SOME STUDIES

OF

TRANSITION METAL NITRITE COMPLEXES

A Thesis

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by

Michael Anthony Hitchman

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Chemistry Department

Imperial College

London S. W. 7.

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A B S T R A C T

A number of new nitrite complexes were prepared and the manner of nitrite bonding in these was investigated by means of infrared and electronic spectroscopy.

In a series of compounds formed by nickel nitrite with various amines the manner of nitrite coordination apparently depends on the steric nature of the amine substituents. Tetra-N-substituted amines produced complexes of the type Ni(diamine)$(NO_2)_2$ having chelating nitrite groups, di-N-substituted amines yielded nitritocomplexes Ni(diamine)$_2$(-ONO)$_2$, while with mono-N-substituted diamines or ethylenediamine itself, nitrocomplexes were formed. Two solid nitritocomplexes were found to exist in a nitro-nitrito equilibrium in solution.

The properties of bridging nitrite groups were studied in some complexes $NiL_2(NO_2)_2$ [L = a substituted pyridine], and in several of these the anions are bridged via a single oxygen atom, a hitherto unrecognised manner of nitrite coordination.

Compounds containing the anions $M(NO_2)_6^{4-}$ [M = Ni, Co and Cu], $M(NO_2)_5^{3-}$ [M = Ni and Mn], $M(NO_2)_4^{2-}$ [M = Zn, Cd, Hg, Cu, Co and Mn] and $Ni(NO_2)_3^-$ are described and, where possible, structures are proposed for these complexes.

A summary has been made of the different ways in which the nitrite group was observed to coordinate in metal complexes

and of the methods by which these types of bonding can be distinguished. The apparent reasons for the adoption of the particular structures found are also discussed.

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Ligand Abreviations

The following ligand abreviations are used throughout this work.

ligand	abreviation
ethylenediamine	en
N-methylethylenediamine	men
N-ethylethylenediamine	een
N,N-dimethylethylenediamine	a-dimen
N,N-diethylethylenediamine	a-dieen
N,N'-diethylethylenediamine	s-dieen
N,N,N',N'-tetramethylethylenediamine	tetmen
N,N,N',N'-tetraethylethylenediamine	teteen
meso-1,2-diphenylethylenediamine	m-stien
racemic-1,2-diphenylethylenediamine	r-stien
1,2-diamino-2-methylpropane	cc-dimen
pyridine	py
2-methylpyridine	2-mepy
3-methylpyridine	3-mepy
4-methylpyridine	4-mepy
quinoline	quin
isoquinoline	i-quin
triphenylphosphineoxide	Ph_3PO
triphenylarsineoxide	Ph_3AsO
ortho-phenylenediamine	o-phen
o-xylylenebis-(triphenylphosphonium)$^{2+}$	o-Cat^{2+}

CHAPTER I

Introduction and Historical Survey

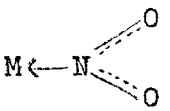
Introduction

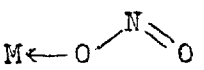
Probably the most interesting feature of the nitrite group as a ligand is its ability to coordinate to a metal ion in several different ways. The present investigations have largely been concerned with identifying the manner in which the nitrite group is bonded in a number of metal complexes, and elucidating the reasons behind the adoption of the particular structures found.

It is pertinent at this stage to consider briefly the information available on the properties of the nitrite ion and metal-nitrite complexes prior to the commencement of this work.

Monodentate nitrite coordination

As a monodentate ligand the nitrite group can coordinate to a metal ion either via nitrogen, forming a nitrocomplex[1] (I), or via oxygen, giving a nitritocomplex (II).

I. 

II. 

A large number of nitrocomplexes have been reported, both mixed ligand complexes such as $Ni(NH_3)_4(-NO_2)_2$ and $\left[Pd\ (NH_3)_3(-NO_2)\right]Cl$ and compounds containing polynitrite ions, eg. $Na_3Co(-NO_2)_6$ and $K_2Pd(-NO_2)_4$.

Oxygen coordination of the nitrite group, however, was

comparatively rare, being limited almost exclusively to a few unstable complexes of Co^{III} and some closely related compounds. The first nitritocomplex to be recognised as such was pink $[Co(NH_3)_5-ONO]Cl_2$. However, this was found to rearrange within a matter of hours to the more stable nitro-isomer, yellow $[Co(NH_3)_5-NO_2]Cl_2$, and almost all the other nitritocomplexes behaved in the same manner. The kinetic mechanisms involved in the linkage isomerism of these nitrite complexes have been the subject of much investigation.

Kinetic studies The formation of $[Co(NH_3)_5-ONO]Cl_2$, together with one or two similar complexes of Co^{III} was studied by Basolo et al.[3] and Murmann and Taube[4] and the following unusual reaction sequences were shown to occur: -

1. $$\begin{cases} [Co(NH_3)_5Cl]^{2+} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{3+} \longrightarrow [Co(NH_3)_5-OH]^{2+} \\ 2HNO_2 \longrightarrow NO^+ \cdots NO_2^- + H_2O \end{cases}$$

2. $$Co(NH_3)_5 - O \begin{matrix} \nearrow H \\ ON^+ \cdots NO_2^- \end{matrix} \longrightarrow [Co(NH_3)_5-ONO]^{2+} + HNO_2$$

The production of the nitrito-isomer was thus due to attack by the N_2O_3 present under the specific conditions of pH and temperature required for the isolation of this form of the complex. The nitrito-complex was formed without breaking the cobalt-oxygen bond of an intermediate hydroxo-species, and subsequently rearranged in a few

hours to the corresponding nitrocomplex, by an intramolecular process[3,4,5]. It was realised by Basolo et al.[3] that the isolation of these unstable nitritocomplexes was due only to the high activation energy of this intramolecular rearrangement and that this was related to the 'inert' nature of metal ions having a d^3 or spin-paired d^6 electron configuration. They were thus able to predict the formation of nitritocomplexes with other similar metal ions and the compounds $\left[M(NH_3)_5\text{-}ONO\right]Cl_2$ [M = Cr, Ir and Rh] and $\left[Pt(NH_3)_5\text{-}ONO\right]Cl_3$ were subsequently isolated[6,7] by a preparative technique similar to that used for the cobalt complex. All these nitritocomplexes, with the exception of the chromium one, also rearranged to the corresponding nitrocomplexes within a few hours. The nitro-isomer of $\left[Cr(NH_3)_5\text{-}ONO\right]Cl_2$ is as yet, however, unknown.

In determining the nature of the metal-nitrite bonding in metal complexes three physical techniques have been of major importance. These were x-ray crystallography, and the measurement of electronic and infrared absorption spectra.

X-ray studies Single crystal x-ray crystallography is now probably the most accurate method of investigating detailed molecular structures in the solid state. However, the determination of a structure by this means is still often a lengthy and arduous process, and it is not always possible to prepare suitable crystals. X-ray techniques are thus generally used to confirm an interesting structure suggested by other means, or when other techniques fail.

Nitrogen coordination of the nitrite ion has been found in the

crystal structures of a number of compounds[8 - 14]. There was no crystallographic information, however, on nitritocomplexes.

Electronic spectra The 'd-d' electronic transitions in nitrite complexes, as measured by the electronic absorption spectra, have often been used to give an indication of the nature of the metal nitrite bonding.

This is because of the relative positions of the nitro- and nitrito-groups in the spectrochemical series, which is shown below for a number of the more common ligands, in order of decreasing ligand field strength[15].

$CN^- > -NO_2^- >$ o-phenanthroline $>$ en $> NH_3 >$ py $> -NCS^- > H_2O > -ONO^- > OH^- > Cl^- > Br^- > I^-$

Thus, while the nitro-group is a 'strong' ligand, the nitrito-group is fairly 'weak'. This means that for transition metal ions, particularly of the first row, the d-d bands in a nitrocomplex will generally be at considerably higher energy than the corresponding ones in the analogous nitritocomplex. Thus it is often possible, by comparing the electronic spectrum of a nitrite complex with those of similar compounds containing other ligands, to deduce the effective ligand field strength of the nitrite groups, and hence their mode of coordination. This is illustrated in Table 1, which lists the energies of the first spin-allowed electronic transitions for the isomeric forms of $\left[Co(NH_3)_5NO_2\right]Cl_2$ together with those of two related compounds.

Table 1

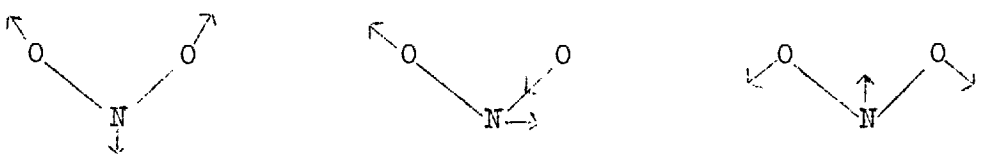
The first spin-allowed electronic transitions of the isomeric forms of $[Co(NH_3)_5NO_2]Cl_2$ and two related compounds.

compound	energy (cm^{-1})	ref.
$[Co(NH_3)_5\text{-}ONO]Cl_2$	20,600	16
$[Co(NH_3)_5\text{-}NO_2]Cl_2$	21,900	16
$[Co(NH_3)_5H_2O]Cl_3$	20,600	17
$Co(NH_3)_6Cl_3$	21,000	17

Infrared spectra The uncoordinated nitrite ion belongs to the point-group C_{2V}, and has three non-degenerate, infrared active fundamental vibrations. These are illustrated in Figure 1, and may be designated ν_s and ν_{as}, the symmetric and antisymmetric nitrogen oxygen stretches, and δ_{no_2} the NO_2 deformation.

Figure 1

The fundamental vibrations of the nitrite ion



ν_s ν_{as} δ_{no_2}

The infrared and raman spectra of sodium nitrite, which

belongs to the space-group Immm(C_{2V}^{20}) [18], have been measured in the solid state and in H_2O and D_2O solution by a number of workers[19-23]. There is general agreement on the observation of three peaks at 828±3 (medium, sharp), 1250±30 (very strong, broad) and 1326±2 cm^{-1} (very weak, sharp), with the exception of the results of Newman, who reported bands at 831, 1325 and 1360 cm^{-1}.[20] The peak at 828 cm^{-1} may be readily assigned as δ_{NO_2}[19-23], and on the basis of the raman polarisability measurements on an aqueous solution[19] and on single crystals[20,23] of $NaNO_2$ the band at 1326 cm^{-1} has been assigned as ν_s. This is also suggested[22] by the fluorescence spectrum of sodium nitrite. This leaves ν_{as} as the broad intense absorption centred at ~1250 cm^{-1}, which is in agreement with the raman spectra of an aqueous solution[19] and a single crystal[23] of sodium nitrite. Potassium nitrite[21], silver nitrite[24] and barium nitrite[25], all have infrared spectra very similar to that of sodium nitrite.

It is thus apparant that NO_2^- is unusual in having ν_s higher than ν_{as}, and in this it resembles O_3[26] (with which it is iso-electronic) and OF_2[27]. This has been explained[21] in terms of the relatively large interaction constant to be expected between the two negatively charged oxygen atoms.

Unfortunately, despite the evidence outlined above, several papers[28-33] concerned primarily with the infrared spectra of coordinated nitrite groups have incorrectly reversed the assignments of ν_{as} and ν_s, apparently on the grounds[31] that an antisymmetric stretching frequency must always be higher than a

symmetric one. However, this is not always the case, and there can be little doubt that the assignments given above are in fact the correct ones.

On coordination the nitrogen-oxygen stretching frequencies of the nitrite group change from their free ion values in a manner quite characteristic of the method of bonding taking place. The frequency δ_{NO_2}, however, has not been found to alter significantly.

Oxygen coordination causes the lowering of one stretching frequency towards that of a nitrogen-oxygen single bond, the other being raised towards that of a nitrogen-oxygen double bond. This may be seen from the values (Table 2) of ν_{as} and ν_s[34] for the nitrito-groups in $\left[Co(NH_3)_5\text{-}ONO\right]^{2+}$, $\left[Pt(NH_3)_5\text{-}ONO\right]^{3+}$ and the limiting covalent compound trans-methylnitrite.

Table 2

The nitrogen-oxygen stretching frequencies (cm^{-1}) in some nitrite compounds

compound	ν_{as}	ν_s	ref.
$NaNO_2$	1250 vsbr	1326 wsp[a]	20 - 23
$\left[Co(NH_3)_5\text{-}ONO\right]Cl_2$	1065 s	1460 s	35
$\left[Pt(NH_3)_5\text{-}ONO\right]Cl_3$	995 s	1505 s	7
trans-CH_3-ONO	814 s	1681 s	36
$Rb_3Co(\text{-}NO_2)_6$	1399 s	1327 s	37
$K_2CaNi(\text{-}NO_2)_6$	1325 vs	1335 wsp	29
$CH_3\text{-}NO_2$	1377 s	1586 s	38

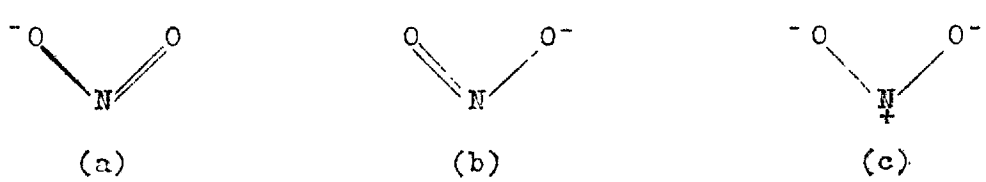
a sp represents sharp peak

It is apparent (Table 2) that nitrogen coordination of the nitrite group has a quite different effect on its vibrational spectrum from bonding via oxygen. Mathieu et al.[39,40] have shown from raman polarisability data and symmetry considerations that in the nitrocomplexes of Co^{III} and Pt^{II} ν_{as} is raised to $\sim$1400 cm^{-1} while ν_s remains virtually unaltered from its free ion value at $\sim$1330 cm^{-1} and it may be noted that ν_{as} is much higher than ν_s in the limiting covalent compound nitromethane[38]. In $K_2CaNi(-NO_2)_6$ the relative intensities of the bands (see Chapter 6) suggest that ν_{as} has been raised to 1325 cm^{-1} while ν_s is at 1335 cm^{-1}. It is thus apparent that bonding via nitrogen tends to raise ν_{as} considerably, while leaving ν_s only slightly above its free ion value. This effect has been explained by Mathieu, Postollec and Poulet[39] in the following manner.

The three main canonic forms of the nitrite ion are illustrated in Figure 2, and it may be seen that the induction of a positive charge on the nitrogen atom (as presumably occurs in a nitrocomplex) increases the contribution of forms (a) and (b) relative to that of (c). This causes a decrease in the negative charge on the oxygen

Figure 2

The three main canonic forms of the nitrite ion



(a) (b) (c)

atoms, and hence the non-bonded interaction term between them, while at the same time increasing the double-bond character of the nitrogen-oxygen bonds. Since the fact that $\nu_s > \nu_{as}$ in free NO_2^- depends on the high value of the non-bonded interaction term, nitrogen coordination would be expected to raise ν_{as} relative to ν_s which is in agreement with the experimental results. Also the increase in double bond character of the N-O bonds should raise ν_s and ν_{as} somewhat, as is indeed the case.

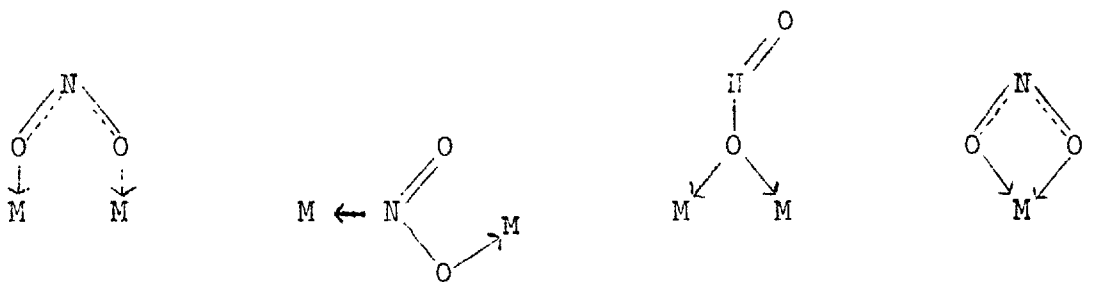
So far only the infrared frequencies of the nitrite group itself have been considered. However, recently interest has also been shown in the vibrations associated directly with the metal-nitrite bond. While these will be considered in more detail in Chapters 6 and 7, it is pertinent to note that the presence of a wagging vibration ρ_w has been suggested[29,41] as a means of identifying nitro-coordination of the nitrite group. This frequency has been assigned at ~ 600 cm^{-1} in many nitrocomplexes of Co^{III} [29,37,41], and at 462 cm^{-1} in $K_2CaNi(NO_2)_6$[29], but was not observed in nitritocomplexes and compounds containing bridged nitrite groups.

Bidentate nitrite coordination

While it had been known for some time that the nitrite group could function as a bridging ligand, the manner in which it accomplishes this was not extensively investigated. The three most probable ways that the nitrite group could bridge are shown in Figure 3 (a), (b) and (c).

Figure 3

The four most likely ways of bidentate nitrite coordination.



The main evidence as to the nature of the bridging actually occurring in metal complexes was provided by the nitrite infrared frequences at ~1200 and ~1500 cm^{-1} in $\left[Co(NH_3)_3\begin{smallmatrix}OH\\OH\\NO_2\end{smallmatrix}Co(NH_3)_3\right]Cl_3$ and some similar compounds[29,31]. The slight lowering of ν_{as} from its free ion value together with the raising of the mean of ν_s and ν_{as} suggested both nitrogen and oxygen coordination of the nitrite group, and it was concluded[29,31] that bridges of the type (b) in Figure 3 were present in these complexes.

Nitrite bonding similar to that illustrated in Figure 3 (c), but involving a linear nitrite group, was proposed [42] in the compound (Ni ethylenediamine$_2$ NO_2)ClO_4, but it has since been suggested [43] that this is incorrect and the structure now proposed for this compound, which in fact involves bridging of type (b) in Figure 3 will be discussed in chapter 5 (A).

A preliminary x-ray analysis of the compound $K_3Hg(NO_2)_4NO_3$ has shown[44] that the mercury ion is surrounded by four nitrite groups,

each chelated as in Figure 3 (d). This is thus a second way that the nitrite group can function as a bidentate ligand.

General Summary

As a monodentate ligand the nitrite ion has usually been found to bond via nitrogen, and oxygen coordination has normally only been observed by virtue of an unusual reaction mechanism which allows the formation of unstable nitritocomplexes with a few kinetically inert metal ions. The type of bonding in any nitrite complex is generally readily distinguishable since the nitro- and nitrito-groups occupy quite different positions in the spectrochemical series and have rather distinctive infrared spectra.

As a bidentate ligand, vibrational spectroscopy suggests that the nitrite group can bridge via nitrogen and an oxygen atom, while an x-ray study has shown that chelation via two oxygen atoms is also possible.

CHAPTER 2

Some Nitro- and Nitritocomplexes of Nickel(II)

Considerable interest has recently been shown[45-48] in the factors influencing the different structures adopted in metal complexes, and the importance of steric hindrance in this respect has been demonstrated in several studies on the compounds formed by various nickel salts with a number of substituted ethylenediamines[45,46]. Thus, in order to investigate the effects of steric interference on the nature of the metal-nitrite bond, a series of compounds of the type $NiD_2(NO_2)_2$ [D = a number of C- or N-substituted ethylenediamines] and $NiL_4(NO_2)_2$ [L = a substituted pyridine or NH_3] were prepared[32]. These complexes are of two quite distinct types depending on the nature of the amine used being blue when D represents m-stien, a-dieen, s-dieen and a-dimen and L = py, 3-mepy and 4-mepy and red when D is en, men, een, cc-dimen, o-phen and r-stien and L = NH_3. The infrared and electronic spectra of the solid complexes suggest that the blue compounds are nitrito-complexes while the red ones contain nitrite groups bonded via nitrogen.

In solution some of the blue complexes undergo structural changes, and these are considered in Chapters 3 and 4.

Electronic spectra

The electronic spectra of the complexes were recorded in the solid state over the range 4000 - 30,000 cm^{-1}, and the energies of

the band maxima are given in Table 3. The spectra of the analogous

Table 3

The electronic reflectance spectra of some nitro- and nitritocomplexes of Ni^{II}

Compound	Band Maxima (cm^{-1})[a]				
$Ni(py)_4(-ONO)_2$	b		16,900	(~13,000sh)	10,400
$Ni(3\text{-}mepy)_4(-ONO)_2$	b	(22,000sh)	17,400	(~13,000sh)	10,600
$Ni(4\text{-}mepy)_4(-ONO)_2$	b	(21,050sh)	17,000	(~13,000sh)	10,500
$Ni(m\text{-}stien)_2(-ONO)_2$	b	(23,300sh)	17,150		10,300
$Ni(a\text{-}dimen)_2(-ONO)_2$	27,250		17,300		10,950, 8,740sh
$Ni(a\text{-}dieen)_2(-ONO)_2$	b	(20,400sh)	16,890	(~14,800sh)	10,350, 7,870sh
$Ni(s\text{-}dieen)_2(-ONO)_2$	27,550	(22,500)	17,000	(~12,400sh)	10,360
$Ni(s\text{-}dieen)_2(CCl_3CO_2)_2$	27,500		17,000	(~11,800sh)	9,700
$Ni(s\text{-}dieen)_2(NCS)_2$	27,600		17,400	(~12,500sh)	10,700
$Ni(NH_3)_4(-NO_2)_2$	b		19,900		11,400
$Ni(en)_2(-NO_2)_2$	b		19,650		12,500, 11,000sh
$Ni(cc\text{-}dimen)_2(-NO_2)_2$	29,240		19,230		11,600
$Ni(r\text{-}stien)_2(-NO_2)_2$	b		19,900		12,500, 10,800sh
$Ni(o\text{-}phen)_2(-NO_2)_2$	b	21,200, 19,600sh			12,500, 11,000sh
$Ni(men)_2(-NO_2)_2$	b		20,120		12,350, 11,000sh
$Ni(een)_2(-NO_2)_2$	b		20,000		12,350, 11,300sh
$Ni(een)_2(CCl_3CO_2)_2$	27,600		17,600	(~13,250sh)	12,020sh, 9,740
$Ni(een)_2(NCS)_2$	28,700		18,200		10,950

a spin-forbidden bands in parentheses

b band obscured by strong ultraviolet absorption

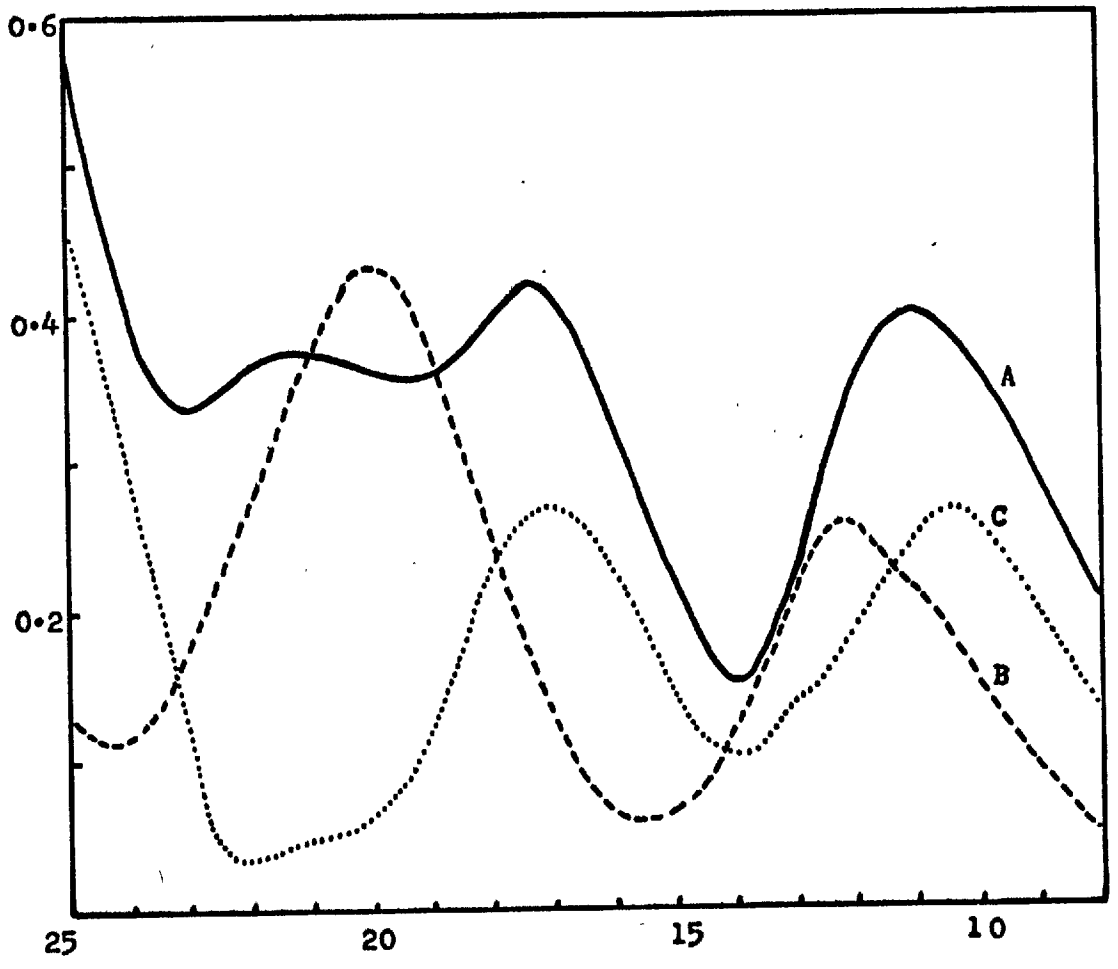
trichloracetate- and isothiocyanate-complexes for one typical blue and one red compound are also given for comparison. The sharp bands in the region 4,000 - 8,000 cm^{-1}, which may be assigned as the vibrational overtones of the organic ligands[46] have been omitted. In some cases very weak peaks were observed in the visible region, and these are probably due to spin-forbidden transitions. The spectra of a typical red complex $Ni(een)_2(-NO_2)_2$ and a typical blue one $Ni(4\text{-mepy})_4(-ONO)_2$ are shown in Figure 4 (b) and (c).

All the compounds listed in Table 3 have electronic spectra characteristic of six-coordinate nickel ions with spin-triplet ground states. Three spin-allowed transitions ($^3A_{2g} \longrightarrow {}^3T_{2g}$, $^3A_{2g} \longrightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \longrightarrow {}^3T_{1g}$ (P) in O_h ligand field symmetry) were observed for some of the complexes though the highest energy band was obscured by electron transfer absorption for most of them. In some cases the first electronic band was split into two components. This has also been observed for a number of other nickel complexes,[45,46,49] and in the compound $Ni(py)_4Cl_2$ it has been ascribed to the removal of the degeneracy of the $^3T_{2g}$ level in the ligand field symmetry which approximates to D_{4h}[49]. In the compounds $Ni(een)_2(-NO_2)_2$, $Ni(men)_2(-NO_2)_2$, $Ni(o\text{-phen})_2(-NO_2)_2$, $Ni(r\text{-stien})_2(-NO_2)_2$ and $Ni(en)_2(-NO_2)_2$ it is also possible that one of the two peaks at ~12,000 cm^{-1} is due to the spin-forbidden transition $^3A_{2g} \longrightarrow {}^1E_g$, which can interact with the first spin-allowed transition, thus gaining intensity[50]. However, it is the approximate energy of the electronic bands in these

FIGURE 4

The Electronic Reflectance Spectra of:-

(A) $Ni(i\text{-}quin)_4(NO_2)_2$ (B) $Ni(een)_2(NO_2)_2$ (C) $Ni(4\text{-}mepy)_4(NO_2)_2$



compounds which are of significance in indicating the manner of bonding of the nitrite groups.

The red complexes $Ni(NH_3)_4(-NO_2)_2$ and $Ni(en)_2(-NO_2)_2$ have been shown to contain nitrite groups coordinated via nitrogen[9,10], and the close similarity of their electronic spectra to those of $NiD_2(-NO_2)_2$ [D = men, een, cc-dimen, r-stien and o-phen] suggests that these compounds are all nitrocomplexes. The relatively high energy of their electronic transitions is in accordance with the position of the nitro-group at the 'strong' end of the spectrochemical series (see Chapter 1).

The band positions of the blue compounds $NiL_4(-ONO)_2$ [L = py, 3-mepy and 4-mepy] and $NiD_2(-ONO)_2$ are all quite different from those of the red nitrocomplexes and are rather similar to those of the thiocyanate and trichloracetate complexes. This suggests that the nitrite groups produce a relatively weak ligand field and are thus coordinated via oxygen.

It is impossible to estimate the ligand field strengths of the nitrite groups in these complexes accurately, since the Δ values (Δ = ligand field splitting parameter) of the substituted amines are unknown. Moreover, it is also possible that the strength of the metal-nitrite bond may vary from one nitritocomplex to another (this possibility is discussed on Page 35). However, some idea of the relative Δ-values may be obtained by the 'average environment' method of Jørgensen[51]. For Ni^{II} in O_h ligand field symmetry the first electronic transition approximates to Δ and this is at

$\sim$12,000 cm^{-1} in a typical nitrocomplex $Ni(een)_2(-NO_2)_2$, and at 10,360 cm^{-1} in a typical nitritocomplex $Ni(s\text{-}dieen)_2(-ONO)$. Taking the Δ-value of the diamines as 11,500 cm^{-1} [52], that of the nitro-groups in $Ni(een)_2(NO_2)_2$ is $\sim$13,000 cm^{-1} and that of the nitrito-groups in $Ni(s\text{-}dieen)_2(-ONO)_2$ is $\sim$8,100 cm^{-1}. These values may be compared with Δ = 8,500 cm^{-1} for H_2O and Δ = 10,800 cm^{-1} for NH_3 [53], and are quite similar to those observed for the nitro- and nitrito-groups in the isomeric forms of $\left[Co(NH_3)_5NO_2\right]Cl_2$ (Table 1), if the difference in oxidation state of the metal ion is taken into account.

Infrared spectra

The spectra of the nickel nitrite complexes listed in Table 3 were determined over the range 2000 - 400 cm^{-1} and the bands due to the nitrite groups (Table 4) were identified by comparison with the spectra of the corresponding nickel thiocyanate and, in many cases, halide complexes. The spectra of $Ni(en)_2(-NO_2)_2$ and $Ni(NH_3)_4(-NO_2)_2$ are shown in Figure 5, and that of $Ni(py)_4(-ONO)_2$ in Figure 13 (Page 71).

In the case of $Ni(o\text{-}phen)_2(-NO_2)_2$, although a strong band occurred at $\sim$1280 cm^{-1} which could be due to nitro-groups, the nitrite frequencies could not be identified with any certainty, because the infrared spectrum of the coordinated amines altered on going from one control compound to another, a feature which has also been noted by other workers [54]. The compound $Ni(py)_4(-ONO)_2$ loses pyridine readily and the spectrum of nujol mulls of this complex showed, in

Table 4

The nitrite infrared frequencies in some nitro- and nitritocomplexes of Ni^{II}

Compound[a]	Band Maxima (cm^{-1})		
	δ_{NO_2}	Nitrogen-Oxygen Stretches	
$Ni(4\text{-mepy})_4(-ONO)_2$	b	1119vs, 1144vs	1401s
$Ni(3\text{-mepy})_4(-ONO)_2$	b	1126vs	1389s
$Ni(py)_4(-ONO)_2$	825m	1114vs	1393s
$Ni(a\text{-dimen})_2(-ONO)_2$	817s	1130vs	1387s
$Ni(a\text{-dieen})_2(-ONO)_2$	824m	1163vs	1361s
$Ni(s\text{-dieen})_2(-ONO)_2$	821w	1205vs	1337s
$Ni(m\text{-stien})_2(-ONO)_2$	b	1221s	1350ms
$Ni(r\text{-stien})_2(-NO_2)_2$	814	~1300[c]	~1320sh[c]
$Ni(cc\text{-dimen})_2(-NO_2)_2$	832w, 818m	~1325[c]	b
$Ni(een)_2(-NO_2)_2$	837m	1303vs	1333w[c]
$Ni(men)_2(-NO_2)_2$	813	1335vs	1353w[c]
$Ni(en)_2(-NO_2)_2$	807m	1299vs	b
$Ni(NH_3)_4(-NO_2)_2$	814w	1300vs	1360[c]

a nujol and hexachlorobutadiene mulls

b band obscured by other ligand vibrations

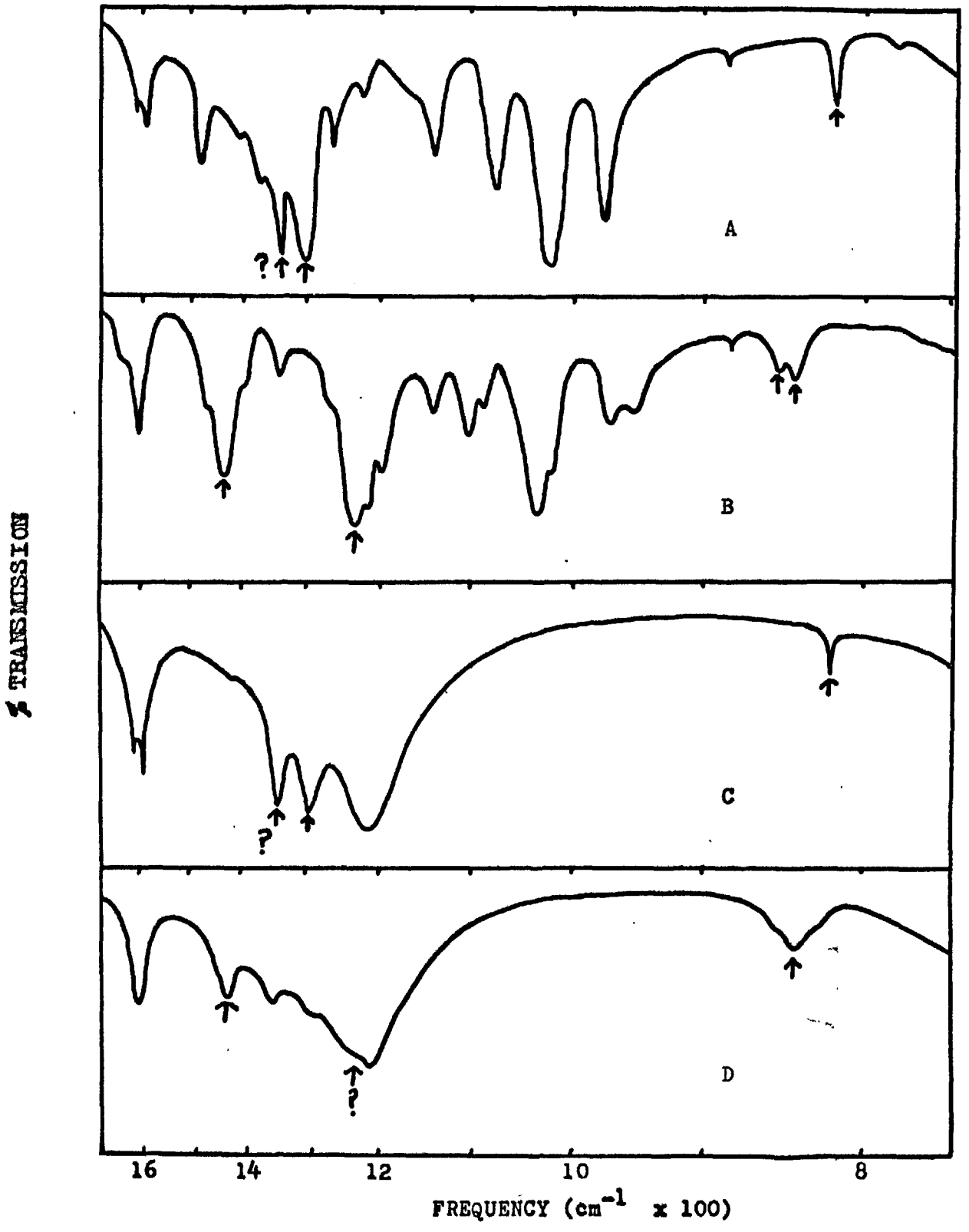
c exact position of band maximum rendered uncertain by other ligand absorption.

FIGURE 5

The Infrared Spectra of:-

(A) $Ni(en)_2(NO_2)_2$ (B) $Ni(en)(NO_2)_2$

(C) $Ni(NH_3)_4(NO_2)_2$ (D) $Ni(NH_3)_2(NO_2)_2$



The nitrite bands are indicated by arrows.

addition to the strong bands listed in Table 4, weak peaks at 1311 and 841 cm^{-1} due to $Ni(py)_2(NO_2)_2$. These peaks disappeared when the compound was mulled in a little pyridine.

