

Spectroscopic Studies on Cyanide Hydride

Complexes and Related Species

by

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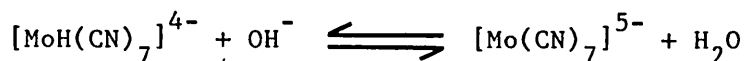
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ABSTRACT

The eight co-ordinate cyanide hydride complex, $[\text{MoH}(\text{CN})_7]^{4-}$, has been prepared and spectroscopic (infrared, Raman, ^1H and ^{13}C n.m.r.) and electrochemical studies were used to demonstrate the existence of the equilibrium:



The cyanide hydride species, $[\text{MH}(\text{CN})_5]^{3-}$ (M = Rh, Ir), have been studied in both solid and solution using infrared and Raman spectroscopy. A controversy in the literature concerning the structure of the rhodium complex in solution has been resolved by the use of ^{13}C n.m.r. spectroscopy and a single crystal X-ray study has confirmed the solid to be $\text{K}_3[\text{RhH}(\text{CN})_5] \cdot \text{H}_2\text{O}$.

Chemical reactions of the cyanide hydride complexes with a variety of organic and inorganic substrates are described. A search for other cyanide hydride species has been carried out.

Studies on the ^{13}C , ^{14}N and ^{15}N n.m.r. spectra of complexes of the type $[\text{MX}(\text{CN})_5]^{n-}$ and related species are reported. Correlations are drawn between the chemical shift values, the Cotton-Kraihanzel force constants for the CN bonds obtained from infrared and Raman spectroscopy and the trans-influence of the ligand, X. An X-ray crystal structure of the dimeric species $\text{K}_5[\text{Ru}_2\text{N}(\text{CN})_{10}] \cdot 3\text{H}_2\text{O}$ has been undertaken.

Attempts to prepare complexes of tantalum and uranium containing the cyanide or isocyanide ligand are reported.

Studies on the synthesis and characterisation of some complexes containing isocyanide - CNR, nitrile - NCR, hydrogen cyanide - NCH and cyanogen - NCCN ligands have been undertaken. A brief study has been made of complexes thought to contain the isocyano ligand, -NC. The complex formulated as $[\text{Co}(\text{NC})(\text{H}_2\text{O})(\text{dmgH})_2]$ has been shown by X-ray crystallography to contain the cyano ligand, $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$.

CONTENTS

	<u>PAGE</u>
ABSTRACT	2
CONTENTS	4
LIST OF TABLES	7
LIST OF FIGURES	9
ACKNOWLEDGEMENTS	11
DEDICATION	12
ABBREVIATIONS AND SYMBOLS	13
 CHAPTER ONE INTRODUCTION	 14
Section 1.1 General Introduction	14
Section 1.2 Bonding in Cyanide and Its Complexes	14
 CHAPTER TWO CYANIDE HYDRIDE COMPLEXES	 21
Section 2.1 General Introduction	21
Section 2.2 Molybdenum and Tungsten Complexes	21
2.2.1 Introduction	21
2.2.2 Preparation of $K_4[MoH(CN)_7] \cdot 2H_2O$	23
2.2.3 Infrared and Raman Spectroscopy of $K_4[MoH(CN)_7] \cdot 2H_2O$	24
2.2.4 N.M.R. Spectroscopy of $K_4[MoH(CN)_7] \cdot 2H_2O$	27
2.2.5 Electrochemical Studies	33
2.2.6 Chemical Reactions of $K_4[MoH(CN)_7] \cdot 2H_2O$	3
2.2.7 Vibrational Spectra of $[Mo(CN)_7]^{4-}$ and $[Mo(CNBut)_7]^{2+}$	35
Section 2.3 Rhodium and Iridium Complexes	38
2.3.1 Introduction	38
2.3.2 Infrared and Raman Spectroscopy	43

2.3.3	N.M.R. Spectroscopy	48
2.3.4	X-ray Crystal Structure of $K_3[RhH(CN)_5] \cdot H_2O$	54
2.3.5	Reactions of $K_3[MH(CN)_5] \cdot H_2O$	58
Section 2.4	Cyanide Hydride Complexes of Other Transition Metals	59
2.4.1	Nickel, Palladium and Platinum	59
2.4.2	Rhenium	60
Section 2.5	Hydrocyanation Reactions	60
Section 2.6	Experimental	62
CHAPTER THREE	VIBRATIONAL SPECTROSCOPIC AND N.M.R. STUDIES OF TRANSITION METAL CYANO COMPLEXES AND RELATED SPECIES	69
Section 3.1	General Introduction	69
Section 3.2	Vibrational Spectroscopic and N.m.r. Studies of Transition Metal Cyano Complexes	69
3.2.1	Introduction	69
3.2.2	The ' <u>trans</u> -influence' and its measurement	70
3.2.3	N.m.r. Studies on Transition Metal Cyano and Carbonyl Species	75
3.2.4	^{13}C n.m.r. Studies of $[MX(CN)_5]^{n-}$ Species	78
3.2.5	Force Constants in Metal-Cyano Complexes - the Cotton-Kraihanzel Model	88
3.2.6	Infrared and Raman Studies of $[MX(CN)_5]^{n-}$ Species	94
3.2.7	X-ray crystal Structure of $K_5[Ru_2N(CN)_{10}] \cdot 3H_2O$	107
3.2.8	Concluding Remarks	113
3.2.9	Vibrational Spectroscopic and N.m.r. Studies on Other Cyano Complexes	114
3.2.10	^{14}N n.m.r. Studies on Transition Metal Cyano Complexes	125
Section 3.3	Tantalum Cyano Complexes	128
3.3.1	Introduction	129
3.3.2	Results	129
3.3.3	Conclusions	134

Section 3.4	Uranium Cyano Complexes	135
3.4.1	Introduction	135
3.4.2	Results and Discussion	138
Section 3.5	Experimental	144
CHAPTER FOUR	PRELIMINARY STUDIES OF COMPLEXES CONTAINING CYANOGEN, HCN, NITRILE AND ISOCYANO LIGANDS	155
Section 4.1	General Introduction	155
Section 4.2	Complexes containing HCN and Cyanogen as Ligands	155
4.2.1	Introduction	155
4.2.2	Results and Discussion	160
Section 4.3	Acetonitrile Complexes of Rhodium(III)	164
Section 4.4	Isocyano Complexes	167
Section 4.5	Experimental	176
PHYSICAL MEASUREMENTS		178
REFERENCES		179

LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
2.1	Infrared and Raman Data for $K_4[MoH(CN)_7] \cdot 2H_2O$	25
2.2	Equilibrium Study of $[MoH(CN)_7]^{4-} / [Mo(CN)_7]^{5-}$	29
2.3	Electrochemical Data for $[M(CN)_7]^{5-}$ species	34
2.4	Infrared and Raman Data for $[Mo(CN)_7]^{4-}$ and $[Mo(CNBu^t)_7]^{2+}$	37
2.5	Species present in solutions of $[Rh(CO)_2Cl]_2$ on reaction with Sodium Cyanide.	40
2.6	Infrared Data for Rhodium Cyanide Hydride Species	44
2.7	Raman Data for $K_3[RhH(CN)_5] \cdot H_2O$	45
2.8	Infrared and Raman Data for $K_3[IrH(CN)_5] \cdot H_2O$	46
2.9	1H chemical shifts for $[RhH(CN)_5]^{3-}$	49
2.10	Bond lengths and bond angles for $K_3[RhH(CN)_5] \cdot H_2O$	57
2.11	Yields of 2-phenylpropionitrile from reactions between phenylacetylene and Transition Metal Cyanide Hydride Complexes	61
3.1	^{13}C chemical shifts for Diamagnetic Cyano Complexes	77
3.2	^{13}C n.m.r. data for Complexes of the type $[MX(CN)_5]^{n-}$	79
3.3	Comparison of <u>cis</u> and <u>trans</u> resonances in $[MX(CN)_5]^{n-}$ with those of $[M(CN)_6]^{n-}$	87
3.4	Cotton-Kraihanzel force constants for Metal Cyano Complexes	92
3.5	Infrared and Raman Data and Cotton-Kraihanzel force constants for $[MX(CN)_5]^{n-}$ species.	97
3.6	Comparison between experimental and literature data for $[PtX(CN)_5]^{2-}$	98
3.7	Comparison between CN force constants for Hexacyano and Monosubstituted Hexacyano Complexes	103
3.8	Bond lengths and Bond angles for $K_5[Ru_2N(CN)_{10}] \cdot 3H_2O$	109
3.9	Infrared and Raman data for $[Ru_2N(CN)_{10}]^{5-}$	111
3.10	Infrared and Raman data for $K_3[Co(NO)(CN)_5] \cdot 2H_2O$	116
3.11	Infrared Data for the Hyponitrito Ligand	117
3.12	^{13}C and Infrared and Raman data for Cyano Complexes	120
3.13	^{14}N n.m.r. data for Cyano and Substituted Cyano Complexes of the Transition Metals	127

3.14	Reactions between Tantalum Complexes and Cyanide	132
3.15	Expected Raman and Infrared Active Modes for Eight Co-ordination	137
3.16	Reactions of Uranyl and Uranium(IV) Salts with Cyanide	139
3.17	Raman data for $[\text{NEt}_4]_4[\text{U}(\text{NCS})_8]$ and $\text{Cs}_4[\text{U}(\text{NCS})_8]$	141
4.1	Summary of Known Complexes of HCN with Transition Metals	157
4.2	Summary of Known Complexes of Cyanogen with the Transition Metals	158
4.3	Infrared Data for Copper Cyanogen Complexes	162
4.4	Infrared and Raman data for Cyanogen Complexes with $[\text{RhCl}(\text{PPh}_3)_3]$	164
4.5	Raman data for <u>fac</u> and <u>mer</u> - $[\text{RhCl}_3(\text{CH}_3\text{CN})]$	165
4.6	Infrared data for $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$ and $[\text{Co}(\text{NC})(\text{H}_2\text{O})(\text{dmgH})_2]$	171
4.7	Raman data for $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$ and $[\text{Co}(\text{NC})(\text{H}_2\text{O})(\text{dmgH})_2]$	172
4.8	Crystal Data for the Complexes $[\text{Co}(\text{XY})(\text{H}_2\text{O})(\text{dmgH})_2]$	169

LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE</u>
1.1	Diagrammatic Representation of the Molecular Orbitals of the Cyanide Ion.	18
1.2	Molecular Orbital Diagram for the Cyanide Ion	19
2.1	Infrared Spectrum of $K_4[MoH(CN)_7] \cdot 2H_2O$	26
2.2	Raman Spectra of $[MoH(CN)_7]^{4-}$	28
2.3a	^{13}C n.m.r. spectrum of $[MoH(CN)_7]^{4-}$	31
2.3b	^{13}C n.m.r. spectrum of an aqueous solution of $[Mo(CN)_7]^{5-}$	32
2.4	Raman Spectrum of $[RhH(CN)_5]^{3-}$	47
2.5	^{13}C n.m.r. spectrum of $[RhH(CN)_5]^{3-}$	50
2.6	^{13}C n.m.r. spectrum of $[IrH(CN)_5]^{3-}$	52
2.7	^{15}N n.m.r. spectra of $[RhH(CN)_5]^{3-}$	53
2.8	The structure of the $[RhH(CN)_5]^{3-}$ anion	56
3.1	Grinbergs Polarisation Theory	71
3.2	Relationship between ^{13}C chemical shifts and oxidation state	83
3.3	Representation of the Normal Modes of Vibration in the C_{4v} molecule, $[MX(CN)_5]^{n-}$	95
3.4	Relative Energy Levels of the Metal-Pentacyanonitrosyls	102
3.5	Relationship between $\delta_{cis}(CN)$ and $k_{cis}(CN)$	105
3.6	Relationship between $\delta_{trans}(CN)$ and $k_{trans}(CN)$	106
3.7	The structure of the $[Ru_2N(CN)_{10}]^{5-}$ anion	108
3.8	Infrared and Raman spectra of $[Ru_2N(CN)_{10}]^{5-}$	110
3.9	Crystal Structures of the Red and Black isomers of $[Co(NO)(CN)_5]^{3-}$	115
3.10	Structure of the $[Ta_6Cl_{12}(CN)_6]^{4-}$ Cluster Anion	128
3.11	A Summary of Tantalum(III) Chemistry	130
3.12	Raman Spectra of $[NEt_4]_4[U(NCS)_8]$ and $Cs_4[U(NCS)_8]$	142

4.1	Modes of Co-ordination of Cyanogen	159
4.2	Reactions of Cyanogen with $[\text{RhCl}(\text{PPh}_3)_3]$	163
4.3	The $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$ Molecule	169
4.4	Raman Spectra of $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$ and $[\text{Co}(\text{NC})(\text{H}_2\text{O})(\text{dmgH})_2]$	173
4.5	Raman Spectra of $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$ and $[\text{Co}(\text{NC})(\text{H}_2\text{O})(\text{dmgH})_2]$	174

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ABBREVIATIONS AND SYMBOLS

Throughout this thesis, various abbreviations and symbols have been used. Frequencies for infrared and Raman spectra are quoted in wavenumbers, cm^{-1} . The bands are described as s, strong; m, medium; w, weak; br, broad; shp, sharp in the infrared spectra. In the Raman spectra, the strongest band is quoted as (10); other band intensities are then given in ratio to this band. Raman bands in solution spectra are also described as p, polarised; dp, depolarised or pp, partially polarised.

Nuclear magnetic resonance (n.m.r.) chemical shift values (δ) are quoted in parts per million (p.p.m.) from the accepted standards for the respective nuclei which are given in the text.

CHAPTER ONE

SECTION 1.1 GENERAL INTRODUCTION

The first synthetic co-ordination complex was a cyano complex, Prussian Blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$, prepared in 1704 by the German artist Diesbach who heated animal refuse and sodium carbonate together in an iron pot.¹ Subsequent work led to the isolation of potassium ferrocyanide, $\text{K}_4[\text{Fe}(\text{CN})_6]$.²

Since then, cyanide complexes of nearly all the d-block transition metals have been prepared. The versatility of the cyanide ligand is well established in that, as well as a wide variety of $[\text{M}(\text{CN})_x]^{n-}$ complexes, it also forms many partially substituted species with ligands such as oxide, halides, nitrosyl, carbonyl and tertiary phosphines occupying some of the co-ordination sites. Co-ordination numbers from two to eight are known involving transition metals in a variety of oxidation states.

Several comprehensive reviews of cyanide chemistry have appeared^{3,4}, that by Sharpe³ being the most notable.

SECTION 1.2 BONDING IN CYANIDE AND ITS COMPLEXES

1.2.1 MODES OF BONDING

(i) Terminal

The cyanide ion functions as a terminal ligand in the great majority of its complexes with transition metals. In such cases, the bond is formed between the carbon atom and the metal, rather than the nitrogen atom, since the latter is more electronegative and its lone pair is consequently less available for σ -donation.

Since the electron densities around carbon and nitrogen are similar, it is only X-ray studies of more recent years which have demonstrated that bonding is via carbon and this is confirmed by e.p.r. and vibrational spectroscopic studies.

A few cases of N-bonded cyanide have been reported. An unstable isocyano complex, $[\text{Cr}(\text{NC})(\text{H}_2\text{O})_5]^{2+}$ was claimed as a reaction intermediate.⁵ Johnson et al.⁶ reported that the nitrogen atoms of the ligands in $\text{K}_2[\text{ReN}(\text{CN})_4] \cdot \text{H}_2\text{O}$ were co-ordinated to rhenium; but this conclusion was reached only on the basis of consideration of the isotropic temperature factors in the structure determination. The CN distance was found to be $1.31\text{\AA}$ as compared to the 'usual' value of $1.16\text{\AA}$ although the $\text{C}\equiv\text{N}$ stretching vibration occurred at the typical frequency of 2120 cm^{-1} ⁷; and the $\text{N}-\hat{\text{Re}}-\text{NC}$ angle was, rather surprisingly, reported as 80.6° .

Linkage isomerism has been reported in the complex $[\text{Co}(\text{NC})(\text{H}_2\text{O})(\text{dmgH})_2]^{8+}$. Heating the isocyano complex at $250-260^\circ$ for one hour yielded the cyano isomer and an X-ray crystal structure determination was completed on both isomers.⁹ This compound is discussed in more detail in Chapter 4.

(ii) Bridging

(a) Linear Bridges

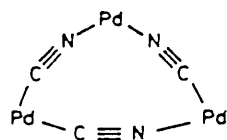
Complexes of the type $\text{M}-\text{C}\equiv\text{N}-\text{M}'$ in which the cyanide ion acts as an ambidentate ligand are well known. Linear bridges are found in simple polymeric species such as silver(I) cyanide and gold(I) cyanide and in 'giant' complexes of the Prussian Blue type. These complexes have been well reviewed by Ludi and Gudel.¹⁰

A recent example is the complex $[\text{Mo}(\text{CNBu}^t)_4(\text{bipy})]_2(\mu-\text{CN})]^{3+}(\text{PF}_6)_3$ in which the geometry around each molybdenum atom is capped trigonal

prismatic with a distorted linear bridging cyanide at the capping position.¹¹

The bridges may, however, deviate quite considerably from linearity. In the binuclear isomers $[(\text{CN})_5\text{-Co}^1\text{-C}\equiv\text{N-Co}^2\text{-(NH}_3)_5]\cdot\text{H}_2\text{O}$ (I) and $[(\text{CN})_5\text{-Co}^1\text{-N}\equiv\text{C-Co}^2\text{-(NH}_3)_5]\cdot\text{H}_2\text{O}$ (II), the $\text{Co}^1\text{-}\hat{\text{C}}\equiv\text{N}$ and $\text{Co}^2\text{-}\hat{\text{N}}\equiv\text{C}$ angles are 172.4° and 159.8° in (I) with $\text{Co}^1\text{-}\hat{\text{N}}\equiv\text{C}$ and $\text{Co}^2\text{-}\hat{\text{C}}\equiv\text{N}$ angles of 166° in (II). These deviations from linearity were attributed to intermolecular repulsion effects rather than to electronic or bonding differences.¹²

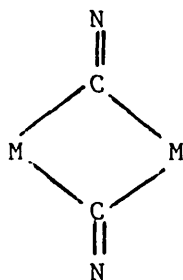
Hartley et al¹³ prepared the complex, $[\text{Pd}_3(\text{dppe})_3(\mu\text{-CN})_3](\text{ClO}_4)_3$, the structure of which is based on a cyclic trimer unit and, in which the ^{31}P n.m.r. indicates the unsymmetrical arrangement of the cyano bridges shown below.



The angles $\text{Pd-}\hat{\text{C}}\text{-N}$ (165°) and $\text{Pd-}\hat{\text{N}}\text{-C}$ (166°) make the cyano bridge significantly non-linear at both ends. The $\text{C}\equiv\text{N}$ distance of $1.15(2)\text{\AA}$ is consistent with a triple bond although some rehybridisation is proposed as the bond angles are significantly removed from 180° .

(b) Bent Bridges

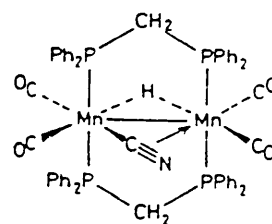
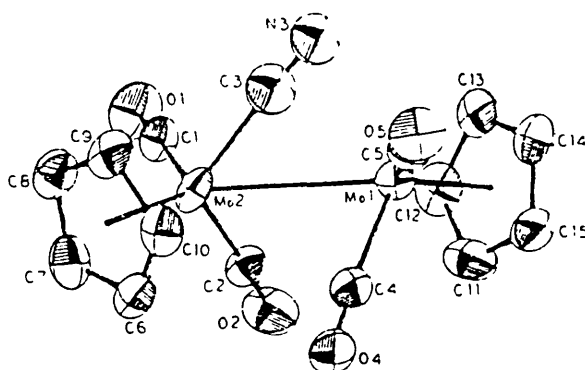
Cyanide complexes of the type



are rare although 'ketonic bridges' are common with CO. One example is $[\text{Cu}(\text{CN})(\text{NH}_3)]_n$ in which two copper atoms are bridged by a carbon atom although the nitrogen atom is further bonded to another copper atom.¹⁴ The $\text{Cu}-\hat{\text{C}}-\text{Cu}$ angle is 69.9° and the $\text{C}\equiv\text{N}$ distance is $1.13\text{\AA}$.

(c) "Semi-Bridging" Cyanide as a Four Electron Donor

There are two examples in the literature of the cyanide ligand acting in this fashion.^{15,16} Carbon monoxide and isocyanides 'have been shown to form bridges in a similar manner.^{17,18} The ligand is bound at one metal atom as in a normal terminal case and η^2 bound at the other. The bonding of the cyanide ion in the adduct $(\text{NEt}_4)[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-CN})]$ ¹⁵ was shown to be such that cyanide donates a total of four electrons to the two molybdenum atoms - two in a normal σ fashion and two more from the cyanide π bonds.



The $\text{Mo}-\hat{\text{C}}-\text{N}$ angle is 170° , consistent with σ donation from an sp orbital on CN^- . An accurate CN bond length was not obtained due to disorder associated with the bridging group.

Low temperature n.m.r. work has recently provided evidence for a similar type of bridge in the molecule, $[\text{Mn}_2\text{H}(\text{CN})(\text{CO})_4(\text{dppm})_2]$.¹⁶ (see above)

1.2.2 BONDING IN FREE CYANIDE

The cyanide ion is isoelectronic with CO, N₂ and the NO⁺ ion. The electronic configuration for the species is $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p)^2(\pi 2p)^2(\pi 2p)^2$ and the molecular orbitals may be represented diagrammatically as in Fig. 1.1.

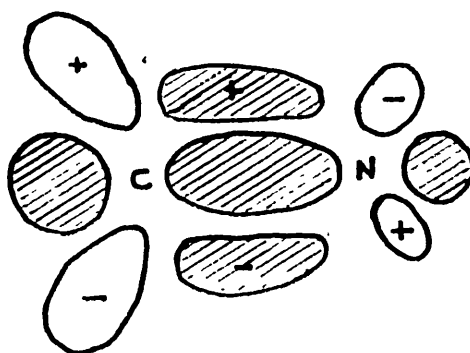


Fig. 1.1

Overlap of the filled 2s orbitals of carbon and nitrogen form σ -bonding and anti-bonding molecular orbitals and overlap of the 2p orbitals form one σ and two π bonding molecular orbitals illustrated schematically in Fig. 1.2 (overleaf)

The alternative approach is to consider formation of a σ -bond between carbon and nitrogen by overlap of sp hybrid orbitals on the carbon and nitrogen atoms leaving a lone pair on each atom. The π bonds are then formed by overlap of the two remaining p orbitals on carbon and nitrogen giving a formal triple bond.

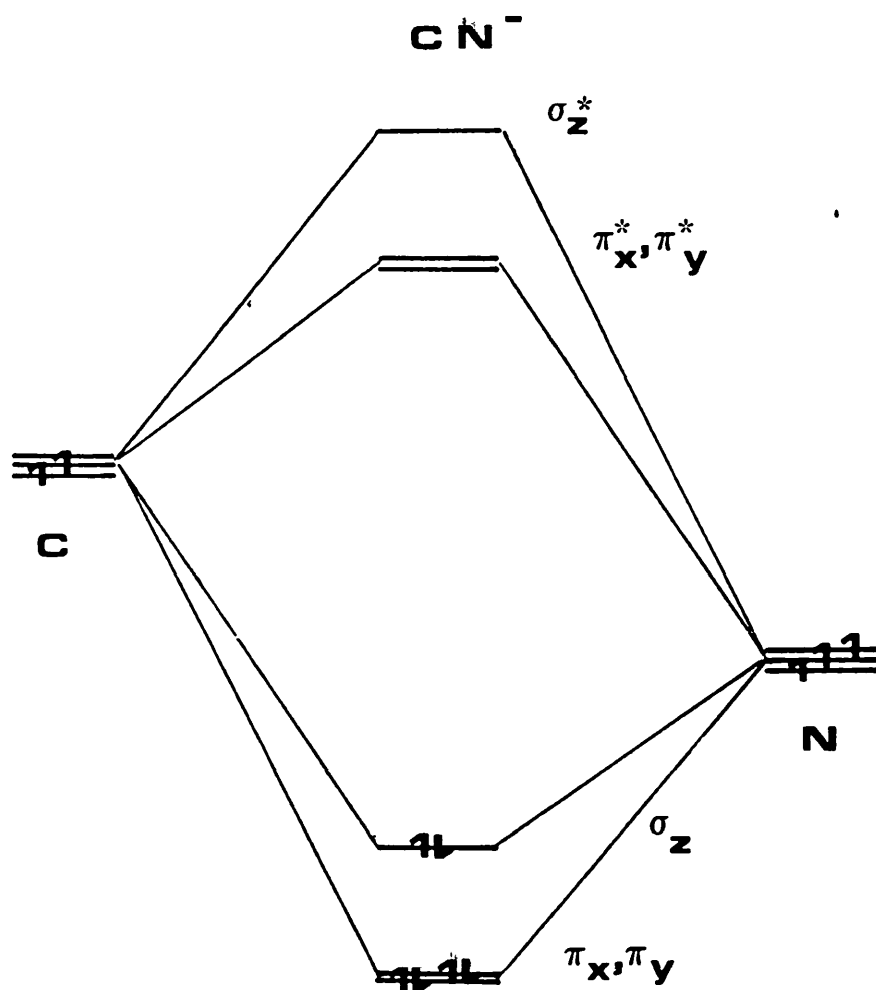


Fig. 1.2 Molecular Orbital Diagram for the Cyanide Ion

1.2.3 BONDING IN CYANO COMPLEXES

Bonding in linear, terminal cyano complexes only will be considered here. Overlap of the σ_{2s} orbital with $nd\sigma$, $(n+1)s$ and $(n+1)p\sigma$ metal orbitals forms a metal-ligand σ bond and the vacant $\pi^* 2p$ orbitals are available for the receipt of $d\pi$ electrons from the metal.

The cyanide ion is a stronger base than CO or NO^+ as a consequence of its negative charge and so has the best σ -bonding capacity. Considering the synergic effect, cyanide would, therefore, be expected to be receptive to back donation from the metal ion forming π bonds. This $d\pi-p\pi$ bonding undoubtedly occurs in cyano complexes (especially those in which the metal has a low oxidation state) but is not as extensive as in carbonyl or isonitrile complexes.

The bonding is discussed in more detail in Chapter 3, where we will be concerned with σ and π bonding effects on the vibrational and n.m.r. spectra of pentacyano complexes.

CHAPTER TWO

CYANIDE HYDRIDE COMPLEXES

SECTION 2.1 GENERAL INTRODUCTION

During investigations¹⁹ of the cobalt(II) cyanide solution which had been shown by Iguchi to absorb molecular hydrogen²⁰ and to act as a hydrogenation catalyst²¹, a hydridic species, $[\text{CoH}(\text{CN})_5]^{3-}$, was detected by ^1H n.m.r. spectroscopy.

Subsequent work has resulted in the isolation of the species $\text{K}_4[\text{WH}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$ ²², $\text{K}_3[\text{RhH}(\text{CN})_5] \cdot \text{H}_2\text{O}$ ²³, $\text{K}_2[\text{RhH}(\text{H}_2\text{O})(\text{CN})_4]$ ²⁴, $\text{K}_3[\text{IrH}(\text{CN})_5] \cdot \text{H}_2\text{O}$ ²⁵ and $[\text{K}(18\text{-crown-6})]_2[\text{PtH}(\text{CN})_3]$ ²⁶.

Preliminary work on the isolation of $\text{K}_4[\text{MoH}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$ had been made²⁷ by passing hydrogen over $\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ at 390°C, but pure samples could not be obtained. We report here the isolation of the new complex $\text{K}_4[\text{MoH}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$ and further studies on the pentacyano hydrido complexes of rhodium and iridium. Studies of reactions of these and the formation of some other cyanide hydride complexes have been undertaken.

SECTION 2.2 MOLYBDENUM AND TUNGSTEN COMPLEXES

2.2.1 INTRODUCTION

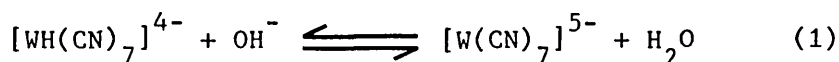
In this section, we will discuss the known cyanide hydride complex of tungsten, $\text{K}_4[\text{WH}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$, and its molybdenum analogue, the new compound, $\text{K}_4[\text{MoH}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$ ²⁸. As these compounds are involved in an acid-base equilibrium with the heptacyano species, $[\text{M}(\text{CN})_7]^{5-}$,

some work has been carried out on the latter species and a brief review of the literature on them is given.

(a) Heptacyano and Cyanide Hydride Complexes of Tungsten

The reaction of $K_3[W_2Cl_9]$ with excess of aqueous cyanide under u.v. light and under anaerobic conditions was found to yield the yellow diamagnetic salt, $K_5[W(CN)_7] \cdot H_2O$.²² This is isomorphous with $K_5[Mo(CN)_7] \cdot H_2O$ which is known to contain a pentagonal bipyramidal anion²⁹ and infrared and Raman studies confirmed that the D_{5h} symmetry was maintained in solution.³⁰

Griffith et al also noted that the reaction of $K_4[W(CN)_8] \cdot 2H_2O$ with molecular hydrogen at 390°C yielded the dark green salt, $K_4[WH(CN)_7] \cdot 2H_2O$.^{22,30} 1H n.m.r. studies confirmed the presence of a hydride and ^{13}C n.m.r. and Raman studies suggested the existence of the equilibrium:



From ^{13}C n.m.r. data, a value of $0.4 \text{ dm}^3 \text{ mol}^{-1}$ for $K = \frac{[W(CN)_7]^{5-}}{[WH(CN)_7]^{4-}[OH^-]}$

was obtained compared with $K=0.2 \text{ dm}^3 \text{ mol}^{-1}$ from Raman studies. The pK_a of $[WH(CN)_7]^{4-}$ is 14.4 so it is a stronger acid than $[CoH(CN)_5]^{3-}$ (pK_a 20.0).³¹

(b) Heptacyano Complexes of Molybdenum

The salts $K_4[Mo(CN)_7] \cdot 2H_2O$ ³², $NaK_3[Mo(CN)_7] \cdot 2H_2O$ ³³, $K_5[Mo(CN)_7]$ ³⁴, $K_5[Mo(CN)_7] \cdot H_2O$ ²⁹ and $Na_5[Mo(CN)_7] \cdot 10H_2O$ ²⁹ have been reported. The anions of the latter two salts have been shown to have pentagonal bipyramidal structures in the solid state.²⁹ Kiernan and Griffith³⁴ suggested at first that $K_5[Mo(CN)_7]$ and its aqueous solution had lower symmetry than D_{5h} but a later study³⁰ implied that this was

in error and that all three heptacyanomolybdate(II) salts retained D_{5h} symmetry in solution.

A single crystal X-ray study of $NaK_3[Mo(CN)_7]$ ³³ showed the anion to be pentagonal bipyramidal. The Raman spectra of the solid and its aqueous solution are similar suggesting little change in structure of the anion from solid to solution.³⁰ The salt is paramagnetic in the solid state (μ_{eff} 1.78 B.M. at 298K) and in aqueous solution (μ_{eff} 1.84 B.M. at 298K) and the e.s.r. spectrum exhibits the features and behaviour expected for a low spin d^3 complex.³⁰

Spectroscopic and e.s.r. evidence^{30,35} suggest that $K_4[Mo(CN)_7].2H_2O$ might contain a capped trigonal prismatic (C_{2v}) structure in the solid state with a pentagonal bipyramidal (D_{5h}) structure in solution. The band splitting in the Raman and infrared spectra in the ν_{CN} region is more complex than in $NaK_3[Mo(CN)_7].2H_2O$ suggesting lower symmetry. X-ray powder diffraction has shown that the potassium salt is not isomorphous with $K_4[M(CN)_7]$ where $M=V, Re$, which are known^{36,37} to contain pentagonal bipyramidal anions.

The crystal structure of $[Mo(CNBut)^t_7](PF_6)_2$ shows this to contain a capped trigonal prismatic structure³⁸ and we report spectroscopic studies on this as a possible model for $K_4[Mo(CN)_7].2H_2O$.

2.2.2 PREPARATION OF $K_4[MoH(CN)_7].2H_2O$

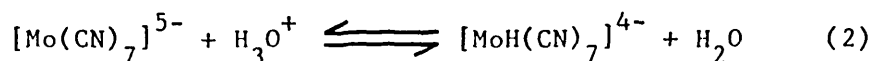
The molybdenum hydride species can be prepared in a similar manner to the tungsten complex by treating $K_4[Mo(CN)_8].2H_2O$ with molecular hydrogen at 400°C.³⁰ This, however, leads to an impure product contaminated with $K_5[Mo(CN)_7]$. We find however, after many attempts, that careful treatment of an ice cold aqueous solution of $K_5[Mo(CN)_7]$ under strictly anaerobic conditions with acetic,

hydrochloric or ascorbic acids, or hydrogen sulphide, gave the dark green diamagnetic salt, $K_4[MoH(CN)_7] \cdot 2H_2O$.

2.2.3 INFRARED AND RAMAN SPECTROSCOPY OF $K_4[MoH(CN)_7] \cdot 2H_2O$

The infrared and Raman data for $K_4[MoH(CN)_7] \cdot 2H_2O$ are given in Table 2.1 and the solid infrared spectrum is shown in Fig. 2.1. In addition to bands in the ν_{CN} region in the infrared spectrum, there are bands at 1805 and 860 cm^{-1} . The 1805 cm^{-1} band shifts to 1830 cm^{-1} in aqueous solution in both infrared and Raman. We assign these bands to the Mo-H stretch and deformation respectively; on deuteration of the complex they shift to 1305 and 625 cm^{-1} . The profiles of the Raman spectra change little between solid and solution, suggesting that the stereochemistry of the anion is maintained in both phases. The profiles are similar to those of $K_4[WH(CN)_7] \cdot 2H_2O$ ³⁰ and X-ray diffraction studies have shown the two complexes to be isomorphous. The infrared spectra show that our hydride complex and $K_5[Mo(CN)_7]$ are the two complexes reported by Kleinberg³⁹ as " $K_3[Mo(CN)_6]$ " and " $K_4[Mo(CN)_6]$ " respectively.

By measuring the Raman spectra of a number of aqueous solutions of known initial concentrations of $[Mo(CN)_7]^{5-}$ (containing 0.60 mol dm^{-3} SO_4^{2-}) with known added amounts of hydrochloric acid (from 0 to 5 mol dm^{-3}) at a constant total ionic strength of 6.0 mol dm^{-3} at 25°C, a value of $K = 2.5 (\pm 0.2) \times 10^{-3}$ mol dm^{-3} was obtained for equation (2):

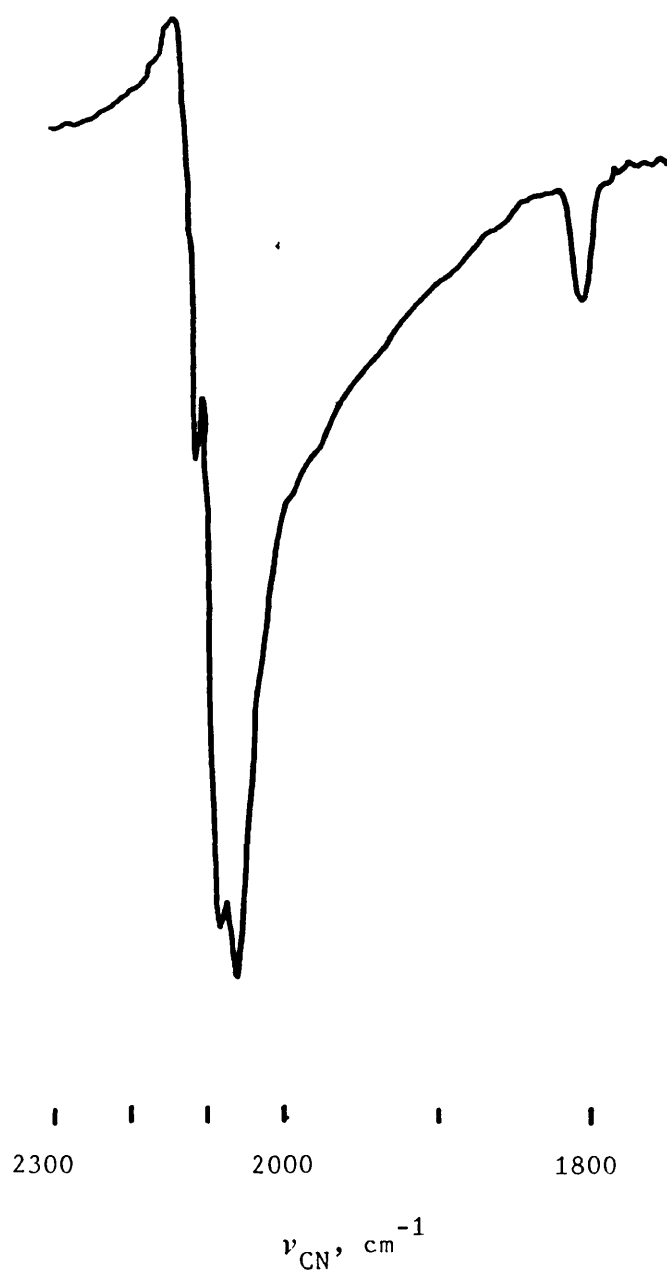


Areas under the peak at 2109 cm^{-1} of $[MoH(CN)_7]^{4-}$ and 1980 cm^{-1} of $[Mo(CN)_7]^{5-}$ were used to determine the concentrations of the

TABLE 2.1 Infrared and Raman data for $\text{K}_4[\text{MoH}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$

ASSIGNMENT	INFRARED (SOLID)	INFRARED (SOLUTION)	RAMAN (SOLID)	RAMAN (SOLUTION)
ν_{CN}	2110sh	2100sh	2118(7)	2123(8)p
	2090vs	2080vs	2106(6)	2107(10)p
	2070vs		2100(9)	2080(9)dp
	2060sh		2082(7)	2065(6)dp
$\nu_{\text{Mo-H}}$	1805w	1830vw	1805(1)	1830(1)p
$\nu_{\text{Mo-}^2\text{H}}$	1305w			
$\delta_{\text{Mo-H}}$	860w			
$\delta_{\text{Mo-}^2\text{H}}$	625w			
$\delta_{\text{MoCN}}, \nu_{\text{MoC}}$	510w			460(1)
	460w			440(1)
	390m			390(1)

Fig 2.1 Infrared Spectrum of $K_4[MoH(CN)_7] \cdot 2H_2O$



two species. The intensity of the peak at 982 cm^{-1} (ν_1 of SO_4^{2-}) was used as an internal reference for the study. The experimental data are summarised in Table 2.2 and three spectra are illustrated in Fig. 2.2. In (a), there is almost pure $[\text{Mo}(\text{CN})_7]^{5-}$; in (c) almost pure $[\text{MoH}(\text{CN})_7]^{4-}$ and in (b) roughly equal concentrations of both species.

From this value of K , the pK_a of $[\text{MoH}(\text{CN})_7]^{4-}$ is 16.6 so it is a weaker acid than $[\text{WH}(\text{CN})_7]^{4-}$ (pK_a 14.4).³⁰ Other comparative data for acid strengths of second and third row hydrido complexes are lacking but $[\text{CoH}(\text{CN})_5]^{3-}$ (pK_a 20.0)³¹ is a weaker acid than $[\text{RhH}(\text{CN})_5]^{3-}$ (pK_a 18.0).³¹ We are unable to offer an explanation for this observation; we would expect the opposite to be true as bonds tend to be stronger from first to second to third row elements.

2.2.4 N.M.R. SPECTROSCOPY

(i) ^1H n.m.r. spectroscopy

The ^1H n.m.r. spectrum of an aqueous solution of $[\text{MoH}(\text{CN})_7]^{4-}$ shows a resonance at δ 2.3 p.p.m., a similar proton shift was observed for aqueous solutions of $[\text{WH}(\text{CN})_7]^{4-}$ (δ 2.4 p.p.m.).³⁰ The low magnitude of these shifts may be connected with the high co-ordination number of the metals.⁴⁰ On addition of strong base to the solution, the ^1H n.m.r. resonance was reduced in intensity and the colour changed to yellow due to the species $[\text{Mo}(\text{CN})_7]^{5-}$. No proton resonance was observed in a solution of $[\text{MoH}(\text{CN})_7]^{4-}$ in $^2\text{H}_2\text{O}$, suggesting that, as with the tungsten analogue³⁰, rapid exchange with $^2\text{H}_2\text{O}$ occurs.

