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A SPECTROSCOPIC STUDY OF THE NITRATE GROUP

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A THESIS SUBMITTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

Department of Chemistry

The City University, London.

June 1973

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I would like to thank Brian Field for his great patience, encouragement and help in the years of our friendship. Also for teaching me Chemistry as a civilised art.

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"How great are your works, O Lord.

Your thoughts are very deep"

Psalm 92.6

INDEX

		Page
1	Abstract	
2	Literature Survey	1
2.1	Structural Discussion	1
2.1.1	Introduction	1
2.1.2	Nitrate Ion	1
2.1.3	Unidentate Nitrato Group	3
2.1.4	Bidentate Nitrato Group	9
2.1.5	Bridging Nitrato Group	15
2.1.6	Other Structural Modes	17
2.2	Vibrational Spectra	21
2.2.1	Nitrate Ion	21
2.2.2	Unidentate Nitrato Group	22
2.2.3	Bidentate Nitrato Group	26
2.2.4	Raman Spectra	32
2.2.5	Bridging Nitrato Group	34
2.3	Spectral Difficulties and Practical Problems	34
2.4	Scope of this Research	39a
3	Experimental	40
3.1.1	Dehydration Methods	40
3.1.2	Preparation and Use of Liquid N_2O_4 and N_2O_5	40
3.2	Analysis	46
3.2.1	Nitrate	46
3.2.2	Metal	47
3.2.3	Water	
3.3	Spectral Recordings	48

		Page
3.3.1	Infra-red spectra	48
3.3.2	Electronic Spectra	49
3.4	Magnetic Susceptibility	49
4	Results	50
4.1	Nickel	50
4.1.1	Introduction	50
4.1.2	$[Ni(H_2O)_6](NO_3)_2$	50
4.1.3	$[Ni(NO_3)_2(H_2O)_4]$	51
4.1.4	$[Ni(NO_3)_2(H_2O)_2]$	53
4.1.5	$[Ni(NO_3)_2]$	56
4.1.6	Infra-red Spectra and Assignments	59
4.2	Cobalt	65
4.2.1	Introduction	65
4.2.2	$[Co(H_2O)_6](NO_3)_2$	65
4.2.3	$[Co(NO_3)_2(H_2O)_4]$	65
4.2.4	$[Co(NO_3)_2(H_2O)_2]$	68
4.2.5	$[Co(NO_3)_2]$	69
4.2.6	Infra-red Spectra and Assignments	73
4.3	Manganese	78
4.3.1	Introduction	78
4.3.2	$[Mn(H_2O)_6](NO_3)_2$	78
4.3.3	$[Mn(NO_3)_2(H_2O)_4]$	78
4.3.4	$[Mn(NO_3)_2(H_2O)_2]$	79
4.3.5	$[Mn(NO_3)_2]$	80
4.3.6	Infra-red Spectra and Assignments	82
5	Concluding Discussion	85
	References	88
	Appendix: Infra-Red Spectra	96

ABSTRACT AND SYNOPSIS

The structures of the NO_3 group have been discussed and the vibrational spectra that may be expected to result from these structures. The various spectral criteria suggested to differentiate between these structures have been reviewed and the experimental problems in obtaining these spectra have been outlined.

The series of compounds $M(NO_3)_2(H_2O)_4$, $M(NO_3)_2(H_2O)_2$, $M(NO_3)_2$ where M = Mn(II), Co(II), Ni(II) have been prepared by dehydration techniques and characterised by analysis, infra-red and electronic spectral measurements and magnetic susceptibility determinations. The infra-red spectra have been examined in detail in the 3600-200cm^{-1} range and related to the structures of the compounds where these are known. The spectra are discussed in relation to the structural criteria found in the literature. It is suggested that the near infra-red region (3600-500 cm^{-1}) can only indicate that the NO_3 group is co-ordinated and give some indication of the strength of the metal-nitrato interaction. The far infra-red region (500-200cm^{-1}) can give information about the environment of the metal atom and hence can indicate the mode of nitrato co-ordination from the number of bands observed, their positions and their shapes. This is probably seen clearly only when oxygen atoms are bonded to the metal, and not so clearly when N-bonded or S-bonded ligands are present. Chloro compounds could probably be fruitfully examined also, as the metal-chlorine bond usually has a higher force constant than the metal-oxygen bond.

