν_{MN}) tend to lie in the region $300\text{-}200\text{ cm}^{-1}$.²⁰⁷ In O-bonded complexes there is little difference in the position of the ν_{CN} bands, the ν_{CO} bands shift to lower wavenumbers ($1070\text{-}1300\text{ cm}^{-1}$) and the deformation modes occur between about 590 and 630 cm^{-1} .¹³⁹ The bands are very intense in the IR and are correspondingly weak Raman scatterers; they are indeed so weak that it is often not possible to measure the Raman spectra of cyanate complexes.²⁸⁰ However electronic spectra, magnetic properties²⁸¹, ^{14}N and ^{13}C NMR data^{112,282} have been measured and indicate that N bonding occurs in most complexes.

Work on mixed complexes of Pd(II) , Pt(II) ²⁸³ and Cu(II) ²⁷⁸ similar to those described earlier²⁶⁵ for thiocyanato complexes has shown that, despite the presence of bulky, electron withdrawing ligands (AsPh_3 , py, bipy) which promote isomerism in the thiocyanato species, the N-bonded *isocyanato* species only are found.

3.3.II Results and discussion.

We have prepared a number of homoleptic and mixed *isocyanato* complexes to confirm the identity of the donor atom and, where possible to measure the Raman spectra for those complexes where these have not previously been measured. The results for homoleptic cyanato complexes are summarised in table 3.3.i, and in table 3.3.ii we present the data measured for substituted complexes.

Table 3.3.i Vibrational spectra for isocyanato complexes.

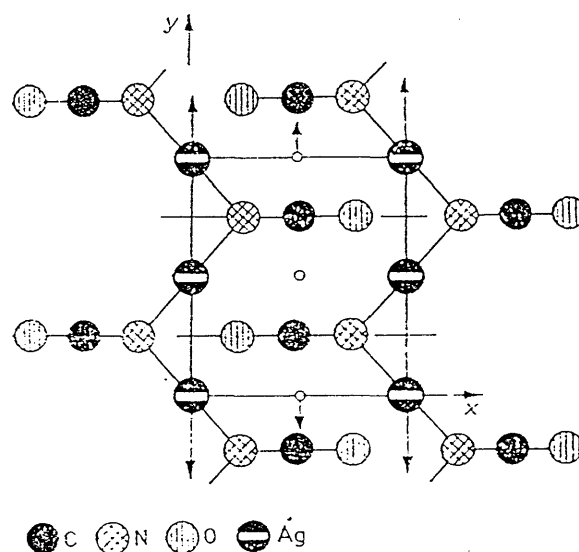
Complex		$\nu_{\text{CN}}(\text{cm}^{-1})$	$\nu_{\text{CO}}(\text{cm}^{-1})$	$\delta_{\text{NCO}}(\text{cm}^{-1})$	$\nu_{\text{M-N}}(\text{cm}^{-1})$	$\delta_{\text{MN}}(\text{cm}^{-1})$
$\text{K}_2[\text{Co}(\text{NCO})_4]$	IR	2220,2200,2188sbr	1344s	654m,642s,631s,623s	384s354s	
	IR ²⁰⁷	2229,2208,2191,2167,2120,2098	1347,1078	657,635,628	-	
	R	2245(2)2180(3)	1348(10),1304(2)	619(1)	-	
$(\text{Et}_4\text{N})_2[\text{Co}(\text{NCO})_4]$	IR	2225sbr	1345m,1338s	611s	348s	
	IR ²⁸⁰	2217,2179	1335	620,617	345	
	R	2271(2),2182(1)	1333(10),1300(1)	613(3)	344(2)	
	R*	-	1356(5)dp,1334(5)p	612(1)p	-	
$(\text{Et}_4\text{N})_2[\text{Zn}(\text{NCO})_4]$	IR	2193sbr,2091s	1333m,1305w	627s	320w	
	IR ²⁴⁶	2200	1333	624,615	328	
	R	-	1359(2)	-	381(4),352(10)	230(10)
	Raq	-	1350(1)	-	359(1)	
$\text{K}[\text{Cu}(\text{NCO})_3]$	IR	2268sbr,2216sbr,2151s	1345m,1316w,1292w	703m,660s,647s,609s	345s	
	IR ²⁰⁷	2270,2251,2220,2163,2150,2105	1348,1318	660,622,609	400,355,340,320	
	R	-	1357(3),1306(4)	739(4),697(1)	382(2),361(1),351(10)	
	Raq	2175(2)	1350(3),1320(3)	633(1)	-	
$\text{K}[\text{Cd}(\text{NCO})_3]$	IR	2249sbr,2214s	1328w,1298w	697m,664s,648s,613s	288s	
	IR ²⁰⁷	2246,2203,2151,2140,2113,2088	1368,1350,1300,1291	658,646,620	290,280	
	R	-	1372(2),1357(6),1306(6)	-	382(2),351(5)	221(10)
AgNCO	IR	2185vsbr	1349m,1303m	654s,618w,594s	374w,305w	
	IR ²⁸⁶	2170	1350	657,598	-	
	R	2292(1),2215(1)	1332(8)	-	380(2),352(4)	220(10)

Key: R* - Raman solution in acetone
 Raq- Raman solution in water

a. Homoleptic complexes.

The only X-ray crystal structures that have been determined of the complexes studied here are those of $\text{K}[\text{Cd}(\text{NCO})_3]$ ²⁸⁴ (see fig 3.3.ii) and AgNCO (fig 3.3.i).²⁸⁵ That there are few structures is probably due to the relative difficulty of preparing the complexes in a pure state and to their instability. $\text{K}[\text{Cd}(\text{NCO})_3]$ has a bridged structure in which each NCO^- bridges with three metal atoms. A bridged structure occurs in AgNCO in which the cyanate group is bound to two metal atoms with a Ag-NCO-Ag angle of around 98° as shown in fig.3.3.i. below.