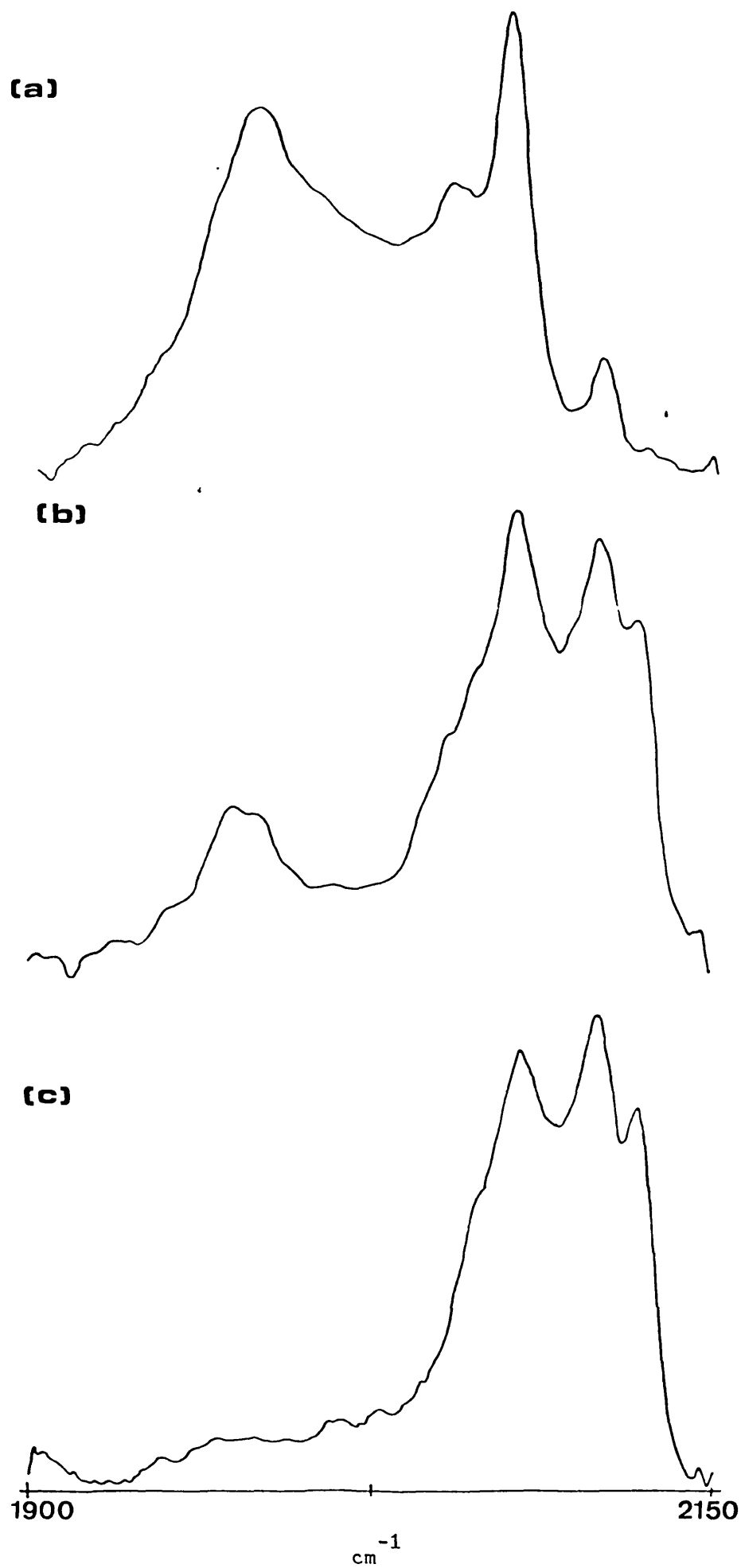


Fig 2.2 Raman Spectra of $[\text{MoH}(\text{CN})_7]^{4-}$

TABLE 2.2 Equilibrium Study of $[\text{MoH}(\text{CN})_7]^{4-}/[\text{Mo}(\text{CN})_7]^{5-}$

Area under peaks at 2110 and 1980 cm^{-1}

$[\text{MoH}(\text{CN})_7]^{4-}$	$[\text{Mo}(\text{CN})_7]^{5-}$	$[\text{H}_3\text{O}^+], \times 10^{-3} \text{ mol dm}^{-3}$	$K, \times 10^{-3}, \text{ mol dm}^{-3}$
0.90	0.10	0.3	2.7
0.76	0.24	0.8	2.5
0.63	0.37	1.6	2.7
0.41	0.59	3.2	2.2
0.37	0.63	4.0	2.3
0.15	0.85	14.2	2.5

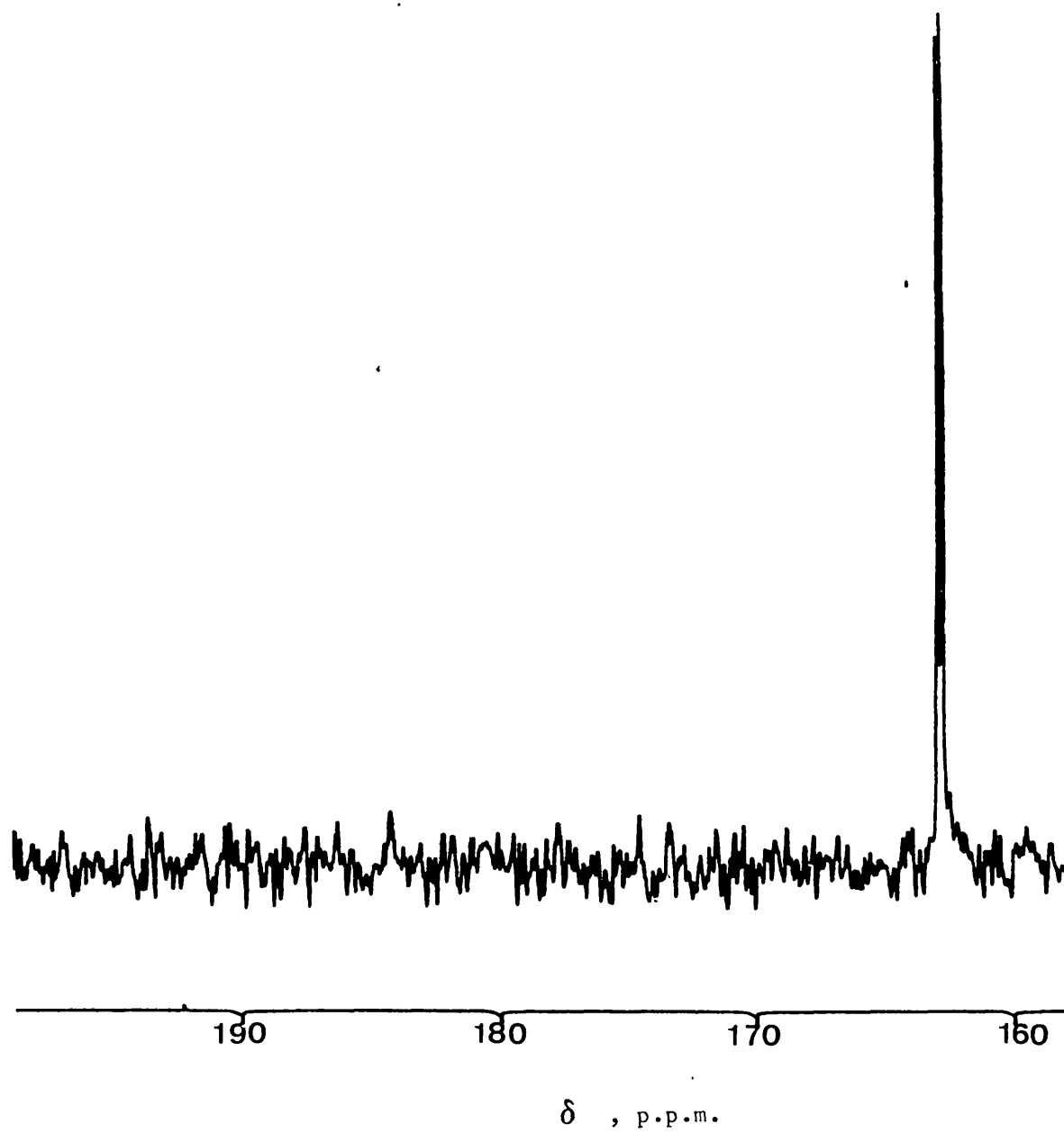
$$K = 2.49 (\pm 0.2) \times 10^{-3} \text{ mol dm}^{-3}$$

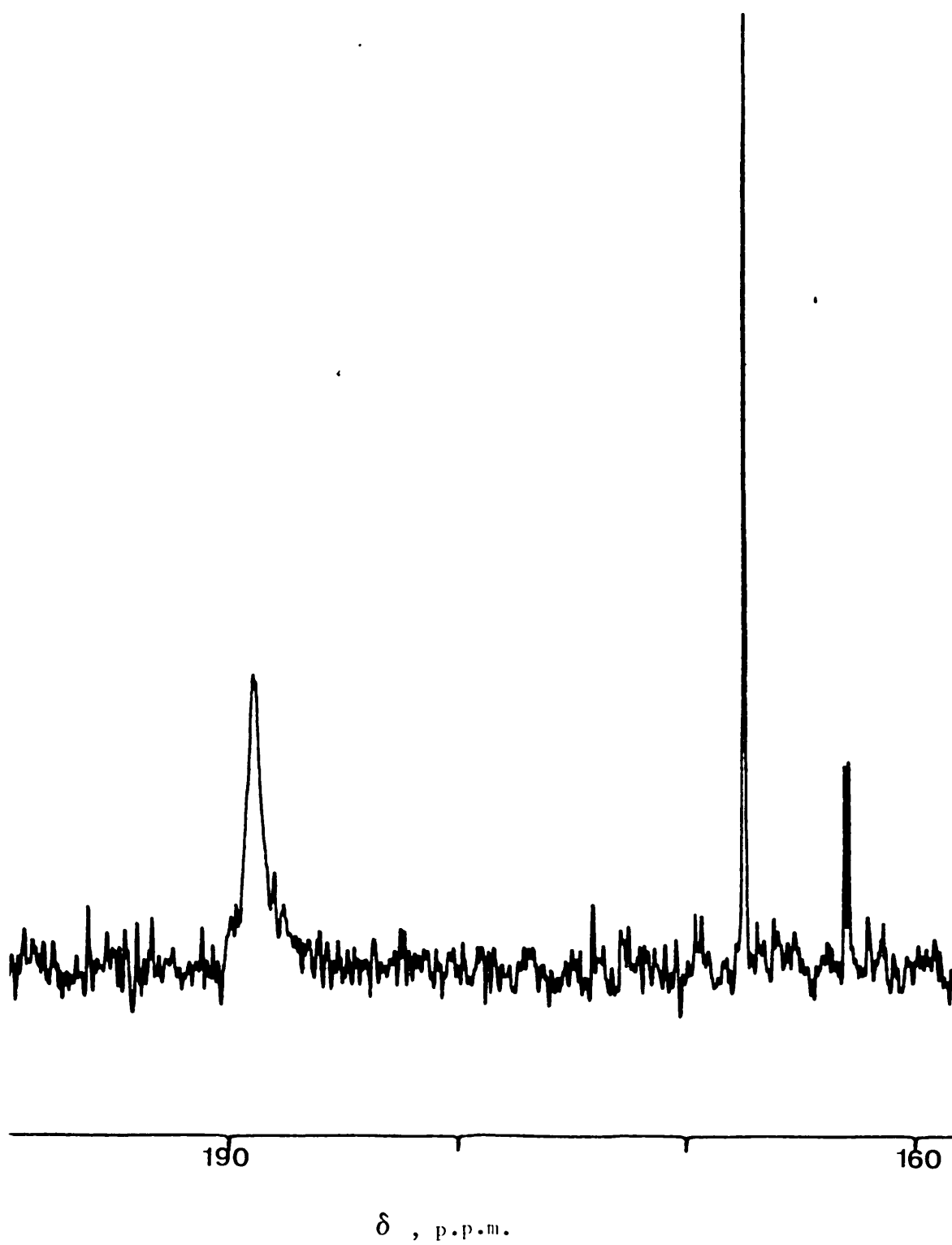
(ii) ^{13}C n.m.r. spectroscopy

The ^{13}C n.m.r. spectrum without proton decoupling of an aqueous solution of $[\text{MoH}(\text{CN})_7]^{4-}$ (Fig. 2.3a) shows a doublet at δ 162.9 and 162.7 p.p.m., $J(^{13}\text{C}, ^1\text{H})$ 11.3 Hz, which collapses to a singlet at δ 163.1 p.p.m. on proton decoupling. The resonance decreased in intensity on addition of strong base and $\text{K}_5[\text{Mo}(\text{CN})_7]$ was isolated from the resultant yellow solution.

The undecoupled ^{13}C n.m.r. spectrum of an aqueous solution of $[\text{Mo}(\text{CN})_7]^{5-}$ in the presence of excess cyanide (0.2 mol dm $^{-3}$) exhibits a similar doublet at δ 163.1 and 162.9 p.p.m.; $J(^{13}\text{C}, ^1\text{H})$ 11.3 Hz, which, again, may be assigned to $[\text{MoH}(\text{CN})_7]^{4-}$ (Fig. 2.3b). In addition to this and the resonance at δ 167 p.p.m. due to free cyanide, a broad resonance occurs at δ 189 p.p.m. which we assign as $[\text{Mo}(\text{CN})_7]^{5-}$. Addition of base to the solution causes the doublet to disappear which we believe supports the equilibrium (2) proposed earlier (p. 24). The sharpness of the hydrido species and CN^- resonances suggest that exchange between free CN^- and $[\text{Mo}(\text{CN})_7]^{5-}$ is not the cause of the broad δ 189 p.p.m. resonance.

This effect is thought to arise from the presence of traces of the paramagnetic Mo(III) species, $[\text{Mo}(\text{CN})_7]^{4-}$; a rapid electron exchange between the two pentagonal bipyramidal anions, $[\text{Mo}(\text{CN})_7]^{5-}$ and $[\text{Mo}(\text{CN})_7]^{4-}$ might be expected. We made measurements of magnetic susceptibility on a number of our n.m.r. solutions using the Evans method⁴¹ and confirmed the presence of a paramagnetic species. In order to reduce this effect, reducing agents such as borohydride, sodium dithionite, sodium hypophosphite, hydrazine, SnCl_2 and zinc powder were added to solutions of $[\text{Mo}(\text{CN})_7]^{5-}$. This did result in solutions containing a lower percentage of $[\text{Mo}(\text{CN})_7]^{4-}$ but the problem has never been completely resolved.

**Fig 2.3a** ^{13}C n.m.r. spectrum of $[\text{MoH}(\text{CN})_7]^{4-}$

**Fig 2.3b**

^{13}C n.m.r. spectrum of an Aqueous Solution of
 $[\text{Mo}(\text{CN})_7]^{5-}$

2.2.5 ELECTROCHEMICAL STUDIES

Cyclic voltammetry of an aqueous solution of $[\text{Mo}(\text{CN})_7]^{5-}$ in 0.1M KCN, (pH 12.0), gave a reversible oxidation at -0.97V (vs SCE) to $[\text{Mo}(\text{CN})_7]^{4-}$; the latter species may be isolated from the green solution after such voltammetry. This couple was further observed by studying the effect of pH change. Hydrochloric acid (2M) was added dropwise under nitrogen with cooling and the redox properties of the solution were studied as $[\text{MoH}(\text{CN})_7]^{4-}$ was formed. We found that as the pH decreased, the redox at -0.9V became irreversible i.e. as the $[\text{Mo}(\text{CN})_7]^{5-}$ was formed in solution it was being converted to the hydrido species and was no longer available for oxidation to the Mo(III) complex. At low pH (5.9), we observed a weak reversible couple at -0.23V possibly due to a process involving the complex $[\text{MoH}(\text{CN})_7]^{4-}$. At pH < 5.9 the addition of further acid caused degradation of the molybdenum species resulting in a black solution. These data are summarised in Table 2.3 overleaf.

In a solution of $[\text{WH}(\text{CN})_7]^{4-}$ treated in the same way, two redox processes were observed from pH 13.0 - 8.25. One redox occurred at -0.98V similar to that observed for the molybdenum complex (both processes are perfectly reversible) and the other at + 0.39V. From pH 8.25 - 8.5, only the latter process was observed in the green solution which we attribute to the species $[\text{WH}(\text{CN})_7]^{4-}$. The observation of the couple at -0.9V suggests the process $[\text{W}(\text{CN})_7]^{5-}/[\text{W}(\text{CN})_7]^{4-}$ as in the molybdenum system. However, the complex $[\text{W}(\text{CN})_7]^{4-}$ has not been previously detected.^{27,30} We were unable to use electrolysis to obtain a great enough concentration of the oxidised species in this couple to carry out further studies. The data are summarised in Table 2.3.

TABLE 2.3 Electrochemical Data for $[\text{M}(\text{CN})_7]^{5-}$, (M=Mo,W)

<u>[Mo(CN)₇]⁵⁻</u>				
pH	E _{1/2} , V	E _{red} -E _{ox} , mV	I _{red} /I _{ox}	
11.1	-0.89	360	1.14	
10.75	-0.89	358	0.95	
10.55	-0.89	332	1.09	
10.45	-0.90	340	1.15	
10.1	-0.92	335	1.45	
9.7	-0.92	267	1.84	
9.0	-0.95	150	2.67	
8.5	-0.93	164	3.05	
5.9	-0.92	-	-	
<u>[W(CN)₇]⁵⁻</u>				
pH	E _{1/2} , V	I _{red} /I _{ox}	E _{1/2} , V	I _{red} /I _{ox}
13.0	-0.97	0.95	+0.40	1.0
12.3	-0.98	1.0	+0.38	1.0
10.3	-0.99	1.2	+0.36	0.93
9.5	-1.0	1.6	+0.36	1.07
8.25	-1.03	1.2	+0.37	1.1
7.15	-	-	+0.37	1.03
6.20	-	-	+0.37	1.0
5.0	-	-	+0.36	1.14

2.2.6 CHEMICAL REACTIONS OF $[\text{MoH}(\text{CN})_7]^{4-}$

Soares and Griffith³⁰ showed that $[\text{WH}(\text{CN})_7]^{4-}$ will stoichiometrically hydrogenate dienes; cyclohexa-1,3-diene and cycloheptadiene giving cyclohexene and cycloheptene in 50 and 25% yields respectively. Solutions of $[\text{MoH}(\text{CN})_7]^{4-}$ in aqueous cyanide were treated with a number of unsaturated hydrocarbons in the presence and absence of hydrogen. A reaction was observed with phenylacetylene (see Section 2.5, p. 60), with cyclohexa-1,3-diene to give cyclohexene in 10% yield and with styrene, which was polymerised in high yield. No reaction was observed with cycloheptadiene, cycloocta-1,5-diene or 2,3-dimethylbuta-1,3-diene. The molybdenum complex does not exhibit the catalytic activity shown by $[\text{CoH}(\text{CN})_5]^{3-}$.

With sulphur dioxide, $[\text{MoH}(\text{CN})_7]^{4-}$ gave $\text{K}_4[\text{Mo}(\text{OSO}_2\text{H})(\text{CN})_7]$ characterised by elemental analysis and vibrational spectroscopy. Reactions with oxygen, nitric oxide and hydrogen peroxide gave $\text{K}_4[\text{Mo}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$; the former via the blue species, $[\text{MoO}(\text{OH})(\text{CN})_4]^{3-}$.⁴²

2.2.7 VIBRATIONAL SPECTRA OF $[\text{Mo}(\text{CNBu}^t)_7]^{2+}$ AND $[\text{Mo}(\text{CN})_7]^{4-}$

It was suggested by Gray et al³⁵ on the basis of e.s.r. and electronic spectral data that the anion in the solid $\text{K}_4[\text{Mo}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$ was capped trigonal prismatic, a structure so far not observed in other heptacyano complexes, and this proposal received further support from more extensive e.s.r. data.³⁰ Despite many attempts, we have been unable to grow crystals of $\text{K}_4[\text{Mo}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$ suitable for X-ray studies. The crystal structure of $[\text{Mo}(\text{CNBu}^t)_7](\text{PF}_6)_2$

shows this to contain a capped trigonal prismatic structure³⁸, and we report here the Raman and infrared spectra of this in the solid and solution states as a model for $K_4[Mo(CN)_7] \cdot 2H_2O$.

For a $[M(CN)_7]^{n-}$ or $[M(CNR)_7]^{n+}$ moiety with capped trigonal prismatic (C_{2V}) geometry, we expect seven Raman active modes ($3A_1 + A_2 + 2B_1 + B_2$, A_1 polarised) of which six ($3A_1 + 2B_1 + B_2$) will also be infrared active; for a pentagonal bipyramid found in many heptacyano complexes³⁰ including $NaK_3[Mo(CN)_7]$ ³³, there should be three Raman active CN stretches ($2A_1' + E_1'$, A_1' polarised) and two infrared active modes ($A_2'' + E_2''$). For solid $[Mo(CNBut)_7](PF_6)_2$ we observe five Raman and four infrared bands in the CN stretching region with three Raman-infrared coincidences; in solid $K_4[Mo(CN)_7] \cdot 2H_2O$ there are four Raman bands and four infrared bands again with three Raman-infrared coincidences (Table 2.4). It, therefore, seems feasible that the cyano complex does contain a similar geometry to the isocyanide one, viz capped trigonal prismatic. In solution, $[Mo(CNBut)_7]^{2+}$ has three Raman bands (2 polarised) with one broad infrared band; if the latter envelops the A_2'' and E_1' modes, this is consistent with pentagonal bipyramidal symmetry; we have earlier shown that $[Mo(CN)_7]^{4-}$ has this structure in aqueous solution.³⁰ The ¹³C n.m.r. spectrum⁴³ of $[Mo(CNBut)_7]^{2+}$ exhibits only one $\underline{CNCMe}_3$ resonance at $\delta 164.3$ p.p.m.; like other pentagonal bipyramidal species³⁰, it is likely to be fluxional on the n.m.r. timescale. The $\underline{CNCMe}_3$ and $\underline{CNCMe}_3$ resonances are at $\delta 57.8$ and 31.0 respectively. The anion $[Mo(CN)_7]^{4-}$ is paramagnetic and an n.m.r. spectrum cannot, therefore, be obtained.

TABLE 2.4 Infrared and Raman data for $[\text{Mo}(\text{CN})_7]^{4-}$ and $[\text{Mo}(\text{CNBu}^t)_7]^{2+}$

	$\text{K}_4[\text{Mo}(\text{CN})_7] \cdot 2\text{H}_2\text{O}^{\text{a},30}$	$[\text{Mo}(\text{CNBu}^t)_7](\text{PF}_6)_2^{\text{b}}$
INFRARED	2110sh	2215sh
(solid)	2100m	2190sh
	2064vs	2140vs,br
	2030sh	2055w,sh
RAMAN	2115w	2217.5(10)
(solid)	2097vs	2192.0(6)
	2080vs	2166.0(9)
	2060w	2152.0(9)
		2142.8(8)
INFRARED	2080m	2140vvs
(solid)	2040m	
RAMAN	2115s	2216(10)p
(solution)	2100sh,p	2179(5)p
	2063w	2147(7)dp

^a Infrared spectra run as nujol mull and in aqueous solution
Raman spectra run in capillary tube and in aqueous solution

^b Infrared spectra run as nujol mull and in acetone and chloroform solution
Raman spectra run as KBr disc and in acetone and chloroform solutions

SECTION 2.3 RHODIUM AND IRIDIUM COMPLEXES

2.3.1 INTRODUCTION

(i) Rhodium Complexes

A rhodium cyanide hydride complex was first detected in solution by ^1H n.m.r. after treatment of rhodium trichloride with excess cyanide and sodium borohydride.⁴⁴ Treatment of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with methanolic KCN gave a compound formulated as $\text{K}_2[\text{RhH}(\text{CN})_4(\text{H}_2\text{O})]$.²⁴ The compound was characterised by infrared and ^1H n.m.r. spectroscopy and its reaction with O_2 , NO and C_2F_4 were reported to give $\text{K}_4[(\text{CN})_4(\text{H}_2\text{O})\text{RhO}_2\text{Rh}(\text{H}_2\text{O})(\text{CN})_4]$, $[\text{Rh}(\text{NO}_2)(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ and $[\text{Rh}(\text{CN})_5(\text{C}_2\text{F}_4\text{H})]^{3-}$ respectively.

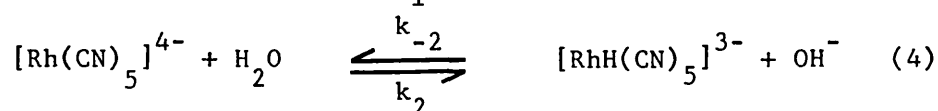
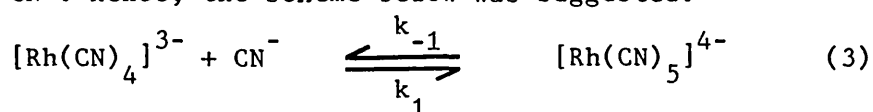
The same authors attempted to prepare the pentacyanohydrido complex by reaction of $\text{Rh}(\text{CN})_3 \cdot 3\text{H}_2\text{O}$ with aqueous cyanide and sodium or potassium amalgam.²⁴ An air-sensitive white product was reported with a doublet in the ^1H n.m.r. at the same place as $[\text{RhH}(\text{CN})_4(\text{H}_2\text{O})]^{2-}$ and $\nu_{\text{Rh-H}}$ at 1965 cm^{-1} as compared to 1976 cm^{-1} . No microanalysis data were reported.

These data were contradicted by Krogmann and Binder²³ who formulated the product of the reaction between $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and methanolic KCN as $\text{K}_3[\text{RhH}(\text{CN})_5] \cdot \text{H}_2\text{O}$. In a later study,⁴⁵ solutions of $[\text{RhH}(\text{CN})_5]^{3-}$ isotopically enriched with $^{13}\text{CN}^-$ were examined by ^1H n.m.r. in the hope that the ^1H , ^{13}C coupling constants could be utilised to provide information concerning the stereochemistry of the compound. The ^1H n.m.r. spectrum comprised the superposition of strong resonances due to species containing only $^{12}\text{CN}^-$ ligands and additional weaker satellite peaks due to ^1H , ^{13}C spin-spin coupling in species containing $^{13}\text{CN}^-$ ligands. The observation of discrete cis and trans ^1H , ^{13}C

coupling constants indicated that a pentacyano species is formed from the reaction of $[\text{Rh}(\text{C}_8\text{H}_{12})\text{Cl}]_2$ and KCN.

Roberts and Symes⁴⁶ reported that $[\text{RhH}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ reacted with oxygen to yield $[\text{Rh}(\text{H}_2\text{O})(\text{CN})_4(\text{OOH})]^{2-}$ after three hours, and Thomas and Wilkinson⁴⁷ mentioned the preparation of $[\text{RhH}(\text{CN})_5]^{3-}$ from $[\text{RhH}(\text{NH}_3)_5]^{2+}$.

A careful study of the reaction of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with potassium cyanide has been reported.^{48,49} The infrared and u.v. spectra of the intermediates in the reaction were observed in solutions resulting from the successive additions of sodium cyanide to $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, both as methanolic solutions. The data and conclusions are summarised in Table 2.5. A successive replacement of CO and Cl^- occurs by CN^- . However, in the first study⁴⁸, the species $[\text{Rh}(\text{CN})_4]^{3-}$ was not observed due to fast oxidative addition of HCN yielding the final product, $[\text{RhH}(\text{CN})_5]^{3-}$. The species $[\text{Rh}(\text{CN})_4]^{3-}$ was detected⁴⁹ using stopped flow techniques. The kinetic measurements showed a first order dependence upon NaCN, indicating that the rate determining step in the reaction involved CN^- . Hence, the scheme below was suggested:



The analogous cobalt species has been postulated by several authors and its rate of formation has been measured by pulse radiolysis.⁵⁰

Halpern et al^{51,52} determined an equilibrium constant for the reaction:

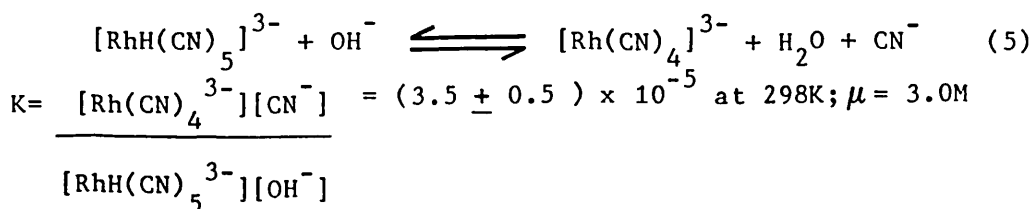


TABLE 2.5 Species present in Solutions of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in methanol on reaction with Sodium Cyanide^{48,49}

Rh:CN ⁻ ratio	Nature of Species	I.R. spectra, cm ⁻¹	U.V. Spectra, (Kk)
1 : 0	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	2088.5, 2015.5	41sh, 37.9, 30.3
1 : 1	$(10^{-3}\text{M}) [\text{Rh}(\text{CO})_2\text{CN}]_x$	2150, 2061, 2009	35.7, 31.1
	$(10^{-4}\text{M}) [\text{Rh}(\text{CO})_2(\text{CN})\text{Cl}]^-$		
1 : 2	$[\text{Rh}(\text{CO})_2(\text{CN})_2]^-$	2078, 2029, 1995	49, 33.6, 25.8
1 : 3	$[\text{Rh}(\text{CO})(\text{CN})_3]^{2-}$	2108, 2085, 1995	49.1, 34.7, 29.3, 25.8
1 : 4	$[\text{RhH}(\text{CN})_5]^{3-}$	2108, 1957	>50, 45sh

The species $[\text{Rh}(\text{CN})_4]^{3-}$ was isolated as its $[\text{Co}(\text{en})_3]^{3+}$ salt by reduction of RhCl_3 in alkaline KCN with zinc powder. The spectra obtained were in good agreement with those reported by Jewsbury and Maher.⁴⁹ Measurements of the rate of approach to equilibrium gave a rate law for reaction (5) in both the forward and reverse directions. These were:

$$\overline{\text{Rate}} = \frac{d[\text{Rh}(\text{CN})_4^{3-}]}{dt} = k_F [\text{RhH}(\text{CN})_5^{3-}] [\text{OH}^-] \quad \text{where } k_F = 8.4 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

$$\overleftarrow{\text{Rate}} = \frac{-d[\text{Rh}(\text{CN})_4^{3-}]}{dt} = k_R [\text{Rh}(\text{CN})_4^{3-}] [\text{CN}^-] \quad \text{where } k_R = 22 \text{ M}^{-1} \text{ s}^{-1}$$

at 25°C, $\mu=3\text{M}$

Assuming a stepwise mechanism via reactions (3) and (4) and using the steady state approximation for $[\text{Rh}(\text{CN})_5]^{4-}$, Halpern reported that $k_1 = 8.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ compared with a value of $1.0 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ for $[\text{CoH}(\text{CN})_5]^{3-}$.⁵³ This difference is in accord with the expectation that $[\text{CoH}(\text{CN})_5]^{3-}$ is a stronger acid than $[\text{RhH}(\text{CN})_5]^{3-}$. Despite this fact, $[\text{RhH}(\text{CN})_5]^{3-}$ shows a much greater dissociation according to equation (5), apparently reflecting the greater tendency of $[\text{Rh}(\text{CN})_5]^{4-}$ to dissociate to the four co-ordinate complex, $[\text{Rh}(\text{CN})_4]^{3-}$.

There is one final mention of a rhodium cyanide hydride species in the literature. Treatment of RhCl_3 or $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in a (Na,K)CN eutectic and subsequent exposure to the atmosphere revealed two intermediate compounds.⁵⁴ These were reported, from their infrared and ^1H n.m.r. spectra, to be $\text{K}_3[\text{RhH}(\text{CN})_5]$ and $\text{K}_2[\text{RhH}(\text{H}_2\text{O})(\text{CN})_4]$. No microanalysis data were given for either compound.

(ii) Iridium Complexes

Unlike its rhodium analogue, there has been little mention of $K_3[IrH(CN)_5] \cdot H_2O$ in the literature, and no controversy as to its formulation. The compound was first prepared by the reaction of excess potassium cyanide in methanol with bis(cyclohexa-1,3-diene)iridium chloride or bis(2,3-dimethylbutadiene)iridium chloride.²⁵ The infrared and electronic spectra and the 1H n.m.r. spectrum were recorded^{25,55} and, from the chemical shift, a charge distribution calculation was carried out using one electron LCAO-MO theory.⁵⁶ A later 1H n.m.r. study of a ^{13}C enriched sample confirmed C_{4v} symmetry for the anion in solution.⁴⁵ The Ag^+ and $(H_3O)^+$ salts have been isolated by cation exchange and no proton exchange was observed after treatment with 2H_2O for seven days.

We decided to investigate the rhodium species more thoroughly in order to resolve the controversy over its structure and to extend the brief data on $[RhH(CN)_5]^{3-}$. The rhodium species was prepared by the literature methods; reaction of cyanide with $[Rh(CO)_2Cl]_2$ ^{23,24} $[Rh(C_8H_{12})Cl]_2$ ⁴⁵ and with $RhCl_3/NaBH_4$ in solution only. In our hands all preparations gave the same product, $K_3[RhH(CN)_5] \cdot H_2O$ characterised by elemental analysis, vibrational spectroscopy and ^{13}C n.m.r. spectroscopy. In the experimental section we report slightly modified preparative procedures for the complex; these give better yields of the compound than do the original methods.

2.3.2 INFRARED AND RAMAN SPECTROSCOPY

For a species $[\text{MH}(\text{CN})_5]^{3-}$ with C_{4V} symmetry, three infrared active fundamentals ($2A_1 + E$) and four Raman active fundamentals ($2A_1 + B_1 + E$) are expected for the ν_{CN} vibrations, while there will be only one infrared and Raman active fundamental (A_1) for the metal-hydrogen stretch. The A_1 Raman modes should be polarised. The species $[\text{RhH}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ also has C_{4V} symmetry but only two infrared active ($A_1 + E$) and three Raman active ($A_1 + B_1 + E$) fundamentals are predicted for the ν_{CN} vibrations. The infrared and Raman data for $[\text{RhH}(\text{CN})_5]^{3-}$ are listed in Tables 2.6 and 2.7 respectively with that from the literature for comparison. The Raman spectra are illustrated in Figure 2.4. The data for $[\text{IrH}(\text{CN})_5]^{3-}$ are given in Table 2.8.

The infrared solution spectrum of $[\text{RhH}(\text{CN})_5]^{3-}$ shows only one peak at 2110 cm^{-1} . However, in carbonyl complexes, it has been found that A_1 modes are higher in frequency than E modes and are either weak or unobserved (see also Chapter 3, p. 96); the 2110 cm^{-1} band may, therefore, be assigned as an E mode.⁴⁸ The solution infrared spectrum of $[\text{IrH}(\text{CN})_5]^{3-}$ does, however, exhibit the expected three bands.

The bands at 1980 and 781 cm^{-1} in the infrared spectrum of solid $\text{K}_3[\text{RhH}(\text{CN})_5] \cdot \text{H}_2\text{O}$ shift to 1430 and 581 cm^{-1} respectively on deuteration and hence may be assigned as the rhodium-hydrogen stretch and deformation.

In the Raman spectrum of an aqueous solution of both complexes, three of the expected four ν_{CN} stretching frequencies are observed. The strongest band at 2147 cm^{-1} (Rh) and 2152 cm^{-1} (Ir), which is polarised, is assigned as an A_1 mode; the depolarised band at

TABLE 2.6 Infrared Data for Rhodium Cyanide Hydride Species

ref	$K_2[RhH(H_2O)(CN)_4]$ 24	$K_3[RhH(CN)_5]$ 25	$K_3[RhH(CN)_5] \cdot H_2O$ 48	$K_2[RhH(H_2O)(CN)_4]$ 54	$K_3[RhH(CN)_5]$ 54	this work
ν_{OH}	3490m					3600m 3530m
ν_{CN}	2103s	2138 2123 2110	2114vs 2093w,sh 2077w	2115	2110	2138sh 2123vs 2110sh
ν_{Rh-H}	1976m	1970	1983m,br	1990	1950	1980m,br
$(\nu_{Rh-H} - 2)$	(1429)	(1427)				(1430)
$\delta_{(HOH)}$	1635		1620m,shp			1615m,shp
δ_{Rh-H}	781	781	782m			781m
$(\delta_{Rh-H} - 2)$		(582)				(581)
ν_{Rh-C}		508	511m			510m
ν_{RhCN}		487	490m 389m 354m 305w			498m 390m

TABLE 2.7 Raman data for $K_3[RhH(CN)_5] \cdot H_2O$

ASSIGNMENT	SOLID	AQUEOUS SOLUTION	METHANOL SOLUTION
	this work	this work	48
ν_{CN}	2163(3)	2147(10)p	2147(10)p
	2153(10)	2127(5)dp	2126(3)
	2140(7)	2119(2)dp	2110(1)
	2130(2)		
	2120(2)		
ν_{Rh-H}	1980(1)	1961(2)p	1952(2)p

2127 cm^{-1} (Rh) and 2125 cm^{-1} (Ir) as the B_1 mode and the weak band at 2119 cm^{-1} (Rh) and 2117 cm^{-1} (Ir) as the E mode. The Raman spectrum of $[RhH(CN)_5]^{3-}$ is similar to that reported by Jewsbury and Maher,⁴⁸ who assumed that the two A_1 modes due to the cis and trans ν_{CN} overlap. This seems unlikely in view of our crystal structure determination (Section 2.3.4, p. 54) and some simple force constant calculations discussed more fully in Chapter 3 (p. 103).

The sharp bands in the ν_{OH} region at 3600 and 3530 cm^{-1} and in the δ_{HOH} region at 1615 cm^{-1} indicate the presence of water which is held in the crystal lattice.

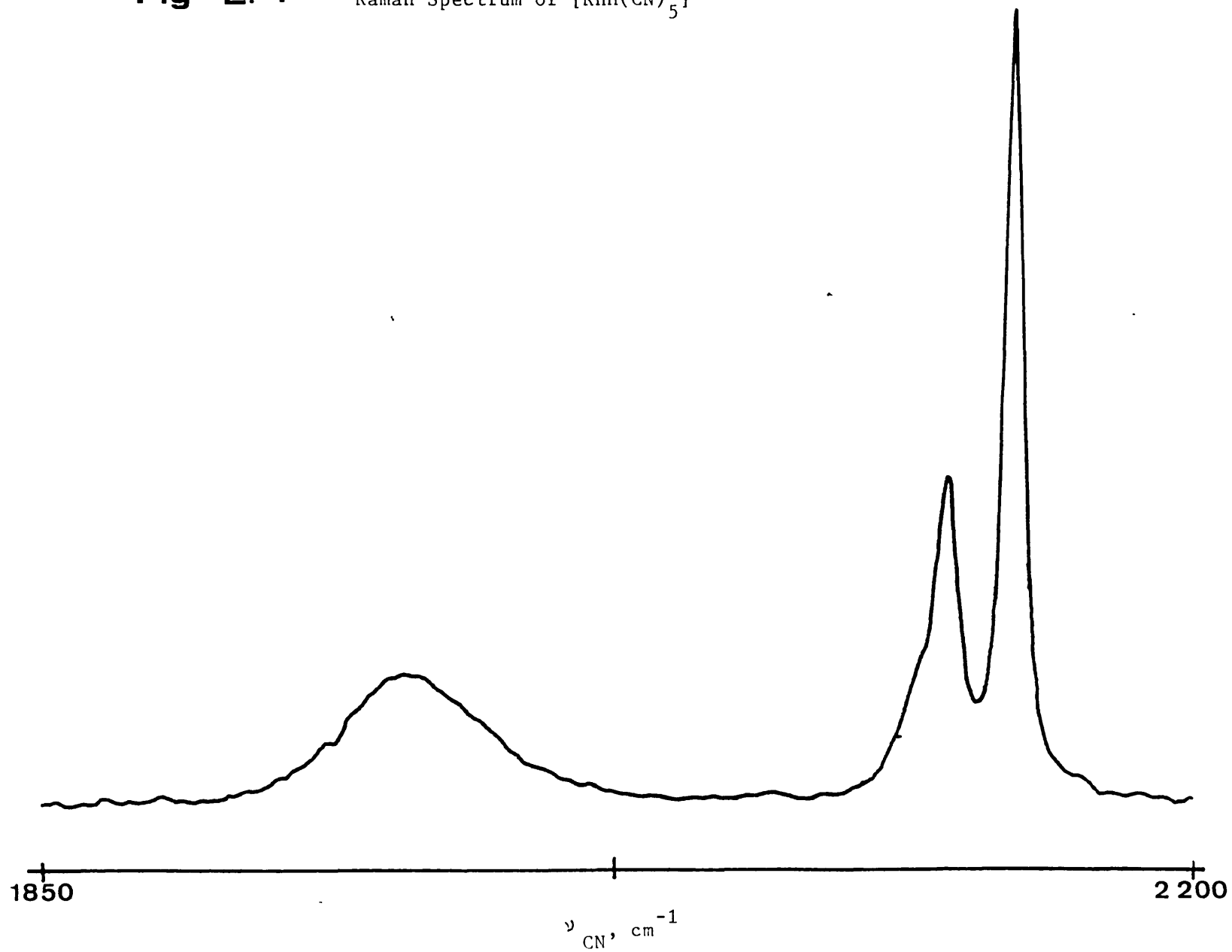
It is interesting to note that the metal-hydrogen stretching frequency increases down the group; ν_{Co-H} : 1860 cm^{-1} ,⁴⁷ ν_{Rh-H} : 1980 cm^{-1} ν_{Ir-H} : 2040 cm^{-1} . This increasing bond strength down the group is

TABLE 2.8 Infrared and Raman data for $\text{K}_3[\text{IrH}(\text{CN})_5] \cdot \text{H}_2\text{O}$

	INFRARED		INFRARED	RAMAN	RAMAN
	25	this work	solution	solid	solution
ν_{CN}	2152sh	2150sh	2125s	2154(10)	2152(10)p
	2127sh	2123sh	2110vs	2130(10)	2125(5)dp
	2110vs	2110vs	2080m		2117(2)dp
$\nu_{\text{Ir-H}}$	2043m	2040m, br	2040m	2043(2)	2037(1)p
$(\nu_{\text{Ir-H}}^2)$		(1450)			
	855sh	855m			
$\delta_{\text{Ir-H}}$	810s	811m			
$(\delta_{\text{Ir-H}}^2)$		(603)			
$\delta_{\text{Ir-C}}$	533m	537m			
$\nu_{\text{Ir-CN}}$	513s	515m			
	454w	452m			
	404s	403m			
	386s	395m			
	333w				
	302w				

Fig 2.4

Raman Spectrum of $[\text{RhH}(\text{CN})_5]^{3-}$



born out by the lability of the hydride ligand. In $[\text{CoH}(\text{CN})_5]^{3-}$, the hydride is readily lost contributing to the catalytic activity of the complex; in $[\text{RhH}(\text{CN})_5]^{3-}$ the hydride exchanges with $^2\text{H}_2\text{O}$ slowly over several days while we find that $[\text{Ir}^2\text{H}(\text{CN})_5]^{3-}$ may only be obtained from treating $[\text{Ir}(\text{C}_6\text{H}_8)_2\text{Cl}]$ with KCN in $\text{CH}_3\text{O}^2\text{H}$; no exchange is observed. The equilibrium (5) has been established for the rhodium species but we could find no evidence for the existence of the species $[\text{Ir}(\text{CN})_4]^{3-}$. It was not possible to study these equilibria either by n.m.r. or Raman spectroscopy as the concentrations of the species required to obtain good spectra would require impossibly high hydroxide concentrations.

The infrared spectrum of 5% ^{15}N enriched $\text{K}_3[\text{RhH}(\text{CN})_5] \cdot \text{H}_2\text{O}$ had an extra band at 2040 cm^{-1} in the $\text{C}\equiv\text{N}$ stretching region which may correspond to the strongest band in the unenriched spectrum at 2123 cm^{-1} .

2.3.3 N.M.R. SPECTROSCOPY

(i) ^1H n.m.r.

The ^1H n.m.r. spectrum of an aqueous solution of $[\text{RhH}(\text{CN})_5]^{3-}$ consists of a doublet arising from spin-spin coupling between ^1H and ^{103}Rh (100% abundant, $I=\frac{1}{2}$). The coupling $J(^1\text{H}, ^{103}\text{Rh})$ is 12.5 Hz. The doublet is observed at δ -11.4 p.p.m., characteristic of the high field values found for metal hydrides.⁵⁸ This shift is comparable with those reported by previous workers (see Table 2.9). The spectrum of $[\text{IrH}(\text{CN})_5]^{3-}$ has a singlet at δ -14.7 p.p.m..

(ii) ^{13}C n.m.r.

The ^1H coupled ^{13}C n.m.r. spectrum of an aqueous solution of $[\text{RhH}(\text{CN})_5]^{3-}$

TABLE 2.9 ^1H CHEMICAL SHIFTS FOR $[\text{RhH}(\text{CN})_5]^{3-}$

δ , p.p.m.	$J(^1\text{H}, ^{103}\text{Rh})$, Hz	Reference
-11.6	13.1	44
-12.6	12.5	24
-11.4	12.8	23
-10.6	12.6	45
-11.4	12.5	47
-11.3	-	54
-11.4	12.5	this work

is shown in Fig. 2.5 and is fully consistent with the pentacyanohydrido formulation. Two sets of double doublets are observed. One set at δ 149 p.p.m. arises from the CN^- group trans to the hydride while that at δ 141 p.p.m., which is four times more intense, arises from the four cis cyanide ligands. These doublets of doublets collapse to doublets on proton decoupling. Coupling between (^{13}C , ^{103}Rh) and (^{13}C , ^1H) gives rise to the observed spectrum. The coupling constants are $J(^{13}\text{C}, ^{103}\text{Rh})$ 34.5, $J(^{13}\text{C}, ^1\text{H}_{\text{trans}})$ 56.6, and $J(^{13}\text{C}, ^1\text{H}_{\text{cis}})$ 5.7 Hz; the latter two being in agreement with those obtained from the ^1H n.m.r. of a ^{13}C enriched sample.⁴⁵ The same spectrum was observed in excess of aqueous cyanide. An extra peak at δ 167 p.p.m. is attributable to free cyanide, its sharpness indicating that no exchange occurs.

It is interesting to note that the trans-CN resonance occurs at a lower field than the cis - a feature which we attribute to the longer trans Rh-C bond (see Section 2.3.4) resulting in deshielding of

Fig 2.5 ^{13}C n.m.r. Spectrum of $[\text{RhH}(\text{CN})_5]^{3-}$



the trans ^{13}C group. This phenomenon is discussed further in Chapter 3, p. 85).

All literature preparations for rhodium hydrido complexes gave a product whose ^{13}C n.m.r. spectrum was as described above. No extra resonances attributable to trans- $[\text{RhH}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ were observed.