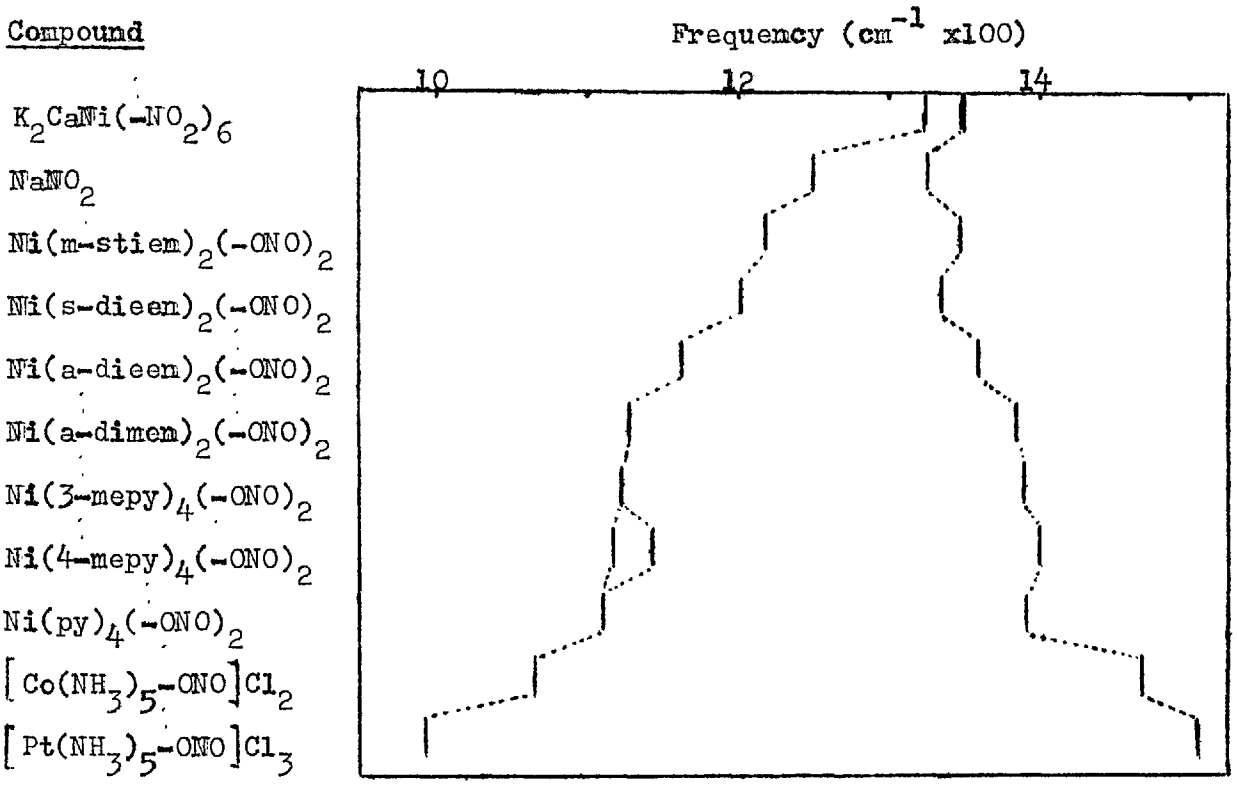
The effects of coordination on the nitrite infrared spectrum have been discussed in Chapter 1

The red compounds $NiD_2(-NO_2)_2$ [D = en, men, een, cc-dimen and r-stien] and $Ni(NH_3)_4(-NO_2)_2$ all had strong nitrite bands at ~1300 cm^{-1} assignable as ν_{as}. In some cases ν_s could also be observed as a weak sharp band at ~1335 cm^{-1}, though generally the feeble nature of this peak prevented its unambiguous assignment. The raising of ν_{as} from its free ion value of ~1250 cm^{-1}, with ν_s remaining virtually unaltered in position and intensity at the uncoordinated value of 1326 cm^{-1}, is quite characteristic of nitrogen bonding of the nitrite group and confirms these compounds to be nitrocomplexes.

In the blue compounds $NiD_2(-ONO)_2$ [D = a-dimen, a-dieen, s-dieen and m-stien] and $NiL_4(-ONO)_2$ [L = py, 3-mepy and 4-mepy], however, ν_{as} occurs in every case below the free ion value, while there is also an increase in the frequency and intensity of ν_s. This divergence of ν_{as} and ν_s from their values in the uncoordinated ion is what is expected for oxygen bonding of the nitrite group, in agreement with the formulation of these blue compounds as nitrito-complexes. It is, however, clear that the frequencies of nitrito-groups can fall over a much wider range than had hitherto been supposed. This is illustrated in Figure 6 which compares ν_{as} and

Figure 6

A Comparison of the Nitrogen-oxygen Stretching Frequencies in some Nitritocomplexes



ν_s in these nickel compounds with the corresponding frequencies in the nitritocomplexes of Co^{III} and Pt^{IV} and a typical nickel nitrocomplex. It is apparent that although the nature of the perturbation on the nitrite ion is the same in each nitritocomplex, the degree is different, and it is the comparison of the nitrite frequencies with those of the free ion which is of value in determining the manner of coordination of the anion.

The presence of a wagging frequency ρ_w, which occurs only in nitrocomplexes and has been assigned at 462 cm^{-1} in $K_2CaNi(-NO_2)_6$[29] has been suggested as a means of distinguishing nitrogen coordination of the nitrite group. However, no band assignable to this vibration was observed above 400 cm^{-1} in any of the nickel nitrite complexes listed in Table 4. The compounds $Ni(a\text{-dieen})_2(-ONO)_2$, $Ni(en)_2(-NO_2)_2$ and $Ni(NH_3)_4(-NO_2)_2$ were also examined in the region 400 - 200 cm^{-1}, but again all the bands present in the nitrite complexes were observed in the control compounds as well. It thus appears that in these nickel amine nitrocomplexes ρ_w is either weak or consistently hidden by other bands and its absence cannot be taken as indicative of the presence of oxygen coordinated nitrite groups.

The Structure of $Ni(a\text{-dimen})_2(-ONO)_2$

In order to confirm the oxygen coordination of the anions in the blue nickel nitrite complexes and to investigate possible structural causes of this method of nitrite bonding, a three-

dimensional x-ray study of $Ni(a\text{-}dimen)_2(\text{-}ONO)_2$ was carried out. While the structural analysis has been described in detail elsewhere[55,56], it is of interest to note the main features of the molecule and these are shown in Figure 7 and Table 5.

Table 5

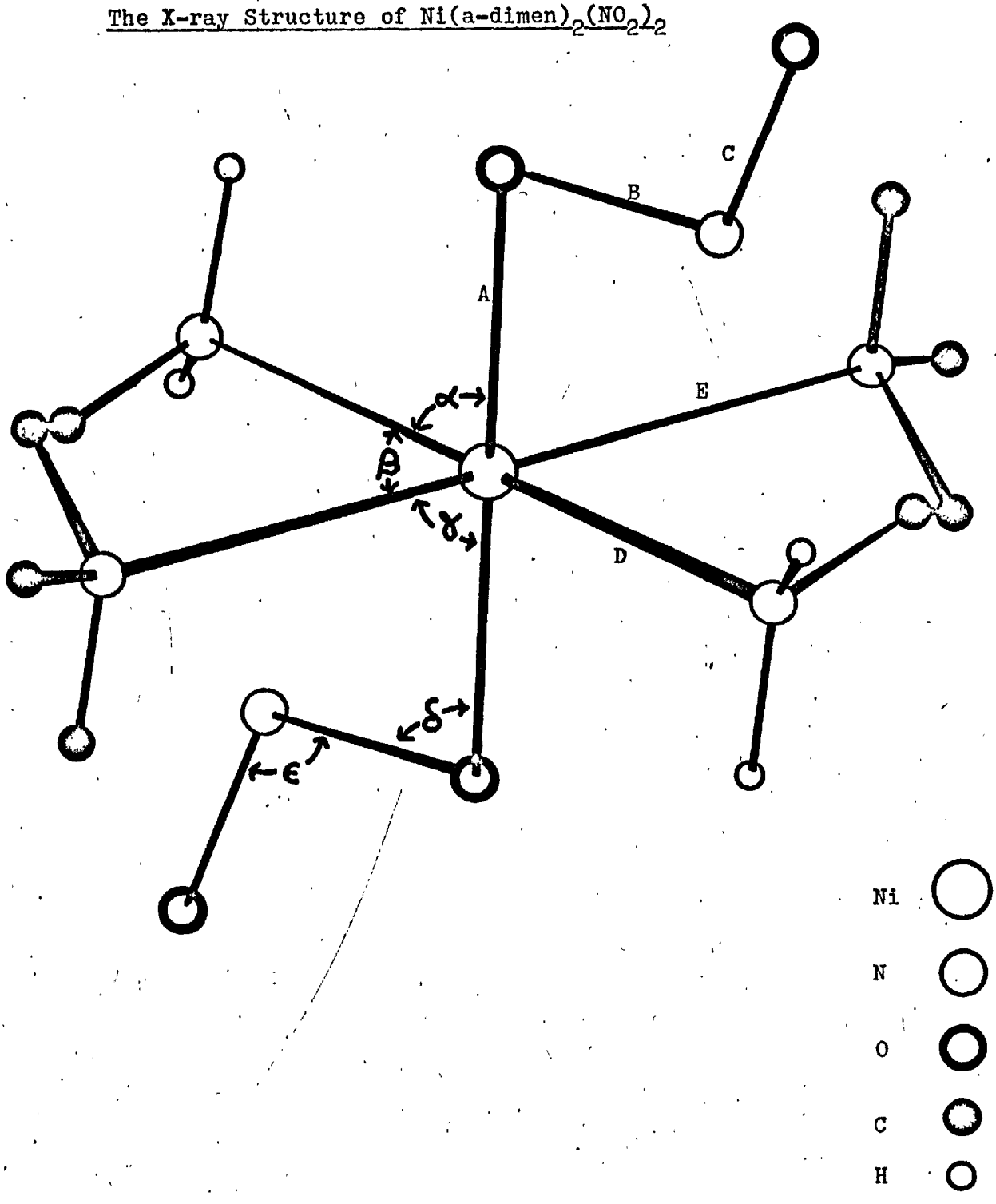
Some molecular dimensions of $Ni(a\text{-}dimen)_2(\text{-}ONO)_2$

	Bond Lengths (Å)		Bond Angles
A	2·107 ± 0·008	α	85·02 ± 0·33°
B	1·290 ± 0·014	β	84·30 ± 0·38°
C	1·207 ± 0·016	γ	92·86 ± 0·34°
D	2·089 ± 0·009	δ	119·53 ± 0·75°
E	2·219 ± 0·012	ϵ	114·97 ± 1·10°

As expected, the nitrite groups are coordinated via oxygen. The bonded oxygen to nitrogen distance (B) is significantly longer than the non-bonded oxygen to nitrogen distance (C). There is quite a large difference in the nickel to nitrogen bond lengths (Ni-N $(CH_3)_2$ = 2·219 Å, Ni-NH_2 = 2·089 Å), and the coordinated oxygen atoms are slightly displaced from axial positions, away from the two nearest methyl groups. The plane of the two O-N-O groups runs nearly through the NH_2-Ni-NH_2 axis, and the nitrite nitrogen atoms overlie the amine nitrogens with the equatorial hydrogens. There are several non-bonding close contacts (3·0 - 3·1 Å) between the

FIGURE 7

The X-ray Structure of $Ni(a\text{-dimen})_2(NO_2)_2$



nitrite groups and the rest of the molecule, and the abnormal length of the Ni-$N(CH_3)_2$ bonds and the positioning of the nitrite groups in the molecule appear to be caused primarily by these steric interactions.

Discussion of the Factors influencing the Nickel-Nitrite Bonding

Prior to the present work almost the only nitritocomplexes known were of the type $M(NH_3)_5$-ONO $^{n+}$, where M = Co^{III}, Cr^{III}, Ir^{III}, Rh^{III} and Pt^{IV}. The cause of this method of nitrite bonding in these compounds is a kinetic one involving attack by N_2O_3 and they usually rearranged fairly quickly to the corresponding nitrocomplexes[3-7]. However, the isolation of the stable nickel nitritocomplexes described here shows that the inert nature of metals with a d^3 or spin-paired d^6 electron configuration is not essential for the formation of nitrito-complexes in general.

The oxygen coordination of the nitrito-groups in these nickel compounds cannot be due to the kinetic effects envisaged for the other complexes mentioned above, since the nickel compounds are far too labile and are formed, moreover, in alkaline solution which presumably precludes the presence of N_2O_3, as this exists in weakly acidic conditions. In the series $NiD_2(NO_2)_2$ nitritocomplexes are formed when D is a di-N-substituted amine, while nitrocomplexes occur when D is a mono-N-substituted diamine or ethylenediamine itself. It thus seems likely that steric factors are important

in deciding the manner of coordination of the nitrite groups in these compcunds.

In a complex such as $Ni(en)_2(-NO_2)_2$ there can be little or no anion-diamine steric interferance. However, when bulky amine substituents are present, coordination via an oxygen atom may cause considerably less steric interaction between anion and diamine than nitrogen bonding. The fact that steric effects are indeed important in this connection is demonstrated by the complexes formed by meso- and racemic-stilbenediamine with nickel nitrite. While $Ni(m\text{-stien})_2(-ONO)_2$ contains anions bonded via oxygen, $Ni(r\text{-stien})_2(-NO_2)_2$ is a nitrocomplex. The only difference between the amines in these compounds is in the position of the benzene rings. In the r-stien complex these are in equatorial positions, while in the m-stien analogue they are axially directed and consequently offer much more steric repulsion to anions situated along the z-axis. It is probably this repulsion which causes many of the complexes of m-stien to be diamagnetic and presumably four-coordinate, while their counterparts with r-stien are paramagnetic and six-coordinate[48,57], and it appears to be this repulsion also, which causes the difference in mode of anion coordination between the two nickel nitrite complexes of stilbenediamine.

It may be noted that Basolo et al.[58] have proposed that steric effects exactly analagous to those envisaged here are important in deciding the manner of bonding of the thiocyanate ion in a number of complexes of palladium.

It is interesting that the aromatic rings in $NiL_4(-ONO)_2$ [L = py, 3-mepy and 4-mepy] apparently provide sufficient steric repulsion to cause oxygen bonding of the nitrite groups, though this is perhaps hardly surprising since the pyridine rings in $Ni(py)_4Cl_2$ are known[59] to be at an angle of ~45° to the $Ni-N_4$ plane. The compound $Ni(o\text{-phen})_2(-NO_2)_2$, in which the benzene rings should offer much less steric interaction, is, moreover, a nitrocomplex.

If the divergence of ν_{as} and ν_s from their free ion values is taken as an approximate measure of the metal-oxygen bond strength, then the bonding in these nickel compounds is weaker than that in the nitritocomplexes of Co^{III} and Pt^{IV}, as expected. Also the values of ν_{as} and ν_s appear to follow a definite sequence (Figure 6). It is possible that the steric hindrance between the anions and in-plane ligands influences not only the manner of coordination of the nitrite group, but also the strength of the metal-donor atom bond. This sequence might then be due to the changes in the Ni-O bond strength caused by the different steric requirements of the amine ligands. However, effects such as hydrogen bonding could also cause a reduction in the divergence of ν_s and ν_{as}, and this might then be responsible for the differences between the nitrogen-oxygen stretching frequencies of some of the compounds.

Preparation of compounds

The complexes $Ni(a\text{-dimen})_2(-ONO)_2$[45], $Ni(a\text{-dieen})_2(-ONO)_2$[46],

$Ni(s\text{-}dieen)_2(NCS)_2$, $Ni(s\text{-}dieen)_2(CCl_3CO_2)_2$, $Ni(een)_2(CCl_3CO_2)_2$ and $Ni(een)_2(NCS)_2$[60] had all been prepared prior to this work. The compounds with men, s-dieen, r-stien, en, o-phen, cc-dimen, 3-mepy and 4-mepy were prepared by methods very similar to that described below for $Ni(een)_2(-NO_2)_2$. Further details for individual complexes are given where appropriate, and analysis results are listed in Table 6.

$Ni(een)_2(-NO_2)_2$ A methanolic solution of nickel nitrite was prepared metathetically from $Ni(NO_3)_2 \cdot 6H_2O$ and an excess of finely powdered $NaNO_2$. The resulting mixture was cooled in CO_2/acetone and filtered. N-ethylethylene-diamine (0·02M) was added dropwise to the vigorously stirred nickel nitrite (0·01M) solution, and the mixture was taken to dryness on the vacuum line. The residue was recrystallised from nitromethane to give red crystals. yield 45%

$Ni(s\text{-}dieen)_2(-ONO)_2$ Blue-green crystals on recrystallisation from ethanol. yield 40%

$Ni(men)_2(-NO_2)_2$ A pink microcrystalline solid on recrystallisation from i-propanol. yield 40%

$Ni(en)_2(-NO_2)_2$ Large red crystals from methanol. yield 50%

$Ni(cc\text{-}dimen)_2(-NO_2)_2$ Large red crystals on recrystallising from nitromethane. yield 30%

$Ni(r\text{-}stien)_2(-NO_2)_2$ A saturated alcoholic solution of r-stien was used. Red crystals were formed and recrystallised from nitromethane. yield 30%

$Ni(o\text{-}phen)_2(\text{-}NO_2)_2$ A saturated solution of o-phenylenediamine in an equivolume mixture of acetone and methanol was used and gave a red, microcrystalline precipitate. yield 40%

$Ni(3\text{-}mepy)_4(\text{-}ONO)_2$ Excess 3-methylpyridine was used and the crude product was recrystallised from acetone containing a little 3-methylpyridine to give large blue crystals. yield 50%

$Ni(4\text{-}mepy)_4(\text{-}ONO)_2$ A method similar to that used for the above compound yielded a pale blue crystalline precipitate. yield 60%

$Ni(py)_4(\text{-}ONO)_2$ The method of Palmer was used[61] and the crude product was recrystallised from i-propanol containing a little pyridine. yield 40%

$Ni(NH_3)_4(\text{-}NO_2)_2$ Large red crystals by the method of Palmer[62]. yield 10%

$Ni(n\text{-}stien)_2(\text{-}ONO)_2$ Sodium nitrite (0·003M) and $Ni(n\text{-}stien)_2(ClO_4)_2$ (0·001M) were heated in ethanol. After a few seconds the desired product formed as a grey-blue microcrystalline precipitate. yield 80%

Table 6

Analysis details for some nitro- and nitritocomplexes of nickel

Compound	Calculated					Found				
	C	H	N	O	Ni	C	H	N	O	Ni
$Ni(een)_2(NO_2)_2$	29·39	7·40	25·71			29·54	7·10	25·99		
$Ni(nen)_2(NO_2)_2$	24·09	6·70	28·11			23·95	6·68	28·41		
$Ni(en)_2(NO_2)_2$	17·73	5·95			21·67	17·95	5·67			21·64
$Ni(NH_3)_4(NO_2)_2$		5·53			26·81		5·44			26·88
$Ni(s\text{-dieen})_2(NO_2)_2$	37·62	8·42	21·94		15·32	37·57	8·51	21·63		15·40
$Ni(n\text{-stien})_2(NO_2)_2$			14·61	11·12	10·20			14·21	11·30	10·10
$Ni(r\text{-stien})_2(NO_2)_2$			14·61	11·12	10·20			14·20	11·04	9·96
$Ni(cc\text{-dimen})_2(NO_2)_2$	29·39	7·40	25·71	19·57		29·31	7·16	25·66	19·47	
$Ni(o\text{-phen})_2(NO_2)_2$	39·26	4·39	22·91			39·00	4·38	23·20		
$Ni(py)_4(NO_2)_2$ [a]					12·57					12·80
$Ni(3\text{-mepy})_4(NO_2)_2$	55·08	5·39	16·07			55·21	5·40	16·08		
$Ni(4\text{-mepy})_4(NO_2)_2$	55·08	5·39		12·23		55·52	5·36		12·39	

a analysis for NO_2^- calc. 19·70; found 19·51

C H A P T E R 3

The Linkage Isomerism of some Nickel Nitrite Complexes

A) A Nitro-Nitrito Solution Equilibrium

In the previous Chapter it was suggested that in the solid compounds $NiD_2(NO_2)_2$ [D = a substituted ethylenediamine] the manner of bonding of the nitrite groups depends primarily on the steric nature of the amine substituents.

The compounds $Ni(a\text{-dimen})_2(NO_2)_2$ and $Ni(s\text{-dieen})_2(NO_2)_2$, which were nitritocomplexes in the solid state, were found to exist in a nitro-nitrito equilibrium in solution in various solvents, and this equilibrium has been studied over a temperature range for $Ni(s\text{-dieen})_2(NO_2)_2$ in chloroform and benzene.

Solutions of $Ni(a\text{-dimen})_2(NO_2)_2$ and $Ni(s\text{-dieen})_2(NO_2)_2$ were found to be monomeric (Table 7) and non-conducting.

Table 7

Molecular weight measurements

Compound	Solvent	conc.M	$M_{obs.}$	$M_{calc.}$
$Ni(s\text{-dieen})_2(NO_2)_2$	$CHCl_3$	0·04	435	383
$Ni(a\text{-dimen})_2(NO_2)_2$	$CHCl_3$	0·01	343	330

Electronic spectra The band maxima in the solution spectra of $Ni(een)_2(NO_2)_2$, $Ni(a\text{-dieen})_2(NO_2)_2$, $Ni(s\text{-dieen})_2(NO_2)_2$ and $Ni(a\text{-dimen})_2(NO_2)_2$ are listed in Table 8.

Table 8

Electronic spectra.

Compound	state	band max. (cm^{-1})		
$Ni(een)_2(NO_2)_2$	$CHCl_3$	a	20200(15)[b]	c
$Ni(a\text{-}dimen)_2(NO_2)_2$	$CHCl_3$	a	20300,~17,000sh	11,100
$Ni(a\text{-}dimen)_2(\text{-}ONO)_2$	solid	27,250	17300	10950,~8740sh
$Ni(s\text{-}dieen)_2(NO_2)_2$	$CHCl_3$	a	20400,~17,000sh	b
$Ni(s\text{-}dieen)_2(\text{-}ONO)_2$	solid	27,550	17,000	10360
$Ni(a\text{-}dieen)_2(NO_2)_2$	CH_2Cl_2	a	17,040(9·5)	9800(6·6)

a band obscured by electron transfer absorption

b figures in parenthesis are molar extinction coefficients

c region below 13500 cm^{-1} not studied

None of the other compounds $NiD_2(NO_2)_2$ were soluble enough in suitable solvents to enable spectra to be obtained.

The solution spectra of $Ni(een)_2(NO_2)_2$ and $Ni(a\text{-}dieen)_2(NO_2)_2$ are very similar to those of the solid complexes (Table 3). The spectra of $Ni(a\text{-}dimen)_2(NO_2)_2$ and $Ni(s\text{-}dieen)_2(NO_2)_2$, however, in chloroform and some other solvents are quite different from those of the solid compounds. In addition to the band at ~17,000 cm^{-1} found for the solid nitritocomplexes, there is in each case a strong peak at ~20,000 cm^{-1}, which is similar to those observed for the solid nitrocomplexes (Table 3). The spectrum of $Ni(s\text{-}dieen)_2(NO_2)_2$ in chloroform (Figure 8), benzene (Figure 9), chlorobenzene

FIGURE 8

(A) The Reflectance Spectrum of:-

$Ni(s\text{-dieen})_2(NO_2)_2$

(B) The Spectrum of 0·015 M

$Ni(s\text{-dieen})_2(NO_2)_2$ in

Chloroform at various

Temperatures

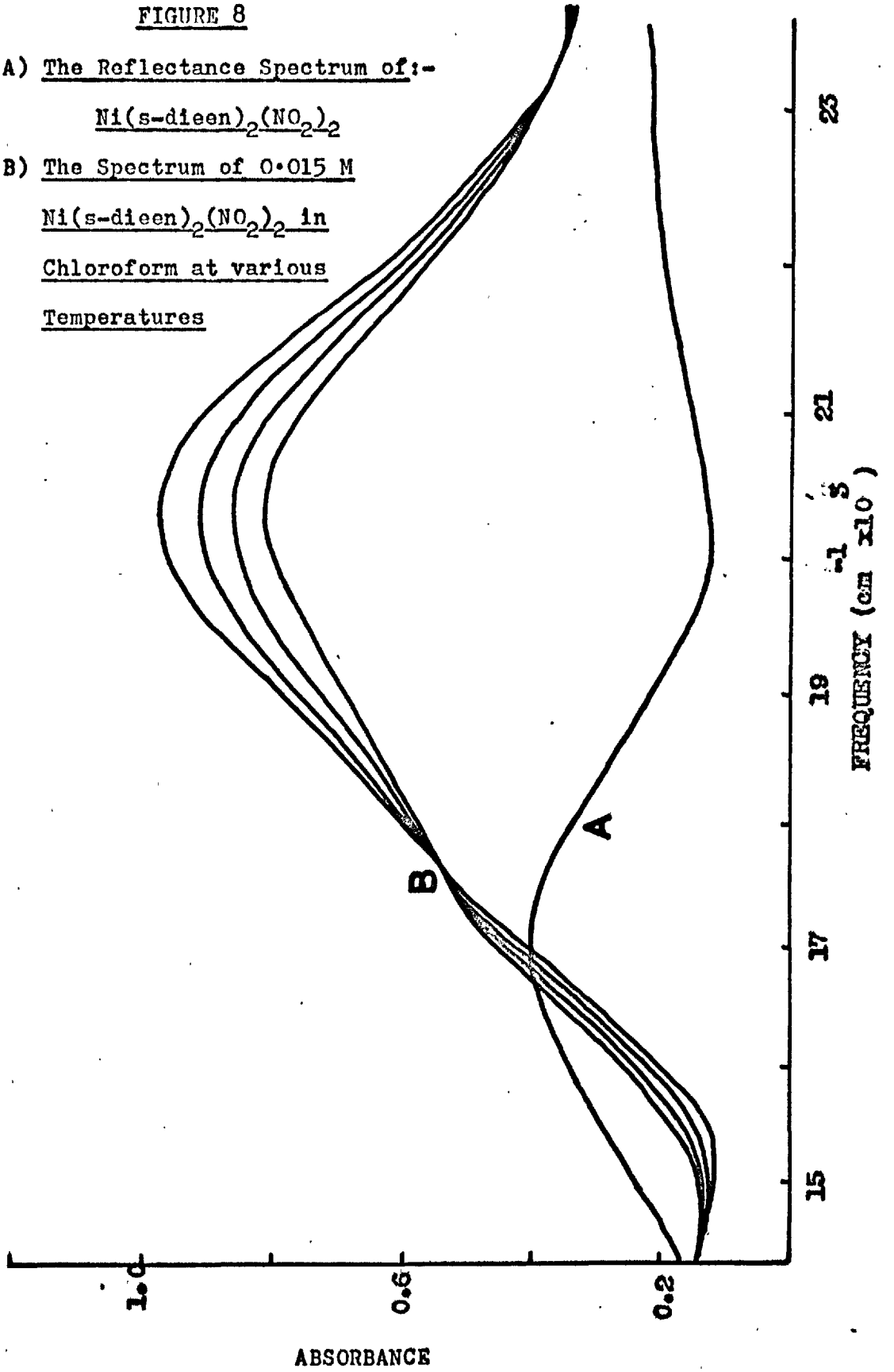
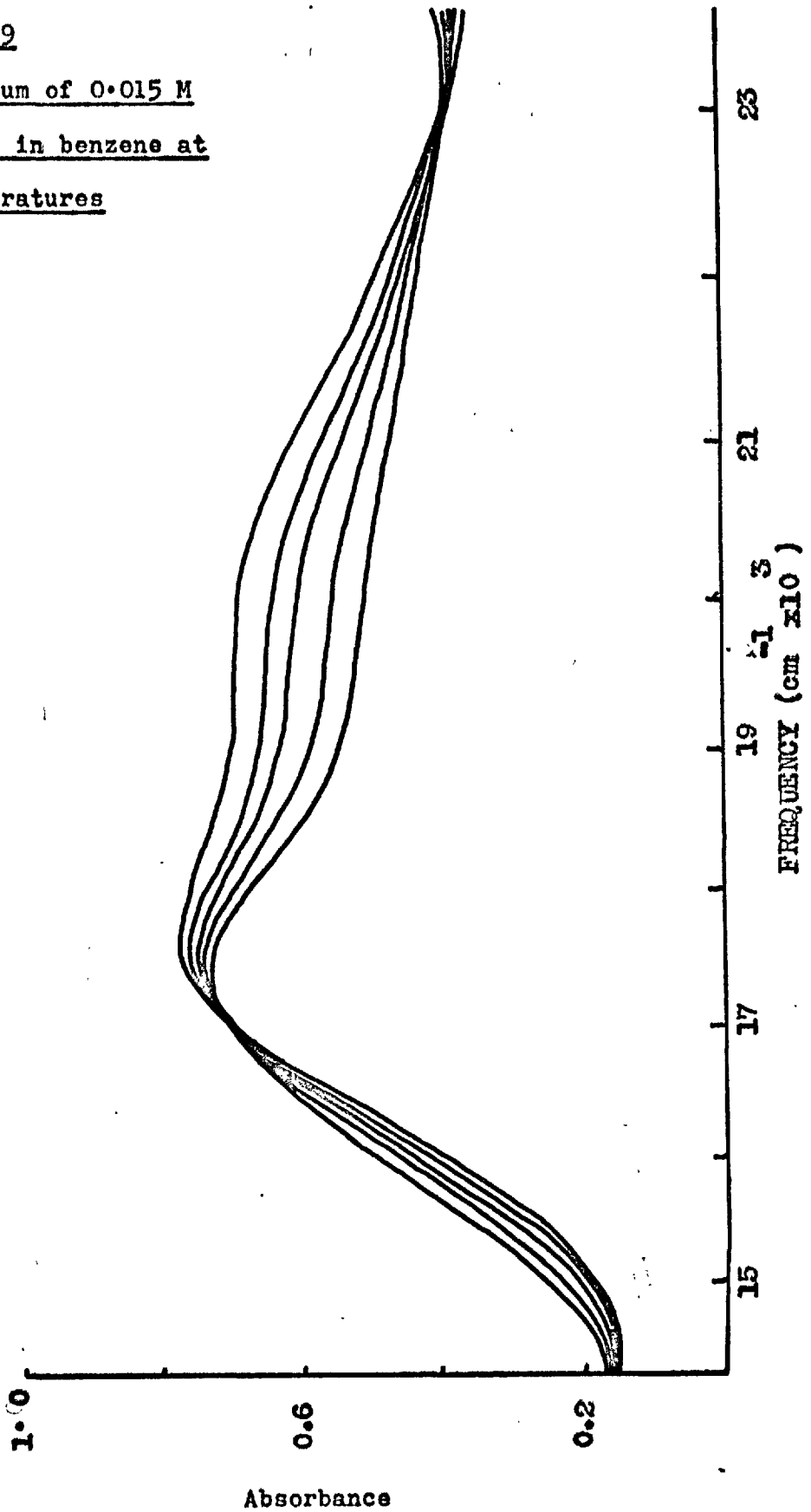


FIGURE 9

The visible spectrum of 0·015 M $Ni(s\text{-dieen})_2(NO_2)_2$ in benzene at various temperatures



and nitromethane was recorded over a temperature range in the region 30,000 - 13,500 cm^{-1} and the band at ~20,000 cm^{-1} was found to decrease with increase in temperature. In each solvent a well-defined isosbestic point occurred at ~17,500 cm^{-1}, indicating the presence of only two species. These results suggest that for $Ni(s\text{-dieen})_2(NO_2)_2$ and $Ni(a\text{-dimen})_2(NO_2)_2$ there is set up in solution an equilibrium of the type: -

$$Ni(diamine)_2(-ONO)_2 \rightleftharpoons Ni(diamine)_2(-NO_2)_2$$

Although other equilibria are perhaps theoretically possible, the one above, which involves species of a known type, fits the experimental observations well, and there is no evidence from the electronic or infrared spectra, or molecular weight and conductivity measurements, for any alternative species.

Infrared spectra

The infrared bands due to the nitrite groups in the complexes are listed in Table 9.

The solution spectra of $Ni(een)_2(NO_2)_2$ and $Ni(a\text{-dieen})_2(NO_2)_2$ are again very similar to those of the solid compounds. The chloroform solution of $Ni(a\text{-dimen})_2(NO_2)_2$, however, showed, in addition to the bands at 1130 and 1389 cm^{-1} also present in the solid nitritocomplex, a strong peak at 1314 cm^{-1} assignable as ν_{as} of nitrite groups coordinated to Ni^{II} via nitrogen. The solution of $Ni(s\text{-dieen})_2(NO_2)_2$ in chloroform also showed a strong band at 1316 cm^{-1} indicative of a nitro-form, but in this case

Table 9

Nitrite infrared bands (cm^{-1})

Compound	state	ν_s	ν_{as}	δ
$Ni(een)_2(NO_2)_2$	$CHCl_3$	a	1320vs	b
$Ni(a\text{-}dimen)_2(NO_2)_2$	$CHCl_3$	1389w	1314s, 1130m	b
$Ni(a\text{-}dimen)_2(\text{-}ONO)_2$	mull	1387s	1130s	817m
$Ni(s\text{-}dieen)_2(NO_2)_2$	$CHCl_3$	a	1316s, b	b
$Ni(s\text{-}dieen)_2(\text{-}ONO)_2$	mull	1337s	1206vs	821w
$Ni(a\text{-}dieen)_2(NO_2)_2$	CH_2Cl_2	a	1130s	b

a band due to nitrite group could not be identified because of other absorption

b band obscured by solvent absorption

the regions where ν_{as} and ν_s would be expected for the nitrito-isomer were obscured by solvent absorption and the strong band due to the nitro-groups.

Thus the solution infrared spectra are quite in accordance with the presence of nitro-nitrito equilibria for $Ni(a\text{-}dimen)_2(NO_2)_2$ and $Ni(s\text{-}dieen)_2(NO_2)_2$.

Temperature dependence of the equilibrium

The equilibrium was studied by measuring the variation with temperature of the visible spectrum of $Ni(s\text{-}dieen)_2(NO_2)_2$ in chloroform (Figure 8) and benzene (Figure 9). The visible spectrum

of $Ni(een)_2(NO_2)_2$ in chloroform was also measured at 293° and 323°K and showed no evidence for any equilibrium. Moreover, the extinction coefficient of the band at 20,000 cm^{-1} did not vary significantly with temperature.

In these studies the temperature was varied by passing water from a thermostatically controlled bath through the cell-holder and measured with a copper/constantan thermocouple encased in a glass tube and placed in the solution under observation. All values of the optical density refer to 0·015M solutions and cells of path length 5 cm were used throughout.

Chloroform solution The constant K for the equilibrium(I)

$$Ni(s\text{-}dieen)_2(\text{-}ONO)_2 \rightleftharpoons Ni(s\text{-}dieen)_2(\text{-}NO_2)_2 \quad \ldots\ldots\ldots (I)$$

is given at any concentration C by the expression $K = \frac{D-D_{ONO}}{D_{NO_2}-D}$ where D is the optical density at any suitable wavelength, and D_{ONO} and D_{NO_2} are the optical densities at this wavelength which would be found for solutions, each of concentration C, of the pure nitrito- and nitro-isomers respectively. Usually the extinction coefficients of the participants in an equilibrium (in this case D_{NO_2} and D_{ONO}) may be found accurately, either by isolation of the two species or by displacement of the equilibrium until one componant is at virtually zero concentration. However, neither of these approaches is possible here; also, in this case there is no other property such as a change in spin

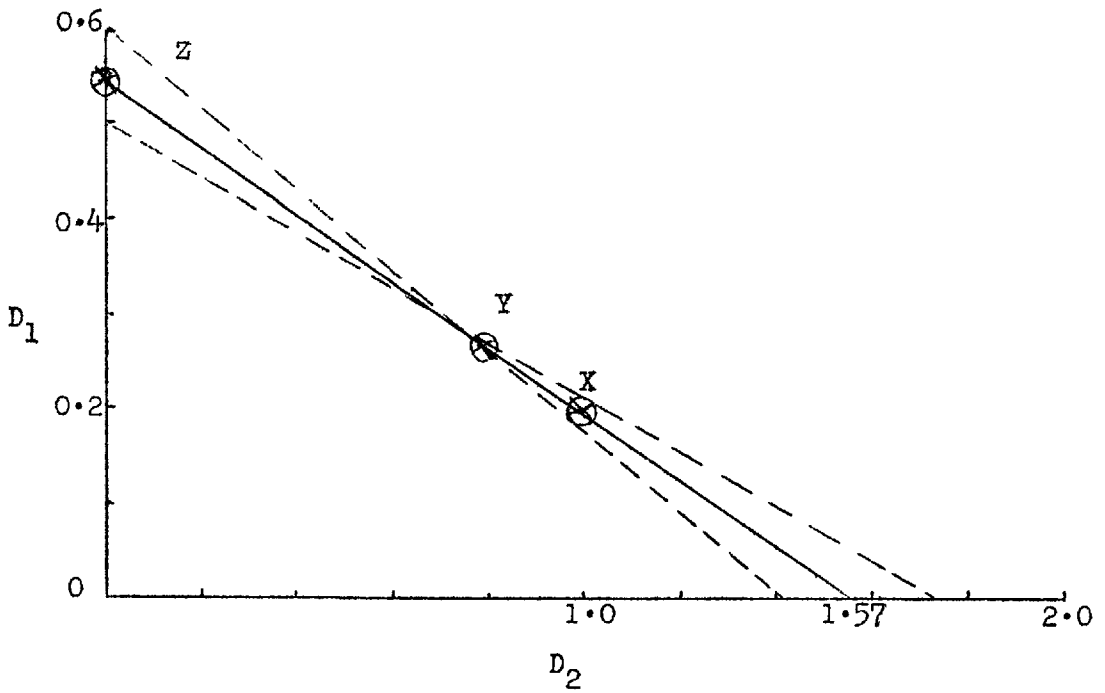
multiplicity to indicate the proportion of the isomers present. The following method of estimating D_{NO_2} and D_{ONO} was thus adopted.

It is apparent (Figure 8) that the band maximum of the nitrito-form of $Ni(s\text{-}dieen)_2(NO_2)_2$ in chloroform is close to that (17,000 cm^{-1}) of solid $Ni(s\text{-}dieen)_2(\text{-}ONO)_2$, though the latter is broader as is usually the case with reflectance spectra. The isosbestic point at 17,650 cm^{-1} must lie on the limiting nitrito-curve as the concentration of the nitro-form vanishes to zero. The proximity of this isosbestic point to the nitrito-band maximum allows the molar extinction coefficient of nitrito-$Ni(s\text{-}dieen)_2(NO_2)_2$ to be estimated fairly accurately as $7{\cdot}5 \pm 0{\cdot}5$ at 17,000 cm^{-1} in chloroform.