It is felt that polarised Raman studies of single crystals, related to the crystal symmetry of the compound is the best method of obtaining clear information about the vibrational frequencies of nitrato compounds.

LITERATURE SURVEY

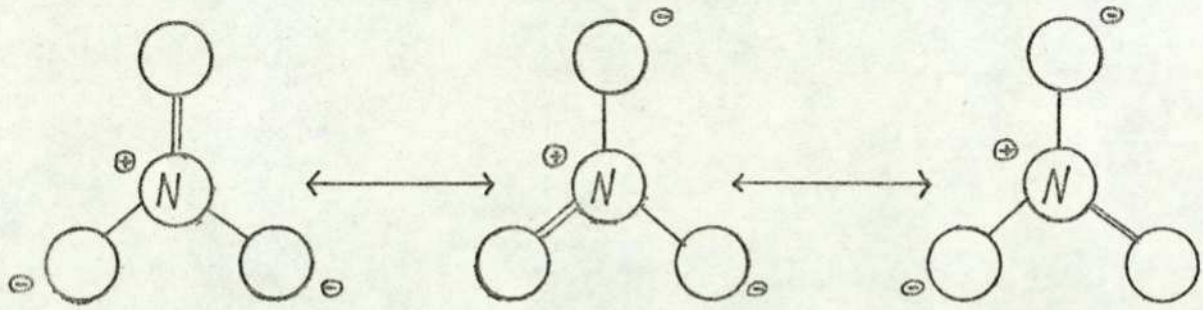
2 LITERATURE SURVEY

2.1.1 Introduction

The NO_3 group has long been recognised as an independent chemical entity by virtue of its ability to take part in substitution reactions without undergoing decomposition. This led to the use of the NO_3 group as a simple counter ion in the preparation of many transition-metal compounds. However, it is now recognised that the NO_3 group can also function as a ligand bonded directly to the metal atom in compounds. Many compounds have now been prepared which indicate that the NO_3 group can function as a strong ambidentate ligand.

2.1.2 The Nitrate Ion

The NO_3 group as an ion has been the subject of many theoretical treatments. The valence-bond approach views the ion as a set of resonance hybrids with the π-bond distributed over the three nitrogen-oxygen bonds [1].



The molecular-orbital treatment[2] divides the twenty-four electrons into σ-bonding and anti-bonding, π-bonding and anti-bonding molecular orbitals: $(3\sigma)^6$, $(3N_{sp})^6$, $(\pi_1)^2$, $(2Np)^4$, $(\pi 2,3)^4$, $(Np)^2$, $\pi 4$, $3\sigma^*$. Delocalization of the $p\pi$ electrons occurs and the electronic charge is spread evenly over the molecular skeleton.

Earlier theoretical treatments have yielded stretching force constants of the order of 10-12[3,4,5] m dynes/Å, but most of the more

recent work places a value of 7-8.5 m dynes/Å[6-10] on this vibrational mode.