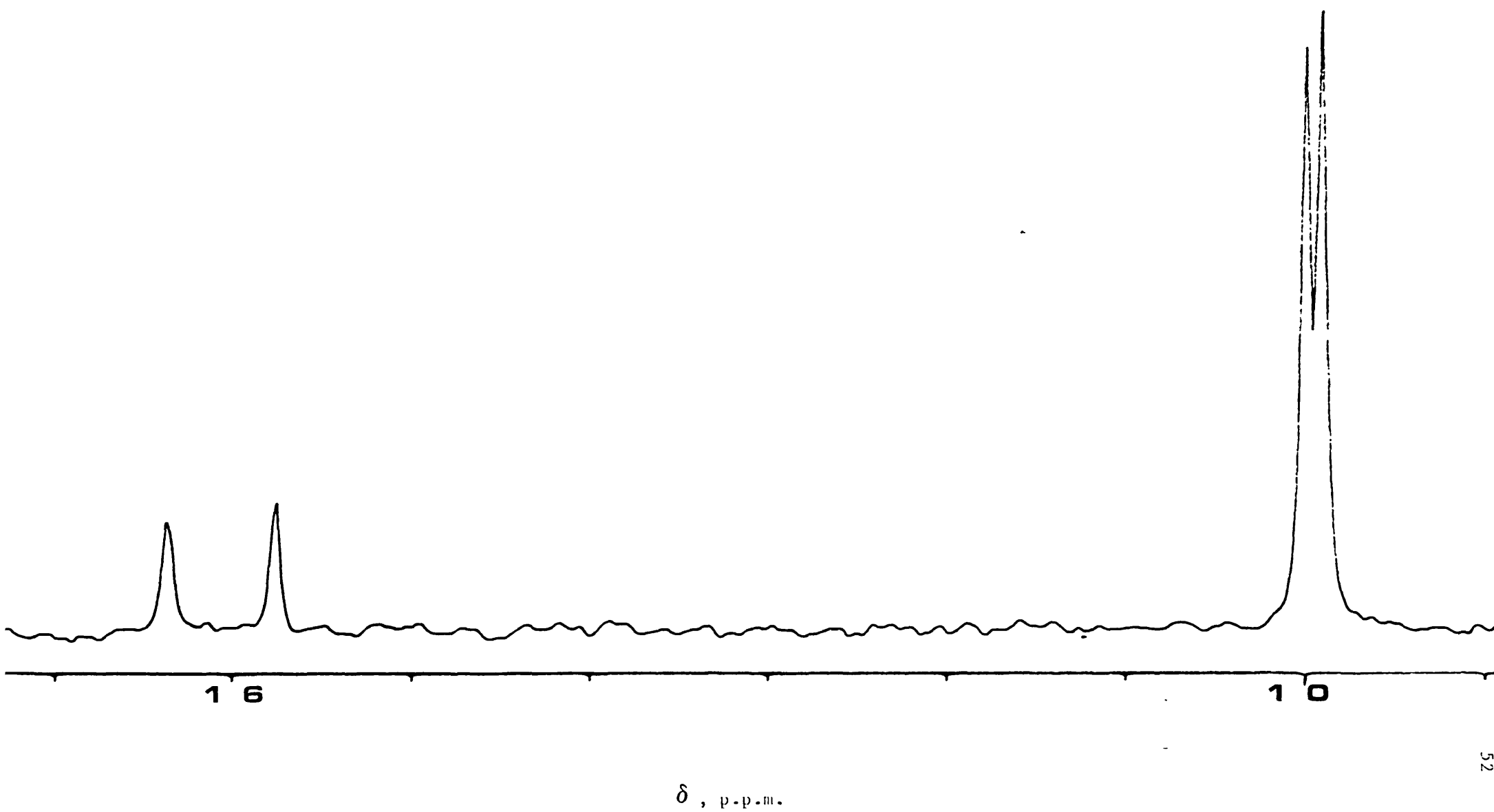
The proton coupled ^{13}C n.m.r. spectrum of $[\text{IrH}(\text{CN})_5]^{3-}$ is illustrated in Fig. 2.6. The structure is much simpler than that of $[\text{RhH}(\text{CN})_5]^{3-}$. There are two doublets, one at $\delta 126$ p.p.m. attributable to CN^- trans to the hydride and one at $\delta 120$ p.p.m., which is four times more intense, attributable to the four cis cyanide ligands. The coupling constants are $J(^{13}\text{C}, ^1\text{H}_{\text{cis}})$ 5.5, $J(^{13}\text{C}, ^1\text{H}_{\text{trans}})$ 38.0 Hz. The cis coupling constant is similar to that observed for the rhodium complex but the trans is somewhat smaller. On proton decoupling the doublets collapse to singlets.

(iii) Nitrogen n.m.r.

There are two naturally occurring isotopes of nitrogen, ^{14}N and ^{15}N . The former has a natural abundance of 99.64%, possesses a spin quantum number, $I=1$ and is consequently endowed with an electric quadrupole moment. ^{15}N is only 0.36% abundant and, since $I=\frac{1}{2}$, there is no quadrupole moment. Hence, although ^{14}N has nearly six times the receptivity of ^{13}C due to its high abundance, its quadrupole moment results in broad lines (100 Hz or more). ^{15}N gives rise to sharp lines but its receptivity is one fiftieth that of carbon.

We have recorded both the ^{14}N and ^{15}N n.m.r. spectra of aqueous solutions of $[\text{RhH}(\text{CN})_5]^{3-}$. The ^{14}N n.m.r. spectrum consisted of a broad line at $\delta -100$ p.p.m. (relative to NH_4NO_3) ; $\omega_{\frac{1}{2}} = 51$ Hz. No

Fig 2.6 ^{13}C n.m.r. Spectrum of $[\text{IrH}(\text{CN})_5]^{3-}$



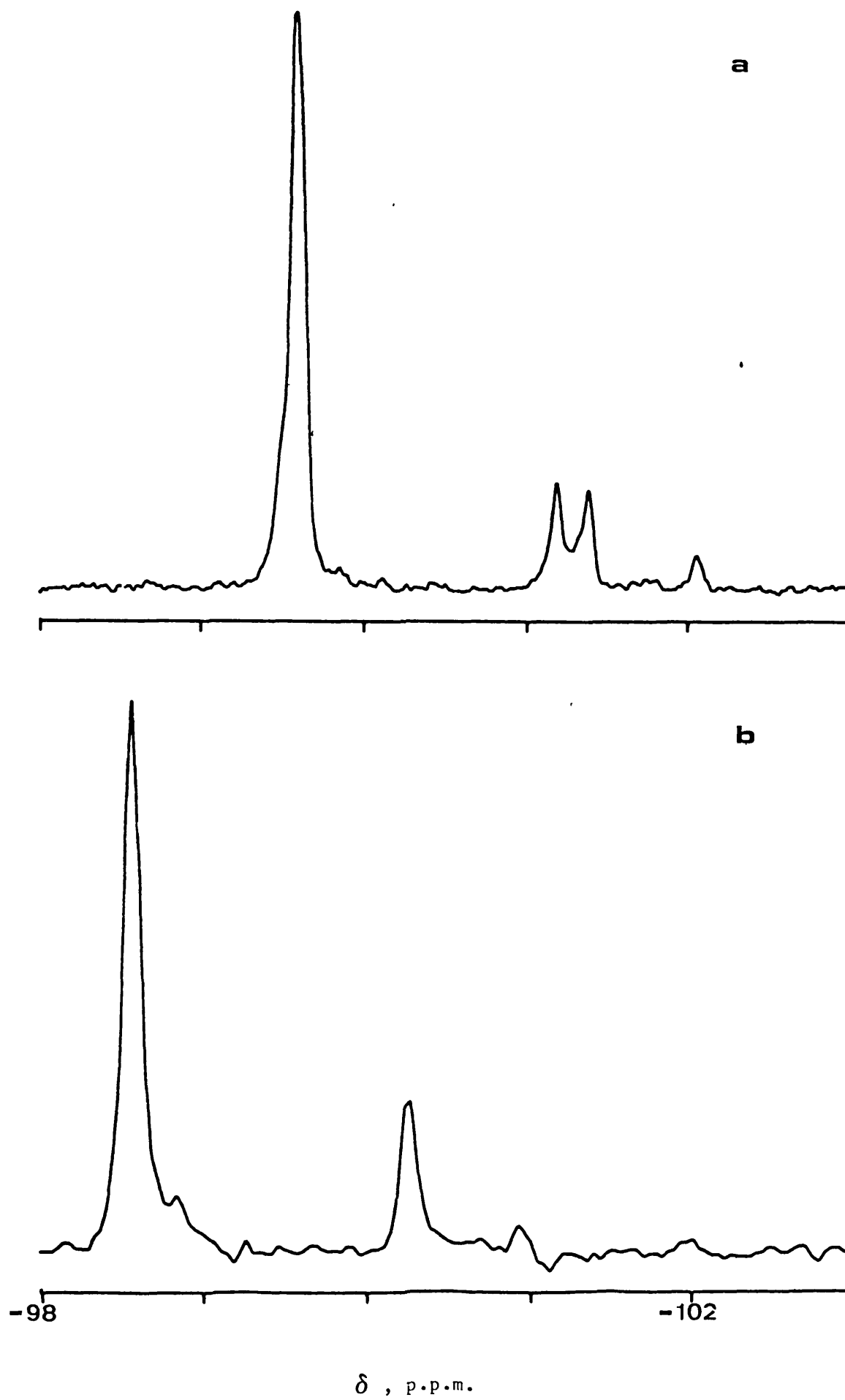


Fig 2.7 ^{15}N n.m.r. spectra of $[\text{RhH}(\text{CN})_5]^{3-}$

rhodium-nitrogen coupling was apparent and the cis and trans environments were not distinguished.

The ^{15}N n.m.r., however, yielded better results. A sample of $\text{K}_3[\text{RhH}(\text{CN})_5]$ was prepared from $[\text{Rh}(\text{C}_8\text{H}_{12})\text{Cl}]_2$ and KC^{14}N (1.5g) and KC^{15}N (0.5g). A ^1H n.m.r. spectrum had the doublet at δ -11.4 p.p.m. but each component of the doublet had a satellite due to (^1H , ^{15}N) coupling. The coupling constant was 4.4 Hz. The proton decoupled ^{15}N n.m.r. spectrum exhibited two resonances, the first at -100.2 p.p.m. (relative to aqueous NO_3^-) and the second, which was approximately four times more intense, at -98.5 p.p.m.. The line width of these resonances was 3.4 Hz at half height indicating broadening of the peak due to unresolved rhodium coupling (Fig. 2.7b). In the ^1H coupled spectrum, there was again a singlet at -99.6 p.p.m. ($\omega_{\frac{1}{2}}=3.4$ Hz) attributable to C^{15}N cis to the hydride and a doublet centred at -101.3 p.p.m. due to C^{15}N trans to the hydride, $J(^{15}\text{N}, ^1\text{H}_{\text{trans}})$ 5.0 Hz. The (^{15}N , ^{103}Rh) and (^{15}N , $^{13}\text{C}_{\text{cis}}$) coupling was too small to be resolved but was responsible for the observed line broadening. (Fig. 2.7a)

The rhodium-nitrogen coupling over two bonds, $\text{Rh}-\text{C}\equiv\text{N}$, is less than 3.4 Hz as compared to direct rhodium-nitrogen coupling in $[\text{RhH}(\text{NH}_3)_5]^{2+}$ where we find that $J(^{15}\text{N}, ^{103}\text{Rh})$ is 14.25 Hz and the doublet is observed at -426.0 p.p.m.. Both compounds exhibit chemical shifts in the regions typical for metal cyano complexes (δ -100 to -150 p.p.m.) and metal ammine complexes (δ -350 to -470 p.p.m.).⁵⁹

2.3.4 THE X-RAY CRYSTAL STRUCTURE OF $\text{K}_3[\text{RhH}(\text{CN})_5]\cdot\text{H}_2\text{O}$

Crystals of $\text{K}_3[\text{RhH}(\text{CN})_5]\cdot\text{H}_2\text{O}$ were prepared by the method of Wilkinson et al²⁴ from $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and methanolic KCN and recrystallized from

water-methanol under argon. This procedure is reported to yield $\text{K}_2[\text{RhH}(\text{H}_2\text{O})(\text{CN})_4]$.²⁴ The crystal used for X-ray work was coated with varnish to minimise decomposition.

Crystal Data: $\text{K}_3[\text{RhH}(\text{CN})_5] \cdot \text{H}_2\text{O}$, triclinic, $a = 7.889(2)$, $b = 8.677(2)$, $c = 8.891(2)$ Å, $\alpha = 88.91(2)$, $\beta = 86.18(2)$, $\gamma = 82.12(2)^\circ$, $U = 601.5$ Å³ (at 19°C), space group $\text{P}\bar{1}$, $z = 2$. A total of 1631 independent reflections were measured of which 105 were 'unobserved'. The structure was solved by Patterson and Fourier methods, and least-squares refinement reached $R = 0.0235$. The program system SHELXTL⁶¹ was used throughout the calculations, and the procedures described in reference 62 were used to help confirm the position of the hydride hydrogen atom derived from least-squares refinement.

Figure 2.8 shows the structure of the anion and the relevant bond lengths and angles are listed in Table 2.10. There is a slight distortion of the octahedral geometry in that the four equatorial cyanide groups are moved towards the hydrogen atom, such that the mean C (axial)-Rh-C (equatorial) angle is 92.5° . The Rh-C distance trans to the hydrido ligand is $2.082(4)$ Å, while the four equatorial Rh-C distances, which are all closely similar, average 2.002 Å. This lengthening of ca. 0.08 Å presumably indicates the higher trans-influence of H as compared with the CN^- ligand. The Rh-H distance of $1.64(4)$ Å is in the range found for transition metal - hydrogen terminal bonds.⁶³

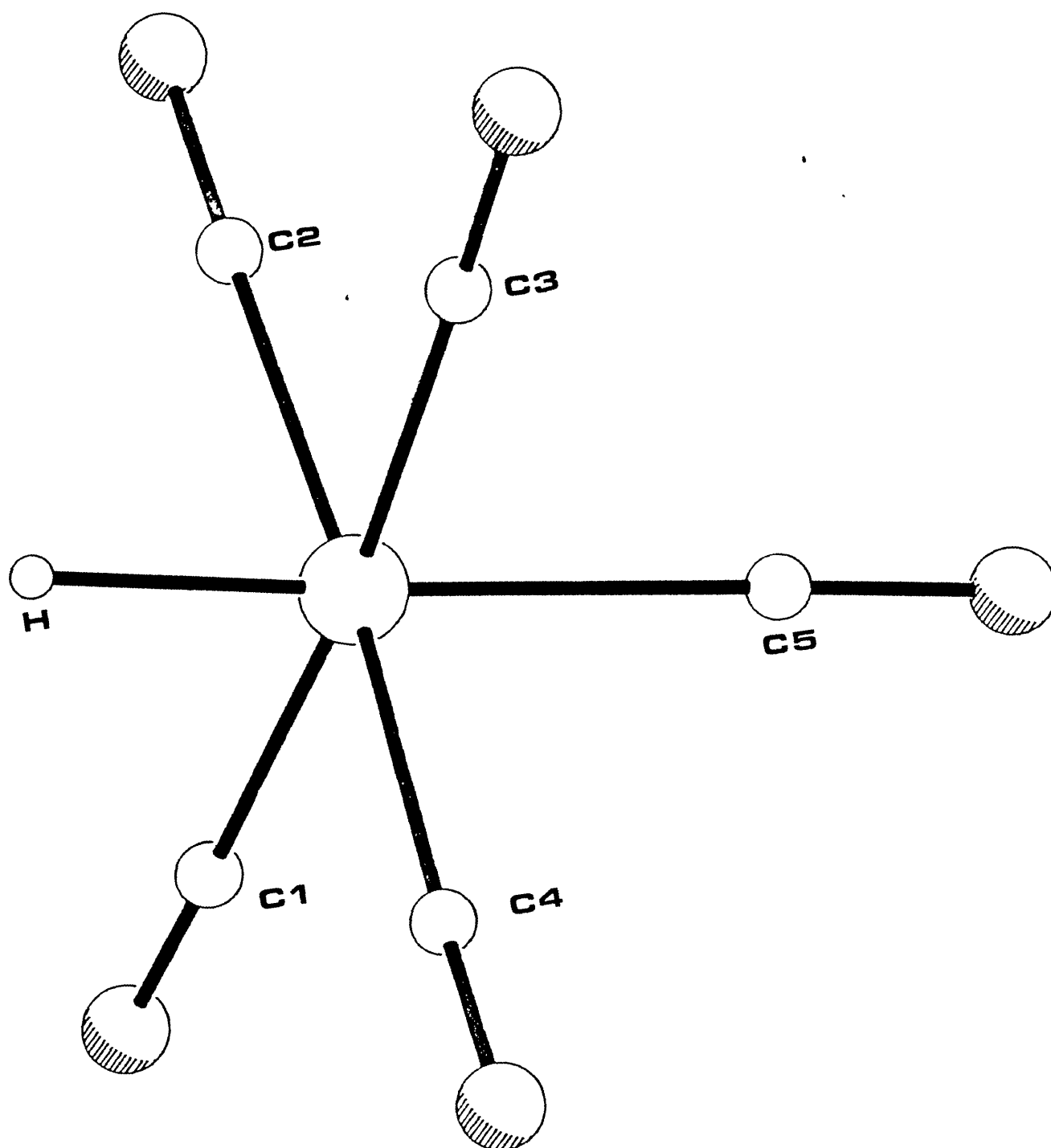


Fig 2.8 The $[\text{RhH}(\text{CN})_5]^{3-}$ Anion

TABLE 2.10 Bond Lengths (Å) and Bond Angles (°) for $K_3[RhH(CN)_5] \cdot H_2O$

Rh(1)-C(1)	2.005(4)	C(1)-N(1)	1.141(6)
Rh(1)-C(2)	2.002(5)	C(2)-N(2)	1.146(6)
Rh(1)-C(3)	2.001(4)	C(3)-N(3)	1.144(6)
Rh(1)-C(4)	2.001(4)	C(4)-N(4)	1.157(6)
Rh(1)-C(5)	2.081(5)	C(5)-N(5)	1.150(7)
Rh(1)-H(1)	1.640(40)		
C(1)-Rh-C(2)	89.6(2)	C(3)-Rh-C(5)	93.2(2)
C(1)-Rh-C(3)	174.5(2)	C(3)-Rh-H	84.7(15)
C(1)-Rh-C(4)	91.1(2)	C(4)-Rh-C(5)	93.2(2)
C(1)-Rh-C(5)	92.4(2)	C(4)-Rh-H	88.7(15)
C(1)-Rh-H	90.3(15)	C(5)-Rh-H	176.6(15)
C(2)-Rh-C(4)	174.6(2)	Rh-C(1)-N(1)	177.7(4)
C(2)-Rh-C(5)	92.1(2)	Rh-C(2)-N(2)	178.6(4)
C(2)-Rh-H	86.0(15)	Rh-C(3)-N(3)	177.7(4)
C(3)-Rh-C(2)	87.5(2)	Rh-C(4)-N(4)	177.9(4)
C(3)-Rh-C(4)	91.4(2)	Rh-C(5)-N(5)	178.5(4)

2.3.5 REACTIONS OF $K_3[MH(CN)_5] \cdot H_2O$ (M = Rh, Ir)

Some reactions of $[RhH(H_2O)(CN)_4]^{2-}$ with oxygen, nitric oxide and tetrafluoroethylene to give $K_4[(NC)_4(H_2O)RhO_2Rh(OH_2)(CN)_4]$, $K_2[Rh(H_2O)(NO_2)(CN)_4]$ and $K_3[Rh(C_2F_4H)(CN)_5]$ respectively have been reported.²⁴ We find that $[RhH(CN)_5]^{3-}$ in aqueous solution reacts with oxygen to give $K_4[(NC)_4(H_2O)Rh]_2(\mu-O_2)$ as reported by Wilkinson *et al*²⁴ but we could detect no trace of a previously reported hydroperoxide.⁴⁶ Reaction with NO and SO₂ respectively yielded $K_2[Rh(H_2O)(CN)_4(NO_2)]$ and $K_2[Rh(SO_3)(CN)_3(H_2O)_2]$.

Reaction of $[CoH(CN)_5]^{3-}$ with $Hg(CN)_2$ in aqueous solution is reported to give $K_6[(NC)_5Co-Hg-Co(CN)_5]$ via an intermediate species $[(CN)_5Co-Hg(CN)]^{3-}$.⁶⁴ We found that a similar reaction with $[RhH(CN)_5]^{3-}$ resulted in formation of $K_3[(NC)_5Rh-Hg(CN)] \cdot H_2O$. A polarised band at 193 cm^{-1} in the Raman spectrum assigned as $\nu(Rh-Hg)$ and a doublet in the ^{199}Hg n.m.r. spectrum, $J(^{199}Hg, ^{103}Rh)$ 270 Hz, indicate the presence of a rhodium-mercury bond.

Reactions were also observed with CO₂, yielding a grey solid with carbonate bands (at 1010, 970, 835, 770, 685, 642 and 385 cm^{-1}) in the infrared spectrum; and with hydrogen peroxide giving the μ -peroxo dimer mentioned above via an unstable peroxy species (ν_{O-O} 870, ν_{CN} 2127 cm^{-1} , % O₂²⁻ 22.2%) Neither of these species could be reproducibly characterised, although the latter may well contain hydrogen peroxide of crystallisation. We could find no reaction with carbon disulphide, sulphur or NO₂.

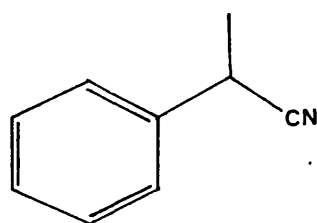
No reaction was observed between $[IrH(CN)_5]^{3-}$ and dienes, oxygen, CO₂, NO or H₂O₂. A reaction did occur with SO₂ to give a product with both sulphito bands and ν_{Ir-H} bands in the infrared and Raman spectra. Microanalysis were consistent with the formulation $K_5[IrH(CN)_3(SO_3)_2] \cdot H_2O$. (see experimental section, p. 67).

SECTION 2.4 CYANIDE HYDRIDE COMPLEXES OF OTHER TRANSITION METAL COMPLEXES

2.4.1 NICKEL, PALLADIUM AND PLATINUM COMPLEXES

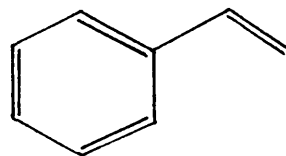
Although nickel phosphine complexes will oxidatively add HCN to yield complexes of the type $[\text{Ni}(\text{H})(\text{PR}_3)_3(\text{CN})]^{65}$, no cyanide hydride complex has been isolated. A species of the type $[\text{NiH}(\text{CN})_3]^{2-}$ was proposed as an intermediate in a hydrocyanation reaction⁶⁶ but no experimental data were presented. Palladium⁶⁷ and platinum⁴⁴ species have been detected by ^1H n.m.r. in solution only and recently the compound $[\text{K}(18\text{-crown-6})]_2[\text{PtH}(\text{CN})_3]$ was isolated.²⁶

We have been unable to isolate or detect in solution a cyanide hydride of nickel. Treatment of $[\text{Ni}(\text{CN})_4]^{2-}$ with sodium amalgam yielded the dark-red dimer, $[\text{Ni}_2(\text{CN})_6]^{4-}$. Treatment of an aqueous solution of $\text{K}_2[\text{Pt}(\text{CN})_4]$ with sodium borohydride or sodium amalgam resulted in the formation of a hydride species observed by ^1H n.m.r.. A 1:4:1 triplet was observed at δ -8.7 p.p.m., $J(^1\text{H}, ^{195}\text{Pt})$ 880 Hz. (Pidcock and Almeida²⁶ reported the ^1H resonance at -12.97 p.p.m. in 2-furyl solution, $J(^1\text{H}, ^{195}\text{Pt})$ 738 Hz.) Attempts to record a ^{13}C n.m.r. spectrum of this solution resulted in one resonance at δ 127 p.p.m., $J(^{13}\text{C}, ^{195}\text{Pt})$ 1029 Hz, attributable to $[\text{Pt}(\text{CN})_4]^{2-}$.⁶⁸ No reaction was observed between $[\text{Pd}(\text{CN})_4]^{2-}$ and sodium borohydride but with sodium amalgam, a solution was obtained whose ^1H n.m.r. spectrum exhibited a resonance at δ -10.6 p.p.m.. Attempts to isolate these hydrido species from solution invariably resulted in loss of hydrogen and precipitation of $\text{K}_2[\text{M}(\text{CN})_4]$ ($\text{M} = \text{Pd}, \text{Pt}$).



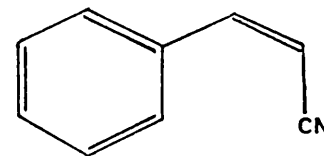
(1)

B.Pt. 230-2°C



(2)

B.Pt. 145.2°C



(3)

B.Pt. cis 249.0°C
trans 263.8°C

We repeated this reaction under the conditions given⁶⁶ (see Experimental Section, p. 67) with a number of cyano complexes and cyanide hydride complexes. The results are summarised in Table 2.11. The reaction mixture was extracted with ether, evaporated to low volume and examined by gas chromatography and by ^1H n.m.r.. The aqueous phase was also examined by ^1H n.m.r. for the presence of hydrides.

Although several hydrides effected the hydrocyanation and hydrogenation reaction, we found that the transformation was stoichiometric rather than catalytic. No trace of a hydride was detected at the end of the reactions and no reaction occurred in the absence of cyanide and /or borohydride. Addition of benzyltriethylammonium chloride as a phase transfer catalyst had no effect upon the reaction rate.

TABLE 2.11 Yields of 2-phenylpropionitrile from reactions between phenylacetylene and transition metal cyano and cyanide hydride complexes.

Cyanide Complex	Reaction	Yield, %
None	None	-
$\text{K}_2[\text{Ni}(\text{CN})_4]$	Yes	85
$\text{K}_2[\text{Pd}(\text{CN})_4]$	None	-
$\text{K}_2[\text{Pt}(\text{CN})_4]$	None	-
$\text{K}_6[\text{Co}_2(\text{CN})_{10}]$	None	-
$\text{K}_3[\text{RhH}(\text{CN})_5]$	Yes	75
$\text{K}_3[\text{IrH}(\text{CN})_5]$	None	-
$\text{K}_4[\text{MoH}(\text{CN})_7]$	Yes	92
$\text{K}_4[\text{WH}(\text{CN})_7]$	Yes	94

SECTION 2.6 EXPERIMENTAL

All operations were carried out under argon unless otherwise stated using standard Schlenk and septum and needle techniques. All organic solvents were dried and distilled before use. All reagents were used as supplied unless otherwise stated.

Preparation of Potassium Heptacyanomolybdate(II)hydrate, $K_5[Mo(CN)_7] \cdot H_2O$

This complex was prepared from dimolybdenum tetraacetate⁶⁹ and potassium cyanide using the method of Kiernan and Griffith.³⁴

Potassium heptacyanohydrogenmolybdate(II)dihydrate, $K_4[MoH(CN)_7] \cdot 2H_2O$

The complex $K_5[Mo(CN)_7] \cdot H_2O$ (0.72g, 1.47 mmol) was dissolved in deoxygenated water and the resultant yellow solution cooled in an ice-salt bath. To the stirred solution was slowly added L-ascorbic acid solution (0.1 mol dm^{-3}), acetic acid (0.1 mol dm^{-3}) or hydrochloric acid (0.1 mol dm^{-3}) from a syringe until the solution was dark green in colour (ca $5\text{-}10 \text{ cm}^3$ required). This reaction could also be effected by passing H_2S through the solution for one hour. Addition of methanol (20 cm^3) precipitated green microcrystals which were filtered, washed with methanol (5 cm^3) and ether (5 cm^3). The product was recrystallised from water/methanol (1:3) and dried in vacuo.

Yield: 0.62g, 89.8%

Found: C, 18.7; H, 0.95; K, 32.9; N, 20.9. $C_7H_5K_4MoN_7O_2$ requires

C, 17.8; H, 1.1; K, 33.2; N, 20.8%.

Potassium heptacyano(hydrogensulphito)molybdate(IV), $K_4[Mo(OSO_2H)(CN)_7]$

Sulphur dioxide was bubbled through a solution of $K_4[MoH(CN)_7] \cdot 2H_2O$

(0.5g, 1.06 mmol) in aqueous potassium cyanide (0.01 mol dm^{-3} , 5 cm^3) for thirty minutes. The colour changed from green to yellow-orange and addition of ethanol (10 cm^3) precipitated an orange solid. This was filtered in air and washed with ethanol (5 cm^3) and ether (5 cm^3).

Yield: 0.44g, 80.0%

Found: C, 16.2; H, 0.18; K, 30.0; N, 19.1; S, 6.2. $\text{C}_7\text{HK}_4\text{MoN}_7\text{O}_3\text{S}$ requires C, 16.3; H, 0.19; K, 30.3; N, 19.0; S, 6.21%.

Infrared Spectrum The following bands were observed:

ν_{CN} 2103vs
1235s,br; 1150vs;br; 1035m,br; 965s
600w, 360m,br

Heptakis(t-butylisocyano)molybdate(II)hexafluorophosphate, $[\text{Mo}(\text{CNBu}^t)_7](\text{PF}_6)_2$

This was prepared using the method of Lippard et al⁷⁰ from $\text{Mo}(\text{CO})_6$ and t-butylisocyanide.

Found: C, 43.5; H, 6.45; N, 10.1. $\text{C}_{35}\text{F}_{12}\text{H}_{63}\text{MoN}_7\text{P}_2$ requires C, 43.4; H, 6.5; N, 10.1%.

Potassium pentacyanohydrogenrhodate(III)monohydrate, $\text{K}_3[\text{RhH}(\text{CN})_5]\cdot\text{H}_2\text{O}$

- (a) This preparation is a modified version of that described by Whitesides and Maglio.⁴⁵ Potassium cyanide (2.0g, 30 mmol) was added, with vigorous stirring, to a refluxing solution of methanol (80 cm^3) under nitrogen. When all the solid had dissolved, finely ground $[\text{Rh}(\text{C}_8\text{H}_{12})\text{Cl}]_2$ ⁷¹ (0.77g, 1.6 mmol) was slowly added to the boiling solution. The resultant purple solution was heated under reflux for fifteen minutes and cooled. The greyish solid was filtered and washed with ethanol and ether. The crude product was redissolved in the minimum volume of water, filtered under nitrogen and ethanol (20 cm^3) added. The white product was filtered, washed with ether (5 cm^3)

and dried in vacuo.

Yield: 1.0g, 86.6%

Found: C, 16.4; H, 0.8; K, 24.3; N, 19.1. $C_5H_3K_3N_5ORh$ requires C, 16.3; H, 0.9; K, 24.6; N, 19.0%.

- (b) This method is that described by Wilkinson et al²⁴ to yield $K_2[RhH(H_2O)(CN)_4]$. To a solution of $[Rh(CO)_2Cl]_2$ (1.0g, 5.3 mmol) in methanol (15 cm³) was added a saturated solution of KCN in methanol until precipitation of a blue solid ceased. To this suspension of $[Rh(CO)_2(CN)]_n$ was added a saturated solution of KCN in aqueous methanol (1:10) until evolution of carbon monoxide ceased. The white product was filtered, washed with methanol (5 cm³) and ether (5 cm³) and recrystallised from water/methanol (1:3).

Yield: 1.73g, 88.7%

Found: C, 16.2; H, 0.8; K, 24.4; N, 19.1. $C_5H_3K_3N_5ORh$ requires C, 16.3; H, 0.9; K, 24.6; N, 19.0. $C_4H_3K_2N_4ORh$ requires C, 15.8; H, 1.0, K, 25.7; N, 18.4%.

Potassium pentacyanohydrogeniridate(III)hydrate, $K_3[IrH(CN)_5] \cdot H_2O$

This is a modified version of the preparation described by Krogmann and Binder.²⁵ Finely powdered $[Ir(C_6H_8)_2Cl]$ ⁷² (0.4g, 1.0 mmol) was slowly added to a refluxing solution of potassium cyanide (0.67g, 10 mmol) in methanol (20 cm³). The mixture was refluxed with stirring for two hours under nitrogen during which time the product precipitated. The solution was cooled and the white product filtered, washed with methanol (5 cm³) and ether (5 cm³) and air-dried.

Yield: 0.36g, 82.0%

Found: C, 13.1; H, 0.6; K, 25.1; N, 14.8. $C_5H_3IrK_3N_5O$ requires C, 13.1; H, 0.7; K, 25.5; N, 15.3%.

Reactions of $K_3[RhH(CN)_5].H_2O$

(i) Reaction with Oxygen

Potassium μ -peroxobis[aquopentacyanorhodate(III)], $K_4[(H_2O(NC)_4Rh(\mu-O_2)(CN)_4(OH_2))_2]$

Oxygen was bubbled through an aqueous solution of $K_3[RhH(CN)_5].H_2O$ (0.5g, 1.36 mmol) for 24 hours. Addition of ethanol produced a white precipitate which was filtered, washed with ethanol and ether and air-dried. The same result was obtained after passing oxygen through the solution for thirty minutes.

Yield: 0.3g, 70.0%

Found: C, 15.4; H, 0.9; K, 24.0; N, 17.5; O_{peroxo}, 5.6. $C_8H_4K_4N_8O_4Rh_2$ requires C, 15.0; H, 0.7; K, 24.5; N, 17.6; O_{peroxo}, 5.1%.

Infrared Spectrum

ν_{OH}	3560s, 3472s
ν_{CN}	2123vs
ν_{O-O}	830m
δ_{RhCN}, ν_{RhC}	513m, 430s, 380s, 365sh

(ii) Reaction with Nitric Oxide

Potassium aquonitrotetracyanorhodate(III), $K_2[Rh(H_2O)(NO_2)(CN)_4]$

Nitric oxide was passed through an aqueous solution (5 cm³) of $K_3[RhH(CN)_5].H_2O$ (0.5g, 1.36 mmol) for thirty minutes. Addition of ethanol precipitated a white solid which was filtered and recrystallised from water/ethanol (1:3).

Yield: 0.40g, 85.0%

Found: C, 13.5; H, 0.4; K, 22.0; N, 20.4. $C_4H_2K_2N_5O_3Rh$ requires C, 13.8; H, 0.6; K, 22.35; N, 20.1%.

Infrared Spectrum

The following bands were observed:

ν_{OH}	3450w
ν_{CN}	2126vs
$\nu_{\text{asym NO}_2}$	1400vs, 1398vs
$\nu_{\text{sym NO}_2}$	1250vs
ρ_{ONO}	830vs

(iii) Reaction with Sulphur Dioxide

Potassium bisaquosulphitotriscyanorhodate(III), $\text{K}_2[\text{Rh}(\text{SO}_3)(\text{H}_2\text{O})_2(\text{CN})_3]$

Sulphur dioxide was bubbled through a solution of $\text{K}_3[\text{RhH}(\text{CN})_5] \cdot \text{H}_2\text{O}$ (0.50g, 1.36 mmol) in water (5 cm³) for one hour. Addition of ethanol precipitated a white product which was filtered, washed with ethanol and ether and air-dried.

Yield: 0.48g, 95.1%

Found: C, 9.2; H, 0.7; K, 19.9; N, 11.5; S, 8.0. $\text{C}_3\text{H}_4\text{K}_2\text{N}_3\text{O}_5\text{RhS}$ requires C, 9.6; H, 1.1; K, 20.8; N, 11.2; S, 8.5%.

Infrared Spectrum

ν_{CN}	2135s, 2127s
ν_{SO}	1145s, 1110vs, 1055s, 1050s, 975vs
	650s, 618s
	555m, 529m, 518m, 433s, 400s, br, 355w

(iv) Reaction with Mercuric Cyanide

Potassium (cyano)(pentacyanorhodate(III))mercury hydrate, $\text{K}_3[(\text{NC})_5\text{RhHg}(\text{CN})] \cdot \text{H}_2\text{O}$

Solid mercuric cyanide (0.1g, 0.4 mmol) was added to an aqueous solution of $\text{K}_3[\text{RhH}(\text{CN})_5] \cdot \text{H}_2\text{O}$ (0.28g, 0.8 mmol) under argon. The resultant solution was stirred overnight. Addition of ethanol precipitated a white solid which was filtered, washed with ethanol and dried in vacuo.

Yield: 0.23g, 98% (based on Hg)

Found: C, 12.2; H, 0.1; K, 19.5; N, 13.9. $\text{C}_6\text{H}_2\text{HgK}_3\text{N}_6\text{ORh}$ requires C, 12.1; H, 0.3; K, 19.7; N, 14.1%.

Infrared Spectrum

Bands were observed at 2145w,sh; 2135s; 2100s (ν_{CN}) and at 1155, 970, 524, 510, 440, 390, 330 cm^{-1} .

Raman Spectrum

In aqueous solution ν_{CN} 2170(6)p, 2144(10)p, 2124(4)dp, 2118(3)dp
 $\nu_{\text{Rh-H}}$ 193(4)p

Reactions of $\text{K}_3[\text{IrH}(\text{CN})_5]\cdot\text{H}_2\text{O}$

Reaction with Sulphur Dioxide

Potassium hydridobis(sulphito)tris(cyano)iridate(III)hydrate, $\text{K}_5[\text{IrH}(\text{CN})_3(\text{SO}_3)_2]$

Sulphur dioxide was bubbled through a saturated solution of $\text{K}_3[\text{IrH}(\text{CN})_5]\cdot\text{H}_2\text{O}$ (0.50g, 1.1 mmol) in water. Addition of ethanol precipitated a white solid which was filtered, washed with ethanol and ether and air-dried.

Yield: 0.65g, 98.0%

Found: C, 5.1; H, 0.5; K, 29.5; N, 6.5; S, 8.7. $\text{C}_3\text{H}_3\text{IrK}_5\text{N}_3\text{O}_7\text{S}_2$ requires C, 5.6; H, 0.5; K, 30.3; N, 6.5; S, 8.9%.

Infrared Spectrum

ν_{CN} 2150sh, 2125s, 2110vs, 2100s
 $\nu_{\text{Ir-H}}$ 2040w
 $\nu_{\text{S-O}}$ 1195s, 1175vs, 1115m, 1095s, 1060m, 970vs
 655s
 567s, 511s, 440s, 430m

Hydrocyanation Reactions

In a typical reaction, $\text{K}_3[\text{RhH}(\text{CN})_5]\cdot\text{H}_2\text{O}$ (0.3g, 0.8mmol), KCN (0.01g, 1.6 mmol) and NaBH_4 (0.008g, 1.6 mmol) were placed in a Schlenk

tube under nitrogen and water (4 cm^3) added from a syringe. This solution was warmed to 45°C in a water bath and phenylacetylene (0.16g , 1.6 mmol) was added. After thirty minutes, ether was added, the organic layer separated, evaporated to low volume and examined by g.l.c. and ^1H n.m.r.. The aqueous layer was also examined by ^1H n.m.r..

CHAPTER THREE

VIBRATIONAL SPECTROSCOPIC AND N.M.R. STUDIES ON TRANSITION METAL CYANO COMPLEXES AND RELATED SPECIES

SECTION 3.1 GENERAL INTRODUCTION

We noted in Chapter Two (Section 2.3.3, p.49) that the trans CN resonance in the ^{13}C n.m.r. spectrum of $[\text{Rh}(\text{CN})_5]^{3-}$ occurs downfield of the cis, a feature which we attribute to the longer trans Rh-C bond. This prompted us to investigate other $[\text{MX}(\text{CN})_5]^{n-}$ species by ^{13}C n.m.r. and infrared and Raman spectroscopy to look for relationships between the trans-influence of the ligand, X; ^{13}C chemical shifts and the force constants of the CN bonds (calculated using the Cotton-Kraihanzel approximation).

We also report ^{13}C , ^{14}N and ^{15}N n.m.r. studies on various other cyano complexes and present an X-ray crystal structure determination of the dimer, $\text{K}_5[\text{Ru}_2\text{N}(\text{CN})_{10}]\cdot 3\text{H}_2\text{O}$.

Attempts to prepare cyano and isocyanide complexes of tantalum and uranium are described and we report extended Raman studies on the complexes $[\text{A}]_4[\text{U}(\text{NCS})_8]$, where $\text{A}=\text{NEt}_4^+$, Cs^+ , in both solid and solution.

SECTION 3.2 VIBRATIONAL SPECTROSCOPIC AND N.M.R. STUDIES ON TRANSITION METAL CYANO COMPLEXES

3.2.1 INTRODUCTION

In this section we present our infrared, Raman and ^{13}C n.m.r.

results. In order to clarify our discussion, we present brief accounts of the 'trans'-influence, the Cotton-Kraihanzel bonding model and n.m.r. studies on cyano complexes.

3.2.2 THE 'TRANS'-INFLUENCE AND ITS MEASUREMENT

The 'trans'-influence of a ligand in a metal complex was defined in 1966 by Pidcock et al⁷³ as the extent to which that ligand weakens the bond trans to itself in the equilibrium state of that complex. The term unambiguously distinguishes this bond weakening effect of a ligand from its trans-effect⁷⁴, defined as the effect of a co-ordinated group, A, upon the rate of substitution reactions of the group trans to it. The 'trans-effect' thus describes a kinetic phenomenon and is a partial description of the transition state in a substitution reaction while the 'trans'-influence manifests itself in the bond strength and bond length of the trans metal-ligand bond in the ground state of the complex. If a substitution reaction proceeds via a dissociative mechanism, the 'trans-effect' and the 'trans-influence' series may often parallel each other; this is not the case in an associative pathway where many other controlling factors are involved.

We will give a brief account of the theories of the 'trans-influence' and its measurement. The literature before 1966 tends to be confused as the 'trans-effect' and 'trans-influence' are not distinguished. An excellent review on the 'trans-influence' is that by Appleton, Clark and Manzer.⁷⁵

The earliest theory of the 'trans-influence' was the polarization theory proposed by Grinberg. The dipole induced in L by the metal, M in turn induces a dipole in M, which tends to repel negative charge

in the trans-ligand, A, hence weakening the M-A bond but not greatly affecting the ligands cis to L. (Fig 3.1). The main disadvantage of

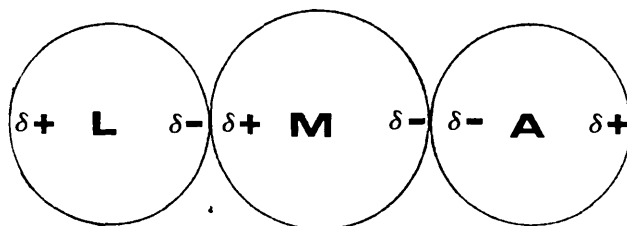


FIGURE 3.1 Grinbergs' Polarization Theory

this theory is that it is electrostatic whilst metals for which the 'trans-influence' is most pronounced are those which form metal-ligand bonds with a high degree of covalency.⁷⁶

Syrkin⁷⁷ gave an explanation of the 'trans-influence' in terms of hybridization of the metal. If a ligand, L, forms a strong covalent bond with the metal, the hybrid orbital used by the metal in this bond will tend to contain a high proportion of metal 5d and 6s orbitals. Since the ligand, L, and the ligand trans to it, A, must both share the same hybrid orbitals, additional d + s participation in the M-L bond will result in decreased availability of these orbitals for bonding by A, which results in a weaker M-A bond. Syrkin predicted a slight strengthening of the bonds to the cis atoms.

The stability of complexes of ligands such as phosphines with "soft" metals (e.g. platinum, gold) was largely ascribed to π back-bonding.⁷⁸ The ability of a ligand to withdraw electrons from the

metal was recognised as possibly being important in stabilising a transition state relative to the ground state in a substitution reaction.^{74,79} In agreement with this hypothesis, π bonding ligands such as ethylene and carbon monoxide had high 'trans-effects' but it was later recognised⁸⁰ that this explanation could not hold for anions with high 'trans-effects' which were not π acceptors e.g. CH_3^- , H^- .

Pidcock et al⁷³ pointed out that metal-phosphine bonds could equally well, or better, be explained in terms of phosphines having a strong σ -inductive effect i.e. high 'trans-influence' which does not depend on extensive M-L π back-bonding. Phosphines would then resemble H^- .⁸⁰ X-ray structural determinations and n.m.r. studies have since shown that phosphines do weaken bonds trans to themselves, irrespective of whether the trans ligand has π -bonding capacity, and conversely M-P bonds are, in turn, weakened when the phosphine is trans to a ligand of high 'trans-influence' with no π -bonding capacity.