Gaussian analysis was carried out on the spectra obtained at 280° and 324°K. The band contours found agreed well with those of related compounds ($Ni(een)_2(NO_2)_2$ in chloroform for the nitro-isomer, and $Ni(a\text{-}dieen)_2(\text{-}ONO)_2$ in CH_2Cl_2 for the nitrito-form). From these analyses the optical density D_1 of the nitrito-isomer at 17,000 cm^{-1} and that of the nitro-form D_2 at 20,400 cm^{-1} were estimated at each temperature. These are points X and Y in Figure 10, a plot of D_1 against D_2. Point Z on this graph was obtained from the molar extinction coefficient of the nitrito-isomer at 17,000 cm^{-1} ($D_1 = 0{\cdot}56$, $D_2 = 0$). The points X, Y and Z should lie on a straight line which, within experimental error,

Figure 10

A graph of D_1 against D_2 (see text for the definition of these parameters). The broken lines indicate the maximum possible error assumed from the experimental results.



is indeed the case. Extrapolation of this line to $D_1 = 0$ then allowed the optical density of the pure nitro-form to be estimated as $D_2 = 1{\cdot}57 \pm 0{\cdot}15$ (corresponding to a molar extinction coefficient of $\epsilon_{NO_2} = 21 \pm 2$) at 20,400 cm^{-1}.

The equilibrium constant K was calculated from $K = (D-D_{ONO})/(D_{NO_2}-D)$ where the values of D, D_{ONO} and D_{NO_2} all here refer to data at 20,400 cm^{-1} (the wavelength where the greatest change in

D with temperature occurred). The value of D_{NO_2} was taken as $1{\cdot}57 \pm 0{\cdot}15$ (see above), while that of D_{ONO}, which is small at 20,400 cm^{-1}, was estimated as $0{\cdot}07 \pm 0{\cdot}05$ (values in the range $0{\cdot}05 - 0{\cdot}09$ were obtained by assuming curve shapes similar to those of related compounds $Ni(diamine)_2X_2$ where X = an oxy-anion). Three separate solutions were studied, and the values of D observed are listed in Table 10. These values were plotted against

Table 10

Experimental optical density values at 20,400 cm^{-1} for 0·015M solutions of $Ni(s\text{-dieen})_2(NO_2)_2$ in chloroform at various temperatures.

Temp. °K	Solution No.	Optical Density D
278	1	1·005
278	2	1·000
280	2	0·975
281	1	0·975
289	2	0·955
292	2	0·915
305	2	0·860
307	3	0·855
311	3	0·835
312	2	0·835
317	2	0·805
322	3	0·785
324	2	0·780

temperature to minimize experimental error, and D-values at seven temperatures (Table 11) were read off from this graph.

Table 11

Values $\log_{10}K$ for the nitro-nitrito equilibrium of 0·015M Ni(s-dieen)$_2$(NO$_2$)$_2$ in chloroform.

D	T°K	$\log_{10}$ K [a]		
		I[b]	II[b]	III[b]
1·005	276	0·219	0·139	0·329
0·985	280	0·194	0·118	0·2985
0·935	290	0·134	0·0665	0·2255
0·890	300	0·081	0·020	0·162
0·840	310	0·023	-0·031	0·094
0·795	320	-0·029	-0·077	0·033
0·775	324	-0·052	-0·0975	0·007

a calc. from $K = (D-D_{ONO})/(D_{NO_2}-D)$

b for I, $D_{ONO} = 0·07$, $D_{NO_2} = 1·57$; II, $D_{ONO} = 0·02$, $D_{NO_2} = 1·72$; III, $D_{ONO} = 0·12$, $D_{NO_2} = 1·42$.

Three sets of $\log_{10}K$ were calculated, one using the mean values of D_{NO_2} and D_{ONO} quoted above, and the others using $D_{ONO} = 0·12$, $D_{NO_2} = 1·42$, and $D_{ONO} = 0·02$, $D_{NO_2} = 1·7$ (the last two sets were the most extreme values of $\log_{10}K$ considered commensurate with the experimental results). These sets were plotted as $\log_{10}K$

against $\frac{1}{T}$, and ΔH and ΔS were calculated from the three graphs using the expression $\log_{10}K = \frac{\Delta S}{2{\cdot}303R} - \frac{\Delta H}{2{\cdot}303RT}$. When the relatively small errors in measuring D were also taken into account, the final values $\Delta H = -2{\cdot}3 \pm 0{\cdot}6$ kcals/mole and $\Delta S = -7{\cdot}3 \pm 1{\cdot}3$ e.u. were obtained for the change $Ni(s\text{-dieen})_2(-ONO)_2 \longrightarrow Ni(s\text{-dieen})_2(-NO_2)_2$.

Equilibrium in benzene It is apparent that the electronic spectrum of 0·015M $Ni(s\text{-dieen})_2(NO_2)_2$ in benzene (Figure 9) at any temperature is rather different from that in chloroform (Figure 8). This could be due to a change either in the proportion of the isomers present, or in the intensity or shape of one or more of the electronic bands, or to a combination of these effects.

The isosbestic point at 17,150 cm^{-1} in the benzene solution of $Ni(s\text{-dieen})_2(NO_2)_2$ allowed the molar extinction coefficient of the pure nitrito-isomer to be estimated as $\epsilon_{ONO} = 10 \pm 0{\cdot}5$ at 16,850 cm^{-1} in this solvent.

Gaussian analysis was carried out on the curves at 283° and 331°K in benzene, and the same procedure described for the chloroform solution was used to estimate the value $\epsilon_{NO_2} = 16 \pm 4$ for the pure nitro-isomer in benzene at 20,200 cm^{-1}. These analyses also showed that the band due to the nitro-isomer in benzene was much broader than that in chloroform, and in agreement with this the isosbestic point was 500 cm^{-1} lower in benzene and at a higher optical density.

Values of D (Table 12) were measured at 20,200 cm^{-1} for two

Table 12

Experimental optical density values at 20,200 cm^{-1} for 0·015M solutions of $Ni(s\text{-dieen})_2(NO_2)_2$ in benzene at various temperatures.

Temp. °K	Solution No.	Optical Density D
283	1	0·676
285·5	2	0·666
286	2	0·674
290	1	0·663
294·5	2	0·648
300	1	0·627
306	2	0·620
309	1	0·596
317	1	0·574
317·5	2	0·583
320·5	1	0·550
327	2	0·550
331	1	0·502
334·5	2	0·509
338·5	1	0·483

solutions of 0·015M $Ni(s\text{-dieen})_2(NO_2)_2$ in benzene, and these were plotted against temperature. D-values were estimated from this graph at seven temperatures (Table 13) and values of $\log_{10}K$ were calculated at each of these from the expression $K = (D-D_{ONO})/(D_{NO_2}-D)$.

Table 13

Values of $\log_{10}K$ for the nitro-nitrito equilibrium of 0·015M $Ni(s\text{-}dieen)_2(NO_2)_2$ in benzene.

D	T°K	$\log_{10} K$ [a]	
		I[b]	II[b]
0·69	280	-0·089	0·423
0·662	290	-0·1225	0·349
0·63	300	-0·161	0·268
0·597	310	-0·222	0·188
0·562	320	-0·246	0·107
0·5225	330	-0·298	0·017
0·486	340	-0·347	-0·066

a calc. from $K = (D-D_{ONO})/(D_{NO_2}-D)$

b for I, $D_{ONO} = 0·03$, $D_{NO_2} = 1·5$ and for II, $D_{ONO} = 0·13$, $D_{NO_2} = 0·9$

In this case D_{NO_2} was taken as $1·2 \pm 0·3$ (from the above value of $\epsilon_{NO_2} = 16 \pm 4$) and D_{ONO} was estimated as $0·08 \pm 0·05$, both at 20,200 cm^{-1}. Two values of $\log_{10}K$ were calculated at each temperature (Table 13), using the most extreme values of D_{ONO} and D_{NO_2} possible. These two sets of $\log_{10}K$ were plotted against $\frac{1}{T}$ to obtain the values $\Delta H = -3 \pm 1·2$ kcals/mole and $\Delta S = -9·5 \pm 3$ e.u. for the equilibrium of $Ni(s\text{-}dieen)_2(NO_2)_2$ in benzene.

Because of the shape of the spectra, the Gaussian analyses

on the curves in benzene were considerably less accurate than those on the chloroform-spectra. This meant that ϵ_{NO_2} and D_{NO_2}, and consequently ΔH and ΔS, could be estimated less accurately in benzene than in chloroform. However, it does seem that, within experimental error, the thermodynamic parameters for the equilibria in the two solvents are rather similar. The difference in the spectra between the two solutions is apparently due to the changes in shape and extinction coefficients of the electronic bands which occur on going from one solvent to the other. In particular, the molar-extinction coefficients of the visible bands of the two isomers are much more similar in benzene than in chloroform.

Equilibria were also observed in solutions of $Ni(s\text{-dieen})_2(NO_2)_2$ in chlorobenzene and nitromethane, but thermodynamic parameters were not calculated for these solvents.

Discussion

The solution nitro-nitrito equilibria described here are particularly interesting in view of the many studies which have been made on the kinetics of formation of nitritocomplexes of Co^{III} and their subsequent rearrangement to the more stable nitro-analogues[3-7]. In the cobalt (III) compounds the nitro-nitrito equilibria lie well to the side of the nitro-isomers, and the nitritocomplexes are only isolated because of the relative

inertness of the Co-O bond. The nickel complexes studied here, however, are labile, and the establishment of the equilibria in solution, where lattice forces are absent, shows that in certain cases the factors deciding the manner of bonding of the nitrite groups must be finely balanced.

In Chapter 2 it was suggested that the main reason for the adoption of oxygen coordination of the nitrite groups in the solid nitritocomplexes $NiD_2(-ONO)_2$ is steric in origin. In the solution equilibrium of $Ni(s\text{-dieen})_2(NO_2)_2$ the enthalpy term favours the nitro-isomer, as expected. However, the entropy term favours the nitrito-form, in agreement with a reduction of the steric interaction and consequent greater freedom of movement, envisaged when the anions bond via oxygen rather than nitrogen. This interpretation of Δ H and Δ S ignores solvent effects, though the variation in ϵ_{NO_2} and ϵ_{ONO} on going from chloroform to benzene indicates that some solvent-solute interaction in fact does occur. However, these effects are likely to be small in the solvents used here, and this is confirmed by the fact that the thermodynamic parameters appear, within experimental error, to be the same in chloroform and benzene. The complexes $Ni(een)_2(-NO_2)_2$ and $Ni(a\text{-dieen})_2(-ONO)_2$ do not exhibit equilibria, and it seems that in the case of solutions of the s-dieen and a-dimen complexes the increase in bond energy on going from the nitrito- to the nitro-isomer is approximately equal to the energy lost through the

increased steric interaction expected when a nitrogen-bonded nitrite group is present compared with one coordinated via oxygen.

The fine balance of the factors deciding the anion coordination in solutions of some of the nickel nitrite complexes raises the question of the possible existence of solid nitro- and nitrito-isomers of stoichiometry Ni(diamine)$_2$(NO$_2$)$_2$ somewhat analogous to the paramagnetic and diamagnetic forms of Ni(m-stien)$_2$(CCl$_3$CO$_2$)$_2$[57]. However, with each of the diamines studied here only one of the potential isomers was stable in the solid state. Recovery of the complexes Ni(s-dieen)$_2$(NO$_2$)$_2$ and Ni(a-dimen)$_2$(NO$_2$)$_2$ from solution, either by addition of ether, or evaporation of the solvent, produced only the solid nitritocomplexes. A pink solid, presumably mainly Ni(s-dieen)$_2$(-NO$_2$)$_2$, was isolated by tipping a frozen chloroform solution of Ni(s-dieen)$_2$(NO$_2$)$_2$ into cold petroleum ether and filtering rapidly, but this reverted to the blue nitritocomplex within a few seconds. Also, although the reaction 1,6-$\left[Co(NH_3)_2(py)_2(-ONO)_2\right]^+ \longrightarrow$ 1,6-$\left[Co(NH_3)_2(py)_2(-NO_2)_2\right]^+$ is thought[63] to involve a mixed nitro-nitrito intermediate, species of the type Ni(diamine)$_2$(-ONO)(-NO$_2$) were not detected in the equilibria studied here.

B) A Mixed Nitro-Nitritocomplex of Nickel(II)

The nature of the metal-anion bonding in compounds of the type $NiL_4(NO_2)_2$ formed with different heterocyclic amines is of particular interest as it is apparently steric interference with the bulky heterocyclic ligands which causes the unusual manner of coordination of the nitrite groups in the blue nitritocomplexes $Ni(py)_4(-ONO)_2$, $Ni(3\text{-mepy})_4(-ONO)_2$ and $Ni(4\text{-mepy})_4(-ONO)_2$.

The complex $Ni(i\text{-quin})_4(NO_2)_2$

The compound $Ni(i\text{-quin})_4(NO_2)_2$ was prepared as a brown microcrystalline precipitate by the slow addition of a methanolic solution of nickel nitrite[64] to a large excess of isoquinoline dissolved in a little methanol. The complex could be recrystallized from acetone and nitromethane to give fairly large purple crystals with infrared and electronic spectra identical to that of the original substance. yield 70%

Analysis details

Calculated:- C, 64·79; H, 4·23; N, 12·60; O, 9·59; NO_2^-, 13·79.

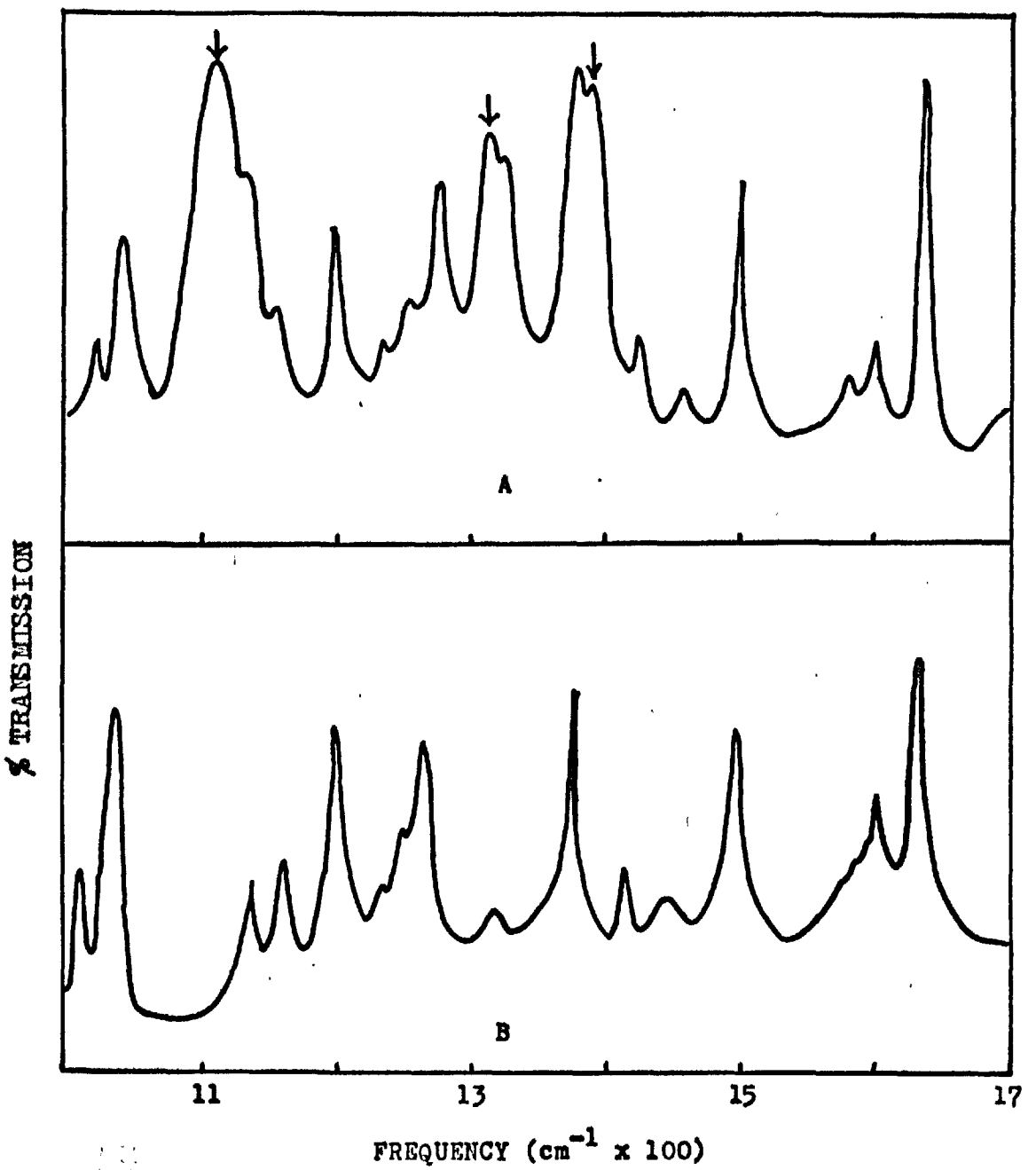
Found:- C, 64·18; H, 4·21; N, 12·70; O, 9·54; NO_2^-, 13·60.

Infrared spectrum The infrared spectrum of solid $Ni(i\text{-quin})_4(NO_2)_2$ (Figure 11) was recorded in the range 2000 - 400 cm^{-1}, and

FIGURE 11

The Infrared Spectra of:-

(A) $Ni(i\text{-}quin)_4(NO_2)_2$ (B) $Ni(i\text{-}quin)_4Br_2$



The nitrite bands are indicated by arrows.

the nitrite bands (at 1124, 1314 and 1397 cm^{-1}) were identified by comparison with the spectra of $Ni(i\text{-quin})_4X_2$ [X = Cl, Br and I]. The bands due to the nitrite groups at 1124 and 1397 cm^{-1} in $Ni(i\text{-quin})_4(NO_2)_2$ are very similar, both in relative intensity and position, to those assigned as ν_{as} and ν_s in the nitritocomplexes $NiL_4(-ONO)_2$ [L = py, 3-mepy and 4-mepy], and suggest that the isoquinoline complex also contains anions coordinated via oxygen. The band at 1314 cm^{-1} in $Ni(i\text{-quin})_4(NO_2)_2$, however, is at considerably lower frequency than ν_s in any of the nitritocomplexes described in Chapter 2, and is very similar to that assigned as ν_{as} for the nitro-groups in the nitrocomplexes $Ni(diamine)_2(-NO_2)_2$. Moreover, this band remained unchanged on mulling in a little isoquinoline, showing that it was not due to any dissociation of the type:- $Ni(i\text{-quin})_4(NO_2)_2 \longrightarrow Ni(i\text{-quin})_2(NO_2)_2 + 2(i\text{-quin})$.

The infrared spectrum thus suggests that $Ni(i\text{-quin})_4(NO_2)_2$ contains both nitro- and nitrito-groups.

Electronic spectrum The electronic reflectance spectrum of $Ni(i\text{-quin})_4(NO_2)_2$ (Figure 4 Page 23) consists of bands at 11,000, 17,400 and 21,280 cm^{-1}. These peaks do not correspond to the three spin-allowed electronic transitions of nickel(II) in near O_h ligand field symmetry[65]. While the bands at 11,000 and 17,400 cm^{-1} may be assigned as the first two spin-allowed transitions ($^3A_{2g} \longrightarrow {}^3T_{2g}$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ in O_h symmetry) of octahedrally coordinated

Ni^{II}, the band due to the third transition ($^3A_{2g} \longrightarrow {}^3T_{1g}(P)$) is then expected at about 28,000 cm^{-1}, which is considerably higher than the observed value of 21,280 cm^{-1}. It is unlikely that the bands at 17,400 and 21,280 cm^{-1} are due to transitions to the A and E components of the level $^3T_{1g}(F)$ split under a ligand field symmetry lower than O_h, since the peak at 11,000 cm^{-1} is not split. Moreover, the separation of the A and E components of the $^3T_{1g}(F)$ level in the tetragonal complex $Ni(i\text{-quin})_4Br_2$ is only 2200 cm^{-1} [66]. The magnetic moment of $Ni(i\text{-quin})_4(NO_2)_2$ is 3·14 B.M. (measured at room temperature and corrected for diamagnetism) and this indicates that no significant concentration of diamagnetic species is present in this compound. It may also be noted that the complexes $Ni(i\text{-quin})_4X_2$ [X = Cl, Br and I] are all paramagnetic[66], which makes it unlikely that any form of $Ni(i\text{-quin})_4(NO_2)_2$ would be diamagnetic.

In fact the electronic and infrared spectra of $Ni(i\text{-quin})_4(NO_2)_2$ somewhat resemble those of the mixtures of nitro- and nitrito-isomers occurring in solutions of $Ni(a\text{-dimen})_2(NO_2)_2$ and $Ni(s\text{-dieen})_2(NO_2)_2$. The reflectance spectrum of $Ni(i\text{-quin})_4(NO_2)_2$ thus appears to be a superimposition of the spectra of two isomeric forms of this compound, one a nitritocomplex and the other a nitrocomplex. The broad band at 11,000 cm^{-1} is a superimposition of the first spin-allowed transitions which occur at ~10,000 cm^{-1} and ~12,000 cm^{-1} in similar nitrito- and nitrocomplexes respectively,

while the greater separation of the second spin-allowed transitions of the two isomers allows these to be resolved as the peaks at 17,400 and 21,280 cm^{-1}. The band at 21,280 cm^{-1} is at rather higher energy than the corresponding bands of similar nitro-complexes (Table 3). However, under the D_{4h} symmetry expected for a species of the type trans-Ni(i-quin)$_4$(-NO_2)$_2$ it is probable that the $^3T_{1g}(F)$ level will split into A and E components[67]. It is possible that the peak at 21,280 cm^{-1} is due to a transition to only one of these components, the transition to the other component being masked by the absorption between the peaks at 17,400 and 21,280 cm^{-1}. The weighted mean of the components of the $^3T_{1g}(F)$ level in nitro-Ni(i-quin)$_4$(-NO_2)$_2$ might then lie somewhat lower than 21,280 cm^{-1}.

The electronic spectrum thus suggests that the formula of Ni(i-quin)$_4$(NO_2)$_2$ is better written as Ni(i-quin)$_4$(-NO_2)$_2$·xNi (i-quin)$_4$(-ONO)$_2$, and this is quite in accordance with the infrared spectrum. It is unlikely that the species Ni(i-quin)$_4$ (-ONO)(-NO_2) is present in any quantity, as this would presumably have an electronic spectrum intermediate between those of a nitro- and nitritocomplex, and not the superimposition of spectra actually observed.

Discussion

The fact that the single crystals of Ni(i-quin)$_4$(-NO_2)$_2$·xNi

$(i\text{-quin})_4(\text{-ONO})_2$ all look rather similar under the polarising microscope suggests that the two linkage isomers are present in the same crystal lattice, rather than as a physical mixture. This compound thus bears a structural resemblance to $Ni\left[(C_6H_{11})(C_6H_5)_2P\right]_2Br_2$ in which both planar and tetrahedral isomers occur in the same crystal lattice[68].

In the previous Chapter it was suggested that nitrocomplexes generally form only when relatively little anion-amine steric interaction is expected (eg. $Ni(NH_3)_4(\text{-}NO_2)_2$), and the compounds $NiL_4(\text{-ONO})_2$ [L = py, 3-mepy and 4-mepy] are all nitritocomplexes. It is consequently rather surprising that $Ni(i\text{-quin})_4(\text{-}NO_2)_2 \cdot xNi(i\text{-quin})_4(\text{-ONO})_2$ should exist in a nitro-form, even as a component in a mixed nitro-nitritocomplex, since isoquinoline might be expected to produce similar or even greater anion-amine steric interference than pyridine. A tentative explanation lies in the relatively large size of the isoquinoline rings, which means that intermolecular packing must be rather important in the lattice energy of any isoquinoline complex. With flat heterocyclic ligands such as these, anion-amine steric interaction must be very sensitive to the positions adopted by the amines in each $Ni(i\text{-quin})_4(NO_2)_2$ molecule. It seems reasonable that in the minimisation of the intermolecular packing energy a certain proportion of the molecules composing the unit cell might adopt amine configurations producing small enough steric interference to

allow coordination of the nitrite groups via nitrogen, while in the remainder of the molecules the anion-amine repulsion is sufficient to stabilise oxygen bonding of the nitrite groups. It may be noted that ν_{as} in the infrared spectrum of $Ni(4\text{-}mepy)_4(\text{-}ONO)_2$ is split by 25 cm^{-1} suggesting that the metal-nitrite bonding also varies among the molecules composing the unit cell of this rather similar compound.

CHAPTER 4

Some Compounds Containing Chelating Nitrite Groups

Prior to the present investigations chelation was virtually unknown as a method of nitrite coordination, being recognised solely from the chelation of the nitrite groups in the compound $K_3[Hg(NO_2)_4]NO_3$[44].

However, several lines of evidence suggest that in the new compounds $CoL_2(NO_2)_2$ [L = Ph_3PO and Ph_3AsO], $NiL_2(NO_2)_2$ [L = py, 2-mepy and quin], $Ni(tetmen)(NO_2)_2$ and $Ni(teteen)(NO_2)_2$ the anions are present as bidentate, chelating ligands. Also, on solution in benzene the solid blue nitritocomplexes $NiL_4(-ONO)_2$ [L = py, 4-mepy and 3-mepy] were found to disproportionate to give the green species $NiL_2(NO_2)_2$ containing chelating nitrite groups.

The compounds $Co(Ph_3PO)_2(NO_2)_2$, $Co(Ph_3AsO)_2(NO_2)_2$ and Ni (tetmen)$(NO_2)_2$ were all found to be monomeric in solution (Table 13).

Table 13

Molecular weight data on some complexes containing chelating nitrite groups.

Compound	Solvent	conc^n	$M_{obs.}$	$M_{calc.}$
$Co(Ph_3PO)_2(NO_2)_2$	acetone	~0·01M	725	708
$Co(Ph_3AsO)_2(NO_2)_2$	acetone	~0·01M	793	795
$Ni(tetmen)(NO_2)_2$	chloroform	~0·05M	270	267

Cobalt Complexes

Electronic spectra The electronic spectra of the purple compounds $Co(Ph_3PO)_2(NO_2)_2$ and $Co(Ph_3AsO)_2(NO_2)_2$, (Table 14) are very similar both in band position and intensity to those of the analogous nitrate complexes (Figure 12)[69]. X-ray studies have shown[70] that the nitrate groups in $Co\left[(CH_3)_3PO\right]_2(NO_3)_2$ are chelating, and similar structures have been proposed for the corresponding complexes with triphenylarsine oxide and triphenylphosphine oxide. The band intensities in these cobalt nitrate compounds are quite distinctive, being midway between those usually observed for Co^{II} in octahedral and in tetrahedral complexes. This unusual feature has been ascribed to the irregularity of the ligand field produced by the assymmetric array of six oxygen atoms around each cobalt ion, and the close similarity of the nitrite to the nitrate electronic spectra suggests similar ligand environments in $Co(Ph_3PO)_2(NO_2)_2$ and $Co(Ph_3AsO)_2(NO_2)_2$ also. Since the two cobalt nitrite complexes are monomeric in acetone with solution spectra very similar to the solid compounds, they are unlikely to contain bridging anions and each nitrite group is probably chelated via two oxygen atoms.

Infrared spectra The nitrite infrared frequencies (Table 15) in solid $Co(Ph_3PO)_2(NO_2)_2$ and $Co(Ph_3AsO)_2(NO_2)_2$ were identified by comparison with the analogous halide complexes. Both the nitrite

FIGURE 12

The Electronic Reflectance Spectra of:-

(A) $Co(Ph_3AsO)_2(NO_2)_2$ (B) $Co(Ph_3AsO)_2(NO_3)_2$

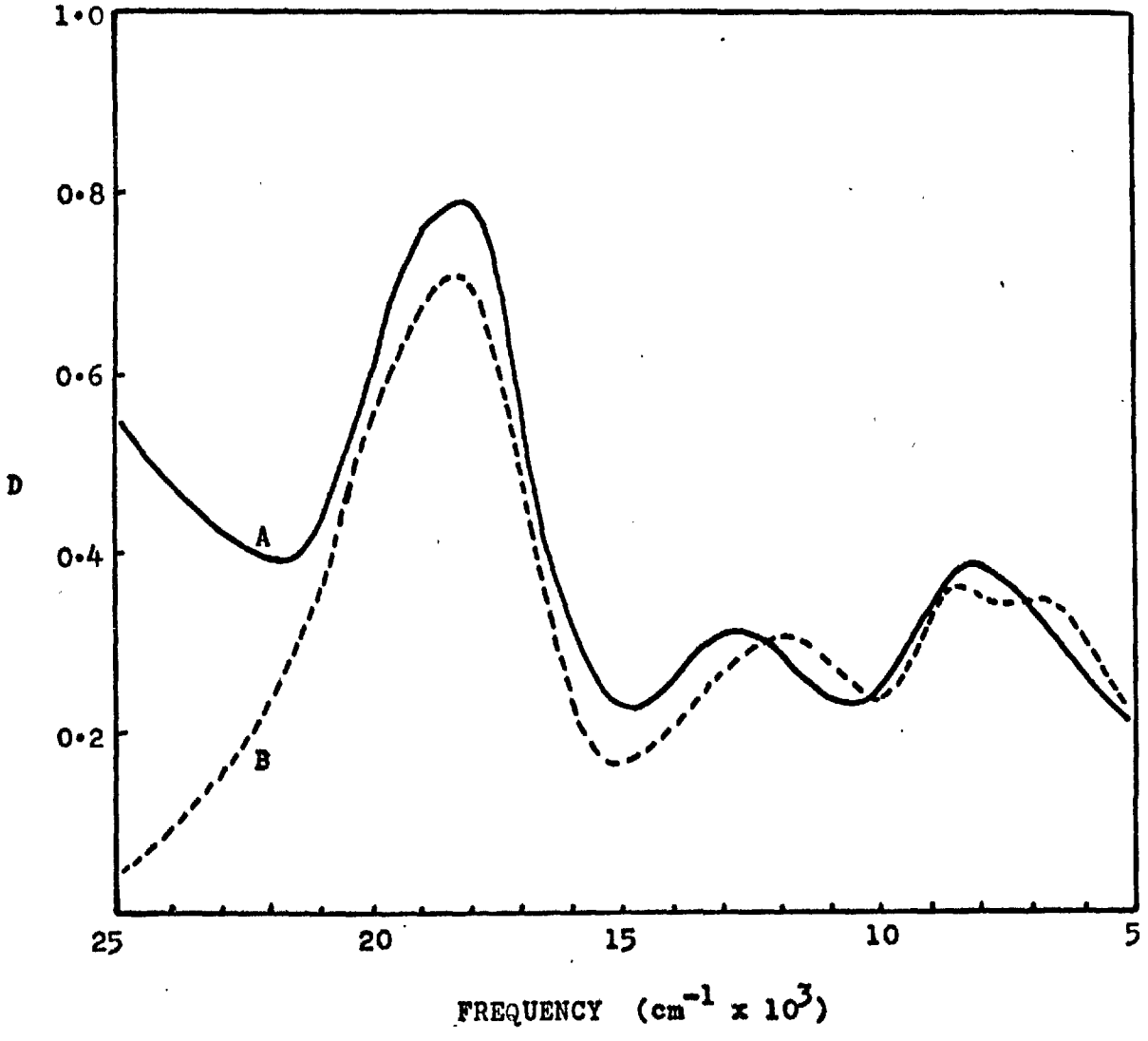


Table 14

The electronic spectral bands of some compounds containing chelating nitrite groups

Compound	State	Band Maxima, cm^{-1} (ϵ_{molar} for solutions)			
$Co(Ph_3PO)_2(NO_2)_2$	solid		17950[a]	12700	7400[b]
	acetone(0·01M)	~20600sh	18400(80)	13000(2)	7800(8·5)[b]
$Co(Ph_3AsO)_2(NO_2)_2$	solid		17000[a]	12700	7870[b]
	acetone(0·01M)		17450(140)[a]	12700sh	7900(14)[b]
$Ni(tetmen)(NO_2)_2$	solid	25800	15900	12500[c]	10000,~8000sh
	$CHCl_3$(0·033M)	25800(35)	15850(15)		10000(6·8)[b]
$Ni(teteen)(NO_2)_2$	solid	25600sh	15600		9300[b]
	benzene(0·01M)	25300sh(~30)	15600(16)		9200(6)[b]
$Ni(py)_2(NO_2)_2$	solid	d 21000[c]	16500		10100
$Ni(2\text{-}mepy)_2(NO_2)_2$	solid	24600	15800	~12500sh[c]	8700
$Ni(quin)_2(NO_2)_2$	solid	24500	15850		8850
$Ni(py)_4(NO_2)_2$	benzene(0·01M)	d	16400(15)		10000(4)[b]
$Ni(3\text{-}mepy)_4(NO_2)_2$	benzene(0·01M)	d	16300(15)		9700(7)[b]
$Ni(4\text{-}mepy)_4(NO_2)_2$	benzene(0·01M)	d	16100(18)		9500(6)[b]

a band assymmetric to higher energy

b band assymmetric to lower energy

c very weak band assigned as a spin-forbidden transition

d band obscured by strong electron transfer absorption

Table 15

The infrared frequencies of the chelating nitrite groups in some complexes.

Compound	State	ν_s	ν_{as}	δ_{NO_2}
$Co(Ph_3PO)_2(NO_2)_2$	solid	~1266mw[a]	1199vs, 1176vs[a]	856m
$Co(Ph_3AsO)_2(NO_2)_2$	solid	1314mw[a]	1193vs, 1183vs	847m
$Ni(tetmen)(NO_2)_2$	solid	1289m[a]	1200vs	863m[a]
	CH_3CN	1284m[a]	1205vs	862m[a]
$Ni(teteen)(NO_2)_2$	solid	b	1199vs	b
	C_6H_6	b	1200vs	b
$Ni(2\text{-mepy})_2(NO_2)_2$	solid	1272m	1199s	866w, 862w
$Ni(py)_2(NO_2)_2$	solid	1304m	1196vs	858m, 838m, 816w
$Ni(quin)_2(NO_2)_2$	solid	1299m, 1289m	1203vs, 1193vs	867m
$Ni(py)_4(NO_2)_2$	C_6H_6	1300m	1190vs	860wbr, 840w
$Ni(3\text{-mepy})_4(NO_2)_2$	C_6H_6	1300m	1195vs	860wbr
$Ni(4\text{-mepy})_4(NO_2)_2$	C_6H_6	b	1190vs	~860wbr

a band position rendered uncertain by organic ligand bands

b band unassigned due to other ligand bands

compounds had a very strong band at ~1190 cm^{-1} assignable as ν_{as} and a medium peak at ~1300 cm^{-1} due to ν_s of the nitrite groups. In each case ν_{as} was split into a doublet, perhaps by the low symmetry which these compounds possess.

The frequencies ν_{as} and ν_s in these complexes are thus both lowered from their free ion values (ν_{as} = ~1250, ν_s = 1326 cm^{-1} in $NaNO_2$). This effect is quite different from that produced by nitro- or nitrito-coordination, or bridging of the nitrite group via nitrogen and oxygen, or a single oxygen atom (see Chapter 5) and is, in fact, quite in accordance with chelation of the anions in these compounds.

For an 'ideal' model in which both metal-oxygen bonds are equivalent, chelation retains the equivalence of the two N-O bonds of the nitrite group, while somewhat reducing their formal bond order and hence the frequencies ν_{as} and ν_s. This is rather similar to the effects observed for the C-O stretching frequencies in some compounds containing bridging carboxylates[71] though for others, eg. $Cr_2(CH_3CO_2)_4 \cdot 2H_2O$, the values of ν_s and ν_{as} are similar to those of the free ion. It should, however, be noted that the infrared spectrum of a nitrite group bridged via two oxygen atoms might closely resemble that of the chelated anions described here.

The band due to ν_s in the chelated nitrite groups is very much weaker than ν_{as}, as is also the case in $NaNO_2$ and many nickel nitrocomplexes. This is in direct contrast to nitrito-complexes and compounds containing nitrite groups bridged via a single oxygen atom or bridged via nitrogen and an oxygen atom, where ν_s is relatively intense.

In $Co(Ph_3PO)_2(NO_2)_2$ and $Co(Ph_3AsO)_2(NO_2)_2$ and in nearly all the nickel complexes also listed in Table 15, δ_{NO_2} is 20 - 30 cm^{-1} higher than in the free ion (828 cm^{-1}). Although such a difference is certainly not diagnostic of chelation, it does appear that this manner of bonding generally raises the frequency δ_{NO_2} somewhat.

Magnetic measurements The room temperature magnetic moments of $Co(Ph_3PO)_2(NO_2)_2$ and $Co(Ph_3AsO)_2(NO_2)_2$ (Table 16) are a little

Table 16

The magnetic moments of some compounds cortaining chelating nitrite groups.

Compound	μ^a B.M.
$Co(Ph_3PO)_2(NO_2)_2$	4·96
$Co(Ph_3AsO)_2(NO_2)_2$	5·03
$Ni(tetmen)(NO_2)_2$	3·37
$Ni(teteen)(NO_2)_2$	3·22
$Ni(py)_2(NO_2)_2$	3·06
$Ni(2\text{-}mepy)_2(NO_2)_2$	3·28
$Ni(quin)_2(NO_2)_2$	3·29

a measured at room temperature and corrected for diamagnetism

higher than those (~4·6 B.M.) of the analogous nitrate complexes[69]. However, the splitting of the ground state ($^4T_{1g}$ in O_h symmetry)

and hence the magnetic properties must depend upon the actual geometry of each individual compound and the ligand field strength of the oxygen atoms involved. Thus some differences between the two groups of compounds might be expected. The higher moments observed for the nitrite complexes suggest that the ligand fields are somewhat more octahedral than in the nitrates. It may be noted in this context that the molar extinction coefficients of the bands at ~18,000 cm^{-1} in the electronic spectra of the nitrite compounds are appreciably lower than those in the corresponding nitrate complexes.

Nickel Complexes

Infrared spectra The nitrite infrared bands (Table 15) in the solid compounds $NiL_2(NO_2)_2$ [L = py, 2-mepy and quin] and Ni(tetmen)$(NO_2)_2$ were identified by comparison with the analogous halide complexes. In the case of Ni(teteen)$(NO_2)_2$ no control compound was available, but the infrared spectrum of this compound was very similar to that of Ni(tetmen)$(NO_2)_2$, so that the strong band ν_{as} could be identified without much ambiguity. The infrared spectrum of $Ni(py)_2(NO_2)_2$ is shown in Figure 13.