Electronic spectral treatments have not been completely successful in accounting for the observed spectrum. Two bands are observed at 200mμ ($\varepsilon \approx 10^4$) and 302mμ ($\varepsilon = 7$). It is generally agreed[11-15] that the 200mμ band is a $\pi \rightarrow \pi^*$ transition ($A_1' \rightarrow E'$), and the fine structure has been identified as the vibrational structure of the D_{3h} symmetry allowed transition. The origin of the 302 mμ band, however, is less clear. Friend and Lyons[11], McConnel[12], McEwens[13], Mookherji and Tandon[14], Nagy et al[15] attribute this band to a forbidden $n \rightarrow \pi^*$ transition. If this is correct then there are two possible transitions, described by Addison and Sutton[16] as $e' \rightarrow a_2''$ ($^1E''$) and $a_2' \rightarrow a_2''(^1A_1'')$ and they assign the latter to the 302mμ band. McEwen[13], however, suggests that this transition is $A_1' \rightarrow E''$ (or $A_1' \rightarrow A_1''$)[11] which could possibly receive some $A_1' \rightarrow E'$ character, borrowing intensity from the 200 mμ band by vibrational perturbation.

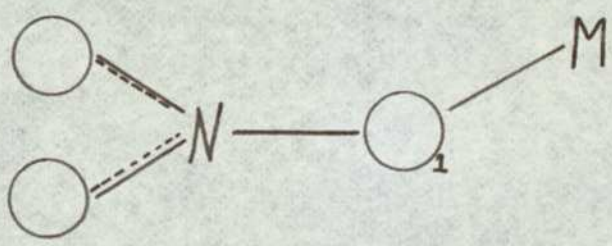
However, McEwens' calculated transition energy does not agree with the observed value of 302mμ. Instead the possibility is raised that this band is a weakly allowed $n \rightarrow \sigma^*$ transition from an E' orbital to an $A_1'\sigma$-antibonding orbital. This is supported by Rotlevi and Treinin[17]. The possibility still remains that both transitions may be occurring within the same envelope.

The ion is planar and symmetric with three equal N-O bonds, the lengths of which are about 1.243Å (average), which is intermediate between the values expected for pure N=O double bonds 1.16Å and pure N-O single bonds 1.43Å[8]. These structural features have been adequately confirmed by many crystal structure determinations, too

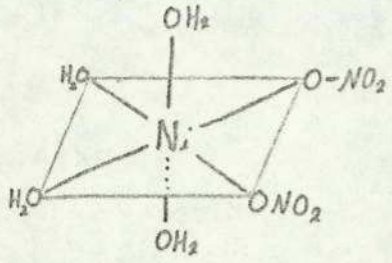
many of which dismiss discussion of the nitrate ion in a few lines because of these consistent features. Only a few papers[5], at present discuss the case of weak interactions giving rise to small deviations from the high symmetry of the unperturbed nitrate ion. Often these deviations are considered to be within the limit of the experimental error for the structural determination and so are not discussed further.

2.1.3 Unidentate Nitrate Group

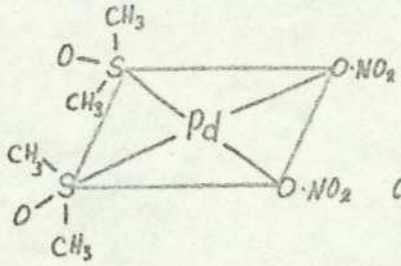
As a unidentate ligand the NO_3 group would be expected to show structural differences from the free ion. The N–O' bond length would be expected to be longer than the value for the free ion, since the bond approaches purer single bond character.



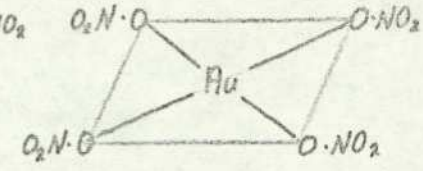
The two remaining N–O bonds would be expected to be shorter than the free-ion value, as they approach double-bond character. Also, the bond angles would be expected to change from three equal angles of 120° to one $>120^\circ$ opposite the M–O–N bond, and two equal angles of $<120^\circ$. This is confirmed by structural analysis. The unidentate nitrate group is by no means as common as was once thought. At the present time the only transition-metal compounds which have been shown to contain unidentate nitrate groups are:



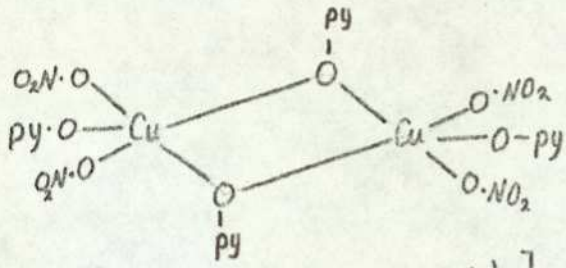
cis-$[Ni(NO_3)_2(H_2O)_4]$



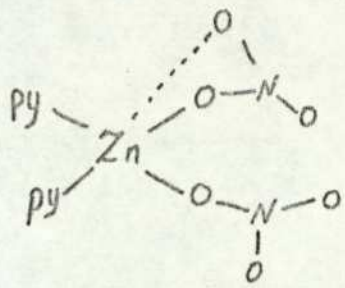
cis-$[Pd(NO_3)_2(DMSO)_2]$



$K[Au(NO_3)_4]$



$[Cu(NO_3)_2(\text{Pyridine N-oxide})_2]_2$



$[Zn(NO_3)_2(Py)_2]$

Figure 1

CIS - $[Ni(NO_3)_2(H_2O)_4]$ (18)

CIS - $[Pd(NO_3)_2(\text{dimethylsulphoxide})_2]$ (19)

$K^+[Au(NO_3)_4]^-$ (20),(21)

$[Zn(NO_3)_2(\text{pyridine})_2]$ (22)

$[Cu(NO_3)_2(\text{pyridine-N-oxide})_2]_2$ (23)

$[Cu(NO_3)_2(CH_3CN)_2]$ half of the nitrato groups are unidentate (24)

$[Mn(NO_3)_3(2,2'\text{-bipyridyl})]$ one unidentate nitrato group (25)

$[VO(NO_3)_3(CH_3CN)]$ one unidentate nitrato group (26)

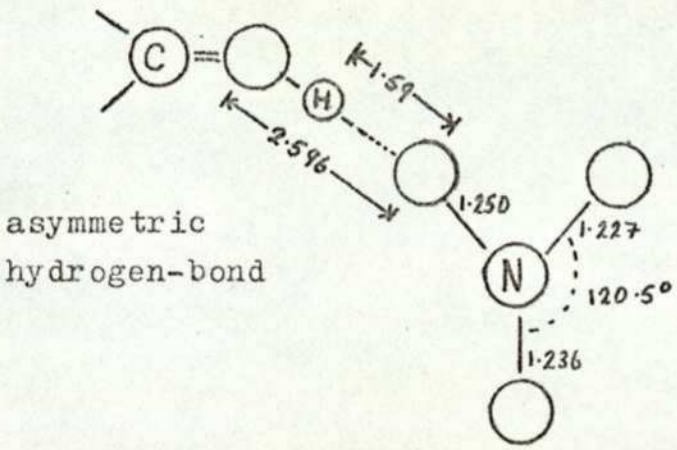
$[Re(NO_3)(CO)_5]$ reported, but not yet published (27)

The others which have been studied are of the type M-ONO_2 where M=F,Cl ,H, CH_3, Li, Na. It is probable that other compounds contain unidentate nitrato groups, e.g. $[Co(NH_3)_5(NO_3)]Cl_2$ and $[Mn(NO_3)(CO)_5]$, but no structural data is available at present.

Weak interactions can also be interpreted in this light. Crystals which are held together by hydrogen bonding between the oxygen atom(s) of the nitrate ion and the protons of the cation show small distortions of the nitrate ions consistent with a very weak unidentate character for the NO_3 groups.