Recent theoretical treatments of the bonding in metal complexes⁸¹⁻⁸⁴ have established the concept of metal rehybridization induced by a ligand, L, forming strong covalent bonds with the metal. Theoretical treatments have given no general agreement on the particular type of metal orbital which tends to concentrate in the M-L bond at the expense of the M-A bond trans to it. Vibrational spectroscopy shows the existence of the 'trans-influence' but provides no information on the orbital rearrangement behind it. A beginning has been made by deducing metal hybridization from X-ray bond lengths⁸⁵ and n.m.r. spin-spin coupling constants in terms of Fermi contact. These results seem to suggest that the M-L bond gains s-character at the expense of the trans M-A bond when L has a high 'trans-influence'.

The bulk of the literature on the 'trans-influence' (and indeed,

the 'trans-effect') refers to square planar complexes, in particular those of Pt (II).⁷⁵ The 'trans-influence' series can be investigated in a number of ways - X-ray crystallography, vibrational spectroscopy, nuclear magnetic resonance spectroscopy, nuclear quadrupole resonance and photoelectron spectroscopy have all been used to obtain series.

If a bond M-A, trans to a ligand L is "unusually long" compared with the sum of covalent radii or with the "normal" bond lengths found in other crystal structures, a high 'trans-influence' is ascribed to the ligand, L.

Mason and Towl⁸³ attempted to determine orders of structural 'trans-influence' for Pt(IV), Ir(III), Rh(III) and Co(III), but the foundation of their argument is weaker than those for Pt(II). They proposed that the relative lengthening of a given metal-ligand (A) bond, expressed as a fraction of the value of the bond length when the trans ligand is A itself is a measure of the trans-influencing ability of the trans ligand, L. We may criticise this approach since if A has a high 'trans-influence' itself, the M-A bond trans to A would be expected to be longer than the M-A bond trans to a ligand of low 'trans-influence', such as Cl⁻. We may illustrate this problem using the structure $K_3[Co(C_2F_4H)(CN)_5]$.⁸⁶ The Co-CN bond trans to $HC_2F_4^-$, 1.927(14) Å is slightly longer than the CN⁻ ligand cis to it, 1.894(14) Å. This enables one to decide that $-C_2F_4H^-$ has a high trans-influence comparable to or slightly greater than cyanide. But, since the 'trans-influence' of the cyanide ligand for Co(III) relative to other ligands is not known from other crystal structures, it does not allow one to place $-C_2F_4H^-$ relative to ligands such as other σ -C bonded groups. Another difficulty is that different 'indicator' groups might have different sensitivities towards the structural

'trans-influence'. In a metal carbonyl bond, for example, the effect of synergic σ - π bonding on the M-CO bond length could well outweigh changes induced by the 'trans-influence' of the ligand trans to the CO group. It is consequently difficult to interpret a result such as the observation of essentially equivalent Mn-CO bond lengths in $\text{MnH}(\text{CO})_5$ and small variations in $\nu_{\text{M-CO}}$ in related complexes.⁸⁷ Frenz and Ibers suggested that in these complexes, CO has a slightly higher trans-influence than H^- .⁸⁷

The assumption is usually made that a decrease in the force constant for an M-A stretching vibration indicates a weakening of the M-A bond. For most complexes that have been examined by vibrational spectroscopy force constants are not available and stretching frequencies are used instead, it being considered that a lower M-A stretching frequency corresponds to a weaker bond. Even where force constants have been calculated, the physical significance of the results has been questioned for all but the simplest molecules.⁸⁸ One problem which occurs when the relative trans-influences of donor atoms of very different masses are examined (e.g. Cl^- , Br^- , I^- , PR_3 , AsR_3 , SbR_3), arises from the possibility of a mass effects on the M-A vibration under consideration. As the mass of the other ligands L attached to the metal increases, the "effective mass" of the ML_n unit increases, which will tend to reduce $\nu_{\text{M-A}}$ even if the M-A force constant does not change. This effect has occasionally been considered as a possible source of "trans-influence", e.g. in the series $[\text{MLCl}_3]^-$ ($\text{M}=\text{Pd}, \text{Pt}$; $\text{L}=\text{SR}_2, \text{PR}_3, \text{AsR}_3$)⁸⁹, but is often ignored. Interpretation of M-A stretching frequencies is also complicated by the possibility of vibrational coupling between $\nu_{\text{M-A}}$ and other molecular vibrations. Most authors seem to consider that this coupling can be ignored provided that the frequency $\nu_{\text{M-A}}$ is well separated from that of other vibrational modes that are likely

to couple, especially when M is a heavy metal like platinum.⁹⁰ An example of vibrational coupling where this condition is not met is provided by ν_{M-H} when the hydride is trans to CN^- e.g. in the complex $[Pt(H)(CN)(PEt_3)_2(TCNE)]$;⁹¹ this can be detected on deuteration of the complex as the ν_{CN} vibration shifts.

Another problem can arise from lattice effects on vibrational modes when the spectra are obtained from solid samples. The spectra may then contain bands which are not observed for solutions⁹² and solid state effects may sometimes cause band splittings.⁹³ Generally close agreement is often found between spectra measured for solids and in solution.⁹⁴ In ionic complexes, the counter-ion can also have an effect on the metal-ligand stretching frequency.⁹⁵

3.2.3 N.M.R. STUDIES ON TRANSITION METAL CYANO AND CARBONYL SPECIES

As Fourier transform instrumentation has become widespread, so the use of ^{13}C n.m.r. as a spectroscopic tool for the investigation of metal complexes with carbon-containing ligands has become extensive. The ^{13}C isotope has a natural abundance of 1.1%, a nuclear spin of $\frac{1}{2}$ and a sensitivity relative to protons of 1.59×10^{-2} . Its low abundance is an advantage in studying samples without labelling as, on average, each molecule will contain only one ^{13}C nucleus and so spectra are not complicated by ^{13}C - ^{13}C coupling. Ligands like the cyanide ion and carbonyls have attracted interest as the carbon is directly bonded to the metal often resulting in large chemical shifts and enabling, if the metal has a nuclear spin, the measurement of spin-spin coupling. Although carbonyl complexes have been widely studied,⁹⁶ comparatively little has been reported for cyano complexes. Hirota et al⁹⁷ reported

chemical shifts for some cyano complexes and several octahedral cyano complexes have been investigated.⁹⁸⁻¹⁰³ Pesek and Mason⁶⁸ presented ¹³C n.m.r. spectra for a number of hexa-, tetra- and dicyano complexes (see Table 3.1). Chemical shift differences were discussed in terms of metal oxidation state and changes in the σ and π bonding of CN^- to the metal ion.

Shporer et al¹⁰⁴ reported ¹⁴N n.m.r. spectra for some simple diamagnetic and paramagnetic cyano complexes and a study on some transition metal nitrosyl and nitrosyl cyanide complexes has been carried out.¹⁰⁵

Two papers on ¹³C n.m.r. of monosubstituted pentacarbonyl complexes of tungsten¹⁰⁶ and vanadium¹⁰⁷, $[\text{MX}(\text{CO})_5]^{n-}$, are helpful in providing a comparison between cyano and carbonyl species. The screening constant for a particular nucleus may be expressed as the sum of three contributions:

$$\sigma = \sigma(\text{dia}) + \sigma(\text{para}) + \sigma(\text{other atoms})$$

The diamagnetic shielding term is concerned with electron density at the particular nucleus, $\sigma_d = k' \sum_i 1/r_i$, where r_i is the mean inverse distance of electron i from the nucleus summed over all the electrons on the nucleus.¹⁰⁸ The paramagnetic shielding term, which arises from the mixing of higher electronic states (especially low lying excited states) with the ground state is generally regarded as dominant. A theoretical expression for this term developed by Pople is as follows:¹⁰⁹

$$\sigma_p = \frac{-k}{\Delta E} \langle r^{-3} \rangle 2p (Q_{AA} + Q_{AB})$$

where ΔE = an average excitation energy

$\langle r^{-3} \rangle$ = mean inverse cube of the distance from the nucleus of a carbon 2p electron

Q_{AA} , Q_{AB} is related to the charge density at the nucleus and to the AB bond order. The remaining anisotropy term includes the contribution of electron currents on neighbouring atoms or functional groups.

TABLE 3.1 Chemical Shifts for Diamagnetic Cyano Complexes in $^2\text{H}_2\text{O}$ ⁶⁸

COMPLEX	δ , p.p.m. ^a	COUPLING CONSTANTS, Hz
<u>Octahedral hexacyano complexes</u>		
$[\text{Fe}(\text{CN})_6]^{4-}$	177.2	
$[\text{Ru}(\text{CN})_6]^{4-}$	162.3	
$[\text{Os}(\text{CN})_6]^{4-}$	142.5	
$[\text{Co}(\text{CN})_6]^{3-}$	140.1	8 line pattern, $J(\text{Co}, \text{C})=126$
$[\text{Rh}(\text{CN})_6]^{3-}$	131.9	doublet, $J(\text{Rh}, \text{C})=33.6$
$[\text{Ir}(\text{CN})_6]^{3-}$	110.9	
$[\text{Pd}(\text{CN})_6]^{2-}$	104.2	
$[\text{Pt}(\text{CN})_6]^{2-}$	84.7	3 line pattern, $J(\text{Pt}, \text{C})=808$
<u>Square-planar tetracyano complexes</u>		
$[\text{Ni}(\text{CN})_4]^{2-}$	136.6	
$[\text{Pd}(\text{CN})_4]^{2-}$	131.9	
$[\text{Pt}(\text{CN})_4]^{2-}$	125.7	3 line pattern, $J(\text{Pt}, \text{C})=1034$
$[\text{Au}(\text{CN})_4]^-$	105.2	
<u>Tetrahedral tetracyano complexes</u>		
$[\text{Cu}(\text{CN})_4]^{3-}$	161.6	
$[\text{Zn}(\text{CN})_4]^{2-}$	147.0	
$[\text{Cd}(\text{CN})_4]^{2-}$	149.8	
$[\text{Hg}(\text{CN})_4]^{2-}$	153.2	
<u>Linear dicyano complexes</u>		
$[\text{Ag}(\text{CN})_2]^-$	150.0	
$[\text{Au}(\text{CN})_2]^-$	154.2	
$\text{Hg}(\text{CN})_2$	144.6	

^aAll δ values relative to TMS

Work on carbonyl complexes^{106,110-112} of the type $[ML_n(CO)_{6-n}]$ has shown that as δ_{CO} increases, ν_{CO} and hence k_{CO} decreases; δ_{CO} increases if CO is replaced by any ligand such as phosphine, arsine, phosphite, amine; δ_{CO} increases with successive replacement of CO by L; $\delta_{COtrans}$ is greater than δ_{COcis} . It is suggested that substituting a better charge donor, L, for CO will increase r and increase bond polarity causing a downfield shift and also that ΔE increases as evidenced by a good correlation between the frequency of the u.v. band corresponding to $M-CO \pi^*$ and δ_{CO} . Changes in ΔE are also used to interpret the relationship $\delta_{trans} > \delta_{cis}$ - a lower ΔE is said to occur for the trans CO which is competing for d-electrons with another ligand rather than CO.

We report here the spectra of $[MX(CN)_5]^{n-}$ and seek correlations between σ and π effects in bonding and chemical shift.

3.2.4 ¹³C N.M.R. STUDIES OF $[MX(CN)_5]^{n-}$ SPECIES

In Table 3.2, we list our data for ¹³C n.m.r. spectra of $[MX(CN)_5]^{n-}$ species measured in aqueous solution. The assignment of bands follows from the appearance of two signals, one being four times the intensity of the other; arising from cis and trans cyanides respectively (see for example, Fig 2.5, p. 50). This 4:1 pattern is unaffected by the addition of free cyanide to the solutions indicating that no exchange is occurring.

Before discussing these results, we will note how changes in σ and π bonding may affect the observed chemical shifts. In carbonyl complexes, a lowfield shift of the ¹³C resonance (usually accompanied

TABLE 3.2 ^{13}C n.m.r. data for complexes of the type $[\text{MX}(\text{CN})_5]^{n-}$
in aqueous solution

COMPOUND	δ , p.p.m.		COUPLING CONSTANTS	X-RAY DATA,
	<u>cis</u> CN	<u>trans</u> CN	Hz	
CN^-	167.4			
$[\text{Mo}(\text{NO})(\text{CN})_5]^{4-}$	168.2	160.7		d Mo-C _{cis} 2.12(5) ¹¹⁵ d Mo-C _{trans} 2.20(4) d Mo-N 1.95(3)
$[\text{Mo}(\text{NO})(\text{CN})_5]^{2-}$	156.0	152.5		
$[\text{Mn}(\text{NO})(\text{CN})_5]^{3-}$	167.0	160.0		d Mn-C _{cis} 1.97(2) ¹¹ d Mn-C _{trans} 2.01(1) d Mn-N 1.66(2)
$[\text{Re}(\text{NO})(\text{CN})_5]^{3-}$	146.7	143.6		
$[\text{Ru}_2\text{N}(\text{CN})_{10}]^{5-}$	141.9	140.1		d Ru-C _{cis} 2.046(17) d Ru-C _{trans} 2.145(17) d Ru-N 1.766(1) (see p.107)
$[\text{RhH}(\text{CN})_5]^{3-}$	141.0	149.0	J(C _{cis} ,Rh) 34.4 J(C _{trans} ,Rh) 36.5 J(C _{cis} ,H) 5.7 J(C _{trans} ,H) 56.6	d Rh-C _{cis} 2.002(4) ⁶¹ d Rh-C _{trans} 2.082(4) d Rh-H 1.64(4)
$[\text{IrH}(\text{CN})_5]^{3-}$	120.0	126.0	J(C _{cis} ,H) 5.5 J(C _{trans} ,H) 38.0	

TABLE 3.2 cont.

$[\text{RhCl}(\text{CN})_5]^{3-}$	140.5	120.0	$J(\text{C}_{\text{cis}}, \text{Rh})$ 35.4 $J(\text{C}_{\text{trans}}, \text{Rh})$ 37.5	
$[\text{RhBr}(\text{CN})_5]^{3-}$	137.7	119.2	$J(\text{C}_{\text{cis}}, \text{Rh})$ 37.6 $J(\text{C}_{\text{trans}}, \text{Rh})$ 39.3	
$[\text{RhI}(\text{CN})_5]^{3-}$	135.4	118.5	$J(\text{C}_{\text{cis}}, \text{Rh})$ 38.7 $J(\text{C}_{\text{trans}}, \text{Rh})$ 39.6	
$[\text{PtCl}(\text{CN})_5]^{2-}$	92.7	75.3	$J(\text{C}_{\text{cis}}, \text{Pt})$ 821	
$[\text{PtBr}(\text{CN})_5]^{2-}$	89.5	74.9	$J(\text{C}_{\text{cis}}, \text{Pt})$ 830	
$[\text{PtI}(\text{CN})_5]^{2-}$	87.3	74.2	$J(\text{C}_{\text{cis}}, \text{Pt})$ 827	
$[\text{Fe}(\text{NO})(\text{CN})_5]^{2-}$	137.0	135.2		d Fe-C _{cis} 1.942(9) ¹ d Fe-C _{trans} 1.920(c) d Fe-N 1.650(7)
$[\text{Fe}(\text{NO}_2)(\text{CN})_5]^{2-}$	179.8	177.2		
$[\text{Fe}(\text{NH}_3)(\text{CN})_5]^{3-}$	183.0	181.7		
$[\text{Fe}(\text{PPh}_3)(\text{CN})_5]^{3-}$	178.9	177.5		
$[\text{Fe}(\text{AsPh}_3)(\text{CN})_5]^{3-}$	178.1	177.1		

TABLE 3.2 cont.

$[\text{Fe}(\text{SO}_3)(\text{CN})_5]^{5-}$	180.3	179.5
$[\text{Fe}(\text{pyr})(\text{CN})_5]^{3-}$	180.2	177.1
$[\text{Fe}(\text{dmsO})(\text{CN})_5]^{3-}$	172.0	169.0

by a decrease in ν_{CO}) has been interpreted as indicative of an increase in π back-bonding.⁹⁶ However, there is a considerable effect from increased σ -bonding. In molecules of the type $\text{X}-\text{C}\equiv\text{N}$, where X is a σ -donor only, the ^{13}C resonance of the nitrile carbon has been observed to shift to high field as the electronegativity of X increases.¹¹³ Yonemoto suggested that this effect was a general feature of $\text{X}-\text{C}\equiv\text{Y}$ systems where $\text{X}=\text{M}$, $\text{Y}=\text{CN}^-$, CO, acetylide. Thus the observed changes in the ^{13}C chemical shift from complex to complex are the result of the combined effects of change in σ -donation (an increase causing a high field shift) and π -acceptance (an increase causing a low field shift). From our vibrational spectroscopic results (p. 97), we predict that differences in the former will be likely to dominate ^{13}CN chemical shifts and, indeed, the high field shifts which are generally observed on complexation of CN^- are consistent with this view.

We have observed shifts to the low field side of aqueous CN^- in low oxidation state, high co-ordination number cyano complexes e.g. $[\text{Mo}(\text{CN})_7]^{5-}$, δ 189.0 p.p.m. where there is a high electron density on the metal resulting in a considerable degree of π back-bonding.

The infrared stretching frequencies support this observation where the CN stretching frequencies are all below that of 2080 cm^{-1} recorded for potassium cyanide.¹¹⁴

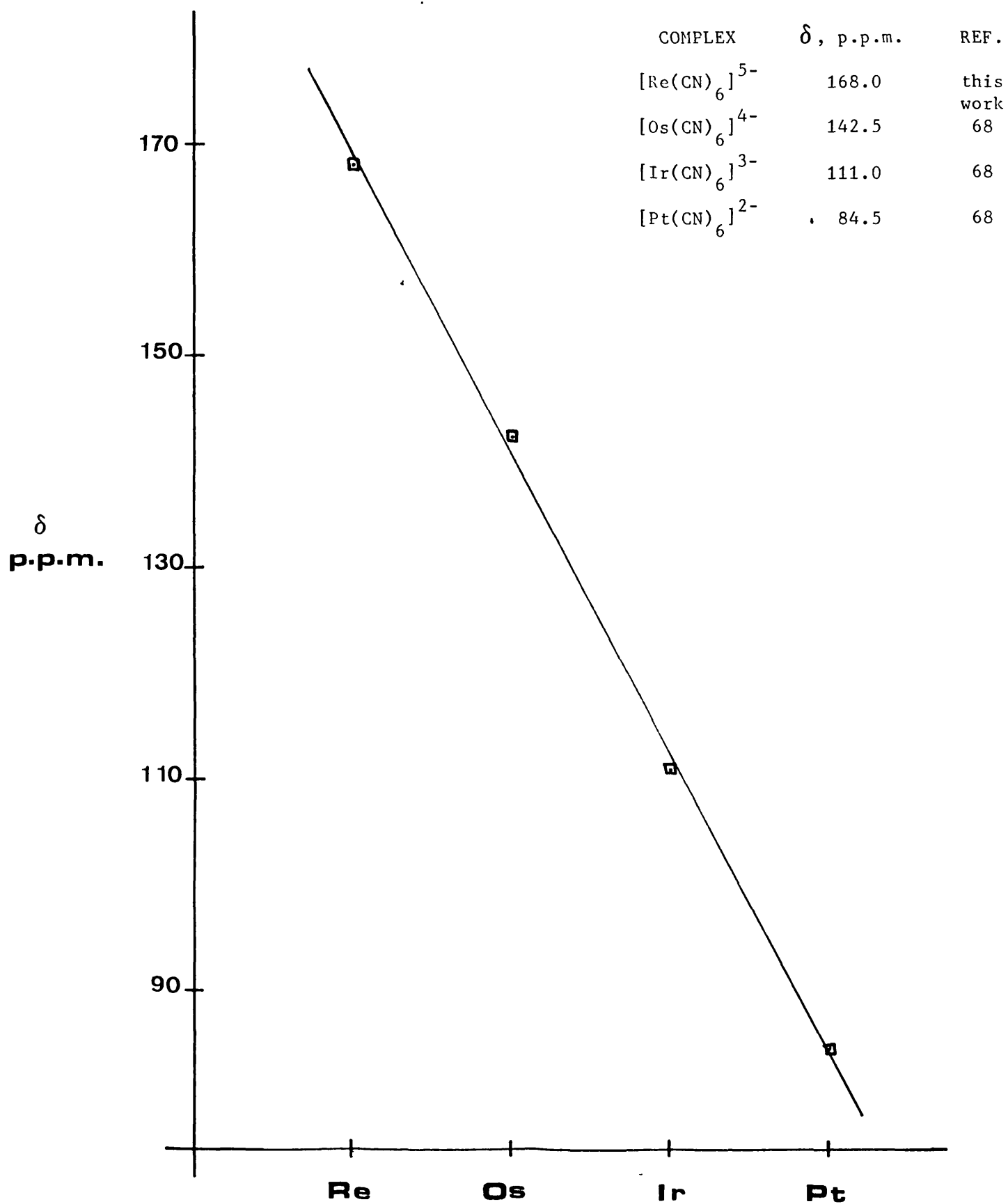
(a) Shifts for isoelectronic species

It is interesting to note that changes in both σ and π bonding operate together to provide a high field shift of the ^{13}C resonance in isoelectronic cyano complexes. Figure 3.2 illustrates the linear relationship between chemical shift and oxidation state in hexacyano complexes of the third row transition elements. Removal of one electron from the metal 5d orbitals causes the resonance to move upfield by ~ 28 p.p.m. (2,800 Hz) e.g. $[\text{Re}(\text{CN})_6]^{5-}$, δ 168.0 p.p.m.; $[\text{Os}(\text{CN})_6]^{4-}$, δ 142.5 p.p.m.. As the metal oxidation state increases, σ -donation increases drawing the CN ligand closer to the filled metal 5d orbitals; any π -back bonding will correspondingly decrease. The shielding of the ^{13}C nucleus by the metal electrons is increased and the resonance is thus observed at higher field. As we would expect, increasing the oxidation state of the same metal in a complex causes the chemical shift to move to higher field for similar reasons e.g. $[\text{Mo}(\text{NO})(\text{CN})_5]^{4-}$ δ 168.2, 160.7 p.p.m.; $[\text{Mo}(\text{NO})(\text{CN})_5]^{2-}$, δ 156.0, 152.5 p.p.m.. The chemical shifts of the pentacyano nitrosyl complexes also move to higher field across the transition metal series (see Table 3.2) e.g. $[\text{Mn}(\text{NO})(\text{CN})_5]^{3-}$ δ 167.0, 160.0 p.p.m.; $[\text{Fe}(\text{NO})(\text{CN})_5]^{2-}$, δ 137.0, 135.2 p.p.m..

(b) Shifts within a vertical triad

There is also a high field shift down a transition metal group,

Fig 3.2 Relationship between ^{13}C chemical shift and Oxidation State



$[\text{Mn}(\text{NO})(\text{CN})_5]^{3-}$, δ 167.0, 160.0 p.p.m.; $[\text{Re}(\text{NO})(\text{CN})_5]^{3-}$, δ 146.7, 143.6 p.p.m. and $[\text{RhH}(\text{CN})_5]^{3-}$, δ 141.0, 149.0 p.p.m.; $[\text{IrH}(\text{CN})_5]^{3-}$, δ 120.0, 126.0 p.p.m..

This effect was also observed in hexacyano and tetracyano complexes by Pesek and Mason⁶⁸ (Table 3.1) who visualised this as a consequence of the penetration of CN^- into the partly filled nd metal orbitals. As n increases from 3 to 5, the expansion of the filled d orbitals around the CN ligands would increase thus shielding the ^{13}C nucleus.

(c) Shifts for halopentacyano species

If we consider the series of complexes $[\text{M}^n\text{X}(\text{CN})_5]^{6-n}$ where $\text{M}=\text{Rh}(\text{III})$, $\text{Pt}(\text{IV})$; $\text{X}=\text{Cl}^-$, Br^- , I^- ; and $[\text{PtX}_2(\text{CN})_4]^{2-}$ where $\text{X}=\text{Cl}^-$, Br^- , I^- (Table 3.12) we observe a small decrease in chemical shift down the halogen series i.e. the ^{13}C resonance shifts to higher field as the electronegativity of X decreases. Interestingly, this observation contradicts Yonemotos' idea¹¹³ that ^{13}C resonances shift to higher field as the electronegativity of X increases. We would suggest that a more electronegative ligand pulls electron density from the metal toward it causing an increase in σ -donation from the CN^- 5σ orbital. The ^{13}C nucleus, therefore, has a lower electron density around it due to the drift of electrons throughout the σ -framework towards the halogen; it is deshielded and resonates at a lower applied field. The decrease of the Cotton-Kraihanzel force constants down the halogen series (Table 3.5, p. 97) is consistent with this idea of less σ -bonding from chlorine to iodine.

(d) Shifts for $[\text{FeX}(\text{CN})_5]^{n-}$

For the series of complexes, $[\text{FeX}(\text{CN})_5]^{n-}$, we observed the ^{13}C

resonances to be shifted to lower field according to the sequence,
 $X = \text{NO}^+ \gg (\text{CH}_3)_2\text{S}=\text{O} > \text{CN}^- \sim \text{N} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{N} \sim \text{PPh}_3 \sim \text{AsPh}_3 > \text{NO}_2^- \sim \text{SO}_3^{2-}$
 $\sim \text{pyridine} > \text{NH}_3$. In a similar experiment, Malin *et al*¹⁰⁰ and Petersen
*et al*¹⁰² reported ^{13}C n.m.r. spectra for several iron(II) complexes
of the type, $[\text{FeX}(\text{CN})_5]^{n-}$, where the ligands, X, were nitrogen donors.
They found that ^{13}C resonances moved to lower field in the series
 $\text{NO}^+ \gg \text{N-methylpyrazinium} > \text{pyrazine} \sim \text{cyanide} \sim \text{isonicotinamide} >$
 $4\text{-methylpyridine} \sim \text{isoquinoline} \sim \text{pyridine}$. If X is a good π -acceptor
and a poor electron donor the resonance appears at a higher field than
that where X is a poor π -acceptor and a good base. In the former case,
the ligand, X, reduces electron density on the metal by forming π -
bonds and so the CN^- ligand is involved in increased σ -donation. This
forms a strong M-C bond and the ^{13}C nucleus is therefore shielded,
causing a high field shift. A pulling in of the cyanide ligand causes
a slight but significant shortening (0.022 Å) of the $\text{Fe-C}_{\text{trans}}$ bond
in $[\text{Fe}(\text{NO})(\text{CN})_5]^{2-}$.¹¹⁷ A good base, however, is competing with CN^-
for σ -donation to the metal with the result that the ^{13}C nucleus is
farther removed from the metal electrons and so is deshielded.

The Mössbauer isomer chemical shifts of known monosubstituted
cyano complexes of iron(II) become less negative along the series
 $\text{NO}^+ > \text{CO} > \text{CN}^- > \text{Ph}_3\text{P} > \text{SO}_3^{2-} > \text{NO}_2^- \sim \text{Ph}_3\text{As} \sim \text{Ph}_3\text{Sb}$ which the authors¹¹⁸
attribute to decreasing π back-donation from the unique ligand to the
iron centre along such series. A higher isomer shift may also be attributed
to strong σ -donation (see Section 3.2.7, p.113) so the series also
corresponds to decreasing σ -donation by the cyano ligands.

(e) Positions of cis vs trans resonances in $[\text{MX}(\text{CN})_5]^{n-}$

If we consider the cis and trans resonances for our complexes,

we may make several observations. The cis CN resonance is at a lower field than the trans, except where $X=H^-$. $\Delta(\delta_{cis} - \delta_{trans})$ tends to be quite small, typically ~ 3 p.p.m. except when $X=H^-, Cl^-, Br^-, I^-$ when it ranges from -6 ($[IrH(CN)_5]^{3-}$) to +17 ($[PtCl(CN)_5]^{2-}$). Finally, when compared to the position of the corresponding hexacyano complex, NO^+ complexes are at higher field, hydride complexes are at lower field, halogen complexes tend to be at lower field and the others are not shifted from this "reference" position by much (Table 3.3). We would suggest that the resonances are at such high field for nitrosyl complexes for the reasons previously discussed. The electron withdrawing power of the nitrosyl ion is so great that the cyanide ligands are pulled in closer to the metal increasing the shielding of the ^{13}C nucleus. The other ligands, X, in this study with the exception of the halogens and H^- do not dominate the bonding in the molecules to such a great extent. We would suggest that the halogens and H^- being strong σ -donors only, lend a directional quality to the bonding, namely the trans ligand is affected more than the cis resulting in the large chemical shift differences between the two.

The position of the cis resonance downfield of the trans implies that the cis CN group is less shielded than the trans. From our previous arguments, this would suggest that the trans CN ligand is closer to the metal than the cis in all cases except for the hydrides where it is less shielded (vis $Rh-C_{trans}$: 2.082 Å. $Rh-C_{cis}$: 2.002 Å, see p. 57). The known X-ray data for the other complexes are summarised in Table 3.2. The trans Fe-C bond in $[Fe(NO)(CN)_5]^{2-}$ is 0.022 Å shorter than the cis¹¹⁷ but in the other two examples of nitrosyl complexes, $[Mo(NO)(CN)_5]^{4-}$ and $[Mn(NO)(CN)_5]^{3-}$ the trans M-C bond is 0.08 and 0.04 Å longer than the cis respectively although, in both cases it should be noted that these differences are very close to the limit

TABLE 3.3 Comparison of cis and trans ^{13}C resonances in $[\text{MX}(\text{CN})_5]^{n-}$ with those of $[\text{M}(\text{CN})_6]^{n-}$

	$[\text{M}(\text{CN})_6]^{n-}$	$[\text{MX}(\text{CN})_5]^{n-}$	
	δ , p.p.m.	δ_{cis} , p.p.m.	δ_{trans} , p.p.m.
M=Re(I), X=NO ⁺	168.0	146.7	143.6
M=Rh(III), X=H ⁻	131.0	141.0	149.0
M=Ir(III), X=H ⁻	110.9	120.0	126.0
M=Rh(III), X=Cl ⁻	131.9	140.5	120.0
M=Rh(III), X=Br ⁻	131.9	137.7	119.2
M=Rh(III), X=I ⁻	131.9	135.4	118.5
M=Pt(IV), X=Cl ⁻	84.7	92.7	75.3
M=Pt(IV), X=Br ⁻	84.7	89.5	74.9
M=Pt(IV), X=I ⁻	84.7	87.3	74.2
M=Fe(II), X=NO ⁺	177.2	137.0	135.2
M=Fe(II), X=dmsO	177.2	172.0	169.0
M=Fe(II), X=AsPh ₃	177.2	178.1	177.1
M=Fe(II), X=PPh ₃	177.2	178.9	177.5
M=Fe(II), X=NO ₂ ⁻	177.2	179.8	177.2
M=Fe(II), X=pyr	177.2	180.2	177.1
M=Fe(II), X=SO ₃ ²⁻	177.2	180.3	179.5
M=Fe(II), X=NH ₃	177.2	183.0	181.7

δ recorded in aqueous solution relative to $(\text{CH}_3)_4\text{Si}$

of the standard deviations and the structures are relatively inaccurate ($R = 6.7$ and 7.2%). The structure of $[\text{Mo}(\text{NO})(\text{CN})_5]^{4-}$ does seem rather unusual as the NO stretching frequency is 1455 cm^{-1} which is in the region characteristic of bent NO groups (which would result in $\text{Mo}(\text{II})$). The NO group is said to be linear, $\text{Mo}-\hat{\text{N}}-\text{O} \ 175.0^\circ$, but the Mo-N bond length of $1.95(3) \text{ \AA}$ is surprisingly long¹¹⁵; ($\text{Mn}-\text{NO}$; $1.66(2)$ ¹¹⁶, $\text{Fe}-\text{NO}$: $1.650(7) \text{ \AA}$ ¹¹⁷). Although we have no n.m.r. data as the complex is paramagnetic, it is interesting to consider the structure of the complex $\text{K}_3[\text{Cr}(\text{NO})(\text{CN})_5]$ which has ν_{NO} at 1643 cm^{-1} but contains a linear Cr-N-O moiety. The trans Cr-C bond ($2.075(14) \text{ \AA}$) is $0.042 \text{ \AA}$ longer than the cis (average $2.033 \text{ \AA}$).¹¹⁹

(f) The use of Coupling Constants

Metal-carbon coupling constants have been of use in determining 'trans-influence' series⁷⁵ as they reflect the amount of interaction occurring between the metal and ligand orbitals. We have observed coupling between (^{13}C , ^{103}Rh) and (^{13}C , ^{195}Pt) in a few of our complexes (Table 3.2) but they have not been commented upon as we do not have sufficient data to draw any valid conclusions.

3.2.5 FORCE CONSTANTS IN METAL CYANO COMPLEXES-THE COTTON-KRAIHANZEL MODEL

The calculation of force constants from the vibrational frequencies is generally referred to as normal co-ordinate analysis. The theory behind the calculations and the mechanics involved¹²⁰ are beyond the scope of this work but one of the major problems associated with this treatment is that there are generally more quadratic force constants than there are vibrational frequencies for a molecular species even

if additional data is obtained from isotopically substituted species.

In 1962, Cotton and Kraihanzel proposed a simple model for analysing¹²⁰ and assigning the infrared active carbonyl stretching frequencies of simple and substituted metal carbonyls of the type $ML_x(CO)_{6-x}$, that is, those with an essentially octahedral distribution of the ligands, L, and carbonyl groups about the metal atom. The method depends on the fact that the CO stretching frequencies lie at much higher frequencies ($> 1850 \text{ cm}^{-1}$) than all other vibrations ($< 700 \text{ cm}^{-1}$). The force constants so obtained are not, therefore, absolute, but in a series of related molecules, the shift from absolute values will probably be essentially constant. The differences between force constants for different but similar molecules should be rather reliably given; such a situation also exists for cyano complexes.

We apply this scheme to the species $[MX(CN)_5]^{n-}$ and so will give a brief account of its derivation and the approximations involved. The derivation of the model from the secular equations governing the vibrations of the complete model involves two approximations. Firstly, no account is taken of the interaction of CN stretching modes with other deformations of the molecule, the so-called effect of high frequency separation. Second, the calculation uses the observed frequencies of the ν_{CN} fundamentals without corrections for anharmonicity.

The secular equation is factored to its maximum extent by modifying the kinetic energy and potential energy matrices. In the former, the coupling between the cyano groups is assumed to be non-mechanical. The secular equations derived for $[MX(CN)_5]^{n-}$ (C_{4v} symmetry) are

$$\text{Species A}_{1-} \quad \begin{vmatrix} k_1 - x & 2k_d \\ 2k_d & k_2 + k_t + 2k_c - x \end{vmatrix} = 0$$

Species B₁₋

$$x = k_2 + k_t - 2k_c$$

Species E

$$x = k_2 - k_t$$

where k_1 = the CN stretching constant for the trans-CN group

k_2 = the CN stretching constant for the cis-CN groups

k_t = the interaction constant for the cis-CN groups trans to each other

k_c = the interaction constant for the cis-CN groups cis to each other

k_d = the interaction constant for pairs of CN groups consisting of the trans-CN group and one of the cis-CN groups.

In systems for which the number of CN stretching frequencies observed suffices to calculate approximate force constants; the force constants can be calculated according to all possible band assignments and it is then necessary to assume a relationship between the force constants that can be used as a criterion of the correct band assignment. It was suggested that all CN stretch-stretch interaction constants, k_i , are positive¹²⁰ - this can be deduced using Molecular Orbital theory and has been established for a number of other compounds by other methods.¹²¹

In order to reduce the number of unknown force constants, a quantitative relationship was assumed between some of them; Cotton and Kraihanzel¹²⁰ suggested that the relationship

$$\frac{1}{2}k_t = k_c = k_d$$

is valid for these systems. Their arguments were based on the symmetry properties of the atomic $d\pi$ orbitals of the metal. It follows from this assumption that CN groups cis to the ligand, L, have a higher stretching force constant than those trans to it.

The secular equations, using the approximation

$$k_i = k_c = \frac{1}{2}k_t = k_d$$

become:

$$\text{Species A}_{1-} \begin{vmatrix} k_1 - x & 2k_i \\ 2k_i & k_2 + 4k_i - x \end{vmatrix} = 0$$

$$\text{Species B}_{1-} \quad x = k_2$$

$$\text{Species E} \quad x = k_2 - 2k_i$$

$$\text{where } x = \frac{\lambda}{\mu} \quad \text{and } \lambda = (5.889 \times 10^{-2}) \nu^2$$

$\mu = \text{reciprocal of the reduced mass of CN}$

For some carbonyl compounds, correct band assignments have been predicted as compared to assignments by other methods.^{120,122} Although the model has been criticised for its general approximations,¹²¹ it is generally acknowledged that the force constants are of the right order and that trends among similar compounds e.g. $[\text{MLX}_5]^{n-}$ are meaningful.¹²³

Turner et al¹²⁴ reported that the application of the approximation to metal cyano complexes gave good agreement with general quadratic valence force field calculations but the authors did not, unfortunately, tabulate any of their results. They showed that errors in the approximation could be accounted for by a combination of anharmonicity and MC-CN coupling. Jones and Swanson¹²⁵ carried out calculations on simple molecules such as $[\text{Au}(\text{CN})_2]^-$ and $\text{Hg}(\text{CN})_2$ but they used vibrational data obtained from solid samples. Alvarez¹²⁶ compared Cotton-Kraihanzel force constants with the GVFF constants for a number of $[\text{M}(\text{CN})_6]^{n-}$ cyano complexes and concluded that the approximation was valid to use as, in many cases, the effect of high frequency separation is much less than in carbonyl

complexes. Recently, Alvarez et al¹²⁷ calculated Cotton-Kraihanzel force constants for a large number of polycyano complexes and showed that the C≡N bond strengths in these complexes depended only on the co-ordination number and oxidation state of the central metal atom. The trans-interaction constants, k_t , increase with co-ordination number and decrease with oxidation state of the central metal ion. Alvarez also reported calculations on trans-[PtX₂(CN)₄]²⁻ (X=Cl, Br, I) and on heptacyano, octacyano and bridging cyano complexes. These results are summarised in Table 3.4.

TABLE 3.4 Cotton-Kraihanzel Force Constants for Metal-Cyano Complexes^{126,127}

<u>COMPLEX</u>	<u>FORCE CONSTANTS</u>		
	k_{CN}	k_t	
[Ag(CN) ₂] ⁻	17.48	0.005	
[Au(CN) ₂] ⁻	17.61	-	
[Hg(CN) ₂]	18.79	0.002	
	k_{CN}	k_t	k_c
[Ni(CN) ₄] ²⁻	17.39	0.12	0.03
[Pd(CN) ₄] ²⁻	17.56	0.10	0.06
[Pt(CN) ₄] ²⁻	17.67	0.07	0.06
		k_{CN}	
[Mn(CN) ₆] ⁵⁻		14.75	
[Tc(CN) ₆] ⁵⁻		14.98	
[Re(CN) ₆] ⁵⁻		14.87	

TABLE 3.4 cont.

	k_{CN}					
$[\text{V}(\text{CN})_6]^{4-}$	16.15					
$[\text{Mn}(\text{CN})_6]^{4-}$	16.24					
$[\text{Fe}(\text{CN})_6]^{4-}$	16.14					
$[\text{Ru}(\text{CN})_6]^{4-}$	16.20					
$[\text{Os}(\text{CN})_6]^{4-}$	16.11					
$[\text{Cr}(\text{CN})_6]^{3-}$	17.25					
$[\text{Mn}(\text{CN})_6]^{3-}$	17.11					
$[\text{Fe}(\text{CN})_6]^{3-}$	17.18					
$[\text{Co}(\text{CN})_6]^{3-}$	17.37					
$[\text{Rh}(\text{CN})_6]^{3-}$	17.49					
$[\text{Ir}(\text{CN})_6]^{3-}$	17.44					
$[\text{Pt}(\text{CN})_6]^{4-}$	18.37					
	k_{trans}	k_{cis}	k_i			
$[\text{PtCl}(\text{CN})_5]^{2-}$	18.34	18.36	0.06			
$[\text{PtBr}(\text{CN})_5]^{2-}$	18.35	18.33	0.06			
$[\text{PtI}(\text{CN})_5]^{2-}$	18.10	18.10	0.06			
	k_{CN}	k_t	k_c			
<u>trans</u> - $[\text{PtCl}_2(\text{CN})_4]^{2-}$	18.15	0.12	0.04			
<u>trans</u> - $[\text{PtBr}_2(\text{CN})_4]^{2-}$	18.07	0.11	0.06			
<u>trans</u> - $[\text{PtI}_2(\text{CN})_4]^{2-}$	17.89	0.12	0.05			
	k_{trans}	k_{cis}	k_w	k_t	k_c	k_o
$[\text{Mo}(\text{CN})_7]^{4-}$	16.41	16.43	16.42	0.57	0.03	0.16
$[\text{Re}(\text{CN})_7]^{4-}$	16.31	16.45	16.41	0.79	0.04	0.20
$[\text{V}(\text{CN})_7]^{4-}$	16.63	16.81	16.76	0.29	-0.01	0.04

$k_w = 2k_{\text{trans}} + 5k_{\text{cis}}$, k_t = trans-trans interaction, k_c = trans-cis interaction,
 k_o = opposite cis-cis interaction

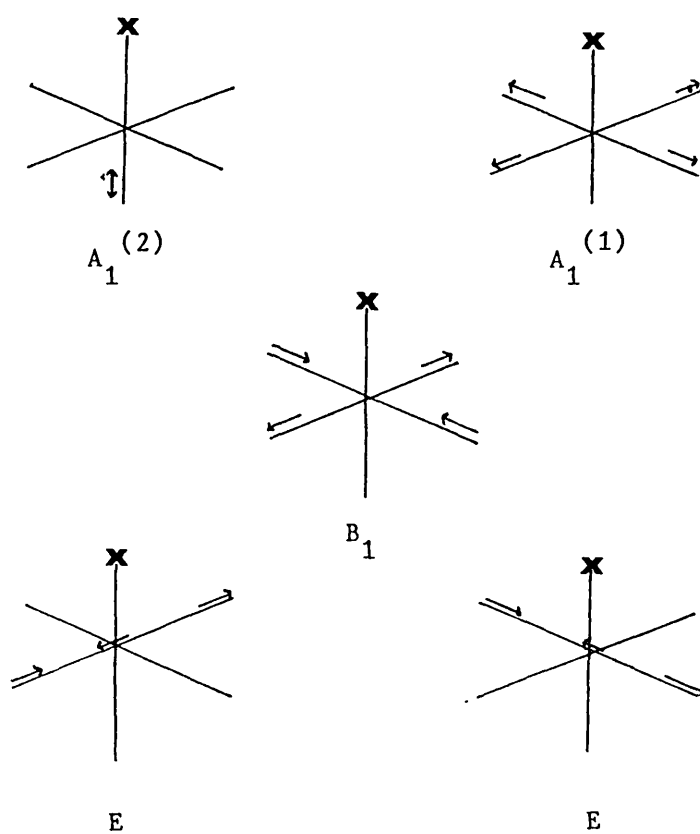
3.2.6 INFRARED AND RAMAN STUDIES OF $[\text{MX}(\text{CN})_5]^{n-}$ COMPLEXES

We have already mentioned (Section 2.3.2, p. 43) that three infrared active fundamentals ($2A_1 + E$) and four Raman active fundamentals ($2A_1 + B_1 + E$) are expected for the ν_{CN} vibrations in a molecule of C_{4v} symmetry. Approximate representations of these modes are illustrated in Figure 3.3. The infrared and Raman assignments and the Cotton-Kraihanzel force constants calculated using the equations below are presented in Table 3.5.

$$k_1 = \frac{\lambda_2}{\mu} \qquad k_2 = \frac{\lambda_9}{\mu} \qquad k_i = \frac{(\lambda_9 - \lambda_{15})}{\mu} \approx \frac{k_t}{2}$$

where λ_2 is derived from the A_1 mode, λ_9 from the B_1 mode and λ_{15} from the E mode. Henceforth, k_1 will be referred to as k_{trans} and k_2 will be referred to as k_{cis} . All infrared and Raman data reported here were recorded on aqueous solutions of the complexes and the full spectroscopic details are given in the experimental section at the end of this chapter (p.144).