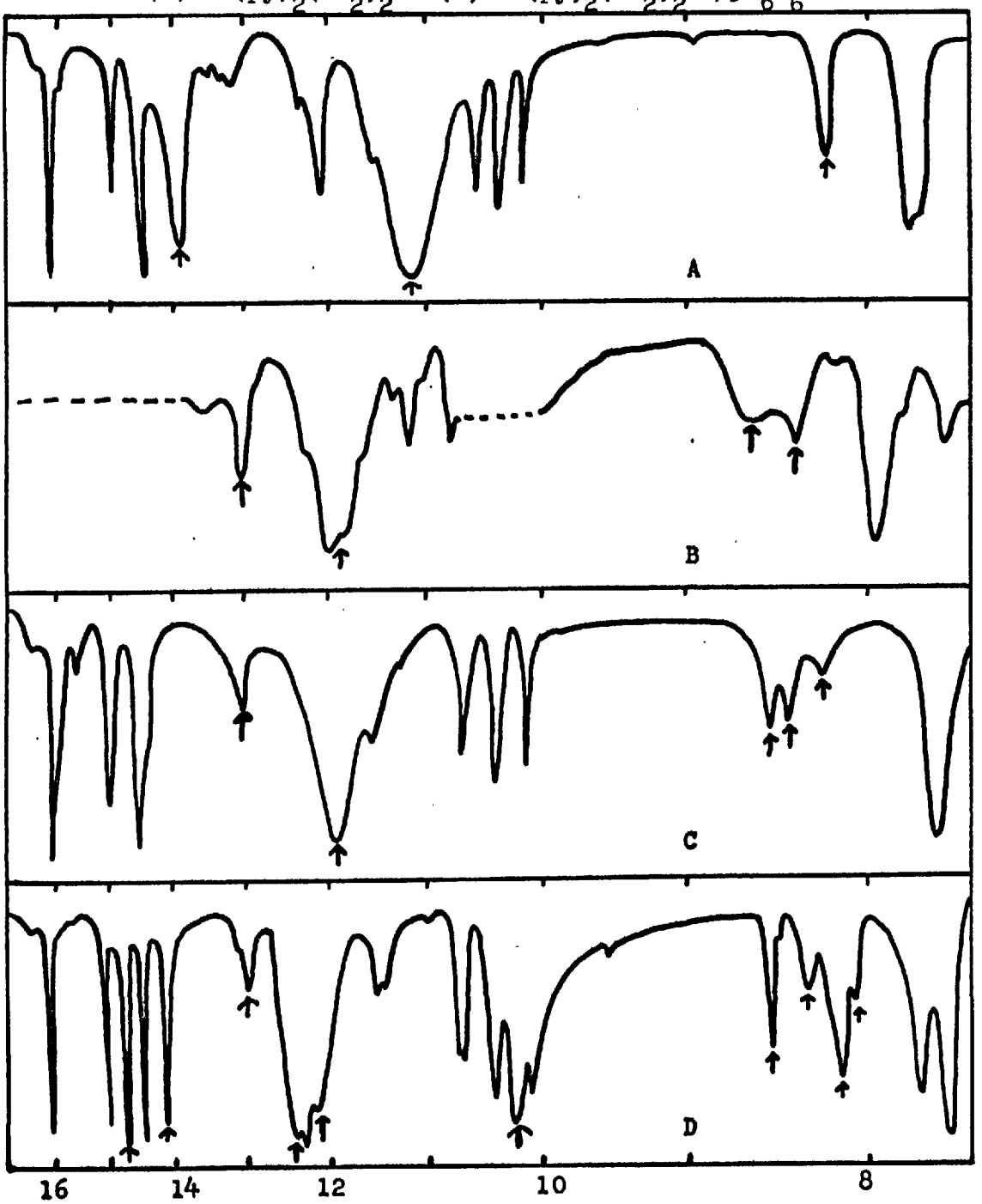
The frequencies ν_s, ν_{as} and δ_{NO_2} in the solid nickel complexes listed in Table 15 are very similar to those in $Co(Ph_3PO)_2(NO_2)_2$ and $Co(Ph_3AsO)_2(NO_2)_2$, and the remarks made on the nitrite infrared peaks in the cobalt compounds apply to the nickel ones

FIGURE 13

The Infrared Spectra of:-

(A) $Ni(py)_4(NO_2)_2$ (B) Solution of $Ni(py)_4(NO_2)_2$ in Benzene

(C) $Ni(py)_2(NO_2)_2$ (D) $Ni(py)_2(NO_2)_2 \cdot 1/3C_6H_6$



The nitrite bands are indicated by arrows.

as well. It thus seems probable that the nickel complexes also contain nitrite groups chelated via two oxygen atoms.

The solid, blue nitritocomplexes $NiL_4(-ONO)_2$ [L = py, 3-mepy and 4-mepy] dissolved in benzene to give emerald green solutions, having nitrite infrared bands quite different from those of the solid compounds (Figure 13). The strong bands at ~1120 and ~1400 cm^{-1}, due to ν_{as} and ν_s of the nitrito-groups in the solid complexes, were replaced in the benzene solutions by a strong band at ~1200 cm^{-1} and a medium one at ~1300 cm^{-1}, and these are very similar in position and relative intensity to those assigned as ν_{as} and ν_s of the chelating nitrite groups in the solid compounds $NiL_2(NO_2)_2$ [L = py, 2-mepy and quin]. Consequently, it seems very probable that solution of the 4:1 complexes in benzene produces extensive dissociation of the type:- $NiL_4(-ONO)_2 \longrightarrow NiL_2(NO_2)_2 + 2L$ [L = py, 3-mepy and 4-mepy] with the nitrite groups in the species $NiL_2(NO_2)_2$ being present as chelating ligands.

Electronic spectra The band maxima in the solid, green compounds $NiL_2(NO_2)_2$ [L = py, 2-mepy and quin], $Ni(tetmen)(NO_2)_2$ and $Ni(teteen)(NO_2)_2$, and in the species $NiL_2(NO_2)_2$ [L = py, 3-mepy and 4-mepy] present in the benzene solutions of the solid compounds $NiL_4(-ONO)_2$ are listed in Table 14 and the electronic spectrum of $Ni(py)_2(NO_2)_2$ is shown in Figure 16 (Page 90).

The electronic spectra suggest that each of the complexes contains six-coordinate Ni^{II} in a fairly weak ligand environment. This is quite consistent with chelation of the anions in these complexes, since the oxygen-coordinated nitrite group is a relatively 'weak' ligand.

It may also be noted that the electronic spectra of the nickel complexes in Table 14 are very similar to those reported[73] for the compounds $NiL_2(NO_3)_2$ [L = 2,3-, 2,4-, and 2,5- lutidine] which are thought to contain chelating nitrate groups.

Magnetic measurements The room temperature magnetic moments (Table 16) of the complexes $NiL_2(NO_2)_2$ [L = py, 2-mepy and quin], $Ni(tetmen)(NO_2)_2$ and $Ni(teteen)(NO_2)_2$, all lie within the range (2·9 - 3·3 B.M.) normally found for six-coordinate, paramagnetic nickel(II).

The structure of $Ni(tetmen)(NO_2)_2$

In order to confirm the manner of anion coordination and to investigate the detailed geometry of a typical complex containing chelating nitrite groups, the structure of $Ni(tetmen)(NO_2)_2$ was determined by x-ray crystallography[56,74].

The molecular configuration (Figure 14) confirmed the presence of chelating nitrite groups. Some bond lengths and angles are listed in Table 17.

FIGURE 14

The X-ray Structure of $Ni(tetmen)(NO_2)_2$

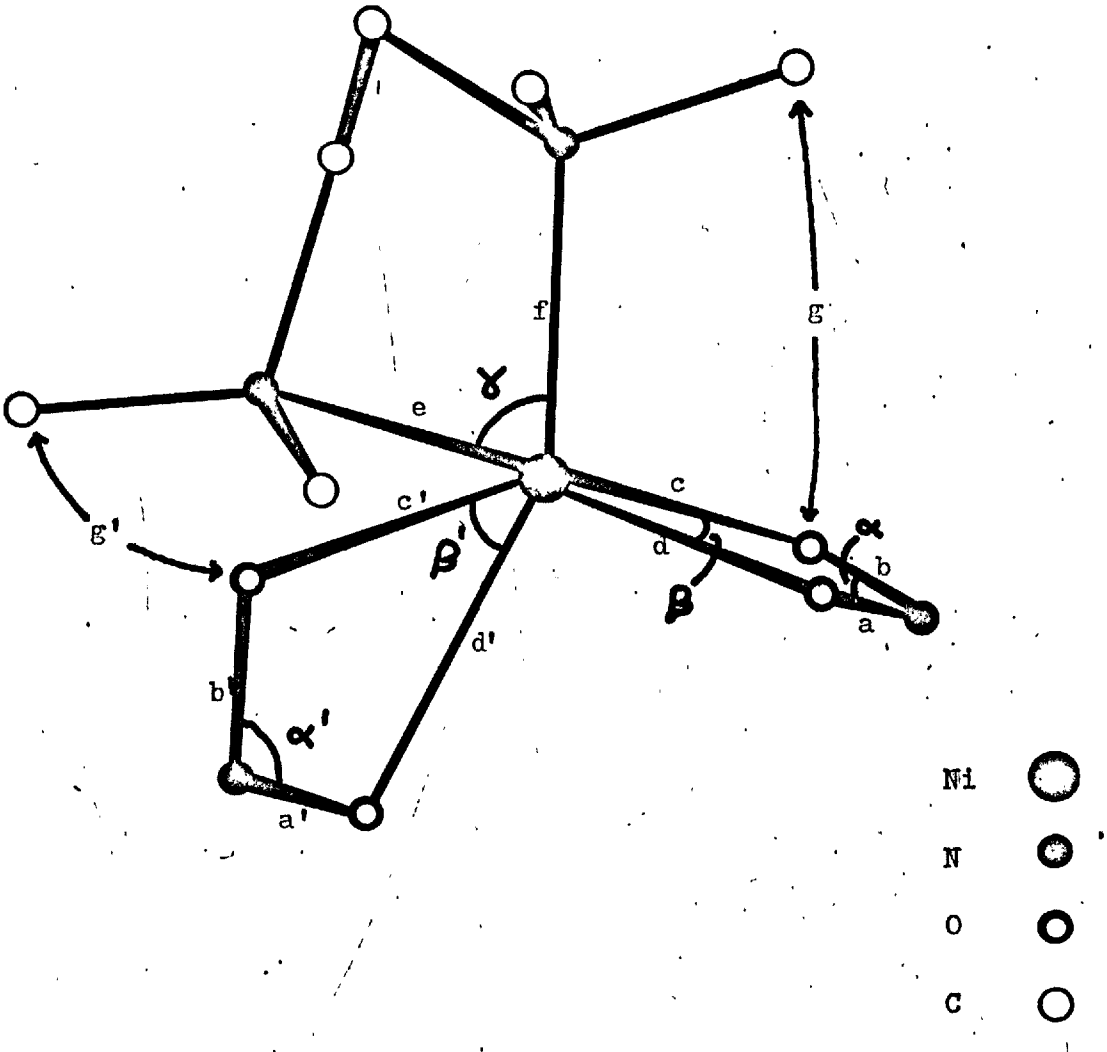


Table 17

Some dimensions of $Ni(tetmen)(NO_2)_2$.

Bond Lengths (Å), Angles (°).

a	1·259 ± 0·015	a'	1·218 ± 0·014
b	1·245 ± 0·016	b'	1·326 ± 0·014
c	2·066 ± 0·009	c'	2·059 ± 0·009
d	2·150 ± 0·009	d'	2·117 ± 0·008
∝	111·65 ± 1·69	∝'	111·69 ± 1·38
β	58·83 ± 0·51	β'	60·57 ± 0·51
ɣ	85·55 ± 0·34		
e	2·087 ± 0·009		
f	2·086 ± 0·009		
g	3·109 ± 0·016	g'	3·066 ± 0·016

The molecule was appreciably distorted from a regular octahedron and this was achieved by an angular distortion of ~15° by each of the four oxygen atoms away from the octahedral positions defined by the two $Ni-N(CH_3)_2$ bonds. In $K_3Hg(NO_2)_4NO_3$, which contains four chelating nitrite groups around each mercury ion, the four Hg-N vectors are arranged in a good approximation to a tetrahedron[44]. Similarly, in $Co[(CH_3)_3PO]_2(NO_3)_2$ the phosphine oxide oxygen atoms and the nitrogen atoms of the chelating nitrate groups lie on the vertices[70] of a tetrahedron. It has thus been suggested[44,70] that each of the coordinated anions

in $Hg(NO_2)_4^{2-}$ and $Co[(CH_3)_3PO](NO_3)_2$ can be considered as occupying essentially a single, tetrahedrally directed coordination position. In Ni(tetmen)$(NO_2)_2$, however, the $N(CH_3)_2$-Ni-$N(CH_3)_2$ plane and the plane defined by the two nitrite nitrogen atoms and the nickel ion are at an angle of 63°, and it seems better to regard the nickel complex as having a distorted octahedral structure.

Discussion

The reasons for the adoption of the chelating structure by the nitrite groups in the complexes described in this Chapter are not completely clear. It is hardly surprising that the nitrite group can coordinate in this manner, since both the nitrate[75] and carboxylate ions[75,76] do this. What is less obvious is why it should bond in this way in preference to other methods. It may be significant in this context that the solid complexes $NiL_2(NO_2)_2$ [L = py, 2-mepy and quin] and $CoL_2(NO_2)_2$ [L = Ph_3PO and Ph_3AsO] are formed, with the exception L = py, with ligands L reluctant to give compounds of stoichiometry ML_4X_2 with other Co^{II} or Ni^{II} salts. Moreover, the complexes ML_2X_2 are generally pseudo-tetrahedral. Thus Ph_3PO and Ph_3AsO form tetrakis-complexes only when the anions have poor coordinating ability[77,78], e.g. I^- and ClO_4^-, and the bis-complexes with the metal halides are pseudo-tetrahedral[78,79]. Both quinoline[80] and

2-methylpyridine[81] form pseudo-tetrahedral complexes with nickel chloride and bromide though the corresponding iodides are planar[80,82] and a polymeric octahedral form of $Ni(quin)_2Cl_2$ is also known[80]. In the case of the species $NiL_2(NO_2)_2$ [L = py, 3-mepy and 4-mepy] which contain chelated anions and are formed on solution of the solid nitritocomplexes $NiL_4(-ONO)_2$ in benzene, it is known that the compounds NiL_4X_2 [L= py and 3-mepy, X = I] dissociate in solution to form the pseudo-tetrahedral species NiL_2X_2 [83]. Quinoline, 2-methylpyridine, tetmen and teteen do not form complexes of stoichiometry $NiL_4(NO_2)_2$ or $Ni(diamine)_2(NO_2)_2$, and this is probably due to the steric requirements of these bulky ligands. It seems likely that it is also these steric requirements which prevent anion bridging in the compounds $NiL_2(NO_2)_2$ and $Ni(diamine)(NO_2)_2$ formed with these amines. Halide bridges in NiL_2X_2 are known to form less readily when L is one of the more sterically hindered heterocyclic ligands[82]. The adoption of chelation, rather than monodentate nitro-coordination in these complexes, is probably due to a more favourable bond energy resulting from the formation of four M - O bonds than two M - N bonds. In the nickel complexes, which are apparently as near octahedral as the presence of the four-membered rings will allow, this can be related to the tendency of nickel(II) to attain six-coordination wherever possible, though it should be noted that the anions in $Ni\left[(n\text{-}C_4H_9)_3P\right]_2(-NO_2)_2$ are bonded via nitrogen[84].

However, nickel complexes with trialkylphosphines are usually diamagnetic trans-planar[85], and the spin-pairing would favour M-NO_2 bonding since the nitro-group lies higher in the spectrochemical series than the nitrito-group.

Preparation of compounds

$Co(Ph_3PO)_2(NO_2)_2$ A solution of $Co(Ph_3PO)_2Cl_2$ in dry acetone was shaken with a two-fold excess of finely powdered $AgNO_2$ until the colour had changed from dark blue to mauve (about two minutes). The resulting solution was filtered and then evaporated in vacuo until mauve crystals formed, together with a small amount of brown solid. The solid products were filtered off, the brown impurity was removed by washing with nitromethane, and the mauve crystals were dried in vacuo.

yield 40% m.p. 200·5°

$Co(Ph_3AsO)_2(NO_2)_2$ This complex was obtained as mauve crystals by a method similar to that used for the previous compound.

yield 50% m.p. 183°

$Ni(tetmen)(NO_2)_2$ A four-molar excess of tetmen was added to a solution of nickel nitrite[64]. Bright green crystals formed and were recrystallised from chloroform.

yield 60% m.p. 174°

$Ni(teteen)(NO_2)_2$ This was prepared as bright green crystals by the method used for the previous compound.

yield 70%

$\underline{Ni(2\text{-mepy})_2(NO_2)_2}$ This was obtained in 60% yield as emerald green crystals by the procedure described for the tetmen complex. The compound turned yellow with decomposition at ~150°.

$\underline{Ni(quin)_2(NO_2)_2}$ This compound was prepared by the method used for the tetmen complex and recrystallised from quinoline as bright green crystals.

yield 70% m.p. 219° dec.

$\underline{Ni(py)_2(NO_2)_2}$ A dark green compound approximating to this stoichiometry was prepared by heating finely ground $Ni(py)_4(-ONO)_2$ in vacuo at 100° until the weight drop showed that about two moles of pyridine had been lost (about two hours).

weight loss of $Ni(py)_4(NO_2)_2 \longrightarrow Ni(py)_2(NO_2)_2$

calc. 33·85%, found 34·46%

An attempt was also made to prepare a 'low-temperature' form of this compound by exchanging an acetone solution of $Ni(py)_2Cl_2$ with excess $AgNO_2$, filtering and removing the solvent under vacuum. The dark green solid formed, which was not analysed, had an infrared spectrum identical with that of the above compound, but with addition of bands at 3500 and 1650 cm^{-1}, showing the presence of water.

Table 18

Analysis data on some complexes containing chelating nitrite groups

Compound	Calculated					Found				
	C	H	N	O	Ni	C	H	N	O	Ni
$Co(Ph_3PO)_2(NO_2)_2$	61·12	4·28		13·57		60·87	4·19		13·15	
$Co(Ph_3AsO)_2(NO_2)_2$	54·37	3·80	3·52	12·07		53·76	3·96	3·51	12·08	
$Ni(tetmen)(NO_2)_2$	27·00	6·04	20·99		21·99	27·36	6·12	20·46		22·20
$Ni(teteen)(NO_2)_2$	37·18	7·49	17·35			37·37	7·26	17·56		
$Ni(2\text{-mepy})_2(NO_2)_2$	42·77	4·19	16·63	19·00		42·39	4·17	16·61	19·20	
$Ni(quin)_2(NO_2)_2$	52·86	3·45	13·71			52·93	3·63	13·41		
$Ni(py)_2(NO_2)_2$	38·87	3·26			19·00	38·18	3·22			19·21

CHAPTER 5

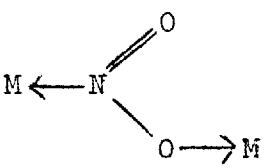
Some Complexes Containing Bridging Nitrite Groups.

While it had been known for some time that the nitrite group could function as a bridging ligand, the method by which it accomplished this was not extensively investigated.

This Chapter describes some new nickel complexes thought to contain bridging nitrite groups. The electronic and infrared spectra are discussed in terms of the manner of nitrite bonding envisaged in these compounds.

A) Some Complexes Containing Nitrite Groups Bridged via Nitrogen and a Single Oxygen Atom

The complexes $\left[Ni(en)_2NO_2\right]X$ $\left[X = ClO_4 \text{ and } BF_4\right]$ and $NiD(NO_2)_2$ $\left[D = en \text{ and } men\right]$ were prepared. In contrast to the bright green nickel nitrite complexes containing chelating nitrite groups, the above compounds were all red. Crystallographic evidence showed that the compounds $\left[Ni(en)_2NO_2\right]$ X $\left[X = ClO_4 \text{ and } BF_4\right]$ contain nitrite groups bridged via nitrogen and an oxygen atom (as illustrated below), and the infrared and electronic spectra of



$Ni(en)(NO_2)_2$ and $Ni(men)(NO_2)_2$ suggest a similar manner of anion

coordination in these complexes also. The term nitrite bridging(NO) will be used to specify the above manner of nitrite coordination.

The compound $Ni(NH_3)_2(NO_2)_2$ was formed as a grey powder by heating $Ni(NH_3)_4(NO_2)_2$ in vacuo at ~100°. It seems that $Ni(NH_3)_2(NO_2)_2$ contains two types of nickel ion, one coordinated to bridged(NO) nitrite groups and the other probably bonded to chelating anions.

The structures of $[Ni(en)_2NO_2]ClO_4$ and $[Ni(en)_2NO_2]BF_4$

A recent, two-dimensional x-ray study on the red compound $[Ni(en)_2NO_2]ClO_4$ was interpreted[42] as indicating an approximately linear nitrite group bonded via one of its oxygen atoms to two equidistant nickel ions in a polymeric chain. This novel form of nitrite coordination seemed improbable for several reasons.

A linear nitrite group is in itself rather unlikely, since it requires the promotion of the non-bonded lone-pair of electrons associated with the nitrogen atom of the angular nitrite ion ($\widehat{ONO} \simeq 115°$) into some other orbital. The Ni-O bonds were improbably long (2·58 Å) in the proposed structure and inconsistent with the electronic reflectance spectrum of $[Ni(en)_2NO_2]ClO_4$ (Figure 16, Page 90), which showed bands at 20,240, 12,500 and ~10,900 cm^{-1} (Table 20). These band energies are very similar to those found for $Ni(en)_2(-NO_2)_2$, but are considerably higher than those observed for the nitritocomplexes $Ni(diamine)_2(-ONO)_2$

(Table 3). Since the crystallographic evidence for the postulated structure was unconvincing, the nitrite group being rather poorly defined, a reinvestigation of the structure of $[Ni(en)_2NO_2]ClO_4$ seemed desirable.

Only two nitrite group frequencies could be found in the infrared spectrum of $[Ni(en)_2NO_2]ClO_4$, at 1256 and 814 cm^{-1} (Table 21). These were identified by comparison with the spectra of $Ni(en)_2(NCS)_2$ and $Ni(en)_2(-NO_2)_2$. The peak at 814 cm^{-1} could be assigned as δ_{NO_2}, but the observation of only one of the two nitrogen-oxygen stretching frequencies made it impossible to use the nitrite infrared spectrum as a guide to the nature of the nickel-nitrite bonding. A three-dimensional x-ray analysis thus seemed the only way of determining the structure of $[Ni(en)_2NO_2]ClO_4$.

The red compound $[Ni(en)_2NO_2]BF_4$ was prepared and had identical electronic and infrared spectra to the perchlorate, except for the differences between the infrared bands of ClO_4^- and BF_4^-. The two compounds also proved to be isomorphous and, as it appeared more suitable, the fluoborate was chosen for the crystallographic study.

It was found[56,86] that the structure involving the linear, single-oxygen bridged nitrite groups was incorrect and the actual structure of $[Ni(en)_2NO_2]BF_4$ is shown in Figure 15(a) with bond lengths and angles being listed in Table 19. Each nickel ion in the polymer chain is coordinated to two bridged(NO) nitrite groups,

Ni N C O F B

FIGURE 15

The X-ray Structure of $[Ni(en)_2(NO_2)]BF_4$

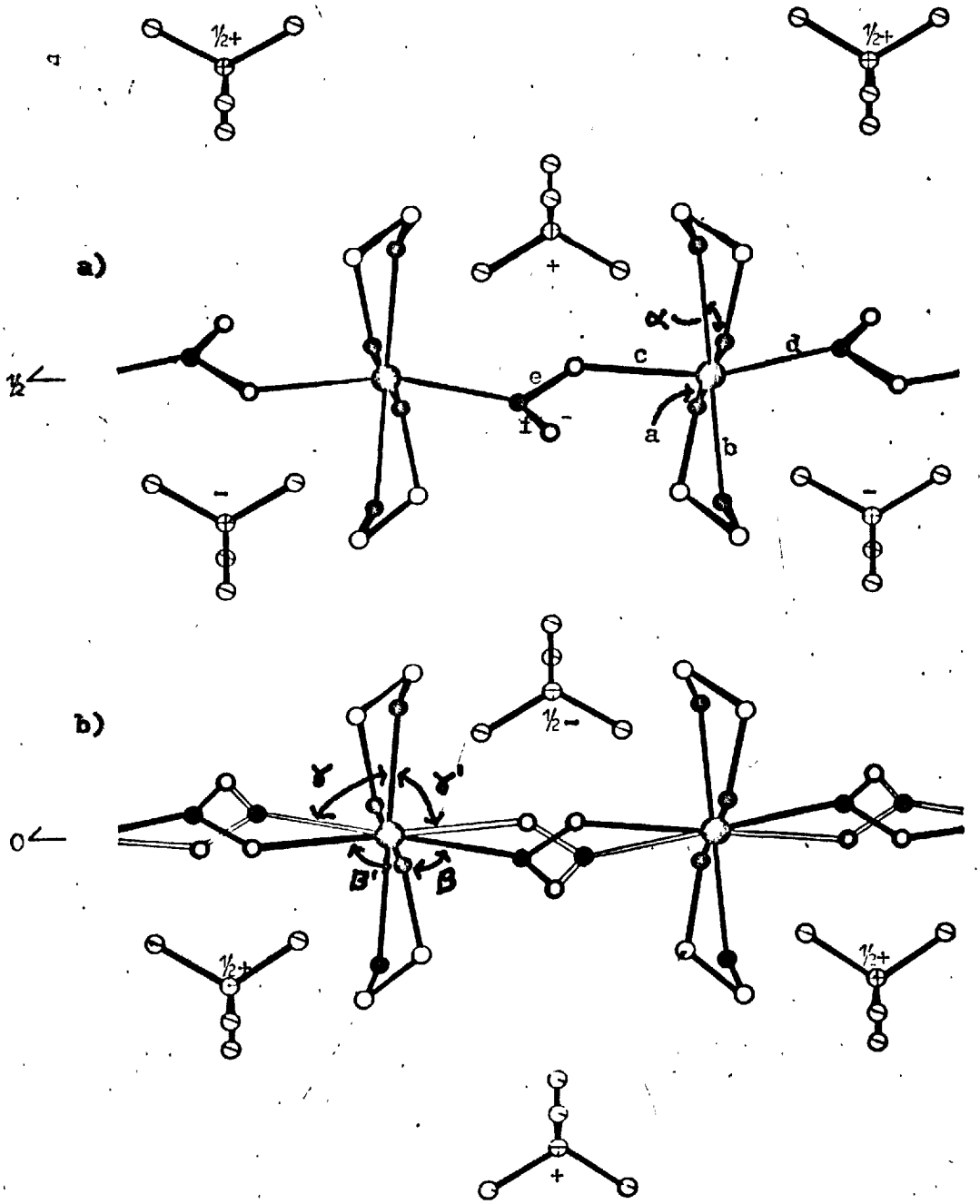


Table 19

Some molecular dimensions in $[Ni(en)_2NO_2]BF_4$

Bond Length (Å), Angles (°)

a	2·117 ± 0·011	α	84·14 ± 0·46
b	2·097 ± 0·012	β	94·08 ± 0·67
c	2·215 ± 0·017	β'	100·68 ± 0·57
d	2·155 ± 0·019	γ	83·39 ± 0·69
e	1·276 ± 0·026	γ'	81·11 ± 0·59
f	1·224 ± 0·025	δ	110·78 ± 1·71

one via nitrogen and the other via oxygen. The grouping Ni←N(=O)→Ni is virtually planar and the angle N-$\hat{N}$i-O is 155·8° with the oxygen atom being more displaced from the axial position than is the nitrite nitrogen atom.

Although the nitrite groups in any one chain are probably ordered, at least for long distances along the chain, the structure as a whole is disordered in the manner illustrated in Figure 15(b). This disorder arises from the reversal of all the NO_2 groups in either adjacent chains or domains of chains.

The similarity of the electronic spectra of $[Ni(en)_2NO_2]BF_4$ and $Ni(en)_2(-NO_2)_2$ suggests that the Δ-value of a bridged(NO) nitrite group is very high and close to that produced by a nitro-group. This is in agreement with the electronic spectrum of $[N(CH_3)_4]Ni(NO_2)_3$ (see Chapter 6), which contains three nitrogen-

oxygen bridged nitrite groups and for which a Δ-value of 12,900 cm^{-1} is found. This may be compared with $\Delta \simeq 13{,}400$ cm^{-1} for six nitro-groups[32,87].

It might be expected that coordination to a nitrogen and oxygen atom of two bridged(NO) nitrite groups, as in $[Ni(en)_2NO_2]BF_4$, would provide a ligand field midway between those of a monodentate nitro- and nitrito-group (i.e. $\Delta \sim 11{,}500$ cm^{-1}) but, at least in the compounds discussed above, this is apparently not the case. However, it seems likely that π-bonding plays an important part in determining the energies of the electronic transitions in nickel nitrite complexes, and the π-bonding properties of a bridged(NO) nitrite group may be rather different from those of monodentate nitro- and nitrito-groups.

The Compounds $Ni(en)(NO_2)_2$, $Ni(men)(NO_2)_2$ and $Ni(NH_3)_2(NO_2)_2$

Infrared spectra The infrared peaks due to the nitrite groups in $Ni(en)(NO_2)_2$ and $Ni(men)(NO_2)_2$ (Table 20), were identified by comparison with the corresponding bisdiamine nitro- and isothiocyanato-complexes. The infrared spectrum of $Ni(en)(NO_2)_2$ is shown in Figure 5 (Page 27).

Although there were slight differences, mainly in intensity, between the bands assigned to the amines in $Ni(en)(NO_2)_2$ and $Ni(men)(NO_2)_2$ and those in the corresponding $Ni(diamine)_2(-NO_2)_2$ complexes, some changes might be expected and the relatively great

Table 20

The nitrite infrared frequencies in some complexes containing bridged(NO) nitrite groups.

Compound	Frequency (cm^{-1})		
	ν_s	ν_{as}	δ_{NO_2}
$[Ni(en)_2NO_2]ClO_4$	a	1256s	863w
$Ni(en)(NO_2)_2$	1429s	1241vs	826w, 836w
$Ni(men)(NO_2)_2$	1429s	1241vs	a
$Ni(NH_3)_2(NO_2)_2$	1433s	~1235sh[b]	839w br

a band unassigned because of peaks due to the amine ligands

b band position rendered uncertain by the amine band at 1210 cm^{-1}

intensity of the bands at 1241 and 1429 cm^{-1} meant that these could confidently be assigned as ν_{as} and ν_s of the nitrite groups.

The infrared spectrum of $Ni(NH_3)_2(NO_2)_2$ (Figure 5) was somewhat more difficult to interpret. The strong, broad band at 1210 cm^{-1} and the medium peak at 1357 cm^{-1} also occur in $Ni(NH_3)_4(-NO_2)_2$ and may thus be assigned to the amine ligands. The peak at 1433 cm^{-1} in $Ni(NH_3)_2(NO_2)_2$ may be assigned as the frequency ν_s of the nitrite groups, with ν_{as} probably occurring as the shoulder at ~1235 cm^{-1}. The very weak band at 1302 cm^{-1} in $Ni(NH_3)_2(NO_2)_2$ could possibly be due to ν_s of chelated nitrite groups, but it could also be caused by a small amount of $Ni(NH_3)_4(-NO_2)_2$ impurity, as this has a very strong band at 1299 cm^{-1}.

Thus, in each of the complexes $Ni(en)(NO_2)_2$, $Ni(nen)(NO_2)_2$ and $Ni(NH_3)_2(NO_2)_2$ the nitrogen-oxygen stretching frequencies occur at ~1240 and ~1430 cm^{-1}. This divergence of ν_{as} and ν_s from their free ion frequencies (ν_{as} = ~1250 cm^{-1}, ν_s = 1326 cm^{-1} in $NaNO_2$) together with the raising of their mean value is a combination of the effects that nitrogen and oxygen coordination have on the nitrite infrared spectrum, as may be seen from Figure 18 (Page100). Such a combination is in accordance with bridging(NO) of the anions similar to that occurring in $[Ni(en)_2NO_2]BF_4$. Bridging of this type has been suggested in $\left[Co(NH_3)_3 \begin{smallmatrix} OH \\ OH \\ NO_2 \end{smallmatrix} Co(NH_3)_3\right]^{3+}$ which has nitrite infrared frequencies at 1200 and 1516 cm^{-1} [29].

However, since chelating nitrite groups have a strong band at ~1200 cm^{-1} and only a weak one at ~1300 cm^{-1} (Table 15), the possibility that anions bonded in this manner are present in addition to the bridged(NO) groups must be considered. The relative sharpness of the peaks at 1241 cm^{-1} in $Ni(nen)(NO_2)_2$ and $Ni(en)(NO_2)_2$ makes this unlikely for these two compounds. However, as there is a strong amine band at 1210 cm^{-1} in $Ni(NH_3)_2(NO_2)_2$, it is impossible to tell from the infrared spectrum of this compound whether it also contains chelating nitrite groups or not.

Electronic Spectra and Discussion

The band maxima of $Ni(en)(NO_2)_2$ and $Ni(nen)(NO_2)_2$ are listed

in Table 21, and the reflectance spectrum of $Ni(en)(NO_2)_2$ is

Table 21

The electronic reflectance spectra of some complexes containing bridged(NO) nitrite groups

Compound	Band Maxima (cm^{-1})	
$[Ni(en)_2NO_2]ClO_4$	20,240	12,500, ~10,900sh
$Ni(en)_2(-NO_2)_2$ [a]	19,650	12,500, ~11,000sh
$Ni(en)(NO_2)_2$	19,900	11,900
$Ni(men)(NO_2)_2$	20,000	12,000
$Ni(NH_3)_2(NO_2)_2$	20,800, 17,100	10,700br

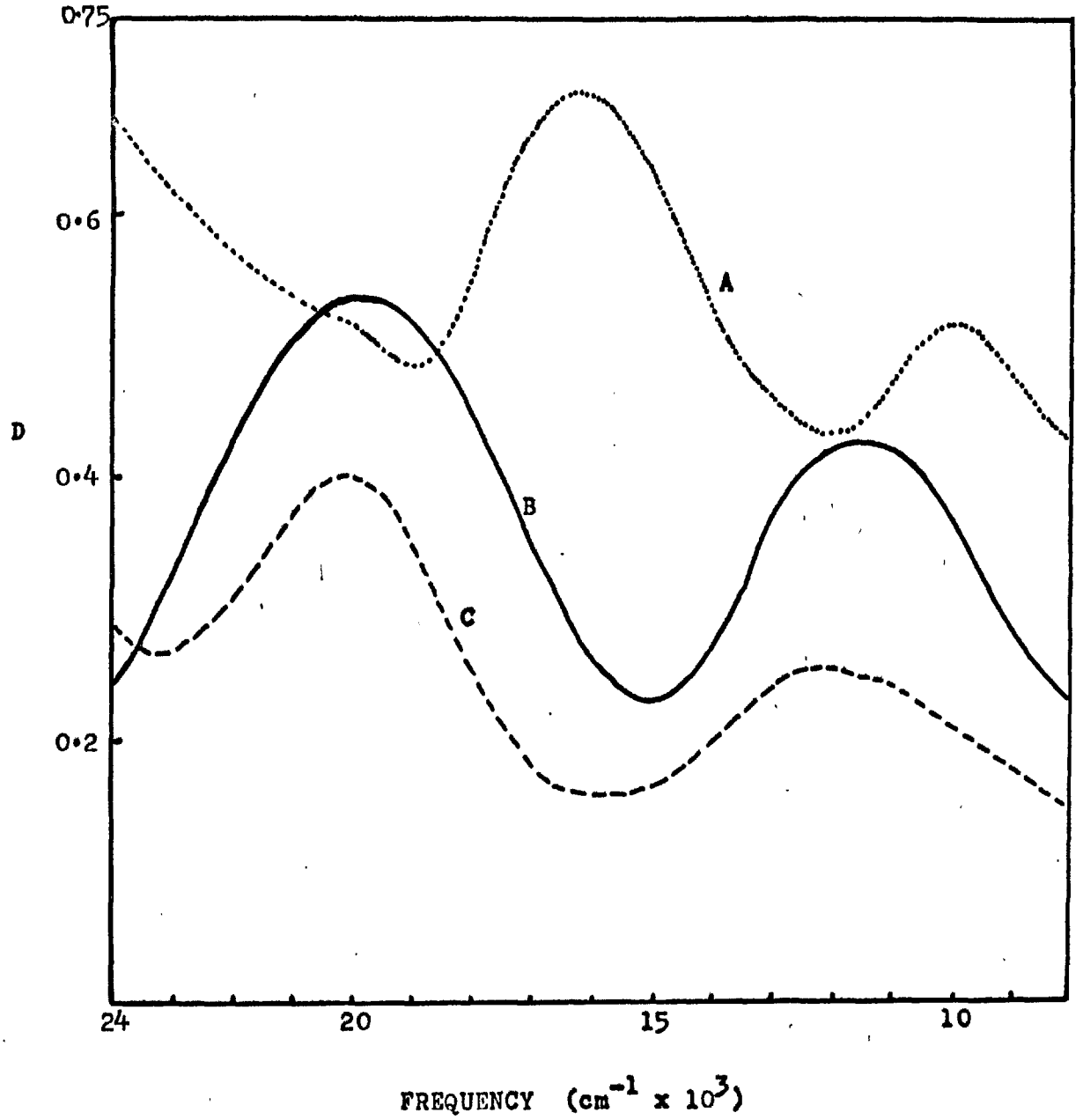
a this compound contains nitro-groups, not bridging(NO) nitrite groups, and is included for comparative purposes.

shown in Figure 16. The two bands observed for each compound may be assigned as the first two spin-allowed transitions of Ni^{II} in a pseudo-octahedral ligand environment. The high energies of the band maxima (~12,000 and ~20,000 cm^{-1}) suggest a relatively strong ligand field around each nickel ion, in contrast to the fairly weak ligand field (with bands at ~10,000 and~17,000 cm^{-1}) observed for the complexes $Ni(diamine)(NO_2)_2$ containing chelating anions. This is consistent with the compounds $Ni(en)(NO_2)_2$ and $Ni(men)(NO_2)_2$ having bridging(NO) nitrite groups, since this form of nitrite bonding produces a high ligand field as it

FIGURE 16

Electronic Reflectance Spectra of:-

(A) $Ni(py)_2(NO_2)_2$ (B) $Ni(en)(NO_2)_2$ (C) $[Ni(en)_2(NO_2)]ClO_4$



involves nitrogen coordination of the anion.