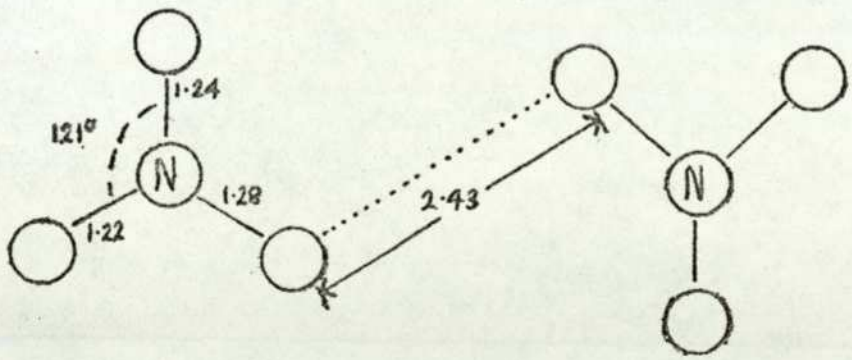
Some examples of this are:

(i) <u>uronium nitrate</u> $(NH_2)_2COH^+.NO_3^-$ (28)



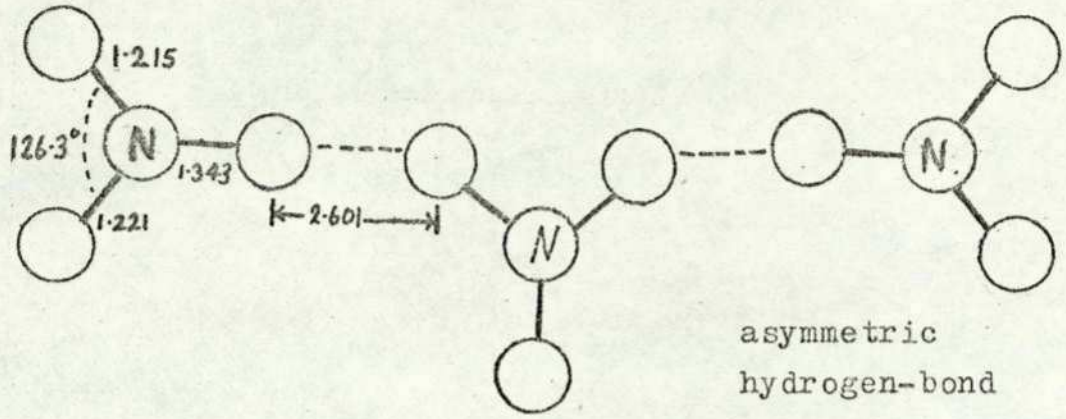
asymmetric hydrogen-bond

(ii) <u>Hydrogen dinitrate ion</u> $[H(NO_3)_2]^-$ (29)



symmetric hydrogen-bond

(iii) $\underline{NH_4NO_3 \cdot 2HNO_3}$ $[H_2(NO_3)_3]^-$ (30)



(iv) $\underline{[UO_2(H_2O)(urea)_4](NO_3)_2}$ (31)

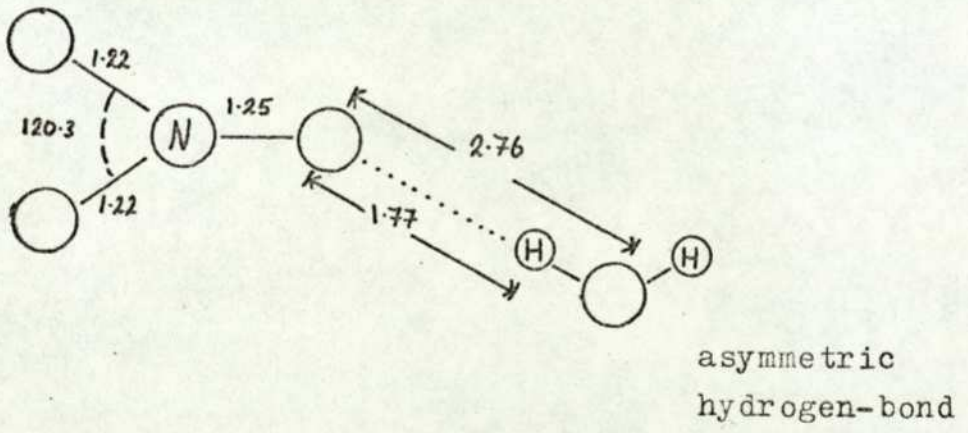


Figure 2

It appears from this that the bond lengths are more sensitive to these weak interactions than the bond angles, as the hydrogen-bonded nitrogen-