It is pertinent, at this point, to consider the assignment of the bands. The Cotton-Kraihanzel model was developed for carbonyl complexes which have well resolved infrared spectra and at a time when Raman spectroscopy was not a widely used technique. A problem of resolving CN stretching frequencies is commonly encountered in the vibrational spectroscopy of metal cyanides. The symmetric and antisymmetric $\text{C}\equiv\text{N}$ stretching frequencies of individual cyano complexes lie fairly close together, whereas the corresponding carbonyl complexes exhibit $\text{C}\equiv\text{O}$ stretching frequencies in a much broader range e.g. for $\text{Cr}(\text{CO})_6$, the CO frequencies range from 2119 to 2000 cm^{-1} ¹²⁸ whilst for $[\text{Co}(\text{CN})_6]^{3-}$, CN frequencies range from 2151 to 2128 cm^{-1} .¹²⁹ This slight separation of CN stretching

**Fig 3.3**

Approximate Representations of the Normal Modes on the C_{4v} molecule, $[MX(CN)_5]^n$

frequencies results from relatively small CN-CN interactions. The carbonyls however, exhibit considerable CO-CO interaction, apparently due to dipole-dipole coupling.¹²⁸

The assignment of the cis A_1 and E vibrations is fairly straightforward and utilises rationale developed for monosubstituted metal carbonyls. The weak infrared band located at highest energy is due to the planar A_1 (ν_1) mode and corresponds to the intense, polarised Raman band. The antisymmetric E mode (ν_{15}) should exhibit the strong intense infrared absorption by virtue of the fact that a large change in dipole moment of the complex accompanies this vibration. Thus, the E mode is assigned to the strong band found in all the infrared spectra of the complexes. This fundamental is generally too weak to be observed in the Raman spectrum; its absence has also been noted in metal pentacarbonylhalides.¹³⁰ The B_1 mode (ν_9) is Raman active only and appears with medium to strong intensity; it is depolarised. The exact position of the axial CN stretching band (ν_2) is difficult to establish because of overlapping by other bands although some complexes do exhibit three Raman bands in this region. In the infrared spectrum, the peak is often obscured by the intense E mode. We have, however, been able to assign this band in most of our complexes using both infrared and Raman spectra. The set of figures in brackets in Table 3.5 are calculated from all four vibrations using a least squares approach:

$$k_{\text{trans}} = \frac{\lambda_2}{\mu} \quad k_{\text{cis}} = \frac{(3\lambda_1 + 5\lambda_9 + 6\lambda_{15})}{14\mu} \quad k_i = \frac{(5\lambda_1 - \lambda_9 - 4\lambda_{15})}{28\mu}$$

We also used the force constants to recalculate the observed frequencies using the equations on p. 94. Some of these results are presented in Table 3.6 with some force constants calculated by Alvarez and Lopez¹²⁷

TABLE 3.5 Infrared and Raman Data and Cotton-Kraihanzel Force Constants
for $[\text{MX}(\text{CN})_5]^{n-}$ Complexes

COMPLEX	CN, cm ⁻¹				FORCE CONSTANT,		
	A ₁ ⁽¹⁾ , ν ₁	A ₁ ⁽²⁾ , ν ₂	B ₁ , ν ₉	E, ν ₁₅	k _{trans}	k _{cis}	k _i
[CoH(CN) ₅] ³⁻	2127	2110	2100	2097	16.95 (16.95)	16.79 (16.87)	0.05 (0.09)
[RhH(CN) ₅] ³⁻	2147	2119	2127	2105	17.10 (17.10)	17.23 (17.15)	0.18 (0.11)
[IrH(CN) ₅] ³⁻	2152	2117	2125	2110	17.07 (17.10)	17.20 (17.19)	0.12 (0.11)
[Mn(NO)(CN) ₅] ³⁻	2123	2110	2096	2100	16.95 (16.95)	16.73 (16.85)	0.03 (0.07)
[Fe(NO)(CN) ₅] ²⁻	2173	2160	2155	2143	17.77 (17.77)	17.69 (17.66)	0.10 (0.08)
[Fe(CO)(CN) ₅] ³⁻	2090	2089	2085	2070	16.61 (16.61)	16.56 (16.47)	0.12 (0.05)
[Mo(NO)(CN) ₅] ⁴⁻	2139	2119	2112	2120	17.09 (17.01)	16.99 (17.14)	0.06 (0.06)
[Mo(NO)(CN) ₅] ²⁻	2139	2135	2131	2120	17.36 (17.36)	17.29 (17.25)	0.09 (0.05)
[PtCl(CN) ₅] ²⁻	2205	2195	2193	2187	18.35 (18.35)	18.31 (18.31)	0.05 (0.05)
[PtBr(CN) ₅] ²⁻	2203	2193	2192	2186	18.31 (18.31)	18.30 (18.29)	0.05 (0.05)
[PtI(CN) ₅] ²⁻	2201	2191	2188	2181	18.28 (18.28)	18.23 (18.22)	0.12 (0.05)
[Fe(NO ₂)(CN) ₅] ²⁻	2089	2068	2064	2060	16.28 (16.28)	16.22 (16.28)	0.03 (0.08)
[Fe(NH ₃)(CN) ₅] ³⁻	2060	2057	2055	2040	16.11 (16.11)	16.08 (15.99)	0.12 (0.05)
[Re(NO)(CN) ₅] ³⁻	2137	2115	2091	2110	17.03 (17.03)	16.65 (16.94)	0.15 (0.09)
[Fe(PPh ₃)(CN) ₅] ³⁻	2087	2040	2057	2030	15.84 (15.84)	16.11 (16.03)	0.21 (0.14)

TABLE 3.5 cont.

$[\text{Fe}(\text{AsPh}_3)(\text{CN})_5]^{3-}$	2087	2040	2057	2030	15.85 (15.85)	16.11 (16.03)	0.21 (0.21)
$[\text{RhCl}(\text{CN})_5]^{3-}$	2150	2140	2154	2130	17.44 (17.44)	17.67 (17.49)	0.20 (0.04)
$[\text{RhBr}(\text{CN})_5]^{3-}$	2148	2137	2143	2128	17.39 (17.39)	17.49 (17.40)	0.12 (0.05)
$[\text{RhI}(\text{CN})_5]^{3-}$	2145	2133	2140	2123	17.33 (17.33)	17.34 (17.36)	0.14 (0.05)
$[\text{Ru}_2\text{N}(\text{CN})_{10}]^{5-}$	2149	2124	2135	2121	17.18 (17.18)	17.36 (17.31)	0.11 (0.07)

TABLE 3.6 Comparison between Experimental and Literature Data and Force Constants for $[\text{PtX}(\text{CN})_5]^{2-}$, X = Cl, Br, I

		$A_1^{(1)}$	$A_1^{(2)}$	B_1	E	k_{trans}	k_{cis}	k_i
$[\text{PtCl}(\text{CN})_5]^{2-}$	127	2210	2195	2198	2187	18.34	18.36	0.06
	this work	2205	2195	2193 (2191)	2187	18.35	18.31	0.05
$[\text{PtBr}(\text{CN})_5]^{2-}$	127	2209	2196	2196	2186	18.35	18.33	0.06
	this work	2203	2193	2192 (2189)	2186	18.31	18.30	0.05
$[\text{PtI}(\text{CN})_5]^{2-}$	127	2203	2181	2192	2182	18.10	18.10	0.06
	this work	2200	2191	2188 (2185)	2181	18.28	18.23	0.12

Note: The figure in brackets indicates the calculated value for ν_9 using all four stretching frequencies

using their own infrared data.

Molecular orbital calculations on cyano complexes¹³¹ indicate that the ligand 5σ orbital involved in forming the M-C σ bond is slightly anti-bonding with respect to the CN moiety and that the π^* CN levels are strongly anti-bonding. Thus, an increase in M-L σ bonding should result in a slight increase in the CN bond strength and, conversely, an increase in $d\pi - p\pi^*$ overlap should result in a decrease in CN bond order.

Several trends become apparent on inspection of the data in Table 3.5 which we will discuss in some detail here in conjunction with the ¹³C n.m.r. data presented in Section 3.2.4, p. 78.

(a) Force Constants and Oxidation State

As we move across the transition metal series from left to right, the force constants k_{trans} and k_{cis} increase suggesting that the CN bond is becoming stronger. Thus the oxidation state of the metal in the complex anion increases across the series e.g. Mn(I) in $[\text{Mn}(\text{NO})(\text{CN})_5]^{3-}$ where $k_{trans} = 16.95$, $k_{cis} = 16.70$ and Pt(IV) in $[\text{PtCl}(\text{CN})_5]^{2-}$ where $k_{trans} = 18.35$, $k_{cis} = 18.31$. As the oxidation state of the metal increases the electrons on the metal are pulled closer to the nucleus and the extent of σ -donation by the CN^- is correspondingly greater. Although this σ -effect is predominant, it is slightly reduced by the fact that any $d\pi - p\pi^*$ bonding will be reduced as the oxidation state increases. This net strengthening of the CN bond is reflected in the higher CN stretching frequencies at 2200 cm^{-1} in the Raman spectra of the Pt(IV) complexes, $\sim 30 \text{ cm}^{-1}$ higher than any others that we recorded. Another good example of the effect of oxidation state on k are the two complexes, $[\text{Mo}(\text{NO})(\text{CN})_5]^{n-}$, where $n = 2, 4$. The force constants for the purple

Mo(0) complex are smaller than those of the yellow Mo(II) complex.

The diminishing availability of electrons on the metal is also reflected in the nitrosyl stretching frequency, ν_{NO} , in the infrared spectrum which we find to be 1455 and 1645 cm^{-1} in the Mo(0) and Mo(II) complexes respectively (ν_{NO} in $[\text{Mo}^{\text{I}}(\text{NO})(\text{CN})_5]^{3-}$ is 1585 cm^{-1} ¹³²). At this point we must recall the comments made in Section 3.2.4, p. 88 regarding the nature of the NO group in the Mo(0) complex. It is also true that as the metal oxidation state increases, the value of the interaction constant, k_i , decreases. This, too, follows from the above explanation as reduced electron density on the metal results in a more "localised" bonding situation.

(b) Force Constants for Halopentacyano Species

An interesting trend occurs in the series of complexes $[\text{PtX}(\text{CN})_5]^{2-}$ and $[\text{RhX}(\text{CN})_5]^{3-}$, where $X = \text{Cl}, \text{Br}, \text{I}$; we observe that the cis and trans force constants decrease down the halogen series. We can envisage this as an inductive effect caused by the electronegativity of the halogens. In the chloro complex, there will be a small but net drift of electrons through the σ -framework towards the halogen. This, of course, increases σ -donation by the cyanide moiety and strengthens the CN bond. This effect is reduced in the bromo and iodo complexes, reducing σ -donation from the slightly anti-bonding CN orbital causing k to decrease. The changes in k_{trans} and k_{cis} are small, k_{trans} for $[\text{PtCl}(\text{CN})_5]^{2-}$ is 18.35 and for $[\text{PtBr}(\text{CN})_5]^{2-}$ is 18.31 so that we would expect to see no effect on k_i where the variation would be undetectable. It is notable that in the case of $[\text{FeX}(\text{CN})_5]^{3-}$, $X = \text{PPh}_3, \text{AsPh}_3$, and indeed in $[\text{FeX}(\text{CO})_5]$, $X = \text{PPh}_3, \text{AsPh}_3$, ¹³³ the Cotton-Kraihanzel force

constants are the same. This is presumably because phosphorus and arsenic are much less electronegative than the halogens and the differences between them are very small.

(c) Variations in Force Constants within a Vertical Triad

If the substituted ligand, X, remains the same but the metal is replaced by another of the same vertical metal triad, e.g. $[\text{MH}(\text{CN})_5]^{3-}$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$) and $[\text{M}(\text{NO})(\text{CN})_5]^{3-}$ ($\text{M} = \text{Mn}, \text{Re}$), we observe an increase in force constant from the complex containing the first row metal to that incorporating the third row metal. This effect is more difficult to rationalise. In general, metal-ligand bonding is regarded as being increasingly covalent from first row to third row complexes, implying greater interaction between the metal and ligand orbitals. Greater σ -interaction in this manner would result in the observed trend.

(d) Variations in Species with M Constant and Varying X

In complexes where the metal remains the same but the ligand, X, changes e.g. $[\text{FeX}(\text{CN})_5]^{n-}$, we may draw some conclusions concerning the nature of the ligand, X. In $[\text{Fe}(\text{CN})_6]^{4-}$, k is 16.14×10^{12} which, for the purposes of this discussion, we will use as a "reference" value. When X is a good base and a poor π -acceptor e.g. NH_3 , NO_2^- , k_{trans} and k_{cis} are less than $[\text{Fe}(\text{CN})_6]^{4-}$; but when X is a good π -acceptor and a poorer base e.g. NO^+ , CO , PPh_3 , AsPh_3 ; the force constants are greater. A good base like NH_3 is a good σ -donor and pushes electrons strongly towards the metal centre. This "inhibits" σ -donation by the CN ligand causing the force constant to decrease relative to the

hexacyano complex. The opposite effect is observed when X is a good π -acceptor like NO^+ or CO. These ligands remove electron density from the metal by π -bonding and σ -donation by CN^- correspondingly is increased resulting in an increase in k. These results correspond well with the n.m.r. results discussed in Section 3.2.4..Table 3.7 shows the effect of replacing cyanide in an octahedral hexacyano complex with either the nitrosyl or the hydride ligand.

Fenske and DeKock¹³⁴ carried out detailed molecular orbital calculations for transition metal pentacyanonitrosyls, $[\text{M}^{\text{X}}(\text{NO})(\text{CN})_5]^{(4-x)-}$ where $\text{M} = \text{Fe}(\text{II}), \text{Mn}(\text{I}), \text{Mn}(\text{II}), \text{Cr}(\text{0}), \text{Cr}(\text{I})$. They noted that although the 5σ level in free NO^+ is 35eV lower than the 5σ in free CN^- ; in their complexes the separation did not exceed 15eV and was frequently less. Such an alteration reflects the loss of electron density of the CN^- group and accumulation of electron density of the NO^+ group upon complex formation. In all cases (see Fig. 3.4) the NO^+ 5σ is well removed from and the CN^- 5σ is in close proximity to the metal 3d orbitals. This

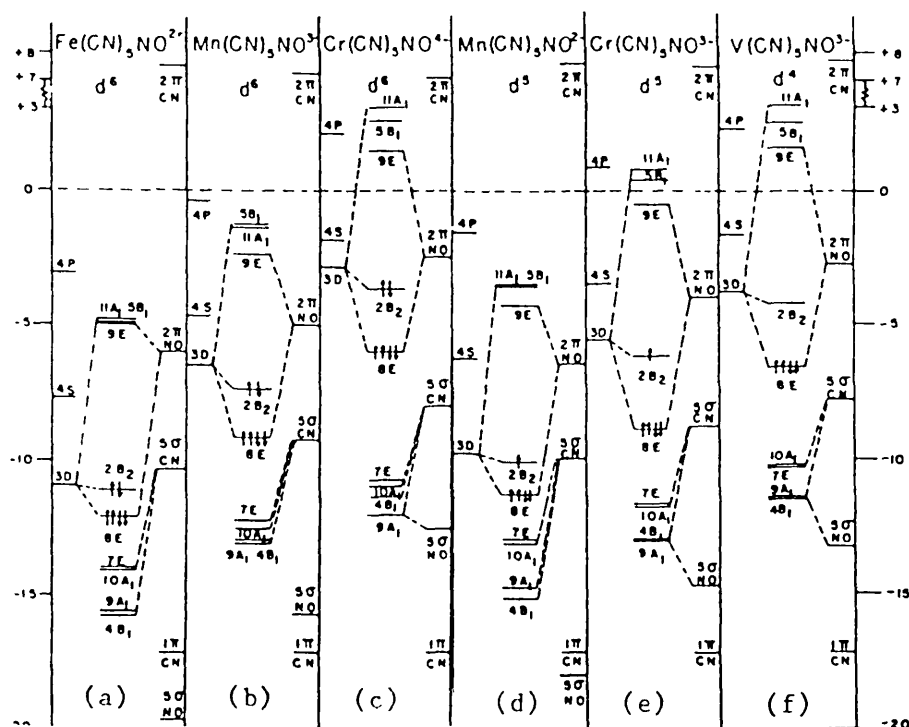


FIGURE 3.4 Relative Energy Levels of Metal-Pentacyanonitrosyl Complexes
Energy scale factors: (a)-7.00,(b)-11.46,(c)-6.50,(d)-20.37,(e)-11.15,(f)-10.61eV

TABLE 3.7 Comparison between CN Force Constants for Hexacyano and Monosubstituted Hexacyano Complexes

COMPLEX	$k_{\text{oct}}^{126,127}$	k_{trans}	k_{cis}
$[\text{Co}(\text{CN})_6]^{3-}$	17.37	-	-
$[\text{CoH}(\text{CN})_5]^{3-}$	-	16.95	16.87
$[\text{Rh}(\text{CN})_6]^{3-}$	17.49	-	-
$[\text{RhH}(\text{CN})_5]^{3-}$	-	17.10	17.23
$[\text{Ir}(\text{CN})_6]^{3-}$	17.44	-	-
$[\text{IrH}(\text{CN})_5]^{3-}$	-	17.07	17.19
$[\text{Mn}(\text{CN})_6]^{5-}$	14.75	-	-
$[\text{Mn}(\text{NO})(\text{CN})_5]^{3-}$	-	17.09	16.99
$[\text{Re}(\text{CN})_6]^{5-}$	14.87	-	-
$[\text{Re}(\text{NO})(\text{CN})_5]^{3-}$	-	17.03	16.95
$[\text{Fe}(\text{CN})_6]^{4-}$	16.14	-	-
$[\text{Fe}(\text{NO})(\text{CN})_5]^{2-}$	-	17.77	17.66

means that the σ -donation of the cyanide group should be greater than the σ -donation of the nitrosyl group and variations in the metal 3d orbital energies should result in substantial changes in the degree of σ -donation by the cyanides but cause only minor variations in that of the nitrosyl group. The converse is true for the 2π orbital interaction where that of the nitrosyl group should be stronger than that of cyanide and be more susceptible to the nature of the metal orbitals. This is in keeping with the view of NO^+ being a stronger π -acceptor than CN^- . Figure 3.4 shows the trend across the transition metal series where the metal 3d orbitals become more stabilised - from the 3d levels above the 2π NO^+ and far above the 5σ CN^- in the case of chromium to just below 5σ CN^- and far below the 2π NO^+ in nitroprusside. This reflects weaker 2π NO^+ participation and stronger 5σ CN^- interaction across the series. Hence (Table 3.7) we see an increase in the CN force constant on replacing CN^- by NO^+ .

The effect of replacing CN^- by H^- is not as obvious. Here, we are replacing a ligand capable of σ -donation and some π -acceptance by a ligand capable of σ -donation only. The lengthening of the $\text{Rh-C}_{\text{trans}}$ bond in $[\text{RhH}(\text{CN})_5]^{3-}$ (Section 2.3.4, p. 55) suggests that the predominant effect is a σ one. The contribution to the σ -bonding framework by H^- is sufficient to suppress slightly that by CN^- resulting in a longer $\text{Rh-C}_{\text{trans}}$ bond and a slight increase in the force constant. This is true for the rhodium and iridium complexes but not for $[\text{CoH}(\text{CN})_5]^{3-}$ where k_{trans} and k_{cis} are smaller than $[\text{Co}(\text{CN})_6]^{3-}$.

(e) Relationship between Chemical Shift and Force Constant

We mentioned in the introduction to the n.m.r. section that work on carbonyl complexes^{106,107} had shown a relationship between δ and k .

FIGURE 3.5 Relationship between $\delta_{\text{cis}}(\text{CN})$ and k_{CN}

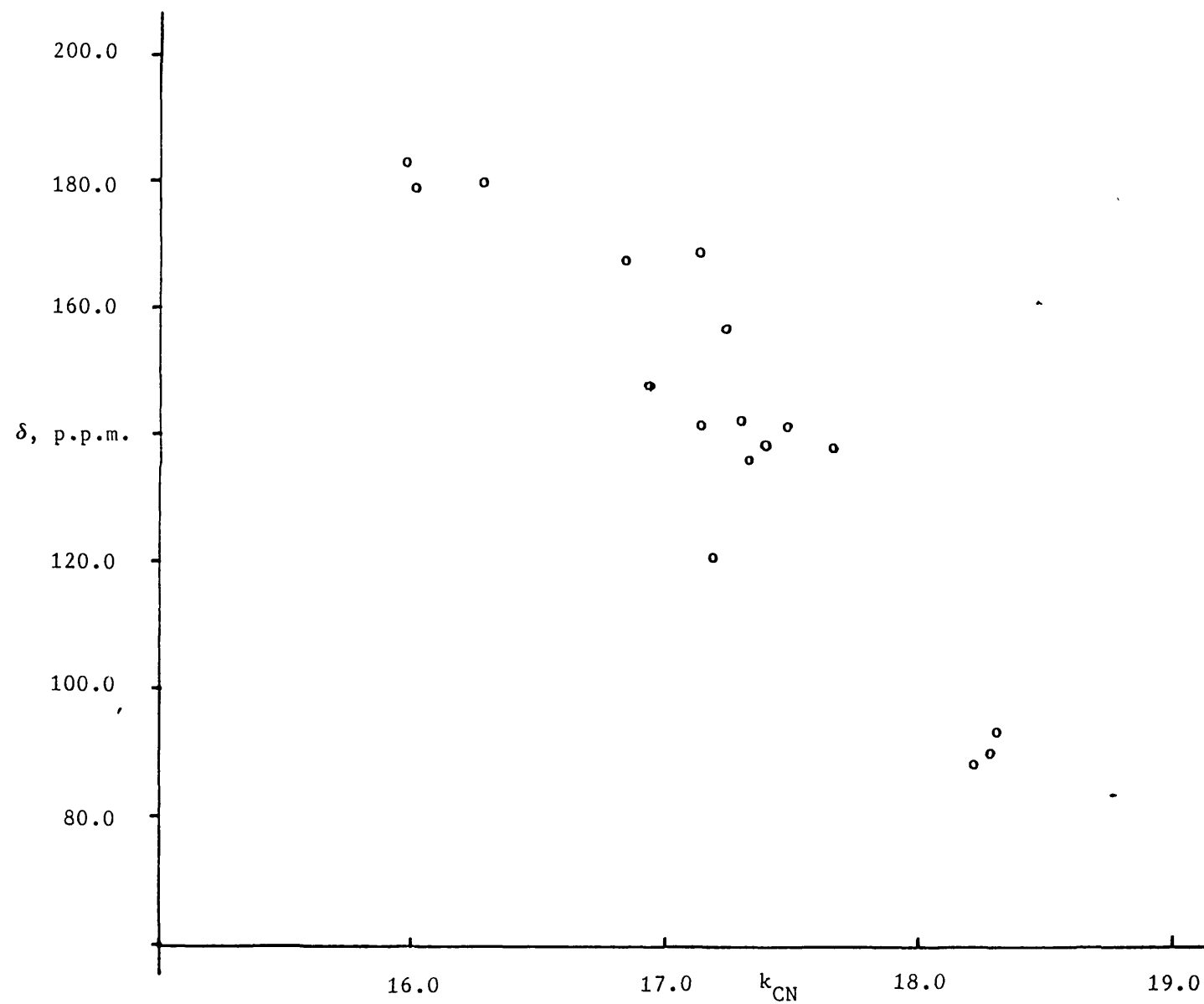
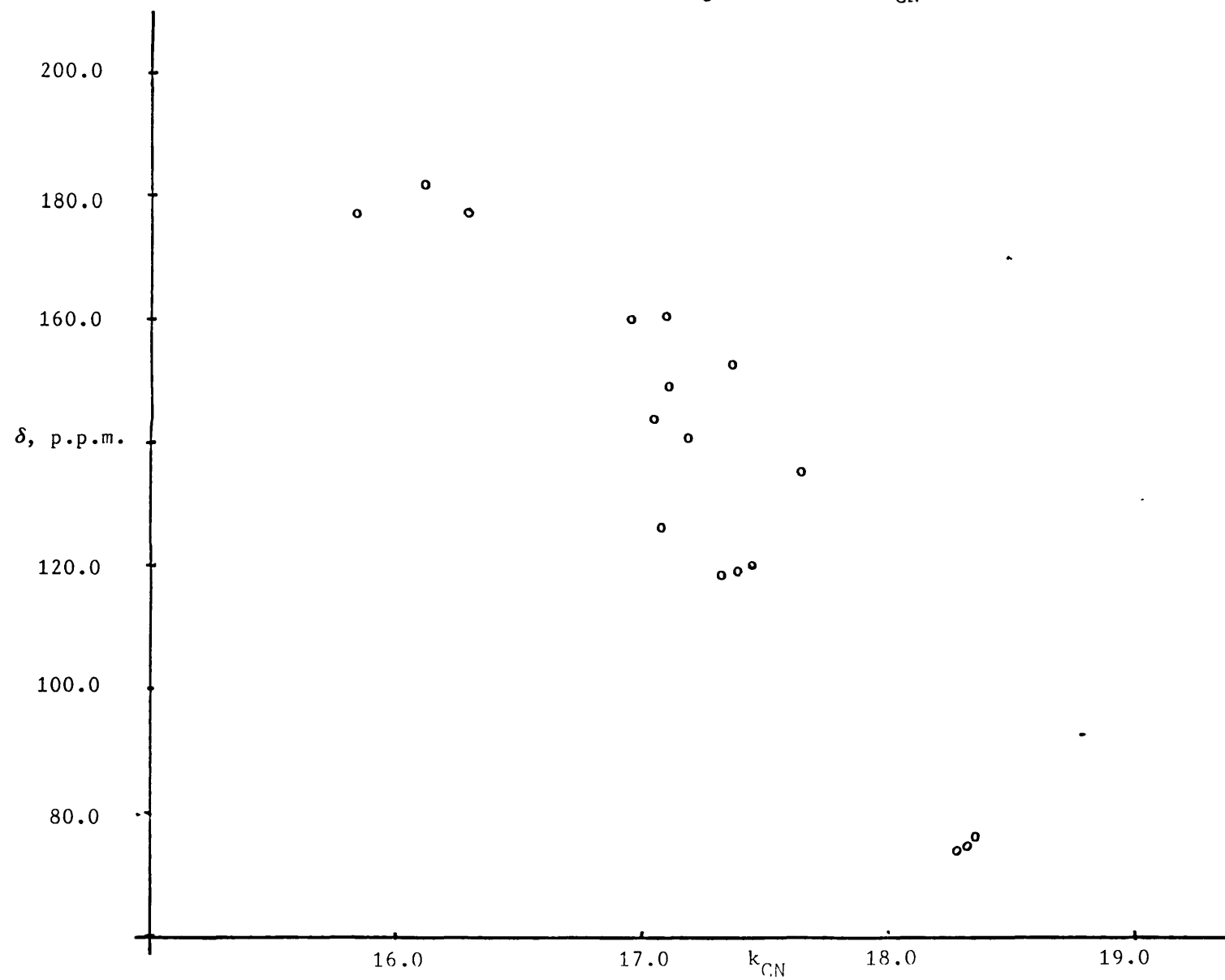


FIGURE 3.6 Relationship between $\delta_{\text{trans}}(\text{CN})$ and k_{CN}



Figures 3.5 and 3.6 show that a similar relationship is found in cyano complexes, namely as δ increases, k_{CN} decreases. A stronger CN bond is associated with a higher field shift in the ^{13}C n.m.r. signal, i.e. with a ^{13}C nucleus that is shielded. From our previous discussions, this implies that the CN^- is closer to the metal and is participating in σ -bonding which from our infrared and Raman results we know strengthens the CN bond.

3.2.7 THE X-RAY CRYSTAL STRUCTURE OF $\text{K}_5[\text{Ru}_2\text{N}(\text{CN})_{10}]\cdot 3\text{H}_2\text{O}$

The nitride ion, N^{3-} , is a strong π -donor and capable of stabilising metals in relatively high oxidation states. In recent years, a variety of terminal and bridged nitrido complexes of ruthenium and osmium have been prepared and characterised¹³⁵⁻⁷ e.g. $[\text{Ru}_2\text{NCl}_8(\text{H}_2\text{O})_2]^{3-}$. The only μ -nitrido complex, however, of this type in which the two axial ligands are the same as the cis ligands is the cyano complex, $\text{K}_5[\text{Ru}_2\text{N}(\text{CN})_{10}]\cdot 3\text{H}_2\text{O}$ first prepared by Griffith and Pawson.¹³⁶ We were interested in this complex as part of our studies on species containing the $[\text{MX}(\text{CN})_5]^{n-}$ moiety and report extended infrared and Raman studies, ^{13}C n.m.r. studies and an X-ray crystal structure determination.

(a) X-Ray Crystal Structure of $\text{K}_5[\text{Ru}_2\text{N}(\text{CN})_{10}]\cdot 3\text{H}_2\text{O}$

The molecule was found to be centrosymmetric but there is some disorder in the positions of the K^+ and H_2O atoms in the unit cell; hence the structure is not particularly accurate, R is 0.073%. The relevant bond lengths and angles are summarised in Table 3.8 and the anion is illustrated in Figure 3.7. We observe that the Ru-C bond trans to the nitrido ligand is longer than those cis by 0.099 Å. It should

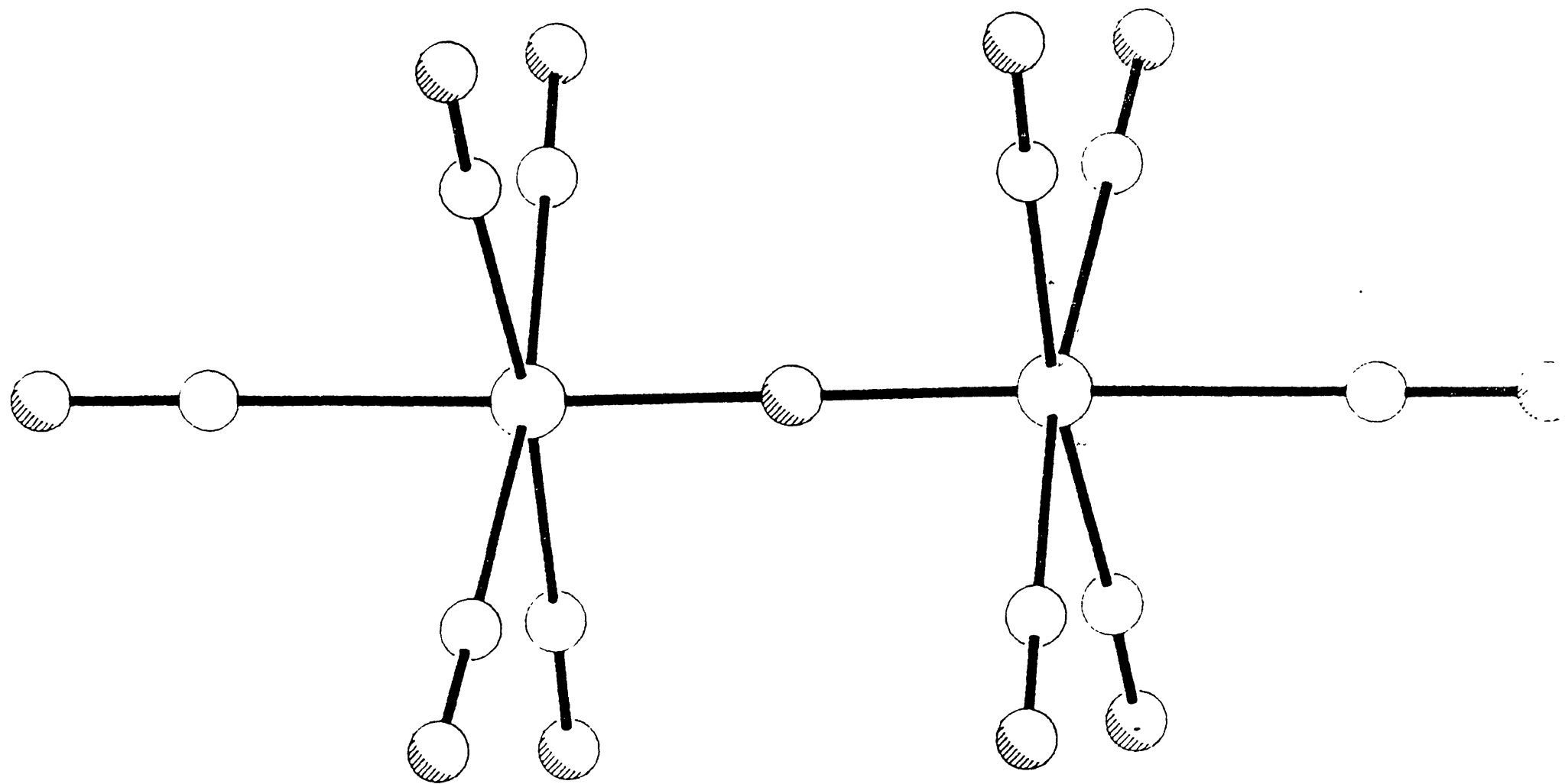


FIGURE 3.7 The $[\text{Ru}_2\text{N}(\text{CN})_{10}]^{5-}$ Anion

TABLE 3.8 Bond Lengths and Bond Angles for $K_5[RuN(CN)_{10}].3H_2O$

	BOND LENGTHS, Å BOND ANGLES, °
Ru - N	1.766(1)
mean Ru - C _{cis}	2.046(17)
Ru - C _{trans}	2.145(17)
N - Ru - C _{cis}	93.1(4)

also be noted that the mean N-Ru-C_{cis} angle is 93.1(4)° indicating a significant displacement of the four cis-cyanide ligands away from the N³⁻ (a similar situation occurs in $[Ru_2NCl_8(H_2O)_2]^{3-}$)¹³⁸; in $[RhH(CN)_5]^{3-}$, the H-Rh-C_{cis} angle was 87.5° (see p. 55).

(b) Infrared and Raman Spectroscopy

The infrared and Raman data are given in Table 3.9 and the spectra are illustrated in Figure 3.8. The spectra are similar in both the solid state and in solution suggesting that there is no change in geometry in solution. In all, seven CN bands, four Raman (two polarised) and three infrared are observed in solution. If the cyano groups were eclipsed, the molecule would have D_{4h} symmetry and, if staggered, D_{4d} symmetry but both configurations give rise to this number of bands:

D _{4h}	Raman	2A _{1g} + B _{1g} + E _g	D _{4d}	Raman	2A ₁ + E ₂ + E ₃
	I.R.	2A _{2u} + E _u		I.R.	B ₂ + E ₁

We provisionally assign the intense polarised Raman band at 2149.5 cm⁻¹

FIGURE 3.8 Infrared and Raman Spectra of $[\text{Ru}_2\text{N}(\text{CN})_{10}]^{5-}$

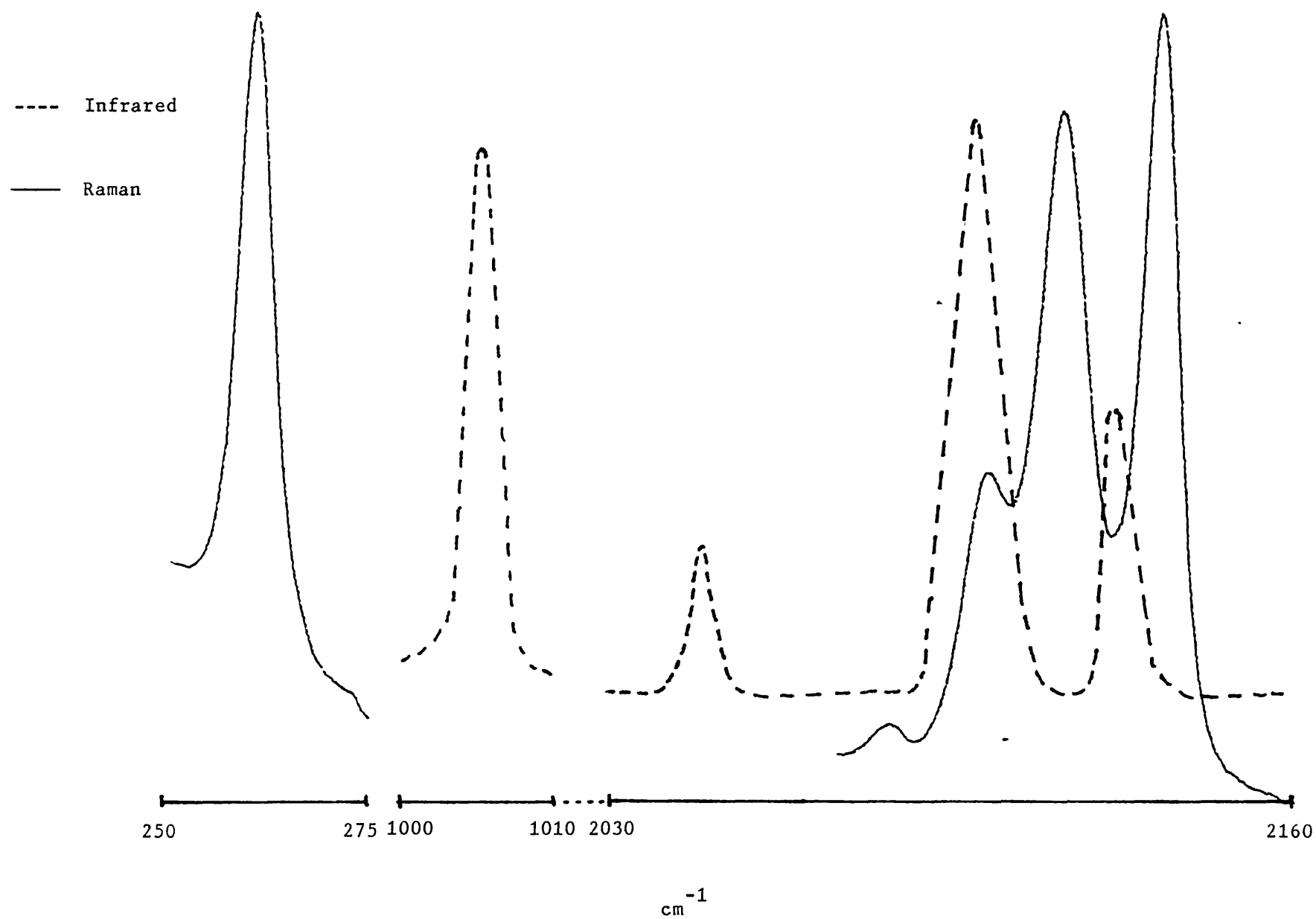


TABLE 3.9 Infrared and Raman Data for $[\text{Ru}_2\text{N}(\text{CN})_{10}]^{5-}$

	INFRARED, cm^{-1}		RAMAN, cm^{-1}	
	SOLID	SOLUTION	SOLID	SOLUTION
ν_{CN}	2143s	2142m	2155(7)	
	2138s			2149.5(10)p
	2130s		2142(6)	
	2120s	2121vs	2134(7)	2135.0(9)dp
	2110s		2123(1)	2124.0(5)p
	2080m,sh			2109.0(1)dp
	2040m,sh	2044m		
δ_{OH_2}	1620s			
$\nu_{\text{as}}, \text{Ru}_2\text{N}$	1010s	1006s		
	985s			
$\nu_{\text{Ru-C}}$				489(4)
				403(1)
$\delta_{\text{Ru-CN}}$				385(1)
				364(2)
$\nu_{\text{sym}}, \text{Ru}_2\text{N}$			262(4)	259(5)p

to the symmetric CN stretch (A_1) and the polarised band at 2124 cm^{-1} to the symmetric stretch of the cyano ligands trans to the nitrido group. This lower frequency probably occurs because the trans cyanide is opposite the strongly 'trans-influencing' nitrido ion. This leads to a weaker $\text{Ru-C}_{\text{trans}}$ bond and hence a weaker CN bond.

The asymmetric Ru_2N stretch is observed in the infrared spectrum at 1006 cm^{-1} in solution ($1010, 985 \text{ cm}^{-1}$ in the solid) and the symmetric stretch is observed in the Raman spectrum at 259 cm^{-1} (polarised).

(c) ^{13}C n.m.r. Spectroscopy and Conclusions

In the ^{13}C n.m.r. spectrum of an aqueous solution of $[\text{Ru}_2\text{N}(\text{CN})_{10}]^{5-}$ two resonances were observed at δ 141.9 and 140.1 p.p.m., which integrated in the ratio 4:1. Although this difference is small, it is comparable in magnitude to that found for $\text{X} = \text{NO}^+$, NO_2^- , NH_3 , PPh_3 , AsPh_3 in $[\text{MX}(\text{CN})_5]^{n-}$. The fact that the trans-resonance is at higher field than the cis is surprising in view of the fact that the trans-Ru-C distance (2.145 Å) is slightly but significantly longer than the cis-Ru-C (2.046 Å); a similar situation is $[\text{RhH}(\text{CN})_5]^{3-}$ (p. 55) where cis Rh-C is 2.002 Å and trans Rh-C is 2.081 Å, which give rise to ^{13}C resonances at δ 141 p.p.m. and 149 p.p.m. respectively, in the opposite sense to the situation for the ruthenium complex.

In the other $[\text{MX}(\text{CN})_5]^{n-}$ complexes which have been studied by X-ray methods, the trans bond is longer than the cis in $[\text{Mo}(\text{NO})(\text{CN})_5]^{4-}$ 115 and $[\text{Mn}(\text{NO})(\text{CN})_5]^{3-}$ 116 but shorter in $[\text{Fe}(\text{NO})(\text{CN})_5]^{2-}$ and the trans- ^{13}C shift is at higher field than the cis except for $[\text{RhH}(\text{CN})_5]^{3-}$. The ruthenium complex is, therefore, not abnormal in its behaviour.

One possibility that we may consider for this behaviour is that all the complexes except $[\text{RhH}(\text{CN})_5]^{3-}$ have the four cis cyanide ligands displaced away from the unique ligand, X. e.g. $\text{N}-\widehat{\text{Ru}}-\text{C}_{\text{cis}} 93.1(4)^\circ$ in $[\text{Ru}_2\text{N}(\text{CN})_{10}]^{5-}$, mean $\text{ON}-\widehat{\text{Fe}}-\text{C}_{\text{cis}} 95.0^\circ$ in $[\text{Fe}(\text{NO})(\text{CN})_5]^{2-}$ 117. The hydride complex, however, has an $\text{H}-\widehat{\text{Rh}}-\text{C}_{\text{cis}}$ angle of 87.5° . We may therefore envisage the trans-CN in the rhodium hydride complex as deshielded relative to the cis ligands, whilst in the other complexes, the opposite is true, as the cis ligands are pushed towards the trans. The deshielded trans-CN in the rhodium hydride complex is therefore observed downfield of the cis.

A recent paper¹³⁸ has mentioned the ^{99}Ru Mössbauer spectroscopy

of some nitrido bridged dimers. The isomer shift is sensitive to the oxidation state of the metal since the removal of s-electrons decreases the electron density of the metal atom, whereas the removal of electrons of higher l decreases the s-electron shielding of the nucleus and leads to an increase in electron density of the metal atom. Ligands that are good σ -donors will directly cause an increase in the s-electron density at the nucleus and thereby increase the isomer shift. If the ligand is a good $L \rightarrow M$ π donor, it will cause an increase in the d-orbital population of the electrons on the metal ion and thereby increase the shielding of s electrons from the nucleus thus causing a lowering of the isomer shift. When there is $M \rightarrow L$ π -bonding, the effect is reversed; there is a decrease in the d-orbital occupancy and therefore less shielding of the s-electrons and consequently an increase in the isomer shift. The low values of the isomer shift for the complexes $[\text{Ru}_2\text{NX}_8(\text{H}_2\text{O})_2]^{3-}$ where $X = \text{Cl}^-$, Br^- , (-0.36 and -0.42 mms^{-1}) is attributed to greater d-electron shielding of s electrons due to $L \rightarrow M$ $p\pi - d\pi$ bonding whilst the high value observed for the cyano complex (-0.025 mms^{-1}) is attributed to loss of 4d electrons from the metal by back donation¹³⁸, although we would suggest that the earlier explanation of increased σ -bonding is more applicable here.