Fig. 3.3.i. Structure of AgNCO .²⁸⁵



We assume that the symmetry of the anions in $(\text{Et}_4\text{N})_2[\text{Zn}(\text{NCO})_4]$, $\text{K}_2[\text{Co}(\text{NCO})_4]$ and $(\text{Et}_4\text{N})_2[\text{Co}(\text{NCO})_4]$ are the same as for their isothiocyanato equivalents. If this is so they should have tetrahedral symmetry with A_1 (Raman active polarised, IR inactive) and T_2 (IR and Raman active, the Raman being depolarised) bands in each of the stretching regions, ν_{CN} , ν_{CO} and ν_{MN} ; in the δ_{NCO} region there should be E (Raman active, depolarised, IR inactive) and T_2 (IR and Raman active, the Raman being depolarised) bands.

K₂[Co(NCO)₄] and (Et₄N)₂[Co(NCO)₄].

The vibrational spectra of the potassium salt were rather more complicated than those measured for the tetraethyl ammonium analogue, as was also seen with K₄[Ni(NCS)₆] and (Et₄N)₄[Ni(NCS)₆] (section 3.2.II). This effect was also observed for K₂[Co(NCO)₄] and (Et₄N)₂[Co(NCO)₄] by Forster and Goodgame²⁸⁰ and was attributed to the loss of symmetry in the former due to strong interactions between the O atoms and K ions. Another reason could be that the larger tetraethylammonium cations separate the complex anions more effectively so that coupling of vibrations between the anions are reduced. The IR spectrum of solid K₂[Co(NCO)₄] had three bands in the ν_{CN} region and two peaks were seen in the Raman (theory predicted one IR and two Raman). In the literature^{207,246,280} the number of bands reported for all the homoleptic isocyanato complexes was consistently greater than the number predicted which suggests that the salts crystallise in rather more complicated lattices than do the analogous thiocyanate complexes. However, we observed the predicted number of bands in both the Raman (two) and IR spectra (one) for the ν_{CO} vibration in these salts and two strong peaks were observed at 384 and 354 cm⁻¹ which we attribute to ν_{MN} . We saw four strong bands in the IR which we assign to δ_{NCO} but only one very weak band occurred at 619 cm⁻¹ in the Raman of the solid.

The number of bands observed in the spectra of (Et₄N)₂[Co(NCO)₄] were closer to the predicted number although we saw one extra ν_{CO} band at 1345 cm⁻¹ in the IR spectrum of the solid and only one weak IR band in each of the ν_{MN} and δ_{NCO} regions. In the Raman spectrum of [Co(NCO)₄]²⁻ in acetone we saw only two moderately strong ν_{CO} bands and one weak ν_{CO} band. No peaks were observed in either the ν_{CN} or ν_{MN} regions.

(Et₄N)₂[Zn(NCO)₄].

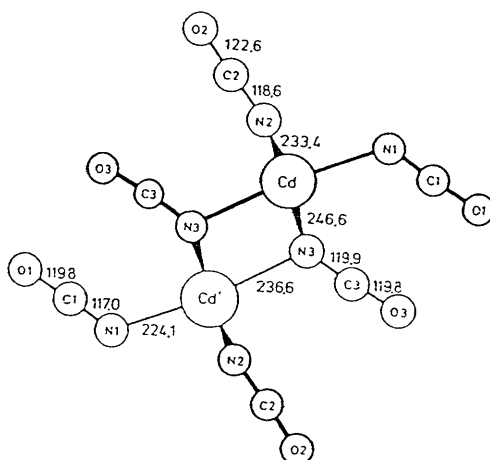
The IR spectrum of white solid (Et₄N)₂[Zn(NCO)₄] had one extra band in each of the ν_{CN} , ν_{CS} and ν_{MN} regions, presumably due to solid state splitting. There

was a single strong δ_{NCO} band at 627 cm^{-1} in the IR but in the Raman spectrum of the solid, no bands were seen which could be attributed to either ν_{CN} or δ_{NCO} . There was one rather weak Raman band at 1359 cm^{-1} which we assigned as ν_{CO} and the two bands at 381 and 352 cm^{-1} occurred in the region expected for ν_{MN} . In the Raman spectrum of a solution of the complex dissolved in water, we saw only two weak bands at 1350 and 359 cm^{-1} . No bands were observed in the ν_{CN} and δ_{NCO} regions.

K[Cu(NCO)₃] , K[Cd(NCO)₃] and AgNCO.

It is reasonable to assume that $\text{K}[\text{Cu}(\text{NCO})_3]$ has the same bridged structure as $\text{K}[\text{Cd}(\text{NCO})_3]$ and it is reported that this latter structure has a pseudotetrahedral arrangement of ligands around the cadmium atom.²⁸⁴ (see fig 3.3.ii) below.

Fig. 3.3.ii. Structure of $\text{K}[\text{Cd}(\text{NCO})_3]$.²⁸⁴



Their spectra were both very complicated with a number of strong, broad ν_{CN} bands above 2200 cm^{-1} which might obscure any other bands reported in the literature.²⁰⁷ No Raman active bands were observed in this region apart from a very weak peak at 2175 cm^{-1} in the solution of copper(II) chloride (0.5M) in excess KNCO (3M). The bands in the other regions were close to those reported in the literature and

the Raman spectra gave similar bands of lower intensities for all modes. The most intense Raman band in $\text{K}[\text{Cd}(\text{NCO})_3]$ occurred at 221 cm^{-1} and we assigned this to δ_{MN} , rather than to a ν_{MN} mode which would be both weaker and occur at higher wavenumbers. The IR spectrum of AgNCO agreed well with that reported in the literature²⁸⁶ but the ν_{CN} at 2185 cm^{-1} was rather low for a bridging species. The Raman bands observed in this region were very weak but much higher than the IR bands, occurring at 2292 and 2215 cm^{-1} . In the spectra of all the above complexes it was the ν_{MN} and ν_{CO} bands which were the strongest in the Raman and correspondingly these were the weakest in the IR. The strongest IR modes were the other vibrations, the ν_{CN} and δ_{NCO} .

b. Mixed Complexes.