oxygen bond is longer than the free ion value, and the other nitrogen-oxygen bond lengths are shorter than the free ion value of 1.243A. Tanaka[32] et al, however, have carried out a force constant calculation on the compound $[Co^{III}(NH_3)_5(NO_3)]Cl_2$ and draw the opposite conclusion, that the bond angles are more sensitive to bonding interactions than the bond lengths.

It is noticeable that for those simple nitrate compounds $M-O-NO_2$, where M = F,Cl,H,CH_3,Li,Na, the ONO bond angle opposite to the M-O-N bond is very large (125-135°). (Table 2a).

Compound	M-O_1 (Å)	N-O_1 (Å)	N-O_2 N-O_3	$O\hat{N}O_3$	Method of Determination	Ref.
HNO_3	H-O 0.964	1.406	1.199,1.21	131°2'	Microwave	33
HNO_3	-	1.41(2)	1.22(2),1.22(2)	130(2)°	Electron diffraction	34
$F.NO_3$	F-O 1.42	1.39	1.29,1.29	125°	-"-	35
$Cl.NO_3$	Cl-O 1.70	1.41	1.22,1.22	130°	Estimated	36
$CH_3.NO_3$	C-O 1.43	1.36	1.26,1.26	125°	Electron diffraction	35
$LiNO_3$	Li-O 1.60	1.40	1.22,1.22	134°	-"-	37
$NaNO_3$	Na-O 1.90	1.40	1.22,1.22	134°	-"-	37
N_2O_5	N-O 1.46(2)	1.46	1.21(1),1.21(1)	134(5)°	-"-	38
pentaerythritol tetranitrate	C-O 1.462	1.404	1.203,1.225	130.4°	X-ray	39
CIS-1,2-acenaphthene diol dinitrate	C-O 1.47	1.41	1.19,1.23	133°	X-ray	40

Table 2a

It is to be expected that as the nitrogen-oxygen bond ($N-O_1$) becomes longer the bond electron pairs on the remaining two nitrogen-oxygen bonds are able to move further apart, thus reducing the electronic repulsion between them. This results in the observed increase in ONO bond angle.

The compounds listed in Table 2a all have 'normal' M-O bond lengths and (yet) the nitrogen-oxygen bond ($N-O_1$) approaches the 'normal' nitrogen-oxygen single bond length of 1.43Å. However, for the transition-metal compounds the metal-oxygen bond length is 'normal' for the metal in that oxidation state, whilst the nitrogen-oxygen bond length ($N-O_1$) is shorter than the single bond length at about 1.31Å (Table 2b) with smaller O_2NO_3 bond angles. Why this should be so is not clear.

Perhaps the compounds in Table 2a are able to form stronger bonds to the nitrato group because they also use s- and p-orbitals similar to those on the nitrato group. The transition metals, on the other hand, use d-orbitals for bonding and the overlap with the sp-hybrid orbitals of the nitrato group is not so complete.