3.2.8 CONCLUDING REMARKS

We would suggest that ^{13}C n.m.r. spectroscopy and the Cotton-Kraihanzel bonding model are useful methods for studying substituted cyano complexes. It seems that k, the force constant of the CN bond and δ vary in approximately the same way (Fig. 3.5 and 3.6) and that both are dependent upon changes in the metal oxidation state, and the nature of the ligand, X. For a detailed trans-influence series, it

is advantageous to study complexes of a metal with a nuclear spin as coupling constants are then of use but, from our results we would suggest the following trans-influence series of ligands towards Fe(II): $\text{NH}_3 > \text{pyridine} \sim \text{SO}_3^{2-} \sim \text{NO}_2^- > \text{AsPh}_3 \sim \text{PPh}_3 \sim \text{pyrazine} \sim \text{CN}^- > \text{Me}_2\text{S}=\text{O} > \text{NO}^+$. This series is similar to those reported for Pt(II)-Cl complexes e.g. $\text{pyridine} > \text{NH}_3 > \text{S-donors} > \text{AsPh}_3 \sim \text{PPh}_3$.⁷⁵ The ligands H^- and N^{3-} also exhibit high trans-influences in the complexes $[\text{RhH}(\text{CN})_5]^{3-}$, and $[\text{Ru}_2\text{N}(\text{CN})_{10}]^{5-}$ respectively.

There are clearly a few problems to solve and we would suggest that further work in this area should concentrate on complexes of metals such as rhodium and platinum which have nuclear spins. More data should enable assessment of ΔE in the shielding terms and hence a better understanding of chemical shifts. Some ^{15}N n.m.r. work could prove interesting as a recent report¹¹⁵ on tungsten carbonyl species found some strange and unexpected effects in ^{17}O n.m.r. as the ligand, X was varied. In conjunction with the n.m.r. work, it would be useful to obtain more crystallographic data on the substituted complexes - the difference in bond lengths and, as we noted in the previous section, the variations in bond angles are valuable aids in explaining the other experimental results.

3.2.9 VIBRATIONAL SPECTROSCOPIC AND N.M.R. STUDIES ON OTHER CYANO COMPLEXES

In this section, we report studies on two pentacyanonitrosyl complexes and ^{13}C n.m.r. studies on a number of other complexes.

(a) $\text{K}_3[\text{Co}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$

There was, at one time, much controversy in the literature^{139,140}

about the nature of the black and red isomers of the nitrosylpentaamine cobalt(III) ion. However, crystal structure studies have shown that the complex ion of the black chloride is monomeric and octahedral with a bent NO group¹⁴¹ (previous studies which reported the NO group as linear were incorrect¹⁴²) and that the red salt, $[\text{Co}(\text{NH}_3)_5(\text{NO})]_2 \cdot \text{Br}_{2.5}(\text{NO}_3)_{1.5} \cdot 2\text{H}_2\text{O}$ is binuclear with an asymmetric cis-hyponitrito bridge.¹⁴³ (Figure 3.9) The pentacyanonitrosyl cobaltate(III) ion¹³⁹ was prepared by treatment of the red and black pentaamminenitrosyl complexes with cyanide. Raynor¹⁴⁴ suggested that the complex should be formulated as trans- $[(\text{CN})_5\text{CoN}_2\text{O}_2\text{Co}(\text{CN})_5]^{6-}$ as $\nu_{\text{as}} \text{N}=\text{O}$ 1120 cm^{-1} corresponded to ν_{as} 1020 cm^{-1} found in the $\text{N}_2\text{O}_2^{2-}$ ion. Toyuki¹⁴⁵ examined the infrared spectrum and, on the basis that the NO stretch in the cobalt complex was much too low for the trend observed in $[\text{M}^x(\text{NO})(\text{CN})_5]^{4-x}$, $\text{M} = \text{Cr}(\text{I}), \text{Mn}(\text{I}), \text{Fe}(\text{II})$, concluded that the species was dimeric with a cis or skew hyponitrito group (a trans-configuration would have fewer infrared bands). Our infrared and Raman data for the complex are presented in Table 3.10 with infrared data from the literature for comparison.

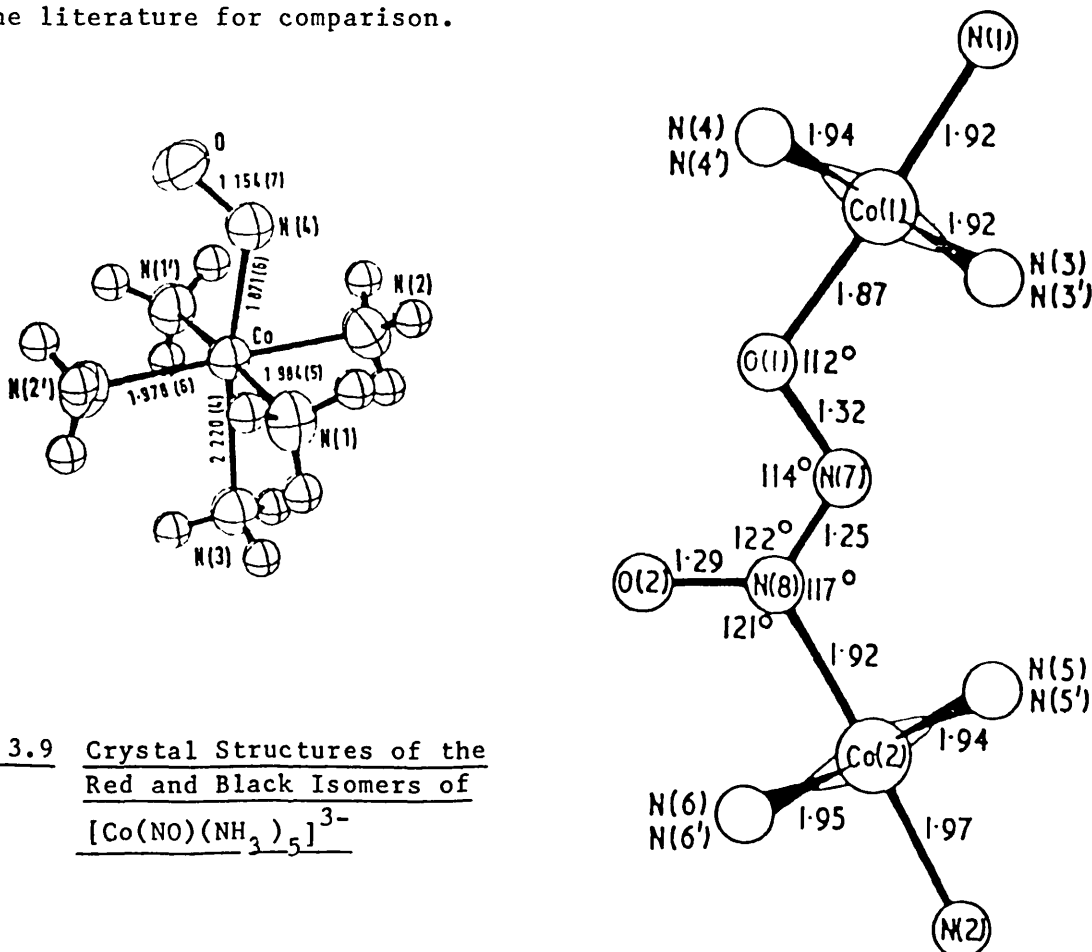


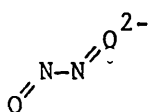
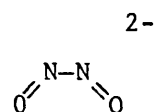
FIGURE 3.9 Crystal Structures of the Red and Black Isomers of $[\text{Co}(\text{NO})(\text{NH}_3)_5]^{3-}$

TABLE 3.10 Infrared and Raman Data for $K_3[Co(NO)(CN)_5] \cdot 2H_2O$

ASSIGNMENT	INFRARED, cm^{-1}				RAMAN, cm^{-1}	
	139	144	145	this work	SOLID	this work SOLUTION
ν_{OH}			3333vs			
ν_{CN}	2141s	2141	2123vs	2120vvs	2152.5(10)	2154(10)p
	2104sh	2104			2141.0(5)	2141(5)dp
δ_{OH_2}	1630m		1603m	1620s,br		
				1335m	1342($\frac{1}{2}$)	1341($\frac{1}{2}$)
$\nu_{N=O}$	1120m	1120	1114m	1160sh		
				1120vvs,br		
			1052w		1032($\frac{1}{2}$)	
ν_{N-O} in in N_2O_2			971vs	980w 832m	986(2) 838(1)	980(2)p 831(1)p
$\nu_{Co-N_2O_2}$			615w 561m	617s 570m	622($\frac{1}{2}$)	
ν_{Co-N}			536w			
ν_{Co-CN}			460w		497($\frac{1}{2}$) 458($\frac{1}{2}$)	
			412vs	418vs	409(5)	410(5)dp
δ_{Co-CN}			380w			
δ_{N-N-O}			370w			
δ_{Co-C-N}			330w 290w		291($\frac{1}{2}$)	292($\frac{1}{2}$)
$\delta_{NC-Co-CN}$			270vw			

In the infrared spectrum, we observed a strong $\nu_{\text{C}\equiv\text{N}}$ stretching frequency at 2120 cm^{-1} similar to Toyuki¹⁴⁵ but somewhat different to the observations of Griffith *et al*¹⁴⁰ and Raynor¹⁴⁴ who reported that ν_{CN} was 2141 cm^{-1} . Griffith *et al*¹⁴⁰ and Raynor¹⁴⁴ further reported a strong band at 1120 cm^{-1} which they attributed to $\nu_{\text{N}=\text{O}}$; we also observed this band with a shoulder at 1160 cm^{-1} . Toyuki¹⁴⁵ reported bands at 1114, 1052 and 971 cm^{-1} which he assigned as $\nu_{\text{N}=\text{N}}$ in $\text{N}_2\text{O}_2^{2-}$, $\nu_{\text{N}-\text{O}}$ in $\text{N}_2\text{O}_2^{2-}$ and $\nu_{\text{N}-\text{O}}$ in $\text{N}_2\text{O}_2^{2-}$ respectively. Griffith¹⁴⁰ and Raynor¹⁴⁴ reported no other data but, like Toyuki¹⁴⁵, we observed a strong band at 418 cm^{-1} which we assign as $\nu_{\text{Co-CN}}$. Table 3.11 lists the relevant infrared stretching frequencies for trans- $\text{N}_2\text{O}_2^{2-}$ and cis- $\text{N}_2\text{O}_2^{2-}$ along with those observed for the complex. We would tentatively suggest from these data that the species contains a cis- $\text{N}_2\text{O}_2^{2-}$ group.

TABLE 3.11 Infrared Data for The $\text{N}_2\text{O}_2^{2-}$ Group

139	145	this work			
1120	1114m	1335m	$\nu_{\text{N}-\text{N}}$	1383 ^a	1314 ^b
	1052w	1120vvs	$\nu_{\text{s}}, \text{N}-\text{O}$	1115	1047
	971vs	832m	$\nu_{\text{as}}, \text{N}-\text{O}$	1020	830

^areference 146

^breference 147

There is little difference between the Raman spectra of the solid and aqueous solution of $K_3[Co(NO)(CN)_5]$ which suggests that there is no change in configuration. If the molecule is indeed binuclear, this structure would appear to be maintained in solution.

We were unable to obtain crystals of this complex suitable for X-ray studies and ^{13}C n.m.r. proved of little use. For the monomeric species, we would expect two ^{13}C resonances in the ratio 4:1, for the CN cis and trans to NO respectively. The ^{13}C n.m.r. study should, however, distinguish between CN^- trans to the O and CN^- trans to N in the binuclear species unless the $N_2O_2^{2-}$ bridge is labile on the n.m.r. timescale. We observed a complicated pattern of ten lines of unequal intensity which were difficult to analyse due to ^{59}Co splitting, $I = 7/2$.

It may be that an ^{15}N n.m.r. spectrum would prove more informative; it is now well established that ^{15}N n.m.r. can distinguish between linear and bent nitrosyl groups¹⁴⁸ so a study of this complex could prove to be of interest.

(b) $K_3[Re(NO)(CN)_5] \cdot 2H_2O$

The cyanonitrosyl complex of rhenium has been variously reported as $Ag_3[Re(NO)(CN)_7]$ prepared by the reaction of $[Re(CN)_8]^{3-}$ (now known to be $[Re(CN)_7]^{4-}$ ¹⁴⁹) with HNO_3 .¹⁵⁰ The species $[Re(NO)(CN)_5]^{2-}$ was obtained by treating $[Re(H_2O)(CN)_5]^{3-}$ with HNO_3 ¹⁵¹ and $K_3[Re(NO)(CN)_7] \cdot 4H_2O$ prepared by reductive nitrosylation of $KReO_4$ using hydroxylamine and KCN in aqueous alkaline solution.¹⁵²

We have repeated the latter preparation and obtain a red solid whose microanalysis is consistent with the formulation, $K_3[Re(NO)(CN)_5] \cdot 2H_2O$. We have recorded the infrared, Raman and ^{13}C n.m.r. spectra of this complex. During the course of our work, a further paper on this compound

has appeared which we feel warrants further comment here.¹⁵³ The authors used an identical preparation to that of Sergeova¹⁵² except that an oil was obtained on precipitation of the product with isopropanol (cold ethanol precipitates the solid product). The product analyses to the above formulation and the infrared spectra are comparable although with a slight difference in the ν_{CN} region. Some discrepancy arises, however, in the ^{13}C n.m.r. spectrum. We observe two resonances in intensity ratio 4:1 at 146.7 and 143.6 p.p.m. attributable, as previously discussed, to the cis and trans cyanó groups respectively. Bhattacharyya and Roy¹⁵³ produced a ^{13}C n.m.r. spectrum with eight signals which they assign to two isomeric structures arising from two different modes of hydrogen bonding of the water molecules simultaneously with the NO and a CN^- group. These isomers have C_s symmetry and so ten cyanide resonances should be observed but the authors account for the lack of two signals by accidental degeneracy of three of the groups. Although we cannot discount this observation, we have never observed this phenomenon in any of our complexes reported in this chapter. We would, however, point out that this class of compounds are hygroscopic and, in our experience the solids are somewhat unstable. Since Bhattacharyya and Roys sample was prepared in India and had its ^{13}C n.m.r. spectrum recorded in America, we would suggest that the sample may have degraded.

(c) Other ^{13}C n.m.r. and Spectroscopic Studies

The data to be discussed in this section are presented in Table 3.12 overleaf. The chemical shift of $[\text{Re}(\text{CN})_6]^{5-}$ has been discussed in Section 3.2.4, p. 82. The seven co-ordinate hexacyanonitrosyl complex of vanadium(I) is, like the seven co-ordinate heptacyano complexes fluxional on the n.m.r. timescale and exhibits only one resonance at

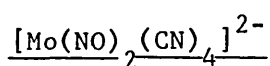
TABLE 3.12 ^{13}C n.m.r. and Infrared and Raman Data for Cyano Complexes
Studied in aqueous Solution

COMPLEX	δ , p.p.m.	INTENSITY	COUPLING CONSTANT, Hz	RAMAN SPECTRA cm ⁻¹	INFRARED SPECTRA cm ⁻¹
$[\text{Re}(\text{CN})_6]^{5-}$	168.0				
$[\text{V}(\text{NO})(\text{CN})_6]^{4-}$	171.3				
$[\text{Mo}(\text{NO})_2(\text{CN})_4]^{2-}$	149.5 146.5	1 1		2145.0(10)p 2139.5(8)dp 2132.5(5)dp 1685.0(10)p 1637.0(6)dp	
$[\text{W}(\text{CN})(\text{CO})_5]^-$	208.5 204.5 158.7	4 cis-CO 1 trans-CO 1 CN	$J(\text{C}, \text{W})$ 124 $J(\text{C}, \text{W}_t^c)$ 139	2125(6)p 1988(5)p 1982(4)dp 1854(10)p 1843(3)p	2118w 2060w 1977w 1920vs 1810s 595vs 375s
$[\text{Ru}_2\text{OCl}_{10}]^{4-}$ + CN^-	121.4 109.6	1 1			2110vs 2080s(CN^-)
$\text{OsO}_4 + \text{CN}^-$ $[\text{OsO}_2(\text{CN})_4]^{2-}$	115.4				
$\text{K}[\text{OsO}_3\text{N}] + \text{CN}^-$	118.0				
Claus salt + CN^- $[\text{Os}_3\text{N}_2(\text{CN})_8(\text{OH})_4(\text{H}_2\text{O})_2]$	145.5				
Osmium violet + CN^- $[\text{Os}_3\text{N}_2(\text{CN})_{10}(\text{H}_2\text{O})_4]$	147.0 143.3	4 1			

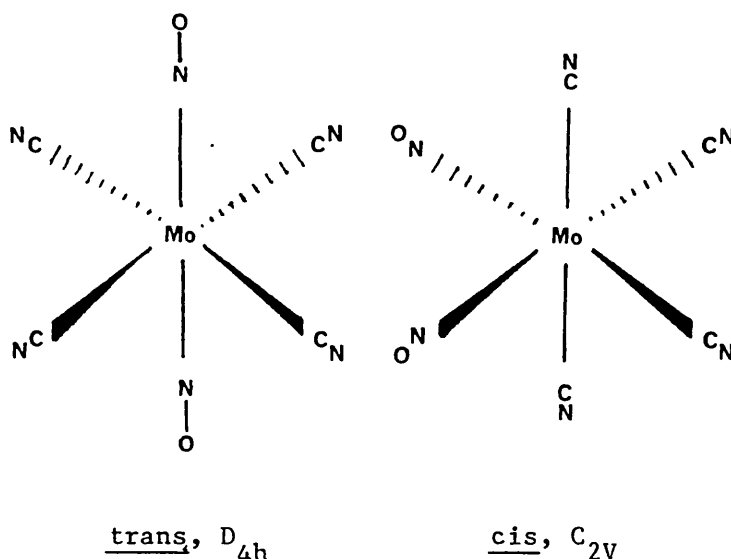
TABLE 3.12 cont.

$[\text{Ni}_2(\text{CN})_6]^{4-}$	148.0	$\omega_{\frac{1}{2}}$ 500 Hz
$[\text{PtCl}_2(\text{CN})_4]^{2-}$	98.9	J(C,Pt) 851
$[\text{PtBr}_2(\text{CN})_4]^{2-}$	96.3	J(C,Pt) 854
$[\text{PtI}_2(\text{CN})_4]^{2-}$	90.8	J(C,Pt) 853

δ 171.3 p.p.m.. Although the signal is broad, ($\omega_{\frac{1}{2}}$ 440 Hz) there is no obvious ^{51}V coupling (^{51}V , 100% abundant, $I = 7/2$). The high co-ordination number and low oxidation state of the vanadium cause the signal to be shifted downfield of that for CN^- as we have mentioned previously (p. 81).



The Mo(0) complex $[\text{Mo}(\text{NO})_2(\text{CN})_4]^{2-}$ was recently reported by Saha et al.¹⁵⁴ They concluded that the compound contained cis-NO groups as there were two NO stretching frequencies in the solid infrared spectrum. A trans- $[\text{Mo}(\text{NO})_2(\text{CN})_4]^{2-}$ species would belong to the point group D_{4h} for which we predict one infrared active (E_u) and two Raman active ($A_{1g} + B_{1g}$, A_{1g} pol) ν_{CN} stretches and one infrared (A_{2u}) and one Raman (A_{1g} , pol) ν_{NO} stretch. The cis-isomer has C_{4v} symmetry and so we would expect four infrared and four Raman active fundamentals ($2A_1 + B_1 + B_2$, $2A_1$ pol) for the cyanide stretch and two infrared and Raman active ν_{NO} fundamentals ($A_1 + B_2$, A_1 pol). In the ^{13}C n.m.r. spectrum of the trans-isomer, we would expect to see one



resonance as all the CN^- groups are equivalent but for the cis-isomer two signals of equal intensity would be predicted assigned to CN trans to NO and CN cis to NO. The data presented in Table 3.12 indicate the presence of a cis-(NO)₂ moiety. The Raman spectrum of an aqueous solution showed one strong polarised band at 2145 cm^{-1} which we assign as an A_1 mode and two depolarised ν_{CN} stretches which we assign as B_1 and B_2 . The second A_1 mode was not observed and is either very weak or coincident with the other A_1 mode. There are two ν_{NO} stretches at 1685 cm^{-1} (A_1) and 1637 cm^{-1} (B_2).

The ^{13}C n.m.r. spectrum consisted of two resonances of equal intensity at δ 149.5 and 146.5 p.p.m.. From our previous work (Table 3.2, p. 79), we might expect that the resonance at δ 146.5 p.p.m. is due to CN⁻ trans to NO. The ^{95}Mo n.m.r. spectrum of the complex was recorded by Enemark *et al*¹⁵⁵ who observed a single resonance at δ -105 p.p.m. relative to MoO_4^{2-} ($w_{1/2}$ 20Hz, pH 11). Our attempts to observe ^{95}Mo - ^{14}N coupling from the NO ligand as reported in $[\text{CpMo}(\text{NO})(\text{CO})_2]^{-}$ ¹⁵⁶ were unsuccessful. It is interesting to note that replacing a cyanide ligand in $[\text{Mo}(\text{NO})(\text{CN})_5]^{4-}$ by a nitrosyl ligand to give $[\text{Mo}(\text{NO})_2(\text{CN})_4]^{2-}$ causes the ^{13}CN resonance to shift upfield from ~ 164 p.p.m. to ~ 147 p.p.m.. This is opposite to the effect observed in carbonyl complexes where δ_{CO} moves downfield with successive replacement of CO by ligands such as phosphines.¹¹⁰

Reaction of $[\text{Ru}_2\text{OCl}_{10}]^{4-}$ with CN^-

We found that reaction of $[\text{Ru}_2\text{OCl}_{10}]^{4-}$ with excess of cyanide in hydrochloric acid solution yielded a yellow solution whose ^{13}C n.m.r. spectrum had two peaks of equal intensity at 121.4 and 109.6 p.p.m.. An infrared spectrum of the same solution had a cyanide stretch at 2110 cm^{-1} . We were unable to isolate a complex from the solution. If CN^- had replaced all ten chloride ligands, we would expect to see two ^{13}C resonances in ratio 4:1. It is possible that the dimer decomposed yielding monomeric species containing the cyano ligand; $[\text{Ru}(\text{CN})_6]^{4-}$ was not formed as its chemical shift is reported at 162.3 p.p.m..⁶⁸

Reaction of OsO_4 with CN^-

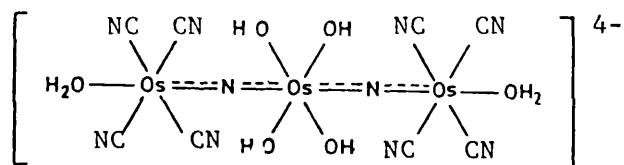
The action of aqueous KCN on OsO_4 was reported to yield the complex $[\text{OsO}_2(\text{CN})_4]^{2-}$, $\nu_{\text{CN}}\ 2152\text{ cm}^{-1}$.¹⁵⁷ The ^{13}C spectrum of the orange solution had one resonance at $\delta 115.4$ p.p.m. consistent with this formulation. The chemical shift is at a much higher field than that of $[\text{Os}(\text{CN})_6]^{4-}$ ⁶⁸ (142.5 p.p.m.) due to the high oxidation state of the osmium in the dioxo complex and the effect of the trans- OsO_2 moiety.

Reaction of $\text{K}[\text{OsO}_3\text{N}]$ with CN^-

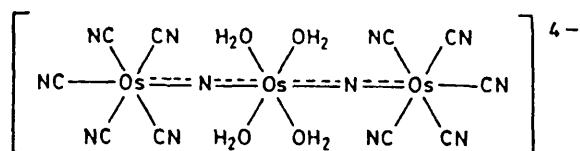
We observed only one resonance at 118.0 p.p.m. in a ^{13}C n.m.r. spectrum of an aqueous solution of potassium osmiamate, $\text{K}[\text{OsO}_3\text{N}]$, and potassium cyanide. This is similar to the ^{13}C chemical shift of $[\text{OsO}_2(\text{CN})_4]^{2-}$ and we would suggest that the species present was trans- $[\text{OsN}(\text{H}_2\text{O})(\text{CN})_4]^-$ reported by Griffith¹⁵⁸ on treatment of $[\text{OsO}_3\text{N}]^-$ with hydrocyanic acid.

Reaction of Claus Salt and Osmium Violet with Potassium Cyanide

The ^{13}C n.m.r. spectra of the product of the reaction of Claus salt with cyanide¹⁵⁹ and the product of the reaction of cyanide with osmium violet¹⁵⁹ consisted of one signal at δ 145.4 and two signals at δ 147.0 and 143.3 p.p.m. (in the ratio 4:1) respectively. It is interesting to note that the Claus salt derivative contains the $[\text{OsN}(\text{H}_2\text{O})(\text{CN})_4]^-$ unit mentioned above but the chemical shift is quite different presumably due to the extended delocalisation over the Os_3N_2 skeleton.

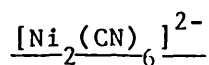


Claus salt derivative



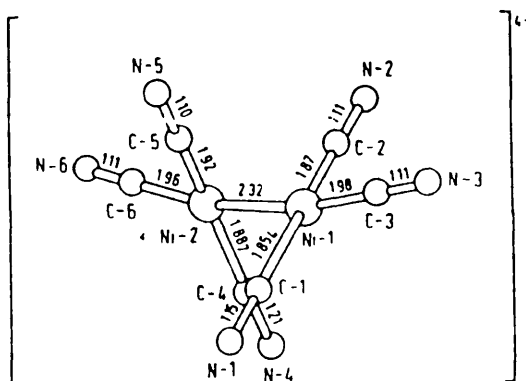
Osmium violet derivative

The ^{13}C n.m.r. spectra illustrate quite clearly the difference between the two complexes. The osmium violet derivative contains both cis and trans-CN groups co-ordinated to the osmium.



The dark red complex, $\text{K}_4[\text{Ni}_2(\text{CN})_6]$ made by reduction of an aqueous solution of $\text{K}_2[\text{Ni}(\text{CN})_4]$ with sodium amalgam under nitrogen has been studied by infrared and Raman spectroscopy¹⁶⁰ and by X-ray crystallography.¹⁶¹

The structure of the rubidium salt has also been determined.¹⁶² In both complexes, the anion consists of two almost planar tricyanonickelate(I) units linked via an Ni-Ni bond about which they are twisted by 82° with respect to each other. (see below)



It is not possible to distinguish between the cyano groups in the ^{13}C n.m.r. spectrum. We observed only one resonance at δ 148.0 p.p.m. which was very broad, $w_{1/2}$ 500 Hz, presumably, this is due to the fluxionality of the molecule in solution.

3.2.10 ^{14}N N.M.R. STUDIES ON TRANSITION METAL CYANO COMPLEXES

^{14}N n.m.r. spectroscopy is dominated by quadrupolar relaxation, since the nuclear electric quadrupole is coupled to the nuclear spin. As the molecule tumbles, the change in the electric field gradient, (q), round the ^{14}N nucleus relaxes the electric quadrupole, and this relaxes the spin also. The lower the local symmetry about nitrogen, the larger q, the faster the quadrupole relaxation and the broader the line by the uncertainty principle.¹⁶³

Our ^{14}N n.m.r. spectra were recorded at 6.43MHz on a Jeol FX 90Q machine, we found that best results were obtained using a pulse delay of one second and a pulse width of 30 μs ; typically 500 to 1000 scans were required to obtain good spectra. A 2M aqueous solution of NH_4NO_3

was used as a standard, with the NH_4^+ line at δ 0 and the NO_3^- line at δ 355.8 p.p.m..

The results are presented in Table 3.13 with those from the literature for comparison and reference. The di-, tetra- and hexacyano complexes all lie in the chemical shift range 227 - 280 p.p.m. with no apparent relationship between the co-ordination number and the chemical shift of metal oxidation number and chemical shift. The latter is perhaps to be expected since the nitrogen is well removed from the vicinity of the metal. The resonances are all broad, typically 800 Hz at half height. The octacyano complexes, $[\text{M}(\text{CN})_8]^{4-}$ where $\text{M} = \text{Mo}, \text{W}$, appear at lower field as do the substituted pentacyano species. It is interesting to note that there is no distinction between cis and trans-CN in these spectra although it is not possible to conclude whether this is a result of the line broadening or of the ^{14}N environments in the molecule. Neither Nikolskii et al¹⁰⁵ or our results show a resonance due to NO^+ in the pentacyanonitrosyl complexes, although M-NO^+ resonances are reported to occur in the region 270 - 400 p.p.m..¹⁶³ Despite the lowering of symmetry in the complexes $[\text{MX}(\text{CN})_5]^{n-}$ compared with $[\text{M}(\text{CN})_x]^{n-}$ where $x = 2, 4, 6$, the resonances do not appear to broaden significantly with the exception of $[\text{W}(\text{CN})_8]^{4-}$ ($w_{1/2}$ 1133 Hz), $[\text{Fe}(\text{NO})(\text{CN})_5]^{2-}$ ($w_{1/2}$ 4500 Hz) and $[\text{RhH}(\text{CN})_5]^{3-}$ ($w_{1/2}$ 51 Hz). In no example was metal- ^{14}N coupling observed.

We concluded, therefore, that ^{14}N n.m.r. was not, for our purposes, particularly useful mainly due to the broadness of the lines; ^{15}N n.m.r., although practically more difficult to obtain, would be more informative due to observation of couplings and sharp lines.

Note: We found in all our n.m.r. experiments that addition of 6mM $[\text{Gd}(\text{EDTA})]^-$ as a relaxation reagent enabled us to accumulate spectra more rapidly. It is not advisable to use this method in cases where small splittings of the resonances are likely as line broadening renders such splittings unobservable.

TABLE 3.13 ^{14}N N.M.R. Data for Cyano and Substituted Cyano Complexes of Transition Metals

COMPOUND	$\delta^{14}\text{N}$, p.p.m.	WIDTH OF ^{14}N RESONANCE AT HALF HEIGHT, Hz	REFERENCE
NH_4NO_3	0 (NH_4^+)	13.5	this work
	355.8 (NO_3^-)	16.9	this work
CN^-	280.0	67.0	this work
$[\text{Mn}(\text{CN})_6]^{3-}$	227	860	104
$[\text{Fe}(\text{CN})_6]^{2-}$	241	645-860	104
$[\text{Fe}(\text{CN})_6]^{3-}$	231	774-946	104
$[\text{Co}(\text{CN})_6]^{3-}$	241	860-1290	104
$[\text{Ni}(\text{CN})_4]^{2-}$	241	860	104
$[\text{Pd}(\text{CN})_4]^{2-}$	266	846	this work
$[\text{Pt}(\text{CN})_4]^{2-}$	280	850	this work
$[\text{Cu}(\text{CN})_2]^-$	241	860-1290	104
$[\text{Ag}(\text{CN})_2]^-$	241	860	104
$[\text{Mo}(\text{CN})_8]^{4-}$	355	800	this work
$[\text{W}(\text{CN})_8]^{4-}$	290	1133	this work
$[\text{Fe}(\text{NO})(\text{CN})_5]^{2-}$	397	4500	105
$[\text{Co}(\text{NO})(\text{CN})_5]^{3-}$	440	800	105
	365	868	this work
$[\text{RhH}(\text{CN})_5]^{3-}$	259	51	this work
$[\text{PtCl}(\text{CN})_5]^{2-}$	300	760	this work

SECTION 3.3 TANATALUM CYANO COMPLEXES

3.3.1 INTRODUCTION

The high co-ordination number cyano complexes $[\text{V}(\text{CN})_7]^{4-}$ ¹⁶⁴, $[\text{Nb}(\text{CN})_8]^{4-/5-}$ ¹⁶⁵, $[\text{Mo}(\text{CN})_8]^{4-/3-}$ ¹⁶⁶, $[\text{Mo}(\text{CN})_7]^{4-/5-}$ ^{32,39}, $[\text{W}(\text{CN})_7]^{5-}$ ²², $[\text{Tc}(\text{CN})_7]^{4-}$ ¹⁶⁷ and $[\text{Re}(\text{CN})_7]^{4-}$ ¹⁶⁸ are all well known. Of this block of the early transition metals, the only element which has not been studied is tantalum. It was, therefore our aim to prepare a high co-ordination number cyano complex of tantalum.

The octacyanonionobates are stable species and so it would seem that the corresponding tantalum complexes should be accessible. Unfortunately the electrolytic methods used for transforming NbCl_5 in the presence of cyanide¹⁶⁵ are not viable with TaCl_5 due to its high reduction potential.

Basson and Leipoldt¹⁶⁹ attempted the preparation of an octacyanotantalate by treating the cluster ions $[\text{Ta}_6\text{Cl}_{12}]^{2+}$, $[\text{Ta}_6\text{Cl}_{12}]^{3+}$ and $[\text{Ta}_6\text{Cl}_{12}]^{4+}$ with aqueous potassium cyanide. This led only to formation of Ta_2O_5 and in methanol as solvent they were still unable to break down the Ta_6 unit although some substitution occurred to give $[\text{Ta}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$. This anion (Figure 3.10) consists of a regular Ta_6 octahedron with each edge bridged by Cl^- and with metal cyanide bonding at the terminal positions. The Ta-C bond length was 2.21(4) Å and the C≡N distance 1.16(5) Å; these complexes are comparable to those of normal cyano complexes although Leipoldt and Basson point out that the situation is complicated by metal-metal bonding and a formal oxidation state of 2.33 on each tantalum ion.

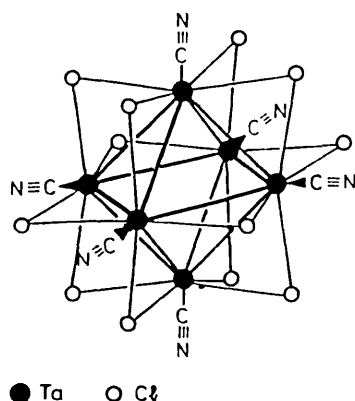


FIGURE 3.10 The $[\text{Ta}_6\text{Cl}_{12}(\text{CN})_6]^{4-}$ Cluster Anion

Our strategy, therefore, was to prepare some tantalum(III) complexes and react them with cyanide under a variety of conditions. There are relatively few tantalum(III) complexes in the literature and so we summarise their reactions in Figure 3.11. During the course of this work, a facile preparation of $[\text{Ta}(\text{CO})_6]^-$ appeared in the literature¹⁸⁵ and so we also studied its reaction with cyanide.

3.3.2 RESULTS

The various reactions and their results are summarised in Table 3.14. Reaction of the tantalum(III) dimer, $\text{Ta}_2\text{Cl}_6(\text{THT})_3$, with cyanide under various conditions (reactions 1-6) was not successful in breaking down the dimeric unit, and, although the tetrahydrothiophene ligands were removed, the chlorides were not (hence the peak in the infrared spectrum at 315 cm^{-1} assigned as $\nu_{\text{Ta-Cl}}$). As there were solubility problems with sodium and potassium cyanide, we tried using tetraethylammonium cyanide and $[\text{K}(18\text{-crown-6})][\text{CN}]$ both of which are soluble in organic solvents. Silver cyanide was used in an attempt to remove the chloride ligands as silver chloride. We found no evidence of reaction in any of these experiments. The infrared spectrum of the product of the reactions with KCN or NaCN had very weak bands at 2120 cm^{-1} but nothing could be characterised.

Reaction of TaCl_5 with CN^- under reducing conditions yielded a greyish product with an infrared band at 2080 cm^{-1} due to free cyanide; reaction in the presence of u.v. light gave similar results. A product was isolated from a KCN/KSCN melt at 250° but infrared spectroscopy and microanalysis showed this to be the known isothiocyanato complex, $[\text{Ta}(\text{NCS})_6]^-$.¹⁸⁶

Figure 3.11 cont.

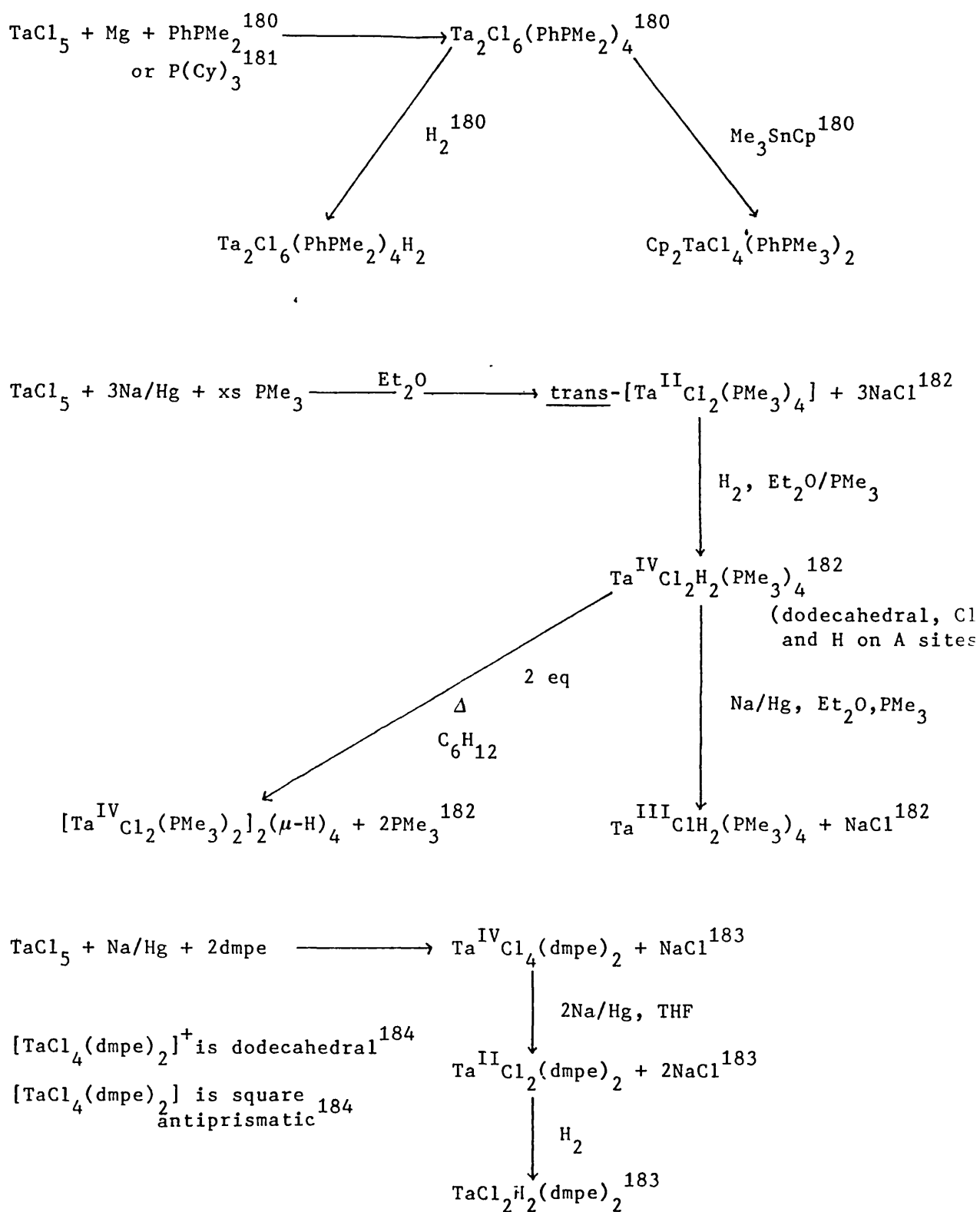


TABLE 3.14 Reactions between Tantalum Complexes and Cyanide

REACTION	PRODUCT	I.R. SPECTRUM OF PRODUCT, cm^{-1}
1 $\text{TaCl}_2(\text{SC}_2\text{H}_4)_3 + \text{aq KCN}$	Purple solution $\longrightarrow$ brownish ppt	2120w,br; 1630w,br; 1155,1080,315vvs
2 $\text{TaCl}_2(\text{SC}_2\text{H}_4)_3 + \text{NaCN/MeOH}$	White precipitate	2130w,br; 2120, 2190, 1155, 1068, 1030, 315vvs
3 $\text{TaCl}_2(\text{SC}_2\text{H}_4)_3 +$ [NEt ₄][CN] in MeCN	Brown precipitate	No ν_{CN} Analysis: C, 32.4; H, 7.1; N, 6.1; Cl, 17.4%
4 $\text{TaCl}_2(\text{SC}_2\text{H}_4)_3 +$ [NEt ₄][CN] in THF	Brown precipitate	No ν_{CN} 1260m, 1172m, 1125w, 1047w, 1010s, 970w, 920m, 849s, 800m, 620w, 517m, 315vvs
5 $\text{TaCl}_2(\text{SC}_2\text{H}_4)_3 +$ [k(18-crown-6)][CN] in MeOH	No product	
6 $\text{TaCl}_2(\text{SC}_2\text{H}_4)_3 + \text{AgCN/MeOH}$	No product obtained with refluxing or with $h\nu$	
7 $\text{TaCl}_5 + \text{Na/Hg} +$ [K(18-crown-6)][CN]	Grey precipitate	2080, 2060sh, 1980br, 1285, 1250, 1110, 960, 837, 535, 315vs Analysis: C, 33.8; H, 6.0; N, 1.2; Cl, 16.3%
8 $\text{TaCl}_5 + \text{NaCN/AgCN}$ in MeOH + $h\nu$	Purple solution $\longrightarrow$ red-brown solution yielding a white precipitate	2080vvw

TABLE 3.14 cont.

9 $\text{TaCl}_5 + \text{KCN} + \text{KSCN}$ at 250° in a melt	Orange fumes given off —————> dark brown melt	
	(i) extracted with methanol, filtered. Solid recrystallised from water/methanol-no product	
	(ii) to filtrate from (i) add acetone/ether —> white ppt.	2170w, 2050s, 1450, 1040w, 970w, 950w, 890w, 880w, 745m, 705m, 487s
	(iii) filtrate from (ii) re- duced in vacuo —> brown solid	2170w, 2080vs, 1630s, 965s, 950s, 745s, 485vs, 473vs
10 $\text{TaCl}_4(\text{MeCN})_3 + \text{NaCN}$ in MeCN	Orange precipitate Colourless solution	2260, 2180, 2090, 320
11 $\text{TaCl}_4(\text{MeCN})_3 + \text{AgClO}_4$ $\xrightarrow[-\text{AgCl}]{+\text{NaCN}}$	Orange solid after stirring and refluxing for 20 hours	2300w, 2260w, 1100vs(ClO_4^-), 620m, 320m
12 $\text{TaCl}_4(\text{MeCN})_3 + \text{NaCN}$ with hv	No reaction	
13 $[\text{Ta}(\text{CO})_6]^- + \text{NaCN}$ or $[\text{NEt}_4][\text{CN}] \xrightarrow[\text{reflux}]{\text{MeOH}}$	No reaction	
14 $[\text{Ta}(\text{CO})_6]^- +$ $\text{NaN}(\text{SiMe}_3)_2$ in C_6H_6	No reaction	
15 $[\text{Ta}^{\text{V}}(\text{edta})_3]^- + \text{Na/Hg} + \text{NaCN}$	No reaction	

We also tried reactions of the tantalum(IV) monomer, $[\text{TaCl}_4(\text{MeCN})_3]$ with NaCN and with $\text{AgClO}_4/\text{NaCN}$. There was no reaction in the former case and the product obtained in the latter case had infrared bands assigned to acetonitrile and the perchlorate ion only. We could obtain no product from the reaction of $[\text{Ta}(\text{CO})_6]^-$ with CN^- or with sodium bis(trimethylsilyl)amide, the latter being a reagent which smoothly converts $[\text{M}(\text{CO})_6]$ to $[\text{M}(\text{CO})(\text{CN})]^-$ (where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$).¹⁸⁷ We could find no change in chemical shift of the $^{13}\text{CN}^-$ resonance on addition of any of the tantalum species mentioned.