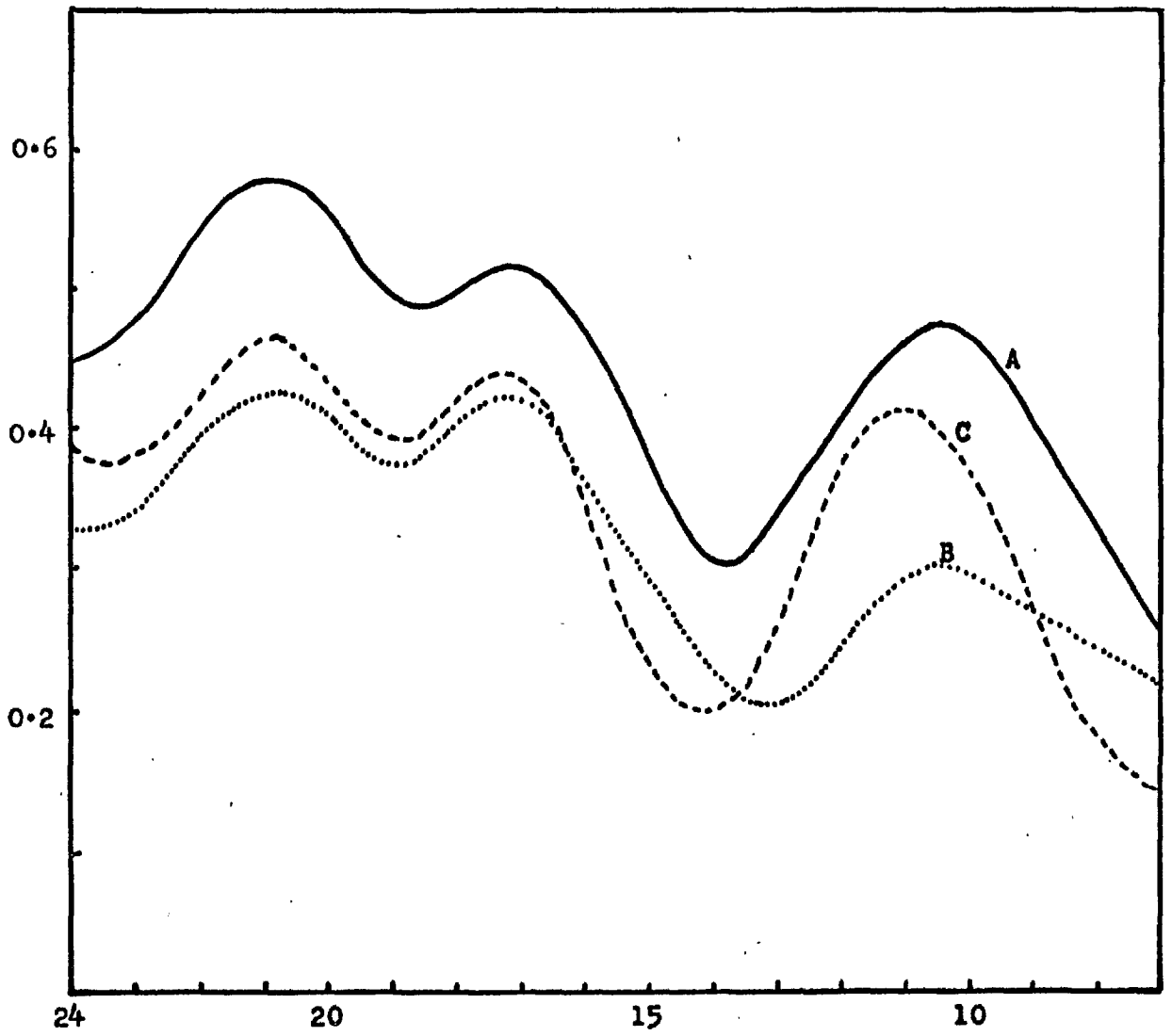
It is perhaps surprising that the electronic spectra of $NiD(NO_2)_2$ [D = en and men] are very similar to that of $[Ni(en)_2NO_2]ClO_4$ (Figure 16), since in the former compounds four coordination positions are occupied by nitrite groups, while in the latter only two coordination positions are taken up by NO_2^-. However, as has already been mentioned, the high ligand field strength of the nitrite group in $[Ni(en)_2NO_2]ClO_4$ is probably related to its π-bonding properties, and these may well depend upon the actual molecular configuration involved. Since the electronic spectra of $Ni(en)(NO_2)_2$ and $Ni(men)(NO_2)_2$ suggest that only nickel ions in essentially similar ligand environments are present (or the bands would be broad or split, as in $Ni(NH_3)_2(NO_2)_2$), each Ni^{II} is probably bonded to two nitrogen and two oxygen atoms of the bridging nitrite groups. Because of the presence of the chelating diamines, two of the coordinated nitrite atoms presumably cannot adopt the 'trans' positions found in $[Ni(en)_2NO_2]BF_4$, and this could well decrease the effective ligand field of the anions in $Ni(en)(NO_2)_2$ and $Ni(men)(NO_2)_2$.

The electronic spectrum of $Ni(NH_3)_2(NO_2)_2$ (Figure 17), suggests the presence of nickel ions in two different ligand environments, one relatively 'weak' and the other 'strong'. The peak at 17,100 cm^{-1} is rather similar to the corresponding band

FIGURE 17

Electronic Reflectance Spectra of:-

(A) $Ni(NH_3)_2(NO_2)_2$ (B) $Ni(py)_2(NO_2)_2 \cdot 1/3C_6H_6$ (C) $Ni(a\text{-dieen})(NO_2)_2$



in the compounds $NiL_2(NO_2)_2$, in which chelating nitrite groups are present, while the band at 20,800 cm^{-1} resembles those of the complexes containing bridging(NO) nitrite groups. The band at 10,700 cm^{-1} is broad, in agreement with its being a superimposition of the two lower energy bands (at ~10,000 and ~12,000 cm^{-1}) expected in conjunction with the peaks at 17,100 and 20,800 cm^{-1}.

It seems thus probable that in $Ni(NH_3)_2(NO_2)_2$ some nickel ions are coordinated to nitrite groups solely (or, at least, mainly) via oxygen atoms, while the rest are bonded to bridged(NO) nitrite groups. It is impossible on the present data to be much more specific about the structure of this compound, since several configurations could conceivably give rise to the observed infrared and electronic spectra. One such structure which, it must be stressed, is only a possibility, is a mixture of $Ni(NH_3)_2(NO_2)_2$ molecules having bridged(NO) nitrite groups with $Ni(NH_3)_2(NO_2)_2$ molecules having chelating nitrite groups. It may be noted that, with the NH_3 molecules in the expected 'trans' positions, the $Ni(NH_3)_2(NO_2)_2$ molecules having the bridging(NO) nitrite groups might easily adopt a 'sheet' configuration. The bulk structure of $Ni(NH_3)_2(NO_2)_2$ might then consist of such 'sheets' interspersed by layers of discrete $Ni(NH_3)_2(NO_2)_2$ molecules having chelating nitrite groups. In $Ni(en)(NO_2)_2$ and $Ni(men)(NO_2)_2$, where the amines presumably occupy 'cis' positions,

such polymeric 'sheets' could not form, and this could possibly explain the structural difference between $Ni(NH_3)_2(NO_2)_2$ and these two compounds.

Any inter- or intramolecular steric interference in the compounds $[Ni(en)_2NO_2]X$ [X = BF_4 and ClO_4] and $NiD(NO_2)_2$ [D = en and men] is likely to be small, and it may be noted that these complexes are formed with diamines which also give stable nitro-complexes $Ni(diamine)_2(-NO_2)_2$. This suggests that the bridging(NO) found in $[Ni(en)_2NO_2]X$ and $Ni(diamine)(NO_2)_2$ is the manner of nitrite coordination generally adopted in compounds of this type when steric considerations are relatively unimportant. However, this is not always the case, since although there can be little steric interaction in $Ni(NH_3)_2(NO_2)_2$, this compound apparently contains chelated anions in addition to bridged(NO) ones.

Preparation of compounds

$[Ni(en)_2NO_2]ClO_4$ Ethylenediamine (0·015 M) was added to an aqueous solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0·01 M) and $NaNO_2$ (0·005 M). On allowing the solution to evaporate large red crystals of the desired product formed and these were filtered off, washed with ethanol and air dried. yield 30%

$[Ni(en)_2NO_2]BF_4$ This was prepared as large red crystals by the method for the previous compound. yield 20%

$Ni(en)(NO_2)_2$ A solution of ethylenediamine (0·01 M) in methanol

(5 mls) was added slowly to a solution of nickel nitrite[64] (0·02 M) and the resulting, slow-forming red precipitate was recrystallised from methanol. yield 40%

Ni(men)$(NO_2)_2$ Red crystals by the method used for Ni(en) $(NO_2)_2$ yield 50%

$Ni(NH_3)_2(NO_2)_2$ Finely ground $Ni(NH_3)_4(-NO_2)_2$ was heated at 116° to constant weight in vacuo to yield a brown powder. Weight loss for $Ni(NH_3)_4(NO_2)_2 \rightarrow Ni(NH_3)_2(NO_2)_2$ calc.16·80% found 16·95%

The preparation of the compounds Ni(en)$(NO_2)_2$ and Ni(men) $(NO_2)_2$ was also attempted by heating the bis-diamine nitrocomplexes in vacuo at 120° and 144° respectively. However, even after several hours no significant weight loss was observed. It has been reported[88] that $Ni(en)_2(-NO_2)_2$ turns blue on heating to 130°, but this effect was not observed in the present experiment.

Table 22

Analysis details of some complexes containing bridged(NO) nitrite groups.

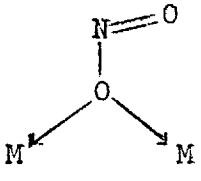
Compound	Calculated					Found				
	C	H	N	O	Ni	C	H	N	O	Ni
$[Ni(en)_2NO_2]BF_4$	15·41	5·17				15·72	5·23			
$[Ni(en)_2NO_2]ClO_4$	14·81	4·97	21·60			15·04	4·94	21·50		
Ni(en)$(NO_2)_2$	11·40	3·82		30·37	27·85	11·71	4·22		30.37	28·30
Ni(men)$(NO_2)_2$	16·03	4·48		28·47		16·04	4·69		28·78	
$Ni(NH_3)_2(NO_2)_2$			30·33	34·63	31·77			30·62	34·28	31·62

B) Complexes Containing Nitrite Groups Bridged via a Single Oxygen Atom

The compounds $NiL_2(NO_2)_2$ [L = 3-mepy, 4-mepy and i-quin] and $Ni(a\text{-dieen})(NO_2)_2$ were prepared by heating the corresponding nitritocomplex $NiL_4(-ONO)_2$ and $Ni(a\text{-dieen})_2(NO_2)_2$ at ~100° in vacuo; the complexes $Ni(py)_2(NO_2)_2 \cdot 1/3C_6H_6$, $Ni(3\text{-mepy})_2(NO_2)_2 \cdot 1/3C_6H_6$ and $Ni(4\text{-mepy})_2(NO_2)_2 \cdot 1C_6H_6$ were obtained as black crystals from benzene solutions of the nitritocomplexes $NiL_4(-ONO)_2$.

All these compounds had very similar electronic spectra and nitrite infrared spectra, which suggests that the benzene molecules present in those obtained from solution are clathrated and do not take part in any formal bonding (benzene is known to be clathrated in this manner in a number of similar complexes[89,90]).

All of the above nitrite complexes apparently contain anions bridged via a single oxygen atom (as illustrated below), a hitherto unrecognised manner of nitrite coordination. This form of bonding will be referred to as bridging(O) of the nitrite group.



Magnetic susceptibility measurements

The magnetic moments of $NiL_2(NO_2)_2$ [L = 3-mepy, 4-mepy and i-quin] and $Ni(3\text{-mepy})_2(NO_2)_2 \cdot 1/3C_6H_6$ are listed in Table 23. The observed values all lie within the range (μ = 2·9 - 3·3) normally

Table 23

The magnetic moments of some compounds containing bridged(O) nitrite groups.

Compound	μ^a
$Ni(3\text{-mepy})_2(NO_2)_2 \cdot 1/3C_6H_6$	3·11
$Ni(i\text{-quin})_2(NO_2)_2$	3·01
$Ni(3\text{-mepy})_2(NO_2)_2$	3·16
$Ni(4\text{-mepy})_2(NO_2)_2$	3·09

a measured at room temperature and corrected for diamagnetism

found for six-coordinate, spin-free nickel(II).

Infrared spectra The infrared bands due to the nitrite groups in $NiL_2(NO_2)_2$ [L = 3-mepy, 4-mepy and i-quin], $Ni(a\text{-dieen})(NO_2)_2$, $Ni(py)_2(NO_2)_2 \cdot 1/3C_6H_6$, $Ni(3\text{-mepy})_2(NO_2)_2 \cdot 1/3C_6H_6$ and $Ni(4\text{-mepy})_2(NO_2)_2 \cdot 1C_6H_6$ are listed in Table 24 and the spectrum of $Ni(py)_2(NO_2)_2 \cdot 1/3C_6H_6$ is shown in Figure 13. The bands due to NO_2^- in $Ni(a\text{-dieen})(NO_2)_2$ were identified by comparison with the infrared spectrum of $Ni(a\text{-dieen})(NCS)_2$. The nitrite peaks in the other compounds were identified by comparison with the spectra of the corresponding halide complexes NiL_2X_2 [X = Cl, Br and I], and the spectra of the compounds containing clathrated benzene were also compared with those of appropriate mixtures of the amines with

Table 24

The nitrite infrared bands in some complexes containing bridged(O) nitrite groups.

Compound	δ_{NO_2}	ν_{as}	ν_s
$Ni(i\text{-quin})_2(NO_2)_2$	a	1010s[b] 1220vs[b]	a 1437s 1486s
$Ni(3\text{-mepy})_2(NO_2)_2$	829m 844w 861m	1025vs 1209vs[b]	1294m 1437s[b] a
$Ni(4\text{-mepy})_2(NO_2)_2$	831w 846m 861m 876vw	1026vs[b] 1225vs[b]	a 1429s[b] 1471m 1488s
$Ni(a\text{-dieen})(NO_2)_2$	838w 846vw 861vw	1020s 1220vsbr	a 1429sbr a
$Ni(py)_2(NO_2)_2$	810vw 823m 840w	1020s 1206sh	1283m 1420s 1475s
$\cdot 1/3C_6H_6$	863w	1233vs[b]	
$Ni(3\text{-mepy})_2(NO_2)_2$	843m 863m	1019vs 1236vs	1299m 1412s[b] 1460s
$\cdot 1/3C_6H_6$			
$Ni(4\text{-mepy})_2(NO_2)_2$	839w 859m 875vw	1007s[b] 1209vs[b]	a 1437s[b] a
$\cdot 1C_6H_6$			

a nitrite band obscured by amine or benzene bands

b exact position of nitrite band maximum rendered uncertain by presence of amine or benzene bands.

benzene. In the compounds $Ni(py)_2(NO_2)_2 \cdot 1/3C_6H_6$ and $Ni(3\text{-mepy})_2(NO_2)_2 \cdot 1/3C_6H_6$ the bands due to the benzene did not interfere with the identification of the nitrite bands, as in 6:1 molar mixtures of pyridine and 3-methylpyridine with benzene the infrared peaks of the benzene were very weak compared with those of the amines.

In $Ni(4\text{-mepy})_2(NO_2)_2 \cdot 1C_6H_6$, however, the benzene bands at ~1500 and ~1000 cm^{-1} made the identification of nitrite bands in these regions rather difficult.

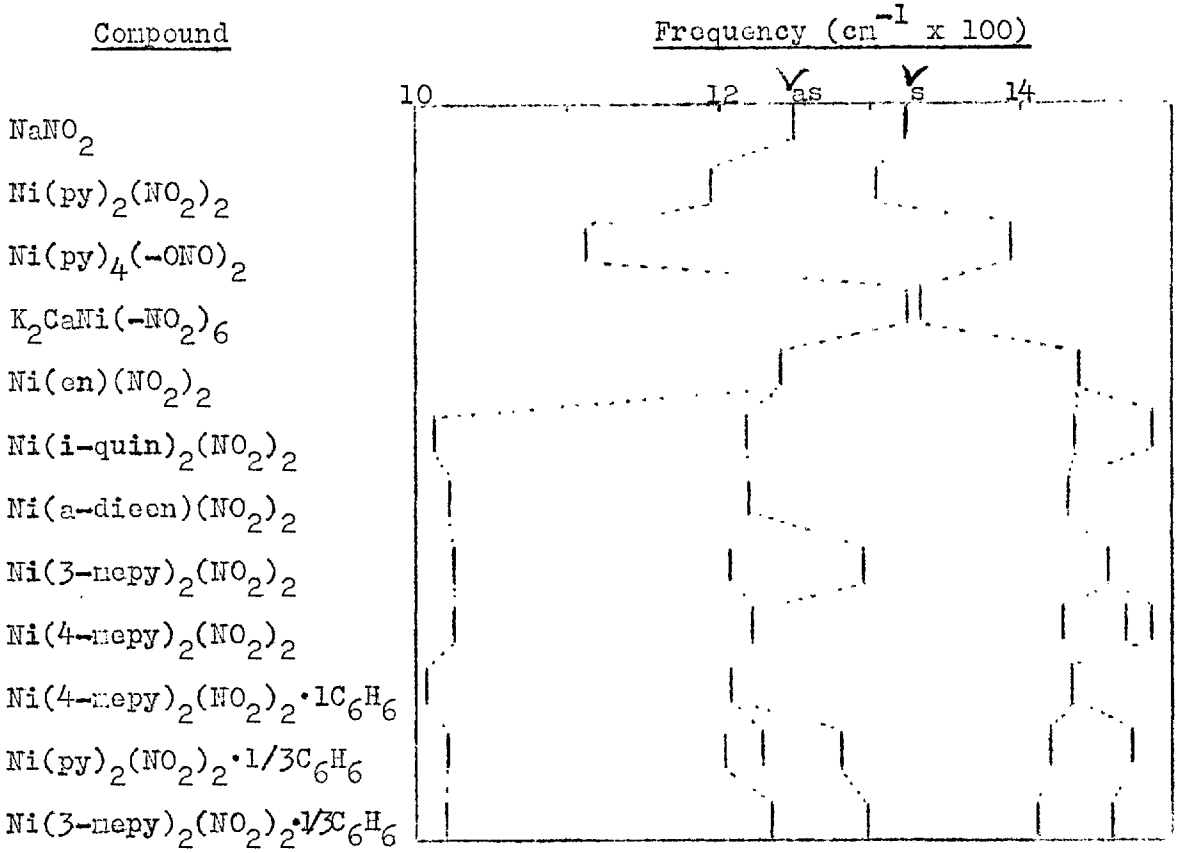
The nitrite infrared spectra of the compounds listed in Table 24 are rather complicated. The sharp bands in the region 800 - 900 cm^{-1} may be assigned as δ_{NO_2}. The other bands may be attributed to the nitrite nitrogen-oxygen stretching frequencies, and Figure 18 compares the values of ν_s and ν_{as} in these nickel nitrite complexes with the values found for nitrite groups coordinated in several different ways.

Each of the compounds in Table 24 has a very strong, broad band (ν_{as}) at ~1220 cm^{-1} and a strong band (ν_s) at ~1430 cm^{-1}, and these are very similar to those found for bridged(NO) nitrite groups in related compounds. The complexes $Ni(py)_2(NO_2)_2 \cdot 1/3C_6H_6$, $Ni(3\text{-mepy})_2(NO_2)_2 \cdot 1/3C_6H_6$ and $Ni(3\text{-mepy})_2(NO_2)_2$ also have a medium peak (ν_s) at ~1290 cm^{-1} and this, together with the broad band (ν_{as}) at ~1220 cm^{-1}, is characteristic of nitrite groups bonded via two oxygen atoms, probably by chelation. The compounds $Ni(i\text{-quin})_2(NO_2)_2$, $Ni(a\text{-dieen})(NO_2)_2$, $Ni(4\text{-mepy})_2(NO_2)_2$ and $Ni(4\text{-mepy})_2(NO_2)_2 \cdot 1C_6H_6$ all have amine bands at ~1300 cm^{-1}, so that it is impossible to tell from their infrared spectra whether they contain chelated nitrite groups or not.

In addition to the frequencies mentioned above, all of the complexes listed in Table 24 have a very strong band (ν_{as}) at ~1020 cm^{-1} and most of them also have a strong peak (ν_s) at

Figure 18

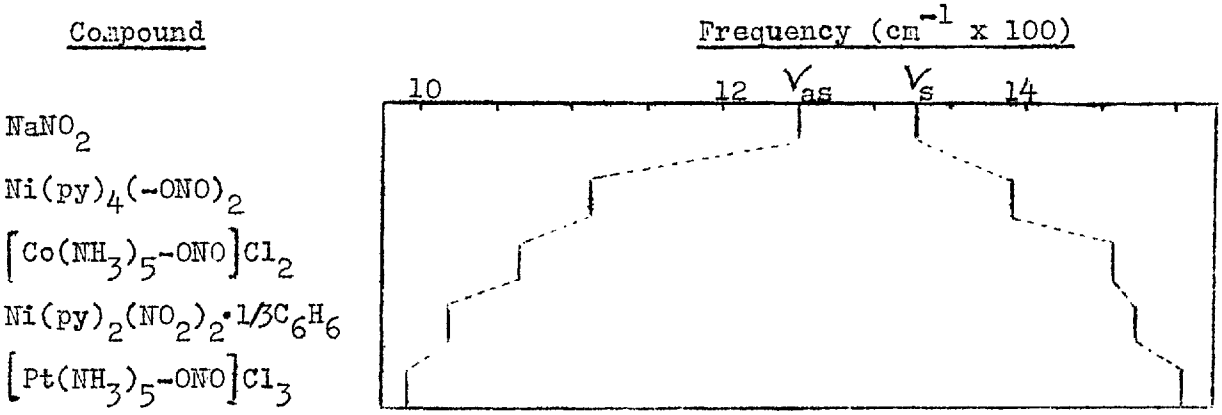
A comparison of ν_s and ν_{as} for some nitrito complexes



~1475 cm^{-1} (in the compounds $Ni(a\text{-dieen}(NO_2)_2$, $Ni(3\text{-mepy})_2(NO_2)_2$ and $Ni(4\text{-mepy})_2(NO_2)_2 \cdot 1C_6H_6$ the presence of amine or benzene bands at ~ 1475 cm^{-1} makes the unambiguous identification of a nitrite band in this region impossible.) These two frequencies are quite different from those observed for the bidentate nitrite groups already mentioned, particularly in the low value of ν_{as} at ~ 1020 cm^{-1}. In fact the bands at ~ 1020 and ~ 1475 cm^{-1} are rather similar to those found for monodentate nitrito-groups (Figure 19). However, since the magnetic moments and electronic

Figure 19

A comparison of ν_s and ν_{as} in some nitrite complexes.



spectra suggest that each nickel ion in the complexes listed in Table 24 is six-coordinate, each nitrite group is presumably two-coordinate. The only two-coordinate nitrite bonding likely to have infrared frequencies similar to those of a monodentate nitrito-group is bridging via a single oxygen atom.

The magnitude of the divergence of ν_{as} and ν_{s} from their free ion values is also in accordance with this manner of nitrite bonding. The effect on the nitrite infrared spectrum of two nickel ions attached to a single oxygen atom of a nitrite group should be considerably greater than that produced when one nickel ion is so bonded. It is apparent (Figure 19) that this is the case with the complexes in Table 24, and the frequencies at ~1020 and ~1475 cm^{-1} lie between those observed for monodentate nitrito-groups coordinated to Co^{III} and Pt^{IV}.

Electronic spectra and Discussion

The electronic spectra of the complexes (Table 25) closely

Table 25

Reflectance spectra of some complexes containing bridged(O) nitrite groups.

Compound	Band Maxima (cm^{-1})		
$Ni(i\text{-quin})_2(NO_2)_2$	20,900	17,200	11,000br[a]
$Ni(3\text{-mepy})_2(NO_2)_2$	20,500	17,400	10,650br[a]
$Ni(4\text{-mepy})_2(NO_2)_2$	20,750	17,400	10,650br[a]
$Ni(a\text{-dieen})(NO_2)_2$	20,900	17,400	11,070
$Ni(py)_2(NO_2)_2 \cdot 1/3C_6H_6$	20,700	17,200	10,600br[a]
$Ni(3\text{-mepy})_2(NO_2)_2 \cdot 1/3C_6H_6$	20,600	17,400	10,600br[a]
$Ni(4\text{-mepy})_2(NO_2)_2 \cdot 1C_6H_6$	20,800	17,100	10,600br[a]

a band assymmetric to lower energy

resemble that of $Ni(NH_3)_2(NO_2)_2$ (Figure 17) and the discussion of the spectrum of this compound also applies to the complexes listed in Table 25. The reflectance spectra of $Ni(py)_2(NO_2)_2 \cdot 1/3C_6H_6$ and $Ni(a\text{-dieen})(NO_2)_2$ are shown in Figure 17.

The electronic spectrum of each of the complexes in Table 25 thus apparently consists of the superimposition of the spectra of two types of six-coordinate nickel ion, one in a relatively weak ligand field produced by anions bonded via oxygen atoms, and the other in a strong ligand field and coordinated to bridged(NO) nitrite groups. The infrared spectra suggest that bridged(NO), bridged(O) and probably also chelated nitrite groups are present in these compounds. These three types of anion coordination could provide the two sorts of nickel environment in several different ways, and on the present data it is impossible to distinguish between these alternatives. A structure which would explain the observed electronic and infrared spectra would be 'sheets' of $NiL_2(NO_2)_2$ molecules connected by the two sorts of bridging nitrite groups, interspersed with layers of discrete $NiL_2(NO_2)_2$ molecules having chelating nitrite groups. It must be emphasised, though, that this is only one of several possible structures and it should be noted that $Ni(a\text{-dieen})(NO_2)_2$, having a chelating diamine, probably could not adopt such a 'layer' configuration.

It is hardly surprising that the compounds $Ni(py)_2(NO_2)_2 \cdot 1/3C_6H_6$,

$Ni(3\text{-mepy})_2(NO_2)_2 \cdot 1/3C_6H_6$ and $Ni(4\text{-mepy})_2(NO_2)_2 \cdot 1C_6H_6$ should contain clathrated benzene, considering the loose, polymeric structures envisaged for these complexes, and the similarity in size and shape between benzene and the heterocyclic amines. The compounds $Ni(py)_4(ClO_4)_2$ and $Ni(4\text{-}\underline{i}\text{-propylpyridine})_4(ClO_4)_2$ have also been found to contain clathrated benzene on crystallisation from this solvent[90]. In the nitrite complexes, the benzene molecules apparently contribute quite significantly to the lattice energy, since the compounds $NiL_2(NO_2)_2$ [L = py, 3-mepy and 4-mepy] could not be prepared from other solvents, and the benzene in $Ni(3\text{-mepy})_2(NO_2)_2 \cdot 1/3C_6H_6$ could not be removed without the complete decomposition of the complex (see preparative section). Similarly, the benzene in $Ni(py)_4(ClO_4) \cdot x$benzene is reported to be strongly held, and solvent molecules are not clathrated on crystallisation of $Ni(4\text{-}\underline{i}\text{-propylpyridine})_4(ClO_4)_2$ from acetone, cyclohexane and chloroform[90].

Since bridged(O) nitrite groups only occur in conjunction with nitrite groups bonded in other ways, any correlation between this manner of nitrite coordination and the nature of the other ligands present is impossible. However, it may be noted that the complexes $NiL_2(NO_2)_2$ [L = 3-mepy, 4-mepy and i-quin], $NiL_2(NO_2)_2 \cdot xC_6H_6$ [L = py, 3-mepy and 4-mepy] and $Ni(a\text{-dieen})(NO_2)_2$ which all contain bridged(O), bridged(NO) and probably also chelated nitrite groups, are formed with amines which give stable nitrito-

complexes $NiL_4(-ONO)_2$ or Ni(diamine)$(-ONO)_2$. It seems likely that the anion-amine steric interference in the above complexes $NiL_2(NO_2)_2$ and Ni(a-dieen)$(NO_2)_2$ is large enough to preclude the presence of only bridged(NO) nitrite groups (such as occur in Ni(en)$(NO_2)_2$), but is not large enough to prevent all nitrite bridging from taking place. Structures are thus adopted in which several different modes of anion coordination occur in the same lattice.

A preliminary x-ray investigation of Ni(3-mepy)$_2(NO_2)_2 \cdot 1/3C_6H_6$ confirms the effective molecular weight of this compound[91]. Although the refinement of the structure is still at a very early stage, the two-dimensional Patterson projections show strong nickel-nickel vectors at a distance of ~3·7 Å. This is in good agreement with the presence of bridged(O) nitrite groups in the complex, since these would require a nickel-nickel distance of about this value.

Preparation of compounds and analysis details

Ni(a-dieen)$(NO_2)_2$ The complex Ni(a-dieen)$_2(-ONO)_2$ was heated in a drying pistol at 116° to constant weight to yield a grey powder. weight loss calculated 30·34%, found 30·38%. analysis:- calc. C, 27·00; H, 6·04; N, 20·99.

found C, 27·18; H, 6·30; N, 20·91.

Ni(i-quin)$_2(NO_2)_2$ This was prepared as a grey solid (sample a)

by heating finely powdered $Ni(i\text{-quin})_4(NO_2)_2$ in a drying pistol to constant weight at 115° (~six hours).
weight loss calculated 38·37%, found 38·72%.

The compound $Ni(i\text{-quin})_2(NO_2)_2$ was also prepared as a grey-brown crystalline precipitate (sample b) by adding i-quinoline (0·015 M) in methanol (5 ml.) to nickel nitrite solution[64] (0·01 M).

The two samples had identical infrared and electronic spectra.
analysis:- sample a) calc. N, 13·71; O, 15·65; NO_2^-, 22·50.
found N, 13·92; O, 15·79; NO_2^-, 22·60.
sample b) calc. C, 52·86; H, 3·45; NO_2^-, 22·50.
found C, 52·88; H, 3·70; NO_2^-, 22·68.

$Ni(3\text{-mepy})_2(NO_2)_2$ A grey powder by heating $Ni(3\text{-mepy})_4(\text{-ONO})_2$ in a drying pistol at 90°.
weight loss calculated 35·60%, found 35·49%.
analysis:- calc. C, 42·77; H, 4·19; Ni, 17·42; NO_2^-, 27·31.
found C, 42·80; H, 4·37; Ni, 17·34; NO_2^-, 27·25.

$Ni(4\text{-mepy})_2(NO_2)_2$ A grey powder by the method used for the previous compound.
weight loss calculated 35·60%, found 35·32%.
analysis:- calc. C, 42·77; H, 4·19; Ni, 17·42; NO_2^-, 27·31.
found C, 43·07; H, 4·41; Ni, 17·70; NO_2^-, 27·00.

$Ni(py)_2(NO_2)_2 \cdot 1/3C_6H_6$ A mixture of $Ni(py)_4(\text{-ONO})_2$ (½g.) and $Ni(py)_2(NO_2)_2$ (½g.) was boiled in benzene (50 ml.) for two

minutes and the bright green solution was filtered and stoppered to prevent atmospheric oxidation of the nitrite ion. After several days large black crystals formed and these were filtered off, washed with benzene and dried quickly in vacuo.

yield 30%

analysis:- calc. C, 43·03; H, 3·61; N, 16·73; Ni, 17·53; NO_2^-, 27·48.

found C, 43·00; H, 3·52; N, 16·66; Ni, 17·80; NO_2^-, 27·50.

$Ni(3\text{-mepy})_2(NO_2)_2 \cdot 1/3C_6H_6$ The compound $Ni(3\text{-mepy})_4(\text{-ONO})_2$ (1g.) was dissolved in boiling benzene (200 ml.) and the green solution was filtered and left, stoppered for three days, when large black crystals formed.

yield 70%

analysis:- calc. C, 46·31; H, 4·44; N, 15·44; O, 17·63; Ni, 16·17; NO_2^-, 25·35.

found C, 46·72; H, 4·70; N, 15·50; O, 17·93; Ni, 15·99; NO_2^-, 25·48.

$Ni(4\text{-mepy})_2(NO_2)_2 \cdot 1C_6H_6$ The compound $Ni(4\text{-mepy})_4(\text{-ONO})_2$, (1g.) was dissolved in boiling benzene (150 ml.) and the solution was filtered, stoppered and left for three days when large black crystals formed.

yield 70%

analysis:- calc. C, 52·10; H,4·86; N, 13·50; O, 15·42; NO_2^-, 22·17.

found C, 52·05; H, 5·11; N, 13·52; O, 15·36; NO_2^-, 21·80.

Attempts were made to prepare compounds of stoichiometry $NiL_2(NO_2)_2$ from solutions of $Ni(py)_4(-ONO)_2$ and $Ni(3\text{-mepy})_4(-ONO)_2$ in acetone, ethylacetate and chloroform, but these were unsuccessful, producing only the starting material on slow evaporation of the solvent. The preparations of $Ni(a\text{-dieen})(NO_2)_2$, $Ni(s\text{-dieen})(NO_2)_2$, $Ni(a\text{-dimen})(NO_2)_2$, $Ni(py)_2(NO_2)_2$ and $Ni(3\text{-mepy})_2(NO_2)_2$ were all attempted by mixing dry, methanolic solutions of nickel nitrite[64] with an appropriate quantity of each amine. However, on slow evaporation of the solvent basic compounds were formed in each case.

The thermal decomposition of $Ni(3\text{-mepy})_2(NO_2)_2 \cdot 1/3C_6H_6$ was studied, but the compound was found to lose weight gradually at 80°, and no phase corresponding to $Ni(3\text{-mepy})_2(NO_2)_2$ was observed.

CHAPTER 6

Some Compounds Containing Anions of the Type $M(NO_2)_6^{4-}$, $M(NO_2)_5^{3-}$ and $M(NO_2)_3^{-}$

Hexanitrocomplexes

Compounds of the type $CC'_2\,M(NO_2)_6$, where C and C' are cations and M represents one of a number of first and second row transition metal ions, have been known for many years. From an extensive study of their x-ray powder patterns Ferrari and his co-workers found[11] that most of these compounds (including those in which M = Co^{II}, Ni^{II}, Fe^{II} and Cu^{II}) have very similar crystal structures in which the metal ions M are surrounded by six octahedrally coordinated nitro-groups. Although the infrared spectra of numerous hexanitrocomplexes have been reported[39,40,92], and detailed band assignments have been made on several compounds containing the ion $Co(-NO_2)_6^{3-}$ [37,41,93] the infrared spectra of ions of the type $M(-NO_2)_6^{4-}$ have been much less well characterised.

During the present investigations the buff-coloured $K_2BaNi(NO_2)_6$, yellow brown $Na_2CaNi(NO_2)_6$, green $K_2SrCu(NO_2)_6$ and green $K_2BaCo(NO_2)_6$ were prepared, all from aqueous solution. With the exception of the copper complex which decomposed within a few weeks, evolving nitrogen dioxide, the compounds were quite stable and only $Na_2CaNi(NO_2)_6$ and $K_2SrCu(NO_2)_6$ had not been described previously.

Infrared spectra The spectra of the four compounds were recorded in the range 2000 - 200 cm^{-1} and those of $K_2BaM(NO_2)_6$ [M = Co and Ni] are shown in Figure 20, together with that of $Rb_3Co(NO_2)_6$ for comparison.

The spectra will be considered in two sections: -

a) the vibrational frequencies of the nitrite groups (2000 - 800 cm^{-1})

b) the vibrational frequencies associated directly with the metal-nitrite bond (800 - 200 cm^{-1})

a) The nitrite infrared frequencies

Before discussing the infrared spectra of the compounds it is of value to recall the effects that nitrogen-coordination has on the nitrite infrared frequencies. In sodium nitrite ν_{as} occurs as a strong band at ~1250 cm^{-1} and ν_s as a weak, sharp peak at 1326 cm^{-1}. Coordination of the nitrite group via nitrogen raises ν_{as} (to ~1400 cm^{-1} in $Co(-NO_2)_6^{3-}$) while leaving ν_s at about its free ion value. The frequency δ_{NO_2} at ~830 cm^{-1} does not alter significantly on coordination and will not be considered further in this section.