Only a few mixed complexes have been prepared and of these the only crystal structure determined has been that of $[\text{Cu}(\text{py})_2(\text{NCO})_2]$ which has *trans* square planar symmetry and a bridging bond of the type Cu-NCO-Cu ²⁸⁷ out of plane to make the copper effectively six coordinate (see fig.3.3.iii below). We expect the same symmetries, and thus the same numbers of bands in the vibrational spectra as discussed in section 3.2.II for the mixed thiocyanate complexes. The effect of changing the organic ligand on the ν_{CN} mode in $\text{Pd}(\text{II})$ cyanato complexes has been examined in detail by Norbury and Sinha^{283,288} and contrasted with similar effects in thiocyanate and selenocyanate complexes. It is true to say that the ligands used in this work were not sufficiently bulky or electron withdrawing to effect a change in coordination and our results agree with the literature values.^{283,288} We believe that the Raman spectra are the first to be measured on cyanate complexes of this nature, and they support the above conclusions.

Table 3.3.ii Vibrational spectra for substituted isocyanato complexes.

Complex		$\nu_{\text{CN}}(\text{cm}^{-1})$	$\nu_{\text{CO}}(\text{cm}^{-1})$	$\delta_{\text{NCO}}(\text{cm}^{-1})$	$\nu_{\text{M-N}}(\text{cm}^{-1})$
[Pd(bipy)(NCO) ₂]	IR	2203sbr	1343m,1323m,1308w	624w,587m	421m,391m,370vw
	IR ^{283,288}	2215-2195	1340	587	389,374
	R	2202(1)	1337(2),1323(10)	-	393(2),378(3),302(4)
[Pd(phen)(NCO) ₂]	IR	2236sbr,2204s	1348m,1340m,1323w	616w,590s	383s
	IR ^{283,288}	2240,2202	1340	600	380,353
	R	-	1351(5),1340(3),1318(10)	566(3)	378(4),316(1)
[Pd(Asph ₃) ₂ (NCO) ₂]	IR	2217sbr	1348m	618w,605w,586m	338m
	IR ^{283,288}	2220-2210	1340-1325	585,471,466	340
	R	2230(1)	1352(2)	-	361(8),336(6),327(10)
[Pd(py) ₂ (NCO) ₂]	IR	2206sbr	1338m,1301w	654m,626m,588s	405m,300m
	IR ^{283,288}	2202	1332	586	408,406,269
	R	2213(1)	1355(sh3),1343(10)	658(4),625(6),607(1)	434(2),350(10)
[Cu(py) ₂ (NCO) ₂]	IR	2204sbr	1325s	672w,639m,625m,611s	437m,374s
	IR ²⁷⁸	2208	1320	625,611	378
	R	2220(2)2195(10)2181(8)	1339(1),1328(9)	653(5),638(6),625(7),614(8)	
[Cu(bipy)(NCO) ₂]	IR	2200sbr	1341m,1326w,1309m	641m,630m,616m	420m,377m,350m
	IR ²⁷⁸	2236,2189	1322,1310	617,606	-
	R	2219(2),2180(1)	1344(2),1327(10),1314(3)	662(2),650(2),639(2)619(2)	381(4),371(2),352(6)

[Pd(bipy)(NCO)₂].

As the 2,2-bipyridyl ligand is *cis*-bidentate this complex obviously adopts a *cis* conformation and in the spectra there were similarities with the analogous *isothiocyanato* complex, such as the observation of coincident bands which in this complex occurred at 2203 cm⁻¹ in the ν_{CN} region, at 1323 cm⁻¹ in the ν_{CO} region and also in the ν_{MN} region at 391 cm⁻¹ (see section 3.2.II.b for the coincident bands that were observed in the vibrational spectra of [Pd(bipy)(NCS)₂]). The band at 2203 cm⁻¹ was actually the only peak observed in the ν_{CN} region in either of both the Raman and IR spectra, although the band was very strong and broad in the IR, and weak in the Raman.

In the ν_{CO} region we observed three IR and two Raman bands; the one at 1323 cm⁻¹ was more intense in the Raman than it appeared in the IR. There were three IR and three Raman bands in the ν_{MN} region whilst in the δ_{NCO} region we saw two bands in the IR at 624 and 587 cm⁻¹ but none in the Raman.

[Pd(phen)(NCO)₂].

This complex also has a *cis* structure by virtue of the *cis* bidentate phenanthroline ligand, although only one band was observed at 1340 cm⁻¹ that was coincident in both the IR and Raman spectra. There were two ν_{CN} bands at 2236 and 2204 cm⁻¹ which were in good agreement with those reported in the literature²⁸³ but no Raman bands were observed in this area. Three bands attributable to ν_{CO} vibrations were seen in both the IR and Raman spectra, and as in the above complex, the Raman active bands at 1351, 1340 and 1318 cm⁻¹ were more intense than the IR active bands, which lay at 1348, 1340 and 1323 cm⁻¹. A single strong band at 383 cm⁻¹ was seen in the ν_{MN} region of the IR spectrum, and there were two weak Raman bands. In the δ_{NCO} region we saw two IR bands at 616 and 590 cm⁻¹ and in the Raman, one at 566 cm⁻¹.