3.3.3 CONCLUSIONS

In our experience, a tantalum cyano complex is an elusive species. The complex should exist but the major problem seems to be that of obtaining a suitable starting material. A monomer is more desirable than a dimer but it seems that cyanide will not replace the chloride ligand. It is possible that the corresponding bromide or iodide complexes would prove more reactive. Forcing reaction conditions such as cyanide in liquid ammonia may prove fruitful. The hexacarbonyl complex should react with isocyanides in a similar manner to $[\text{V}(\text{CO})_6]^-$ which yielded $[\text{V}(\text{CNBu}^t)_6]^-$.¹⁸⁸

SECTION 3.4 URANIUM CYANO COMPLEXES

3.4.1 INTRODUCTION

(a) Cyano Complexes of Uranium

The earliest mention of a cyano complex of uranium was the precipitation of a uranyl(VI) species, $K_2[UO_2(CN)_4]$, from aqueous solutions of uranyl(VI) acetate on the addition of a large excess of potassium cyanide.¹⁸⁹ This formulation seems unlikely in view of the higher co-ordination number exhibited by uranium(VI) in the thiocyanates - $(pyridinium)_3[UO_2(NCS)_5]$.¹⁹⁰ Recently, however, cyano complexes of uranium(VI) and uranium(V) were said to be observed by spectrophotometric and electrochemical methods in a limited pH range.¹⁹¹

The preparation of a uranium(IV) cyanide-DMA (N,N'-dimethylacetamide) complex was attempted by reaction of $[U(SCN)_4 \cdot 4DMA]$ or $[UCl_4 \cdot 2.5DMA]$ with mercuric cyanide or iodine monocyanoide in acetonitrile but the products were unstable and not characterised.¹⁹² A uranium(IV) chlorocyanide, $[UCl_3(CN) \cdot 4NH_3]$, and a chlorocyanouranate(IV), $[NEt_4][UCl_4(CN)_2]$ have been reported;¹⁹³ both were isolated from the reaction of UCl_4 with CN^- in liquid ammonia. Further replacement of chlorine by cyanide could not be achieved. Changes in the visible spectrum of $U(ClO_4)_4$ in acetonitrile were reported to occur on the addition of HCN,¹⁹⁴ a possible indication of the formation of a chlorocyano complex in solution.

It was our intention, therefore, to confirm or refute the observations of uranium(VI) species made by Aloy¹⁸⁹ and Musikas et al¹⁹¹ and to carry out some work on uranium(IV) systems.

(b) Isothiocyanato Complexes of Uranium(IV)

There has been considerable interest in the salts of the $[\text{U}(\text{NCS})_8]^{4-}$ anion. The complex was first reported by two groups of workers^{195,196} who reacted UCl_4 with SCN^- . An infrared study of the Rb^+ , Cs^+ and NH_4^+ salts in both solid and acetone solution was undertaken by Gray and Smith.¹⁹⁷ In the solid four ν_{CN} bands were observed which is consistent with D_{2d} (dodecahedral) symmetry (see Table 3.12) but in solution, two bands were observed, consistent with D_{4d} symmetry. Further studies were made on the tetraethylammonium salt and caesium salt by Bagnall et al¹⁹⁸. X-ray powder diffraction showed that the salts were not isomorphous. The infrared spectrum of the solid NEt_4^+ salt showed only one ν_{CN} band characteristic of an anion with cubic symmetry while the Cs^+ salt exhibited more than one band. In nitromethane or acetonitrile solution, both salts exhibited only one ν_{CN} band in the infrared (contrary to the observations of Gray and Smith¹⁹⁷ in acetone solution). Bagnall et al suggested, therefore, that on dissolution, the cubic stereochemistry of $[\text{U}(\text{NCS})_8]^{4-}$ in the tetraethylammonium salt is destroyed, the arrangement of the NCS groups changing to that of the anion in $\text{Cs}_4[\text{U}(\text{NCS})_8]$, probably either D_{2d} or D_{4d} . The presence of only one infrared band in the solution did not permit these authors to assign the configuration of the anion in solution.

Countryman and McDonald¹⁹⁹ determined the X-ray crystal structure of $[\text{NEt}_4][\text{U}(\text{NCS})_8]$ and confirmed that the anion was indeed cubic. They suggested that the cruciform shape in which the cations are packed against the faces of the cube may be responsible for forcing the anion to adopt the unusual cubic configuration.

Kettle and Smith²⁰⁰ have discussed the possible participation of

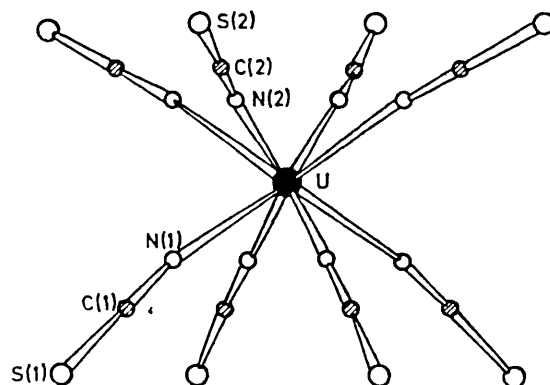
f-orbitals in bonding and pointed out that cubic co-ordination is a case where the stereochemistry may be indicative of bonding using f-orbitals. The A_{2u} irreducible representation of the metal-ligand σ -bonds is spanned by the metal f_{xyz} orbital, but not by metal s, p or d orbitals. In a covalent description of the bonding, the ligands could, therefore, be bonded to the metal by means of hybrid metal orbitals between $fd^3 sp^3$ and $f^4 d^3 s$, both of which provide eight equivalent orbitals directed to the cube vertices.

TABLE 3.15 Expected Raman and Infrared Active modes for Eight Co-ordination

SYMMETRY	INFRARED ACTIVE	RAMAN ACTIVE	COINCIDENCES
O_h (cubic)	T_{1u}	$A_{1g} + T_{2g}$ 1 polarised	0
D_{4d} (square antiprism)	$B_2 + E_1$	$A_1 + E_2 + E_3$ 1 polarised	0
D_{2d} (dodecahedral)	$2B_2 + 2E$	$2A_1 + 2B_2 + 2E$ 2 polarised	4

Preparation, electronic structure and magnetic measurements have also been reported for the tetraethylammonium salt^{192,201} and an infrared, Raman and ^{13}C n.m.r. study reported that the anion retained its cubic geometry in solution.²⁰² Three ν_{CN} bands were observed in the solid Raman spectrum and two in solution of which one was polarised.

The $\text{Cs}_4[\text{U}(\text{NCS})_8]$ salt has been subjected to X-ray studies²⁰³ and the configuration of the anion found to be very close to square antiprismatic



with the Cs^+ ions packed against the triangular faces of the square antiprism.

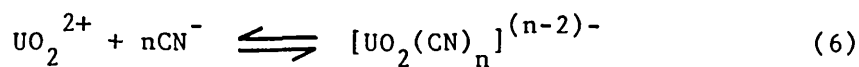
We proposed to record Raman spectra for the two salts in solution to confirm the change in geometry of $[\text{NEt}_4][\text{U}(\text{NCS})_8]$.

3.4.2 RESULTS AND DISCUSSION

(a) Cyano Complexes of Uranium

Our experimental results are given in Table 3.16. All attempts to produce a uranyl cyano complex resulted in precipitation of a yellow hydrolysis product of the type, $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$ or $[(\text{UO}_2)_3(\text{OH})_5]^+$.²⁰⁴ We concluded that the yellow compound formulated by Aloy¹⁸⁹ as $\text{K}_2[\text{UO}_2(\text{CN})_4]$ is also a hydrolysis product; his formulation was arrived at with a mixture of KCN which he used in vast excess in his preparation.

Musikas et al¹⁹¹ identified the two competing reactions in solution as:



and

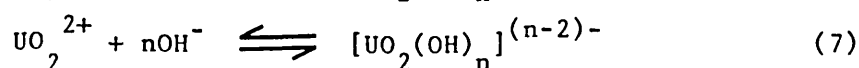


TABLE 3.16 Reactions of Uranyl and U(IV) Salts with Cyanide

URANIUM SALT	REACTION CONDITIONS	PRODUCT
1 Uranyl nitrate or uranyl acetate	stir with aqueous KCN	Yellow precipitate, no ν_{CN} Analysis: C, nil; H, 0.6; N, nil%
2 Uranyl nitrate or uranyl acetate	stir with aqueous KCN at pH 10.6	Yellow product I.R. 1550vs, 1450vs, 1350vs, 1062vs, 850vs, br, 830, 730s, 700m, 310s ^{13}C n.m.r. 176.0 p.p.m. (CN^-) 172.5 p.p.m.
3 Uranyl nitrate or uranyl acetate	KCN in ethanol or ether	as 1
4 Uranyl nitrate or uranyl acetate	KCN in methanol, reflux	as 1
5 Uranyl nitrate or uranyl acetate	aqueous KCN, HCl, pyridine (cf pyridinium salt of $[\text{UO}_2(\text{NCS})_5]^{3-}$)	as 1
6 Uranyl nitrate in MeCN, reduce in presence of $[\text{NEt}_4][\text{CN}]$	$E_{1/2} -0.42\text{V}$ Irreversible	$\text{UO}_2^{2+} \longrightarrow \text{U}^{4+}$ no reaction with CN^-
7 Uranyl nitrate	Na/Hg, KCN	Green product, no ν_{CN}
8 Uranyl nitrate	dilute HCl, sodium dithionite $\longrightarrow \text{U(IV)}$ in solution + CN^-	Green product, no ν_{CN}
9 Uranium tetrachloride	aqueous NaCN	No reaction
10 Uranium tetrachloride	KCN in acetonitrile	No reaction

TABLE 3.16 cont.

11	Uranium tetrachloride	$[\text{NEt}_4][\text{CN}]$ in acetonitrile, reflux	No reaction
12	Uranium tetrachloride	NaCN in methanol, $h\nu$	No reaction
13	Uranium tetrachloride	methanolic AgCN, $h\nu$	I.R. indicates a chloro uranyl species
14	Uranium tetrachloride	methanolic AgCN, reflux	No reaction

and claimed, from u.v. studies of the solutions, that in the pH range 8.5-11.0, reaction (6) was dominant yielding a complex containing five or six cyanide ligands. We find that at all pH ranges, only a hydrolysis product is obtained. There was never any sign of a ν_{CN} stretch in the infrared spectrum. We did, however, examine the ^{13}C n.m.r. spectrum of an aqueous solution of uranyl nitrate and excess KCN. As well as the resonance at 176.0 p.p.m. due to free cyanide, there was a small peak at 172.5 p.p.m.. Infrared spectra of the solution showed a broad band in the ν_{CN} region but no distinguishable peaks (the pH of the solution was 10.6, that at which Musikas *et al*¹⁹¹ claimed cyano complexes should exist). The solution was reduced in volume in vacuo and a yellow product isolated which contained no C or N by microanalysis and no ν_{CN} bands in the infrared spectrum.

Reaction of the $(\text{UO}_2)^{2+}$ moiety under reducing conditions in the presence of cyanide yielded green U(IV) species but no cyanide was incorporated in the product. Similarly electrochemical reduction of $(\text{UO}_2)^{2+}$ in the presence

of cyanide did not indicate the presence of any new species. Uranium tetrachloride could not be made to react with cyanide under any conditions.

We would suggest that this lack of reaction is due to the nature of the metal and ligand involved. Uranium is a large ion surrounded, as it employs f-orbitals in its bonding, by an almost spherical diffuse electron density - a 'soft' ion. Cyanide, however, is a 'hard' ligand and a relatively poor π -acceptor.

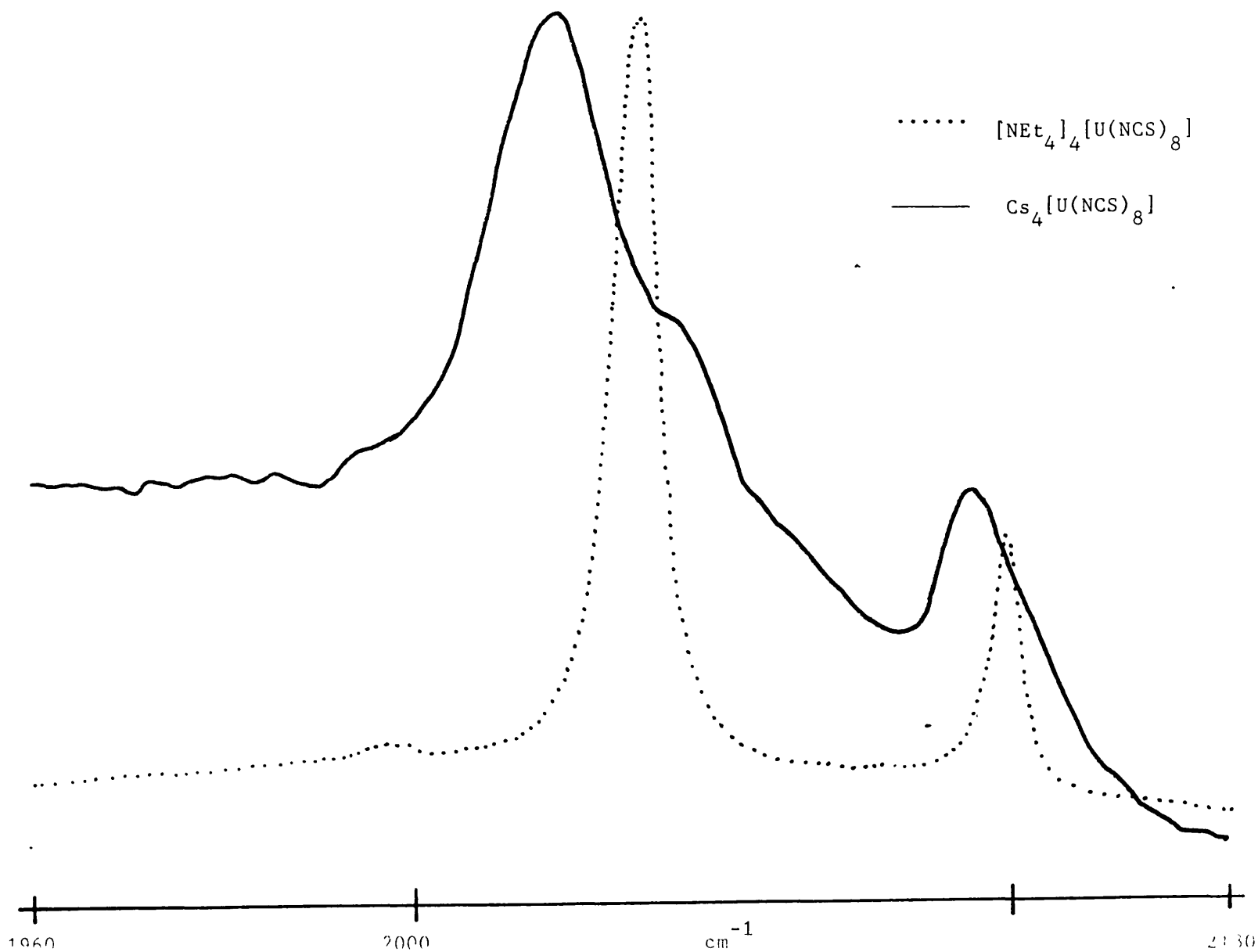
(b) Raman Study of $[\text{U}(\text{NCS})_8]^{4-}$

As we have discussed earlier, $\text{Cs}_4[\text{U}(\text{NCS})_8]$ is square antiprismatic in both solid²⁰³ and solution¹⁹⁸ whilst $[\text{NEt}_4][\text{U}(\text{NCS})_8]$ is cubic in the solid¹⁹⁹ and has been proposed from infrared data to be square antiprismatic or dodecahedral in solution¹⁹⁸ or, from Raman data, to be cubic in solution.²⁰² We have recorded the Raman spectra of both complexes in both solid and solution and our results are tabulated in Table 3.17 and illustrated in Figure 3.12.

TABLE 3.17 Raman Data for $[\text{NEt}_4][\text{U}(\text{NCS})_8]$ and $\text{Cs}_4[\text{U}(\text{NCS})_8]$

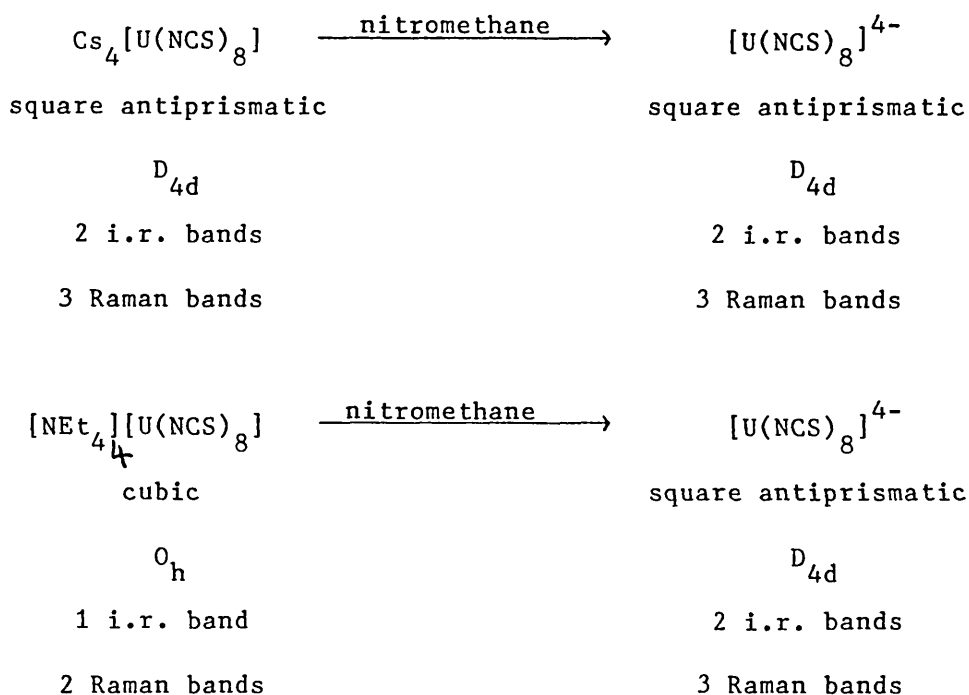
ν_{CN} in	$[\text{NEt}_4][\text{U}(\text{NCS})_8]$		$\text{Cs}_4[\text{U}(\text{NCS})_8]$
	ref. 202	this work	this work
Solid	2092(2)	2099(3)	2093(4)
	2047(10)	2046(10)	2050(4)sh
	2040(8)		2035(10)
Solution (nitromethane)	2093(5)p	2098(3)dp	2095(4)dp
	2052(10)dp	2054(4)dp	2053(4)dp
		2044(10)p	2037(10)p

FIGURE 3.12 Raman Spectra of $[\text{NEt}_4]_4[\text{U}(\text{NCS})_8]$ and $\text{Cs}_4[\text{U}(\text{NCS})_8]$ (solid)



Soulié et al²⁰² suggested that the anion is cubic in solution as only two ν_{CN} fundamentals are observed, one of which is polarised (Table 3.15, p. 137). We, however, observed three ν_{CN} stretches of which one was polarised for both the Cs^+ and tetraethylammonium salts consistent with $\text{D}_{4\text{d}}$ symmetry, In the cubic solid, we observe, by contrast, only two Raman bands (consistent with O_h symmetry) while Soulié et al²⁰² observed three bands which they state as consistent with the distortion of the symmetry to $\text{D}_{4\text{h}}$.

We conclude that the following changes in molecular configuration occur in these complexes:



SECTION 3.5 EXPERIMENTAL

In Section 3.5.1, many of the preparations are directly from the literature. In these cases, we have given only the reference, the microanalysis data and the spectral data; no experimental details are given unless modifications were made. Infrared and Raman data are given for aqueous solutions in the ν_{CN} region unless otherwise stated.

3.5.1 CYANO COMPLEXES AND COMPLEXES OF THE TYPE $[\text{MX}(\text{CN})_5]^{n-}$

Preparation of the $[\text{CoH}(\text{CN})_5]^{3-}$ Ion ²⁰⁵

Prepared 'in situ', therefore no analytical data

Infrared 2125w, 2097s

Raman 2127(10)p, 2110(5)p, 2100sh

Preparation of $\text{K}_3[\text{RhH}(\text{CN})_5] \cdot \text{H}_2\text{O}$ and $\text{K}_3[\text{IrH}(\text{CN})_5] \cdot \text{H}_2\text{O}$

See Chapter 2, for all details

Preparation of $\text{K}_3[\text{Mn}(\text{NO})(\text{CN})_5]$ ²⁰⁶

Found: C, 18.4; H, trace or nil; K, 35.16; N, 25.47. $\text{C}_5\text{K}_3\text{MnN}_6\text{O}$ requires C, 18.07; K, 35.3; N, 25.31%

Infrared 2100

Raman 2123p, 2110p, 2096dp

Preparation of $\text{K}_4[\text{Mo}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$ ²⁰⁷

Found: C, 9.8; H, 0.68; K, 27.8; N, 14.9. $\text{C}_5\text{H}_4\text{K}_4\text{MoN}_6\text{O}_3$ requires C, 10.7; H, 0.7; K, 27.9; N, 15.0%

Infrared 2120

Raman 2139p, 2119p, 2112dp

Preparation of $\text{Cs}_2[\text{Mo}(\text{NO})(\text{CN})_5] \cdot 3\text{H}_2\text{O}$ ¹³²

Found: C, 9.7; H, 0.8; N, 14.0. $\text{C}_5\text{Cs}_2\text{H}_6\text{MoN}_6\text{O}_4$ requires C, 10.4; H, 1.1; N, 14.6%

Infrared 2120

Raman 2139(10)p, 2135(3)p, 2131(7)dp

Preparation of $\text{K}_3[\text{Re}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$ ¹⁵²

The complex was prepared using the method described for $\text{K}_3[\text{Re}(\text{NO})(\text{CN})_7] \cdot 4\text{H}_2\text{O}$
 Found: C, 11.8; H, 0.8; N, 16.75. $\text{C}_5\text{H}_4\text{K}_3\text{N}_6\text{O}_3\text{Re}$ requires C, 12.0; H, 0.8; N, 16.8%

Infrared 2110

Raman 2137p, 2115p, 2091dp

Preparation of $[\text{RhX}(\text{CN})_5]^{3-}$ ²⁰⁸

The halopentacyano complexes were prepared in solution and not isolated.

$\text{X} = \text{Cl}^-$

Infrared 2130s, 2140vw

Raman 2150(10)p, 2143(7)dp

$\text{X} = \text{Br}^-$

Infrared 2128s, 2137vw

Raman 2148(10)p, 2143(7)dp

$\text{X} = \text{I}^-$

Infrared 2123vs, 2133vvw

Raman 2145(10)p, 2140(5)dp, sh

Preparation of $[\text{PtX}(\text{CN})_5]^{2-}$ ²⁰⁹

The complexes were prepared in solution and not isolated.

$\text{X} = \text{Cl}^-$

Infrared 2210w, 2195sh, 2187s

Raman 2205p, 2193dp

$\text{X} = \text{Br}^-$

Infrared 2193w, 2186s

Raman 2203p, 2192dp

$\text{X} = \text{I}^-$

Infrared 2191w, 2181s

Raman 2201p, 2188dp

Preparation of $\text{K}_5[\text{Ru}_2\text{N}(\text{CN})_{10}]\cdot 3\text{H}_2\text{O}$ ¹³⁶

Found: C, 16.4; H, 0.8; K, 26.8; N, 21.2. $\text{C}_{10}\text{H}_6\text{K}_5\text{N}_{11}\text{O}_3\text{Ru}_2$ requires C, 16.6; H, 0.8; H, 26.9; N, 21.2%

For spectral data, see Section 3.2.5, Table 3.9, p. 111

$\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5]\cdot 2\text{H}_2\text{O}$

The compound was used as supplied.

Infrared 2143

Raman 2173(10)p, 2162(9)p, 2155(5)dp

Preparation of $\text{Na}_3[\text{Fe}(\text{NH}_3)(\text{CN})_5]\cdot 3\text{H}_2\text{O}$ ²¹⁰

Found: C, 18.3; H, 2.8; N, 25.5. $\text{C}_5\text{FeH}_9\text{N}_6\text{Na}_3\text{O}_3$ requires C, 18.4; H, 2.8; N, 25.8%

Infrared 2057w, 2040

Raman 2060(10), 2055(7)dp

Preparation of $\text{Na}_3[\text{Fe}(\text{CO})(\text{CN})_5]$ ²¹⁰

A solution of $\text{Na}_3[\text{Fe}(\text{NH}_3)(\text{CN})_5]$ prepared as above was treated with carbon monoxide gas until the colour changed from yellow to colourless. This solution was used for all measurements.

Infrared 2089vvw, 2070s

Raman 2090(10)p, 2085(6)dp

Preparation of $\text{Na}_3[\text{Fe}(\text{PPh}_3)(\text{CN})_5] \cdot 2\text{H}_2\text{O}$ ²¹¹

Found: C, 49.5; H, 3.4; N, 12.3. $\text{C}_{23}\text{FeH}_{19}\text{Na}_3\text{O}_2\text{P}$ requires C, 49.9; H, 3.4; N, 12.7%

Infrared 2040w, 2030

Raman 2087(10)p, 2057(5)dp

Preparation of $\text{Na}_3[\text{Fe}(\text{AsPh}_3)(\text{CN})_5] \cdot 2\text{H}_2\text{O}$ ²¹⁰

Found: C, 45.2; H, 3.2; N, 11.8. $\text{AsC}_{23}\text{FeH}_{19}\text{Na}_3\text{O}_2$ requires C, 46.2; H, 3.2; N, 11.7%

Infrared 2040w, 2030s

Raman 2087(10)p, 2057(6)dp

$\text{Na}_3[\text{Fe}(\text{dmsO})(\text{CN})_5]$,²¹² $\text{Na}_3[\text{Fe}(\text{pyridine})(\text{CN})_5]$,²¹² and $\text{Na}_5[\text{Fe}(\text{SO}_3)(\text{CN})_5]$ ²¹³ were prepared by literature methods.

Preparation of $\text{K}_3[\text{Co}(\text{NO})(\text{CN})_5] \cdot 2\text{H}_2\text{O}$ ¹⁴⁰

Found: C, 16.8; H, 1.1; N, 23.4. $\text{C}_5\text{CoH}_4\text{K}_3\text{N}_6\text{O}_2$ requires C, 16.9; H, 1.1; N, 23.6%

Spectral details are given in Table 3.10, p. 116.

Preparation of $K_5[Re(CN)_6]$

The complex was prepared by a modification of the method of Clauss and Lissner.²¹⁴ A 0.5% potassium amalgam was prepared from potassium (0.1g, 2.56 mmol) and mercury (23cm³). Solutions of KCN (6.5g, 0.1 mol) in water (15 cm³) and K_2ReCl_6 (1.0g, 2.10 mmol) in water (25 cm³) were degassed and added (cyanide first) to the amalgam. There was an immediate colour change from light to dark green, the solution was filtered from the amalgam and ethanol (40 cm³) added. The solution was cooled at -20° and the green precipitate filtered, washed with ether and dried in vacuo.

Found: C, 13.3; N, 15.6. $C_6K_5N_6Re$ requires C, 13.4; N, 15.6%

Preparation of $[Ph_4P][Mo(NO)_2(CN)_4]$ ¹⁵⁴

Found: C, 63.8; H, 4.0; N, 8.4. $C_{52}H_{40}N_6O_2P_2Mo$ requires C, 64.1; H, 4.1; N, 8.6%

Preparation of $K_2[PtX_2(CN)_4]$ ²⁰⁹

X = Cl⁻

Found: C, 10.6; N, 12.4. $C_4Cl_2K_2N_4Pt$ requires C, 10.7; N, 12.5%

X = Br⁻

Found: C, 8.8; N, 10.5; $Br_2C_4K_2N_4Pt$ requires C, 8.9; N, 10.4%

X = I⁻

Found: C, 7.7; N, 8.8. $C_4I_2K_2N_4Pt$ requires C, 7.6; N, 8.9%

Preparation of $[Ni_2(CN)_6]^{4-}$

A solution of $K_2[Ni(CN)_4]$ was added to sodium amalgam under nitrogen. The resultant dark-red solution was transferred under nitrogen to an n.m.r. tube as required.

Preparation of $K_4[Os_3N_2(CN)_8(OH)_4(OH_2)_2]^{159}$

The complex $[Os_3N_2(NH_3)_4(OH)_8(OH_2)_2]^{159}$ (1.0g, 1.2 mmol) was dissolved in potassium cyanide solution (2.5g in 75 cm³ water) and the mixture heated under reflux for 7 hours. When cold, the brown solution was added to methanol (150 cm³) and the brown product filtered off and washed with methanol and ether.

Found: C, 8.9; H, 1.0; N, 13.7. $C_8H_8K_4N_{10}O_6Os_3$ requires C, 9.0; H, 0.8; N, 13.1%

Preparation of $K_4[Os_3N_2(CN)_{10}(OH)_2] \cdot 4H_2O^{159}$

The complex $[Os_3N_2(NH_3)_8(OH)_6]Cl_6^{159}$ (0.35g, 0.33 mmol) was dissolved in potassium cyanide solution (2.0g in 5 cm³ water) and the mixture stirred and heated under reflux for 7 hours. The brown solution was added to methanol (20 cm³), the product filtered and washed with methanol and ether. The product was recrystallised from water/methanol.

Found: C, 9.8; H, 1.4; N, 14.6. $C_{10}H_{16}K_4N_{12}O_8Os_3$ requires C, 10.4; H, 1.4; N, 14.5%

3.5.2 TANTALUM COMPLEXES

All reactions were carried out under argon unless otherwise stated. All solvents, reagents and apparatus were dried before use and solvents were thoroughly degassed. Tetraethylammonium cyanide²¹⁵ and sodium bis(trimethylsilyl)amide²¹⁶ were prepared by literature methods.

Preparation of $Ta_2Cl_6(SC_4H_8)_3^{170}$

Sodium (0.12g, 5.22 mmol) was added to mercury (30g) and the resulting amalgam transferred to a dropping funnel attached to a three-

necked 100 cm³ flask which was degassed for 30 minutes. To this was added TaCl₅ (1.037g, 2.89 mmol) along with dry toluene (15 cm³) - a yellow solution resulted. Dry tetrahydrothiophene (0.75 cm³, 9.0 mmol) was syringed into the flask and a bright orange colour appeared as the TaCl₅-THT adduct formed. The amalgam was then added dropwise with vigorous stirring yielding finally a plum coloured solution. The mixture was then evaporated to dryness on the line and stored overnight. The residue was taken up in dry toluene (10 cm³) and the plum coloured solution filtered into a clean, dry Schlenk tube. The extract was slowly evaporated to yield the red-violet product.

Found: C, 17.0; Cl, 24.9; H, 3.2. C₁₂Cl₆H₂₄S₃Ta₂ requires C, 17.2; Cl, 25.3; H, 2.9%

Preparation of TaCl₄(CH₃CN)₃

This compound was prepared by a modification of the method used to prepare NbCl₄(THF)₂.²¹⁷ Into a dry Schlenk tube under dry argon was placed aluminium powder (0.8g, 30 mmol) and dry acetonitrile (25 cm³). TaCl₅ (2.6g, 7.25 mmol) was slowly added with vigorous stirring. After stirring under argon for 4 hours, an orange solution and a pale yellow powder was obtained. The solution was filtered and the filtrate reduced in volume and cooled. An orange-yellow product was obtained which was filtered, washed with acetonitrile and dried in vacuo.

Yield: 2.4g, 74%

Found: C, 16.0; Cl, 31.3; H, 2.1; N, 9.3. C₆Cl₄H₉N₃Ta requires C, 16.1; Cl, 31.8; H, 2.0; N, 9.4%

Infrared Spectrum ν_{CN} 2330m, 2300w, 2120w

965m, 475s

ν_{Ta-Cl} 320vs

Preparation of $[\text{PPh}_4][\text{Ta}(\text{CO})_6]$ ¹⁸⁵

A solution of sodium naphthalenide was prepared by adding naphthalene (4.3g, 33.6 mmol) and sodium metal (0.77g, 33.6 mmol) to dimethoxyethane (60 cm³) under dry, anaerobic conditions. The mixture was stirred overnight yielding a green solution which was filtered and used as required. TaCl_5 (2.0g, 5.58 mmol) was slowly added with vigorous stirring to the above solution of sodium naphthalenide at -80°C (solid CO_2 /ethanol bath). Carbon monoxide was then bubbled through the stirred solution at atmospheric pressure ('at -80°C) for 20 hours. During this time, the colour changed from green through mauroon to orange-red. The solution was filtered into a flask containing $[\text{PPh}_4]\text{Cl}$ (2.09g, 5.58 mmol), the solvent removed on the line, the residue washed with pentane, dissolved in THF (20 cm³) and filtered. The orange solution was reduced in volume to approximately 2 cm³ and ether (2 cm³) added. The product was filtered, washed with ether and dried in vacuo.

Yield: 1.3g, 33.0%

Found: C, 52.1; H, 2.7. $\text{C}_{30}\text{H}_{20}\text{O}_6\text{PTa}$ requires C, 52.3; H, 2.9%

Infrared Spectrum ν_{CO} 1859vs,br; 1837vs,br

Reactions between Tantalum Complexes and Cyanide

These reactions are described in Table 3.14, p. 133). However, some typical reactions are described here in detail. All others were carried out in a similar manner. The nature of the products are detailed in the Table.

Reaction between $\text{Ta}_2\text{Cl}_{10}(\text{SC}_4\text{H}_8)_3$ and Tetraethylammonium Cyanide

To a solution of $\text{Ta}_2\text{Cl}_{10}(\text{SC}_4\text{H}_8)_3$ (1.05g, 0.15 mmol) in dry toluene (5 cm³)

was added a solution of $[\text{NEt}_4][\text{CN}]$ (0.41g, 2.6 mmol) in toluene (5 cm^3). On stirring, the solution became yellow-brown in colour and, when the solvent was removed, a brown residue was obtained. This was dissolved in acetonitrile (5 cm^3), filtered and reduced in volume yielding a brown product which was filtered and dried in vacuo.

Reaction between Tantalum Pentachloride and Cyanide

TaCl_5 (0.76g, 2.12 mmol) was dissolved in dry degassed toluene (20 cm^3) and $[\text{K}(18\text{-crown-6})][\text{CN}]$ (5.8g, 17.6 mmol) added. This solution was slowly added, with vigorous stirring, to sodium amalgam (0.12g Na, 30 cm^3 mercury). An whitish precipitate formed instantly which was filtered and dried. The filtrate was reduced in volume but no further product was obtained.

Reaction between $\text{TaCl}_4(\text{CH}_3\text{CN})_3$ and Cyanide

$\text{TaCl}_4(\text{CH}_3\text{CN})_3$ (0.5g, 1.37 mmol) in acetonitrile (10 cm^3) was treated with silver perchlorate (0.41g, 2.0 mmol). An immediate precipitate of silver chloride was formed. The precipitate was filtered and to the resultant yellow solution was added sodium cyanide (0.67g, 13.7 mmol). The solution was stirred overnight and the orange precipitate which had formed was filtered, washed with acetonitrile and dried in vacuo. The infrared spectrum showed bands due to CH_3CN and ClO_4^- .

3.5.3 URANIUM COMPLEXES

Unless otherwise stated, all uranium(IV) reactions were carried out under anaerobic, anhydrous conditions. Again, we will describe a few representative reactions as full details are given in Table 3.16, p. 139).

Reaction of Uranyl Acetate with Potassium Cyanide

Uranyl acetate (1.0g, 2.36 mmol) was slowly added to a stirred solution of potassium cyanide (3.07g, 47.2 mmol). A dark yellow precipitate was formed immediately. This was filtered, washed with water, ethanol and ether and air-dried.

Found: C, trace or nil; H, 0.57; N, trace or nil.

Reaction of Uranium(IV) Tetrachloride with Silver Cyanide

A solution of uranium tetrachloride (0.2g, 0.53 mmol) in dry methanol (5 cm³) was treated with a solution of silver cyanide (0.7g, 5.3 mmol) in methanol (5 cm³). We found that refluxing the solution for one hour, or treating it with u.v. light for one hour resulted in a colour change from green to yellow. The solution was reduced in volume and dry [NEt₄]Br (0.13g, 0.6 mmol) added. A yellow solid was obtained which was filtered and dried in vacuo.

Infrared Spectrum

$\nu_{\text{U=O}}$ 927vs, 920vs

$\nu_{\text{U-Cl}}$ 260 vs and bands due to NEt₄⁺.

Preparation of [NEt₄]₄[U(NCS)₈]

This method is similar to that of Bagnall et al.¹⁹⁸ Uranium tetrachloride (0.6g, 1.58 mmol) was added to a mixture of potassium thiocyanate (1.23g, 12.6mmol)

and tetraethylammonium chloride (1.05g, 6.32 mmol) in dry acetonitrile (10 cm^3) under argon. The mixture was gently warmed for several minutes and filtered to remove precipitated potassium chloride. The light green filtrate was cooled at -20°C to yield green crystals.

Found: C, 47.3; H, 8.0; N, 16.3; S, 25.0. $\text{C}_{40}\text{H}_{80}\text{N}_9\text{S}_8\text{U}$ requires C, 47.7; H, 7.9; N, 16.7; S, 25.4%

Infrared Spectrum

ν_{CN}	2120sh, 2110sh, 2050vvs
	1185w, 1171s, 1067m, 1050m, 997s, 970m, 782s
δ_{NCS}	482s
	418w, 390w

Preparation of $\text{Cs}_4[\text{U}(\text{NCS})_8]$ ¹⁹⁸

Uranium tetrachloride (1.12g, 2.95 mmol) was added to a solution of caesium ~~hydroxide~~ (4.5g, 20 mmol) in acetone (20 cm^3). The solution was warmed with stirring and caesium chloride precipitated. The solution was filtered hot and the filtrate allowed to cool. The acetone was removed on the vacuum line and the residue taken up in nitromethane (10 cm^3). This was filtered and dichloromethane (20 cm^3) added. Cooling overnight at -20°C produced green crystals which were filtered and dried in vacuo.

Found: C, 7.5; N, 7.1; S, 19.9. $\text{C}_8\text{Cs}_4\text{N}_8\text{S}_8\text{U}$ requires C, 7.8; N, 9.1; S, 20.8%

Infrared Spectrum

ν_{CN}	2098sh, 2086sh, 2064vvs
δ_{NCS}	482m

CHAPTER FOUR

PRELIMINARY STUDIES OF COMPLEXES CONTAINING CYANOGEN, HYDROGEN CYANIDE, NITRILE AND ISOCYANO LIGANDS

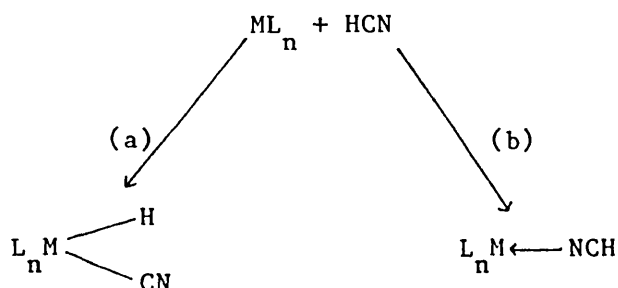
SECTION 4.1 GENERAL INTRODUCTION

In this chapter, we will discuss complexes containing cyanogen and hydrogen cyanide as ligands. We present a ^{13}C and ^{15}N n.m.r. study of some acetonitrile complexes and discuss the bonding of cyanide via nitrogen specifically in cobalt-dimethylglyoximate complexes.

SECTION 4.2 COMPLEXES CONTAINING HYDROGEN CYANIDE AND CYANOGEN AS LIGANDS

4.2.1 INTRODUCTION

An excellent review of this subject is that recently published by Corain.²¹⁸ We will not consider the products of reactions between HCN or cyanogen and potential Lewis acids, e.g. $\text{BF}_3(\text{HCN})$, $\text{FeCl}_3(\text{HCN})_3$,²¹⁸ but only compounds which can be defined as co-ordination compounds. Hydrogen cyanide is a reactive molecule which can interact with metal complexes in two ways:



Reaction (a) is an oxidative addition in which the HCN molecule is behaving as a protonic acid; this usually takes place with low oxidation state metal complexes e.g. $[\text{Pt}(\text{H})(\text{CN})(\text{PPh}_3)_2]$ is formed by the addition of HCN to the platinum(0) complex, $\text{Pt}(\text{PPh}_3)_3$ or 4 .²¹⁹ In reaction (b), the co-ordination mode of HCN is a 'nitrile' end-on type. With two exceptions, the co-ordination of HCN to a metal is accompanied by an increase in ν_{CN} . For $[\text{Ag}(\text{HCN})]^+$ ²²⁰ (in solution) there is no shift and for $[\text{Ru}(\text{NH}_3)_5(\text{HCN})]^{2+}$ ²²¹ a decrease in ν_{CN} from 2096 to 1960 cm^{-1} is observed. Although X-ray data is not available, it is generally accepted that HCN co-ordinates through the nitrogen lone pair. The increase in ν_{CN} on co-ordination has been discussed in detail²²² and is attributed to C≡N bond strengthening as observed in cyano complexes. The effect of co-ordination on $\nu_{\text{C-H}}$ is not as clear; in the majority of cases it decreases, but in $[\text{M}(\text{CO})_5(\text{HCN})]$ ¹⁸⁷ it is observed to increase. Interpretation of this shift as a weakening of the C-H bond is cautious as the ν_{CN} and $\nu_{\text{C-H}}$ vibrations are known to be coupled.²²² It is notable that the ^1H n.m.r. data support a weaker C-H bond as there is a downfield shift (less shielding of the H nucleus) on co-ordination. The relevant data on known HCN complexes are summarised in Table 4.1.

The co-ordination compounds of cyanogen, C_2N_2 , known to date are listed in Table 4.2 along with some relevant data. They are normally prepared by treating cyanogen dissolved in an inert solvent with a convenient metal complex which, upon ligand displacement, accommodates cyanogen in the co-ordination sphere. A glance at the infrared data in Table 4.2 shows that there are complexes in which two well-defined ν_{CN} bands are observed, those in which a single band was detected and those in which a pattern of bands are observed (some given in parentheses).