The nitrite infrared frequencies for the compounds studied here are listed in Table 26(a), and the bands reported by Elliott, Hathaway and Slade[94] for the complexes $K_2BaM(NO_2)_6$ [M = Co and Ni] are shown in part (b) of this Table. The values found in the

FIGURE 20

The Infrared Spectra of:-

(A) $K_2BaNi(NO_2)_6$ (B) $K_2BaCo(NO_2)_6$ (C) $Rb_3Co(NO_2)_6$

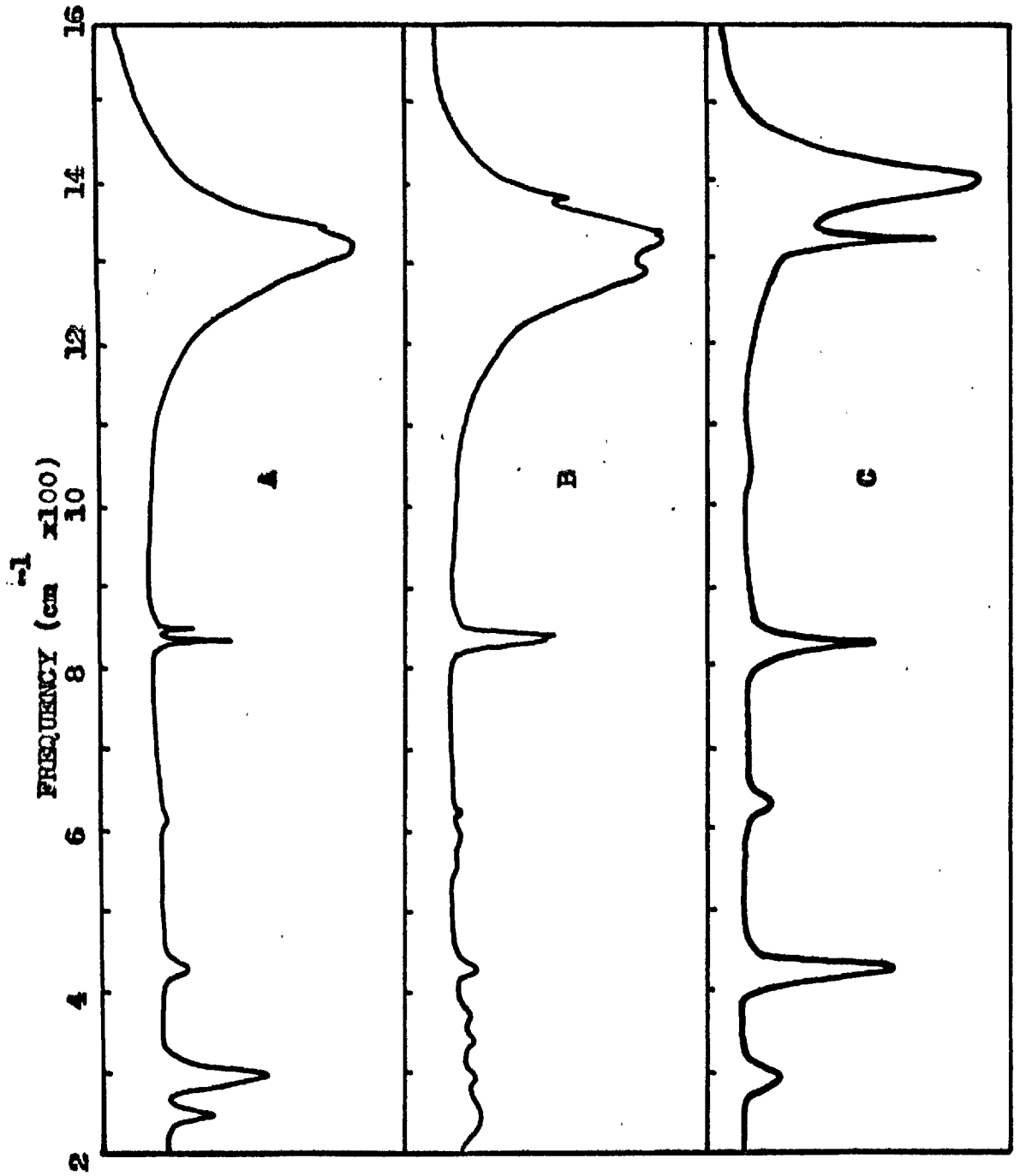


Table 26

a) The nitrite infrared frequencies (cm^{-1}) in some hexanitrocomplexes.

Compound[a]	ν_s	ν_{as}	δ_{NO_2}
$K_2BaNi(-NO_2)_6$	1348w sp	1312vs	840w , 820m
$Na_2CaNi(-NO_2)_6$	1332w sp	~1335vs	833m ,~830w sh
$K_2BaCo(-NO_2)_6$	1395m sp, 1335w sp	1321vs, 1282s	829sp, 825sh m
$K_2SrCu(-NO_2)_6$	1348sh sp	1335vs, 1280s	827m , 818m

a measured as nujol and hexachlorobutadiene mulls using KBr plates. The spectra were also measured using As_2S_3 disks in the region 1300 - 1400 cm^{-1} to ensure that no exchange with the KBr plates had occurred.

b) Nitrite infrared frequencies reported by Elliott et al.[94] for some hexanitrocomplexes.[a]

Compound	ν_s	ν_{as}	δ_{NO_2}
$K_2BaCo(-NO_2)_6$	1330s, 1292sh, 1250sh	1400s, 1650vw	830s
$K_2BaNi(-NO_2)_6$	1348s, 1341vs	1405m sh, 1640vw	836w, 810m sp

a it should be noted that the assignments of ν_s and ν_{as} reported by these workers are incorrect and should be reversed.

present studies will be considered first.

The nickel complexes each have one strong band and one sharp, weak peak in the region 1310 - 1350 cm^{-1}. From the relative intensities the strong band may be assigned as ν_{as} and the weak one as ν_s. In $Na_2CaNi(NO_2)_6$ these two frequencies almost coincide, ν_s occurring as a weak, sharp peak near the top of the broad intense band ν_{as}.

The infrared spectra of the cobalt and copper complexes are more complicated than those of the nickel ones. However, again from the relative intensity of the bands, it seems likely that in $K_2BaCo(NO_2)_6$ and $K_2SrCu(NO_2)_6$ the pair of bands at ~1280 and ~1330 cm^{-1} may be assigned as ν_{as}. In the cobalt complex two sharp peaks, at 1335 and 1395 cm^{-1}, due to ν_s were observed, while in $K_2SrCu(NO_2)_6$ only one peak, at 1348 cm^{-1}, assignable to ν_s could be resolved.

Thus in each of the complexes ν_{as} is raised from its free ion value, while ν_s occurs as a weak, sharp peak generally not far from its position in the uncoordinated ion. This is consistent with the formulation of the compounds as nitrocomplexes.

During the preparation of this thesis Elliott et al. published the infrared spectra of a number of compounds containing the hexanitro-ions of Co^{II}, Cu^{II}, Ni^{II} and Fe^{II} [94]. The nitrite bands and their assignments which they report for $K_2BaM(-NO_2)_6$ [M = Ni and Co] are listed in Table 26(b). It should be noted

that these authors have incorrectly reversed the assignments of ν_s and ν_{as} in free NO_2^-. This presumably means that these assignments should also be reversed in the complexes they have studied. There is generally poor agreement between the bands observed by Elliott et al. and those found by this author. It seems most unlikely that the assignments of the very weak peaks at ~1640 cm^{-1} as nitrite fundamental vibrations by Elliott et al. is correct. These peaks are probably due to a small amount of lattice water. Weak bands were also sometimes observed in this region in the present investigations, but these disappeared on drying the samples in vacuo at ~100°. No explanation can be offered, however, for the other differences between the values listed in Table 26(a) and (b).

It is interesting to speculate on the cause of the doubling of the frequency ν_{as} in the compounds $K_2BaCo(-NO_2)_6$ and $K_2SrCu(-NO_2)_6$. In previous Chapters it was shown that in nitritocomplexes the magnitude of the change in ν_{as} and ν_s from their free ion values was related to the strength of the metal-nitrite bond. A similar effect is also to be expected in nitrocomplexes, as has been noted by Nakamoto[95], and this would explain why ν_{as} occurs at ~1400 cm^{-1} in $Co(-NO_2)_6^{3-}$, ~1320 cm^{-1} in $Ni(-NO_2)_6^{4-}$ and ~1250 cm^{-1} in uncoordinated NO_2^-. The occurrence of <u>two</u> frequencies ν_{as} in $K_2SrCu(-NO_2)_6$ and $K_2BaCo(-NO_2)_6$, one at a value similar to that in $Ni(-NO_2)_6^{4-}$, and one nearer to that of the free ion is

in accordance with distorted, tetragonal structures for the cobalt and copper complexes. The bands at ~1330 cm^{-1} would be due to relatively strongly bonded nitro-groups, while those at ~1280 cm^{-1} would be associated with more weakly bound nitrite groups. Complexes of Cu^{II} and spin-paired Co^{II} often have tetragonal configurations and these distortions are usually explained in terms of the Jahn-Teller theorem[96]. It must, however, be noted that the doubling of ν_{as} in $K_2SrCu(-NO_2)_6$ and $K_2BaCo(-NO_2)_6$ does not necessarily show the existance of two types of metal-nitrite bond. It could also be caused if the $M(-NO_2)_6^{4-}$ ions have a regular octahedral configuration, but occupy a crystal site of low symmetry. The $Co(-NO_2)_6^{4-}$ ion is known to occupy a site of symmetry S_6 in $K_2BaCo(NO_2)_6$ [97], and this should split both ν_{as} and ν_s into two frequencies[37]. It is, however, unlikely that this effect would be large. The ion $Ni(-NO_2)_6^{4-}$ has a site symmetry of C_{3i} in $K_4Ni(-NO_2)_6 \cdot 1H_2O$, from which both ν_{as} and ν_s should be split into two frequencies[40]. No such splitting is observed in practise, though (Figure 24). The structures of $K_2SrCu(-NO_2)_6$ and $K_2BaCo(-NO_2)_6$ will be discussed in connection with the crystallographic information reported on these compounds in the section on electronic spectra.

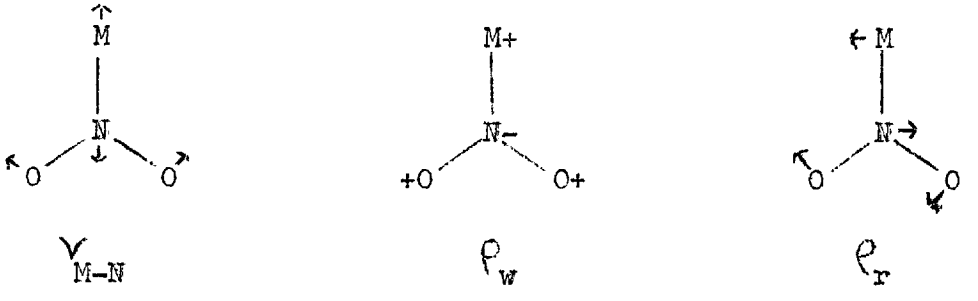
b) Vibrations associated directly with the metal-nitrite bond

If the planar group M - NO_2 is considered in isolation, it

has six normal vibrational modes. Three of these approximate to ν_s, ν_{as} and δ_{NO_2}, of uncoordinated NO_2^-. The other three are illustrated in Figure 21 and may be designated ν_{M-N}, the metal-

Figure 21

Diagram of the stretching, wagging and rocking vibrations associated directly with the $M-NO_2$ group.



nitrogen stretch and ρ_w and ρ_r which are wagging and rocking modes.

In a polynitro-ion of the type $M(-NO_2)_6^{4-}$ the vibrations will be more complicated. However, it is still to be expected that three sets of bands corresponding essentially to the vibrations ν_{M-N}, ρ_w and ρ_r illustrated above will be observed.

The infrared spectra of the complexes were measured in the range 800 - 200 cm^{-1} and the bands observed are listed in Table 27 (a) together with the proposed assignments. The bands in this region and their assignments, reported by Elliott et al. for the compounds $K_2BaM(-NO_2)_6$ [M = Co and Ni] are shown in Table 27(b). There is

Table 27

a) Infrared bands (cm^{-1}) in the region 800 - 200 cm^{-1} in some hexanitrocomplexes.

Compound	ν_{M-N}	ρ_w	ρ_r	Unassigned Bands
$K_2BaNi(-NO_2)_6$	293s	433w	259m[a]	610vw
$Na_2CaNi(-NO_2)_6$	280m	460m	252w[a]	
$K_2BaCo(-NO_2)_6$	323sh[a], 290w[a]	415m[a], 369w[a]	250br[a]	631w, 599vw, 565ws
$K_2SrCu(-NO_2)_6$	294m	460w	255w sh[a], 208w[a]	617vw

a assignment uncertain. See text for a discussion of this band.

b) The infrared bands and assignments reported by Elliott et al.[94] for some hexanitrocomplexes in the region 800 - 200 cm^{-1}.

Compound	ν_{M-N}	ρ_r
$K_2BaCo(-NO_2)_6$	418m, 384w	326w, 293s
$K_2BaNi(-NO_2)_6$	435w	296s, 288s

fairly good agreement between the values found by these authors and those observed in the present work, except that in $K_2BaNi(-NO_2)_6$ Elliott et al. observed a band at 288 cm^{-1}, while this band occurred at 259 cm^{-1} in the sample studied here. It may also be noted that the spectra of $K_2BaM(-NO_2)_6$ [M = Co and Ni] reported in this work showed very weak bands at ~600 cm^{-1}. Although

Elliott et al. do not describe similar peaks in their samples of $K_2BaCo(-NO_2)_6$ and $K_2BaNi(-NO_2)_6$, they do report weak or very weak bands in this region for most of the compounds containing the ions $M(-NO_2)_6^{4-}$ [M = Co, Fe and Cu] which they studied. The band assignments in the present work, however, are quite different from those made by Elliott et al. and the reasons for this will now be discussed.

In the assignment of infrared frequencies in this region the comparison of spectra with those of compounds for which complete band assignments have been made is often very useful. The infrared spectrum of $Rb_3Co(-NO_2)_6$ is shown in Figure 20. The ion $Co(-NO_2)_6^{3-}$ has been studied by several workers and there is general agreement on the following band assignments: -

$$\rho_w \sim 630\ cm^{-1}, \qquad \nu_{M-N} \sim 420\ cm^{-1}, \quad \rho_r\ 250 - 290\ cm^{-1}$$

A normal coordinate analysis has been made on the planar nitro-complex $K_2Pt(-NO_2)_4$ by Nakamoto et al.[29], and this has recently been revised by Postollec, Mathieu and Poulet[39]. The latter workers give the following assignments: -

$$\rho_w\ 610,\ 633\ cm^{-1}, \quad \nu_{M-N}\ 357,\ 377\ cm^{-1}, \quad \rho_r\ 270,-\ 300\ cm^{-1}$$

On the basis of the values for $Co(-NO_2)_6^{3-}$ Elliott et al, made the following band assignments for the ions $M(-NO_2)_6^{4-}$ M = Co, Ni, Cu and Fe : -

$$\rho_w\ 470 - 650\ cm^{-1}, \quad \nu_{M-N}\ 350 - 450\ cm^{-1}, \quad \rho_r\ 270 - 320\ cm^{-1}$$

While at first sight these assignments look quite reasonable,

they do not account for the important fact that the metal-ligand vibrations (particularly the stretches) are expected to be considerably lower in complexes of divalent metal ion such as Ni^{II} than in those of Co^{III}. It is a little difficult to predict exactly where ν_{M-N} should come in the spin-paired ions $Co(-NO_2)_6^{4-}$ and $Fe(-NO_2)_6^{4-}$. However, both $Fe(-NO_2)_6^{4-}$ and $Co(-NO_2)_6^{3-}$ have spin-paired d^6 electron configurations, so that on purely electrostatic grounds, the metal-ligand stretching frequencies should be lower in the iron complex.

In considering the region in which ν_{M-N} is to be expected in the ions $M(-NO_2)_6^{4-}$, it is of interest to compare the metal-nitrogen stretching frequencies in the complex ions $Ni(NH_3)_6^{2+}$, $Co(NH_3)_6^{3+}$, spin-free $Co(NH_3)_6^{2+}$ and $Pt(NH_3)_4^{2+}$. The generally accepted values of these are shown in Table 28. It is apparent

Table 28

Some metal-nitrogen stretching frequencies (cm^{-1}).

Compound	ν_{M-N}	Ref.
$[N(CH_3)_4]_4Ni(-NCS)_6$	245	98
$[N(CH_3)_4]_3Cr(-NCS)_6$	364	98
$Ni(NH_3)_6Cl_2$	334	99
$Co(NH_3)_6Cl_2$	318	100
$Co(NH_3)_6Cl_3$	500, 476, 448	99
$Pt(NH_3)_4Cl_2 \cdot H_2O$	497	101

that on going from $Co(NH_3)_6^{3+}$ and $Pt(NH_3)_4^{2+}$ to $Ni(NH_3)_6^{2+}$ and $Co(NH_3)_6^{2+}$(spin free) there is a drop in ν_{M-N} of some 30%. Similarly ν_{M-N} is considerably lower in $Ni(-NCS)_6^{4-}$ than in $Cr(-NCS)_6^{3-}$. Assuming that an analogous reduction occurs on going from $Co(-NO_2)_6^{3-}$ and $Pt(-NO_2)_4^{2-}$ to $Ni(-NO_2)_6^{4-}$, the frequency ν_{M-N} is to be expected at ~270 cm^{-1} in $Ni(-NO_2)_6^{4-}$. Since a strong band occurs at ~290 cm^{-1} in all of the complexes listed in Table 27(a), this has in each case been assigned as ν_{M-N}. However, so many bands occur in the region 415 - 200 cm^{-1} in the infrared spectrum of $K_2BaCo(-NO_2)_6$, that the <u>definite</u> assignment of any of these as ν_{M-N}, ρ_w or ρ_r is impossible. Considering that ν_{as} and ν_s are also split in this compound, the 'richness' of the infrared spectrum of $K_2BaCo(-NO_2)_6$ in the region 800 - 200 cm^{-1} is hardly surprising. It is also likely that ν_{M-N} is split in $K_2SrCu(-NO_2)_6$, and possible that it is split in the two nickel complexes, as will be discussed later. Nevertheless, in all the compounds containing ions of the type $M(-NO_2)_6^{4-}$ described here it seems highly probable that ν_{M-N} occurs at ~290 cm^{-1} and not as stated by Elliott et al. at ~400 cm^{-1}.

Having assigned ν_{M-N} to the relatively strong bands at ~290 cm^{-1}, the question of the assignments of ρ_w and ρ_r remains. The infrared spectra of $K_2BaNi(-NO_2)_6$, $Na_2CaNi(-NO_2)_6$ and $K_2SrCu(-NO_2)_6$ each show a medium or weak band at ~250 cm^{-1}, and a weak

or medium band at ~450 cm^{-1}. The spectra of $K_2BaNi(-NO_2)_6$, $K_2BaCo(-NO_2)_6$ and $K_2SrCu(-NO_2)_6$ also show very weak bands at ~610 cm^{-1}. The bands at ~450 cm^{-1} are here assigned as ρ_w. This is in agreement with Nakamoto et al.[29] who have assigned ρ_w at 462 cm^{-1} in $K_2CaNi(-NO_2)_6$, and Postollec et al.[39] who have assigned ρ_w at 430 cm^{-1} in $K_4Ni(NO_2)_6 \cdot 1H_2O$. The very weak bands at ~610 cm^{-1} assigned by Elliott et al. as ρ_w are not assigned as fundamental vibrations in this work.

The remaining bands at ~250 cm^{-1} are tentatively assigned as ρ_r. However, it is also possible that they are due to components of the vibration ν_{M-N}. This frequency is triply degenerate in the symmetry T_h expected for a regular $M(-NO_2)_6^{4-}$ ion, but twisting of the $-NO_2$ groups can cause a lowering of the symmetry to S_6 and this gives two frequencies ν_{M-N}. (For a discussion of the number of bands predicted for the $M(-NO_2)_6^{n-}$ ion in different symmetries see reference 37.) It seems highly probable that ν_{M-N} will be split in the apparently distorted compounds $K_2SrCu(-NO_2)_6$ and $K_2BaCo(-NO_2)_6$, and the bands in the region 270 - 200 cm^{-1} in these compounds are probably due both to ν_{M-N} and ρ_r.

Electronic spectra and Discussion

The band maxima in the reflectance spectra of the compounds are listed in Table 29, together with those reported by Elliott

Table 29

The electronic reflectance spectra of some hexanitrocomplexes.

Compound	Band Maxima (cm^{-1})			Ref.
$K_2SrCu(-NO_2)_6$	22,700	16,300	7,600	a
$K_2BaCo(-NO_2)_6$	23,000	15,700	7,350	a
	23,530	15,920	7,140	94
$K_2BaNi(-NO_2)_6$	20,620	13,750		a
	20,660	13,590,	10,990sh[b]	94
$Na_2CaNi(-NO_2)_6$	21,500	13,800,	11,300sh[b]	a

a this work

b weak band assigned as a spin-forbidden transition

et al. for $K_2BaM(-NO_2)_6$ [M = Co and Ni].

Nickel complexes.

The strong bands at ~13,800 and ~21,000 cm^{-1} observed in the two compounds containing $Ni(-NO_2)_6^{4-}$ may be assigned as the transitions $^3A_{2g} \longrightarrow {}^3T_{2g}$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ of spin-free Ni^{II} in an octahedral ligand environment, and suggest a Δ-value of ~13,400 cm^{-1} for six nitro-groups around nickel(II).

The very weak shoulder at 11,300 cm^{-1} in $Na_2CaNi(-NO_2)_6$ is probably due to the spin-forbidden transition $^3A_{2g} \longrightarrow {}^1Eg$.

Cobalt and copper complexes

The reflectance spectra of $K_2BaCo(-NO_2)_6$ (Figure 21) and $K_2SrCu(-NO_2)_6$ are very similar. The bands at ~ 7,500 and ~ 16,000 cm^{-1} may reasonably be assigned to d-d transitions. The peaks at ~ 23,000 cm^{-1} could, however, either be d-d in origin or due to some form of charge transfer. Since none of the compounds $K_3Cu(NO_2)_5$ [102], $(o\text{-}Cat^{2+})Cu(NO_2)_4$ and $(o\text{-}Cat^{2+})Co(NO_2)_4$ (see Chapter 7) have bands in this region, it seems unlikely that the peaks at ~ 23,00 cm^{-1} in the hexanitro-cobalt and copper complexes are due to charge transfer. Nevertheless, this possibility cannot be entirely ruled out, since the nature of the metal-nitrite bonding in the tetra-, penta- and hexanitrite-complexes of Cu^{II} is different, and the electronic ground states of the Co^{II} ions in $Co(NO_2)_4^{2-}$ and $Co(-NO_2)_6^{4-}$ are not the same.

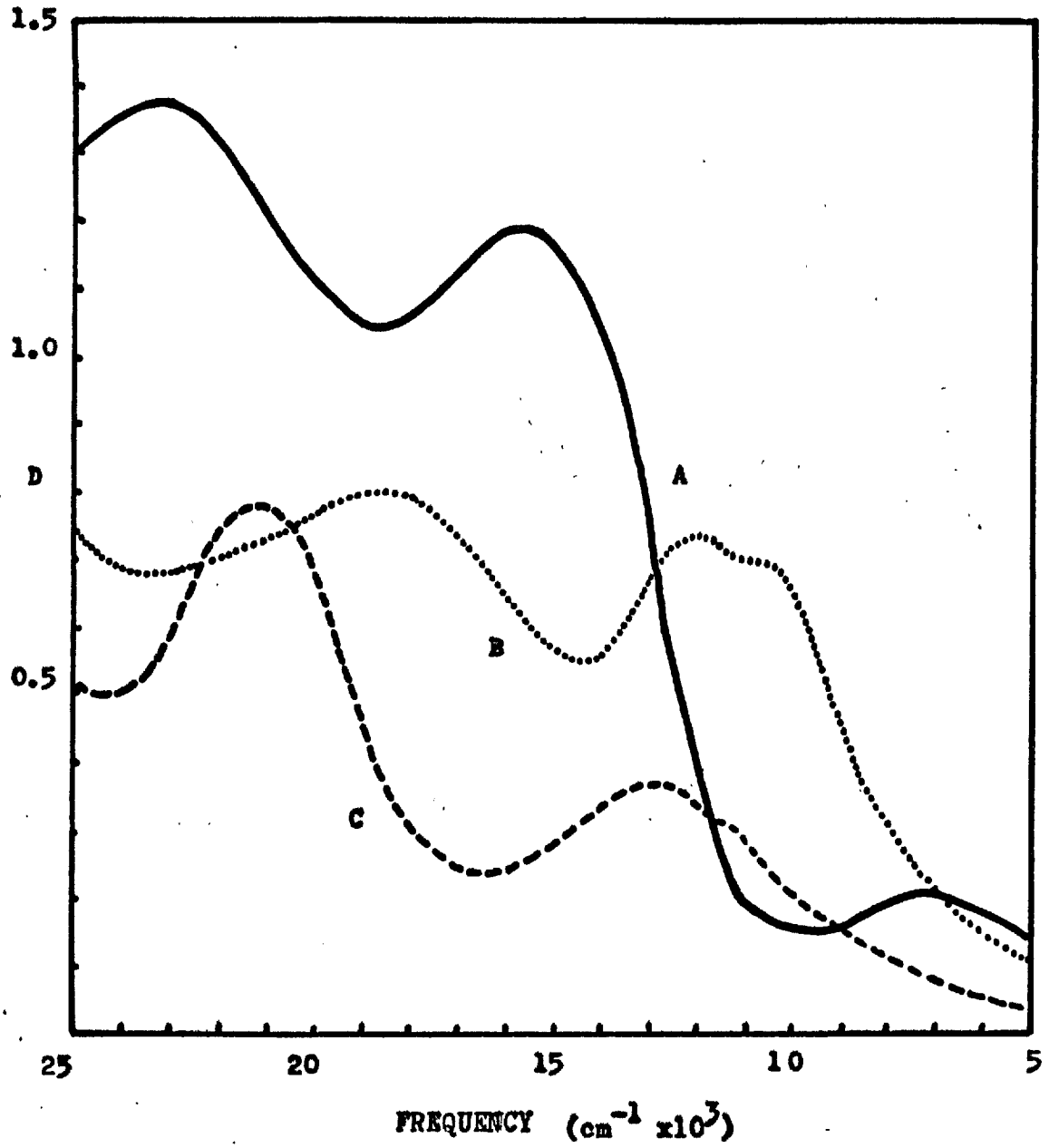
Since only a single, spin-allowed transition in the region 5 - 30,000 cm^{-1} is expected for Cu^{II} and spin-paired Co^{II} in O_h ligand field symmetry, the observation of two or possibly three bands for the hexanitrocomplexes suggests that they have distorted structures. If the bands at ~23,000 cm^{-1} are assigned as d-d bands, then the spectra of the ions $Co(-NO_2)_6^{4-}$ and $Cu(-NO_2)_6^{4-}$ can be explained in terms of a tetragonal structure in the following manner.

The ions are assumed to have four short and two long $M\text{-}NO_2$ bonds with the nitro-groups acting as π-acceptors. Spin-orbit

FIGURE 21

Electronic Reflectance Spectra of:-

(A) $K_2BaCo(NO_2)_6$ (B) $Cs_3Ni(NO_2)_5$ (C) $N(CH_3)_4Ni(NO_2)_3$

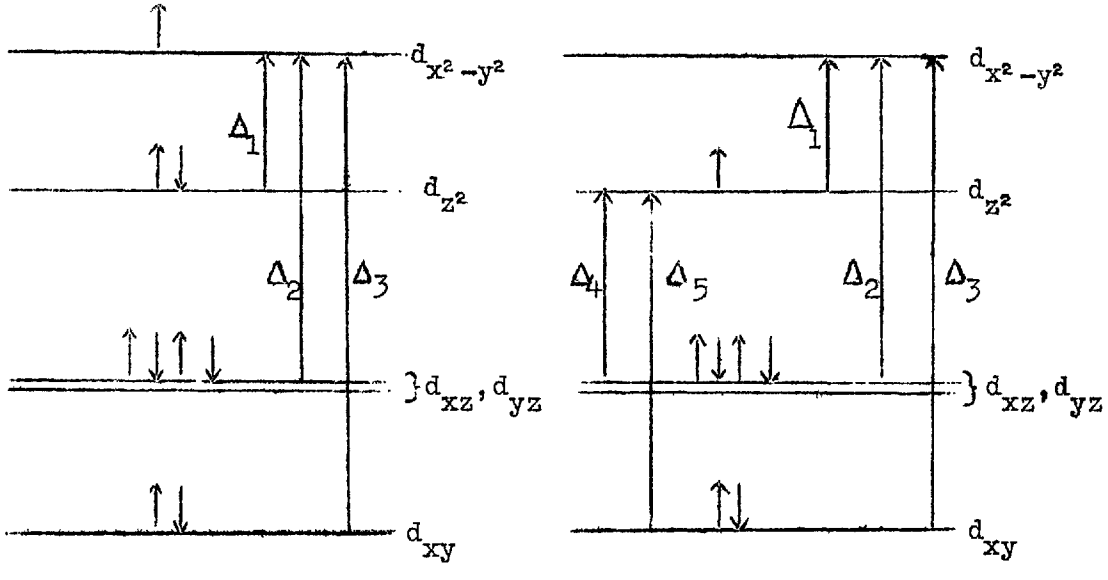


coupling is neglected. In the 'strong field' approach, which is applicable to hexanitrocomplexes, the electronic spectra may be considered in terms of transitions between the individual d-orbitals. The approximate ordering of the d-orbitals are shown in Figure 22.

Figure 22

The approximate ordering of the d-levels in

a) $Cu(-NO_2)_6$ b) $Co(-NO_2)_6$



The three bands in the spectrum of $K_2SrCu(-NO_2)_6$ are then assigned as Δ_1 = 7,600 cm^{-1}, Δ_2 = 16,300 cm^{-1} and Δ_3 = 22,700 cm^{-1}. The value of 10Dq is given approximately by $(2\Delta_2+\Delta_3)/3 - \Delta_1/2$ = 14,600 cm^{-1}, in fairly good agreement with the value

of 10Dq~13,800 cm^{-1} for six nitro-groups around Ni^{II}. The spectrum of $Co(-NO_2)_6^{4-}$ should then consist of three bands (due to Δ_1, Δ_2 and Δ_3) corresponding to the three transitions in $Cu(-NO_2)_6^{4-}$, plus two additional bands due to the transitions Δ_4 and Δ_5. The transition Δ_4 should occur at a wavelength equal to $\Delta_2 - \Delta_1$, and from the spectrum of $K_2SrCu(-NO_2)_6$ this is 16,300 - 7,600 = 8,700 cm^{-1}. Similarly, the transition $\Delta_5 = \Delta_3 - \Delta_1$ = 22,700 - 7,600 = 15,100 cm^{-1}. Thus the bands in the electronic spectrum of $K_2BaCo(-NO_2)_6$ can be assigned as follows. That at 7,350 cm^{-1}, which is somewhat broad, is a superimposition of the peaks due to the transitions Δ_1 and Δ_4, while the band at 15,700 cm^{-1} is due to the transitions Δ_2 and Δ_5. The peak at 23,000 cm^{-1} is due to the transition Δ_3. The similarity between the electronic spectra of $K_2BaCo(-NO_2)_6$ and $K_2SrCu(-NO_2)_6$ is thus purely fortuitous, and it is not generally to be expected that the electronic spectra of distorted, spin-paired Co^{II} complexes will resemble those of their Cu^{II} analogues.

It thus seems that the electronic and infrared spectra of $K_2BaCo(-NO_2)_6$ and $K_2SrCu(-NO_2)_6$ are in accordance with distorted, tetragonal structures for these compounds. While no crystallographic data appears to have been reported for $K_2SrCu(-NO_2)_6$, the x-ray powder patterns suggest[94] that the similar compounds $K_2CaCu(-NO_2)_6$ and $K_2BaCu(-NO_2)_6$ both have tetragonal structures. A three-dimensional x-ray determination of the structure of

$K_2BaCo(-NO_2)_6$ has shown[97] the $Co(-NO_2)_6^{4-}$ group to have an undistorted octahedral configuration. Since such a structure seems to be at variance with the electronic and infrared spectra of this compound, it is probable that the $Co(-NO_2)_6^{4-}$ ion undergoes a dynamic Jahn-Teller distortion in $K_2BaCo(-NO_2)_6$. This possibility has also been suggested by Bertrand and Carpenter [97] and Elliott et al.[94].

Preparation of compounds

$K_2BaNi(NO_2)_6$ An aqueous solution of potassium nitrite was added to one of nickel chloride (0·01 M) until the orange complex potassium nickel nitrite began to precipitate. Water was then added until the solid just redissolved. The resulting solution was filtered into an aqueous solution of barium chloride (0·01 M). A buff-coloured precipitate immediately formed. This was recrystallised from an aqueous solution of sodium nitrite (0·02 M). yield 25%

analysis:- calc. Ba, 24·95; NO_2^-, 50·17.

found Ba, 25·01; NO_2^-, 50·02.

$Na_2CaNi(NO_2)_6$ An aqueous solution of an equimolar mixture of nickel chloride and calcium chloride was added to an aqueous solution of excess sodium nitrite. On leaving the solution to evaporate slowly for several days a brown precipitate formed. This was recrystallised from water to give yellow-brown crystals.

yield 10%

analysis:- calc. Ca, 9·53; Ni, 13·92; NO_2^-, 65·63.

found Ca, 9·30; Ni, 13·46; NO_2^-, 64·10.

$K_2SrCu(NO_2)_6$ An aqueous solution of an equimolar mixture of copper chloride and strontium chloride was added to an aqueous solution of excess potassium nitrite. After a few seconds a dark green microcrystalline precipitate formed which was filtered off and washed with ice cold water. yield 50%

analysis:- calc. Cu, 12·56; NO_2^-, 54·64.

found Cu, 12·60; NO_2^-, 54·60.

$K_2BaCo(NO_2)_6$ Cobalt chloride (0·01 M) was dissolved in a little oxygen-free water and added to an aqueous, oxygen-free solution of potassium nitrite (0·02 M), barium nitrite (0·01 M) and sodium nitrite (0·05 M). After a few minutes a dark green microcrystalline precipitate formed which was filtered off under nitrogen, washed with a little water and dried in vacuo. Since the infrared spectrum showed the presence of a small amount of water, the compound was heated in vacuo at 95° to constant weight, after which the water infrared peaks almost disappeared.

yield 10%

analysis:- calc. Co, 10·70; NO_2^-, 50·12.

found Co, 10·55; NO_2^-, 50·19.

The compounds $K_4Ni(NO_2)_6 \cdot 1H_2O$ and $K_4Ni(NO_2)_6$

It has been known for over a hundred years that addition of

an aqueous solution of a nickel salt to an aqueous solution of excess potassium nitrite produces an orange crystalline precipitate[103]. In previous work this compound has always been formulated as $K_4Ni(NO_2)_6$ and as such its crystal structure has been investigated by Ferrari et al.[104] and its infrared spectrum was reported by Postollec et al.[39,40]. On the basis of two-dimensional x-ray data, Ferrari et al. proposed a tetragonal unit cell of dimensions a = 7·63 Å and c = 22·42 Å with z = 3 for this compound, and suggested that each nickel ion was octahedrally coordinated to six nitro-groups.

In the present work an orange crystalline precipitate was prepared by adding a concentrated aqueous solution of nickel bromide to excess, saturated aqueous potassium nitrite. Careful analysis of the compound showed it to have the formula $K_4Ni(NO_2)_6 \cdot 1H_2O$:-

calc. K, 30·71; Ni, 11·53; NO_2^-, 54·24 %.

found K, 30·99; Ni, 11·49; NO_2^-, 53·93 %.

In agreement with this the infrared spectrum of the compound showed sharp peaks at 3610, 3540 and 1621 cm^{-1}, assignable as the O-H stretching and deformation frequencies of water. All the major lines in the x-ray powder pattern[105] of the complex (Table 30(a)) could be interpreted in terms of a tetragonal unit cell of dimensions a = 7·634 Å, c = 22·450 Å with z = 3 and these are very similar to the values reported for the compound studied

Table 30

d-values for:

a) $K_4Ni(NO_2)_6 \cdot 1H_2O$		b) $K_4Ni(NO_2)_6$
7·4556ms	1·8917w	5·9392s
6·2873s	1·8440w	5·4241ms
5·6552w	1·8128vw	4·7138vw
4·2618vw	1·7246vw	4·3064w
3·7827s	1·6692w	3·8376ms
3·6886ms	1·6588vw	3·5573ms
3·3107w		3·5140ms
3·2415m		3·2995m
3·1431w		3·0145m
2·8665vw		2·9960m
2·8271w		2·8535m
2·6533vs		2·7280vs
2·4614w		2·6970w
2·4195vw		2·5456vw
2·2635m		2·4179vw
2·1843ms		2·3468w
2·1662ms		2·1778vw
2·1255w		2·1588w
2·1124w		2·1460vw
2·0735vw		2·0202vw
1·9573vw		1·9966vw
1·9395w		1·9670vw

by Ferrari et al. Moreover, the monohydrate had an almost identical infrared spectrum to that described for the compound investigated by Postollec et al. except that these workers did not report the three water bands mentioned above. It is possible that they observed the water bands but did not mention them as they were concerned primarily with the infrared frequencies of the nitrite groups. Since, as will be shown, anhydrous $K_4Ni(NO_2)_6$ has quite different properties from those of the hydrated compound, there can be little doubt that the complexes studied by Postollec et al. and Ferrari et al. were in fact $K_4Ni(NO_2)_6 \cdot 1H_2O$, and this will be assumed in considering the results of these workers.

The water in the orange compound was quite strongly held and was not removed even by storage in vacuo over P_2O_5 for several months. However, on heating to ~100° for a few hours, the complex turned brick-red and this was accompanied by a weight loss corresponding to the loss of one mole of water:-

calc. 3·94% found 4·00%

The x-ray powder pattern also altered completely[105] and the d-spacings of the red compound (which could not be identified in terms of unit cell dimensions) are listed in Table 30(b). Moreover, the infrared spectrum changed considerably and the bands at 3610, 3540 and 1621 cm^{-1}, due to water, disappeared. The analysis of the red complex agreed with the formula

$K_4Ni(NO_2)_6$:- calc. Ni, 11·95; NO_2^-, 56·19;
found Ni, 11·86; NO_2^-, 55·85.

Although the anhydrous compound remained unchanged in the absence of water for several months, it was very hygroscopic at room temperature and if exposed to the atmosphere, gained in weight to the extent of one mole of water to form an orange complex identical in all respects with the original monohydrate.