[Pd(AsPh₃)₂(NCO)₂].

The vibrational spectra of this complex were much simpler than for the other mixed *isocyanato* complexes prepared. We observed a single IR band at 2217 cm⁻¹ in the ν_{CN} region and also a weak Raman band at 2230 cm⁻¹. In the ν_{CO} region of this complex there was one moderately strong IR band at 1348 cm⁻¹ and one weak peak in the Raman spectrum at 1352 cm⁻¹. The single IR band at 338 cm⁻¹ in the ν_{MN} region agreed well with those reported in the literature²⁸⁸ and in the Raman spectrum of this area there were three relatively intense bands at 361, 336 and 327 cm⁻¹. In the IR spectrum there were three bending modes but, as for [Pd(bipy)(NCO)₂], we saw none in the Raman.

[Pd(py)₂(NCO)₂].

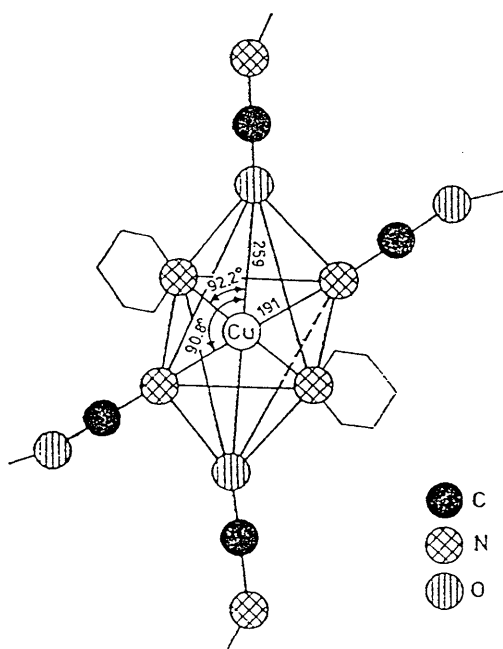
There was only a single coincident band observed in the IR and Raman, occurring in the δ_{NCO} region at 626 cm⁻¹ in the vibrational spectra of this complex and in comparison with the number of coincident bands observed in the spectra of [Pd(bipy)(NCO)₂] (three) it seems likely that both this complex and [Pd(AsPh₃)₂(NCO)₂] adopted *trans* structures in agreement with the literature.²⁸⁸ The spectra were similar to the complexes discussed above; in the ν_{CN} region a single strong peak was observed at 2206 cm⁻¹ in the IR and there was one weak Raman band at 2213 cm⁻¹. We saw two moderately strong IR bands and two weak Raman bands in the ν_{CO} region. The spectra of the remaining fingerprint regions were more complex, with two IR and three Raman bands in the ν_{MN} region and three bands in both the Raman and IR spectra of the δ_{NCO} area.

[Cu(py)₂(NCO)₂]

As mentioned above the X-ray crystal structure of this complex has been reported²⁸⁷ to be square planar with a *trans* conformation and a bridging Cu-NCO-Cu out of the plane (see fig.3.3.iii). Our observations agree with the above determination

and other literature.²⁷⁸ There were no coincident bands in the stretching regions although in the δ_{NCO} region one band was seen at 625 cm^{-1} in both the Raman and IR spectra and a second was seen at 639 cm^{-1} in the IR and 638 cm^{-1} in the Raman. One effect of bridging is the shifting of bands to higher wavenumbers than usual, and as the highest ν_{CN} band lay at 2220 cm^{-1} , comparable to the highest bands in the complexes of Pd(II), it seems likely that these complexes also had some bridging.

Fig.3.3.iii. The structure of $[\text{Cu}(\text{py})_2(\text{NCO})_2]$.²⁸⁷



Another indication of bridging is large splitting of bands ($30\text{-}50\text{ cm}^{-1}$)¹³⁹ and this was apparent in the δ_{NCO} region where the highest of the four IR bands occurred at 672 cm^{-1} and the lowest peak lay at 611 cm^{-1} . In the Raman spectrum of this region there were bands at 653 and 614 cm^{-1} and in the ν_{MN} area the two bands were at 437 and 374 cm^{-1} .

The other aspects of the spectra of this complex were similar to those we have described above. In the ν_{CO} region there was one IR band at 1325 cm^{-1} and two peaks in the Raman, one of which was strong at 1328 cm^{-1} . In the ν_{CN} areas there were four

bands in both the IR and Raman spectra and only two IR bands were observed in the ν_{MN} region.

[Cu(bipy)(NCO)₂].

This complex is, like its Pd(II) analogue, *cis* and there were coincident bands in each of the stretching regions at 2200 cm^{-1} (ν_{CN}), 1326 cm^{-1} (ν_{CO}) and in the ν_{MN} region a band that appeared at 350 cm^{-1} in the IR and 352 cm^{-1} in the Raman. Elsewhere in the IR spectrum we observed bands in agreement with the literature²⁷⁸ with extra peaks at 1341 and 641 cm^{-1} . The Raman spectrum corroborated the IR data and the general trends observed for the Raman bands of these mixed isocyanato complexes; two weak ν_{CN} bands at 2219 and 2180 cm^{-1} , three ν_{CO} bands one at 1327 cm^{-1} which was strong. There were also three ν_{MN} bands and four peaks attributable to δ_{NCO} .

Conclusions.

Our studies on cyanato complexes have confirmed the results of previous investigations^{246,278,280}, that N-bonded complexes are formed in both homoleptic and mixed complexes of those metals used in this study. We have measured new Raman data for these complexes, but have found that generally bands in the ν_{CN} and δ_{NCO} regions are weak, if they are visible at all whilst the bands in the δ_{NCO} region are usually intense.