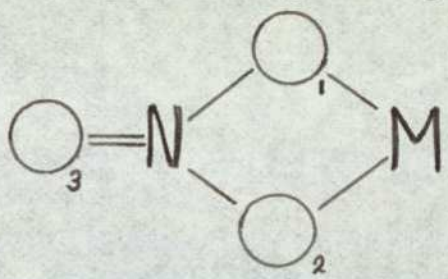
Compound	M-O_1 (Å)	N-O_1 (Å)	N-O_2, N-O_3 (Å)	$O_2\hat{N}O_3$	Ref.
$[Ni^{II}(NO_3)_2(H_2O)_4]$	2.052(9)	1.304(12)	1.264,1.236	121.30°	18
	2.079(9)	1.293(12)	1.244,1.213	123.81°	
$[Pd^{II}(NO_3)_2(DMSO)_2]$	2.066	1.32(1)	1.217(9) 1.217(9)	-	19
$K[Au^{III}(NO_3)_2]$	2.02(2)	1.34(2)	1.14(3),1.24(3)	129°(2)	20
	1.99(1)	1.39(3)	1.20(2),1.22(2)	131°(2)	
$[Cu^{II}(NO_3)_2(CH_3CN)_2]$	1.89	1.31(5)	1.30(7),1.23(5)	130°	24
$[Cu(NO_3)_2(pyNO)_2]_2$	1.996(5)	1.316(9)	1.222(9),1.227(10)	123.1°	23
	1.967(5)	1.304(8)	1.221(8),1.234(9)	125.6°	
$[Zn(NO_3)_2(py)_2]$	2.047(13)	1.31(2)	1.25,1.25(2)	120.4(14)	22
	2.044(12)	1.28(2)	1.28,1.27(2)	120.1(16)	
$(Mn(NO_3)_3(bipy)$	1.864(8)	1.241(13)	1.115(14)	115.6°(15)	25
			1.234(18)		
$[VO(NO_3)_3(CH_3CN)]$	1.92(2)	1.45(3)	1.19,1.24(3)	130.2°(25)	26

Table 2b

2.1.4. Bidentate Nitrato Group

As a bidentate ligand the nitrato group would be expected to show the following structural features: (1) one short N-O bond of near "pure" double bond character; (2) two approximately equal N-O bonds rather longer than those found in the free NO_3 group, but not as long as an N-O bond of

single bond character. (This is due to the limited movement of the oxygen atom along the N-O bond axis conducive to good overlap with the orbitals of the metal atoms). (3) An ONO bond angle much less than 120° opposite the metal atom and, (4) two approximately equal ONO angles slightly greater than 120°. These features are observed in the bidentate nitrato compounds of known structure.(e.g.41, 42)



The actual N-O bond lengths vary quite a lot and it has been suggested that the stronger the metal-oxygen interaction, the shorter is the terminal N-O bond length. For example, the volatile compounds $Ti(NO_3)_4$ [41] and $Sn(NO_3)_4$ [42] both show N-O bond lengths of 1.18Å (average) indicating the strong bonding interaction between the metal and oxygenatoms. It is notable that there are no compounds known in which the NO_3 group is bonded in a bidentate manner to a non-metal, as is more commonly found for the unidentate nitrato group. It is also noteworthy that, at the present time the number of bidentate nitrato compounds (far) exceeds those of the unidentate nitrato compounds, a state of affairs which is the opposite of that originally expected. In the early work all compounds were assumed to possess unidentate nitrato groups. The reasons for this assumption may perhaps be found in the disinclination at one time to contemplate co-ordination numbers greater than six, together with the supposed instability of four-membered rings. In addition, perhaps a lack of appreciation of the changes in molecular properties and reactivity on passing from an aqueous to a non-aqueous system.

It is perhaps suitable to insert here a few words about two compounds of known structure which do not easily fit into either of the two categories outlined above. These are $[Co(NO_3)_4]^{2-}$ [43] and $[Bi(NO_3)_3(H_2O)_3]2H_2O$ [44]. The structures of these two molecules have been interpreted by their respective authors as containing bidentate nitrato groups, but it would seem to be a forced interpretation. The structures could perhaps be more realistically interpreted as containing unidentate nitrato groups (with one normal metal-oxygen bond length per NO_3 group) in which a second oxygen atom of each nitrato group approaches close to the metal atom, giving metal-oxygen distances of 0.3-0.5Å (16-20%) longer than the normal distances. This crystallographic proximity cannot really be considered to be a bonding interaction.