Clearly $K_4Ni(NO_2)_6 \cdot 1H_2O$ and $K_4Ni(NO_2)_6$ are two quite distinct compounds and their properties and possible structures will now be discussed.

Electronic spectra The electronic spectra of $K_4Ni(NO_2)_6 \cdot 1H_2O$ and $K_4Ni(NO_2)_6$ are shown in Figure 23 and the band maxima (cm^{-1}) are listed below:-

$K_4Ni(NO_2)_6 \cdot 1H_2O$	20,700	13,200	~11,000sh[a]
$K_4Ni(NO_2)_6$	19,200	12,050	~10,500sh

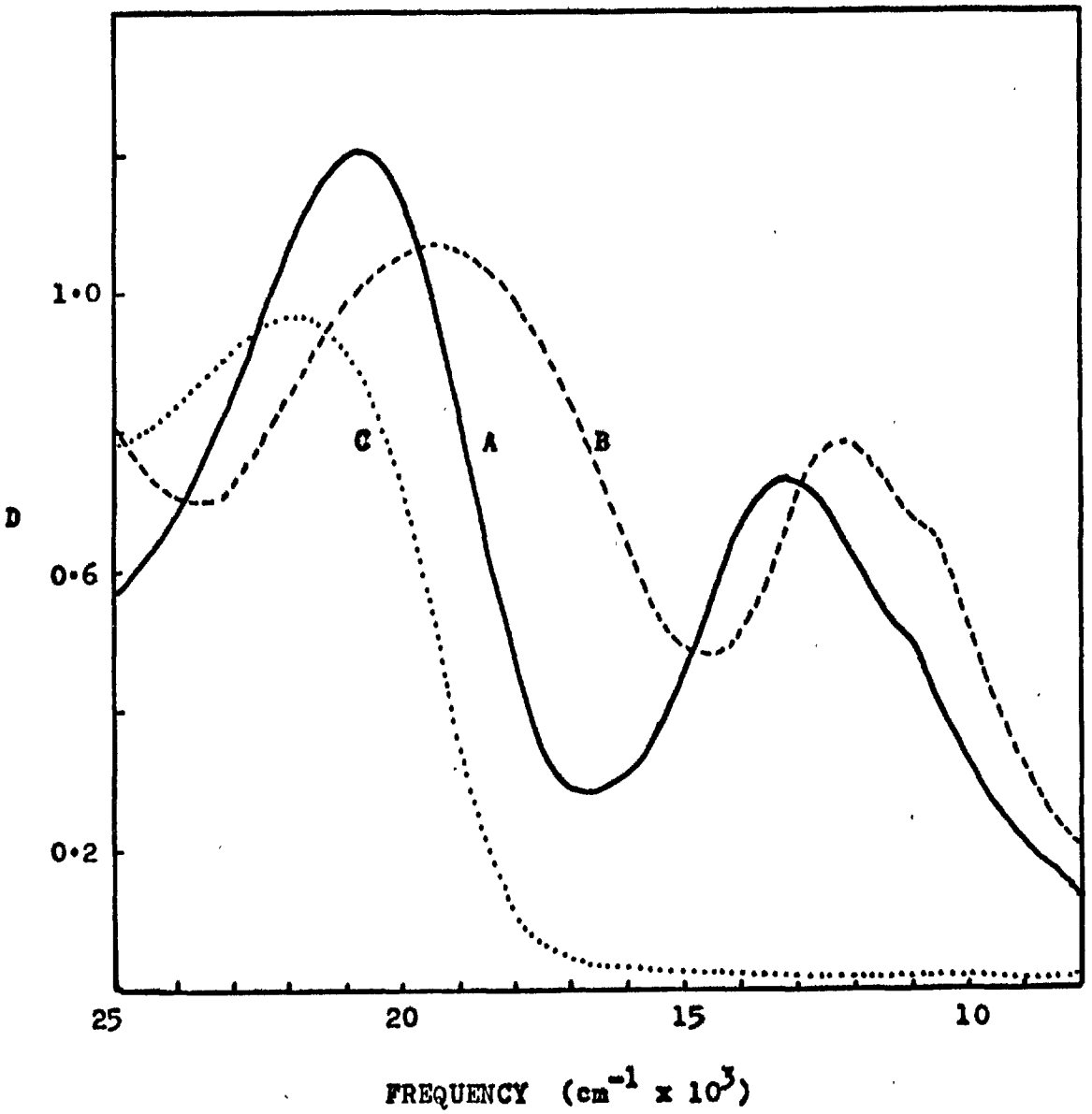
a very weak peak assigned as a spin-forbidden transition

Except that the band at 13,200 cm^{-1} in the spectrum of $K_4Ni(NO_2)_6 \cdot 1H_2O$ is at slightly lower energy than the corresponding bands in the hexanitrocomplexes $K_2BaNi(-NO_2)_6$ and $Na_2CaNi(-NO_2)_6$ (Table 29), the electronic spectra of these three compounds are very similar. Thus $K_4Ni(NO_2)_6 \cdot 1H_2O$ probably contains six nitro-

FIGURE 23

Electronic Reflectance Spectra of:-

(A) $K_4Ni(NO_2)_6 \cdot 1H_2O$ (B) $K_4Ni(NO_2)_6$ (C) $Cs_3Mn(NO_2)_5$



groups octahedrally bonded to each nickel ion and it seems unlikely that the water molecule is coordinated. This is in agreement with the infrared spectrum, as will be discussed later, and with the structure proposed by Ferrari et al.

Although the spectrum of anhydrous $K_4Ni(NO_2)_6$ also suggests a near octahedral coordination for the nickel ion, the bands at 19,200 and 12,050 cm^{-1} are each ~1300 cm^{-1} lower in energy than those in the hydrated complex. The shoulder at ~10,500 cm^{-1} in $K_4Ni(NO_2)_6$ is probably due to the spin-forbidden transition $^3A_{2g} \longrightarrow {}^1E_g$, though it could also be due to a component of the $^3T_{2g}$ level if this were split by a low ligand field symmetry. The lowering in energy of the bands on going from the monohydrate to $K_4Ni(NO_2)_6$ suggests that a considerable weakening of the ligand field accompanies dehydration. The most likely explanation of this is that some of the nitro-groups in $K_4Ni(NO_2)_6 \cdot 1H_2O$ are replaced by oxygen-coordinated nitrite ions in $K_4Ni(NO_2)_6$, as the nitrito-group is considerably lower in the spectrochemical series than the nitro-group. Since for Ni^{II} $\Delta_{-NO_2} \simeq$ 13,400 cm^{-1} and Δ_{-ONO} ~9,000 cm^{-1}, the replacement of one nitro-group by a nitrito-group should cause a shift of ~700 cm^{-1} to lower energy in the spectrum of a six-coordinate nickel complex. The fact that one reasonably sharp band at ~19000 cm^{-1} is observed in the spectrum of $K_4Ni(NO_2)_6$ suggests that only one type of nickel ion is present in this compound, as two bands would

be expected from a mixed species of the type $K_4Ni(-NO_2)_6 \cdot K_4Ni(-NO_2)_2(-ONO)_4$. Thus the spectral shift on going from $K_4Ni(NO_2)_6 \cdot 1H_2O$ to $K_4Ni(NO_2)_6$ is consistent with approximately two of the nitro-groups in the former compound being replaced by nitrito-groups in the latter. The reason for this rather surprising change will be discussed later.

Infrared spectra The infrared spectra of $K_4Ni(NO_2)_6 \cdot 1H_2O$ and $K_4Ni(NO_2)_6$ are shown in Figure 24, and the band maxima due to the nitrite groups are listed in Table 31, together with those

Table 31

The nitrite infrared bands in the compounds $K_4Ni(NO_2)_6 \cdot H_2O$ and $K_4Ni(NO_2)_6$

Compound	ρ_w	δ_{NO_2}	ν_{as}	ν_s
$K_4Ni(NO_2)_6 \cdot 1H_2O$	427m	810s 833m	1319vs	1346w sp
$K_4Ni(NO_2)_6 \cdot 1H_2O$[a]	430m	815s 836m	1320vs	1347sh
$K_4Ni(NO_2)_6$	414m 423w	813m sp 826m sp	1206s 1325vs	1347w sh
		846vw 867m sp		1387m sp

a values taken from references 39 and 40

reported by Postollec et al. for the hydrated complex.

In $K_4Ni(NO_2)_6 \cdot 1H_2O$ the nitrite infrared bands are very similar to those observed in the hexanitrocomplexes listed in

FIGURE 24

The Infrared Spectra of:-

(A) $K_4Ni(NO_2)_6 \cdot 1H_2O$ (B) $K_4Ni(NO_2)_6$

(C) $Cs_3Ni(NO_2)_5$ (D) $Cs_3Mn(NO_2)_5$

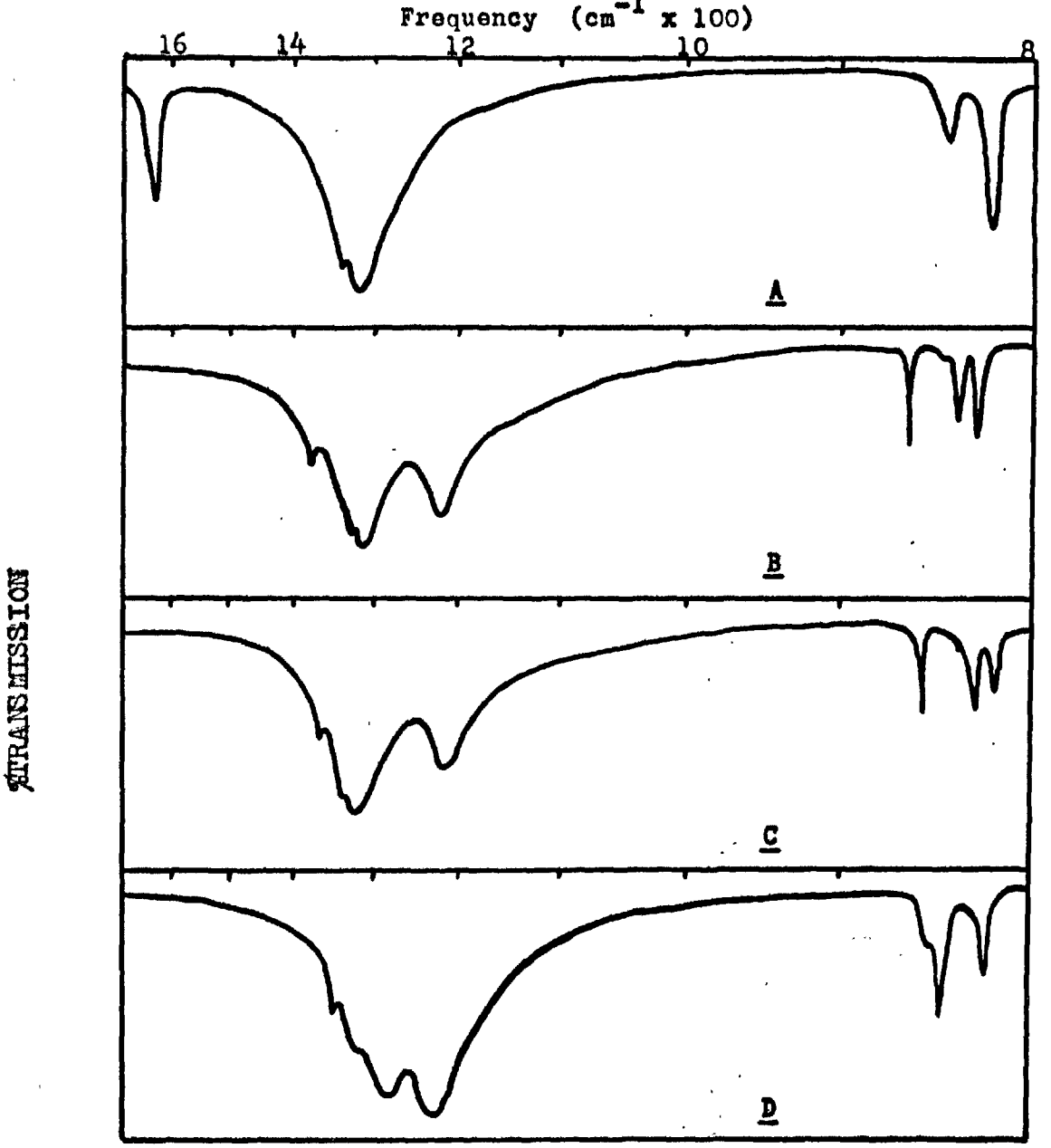


Table 26(a) and the assignments of the frequencies have been made accordingly. This confirms $K_4Ni(-NO_2)_6 \cdot 1H_2O$ to have six coordinated nitro-groups, since no bands were observed in the region in which ν_{as} occurs for uncoordinated nitrite ions (~1250 cm^{-1}). In addition to the peaks listed above $K_4Ni(NO_2)_6 \cdot 1H_2O$ had a broad band centred at 510 cm^{-1} and this was also reported at ~500 cm^{-1} by Postollec et al.[39]. As this band was absent in $K_4Ni(NO_2)_6$ it is probably due to librational vibrations of the water molecule. Similar bands have been reported in a number of other compounds containing water of crystallisation[106].

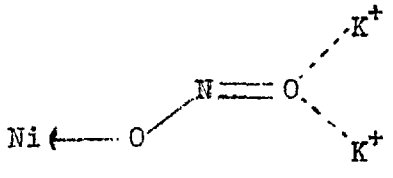
The nitrite infrared spectrum of $K_4Ni(NO_2)_6$ is more complicated than that of the hydrated complex. Four bands due to δ_{NO_2} were observed all at different frequencies from those in $K_4Ni(-NO_2)_6 \cdot 1H_2O$. The strong band at 1325 cm^{-1}, the weak shoulder at 1347 cm^{-1}, and the peaks at 414 and 423 cm^{-1} in $K_4Ni(NO_2)_6$ are all similar to those in $K_4Ni(-NO_2)_6 \cdot 1H_2O$ and analogous hexanitrocomplexes, and may thus be assigned as nitro-group frequencies.

In addition to the bands due to the nitrogen bonded nitrite groups, $K_4Ni(NO_2)_6$ has a strong peak ν_{as} at 1206 cm^{-1} and a medium peak ν_s at 1387 cm^{-1}. These frequencies are similar to the values of ν_{as} and ν_s observed in several nickel nitrito-complexes of the type $Ni(diamine)_2(-ONO)_2$ and to those found in

the tetranitritocomplexes $(o\text{-}Cat^{2+})M(NO_2)_4$ [M = Co^{II}, Cu^{II} and Zn^{II}] discussed in Chapter 7. This suggests that $K_4Ni(NO_2)_6$ contains nitrite groups bonded via oxygen, though it may be noted that ν_{as} is not lowered from its free ion value of ~1250 cm^{-1} by as much as is often observed in nickel nitrito-complexes, i.e. ν_{as} = 1114 cm^{-1} in $Ni(py)_4(-ONO)_2$. The lowering of ν_{as} is dependant on the difference in bond strength between the two nitrite nitrogen-oxygen bonds. If, as is suggested in the discussion, there is rather strong interaction between the potassium ions and the formally 'non-bonded' nitrito-oxygen atoms (Figure 25) the lowering of ν_{as} is in fact expected to be rather

Figure 25

The possible configuration of the nitrito-groups in $K_4Ni(NO_2)_6$



less than that observed in nitritocomplexes of the type $Ni(py)_4(-ONO)_2$, where no such interaction can occur. In the ion $Co(NO_2)_4^{2-}$, in which it is thought that each nitrite group is coordinated to the cobalt ion strongly via one oxygen atom and weakly via the second oxygen atom, ν_{as} is at ~1200 cm^{-1} and ν_s

at 1390 cm^{-1} and these values are very similar to those of the nitrito-groups in $K_4Ni(NO_2)_6$.

The infrared spectra are thus quite in accordance with a change of the type:-

$$K_4Ni(-NO_2)_6 \cdot 1H_2O \longrightarrow K_4Ni(-ONO)_n(-NO_2)_{6-n} + 1H_2O$$

occurring on heating hydrated potassium nickel nitrite.

Discussion

Although the water molecule is apparently not formally coordinated to the nickel ion in $K_4Ni(-NO_2)_6 \cdot 1H_2O$, its presence is clearly of considerable importance in the total energy of this compound, since on dehydration the structure of the complex and the nature of the nickel-nitrite coordination alter radically.

A possible explanation of the part played by the water molecule in $K_4Ni(-NO_2)_6 \cdot 1H_2O$ is suggested by the structure of this compound proposed by Ferrari et al.. Although these workers did not recognise the presence of the water molecule they reported the existence of 'cavities' between certain pairs of potassium ions. Whereas most of the potassium-potassium interactions were 'cushioned' by suitably situated nitrite oxygen atoms, the pairs of potassium ions on either side of these 'cavities' were not. Ferrari et al. could not explain this feature of the structure and it seems probably that the water

molecule in $K_4Ni(NO_2)_6 \cdot 1H_2O$ is situated in this 'cavity', thus reducing the interaction between the positively charged potassium ions. This hypothesis is supported by the fact that the structure suggested one 'cavity' per nickel ion, in agreement with the formula $K_4Ni(NO_2)_6 \cdot 1H_2O$.

Dehydration must remove the 'cushioning' between these pairs of potassium ions and the interaction between them is apparently then so strong that the structure is rendered unstable and alters to that of the nitro-nitritocomplex $K_4Ni(-ONO)_n(-NO_2)_{6-n}$. The reasons why some of the nitrite groups are bonded via oxygen in the anhydrous compound, although this method of nitrite coordination is usually less stable than nitrogen-bonding, are not completely clear. It is possible that it is because better 'cushioning' of the cations by the negatively charged oxygen atoms can be obtained if some of the nitrite groups are bonded via oxygen. (The non-bonded oxygen atom is considerably further from the nickel ion in the grouping $M \leftarrow O-N-O$ than in the grouping $M \leftarrow N\lesssim^{O}_{O}$.) Presumably, the energy gained from the decrease in the potassium-potassium interaction must be greater than that lost by replacing a $Ni-NO_2$ bond by a Ni-ONO bond. The high ratio of the cations to the anion in $K_4Ni(NO_2)_6$ is probably significant, since many anhydrous compounds of the type $(cation)_3M(NO_2)_6$ are known, and in these the nitrite groups are apparently always coordinated via nitrogen.

Two pentanitrite complexes

Although the dark red complex $Cs_3Ni(NO_2)_5$ had been reported previously[107] its structure was unknown. Since compounds of this stoichiometry are comparatively rare it was thought of interest to investigate the nature of the metal-nitrite bonding in this complex. The new bright yellow complex $Cs_3Mn(NO_2)_5$ is also described.

Electronic spectra

Nickel complex The electronic spectrum (Figure 21) of this compound consists essentially of two rather broad bands at 18,300 cm^{-1} and ~11,900 cm^{-1}. This is consistent with a pseudo-octahedral ligand field around the nickel ion and implies that tetrahedral or planar species are absent. Thus, it is unlikely that the structure can be of the type $Cs_3[Ni(NO_2)_4]NO_2$ or $Cs_4Ni(NO_2)_6 \cdot Cs_2Ni(NO_2)_4$. The lower energy band has a very prominent shoulder at ~10,500 cm^{-1}. Since this could either be assigned to the spin-forbidden transition $^3A_{2g} \longrightarrow {}^1E_g$, or to a transition to a component of the $^3T_{2g}$ level split under low symmetry, the energy of the first spin-allowed transition in $Cs_3Ni(NO_2)_5$ cannot be estimated accurately. However, it does seem that it is approximately half-way between that produced by six nitro-groups (~13,800 cm^{-1}) and six nitrito-groups (~9,000 cm^{-1}).

Manganese complex

The electronic spectrum of $Cs_3Mn(NO_2)_5$ (Figure 23) consists of a single band at 21,700 cm^{-1}. Since several electronic transitions are expected for spin-free Mn^{II} in this region, a precise assignment of the band has not been attempted. Although no accurate estimates of the intensity could be made, as solution measurements were not possible, the band was far stronger than those normally observed for Mn^{II} in pseudo-octahedral ligand field symmetry. This suggests that the ligand field in $Cs_3Mn(NO_2)_5$ has no centre of symmetry, because rather similar band intensities have been observed[108] for the tetrahedral ions MnX_4 [X = Br and I] and in pseudo-eight-coordinate $Mn(NO_2)_4^{2-}$ (see Chapter 7).

Infrared spectra and discussion

The infrared spectra of the compounds are shown in Figure 24 and the band maxima are listed below.

	$Cs_3Ni(NO_2)_5$	$Cs_3Mn(NO_2)_5$
ρ_w	406w,433w	
δ_{NO_2}	809m sp,821m sp,	811m sp,837m sp,
	833vw sh, 860m sp	846vw sp
ν_{as}	1208s, 1325vs	1215vs,1287s
ν_s	~1348vw sh,1372w sp	1333vw sh,1353w sp
unassigned bands	~250s,~275s, ~305sh,340m	260s br,319m

Nickel complex The very strong band at 1325 cm^{-1} and the shoulder at 1348 cm^{-1} may be assigned as ν_{as} and ν_s of nitro-groups, with the weak peaks at 406 and 433 cm^{-1} being due to ρ_w.

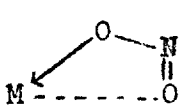
The most likely explanation of the peaks at 1208 and 1372 cm^{-1} is that they are ν_{as} and ν_s of what are essentially nitrito-groups. It is, however, also possible that the peak at 1372 cm^{-1} is ν_s of the nitro-groups, this frequency being split into two components. The band at 1208 cm^{-1} could then be ν_{as} of chelated anions, with ν_s of these masked under the nitro-band at 1325 cm^{-1}. It seems unlikely that the peak at 1372 cm^{-1} is a nitro-frequency, though, since the nitro-band ν_{as} at 1325 cm^{-1} is unsplit. Moreover, the frequency ν_s has not been observed above 1350 cm^{-1} in any other nickel nitrocomplexes. The absence of a band at ~1435 cm^{-1} showed that no bridged(NO) nitrite groups are present.

Manganese complex Except for the inexplicable absence of bands at ~400 cm^{-1} due to ρ_w, the spectrum of $Cs_3Mn(NO_2)_5$ generally resembles that of the nickel pentanitrite complex. The peaks at 1287 and 1333 cm^{-1}, assignable as ν_{as} and ν_s of nitro-groups, are at lower frequency than those in $Cs_3Ni(NO_2)_5$. Similarly, the bands at 1353 and 1212 cm^{-1} due to ν_{as} and ν_s of the nitrito-groups are slightly closer to their free ion values. This is in agreement with metal-ligand bonds being generally slightly weaker in

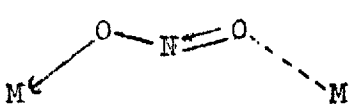
manganese(II) complexes than in the corresponding nickel(II) compounds.

Although the compounds were not found to be isomorphous[91], the general resemblance of the infrared spectra suggests that the metal-nitrite bonding is rather similar in the two complexes.

Discussion Despite the difference in stoichiometry there is a distinct similarity between the infrared spectra of the pentanitrite complexes and the nitro-nitritocomplex $K_4Ni(-ONO)_n(-NO_2)_{6-n}$. In the last compound it was suggested that the formally non-bonded nitrito-oxygen atoms interact with the potassium ions, and that this explains why the nitrito infrared frequencies are relatively close to those of free NO_2^-. In $Cs_3M(NO_2)_5$ [M = Ni and Mn] the nitrito frequencies are even closer to those in $NaNO_2$. However, because of the stoichiometry of the compounds, and as the caesium ion is far less polarising than K^+, it seems probable that in the pentanitrite complexes the formally non-bonded oxygen atoms of the nitrito-groups interact with the manganese and nickel ions. This could either be by unsymmetrical chelation, or unsymmetrical bridging, as illustrated in I and II below.



I



II

The reasons why bonding of this type is adopted in preference to the more usual forms of mono- or bidentate nitrite coordination are obscure. However, five-coordinate complexes are comparatively rare, and are usually only formed when six-coordination is prevented for steric reasons[109]. In several tetranitrite ions with similar metals, e.g. Co^{II}, it seems likely that four unsymmetrical bonds of type I above are formed, and this manner of bonding is probably adopted in order to increase the effective coordination number of the central metal ion. The hexa-nitrite ion $Ni(NO_2)_6^{4-}$ normally contains six nitro-groups and it seems likely that in the penta-nitrite complexes a balance is set up in which some of the nitrite groups coordinate in their generally preferred manner, i.e. via nitrogen, while others coordinate as in I or II in order to raise the effective coordination number of the manganese and nickel ions. Both Ni^{II} and Mn^{II} tend to adopt a relatively high coordination number (usually six) whenever this is not precluded for steric reasons. It is not clear why a structure involving bridged(NO) nitrite groups does not occur, though this may be prevented by the large size of the caesium ions.

Preparation of Compounds

$Cs_3Ni(NO_2)_5$ Aqueous solutions of nickel nitrite (0·01 M) and caesium nitrite (0·03 M) were prepared by treating solutions of

the sulphites with barium nitrite solution and filtering. The nitrite solutions were mixed, filtered and allowed to stand over sulphuric acid. After some days dark red crystals formed and these were washed with a little ice-cold water and dried in vacuo. yield 5%

analysis:- calc. Ni, 8·54; NO_2^-, 33·46.

found Ni, 8·57; NO_2^-, 33·16.

$Cs_3Mn(NO_2)_5$ A methanolic solution of manganous nitrite (0·01 M) was prepared metathetically from manganous bromide and excess finely powdered silver nitrite. This was added to a solution of caesium nitrite (0·05 M) in methanol (200 ml). On leaving in the refrigerator a cream coloured precipitate formed. This was recrystallised from methanol. The compound was slightly photosensitive, slowly darkening after about two weeks. It remained unchanged for several months, however, on being stored under its mother liquor in the refrigerator. yield 15%

analysis:- calc. Mn, 8·04; O, 23·41; NO_2^-, 33·65.

found Mn, 7·83; O, 23·51; NO_2^-, 33·42.

A Trinitrite Complex

No well-authenticated trinitrite complexes had been reported. The compound $N(CH_3)_4Ni(NO_2)_3$ was prepared as a fawn, microcrystalline precipitate by adding a concentrated aqueous solution of nickel bromide (0·01 M) to an aqueous solution of tetramethylammonium bromide (0·01 M) and an excess of sodium nitrite. An identical compound was obtained using a large excess of tetramethylammonium bromide.

yield 70% m.p. 270°

analysis:- calc. Ni, 21·67; N, 20·68; O, 35·44; NO_2^-, 50·94.

found Ni, 21·93; N, 20·80; O, 35·15; NO_2^-, 50·82.

Infrared spectrum The nitrite infrared bands in the compound occurred at:- δ_{NO_2}, 852(m); ν_{as}, 1202(vs); ν_s, 1435(s) cm^{-1}. The bands were identified by comparison with the spectra of $N(CH_3)_4Cl$ and $N(CH_3)_4Br$. These values of ν_s and ν_{as} are similar to those of the bridged(NO) groups in $Ni(en)(NO_2)_2$ and $Ni(nen)(NO_2)_2$ and suggest a similar manner of nitrite coordination in the trinitrite complex. Since chelating nitrite groups have a strong band at ~1200 cm^{-1} and only a weak peak at ~1300 cm^{-1}, the possibility that these are also present must be considered. However, the occurrence of only one, very sharp band due to δ_{NO_2} makes the presence of more than one type of nitrite group rather unlikely.

Electronic spectrum and Discussion The reflectance spectrum of the complex (Figure 21) consists of two strong bands at 13,250 and 21,000 cm^{-1} which may be assigned as the first two spin-allowed transitions ($^3A_{2g} \longrightarrow {}^3T_{2g}$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ in O_h symmetry) of octahedrally coordinated Ni^{II}. The weak shoulder at ~10,900 cm^{-1} is probably due to the spin-forbidden transition $^3A_{2g} \longrightarrow {}^1E_g$. The band at 13,250 cm^{-1} suggests a Δ-value of 12,900 cm^{-1} for three bridged(NO) groups, which is only slightly less than that (~13,400 cm^{-1}) produced by six nitro-groups.

It is of interest to consider why a compound of stoichiometry (cation) $Ni(NO_2)_3$ is formed with $N(CH_3)_4^+$, while other cations yield hexa- or pentanitrite complexes with nickel nitrite. The structure of $Ni(NO_2)_3^-$ probably consists of chains of $\rightarrow Ni \leftarrow N(=O)-O \rightarrow Ni \leftarrow$ groupings running in three dimensions. Every eight nickel ions then form a hollow cube of side ~5Å and there will be one such cube for each nickel ion. Since the volume occupied by a tetramethylammonium ion is ~60$(Å)^3$ [110], it seems likely that this cation is just the right size to fit into such a polymeric structure. An attempt to prepare $N(C_2H_5)_4Ni(NO_2)_3$ by the same method used for the tetramethylammonium complex was unsuccessful, producing no solid product. This is not surprising as the volume of $N(C_2H_5)_4^+$ is ~260$(Å)^3$ [110], which would make it too large to fit into the polymeric 'cagework' of the $Ni(NO_2)_3^-$ ion.

CHAPTER 7

Some Tetranitrite Complexes

Although the planar nitrocomplexes $K_2Pt(NO_2)_4$ and $K_2Pd(NO_2)_4$ were known[39], and the compound $K_3[Hg(NO_2)_4]NO_3$ had been shown[44] to contain four chelated nitrite groups, there were no well-authenticated reports of tetranitrite complexes of first-row transition metal ions.

Since the employment of large cations had been of value in stabilising ions of the type MX_4^{2-} (where X represents a pseudo-halogen[111,112] or nitrate[113] group) in solid compounds it was felt that the use of these might be helpful in the preparation of tetranitrite complexes. A series of compounds $(o\text{-}Cat^{2+})M(NO_2)_4$ [M = Zn, Cu, Co and Mn] and $(cation)_2M(NO_2)_4$ [cation = $N(CH_3)_4$, Cs or K and M = Zn, Cd, Hg and Mn] were prepared, and the infrared and electronic spectra of these are reported here, together with their possible structures.

Electronic Spectra

The spectra of the compounds containing the ions $Co(NO_2)_4^{2-}$, $Cu(NO_2)_4^{2-}$ and $Mn(NO_2)_4^{2-}$ were recorded in the solid state and in solution in acetonitrile containing $\frac{M}{20}$ $N(CH_3)_4NO_2$ in the range 4,000 - 30,000 cm^{-1}, and the band maxima are listed in Table 32.

The spectrum of $(o\text{-}Cat^{2+})Co(NO_2)_4$ is very similar to that reported[113,114] for the compound $[N(CH_3)_4]_2Co(NO_3)_4$ (Figure 26)

FIGURE 26

The Electronic Spectra of:-

(A) $(o\text{-}Cat^{2+})Co(NO_2)_4$ (B) $N(CH_3)_4Co(NO_3)_4$

both in acetonitrile solution

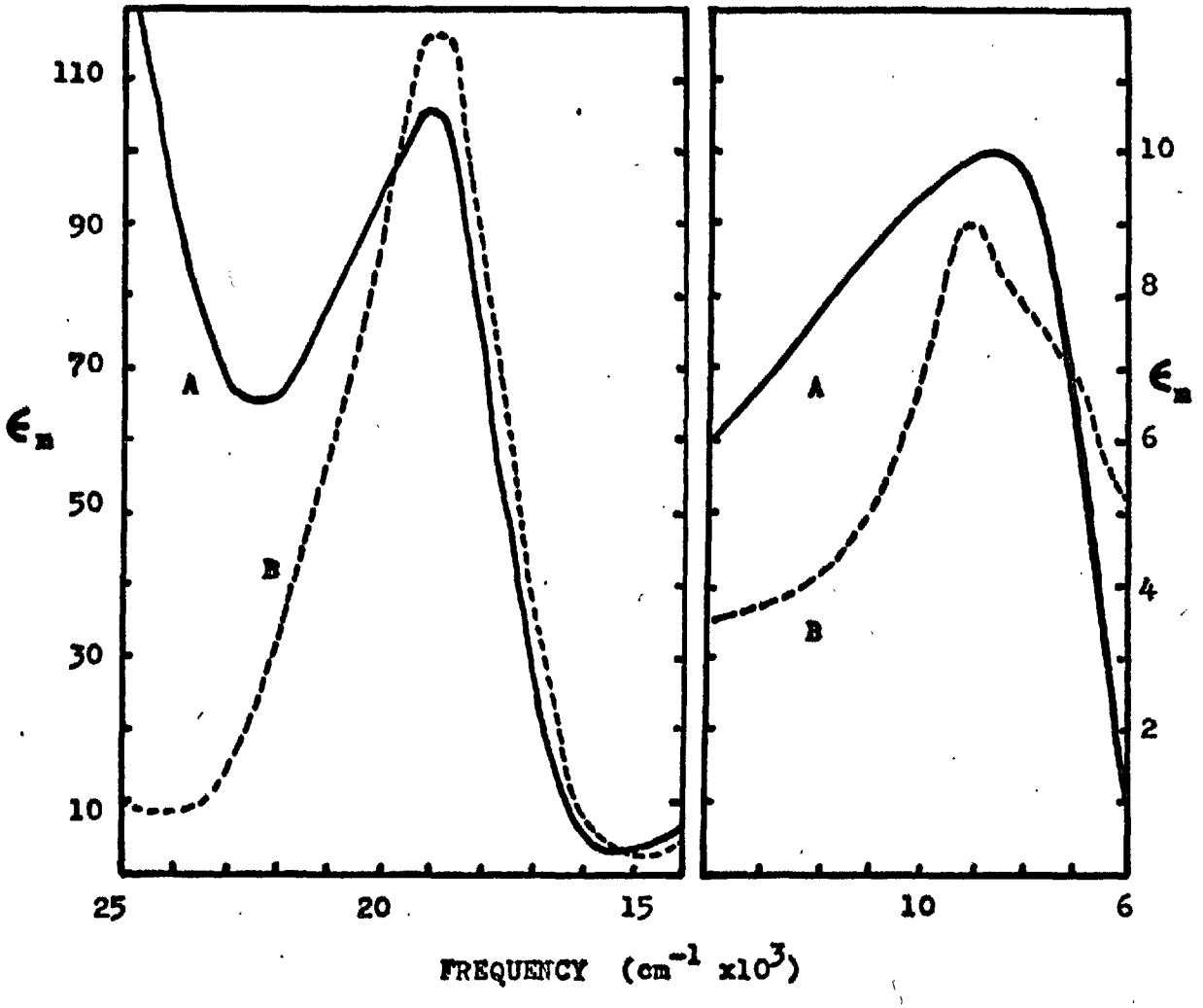


Table 32

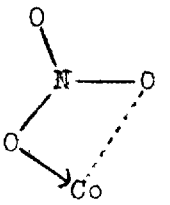
The band maxima in the electronic spectra of some tetranitrite complexes.

Compound	State	Band Maxima (cm^{-1})
$(o\text{-}Cat^{2+})Co(NO_2)_4$	solid	18,000 8,260br
	CH_3CN[a]	19,000(105) 8,300(10br)
$(o\text{-}Cat^{2+})Cu(NO_2)_4$	solid	13,200
	CH_3CN[a]	14,800(108)
$(o\text{-}Cat^{2+})Mn(NO_2)_4$	solid	22,200sh ~18,000sh[b]
$[N(CH_3)_4]_2Mn(NO_2)_4$	solid	22,800
	CH_3CN[a]	23,300(6·9)
$Cs_2Mn(NO_2)_4$	solid	23,200

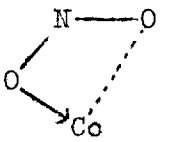
a solution containing $\frac{M}{20}$ $N(CH_3)_4NO_2$

b very weak band probably due to a small amount of $Co(NO_2)_4^{2-}$

and the band intensities are unusual in being midway between those usually observed for Co^{II} in octahedral and tetrahedral ligand fields. In the nitrate complex this has been related to the novel structure of the compound[115], in which each nitrate ion is bonded to the cobalt by one short bond (~2·0 Å) and one relatively long bond (~2·5 Å) as in I below. The similarity of the electronic spectra suggests an essentially analogous manner of coordination for the nitrite groups in $(o\text{-}Cat^{2+})Co(NO_2)_4$, as in II and this possibility will be considered more fully in



I



II

conjunction with the infrared spectra.

The spectra of the compounds $Cs_2Mn(NO_2)_4$, $(o\text{-}Cat^{2+})Mn(NO_2)_4$ and $[N(CH_3)_4]_2Mn(NO_2)_4$ were measured in the solid state, and that of the tetramethylammonium compound was found to be the same in acetonitrile solution, as in acetonitrile containing $\frac{M}{20}$ $N(CH_3)_4NO_2$. The spectrum of the ion $Mn(NO_2)_4^{2-}$ consists of a single, broad band centred at ~23,000 cm^{-1}. The intensity of this (ϵ_m = 7) is much greater than that usually observed for Mn^{II} in an octahedral ligand field, and is similar to that found[108] for the bands at ~23,000 cm^{-1} in the tetrahedral species MX_4^{2-} [X = Br and I]. While in each of the tetrahalo-manganate(II) ions several bands occur in this region, in $Mn(NO_2)_4^{2-}$ only one broad band can be resolved. However, as the manganese ions in the tetranitrite complexes are apparently formally eight-coordinate, as will be discussed later, its electronic spectrum is not necessarily expected to resemble those of the tetrahedral ions mentioned above. In addition to the peak at ~23,000 cm^{-1}, the compound $(o\text{-}Cat^{2+})Mn(NO_2)_4$ had a very weak band at ~18,000 cm^{-1},

This is probably caused by a trace of $(o\text{-}Cat^{2+})Co(NO_2)_4$ impurity, since even a small amount (~5%) of this would produce bands comparable in intensity to those of $Mn(NO_2)_4^{2-}$. The absence of this band in $[N(CH_3)_4]_2Mn(NO_2)_4$ and $Cs_2Mn(NO_2)_4$ can be attributed to the instability of the cobalt tetranitrite complexes with these cations (see preparitive section).