Homoleptic cyanato complexes are difficult to prepare, but polymeric and bridged molecules such as $\text{K}[\text{Cu}(\text{NCO})_3]$ can be formed in aqueous solution and the apparent absence of these species in the oxidation reactions of cyanide complexes suggests that the mechanism of oxidation does not proceed via the formation of cyanate complexes. We cannot conclude whether the observations made for the oxidation of adsorbed complexes, in which adsorbed $[\text{Cu}(\text{NCO})_3]^-$ was formed were due to the

presence of the alumina (see section 3.1.II).

Mixed cyanate complexes can be prepared using the same general methods as their thiocyanate analogues and their vibrational spectra have more bands than homoleptic complexes, confirming that despite the presence of bulky, π -accepting ligands the N-bonded *isocyanato* species are always formed.

3.4 Experimental.

Section 3.1. Preparation of cyanide complexes.

K[Cu(CN)₂].

This was prepared by evaporation of an aqueous solution of equimolar KCN and CuCN, after heating until the solution was clear yellow, to yield light yellow crystals.²⁸⁹ N.B. The sodium salt proved easier to prepare than the potassium analogue which tended to decompose to CuCN and K₂[Cu(CN)₃] (yield = 100%).

(Found: C, 15.51; H, 0.00; N, 18.06; K, 26.00%. C₂N₂KCu requires C, 15.53; N, 18.12; K, 25.28%).

K₂[Cu(CN)₃].

This was prepared using the above method but using different ratios of reactants.²⁸⁹

(Found: C, 16.41; H, 0.00; N, 18.96; K 33.99%,. C₃N₃K₂Cu requires C, 16.40; N, 19.13; K, 35.59%).

K₃[Cu(CN)₄].

This was prepared using the above method but using different ratios of reactants.²⁸⁹

(Found: C, 16.92; H, 0.00; N, 19.32; K 41.66%,. C₄N₄K₃Cu requires C, 16.87; N, 19.68; K, 41.18%).

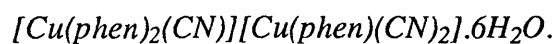
Preparation of Cu(II) cyano complexes.

The complexes below were prepared using the published methods.¹²⁴



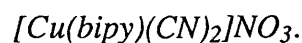
Turquoise powder (yield = 39.9%).

(Found: C, 56.78; H, 3.14; N, 15.15%. $C_{25}H_{18}N_6O_4Cu$ requires C, 56.65; H, 3.42; N, 15.86%).



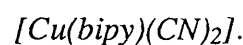
Green solid (yield = 27.3%).

(Found: C, 52.68; H, 2.84; N, 14.10%. $C_{39}H_{36}N_9O_6Cu_2$ requires C, 54.86; H, 3.75; N, 14.75%).



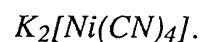
Brown powder (yield = 39.9%).

(Found: C, 50.82; H, 3.00; N, 18.60%. $C_{14}H_8N_5O_3Cu$ requires C, 52.30; H, 3.50; N, 17.34%).



Purple powder (yield = 12.4%).

(Found: C, 52.35; H, 2.84; N, 20.16%. $C_{13}H_8N_2Cu$ requires C, 53.00; H, 2.94; N, 20.61%).



This was prepared using the published method²³⁴ from $NiSO_4.6H_2O$ (60g, 0.23 mol) in H_2O (200 cm³) to which was added KCN (30g, 0.46mol) in H_2O (60 cm³). The precipitate of $Ni(CN)_2$ was washed with H_2O and filtered overnight. To the filter cake was added KCN (28g, 0.43mol) in H_2O (30 cm³) to give a red solution

from which orange crystals of $K_2[Ni(CN)_4]$ (47g, 0.18mol = 80%) were precipitated by the addition of ethanol (200 cm³). These were filtered off, washed with ethanol and dried in vacuo.

(Found: C, 19.89; H, 0.00; N, 26.48; K, 31.97%. $C_4N_4K_2Ni$ requires C, 20.0; N, 26.67; K, 32.50%).

$K_2[Zn(CN)_4]$.

Zinc oxide, ZnO (3.24g, 0.04 mol) was added to a solution of NaOH (4.5M, 100 cm³) and the suspension heated to boiling for thirty minutes. To the hot solution was added KCN (10.42g, 0.16 mol) dissolved in the minimum of hot water and the solution stirred whilst hot for ten minutes until most of the cloudiness had disappeared. This hot solution was filtered to remove unreacted ZnO and when cool, poured into acetone (300 cm³) whereupon a white precipitate was formed. This was filtered off (2.08g) and the mother liquor reduced under vacuum to yield a further portion of $K_2[Zn(CN)_4]$ (7.68g). The crude portions were recrystallised from hot water and ethanol and dried in vacuo. (total yield = 98%)

(Found: C, 19.57; H, 0.00; N, 22.62; K, 31.70%. $C_4N_4K_2Zn$ requires C, 19.39; N, 21.56; K, 31.58%).

$K_2[Cd(CN)_4]$.

This was prepared using the method of Dickinson.²³⁶ To $Cd(NO_3)_2 \cdot 4H_2O$ (3g, 9.73 mmol) in H_2O (20 cm³) was added NH_4OH (2 cm³, 35%) and the white precipitate formed removed by centrifugation. After washing this solid twice with water, a solution of KCN (2.6g, 39 mmol) in H_2O (10 cm³) was added and the mixture stirred until it became clear, whereupon it was added to ethanol (100 cm³) to precipitate out the white product. This was filtered, washed with methanol (25 cm³) and dried in vacuo. (yield 1.97g 7.9 mmol = 69%).

(Found: C, 16.14; H, 0.00; N, 18.66; K 31.20%, $C_4N_4K_2Cd$ requires C, 16.29; N,

19.00; K, 31.33%).