TABLE 4.1 Summary of Known HCN Complexes of the Transition Metals

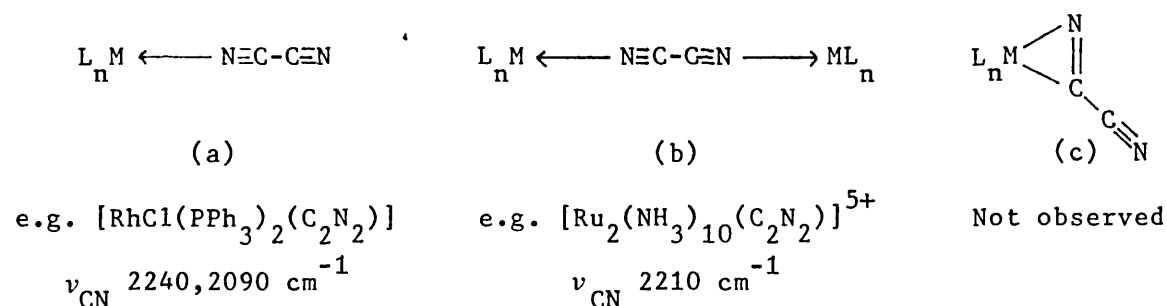
COMPLEX	COLOUR		$\nu_{\text{C-N}}, \text{cm}^{-1}$	$\nu_{\text{C-H}}, \text{cm}^{-1}$	$\delta_{\text{HCN}}, \text{cm}^{-1}$	PHASE	$\delta, \text{p.p.m.}$	REFERENCE
$[\text{TiCl}_4(\text{HCN})_2]$	Yellow	trans	2135	3173	764	Solid	-	222,223
$[\text{TiBr}_4(\text{HCN})_2]$	Red	trans	2127	-	-	Solid	-	223
$[\text{VCl}_4(\text{HCN})_2]$	Black	unstable at 40°C	2140	3205	769	Solid	-	224
$[\text{Cr}(\text{CO})_5(\text{HCN})]$	Yellow	-	2119	3267	-	C_6H_6 soln	5.76	187
$[\text{W}(\text{CO})_5(\text{HCN})]$	Yellow	-	2216	3261	-	"	6.26	187
$[\text{Ru}(\text{NH}_3)_5(\text{HCN})]^{2+}$	White	stable in water at pH<1	1960vs	-	-	Solid	-	221
$[\text{RhCl}(\text{H})(\text{CN})(\text{PPh}_3)_2(\text{HCN})]$	-	-	2145	-	-	Solid		225
$[\text{Ag}(\text{HCN})]^+$	-	characterised in HF soln	2138 2148	3225	770	HF soln Solid	4.83	220
$[\text{Ag}(\text{HCN})_2]^+$	-	in HF	2147	-	-	HF soln	4.88	220
$[\text{Cu}(\text{HCN})]^{2+}$	-	in HF	-	-	-	-	5.19	220
HCN			2096	3215	794	Liquid	4.46	226

TABLE 4.2 Summary of the Cyanogen Complexes of the Transition Metals

COMPLEX	COLOUR	COMMENTS	$\nu_{\text{CN}}, \text{cm}^{-1}$	PHASE	REFERENCE
$[\text{Cr}_2(\text{CO})_{10}(\text{C}_2\text{N}_2)]$	reddish-violet	photochemical	2118,(2263)	CCl_4 soln	227
$[\text{Mo}_2(\text{CO})_{10}(\text{C}_2\text{N}_2)]$	dark brown	"	(2267)	CCl_4 soln	227
$[\text{W}_2(\text{CO})_{10}(\text{C}_2\text{N}_2)]$	violet	"	2107,(2267)	CCl_4 soln	227
$[\text{Ru}_2(\text{NH}_3)_{10}(\text{C}_2\text{N}_2)]^{4+}$	-	-	1960	solid	228
$[\text{Ru}_2(\text{NH}_3)_{10}(\text{C}_2\text{N}_2)]^{5+}$	-	-	2210	solid	228
$[\text{Ru}_2(\text{NH}_3)_{10}(\text{C}_2\text{N}_2)]^{6+}$	-	-	2330	solid	228
$[\text{Ru}(\text{NH}_3)_5(\text{C}_2\text{N}_2)]^{2+}$	-	-	2220,2090	-	228
$[\text{RhCl}(\text{PPh}_3)_2(\text{C}_2\text{N}_2)]$	yellow-brown	$-\text{C}_2\text{N}_2$ at r.t.	2240,2090	solid	229
$[\text{RhCl}(\text{PPh}_3)_2(\text{C}_2\text{N}_2)\text{I}_2]$	brown	$-\text{C}_2\text{N}_2$ in vacuo	2320,2170	solid	230
$[\text{RhCl}(\text{PPh}_3)_2(\text{CN})_2]_2(\text{C}_2\text{N}_2)$	yellow	$-\text{C}_2\text{N}_2$ in vacuo	2115	solid	230
$[\text{RhBr}(\text{PPh}_3)_2(\text{CN})_2]_2(\text{C}_2\text{N}_2)$	white	-	2115	solid	230
$[\text{Ni}(\text{PET}_3)_3(\text{C}_2\text{N}_2)]$	-	in soln only	2232, 2066	toluene soln	231
$[\text{Ni}(\text{P}(\text{O}-\text{p-tolyl})_3)_3(\text{C}_2\text{N}_2)]$	-	in soln only	2215,2088	toluene soln	231
$[\text{Ni}(\text{P}(\text{OPh})_3)_3(\text{C}_2\text{N}_2)]$	-	in soln only	2220,2085	benzene soln	232
$[\text{Cu}(\text{CN})_2(\text{C}_2\text{N}_2)]$	brown	-	2225,(2325)	solid	233
$[\text{Cu}(\text{CN})(\text{H}_2\text{O})(\text{C}_2\text{N}_2)]_n$	brown	-	2160	solid	234
C_2N_2	-	-	2158,2336	liquid	235
			2147	gas	235

On the basis of symmetry considerations, we see that the nitrile-like end-on monodentate co-ordination of cyanogen (Figure 4.1a) is expected to give two infrared active stretching modes whilst an end-on bridging co-ordination (Figure 4.1b) is predicted to give only one ν_{CN} band.

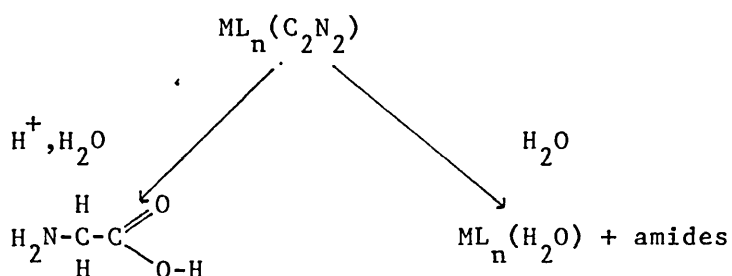
FIGURE 4.1 Modes of Co-ordination of Cyanogen



The complexes $[\text{M}_2(\text{CO})_{10}(\text{C}_2\text{N}_2)]$ where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$, exhibit two bands in the infrared although they are expected to be dinuclear. It is proposed²¹⁸ that the bands at 2118 and 2107 cm^{-1} in the Cr and W complexes are attributable to ν_{asCN} of the bridging group and the other bands ($> 2260 \text{ cm}^{-1}$) are not related to the cyanogen ligand.

In all cases of monodentate behaviour, except in Rh(III) complexes, both the ν_{CN} bands shift to lower frequency on co-ordination; for Rh(III) there is essentially no effect. As in metal cyano complexes, the $\text{C} \equiv \text{N}$ force constant will be increased by good $\text{N} \rightarrow \text{metal } \sigma$ donation and decreased by good $\text{metal} \rightarrow \text{N } \pi$ donation. It has been suggested^{218,228} that the decrease in ν_{CN} , particularly when the metal has a high electron density e.g. Ni(0), Ru(II), strongly suggests the existence of a significant π -bonding component in the metal-cyanogen bond. Some support for this is offered by the decreasing ν_{CN} in the bridged Ru(II), Ru(II-III) and Ru(III) cyanogen complexes.²²⁸

There are two examples in the literature of chemical transformation of co-ordinated cyanogen into another organic species; the complex $[\text{Cu}(\text{CN})(\text{C}_2\text{N}_2)(\text{H}_2\text{O})]^-$ can be hydrolysed to give glycine²³⁴ and other unidentified products while $[\text{Ru}_2(\text{NH}_3)_{10}(\text{C}_2\text{N}_2)]^{4+}$ undergoes irreversible oxidation in water to Ru(III) species²²⁸ in which the cyanogen undergoes hydrolysis to various amides:



It was our intention to study some of these complexes in more detail and, specifically, to obtain some Raman and ^{13}C n.m.r. data.

4.2.2 RESULTS AND DISCUSSION

(a) Copper Cyanogen Complexes

Tobia et al²³³ reported that reaction between Cu^{2+} and CN^- ions in aqueous solution formed a pink solution at a Cu/CN molar ratio of 1:4 and at pH 7.3. On further addition of Cu^{2+} , the colour changed to deep wine-red, at pH 5.7, below which CuCN was precipitated. The coloured solution was attributed to the monocyanogen-dicyano complex ion, $[\text{Cu}(\text{CN})_2(\text{C}_2\text{N}_2)]^-$. The same colour was produced by treating solutions prepared from CuCN and KCN (containing mostly $\text{Cu}(\text{CN})_2^-$) with cyanogen gas. On standing, this complex is reported to polymerise yielding a dark-brown, chemically inert solid which liberates cyanogen gas

on heating. Analysis agrees with the formulation $[\text{Cu}(\text{CN})_2(\text{C}_2\text{N}_2)]_n^-$ and in the infrared spectrum a band at 2100 cm^{-1} was assigned to ν_{CN} of the co-ordinated CN^- group and bands at 2225 and 2325 cm^{-1} were assigned to ν_{CN} of the cyanogen ligand.

Beck et al²³⁴ were unable to reproduce the above results but found that reaction between copper sulphate and sodium cyanide in aqueous solution yielded a dark-brown complex which they formulated as, $[\text{Cu}(\text{CN})(\text{C}_2\text{N}_2)(\text{H}_3\text{O})]^-$. The infrared spectrum exhibited bands characteristic of co-ordinated water and two bands in the ν_{CN} region - one at 2160 cm^{-1} assigned as co-ordinated CN^- and one at 2160 cm^{-1} assigned to end-on bidentate bridging cyanogen.

We repeated both of these preparations and found them to yield dark-brown complexes which were identical by infrared and Raman spectroscopy and by analysis. In the infrared spectrum, we observed two bands in the ν_{CN} region at 2120 and 2230 cm^{-1} whilst in the Raman spectrum there was only one broad ν_{CN} band at 2236 cm^{-1} and a weak band at 2328 cm^{-1} which we attribute to some C_2N_2 produced by decomposition in the laser beam. The infrared spectrum is consistent with a bridging cyanogen group (see introduction) where we expect to see only one ν_{CN} mode. Tobia et al reported two bands which is not expected for a polymeric complex although we observed our high frequency band at 2230 cm^{-1} which is close to their value of 2225 cm^{-1} ²³³ and quite different from that of Beck et al²³⁴ at 2160 cm^{-1} . In the Raman spectrum of the solid, we could see no band due to co-ordinated CN^- but we did observe a band at 2236 cm^{-1} coincident with infrared spectrum. The details are summarised in Table 4.3 overleaf.

As the complex is very insoluble, we were unable to obtain a ^{13}C n.m.r. spectrum which may have been useful in determining the relative intensities of CN^- : C_2N_2 carbon atoms. Our microanalysis results are consistent

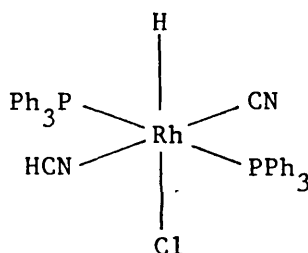
TABLE 4.3 Infrared Data for the Copper Cyanogen Complexes

REFERENCE	$\nu_{\text{CN}}, \text{cm}^{-1} (\text{CN}^-)$	$\nu_{\text{CN}}, \text{cm}^{-1} (\text{C}_2\text{N}_2)$
233	2100	2225, 2325
234	2125	2160
this work	2120	2230

with the formulation of Beck et al²³⁴ namely we would suggest that the complex is $[\text{H}[\text{Cu}(\text{CN})(\text{H}_2\text{O})(\text{C}_2\text{N}_2)]_n$.

(b) Reactions of Cyanogen and Hydrogen Cyanide with Chlorotris(triphenyl phosphine)rhodium(I)

The reaction of HCN with $\text{RhCl}(\text{PPh}_3)_2$ was reported to yield a yellow complex of stoichiometry $\text{RhCl}(\text{HCN})_2(\text{PPh}_3)_2$ which, in the infrared spectrum, as well as phosphine bands had $\nu_{\text{Rh-H}}$ 2163, ν_{CN} 2128 and $\nu_{\text{Rh-Cl}}$ 260 cm^{-1} .²²⁵ In the ^1H n.m.r. spectrum a quartet at δ -9.65 p.p.m. was observed.²²⁵ The complex was formulated as below:



where oxidative addition of HCN has occurred at the rhodium centre and a triphenylphosphine group has been displaced by HCN.

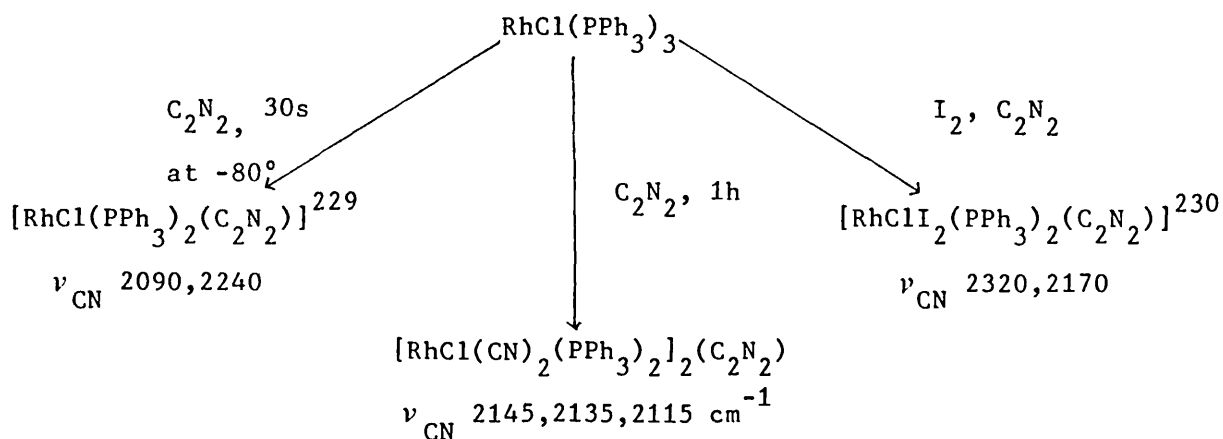
We prepared this complex and attempted to record its ^{13}C n.m.r.

spectrum. The spectrum was rather uninformative as the triphenylphosphine resonances occur at δ 140 p.p.m. which is the region where rhodium-cyano complexes are observed (see Chapter 3). In the Raman spectrum of the solid, we observed bands at 255 cm^{-1} ($\nu_{\text{Rh-Cl}}$) and at 2125 and 2160 cm^{-1} coincident with the infrared spectrum. The infrared spectrum was similar to that observed by Singer and Wilkinson.²²⁵ We observed a weak band at 3255 cm^{-1} in the infrared spectrum which we tentatively assign as $\nu_{\text{C-H}}$.

Corain *et al*^{229,230} reported the reactions of $\text{RhCl}(\text{PPh}_3)_3$ with cyanogen. These reactions are summarised in Figure 4.2.

We prepared these complexes and again found that ^{13}C n.m.r. was uninformative due to masking of the cyano resonances by the triphenylphosphine resonances. We were, however, able to record Raman spectra of the solutions of these complexes in dichloromethane; spectra of the solids could not be obtained as the samples decomposed in the laser beam. The data are presented in Table 4.4. In the complexes $[\text{RhCl}(\text{PPh}_3)_2(\text{C}_2\text{N}_2)]$ and $[\text{RhClI}_2(\text{PPh}_3)_2(\text{C}_2\text{N}_2)]$, the $\nu_{\text{sym.CN}}$ stretch of C_2N_2 is active in both the infrared and Raman spectra. Corain *et al* reported that these bands

FIGURE 4.2 Reactions of Cyanogen with $\text{RhCl}(\text{PPh}_3)_3$



were attributable to cyanogen because they decreased in intensity on standing when the complexes slowly released cyanogen gas. The complex $[\text{RhCl}(\text{CN})_2(\text{PPh}_3)_2]_2(\text{C}_2\text{N}_2)$ had two bands in its Raman spectrum, a weak band at 2127 cm^{-1} and a very strong band at 2326 cm^{-1} which we assign to C_2N_2 . We would suggest that the bridging cyanogen ligand is unstable in the solution and breaks down releasing cyanogen gas.

TABLE 4.4 Infrared and Raman Data for Cyanogen Complexes of Rhodium

COMPLEX	INFRARED SPECTRUM, cm^{-1}			RAMAN SPECTRUM, cm^{-1}
	$\nu_s(\text{C}_2\text{N}_2)$	$\nu_{as}(\text{C}_2\text{N}_2)$	ν_{CN}	
C_2N_2	-	2150	-	2330
$[\text{RhCl}(\text{PPh}_3)_2(\text{C}_2\text{N}_2)]$	2240	2090	-	2240p
$[\text{RhClI}_2(\text{PPh}_3)_2(\text{C}_2\text{N}_2)]$	2320	2170	-	2325p
$[\text{RhCl}(\text{CN})_2(\text{PPh}_3)_2]_2(\text{C}_2\text{N}_2)$	-	2115	2135 2145	2127(1)p 2326(10)p

SECTION 4.3 ACETONITRILE COMPLEXES

We have carried out a Raman and n.m.r. study on the acetonitrile complex of rhodium(III) - $[\text{RhCl}_3(\text{CH}_3\text{CN})]$. This ligand is of interest in this work as it bonds to the metal via nitrogen (-NCR) and we can use it to provide a comparison with -NCH and -NC complexes discussed

elsewhere in this chapter.

(a) Raman Spectroscopy

An octahedral complex of formula MX_3Y_3 may exist in two isomeric forms - the so-called facial or fac and meridional or mer isomers. The former belongs to the C_{3v} point group and so, for the M-X and M-Y stretches, we predict two infrared ($\text{A}_1 + \text{E}$) and two Raman ($\text{A}_1 + \text{E}$) active fundamentals (two coincidences). The mer-isomer belongs to the C_{2v} point group and, hence, exhibits three infrared and three Raman active M-X and M-Y fundamentals ($2\text{A}_1 + \text{B}_1$) with three Raman-infrared coincidences. The infrared data for these complexes are known²³⁶; for the fac-isomer $\nu_{\text{Rh-Cl}}$: 356s and 346s cm^{-1} and for the mer-isomer $\nu_{\text{Rh-Cl}}$ 356s, 350s and 300sh cm^{-1} but in the ν_{CN} region only one band was observed for each isomer at 2310 and 2304 cm^{-1} respectively. Our Raman data are listed in Table 4.5 and are consistent with the above symmetries.

TABLE 4.5 Raman Data for fac- and mer- $[\text{RhCl}_3(\text{CH}_3\text{CN})]$

	fac-isomer		mer-isomer	
	solid ^a	solution ^b	solid	solution
ν_{CN}	2347(10)	2345(10)p	2332(10)	2346(10)p
	2315(6)	2318(7)dp	2317(8)	2337(6)dp
			2306(5)	2316(6)p
$\nu_{\text{Rh-Cl}}$	352(6)	350(5)dp	353(3)	348(3)p
	306(10)	302(10)p	315(5)	331(3)dp
			300(10)	305(10)p

^a Solid recorded as KBr disc

^b Solutions recorded in aqueous solution

These bands occur at higher frequency than in acetonitrile itself indicating that, as in cyano complexes discussed in Chapter 3, donation from the slightly anti-bonding orbital on N strengthens the $\text{N}\equiv\text{C}$ bond on co-ordination. The CN stretching frequencies for these complexes are in the region $2300\text{--}2350\text{ cm}^{-1}$ compared to ν_{CN} of 2145 cm^{-1} in $[\text{RhCl}(\text{H})(\text{CN})(\text{PPh}_3)_2(\text{HCN})]$ and 2216 cm^{-1} in $[\text{W}(\text{CO})_5(\text{HCN})]$.¹⁸⁷

(b) ^{13}C and ^{15}N n.m.r. Spectroscopy

The ^1H coupled ^{13}C n.m.r. spectra of these complexes exhibit resonances attributable to the methyl carbon in the region δ 0 p.p.m. and resonances assigned to the nitrile carbon in the region 120-130 p.p.m.. In the fac-isomer, all the CH_3CN groups are equivalent (each is trans to a Cl) and so we observe a doublet at δ 121.5 p.p.m. assigned to CH_3CN with coupling to ^{103}Rh , $J(^{13}\text{C}, ^{103}\text{Rh})$ 12.4 Hz, and a 1:2:2:1 quartet centred at δ 5.9 p.p.m., $J(^{13}\text{C}, ^1\text{H})$ 138.4 Hertz, assigned to CH_3CN .

The spectrum of the mer-isomer is more complicated as the CH_3CN groups are not equivalent (one is trans to Cl, the other two are trans to CH_3CN). Hence the spectrum consists of two sets of resonances in the ratio 1:2. There are two doublets at 122.3 ($J(^{13}\text{C}, ^{103}\text{Rh})$ 9.5 Hz) and 119.3 p.p.m. ($J(^{13}\text{C}, ^{103}\text{Rh})$ 9.6 Hz) in intensity ratio 1:2 which we assign as the nitrile carbons. The methyl carbon region consists of two superimposed quartets in ratio 1:2 centred at δ 3.62 and 3.79 p.p.m. respectively; in both cases $J(^{13}\text{C}, ^1\text{H})$ was 138.4 Hz.

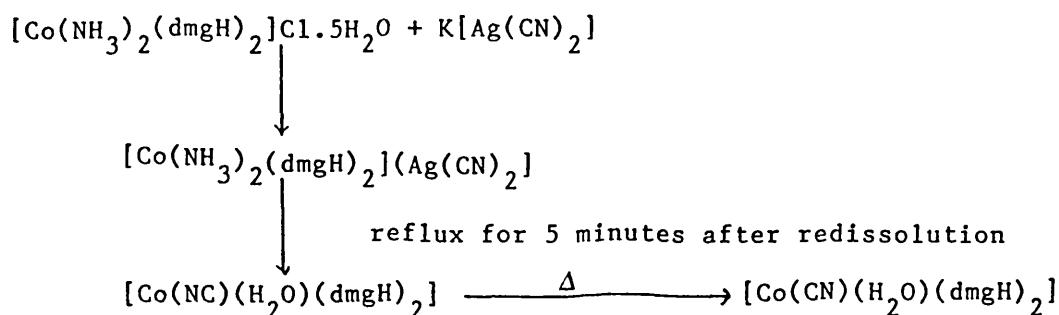
We also recorded the ^{15}N n.m.r. spectra of ^{15}N enriched complexes prepared using 30% ^{15}N enriched $\text{CH}_3^{15}\text{CN}$. As we found for the complex $[\text{RhH}(\text{NH}_3)_5]^{2+}$ (p. 54), ($^{15}\text{N}, ^{103}\text{Rh}$) coupling was observed in both isomers. The fac-isomer exhibited a doublet at - 160 p.p.m., $J(^{15}\text{N}, ^{103}\text{Rh})$ 15.6 Hz,

while the spectrum of the mer-isomer contained two doublets at - 163 and - 170 p.p.m. in the ratio 1:2. The coupling constant observed between ^{15}N , ^{103}Rh for the group trans to a chloride ligand was slightly greater (30 Hz) than that observed for the two acetonitrile groups trans to each other (16 Hz). These resonances occur in the region typical of that reported for nitrile complexes.⁵⁹

SECTION 4.4 ISOCYANO COMPLEXES

We mentioned in Section 1.1.2 (p. 15) that two stable complexes containing the isocyano ligand had been reported. Johnson *et al*⁶ reported that the cyano ligands in the complex $\text{K}_2[\text{ReN}(\text{CN})_4] \cdot \text{H}_2\text{O}$ were co-ordinated to rhenium via the nitrogen atoms; but this conclusion was reached only on consideration of isotropic temperature factors in the structural data. The $\text{N}-\widehat{\text{Re}}-\text{NC}$ angle was, surprisingly, found to be 80.6° and the CN distance was $1.13 \text{ \AA}$ and $\nu_{\text{CN}} 2120 \text{ cm}^{-1}$.⁷ On this evidence, the structural study seems somewhat unreliable but we have been unable to obtain crystals of this complex suitable for further studies.

We have been interested in cobalt-dimethylglyoximate complexes as Vitamin B₁₂ models in the development of potential cyanide antidotes. During the course of this work, we became interested in the complexes $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$ and $[\text{Co}(\text{NC})(\text{H}_2\text{O})(\text{dmgH})_2]$.⁸ Alvarez and Lopez⁸ claimed that employing $[\text{Ag}(\text{CN})_2]^-$ as a source of the cyano group resulted in the formation of $[\text{Co}(\text{NC})(\text{H}_2\text{O})(\text{dmgH})_2]$. The formation of this complex is summarised below:



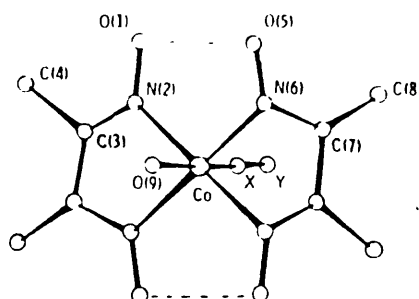
The authors also reported that heating the orange isocyano complex at 250 - 260°C for one hour yielded the brown cyano complex. The C≡N stretch for the cyano complex was reported at 2186 cm⁻¹ and that for the isocyano complex at 2135 cm⁻¹.⁸ Our infrared and Raman data are presented in Tables 4.6 and 4.7 and illustrated in Figures 4.4 and 4.5.

X-Ray Crystallography

Alvarez and Lopez⁸ reported crystal structure data for both complexes which are described more fully in an earlier paper.⁹ Close study of the latter paper gives rise to some confusion. The Co-C and Co-N distances given in the text do not correspond with those in the tables. The red crystals of the cyano isomer were obtained by heating crystals of the orange isomer; we were unable to carry out this transformation and maintain the crystal form - a brown powder was always obtained. The isotropic temperature factors quoted for the CN and NC isomers were satisfactory. However, the data given in the two papers^{8,9} are not the same. We prepared orange crystals of the isocyano complex by the method of Alvarez and Lopez⁸ and redetermined the structure. Relevant details of all the complexes are summarised in Table 4.8 and in Figure 4.3. We find the orange crystals claimed by Alvarez and Lopez as [Co(NC)(H₂O)(dmgH)₂] to be [Co(CN)(H₂O)(dmgH)₂]. As shown in the Table 4.8, the unit cell dimensions and volume of our orange complex correspond to those of the reported brown cyano complex, not the orange "isocyano" complex. The bond lengths are also comparable to those reported by Alvarez and Lopez⁸ and Solans et al.⁹ The isotropic temperature factors increase in the order Co < C < N as one would expect for a cyano complex. Reversing the C and N assignment in our structure to give an isocyano group would make these factors

TABLE 4.8 Crystal Data for the Complexes $[\text{Co}(\text{XY})(\text{H}_2\text{O})(\text{dmgH})_2]$

	$[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$		$[\text{Co}(\text{NC})(\text{H}_2\text{O})(\text{dmgH})_2]$		this work
	8	9	8	9	
Co-N(dmgh), Å	1.89	1.86(1)	1.89	1.91(1)	1.883(5)
Co-O(H ₂ O), Å	1.992(4)	1.992(4)	1.984(3)	2.010(3)	1.981(7)
Co-C(N), Å	1.906(5)	1.906(5)	-	-	1.900(9)
Co-N(C), Å	-	-	1.903(4)	1.927(4)	-
C≡N, Å	1.141(7)	1.140(7)	1.149(6)	1.163(6)	1.130(12)
a, Å	-	10.867(3)	-	10.987(3)	10.837
b, Å	-	9.581(3)	-	9.728(3)	9.544
c, Å	-	7.156(2)	-	7.242(2)	7.147
v, Å ³	-	729.1(6)	-	757.0(6)	723.53
U _{Co}	-	0.0294(5)	-	0.0320(4)	0.0263(7)
U _c	-	0.0350(23)	-	0.0476(24)	0.0271(43)
U _N	-	0.0517(25)	-	0.0453(23)	0.0301(43)
R, %	-	4.9	-	5.3	5.1

FIGURE 4.3 The $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$ Molecule

meaningless. Further work needs to be completed on our structure as the hydrogen atoms in the water molecule are showing some disorder; similarly the hydrogen atoms bridging the two dmg molecules are not yet accurately refined. It is interesting to note that in the structural paper⁹, both of the protons are reported to be associated with one dmg molecule, i.e. the complexes are formulated as $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmg})(\text{dmgH}_2)]$. We feel that this formulation is unlikely.

Infrared and Raman Data

A glance at Tables 4.6 and 4.7 and at Figures 4.4 and 4.5 show the difference between the two complexes. In the light of our structure determination, the ν_{CN} of the orange complex at 2130 cm^{-1} in the infrared and 2136 cm^{-1} in the Raman spectrum is consistent with a cyano complex; the band is also sharp - a usual feature of cyano complexes. The brown complex exhibits ν_{CN} bands at 2180 in the infrared and at 2190 cm^{-1} in the Raman spectrum; both bands are broad. This is quite high for a cyano complex. These bands are observed both for the brown complex obtained by heating the orange complex and in the brown complex formulated as $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$ prepared from cobalt acetate by the method of Yamazaki *et al.*²³⁷

Conclusions and Suggestions for Further Work

The reported "isocyano" complex $[\text{Co}(\text{NC})(\text{H}_2\text{O})(\text{dmgH})_2]$ does not contain the isocyano ligand, but a "normal" terminal cyano group. This leaves us to determine the nature of the brown complex reported by Alvarez and Lopez⁸, Solans *et al.*⁹ and Yamazaki *et al.*²³⁷ as the cyano complex. At this time, X-ray diffraction studies are in progress to determine if the two brown complexes and the orange complex are

TABLE 4.6 Infrared Data for $[\text{Co}(\text{XY})(\text{H}_2\text{O})(\text{dmgH})_2]$

ASSIGNMENT, cm^{-1}	CN ISOMER	NC ISOMER
$\nu_{\text{O-H}}$	3420w,br	3260m 3140m,br
$\nu_{\text{C}\equiv\text{N}}$ or $\nu_{\text{N}\equiv\text{C}}$	2180m,br	2130s,shp
$\nu_{\text{C=N}}$	1555s,br	1560s,br
$\delta_{\text{sym}}(\text{CH}_3)$	1365m	1365w 1325s
ν_{NO}	1238vs 1090s	1232vs 1085s,br
$\delta_{\text{O-H}}$ in dmg	975w	975w 850w
$\delta_{\text{C=N-O}}$	740m	733m
$\nu_{\text{Co-N}}$	520w	518s 460w 442s 393s 300m

TABLE 4.7 Raman Data for $[\text{Co}(\text{XY})(\text{H}_2\text{O})(\text{dmgH})_2]$

ASSIGNMENT, cm^{-1}	CN ISOMER	NC ISOMER
$\nu_{\text{C}\equiv\text{N}}$	2190w, br	2165.5w, br 2136.0vvs
$\nu_{\text{C}=\text{N}}$	1502(4) 1480(7)	1589(1) 1502(3)
	1390(3) 1381(2) 1359(4)	1435(1) 1382(0.5) 1352(2) 1330(2)
ν_{NO}	1154(10) 1003(1) 977(0.5) 851(1) 819(0.5)	1147(1) 1003(1)
	611(3)	731(1)
	583(8)	591(0.5)
		518(1) 491(1) 473(4)
	410(2)	377(3)
	338(2) 255(1)	248(10)

FIGURE 4.4 Raman Spectra of $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$ and $[\text{Co}(\text{NC})(\text{H}_2\text{O})(\text{dmgH})_2]$

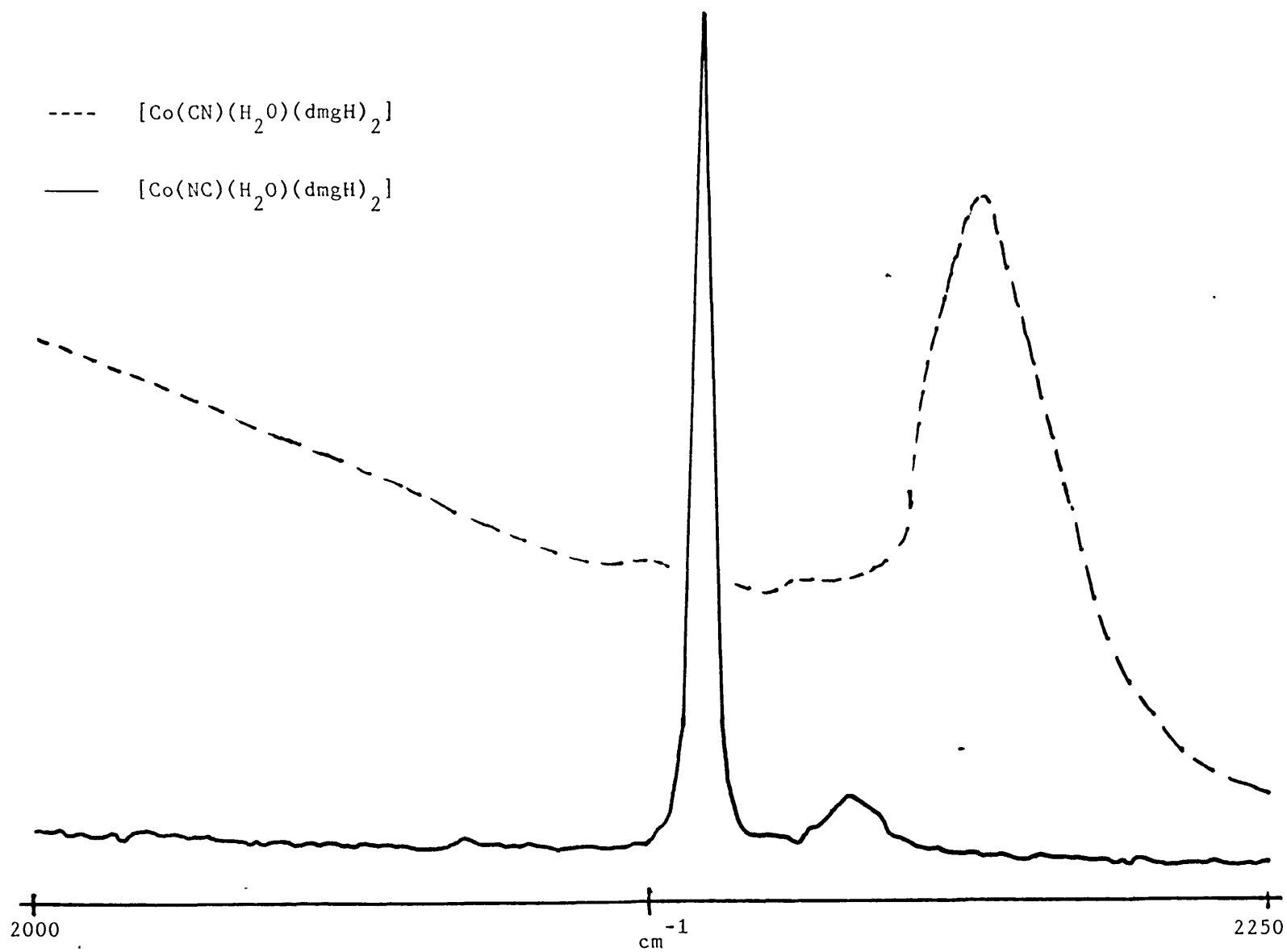
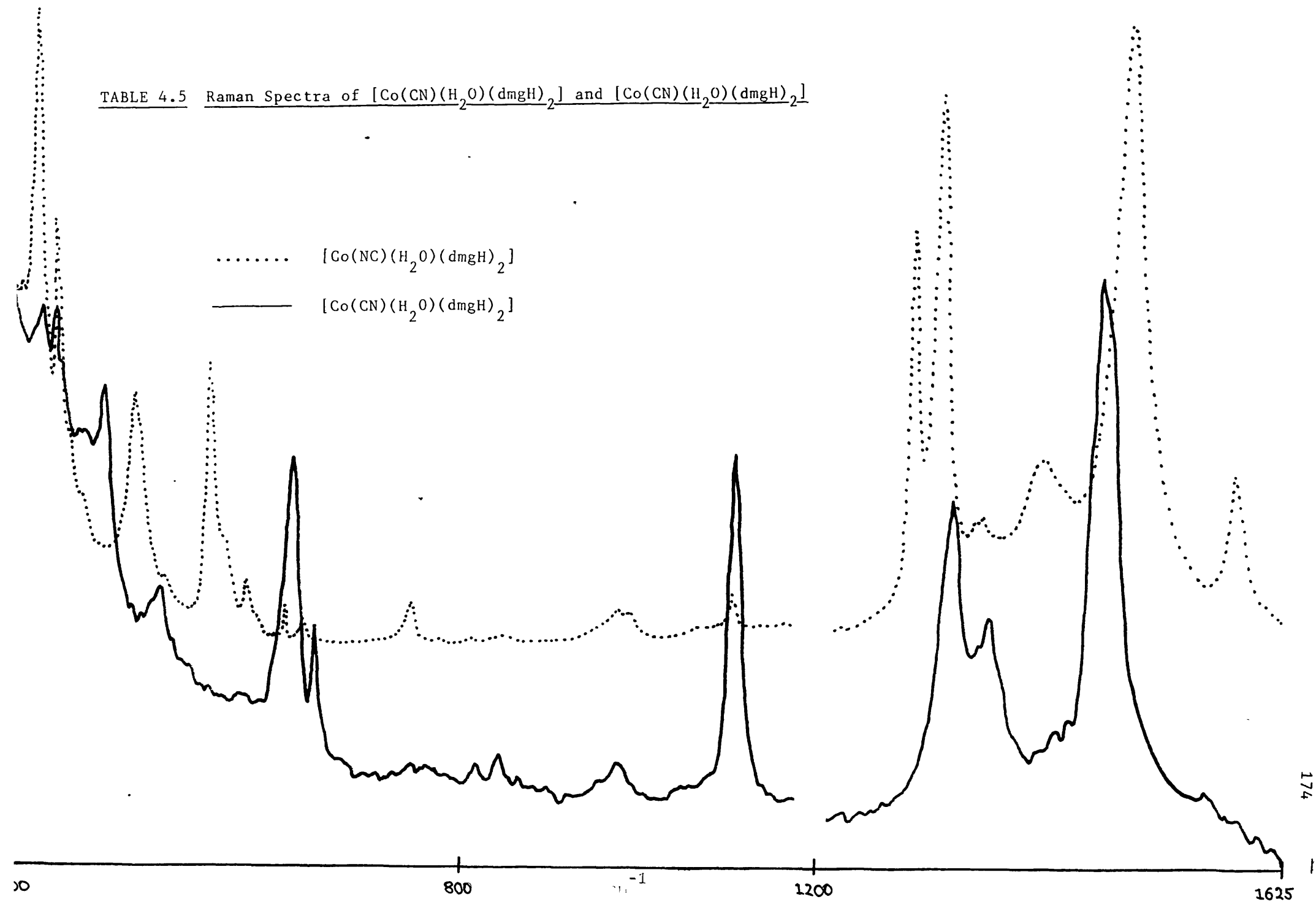


TABLE 4.5 Raman Spectra of $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$ and $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$

..... $[\text{Co}(\text{NC})(\text{H}_2\text{O})(\text{dmgH})_2]$
 ——— $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$



isostructural. From our infrared and Raman data and from the information that the brown complex is obtained from the orange complex by heating, we would tentatively suggest that the brown complex may contain a bridging cyano group. Microanalysis data for the two complexes would be very similar. Alvarez and Lopez²³⁸ report a brown complex, $[\text{Co}(\text{dmgH})_2(\text{CN})-]_x$ obtained from the reaction of $[\text{Co}(\text{dmgH})_2(\text{H}_2\text{O})_2]\text{Cl}$ with sodium cyanide, which has infrared and Raman bands at 2184 and 2179 cm^{-1} respectively.

We feel, therefore, that further studies on this system should resolve the formulation of the brown complex.

SECTION 4.5 EXPERIMENTAL

Preparation of $[\text{RhCl}(\text{PPh}_3)_3]$

The complex was prepared using the method of Osborn and Wilkinson.

Found: C, 70.3; H, 4.95. $\text{C}_{54}\text{ClH}_{45}\text{P}_3\text{Rh}$ requires C, 70.1; H, 4.87%

Preparation of $\text{CuC}_3\text{N}_3\text{H}_3\text{O}$ ²³⁴

To a sodium cyanide solution (60 cm^3 , 10M), cooled in an ice bath was added copper sulphate solution (130 cm^3 , 1.5M) dropwise with vigorous stirring. The colour of the solution became purple and then brown at which point a copious brown precipitate was formed. This was filtered off, washed with cold water and dried in vacuo.

Found: C, 24.48; N, 28.88; H, 1.47. $\text{C}_3\text{CuH}_3\text{N}_3\text{O}$ requires C, 22.4; H, 1.9; N, 26.1%

Preparation of $[\text{RhCl}(\text{HCN})_2(\text{PPh}_3)_2]$ ²²⁵

Hydrogen cyanide gas was bubbled through a solution of $[\text{RhCl}(\text{PPh}_3)_3]$ (0.38g, 0.4 mmol) in dichloromethane (3 cm^3) - petroleum ether (1 cm^3). The colour slowly changed from red to yellow and, as the dichloromethane was removed from the solution, the yellow product precipitated.

Found: C, 60.8; H, 4.4; N, 3.8. $\text{C}_{38}\text{ClH}_{32}\text{N}_2\text{P}_2\text{Rh}$ requires C, 60.8; H, 4.4; N, 3.7%

The complexes $[\text{RhCl}(\text{PPh}_3)_2(\text{C}_2\text{N}_2)]$ ²²⁹, $[\text{RhCl}(\text{CN})_2(\text{PPh}_3)_2](\text{C}_2\text{N}_2)$ ²³⁰ and $[\text{RhClI}_2(\text{PPh}_3)_2(\text{C}_2\text{N}_2)]$ ²³⁰ were prepared according to the literature methods as were the complexes fac and mer- $[\text{RhCl}_3(\text{CH}_3\text{CN})_3]$.²³⁶

Preparation of $[\text{Co}(\text{CN})(\text{H}_2\text{O})(\text{dmgH})_2]$

This complex was prepared according to the method of Yamazaki et al.

To a hot solution of dimethylglyoxime (3.29g, 27.5 mmol) in methanol (100 cm³) was added cobalt(II) acetate (3.115g, 12.5 mmol) with stirring. After 15 minutes, sodium cyanide (0.615g, 12.5 mmol) was added to the deep red solution at room temperature in water (35 cm³). The method states that aeration of the solution for a few hours results in formation of the product but we observed precipitation immediately on cooling. The product was filtered, washed with water, methanol and ether and air-dried.

Yield: 2.977g, 71.9%

Found: C, 32.65; H, 4.29; N, 20.84. $\text{C}_9\text{CoH}_{16}\text{N}_5\text{O}_5$ requires C, 32.45; H, 4.84; N, 21.02%

Preparation of $[\text{Co}(\text{NC})(\text{H}_2\text{O})(\text{dmgH})_2]$

The complex was prepared according to the method of Alvarez and Lopez.⁸

To a solution of $[\text{Co}(\text{NH}_3)_2(\text{dmgH})_2]\text{Cl} \cdot 5\text{H}_2\text{O}$ (2.0g, 4.45 mmol) in water (30 cm³) was added a solution of $\text{K}[\text{Ag}(\text{CN})_2]$ (0.96g, 4.8 mmol) in water (30 cm³).

The resulting yellow solution yielded a precipitate of $[\text{Co}(\text{NH}_3)_2(\text{dmgH})_2] \cdot [\text{Ag}(\text{CN})_2]$. This suspension was heated to reflux and after redissolution

of the precipitate, the solution was heated for a further 15 minutes.

The yellow solution was cooled slowly and orange-yellow crystals were obtained. These were filtered off, washed with a small amount of cold water and air-dried.

Yield: 0.59, 40.0%

Found: C, 32.5; H, 4.8; N, 21.0. $\text{C}_9\text{CoH}_{16}\text{N}_5\text{O}_5$ requires C, 32.45; H, 4.84; N, 21.02%

PHYSICAL MEASUREMENTS

Raman spectra were measured on a Spex Ramalog 5 instrument (Model 14018) using exciting lines from a Coherent Model 52 krypton ion laser. Data were collected using a GaAs photomultiplier tube coupled to a Spex Datamate computer system. Solids were recorded as spinning KBr discs or in capillaries under nitrogen and solutions in a spinning cell under nitrogen.

Infrared spectra were measured on a Perkin-Elmer 683 instrument as mulls in liquid paraffin between caesium iodide plates, as pressed discs in KBr or as aqueous solutions between calcium fluoride plates.

^1H n.m.r. were measured on a Perkin-Elmer R32 90MHz instrument. ^{13}C and ^{15}N n.m.r. were recorded on a Bruker WM 250 Fourier Transform spectrometer (5.9 tesla). ^{13}C spectra were recorded at 62.9MHz (using broad band proton decoupling as necessary) with a digital resolution of $\sim 2\text{Hz/point}$. Chemical shift reference was nominally to external DSS in $^2\text{H}_2\text{O}$. ^{15}N n.m.r. spectra were recorded at 25.4 MHz - digital resolution was 1Hz/point, 0.3Hz/point (not decoupled); similar resolution for line broadening. The shift reference was external NO_3^- of a saturated aqueous solution of NH_4NO_3 . Data were multiplied by an appropriate exponential function to obtain optimum signal/noise ratio. ^{13}C , ^{14}N and ^{199}Hg were recorded on a Jeol FX 90Q Fourier transform spectrometer at 22.51MHz, 6.43MHz and 9.2MHz respectively; other conditions as previously described.

Microanalyses were performed by Mr. K. Jones of the Imperial College Microanalytical Department and by Pascher (Bonn); potassium was determined gravimetrically using tetraphenylboron.

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