The spectrum of $(o\text{-}Cat^{2+})Cu(NO_2)_4$ consists of a single broad band which is at 13,200 cm^{-1} in the solid compound, 12,000 cm^{-1} with possibly a shoulder at ~22,000 cm^{-1} in acetonitrile containing no excess NO_2^-, and 14,800 cm^{-1} in acetonitrile containing $\frac{M}{20}$ $N(CH_3)_4NO_2$. The reason for these differences in the solution spectra is not apparent. If no d-d bands are obscured under the relatively strong electron transfer absorption commencing at ~23,000 cm^{-1}, the occurrence of only a single electronic transition suggests a fairly distortion-free structure for $Cu(NO_2)_4^{2-}$. However, the ion $Cu(NO_3)_4^{2-}$ has bands at ~14,000 and 25,000 cm^{-1} [113], so it seems quite possible that the tetranitrite species may also have a peak at ~25,000 cm^{-1}. No definite conclusions can thus be drawn with regard to the electronic spectrum of $(o\text{-}Cat^{2+})Cu(NO_2)_4$.

Magnetic Measurements

The room temperature magnetic moments of $(o\text{-}Cat^{2+})M(NO_2)_4$ [M = Co, Cu and Mn] are listed in Table 33. The value for the

Table 33

The magnetic moments of some tetranitrite complexes.

Compound	μ(B.M.)[a]
$(o\text{-}Cat^{2+})Co(NO_2)_4$	4·47
$(o\text{-}Cat^{2+})Cu(NO_2)_4$	2·00
$(o\text{-}Cat^{2+})Mn(NO_2)_4$	5·98

a corrected for diamagnetism

cobalt complex is rather similar to that reported (~4·67 B.M.) [113,114] for $Co(NO_3)_4^{2-}$ and is typical of the values generally found for Co^{II} ions in pseudotetrahedral ligand environments.

Infrared Spectra

The infrared spectra of the compounds were measured in the region 2000 - 200 cm^{-1} and the nitrite bands in the compounds having organic cations were identified by comparison with the spectra of the appropriate cation halide and nitrite salts. The frequencies will be considered in two sections:-

a) The infrared frequencies of the nitrite groups 2000 - 800 cm^{-1}

b) The infrared frequencies associated directly with the metal-nitrite bonds (800 - 200 cm^{-1}).

a) The nitrite infrared frequencies The nitrite infrared bands in the region 2000 - 800 cm^{-1} are listed in Table 34.

Table 34

The nitrite infrared frequencies (2000 - 800 cm^{-1}) in some tetranitrite complexes.

Compound	State	ν_{as}	ν_s	δ_{NO_2}
$(o\text{-}Cat^{2+})Zn(NO_2)_4$	mull	1184s	1397m	a
	CH_3CN	~1176s	a	a
$Cs_2Zn(NO_2)_4$	mull	1167vs	1381s	847ms sp
$(o\text{-}Cat^{2+})Co(NO_2)_4$	mull	1191s	1390m	a
	CH_3CN	1218s	a	a
$(o\text{-}Cat^{2+})Cu(NO_2)_4$	mull	1195s	1372s	a
	CH_3CN	1188s	a	a
$(o\text{-}Cat^{2+})Mn(NO_2)_4$	mull	1238vs br	a	a
$[N(CH_3)_4]_2Mn(NO_2)_4$	mull	1211vs br	a	837ms sp
	CH_3CN	1208vs br	a	837ms sp
$Cs_2Mn(NO_2)_4$	mull	1225vs br	1302vw sh	841ms sp
$K_2Cd(NO_2)_4$	mull	1266vs br	b	851m sp, 858w sp
$K_2Hg(NO_2)_4$	mull	1258vs br	b	851m sp, 858w sp

a cation or solvent absorption obscures the region where this frequency is expected.

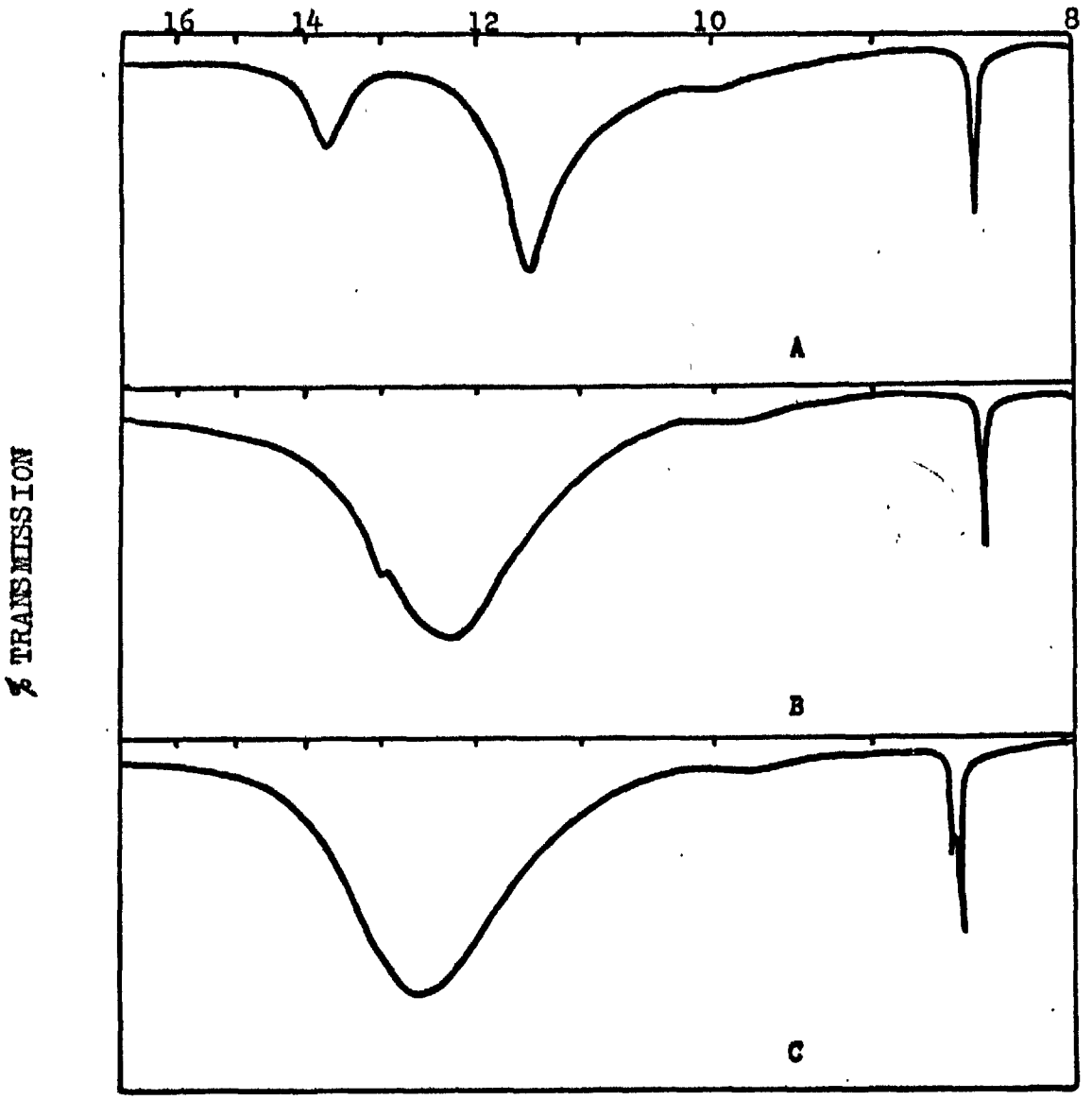
b band probably obscured by ν_{as}.

The solid tetranitrite complexes of Zn (Figure 27a), Co and Cu each have a strong band ν_{as} at ~1180 cm^{-1}, and a medium peak ν_s at ~1380 cm^{-1}. This divergence of ν_{as} and ν_s from their free

FIGURE 27

The Infrared Spectra of:-

(A) $Cs_2Zn(NO_2)_4$ (B) $Cs_2Mn(NO_2)_4$ (C) $K_2Cd(NO_2)_4$



ion values (ν_{as} ~1250, ν_s = 1326 cm^{-1}) is characteristic of oxygen coordination of the nitrite group and suggests that these compounds are nitritocomplexes. However, it may be noted that in $(o\text{-}Cat^{2+})Co(NO_2)_4$ ν_{as} is not as low as in some other nitritocomplexes of Co^{II} [ν_{as} = 1100 cm^{-1}, ν_s = 1410 cm^{-1} in $Co(py)_4(-ONO)_2$]^{116}. This is consistent with some interaction occurring between the formally non-bonded nitrite oxygen atom and the cobalt ion in $Co(NO_2)_4^{2-}$, as is suggested by the electronic spectrum. On dissolving $(o\text{-}Cat^{2+})Co(NO_2)_4$ in acetonitrile the frequency ν_{as} changed from 1191 to 1218 cm^{-1}. This increase was not due to dissociation, as the electronic spectrum of the solution was identical to that containing $\frac{M}{20}$ $N(CH_3)_4NO_2$. However, it is quite possible that the bond lengths in a pseudo-eight coordinate structure of the type suggested for $Co(NO_2)_4^{2-}$ might alter somewhat on solution in a highly polar solvent, and this could cause shifts in the nitrite infrared frequencies.

The frequencies ν_{as} and ν_s in the compounds containing $Mn(NO_2)_4^{2-}$ are different from those in the copper, cobalt and zinc complexes, as may be seen from Figure 27b. In the manganese compounds ν_{as} is a strong, broad band at ~1220 cm^{-1}, and in $Cs_2Mn(NO_2)_4$ ν_s can be resolved as a weak shoulder at 1302 cm^{-1}. These frequencies, and the relative intensities of the bands, are similar to those observed for the chelating nitrite groups in the complexes described in Chapter 4 and suggest a similar manner of anion coordination in $Mn(NO_2)_4^{2-}$. The manganese ion in these

complexes is thus formally eight coordinate ,with each nitrite group bonding via two oxygen atoms.

The infrared spectra of $K_2Cd(NO_2)_4$ (Figure 27c) and $K_2Hg(NO_2)_4$ each show a broad intense band ν_{as} centred at ~1260 cm^{-1}, but in neither of these compounds could a peak assignable as ν_s be resolved. It seems likely that the band due to this latter frequency was obscured under the very strong absorption caused by ν_{as}. The antisymmetric nitrogen-oxygen stretching frequency in these complexes is very similar to that in sodium nitrite, which makes any deductions about the metal-nitrite bonding based on the infrared spectra difficult. It is known[44] that the compound $K_3[Hg(NO_2)_4]NO_3$ contains four chelating nitrite groups, and the frequency ν_{as} was reported[117] at ~1200 cm^{-1} in this compound. The frequency ν_s was apparently not observed, the only other bands in this region (at 1377 and 1394 cm^{-1}) being assignable as ν_{as} of the ionic nitrate. It seems unlikely that the nitrite groups should be chelated in $K_3[Hg(NO_2)_4]NO_3$ and bonded differently in $K_2Hg(NO_2)_4$, and the fact that their infrared spectra are not identical is probably attributable to relatively small differences in the metal-nitrite bonding. By analogy it seems likely that $K_2Cd(NO_2)_4$ also contains chelated nitrite groups.

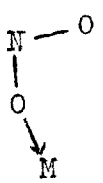
Postollec et al.[39] have reported the following bands for the compounds $K_2Cd(NO_2)_4$:- δ_{NO_2}, 855; ν_{as}, 1250 - 1275; ν_s, 1345 cm^{-1}

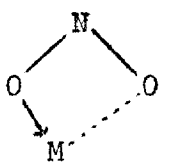
and $K_3Hg(NO_2)_5 \cdot H_2O$:- δ_{NO_2}, 848 - 855; γ_{as}, 1250; γ_s ~1310 cm^{-1}. The mercury compound, which was formulated in the older literature[120] as a pentanitrite monohydrate, has since been shown[44,117] to be $K_3\left[Hg(NO_2)_4\right]NO_3$, but as Postollec et al. reported, no bands assignable to ionic nitrate, they presumably could not have studied this complex. As no analysis figures were quoted the compound they formulated as '$K_3Hg(NO_2)_5 \cdot H_2O$' must be considered doubtful, and may possibly have been the same as the complex $K_2Hg(NO_2)_4$ studied here.

b) Infrared frequencies associated directly with the metal-nitrite bond

As the exact nature of the bonding and thus the overall symmetry of the ions $M(NO_2)_4^{2-}$ are unknown, no rigorous analysis of the infrared spectra has been attempted. However, the observed frequencies (Table 35) can be interpreted in a general manner in terms of the approximate structures suggested by the infrared spectra in the higher energy region. The two extreme forms that the metal-nitrite bonding in the complexes can take are monodentate nitrito-coordination and symmetrical chelation (Figure 28 a and c). Clearly between these limiting forms there are an

Figure 28

(a) 

(b) 

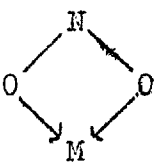
(c) 

Table 35

The infrared spectra (800 - 200 cm^{-1})

of some tetranitrite complexes.

Compound	ν_{M-O}	Unassigned Bands
$(o\text{-}Cat^{2+})Zn(NO_2)_4$	308s	
$Cs_2Zn(NO_2)_4$	~290, 328s	
$(o\text{-}Cat^{2+})Co(NO_2)_4$	~294sh, 332s	
$(o\text{-}Cat^{2+})Mn(NO_2)_4$	~260 [a], 301 [a]	
$[N(CH_3)_4]_2Mn(NO_2)_4$	~255 [a], 301 [a]	
$Cs_2Mn(NO_2)_4$	260s br[a], 315m[a]	
$(o\text{-}Cat^{2+})Cu(NO_2)_4$	283m, 325s	
$K_2Cd(NO_2)_4$	242vs br[a]	323w, 340w
$K_2Hg(NO_2)_4$	227vs br[a]	337w

a peak not assigned with certainty, see text for discussion

infinite number of configurations having one relatively strong and one weak metal-oxygen bond, and this type of coordination is illustrated in Figure 28(b). The metal-ligand vibrations to be expected from these three types of coordination will now be considered.

In a complex having monodentate nitrito-groups, the rocking and wagging vibrations will probably be at relatively low energy and will consequently be ignored in this discussion. If only the

coordinated oxygen atoms are considered, the symmetry around the metal ion is likely to be T_d, though if the nitrogen and non-bonded oxygen atoms are also taken into account the symmetry is lowered, probably to S_4. A single infrared active, triply degenerate metal-oxygen stretching frequency ν_{M-O} is expected in T_d, and this is split into A and E componants under S_4 symmetry.

In compounds in which the monodentate nitrite coordination is distorted into unsymmetrical chelation, as in Figure 28(b), the symmetry of the primary coordination sphere is likely to be lowered, probably to D_{2d}, and the frequency ν_{M-O} is expected to be split into A and E componants.

A complex $M(NO_2)_4^{2-}$ having four chelating nitrite groups is likely to have D_{2d} symmetry. Without making detailed calculations it is difficult to predict the relative energies of the stretching and bending modes in a ring-system, such as M<O>N. However, for this four-membered ring two distinct frequencies ν_{M-O} which are essentially metal-oxygen in character are to be expected. It has been suggested[119] that for the nitrate group chelation should produce two metal-oxygen stretching frequencies and monodentate coordination only a single frequency ν_{M-O}.

The compound $(o\text{-}Cat^{2+})Zn(NO_2)_4$ has only a single band at 308 cm^{-1}, which may be assigned as ν_{M-O}. This suggests that the symmetry of the complex is effectively T_d, and that each nitrite

group is bonded essentially via a single oxygen atom. In $Cs_2Zn(NO_2)_4$ the band at ~310 cm^{-1} is very broad and apparently consists of two components at 328 and ~290 cm^{-1}. This splitting of ν_{M-O} may well be due to solid state effects, as the caesium ions are considerably more polarising than o-Cat^{2+}.

In (o-Cat^{2+})$Co(NO_2)_4$ ν_{M-O} is assymmetric to lower energy and is apparently composed of two components at 332(s) and ~294(m) cm^{-1}. This is consistent with a distortion of the primary coordination sphere from T_d to D_{2d}, and is in agreement with nitrite coordination of the kind shown in Figure 28(b).

The spectra of all the compounds containing $Mn(NO_2)_4^{2-}$ show two quite distinct bands, at ~300 and ~260 cm^{-1}, and these have tentatively been assigned as ν_{M-O}. This is consistent with the nitrite groups chelating in these complexes. It is also possible, however, that the broad band at ~260 cm^{-1} is due to the nitrogen-oxygen stretching frequencies, and the peak at ~300 cm^{-1} is due to an out of plane wagging vibration similar to ρ_w in nitro-complexes (see Chapter 6). This wagging vibration should be at much higher energy for a chelated nitrite group than a mono-dentate nitrito-group.

The compounds $K_2M(NO_2)_4$ [M = Cd and Hg] each have a strong broad band at ~230 cm^{-1}, and a weak sharp peak at ~330 cm^{-1}, the latter being split into two components in the cadmium complex. The observation of two peaks in this region is consistent with

chelation of the nitrite groups in these complexes. It seems likely that the broad band at ~230 cm^{-1} is due in each case essentially to one or more metal-oxygen stretching vibrations and it is possible that this band could have further components below 200 cm^{-1}. The weaker sharp bands at ~340 cm^{-1} could either be due to a component of ν_{M-O}, or to the out of plane wagging vibration already discussed for the manganese(II) complexes.

The unusual nature of the bonding in most of these compounds and the consequent splitting of ν_{M-O} makes a direct comparison with other systems difficult. If the weighted mean of the split bands is taken, the stronger bands being assigned as E modes, the order of decreasing ν_{M-O} is Co > Cu > Zn > Mn > Cd > Hg. This sequence is rather similar to that found for the metal-ligand vibrations of other systems MX_4^{2-}, e.g. for X = NCO the following values of ν_{M-N} have been reported[121]:-

Co, 345; Cu, ~338; Mn, 325; Zn, 321; Cd, 298 cm^{-1}.

The metal-oxygen stretching frequencies in the tetranitrite complexes are at rather similar values to ν_{M-N} (~290 cm^{-1}) in the hexanitro-ions $M(-NO_2)_6$ [M = Ni and Cu]. This seems quite reasonable, since the difference in mass between oxygen and nitrogen is small. Also, although ν_{M-X} generally occurs rather higher in tetrahedral MX_4^{2-} ions than in octahedral MX_6^{4-} ions (e.g. ν_{M-N} is at 287 cm^{-1} in $Mn(NCS)_4^{2-}$ and 220 cm^{-1} in $Mn(NCS)_6^{4-}$ [98]) the force constant of the bond $M-NO_2$ may well be somewhat

greater than that of the bond M-ONO.

It is interesting to compare the region in which ν_{M-O} occurs in these tetranitrite complexes with the metal-oxygen stretching frequencies observed in other compounds. In several complexes of the type $M(Ph_3AsO)_2X_2$ [M = Co, Zn, Ni and Mn; X = a halide] Rodley et al. have assigned[122] ν_{M-O} at ~400 cm^{-1}. Similarly Nakamoto et al. have assigned[123] ν_{M-O} at ~420 cm^{-1} in the acetylacetonates of Ni^{II}, Co^{II} and Zn^{II}. These frequencies are considerably higher than those observed in the compounds studied here. However, the nature of the ligands is so different that it is not really to be expected that the metal-oxygen vibrations should occur in a similar frequency range. The spectra of a number of complexes containing coordinated nitrate and sulphate groups have been reported (Table 36) and, while the structures of these compounds are generally complicated or unknown, the metal-oxygen stretching frequencies have been assigned in a similar frequency range to that in the nitrite complexes described here.

Table 36

The metal-oxygen stretching frequencies of some coordinated sulphate and nitrate groups.

Compound	ν_{M-O}	Reference
$Co(NO_3)_2$	316sh, 271s	124
$Co(Ph_3PO)_2(NO_3)_2$ [a]	313 , 279	125
$Cu(NO_3)_2$	336s, 299sh, 253w sh	124
$Cu(2\text{-mepy})_2(NO_3)_2$	328s, 281s, 273s, 266sh	125
$CuSO_4$	345m	124
$Mn(NO_3)_2$	231s, 199sh	124
$Zn(NO_3)_2$	317s, 284s	124
$Cd(NO_3)_2$	199s, 162sh	124

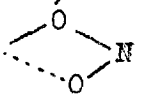
a only ν_{M-O} of the coordinated anions is given

Discussion

It is interesting to speculate on the cause of the manner of coordination adopted by the nitrite groups in the tetranitrite complexes described here. Both $K_2BaCo(-NO_2)_6$ and $K_2SrCu(-NO_2)_6$ are nitrocomplexes, so that the cause of the oxygen coordination of the anions in $Co(NO_2)_4^{2-}$ and $Cu(NO_2)_4^{2-}$ presumably cannot be steric in origin, as more crowding of the ligands is to be expected in the hexanitrite complexes. It is possible that it is the increase in the effective coordination number of the Co^{II} and Cu^{II} ions which occurs on the unsymmetrical chelation of the

nitrite groups which provides the driving force for the adoption of this method of nitrite coordination. Although copper complexes with a coordination number greater than four are comparitively rare, both $K_2SrCu(-NO_2)_6$ and $Cu(NH_3)_4(-NO_2)_2$ [12] are six-coordinate, and both contain nitrite groups bonded via nitrogen. It thus seems reasonable that the cause of the oxygen coordination of the anions in $Cu(NO_2)_4^{2-}$ should be to increase the effective coordination number of the copper ion. Another factor related to this, which is probably important in influencing the manner of nitrite coordination adopted in a complex, is the formal charge of the species involved. In an ion of the type MX_4^{2-} the metal is likely to have a relatively high affinity for negative charge. As the formal charge in NO_2^- is carried on the oxygen atoms, this will tend to favour oxygen coordination of the nitrite groups in a tetranitrite complex. In MX_6^{4-} though, the tendancy will be for the negative charge to be dispersed over the molecule as a whole. Since the nitro-group probably acts as a π-acceptor (and the nitrito-group as a π-donor) this will favour nitrogen-coordination of the nitrite groups in a hexa-nitrite complex.

Nitrite bridging in the compounds $(o\text{-}Cat^{2+})M(NO_2)_4$ is probably precluded by the large size of the cation. It is known[98] that while bridging thiocyanates occur in $[N(CH_3)_4]_2Ni(NCS)_4$, monodentate thiocyanate groups are present in $(p\text{-}Cat^{2+})Ni(NCS)_4$.

The fact that in $M(NO_2)_4^{2-}$ the nitrite groups appear to be essentially monodentate when M = Zn, Co and Cu, but bidentate when M = Mn, Cd and Hg, is probably related to the size of the metal ions. The approximate radii of these, as estimated by Pauling [126], are as follows:- Zn^{2+}, 0·74; Co^{2+}, 0·74; Cu^{2+}, 0·72; Mn^{2+}, 0·80; Cd^{2+}, 0·97; Hg^{2+}, 1·10 Å. With coordination of the type  a balance must be set up between the gain in energy on the formation of the second metal-oxygen bond and the increased steric interaction as eight oxygen atoms are accommodated around the metal ion. With the relatively small ions Zn^{2+}, Co^{2+} and Cu^{2+} only four short metal-oxygen bonds can be tolerated, while with the larger Mn^{2+}, Cd^{2+} and Hg^{2+} eight apparently equivalent oxygen atoms can be positioned around each metal ion.

Both $K_2Pd(NO_2)_4$ and $K_2Pt(NO_2)_4$ are planar nitrocomplexes[39]. However, the spin-paired d^8 electron configurations of Pt^{II} and Pd^{II} usually give rise to the formation of planar compounds, and this would tend to favour nitrogen-coordination of the nitrite groups.

Preparation of Compounds

The o-$Cat(NO_2)_2$ used in the following preparations was made by treating a cold, ethanolic solution of o-$CatBr_2$ with excess finely powdered silver nitrite, shaking vigorously for

about a minute, filtering and precipitating the desired product with ether. Methods essentially similar to that described below for $(o\text{-}Cat^{2+})Mn(NO_2)_4$ were used in the preparation of $(o\text{-}Cat^{2+})M(NO_2)_4$ [M = Cu, Co and Zn]. Details for individual compounds are given below.

$\underline{(o\text{-}Cat^{2+})Mn(NO_2)_4}$ A cold ethanolic solution of $Mn(NO_2)_2$ ($\frac{M}{1000}$) was prepared metathetically from $MnBr_2 \cdot 6H_2O$ and excess finely powdered silver nitrite. This was added to an ethanolic solution of $o\text{-}Cat(NO_2)_2$ ($\frac{1 \cdot 5M}{1000}$) to give a yellow precipitate of $(o\text{-}Cat^{2+})Mn(NO_2)_4$. yield 70%

analysis:- calc. C, 60·88; H, 4·41; O, 14·75.

found C, 60·39; H, 4·48; O, 14·55

$\underline{(o\text{-}Cat^{2+})Cu(NO_2)_4}$ A green, powdery precipitate. yield 60%

analysis:- calc. C, 60·30; H, 4·37; O, 14·61.

found C, 60·50; H, 4·50; O, 14·50.

$\underline{(o\text{-}Cat^{2+})Co(NO_2)_4}$ Oxygen free acetone was used as the solvent in the preparation of this complex. On mixing the solutions of $Co(NO_2)_2$ and $o\text{-}Cat(NO_2)_2$ a faint yellow precipitate formed, which was filtered off and discarded. Addition of ether produced a precipitate of $(o\text{-}Cat^{2+})Co(NO_2)_4$ and this was recrystallised from oxygen free acetone as large purple crystals. yield 15%

analysis:- calc. C, 60·61; H, 4·39; N, 6·43; O, 14·69; NO_2^-, 21·12.

found C, 60·43; H, 4·46; N, 6·48; O, 14·23; NO_2^-, 21·00.

$\underline{(o\text{-}Cat^{2+})Zn(NO_2)_4}$ A methanolic solution of zinc nitrite was

prepared metathetically from $Zn(NO_3)_2 \cdot 6H_2O$ and sodium nitrite and added to a methanolic solution of o-$Cat(NO_2)_2$. On addition of a little ether a white, crystalline precipitate formed.

yield 40%

analysis:- calc. C, 60·17; H, 4·36; N, 6·38; O, 14·57; NO_2^-, 20·95.

found C, 59·91; H, 4·34; N, 6·02; O, 14·45; NO_2^-, 21·17.

$[N(CH_3)_4]_2Mn(NO_2)_4$ Yellow crystals of this compound were prepared by a method similar to that of $(o\text{-}Cat^{2+})Mn(NO_2)_4$ but using $N(CH_3)_4Br$ as a starting material. yield 70%

analysis:- calc. C, 24·81; H, 6·25; O, 33·06.

found C, 25·22; H, 6·36; O, 33·15.

$Cs_2Zn(NO_2)_4$ Caesium nitrite was prepared by mixing equimolar aqueous solutions of caesium sulphate and barium nitrite, filtering off the precipitated barium sulphate, and evaporating the resulting solution to dryness. A methanolic solution of $Zn(NO_2)_2$ ($\frac{3\cdot5M}{1000}$) was prepared metathetically from $Zn(NO_3)_2 \cdot 6H_2O$ and sodium nitrite and added to caesium nitrite ($\frac{8M}{1000}$) in methanol (40 mls.). This yielded a white, crystalline precipitate which was recrystallised from methanol. yield 10%

analysis:- calc. Zn, 12·69; NO_2^-, 35·71.

found Zn, 12·78; NO_2^-, 35·42.

$Cs_2Mn(NO_2)_4$ A methanolic solution of manganous nitrite ($\frac{M}{100}$) was added to caesium nitrite ($\frac{M}{100}$) in methanol (40 mls.) to give a cream precipitate. This was recrystallised from methanol to give

large yellow crystals. These were slightly photosensitive, but remained unchanged for several weeks on being stored at ~0°C under the mother liquor. yield 15%

analysis:- calc. Mn, 10·88; NO_2^-, 36·46.

found Mn, 10·60; NO_2^-, 36·35.

$K_2Cd(NO_2)_4$ Saturated aqueous solutions of cadmium bromide and excess potassium nitrite were mixed and left for several days when large, pale yellow crystals formed. yield 30%

analysis:- calc. Cd, 30·00; NO_2^-, 49·12.

found Cd, 29·91; NO_2^-, 48·93.

$K_2Hg(NO_2)_4$ A solution of mercuric nitrite was prepared metathetically in the minimum of water from mercuric chloride and a slight excess of silver nitrite. This was added to a saturated aqueous solution of excess potassium nitrite. On leaving at 0°C for two days large straw-coloured crystals formed. yield 30%

analysis:- calc. Hg, 43·43; NO_2^-, 39·77.

found Hg, 43·06; NO_2^-, 39·80.

Several attempts were made to prepare a compound by mixing ethanolic solutions of nickel nitrite and o-$Cat(NO_2)_2$. In each case a grey, gelatinous precipitate formed, but although solutions dried with molecular sieves were used, and the reaction was carried out in an enclosed apparatus under dry air, the product was in each case found to be very hygroscopic and to

exhibit infrared bands due to water. No analysis of the compound was made.

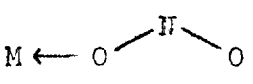
Brown precipitates were also obtained by mixing an ethanolic solution of ferrous nitrite (prepared by exchanging ferrous chloride with silver nitrite) with ethanolic solutions of o-$Cat(NO_2)_2$ or $N(CH_3)_4NO_2$, the reaction being in each case carried out under nitrogen. However, as these products showed infrared bands due to water and gave off brown fumes of nitrogen dioxide on exposure to the atmosphere, they were not analysed. Purple crystals were obtained by adding, under nitrogen, an ethanolic solution of $N(CH_3)_4NO_2$ ($\frac{2M}{100}$) to an ethanolic solution of cobaltous nitrite ($\frac{M}{100}$). On filtering under nitrogen these went brownish-green and exhibited infrared bands due to water. They were not analysed. Addition of an ethanolic solution of $N(CH_3)_4NO_2$ to an ethanolic solution of cupric nitrite produced a brown, unanalysed, precipitate, which had infrared bands due to water and gave off fumes of nitrogen dioxide on exposure to the air.

CHAPTER 8

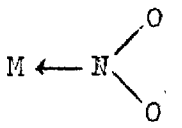
A General Summary

This Chapter summarises the ways in which each of the different methods of nitrite coordination can be identified, and the type of compound in which they are normally found.

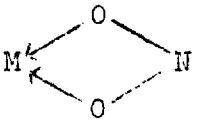
The known methods of nitrite bonding are illustrated below, together with the terminology used in this summary to specify each type of coordination.



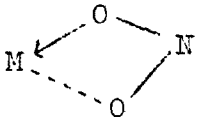
nitrito



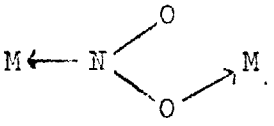
nitro



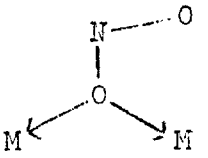
chelating



unsymmetrical chelating



bridging(NO)



bridging(O)

Identification of the method of nitrite coordination

A) Infrared Spectra

The frequencies and relative intensities of the nitrite infrared stretching vibrations ν_s and ν_{as} are usually the best guide to the method of nitrite coordination in a compound. The frequency ranges associated with each type of bonding are given in Table 37.

The frequencies are often dependant upon the nature (and particularly the oxidation state) of the metal ion to which the nitrite group is coordinated. Also, the frequency ranges sometimes overlap; thus the nitrite infrared spectrum of an unsymmetrically chelated group is similar to that of a weakly bound nitrito-group.

The infrared vibrations associated directly with the metal-ligand bond can sometimes act as a guide to the type of nitrite coordination in a complex. However, only a limited number of compounds have been studied in this frequency range, and these have been discussed in Chapters 6 and 7.

Table 37

Type of Nitrite Bonding	Metal Ion	ν_{as} (cm^{-1})	ν_{s} (cm^{-1})	Reference
ionic	Na^{I} K^{I}	1225-1270 vs br	1325-1335 w-vw	19-23
	Ba^{II}		sp	25
nitrito	Ni^{II}	1114-1220 s-vs	1340-1400 ms-s	a
	Co^{III} Rh^{III}	1060-1070 s-vs	1460-1470 s	6, 7, 29
	Ir^{III} Cr^{III}			
	Pt^{IV}	995 s	1505 s	7
nitro	Ni^{II} b	1300-1335 vs	1320-1350 w-vw	a, 29, 39
	Co^{II} c Cu^{II}	1280-1335 vs	1335-1395 m-vw	a, 92, 94
	Co^{III} Rh^{III}	1375-1420 s-vs	1330-1350 s	39, 92
	Ir^{III}			
	Pt^{II} Pd^{II}	1380-1440 s-vs	1310-1350 s	29, 39
	Pt^{IV}	1460-1485 s-vs	1325-1335 s	39
chelating	Ni^{II} Co^{II}	1175-1205 vs	1265-1315 vw-m	a
	Mn^{II}	1205-1240 vs br	1300 vw	a
	Cd^{II} Hg^{II}	1200-1270 vs br	d	a, 39,117
unsymmetrically chelating	Co^{II} Cu^{II}	1195-1205 vs	1370-1390 m-s	a
bridging(NO)	Ni^{II}	1200-1255 s-vs	1410-1440 s	a
	Co^{III}	1180-1200 s	1485-1515 s	29, 31
bridging(O)	Ni^{II}	1005-1025 s	1460-1490 s	a

a this work b spin-free c spin-paired

d this frequency has not been assigned with certainty

B) Electronic Spectra

When investigating the nature of the bonding in a nitrite complex the energies of the d-d electronic transitions are useful in essentially two ways.

Firstly, in conjunction with the magnetic susceptibility, they usually indicate the approximate symmetry of the ligand field, i.e. whether the complex is planar, tetrahedral or octahedral. From the stoichiometry it is then often apparent whether the nitrite groups are expected to be monodentate or bidentate.

Secondly, it is generally possible to tell from the electronic spectrum of a complex whether the nitrite groups are coordinated via nitrogen or oxygen. This is because nitrite groups coordinated solely via oxygen (i.e. as nitrito, chelated, unsymmetrically chelated and bridged(O) groups) are at the weak end of the spectrochemical series, while those bonded solely or partly via nitrogen (i.e. nitro and bridged(NO) groups) are at the strong end. The oxygen bonded nitrite groups have a Δ-value of $\sim$9,000 cm^{-1} when octahedrally coordinated to Ni^{II}, while those bonded via nitrogen have $\Delta \sim 13,000$ cm^{-1}.

Discussion of Compounds containing the different kinds of coordinated nitrite group

Nitro

This is the method of nitrite coordination adopted in most of the complexes of Ni^{II}, Pt^{II}, Pd^{II}, Co^{III}, Rh^{III}, Ir^{III} and Pt^{IV}.

Nitrito

Unstable nitritocomplexes of the 'inert' metal ions Co^{III}, Rh^{III}, Ir^{III} and Pt^{IV} are known, but these have only been isolated by means of an unusual reaction sequence[3-7].

A series of stable nitritocomplexes of Ni^{II} have been prepared, and it has been suggested that the oxygen coordination of the nitrite groups in these is caused primarily by steric interferance with other ligands.

In the only two nitrite complexes of Cr^{III} which have been studied[29,127], oxygen bonded nitrite groups are present. The reasons why this manner of coordination occurs are not known.

It is possible that the nitrite group normally bonds via nitrogen because of the greater crystal field stabilisation energy produced by this manner of coordination. If so, in complexes where this energy is effectively zero (i.e. with metal ions having filled or half-filled d-shells) the nitrite groups might be expected to bond via oxygen rather than nitrogen, particularly as the hydrogen in nitrous acid is attached to an oxygen atom. However, as yet almost no complexes with metal ions

of this kind are known, so that this hypothesis remains to be investigated.

Chelating

Chelating nitrite groups occur in several complexes of the type $ML_2(NO_2)_2$ [M = Co^{II} and Ni^{II}, L = a monodentate ligand]. The stoichiometry of these compounds is apparently limited by the bulky nature of the ligands L, and it is probably also the steric requirements of these ligands which prevents nitrite bridging. The nitrite groups presumably chelate since by this means the effective coordination number of the metal ions is increased from four to six.

Chelating nitrite groups are also present in $M(NO_2)_4^{2-}$ [M = Hg, Cd and Mn].

Unsymmetrical Chelating

This manner of coordination is apparently present in the tetranitrite complexes of Co^{II} and Cu^{II} formed with bulky cations. The size of the cations probably precludes nitrite bridging, and the anions presumably cannot all chelate as this would produce too much steric interaction between the oxygen atoms around the relatively small Co^{II} and Cu^{II} ions. Instead, the effective coordination number of the metal ions appears to be increased by unsymmetrical chelation.

Bridging(NO)

Several complexes of Ni^{II} and Co^{III} have nitrite groups

bonded in this way, and it seems likely that this method of bidentate nitrite coordination is the one generally adopted with these metal ions when steric considerations are unimportant.

Bridging(O)

This type of bonding is at present known only from an isolated series of nickel complexes, and the reasons for its adoption are obscure.

Physical Measurements

Electronic Spectra

These were measured in the solid state by the reflectance technique using Unicam S.P. 500 and Beckman D.K. 2 spectrometers. Solution spectra were observed using a Perkin-Elmer Model 350 spectrometer.

Infrared Spectra

In the range 4000 - 400 cm^{-1} these were obtained using a Grubb-Parsons Spectromaster grating spectrometer, and between 400 and 200 cm^{-1} with a Grubb-Parsons D.M. 2 grating spectrometer.

Magnetic Susceptibility measurements were made using a Gouy balance of the conventional type.

Molecular Weights were determined in solution with a Mechrolab. Inc. vapour pressure osmometer, Model 301 A.

Analysis Methods

The elements C, H, N and O were determined by the Imperial College Microanalytical Laboratory. Metals were usually determined volumetrically by titration with E.D.T.A.[128], though potassium was estimated by flame photometry, and nickel was in some cases determined gravimetrically by precipitation with dimethylglyoxime. Analysis for ionic nitrite was carried out by the method in Vogel[129].

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