K₂[Pd(CN)₄].3H₂O.

This preparation was a modification of that reported by Stefano and Burmeister for K₂[Pd(SCN)₄].²³⁵ An aqueous solution (20 cm³) of PdCl₂ (0.5g, 4.7 mmol) and KCN (1.23g, 19 mmol) was stirred and heated until it was completely clear. The liquor was transferred to a basin and left to evaporate to dryness. The white solid was redissolved in the minimum of hot water (<5 cm³) and ethanol added dropwise until cloudiness was observed. The solution was transferred to the refrigerator and left for the white product to crystallise out. The crystals were filtered and air dried. (Yield 0.347g 1.0 mmol = 21.6%).

(Found: C, 13.96; H, 1.74; N, 16.21%. C₄H₆N₄K₂O₃Pd requires C, 14.02; H, 1.75; N, 16.36%).

K₂[Pt(CN)₄].H₂O.

This was prepared using the above method from PtCl₂ to form yellow crystals which turned white on exposure to the air.

(Found: C, 11.75; H, 0.26; N, 13.41%. C₄H₂N₄K₂OPt requires C, 12.10; H, 0.50; N, 14.17%).

K[Ag(CN)₂].

A solution of AgNO₃ (2g, 12 mmol) in H₂O (30 cm³) was added to KCN (0.77g, 12 mmol) in H₂O (20 cm³). The resulting white precipitate was centrifuged off, washed twice with water and stirred in a solution of hot aqueous KCN (0.77g, 12 mmol in 20 cm³ H₂O) until all had dissolved. The solution was transferred to the refrigerator and left to crystallise out overnight. The first batch (1.23g, 6.2 mmol) of colourless crystals were taken for analysis after filtration and drying in vacuo, but a second portion of solid (0.96g, 4.8 mmol) was precipitated by pouring the liquor into

ethanol (100 cm³). (Total yield = 91.7%).

(Found: C, 11.00; H, nil; N, 12.25; K19.28%,. C₂N₂KAg requires C, 10.08; N, 11.76; K, 19.60%).

Section 3.1.II. Adsorption methods.

Cocrystallizations were carried out using the published method.²³⁸ Other adsorptions were carried out by slurring alumina (as supplied by Aldrich) in a solution of the cyanide complex (0.1M) overnight. The alumina was filtered, washed three times with water and transferred to an oven to dry at 80°C. IR spectra of the adsorbed species were run as KBr discs between 2000 and 2300 cm⁻¹. Electronic spectroscopy was used to measure the concentration in solution of the cyanide complex before and after adsorption in order to calculate the loading.

Oxidations were carried out using the complex adsorbed on alumina (1g) stirred in a solution of H₂O₂ overnight or until the oxidant had decomposed as measured using peroxide test strips (Merck).

Montmorillonite K10 and Bentonite were supplied by Aldrich and Amberlite IRA-904 standard grade by BDH. CR-20 ion exchange was made by Mitsubishi Chemicals and lent to us by Interlox Ltd.

Section 3.1.III. Mass spectrometry.

Negative f.a.b. mass spectra were run on a VG 7070E machine with a Xenon gun by Mr John Bilton. The matrix for all samples was a glycerol water mixture.

Section 3.2. Preparation of thiocyanate complexes.

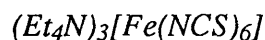
a. Homoleptic thiocyanate complexes.

Unless otherwise stated the following complexes were prepared using the methods published by Sabatini and Bertini.²⁴⁶



Light purple crystals.

(Found: C, 44.23; H, 7.58; N, 15.36%. $C_{30}H_{60}N_9S_6Cr$ requires C, 45.54; H, 7.64; N, 15.93%).



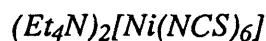
Deep red microcrystalline powder.

(Found: C, 44.62; H, 7.58; N, 15.57%. $C_{30}H_{60}N_9S_6Fe$ requires C, 45.35; H, 7.55; N, 15.87%).



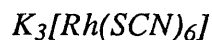
To $NiBr_2 \cdot 3H_2O$ (1.0g, 3.7 mmol) in acetone (20 cm³) was added a solution of KSCN (2.13g, 22 mmol) in H₂O (5 cm³) and acetone (30 cm³), and the resulting green liquid stirred for one hour. The white precipitate formed was filtered and the solution reduced under vacuum to dryness. The solid was taken up in acetone (50 cm³), refiltered and reduced again. This process was repeated three times until both the solution and precipitate were blue. The solution was then poured into ether (100 cm³) and the blue precipitate filtered and dried in vacuo. (yield 0.60g = 28%).

(Found: C, 13.22; H, 0.60; N, 13.71%. $C_6H_2N_6OS_6K_4Ni$ requires C, 12.41; H, 0.34; N, 14.48%).



Light blue crystals (yield= 17%).

(Found: C, 49.23; H, 8.86; N, 15.16%. $C_{38}H_{80}N_{10}S_6Ni$ requires C, 49.24; H, 8.60; N, 15.09%).



This was prepared using the method of Barbieri.²⁹⁰ to form red crystals (yield = 83.8%).

(Found: C, 12.18; H, nil; N, 14.03; K, 18.94%. $C_6N_6S_6K_3Rh$ requires C, 12.72; N, 14.84; K, 20.67%).



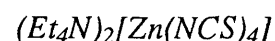
Deep blue crystals prepared using the method described above for $K_4[Ni(NCS)_6]$.

(Found: C, 11.82; H, 0.99; N, 12.83%. $C_4H_4N_4O_2S_4K_2Co$ requires C, 11.85; H, 0.99; N, 13.80%).



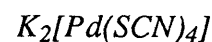
Deep blue crystals (yield 21%).

(Found: C, 43.20; H, 7.53; N, 15.36%. $C_{20}H_{40}N_6S_4Ni$ requires C, 43.51; H, 7.25; N, 15.23%).



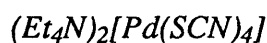
White microcrystalline powder (yield = 85%).

(Found: C, 42.48; H, 7.28; N, 14.74%. $C_{20}H_{40}N_6S_4Zn$ requires C, 43.09; H, 7.18; N, 15.06%).



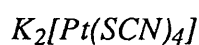
Red orange crystals prepared by the method of Destefano and Burmeister.²³⁵

(Found: C, 11.57; H, nil; N, 12.88; K, 17.45%. $C_4N_4S_4K_2Pd$ requires C, 11.52; N, 13.44; K, 18.06%).



Red crystals (yield = 57%).

(Found: C, 38.97; H, 6.16; N, 13.86%. $C_{20}H_{40}N_6S_4Pd$ requires C, 40.09; H, 6.73; N, 14.03%).



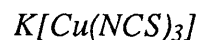
Golden yellow crystals prepared by the method of Destefano and Burmeister.²³⁵

(Found: C, 9.89; H, nil; N, 10.73%. $C_4N_4S_4K_2Pt$ requires C, 9.50; N, 11.08%).



Yellow-orange needle crystals prepared according to the published method.²⁹¹ (yield 66%).

(Found: C, 8.70; H, 0.34; N, 10.07%. $C_5H_4N_5S_5K_3O_4U$ requires C, 8.41; H, 0.56; N, 9.81%).



To $CuCl_2$ (0.5g, 3.7 mmol) in H_2O (50 cm³) was added a solution of KSCN (1.44g, 14.8mmol) in H_2O (20 cm³). The dark green precipitate was filtered and dried in vacuo. (0.45g, yield = 44%).

(Found: C, 13.18; H, nil; N, 14.94%. $C_3N_3S_3KCu$ requires C, 13.01; N, 15.18; K, 14.10%).



Palladium chloride, $PdCl_2$ (0.59g, 3.3 mmol) was heated in conc. HCl (s.g. 1.18 5

cm³) until all the solid had dissolved. To this solution was added a saturated aqueous solution of KSCN (1.3g 13 mmol in approx 5 cm³ H₂O) and the liquid stirred for one hour. The orange precipitate formed was filtered and air dried.

(Found: C, 9.82; H, 0.45; N, 10.93%. C₂N₂S₂Pd requires C, 9.30; H, 1.55; N, 10.50%).

b. Mixed Thiocyanate Complexes.

The following complexes were prepared using the methods of Burmeister and Basolo.²⁶⁵

[Pd(phen)(SCN)₂]

Orange solid, decomposed on heating.

(Found: C, 42.23; H, 1.87; N, 14.07%. C₁₂H₈N₄S₂Pd requires C, 41.76; H, 2.00; N, 13.91%).

[Pd(bipy)(SCN)₂]

Light-yellow solid, turned brown due to isomerisation when heated at 150°C.

(Found: C, 37.28; H, 1.24; N, 14.49%. C₁₄H₈N₄S₂Pd requires C, 38.04; H, 2.13; N, 14.79%).

[Pd(py)₂(SCN)₂]

Bright yellow solid.

(Found: C, 36.72; H, 2.26; N, 14.59%. C₁₂H₁₀N₄S₂Pd requires C, 37.84; H, 2.65; N, 14.71%).

[Pd(Asph₃)₂(SCN)₂]

Yellow solid, turned orange on heating at 150°C due to isomerisation.

(Found: C, 56.33; H, 3.58; N, 3.96%. C₃₈H₃₀N₂S₂AsPd requires C, 54.33; H, 3.62;

N, 3.36%).

[Pt(bipy)(NCS)₂]

Orange solid prepared at room temperature.

(Found: C, 31.81; H, 1.73; N, 11.36%. C₁₄H₈N₄S₂Pt requires C, 30.84; H, 1.71; N, 11.99%).

[Pt(Asph₃)₂(SCN)₂]

Bright yellow powder, which turned light yellow upon heating at 150°C due to isomerisation.

(Found: C, 50.19; H, 3.21; N, 2.85%. C₃₈H₃₀N₂S₂AsPt requires C, 49.41; H, 3.27; N, 3.03%).

[Cu(bipy)(NCS)₂]

Copper (II) chloride, CuCl₂ (0.5g, 3.7 mmol) and KSCN (1.44g, 14.8 mmol) were stirred together in acetone (50 cm³) for thirty minutes and the dark green precipitate filtered off. To the solution was added dropwise a solution of 2,2 bipyridyl (1.15g, 7.4 mmol) in acetone (10 cm³) whilst stirring vigorously. The green precipitate which formed immediately was filtered off and a second, crystalline portion was formed in the flask during the filtration. Both solids were dried in vacuo. (total yield 0.59g, 44%).

(Found: C, 42.39; H, 3.11; N, 16.80%. C₁₄H₈N₄S₂Cu requires C, 42.92; H, 2.38; N, 16.69%).

[Cu(py)₂(NCS)₂]

Copper (II) chloride, CuCl₂ (0.5g, 3.7 mmol) and KSCN (1.44g, 14.8 mmol) were stirred together in H₂O (50 cm³) and pyridine (0.59g, 7.4 mmol) was added dropwise. A dark green precipitate was formed and the solution was stirred for ten minutes before filtration. The solid (0.50g, 1.5 mmol = 40%) was dried in vacuo. When heated at 150°C the compound decomposed and turned brown.

(Found: C, 42.52; H, 2.85; N, 15.24%. $C_{12}H_{10}N_4S_2Cu$ requires C, 42.66; H, 2.96; N, 16.59%).

Section 3.3. Preparation of cyanate complexes.

a. Homoleptic complexes.

$(Et_4N)_2[Co(NCO)_4] \cdot 3H_2O$

A solution containing $CoCl_2 \cdot 6H_2O$ (1g, 4.2 mmol) and KNCO (2.05g, 25 mmol) in H_2O (20 cm³) was stirred whilst a solution of Et_4NBr (1.79g, 8.5 mmol) in ethanol (20 cm³) was added. The liquor was left in the freezer for blue crystals to appear which were filtered, washed with absolute ethanol and dried in vacuo (1.11g, 2.1 mmol = 49%).

(Found: C, 45.05; H, 8.26; N, 15.23%. $C_{20}H_{26}N_6O_7Co$ requires C, 46.07; H, 5.03; N, 16.12%).

$K_2[Co(NCO)_4] \cdot 2H_2O$

A saturated aqueous solution of KNCO (2.56g, 31.5 mmol) was added to a solution of $CoCl_2 \cdot 6H_2O$ (2.5g, 11 mmol) in acetone 15 cm³). A white precipitate was formed which was filtered off from the blue filtrate. The solvent was removed under vacuum to yield blue crystals (0.844g, 2.5 mmol = 23%) which were washed with ethanol and dried in vacuo.

(Found: C, 14.11; H, 0.23; N, 15.79%. $C_4H_4N_4O_6Co$ requires C, 14.08; H, 1.17; N, 16.42%).

$K[Cu(NCO)_3]$

This was prepared by the method of Ripan.²⁹² It was precipitated as a blue solid from aqueous solutions containing $CuCl_2$ and KNCO in a ratio of NCO^- : Cu greater than four. Below this ratio the product did not analyse as below.

(Found: C, 15.24; H, nil; N, 17.60%. $C_3N_3O_3KCu$ requires C, 15.75; N, 18.38%).

$K[Cd(NCO)_3]$

An aqueous solution of KNCO (0.80g, 9.9mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (1.0g, 3mmol) was stirred for one hour after which a white precipitate was observed. To the solution (70 cm³) was added ethanol (50 cm³) and the resulting white precipitate was filtered

and dried in vacuo.

(Found: C, 12.51; H, nil; N, 14.43%. $C_3N_3O_3Kcd$ requires C, 13.00; N, 15.16%).

$(Et_4N)_2[Zn(NCO)_4]$

This was prepared using the published method of Forster and Goodgame.²⁸¹

(Found: C, 49.31; H, 8.44; N, 17.34%. $C_{20}H_{40}N_6O_4Zn$ requires C, 48.62; H, 8.20; N, 17.00%).

$Ag(NCO)$

This light sensitive white solid was formed as a precipitate in reactions between $AgNO_3$ and $KNCO$.

(Found: C, 8.20; H, nil; N, 9.44%. $CNOAg$ requires C, 8.00; N, 9.33%).

b. Mixed cyanate complexes.

$[Pd(phen)(NCO)_2]$

Palladium chloride, $PdCl_2$ (0.2g, 1.1 mmol) was dissolved in 1:1 ethanol/ H_2O (100 cm^3) containing $KNCO$ (0.37g 4.5 mmol). After filtration of the solution to remove unreacted $PdCl_2$ a solution of 1,10 phenanthroline (0.21g, 1 mmol) in ethanol (20 cm^3) was added and the mixture stirred for 15 minutes. The light yellow precipitate formed was separated by centrifugation and washed with ethanol and acetone before drying in vacuo.

(Found: C, 43.42; H, 2.02; N, 14.13%. $C_{12}H_8N_4O_2Pd$ requires C, 45.41; H, 2.16; N, 15.14%).

$[Pd(bipy)(NCO)_2]$

This yellow solid was prepared in the same way as $[Pd(phen)(NCO)_2]$.

(Found: C, 40.31; H, 2.64; N, 15.72%. $C_{14}H_8N_4O_2Pd$ requires C, 41.62; H, 2.89; N, 16.18%).

$[Pd(py)_2(NCO)_2]$

This light yellow solid was prepared in the same way as $[Pd(phen)(NCO)_2]$.

(Found: C, 40.68; H, 2.12; N, 15.87%. $C_{12}H_{10}N_4O_2Pd$ requires C, 41.38; H, 2.87; N, 16.09%).

$[Pd(AsPh_3)_2(NCO)_2]$

This bright yellow solid was prepared in the same way as $[Pd(phen)(NCO)_2]$.

(Found: C, 56.84; H, 3.59; N, 3.35%. $C_{36}H_{30}N_2O_2AsPd$ requires C, 56.86; H, 3.78; N, 3.49%).

[Cu(bipy)(NCO)₂]

A solution of KNCO (0.48g 5.9 mmol) in H_2O (10 cm^3) was added to a solution containing $CuCl_2$ (0.3g 2.3 mmol) and 2,2 bipyridyl (0.4g, 2.3 mmol) in H_2O (50 cm^3). The resulting blue precipitate was filtered and dried in vacuo.

(Found: C, 47.21; H, 2.37; N, 18.35%. $C_{14}H_8N_4O_2Cu$ requires C, 47.45; H, 2.63; N, 18.45%).

[Cu(py)₂(NCO)₂]

This was prepared using the method reported by Davis and Logan.²⁹³ Pyridine (0.58g, 7.3 mmol) was added dropwise to a solution containing $CuCl_2$ (0.5g, 3.7 mmol) and KNCO (1.2g, 14.6 mmol) in water (20 cm^3). The deep blue solid was extracted with chloroform (200 cm^3) and the solvent removed under vacuum to leave a blue powder.

(Found: C, 46.91; H, 3.13; N, 18.15%. $C_{12}H_{10}N_4O_2Cu$ requires C, 47.14; H, 3.27; N, (18.33%).

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