Before the crystal structure was determined, the electronic spectrum was interpreted as indicating a tetrahedral environment for the cobalt (II) atom. The spectrum shows a single broad absorption at 538mμ (εmax = 107 in 0.0045M nitromethane), which was considered to be consistent with tetrahedral co-ordination of the cobalt (II) atom. [45,46,47] In addition, a magnetic moment of 4.67BM [45] was observed, which again was considered to be consistent with a tetrahedral environment for the cobalt (II) atom. These two points are no longer regarded as being so definitive.

(1) The high-spin cobalt (II) ion in both the octahedral and tetrahedral bonding environments has three unpaired electrons, giving a "spin-only" magnetic moment of 3.87BM. However, for an octahedral ligand field there is some contribution to the magnetic moment from the orbital angular momentum, and values are observed in the range 4.7 - 5.2 B.M. [48]

Although no orbital contribution is theoretically expected for a tetrahedral ligand field, molecular distortions do allow some contribution and magnetic moments in the range 4.2-4.8[48] are considered normal. The two nitrato-cobalt (II) compounds of known structure have magnetic moments in the overlap between the octahedral and tetrahedral ranges: for $[Ph_4As]_2[Co(NO_3)_4]$[43] μ_{eff} = 4.67BM[45] and for $[Co(NO_3)_2(Me_3PO)_2]$[44] μ_{eff} = 4.59BM[50]. It has been suggested[51] that the magnetic moments of cobalt (II) compounds indicate only the nature of the orbital ground state. A magnetic moment of 4-4.8BM implies an orbital singlet ground state, and higher values indicate an orbital triplet ground state.

(2) It is difficult to distinguish clearly between tetrahedral and octahedral co-ordination of the cobalt (II) ion from the electronic spectrum. Generally, the band positions for a given donor atom, do not vary much, but the band intensities are expected to be very different. Octahedral cobalt (II) compounds have very low molar absorbances (ε = 5), and tetrahedral compounds exhibit high molar absorbances (ε = 500) for the main transition in the 500-600mμ region. Known nitrato compounds of cobalt (II) have values in the range ε = 50-150, for example:

$[Co(NO_3)_2]$	: ε = 78.8	at 520 mμ (nitromethane)[52]
$[Co(NO_3)_4]^{2-}$	: ε = 107; 135 [45][47]	at 538 mμ (nitromethane)
$[Co(NO_3)_2(Me_3PO)_2]$	: ε = 114	at 560 mμ (dichloromethane)[44]
$[Co(NO_3)_2(EPNO)_4]$	: ε = 48.5	at 534.2mμ(nitromethane-acetone)[53]
$[Co(NO_3)_2(\alpha\text{-picoline})_2]$	: ε = 154	at 539.3mμ(acetone)[51]

These intermediate values for the molar absorbances and the electronic spectra seem to indicate that such nitrato compounds possess distorted tetrahedral environments. Cotton and Bergman[43] showed that $[Co(NO_3)_4]^{2-}$ possesses a point group symmetry of D_{2d} which is a sub-division of T_d (tetrahedral). Hence, the co-ordination is a distorted tetrahedral arrangement, lying somewhere between a true four-co-ordinate and a true eight-co-ordinate structure. There is a greater conflict between the spectral data and the octahedral arrangement found in $[Co(NO_3)_2(Me_3PO)_2]$. This led Cotton[49] to suggest that the nitrato groups act as large diffuse uni-negative anions centred at the nitrogen atom positions. This introduces considerable distortion into the tetrahedral environment of the cobalt (II) ion, as shown by the electronic spectrum. Wood has applied this principle to the structure of $[Ce^{III}(NO_3)_5]^{2-}$(54).

The co-ordination of the nitrato group will be very dependent on packing considerations. Thus, in $[Co(NO_3)_4]^{2-}$ the close proximity of the nitrato groups allows only essentially unidentate co-ordination. In $[Co(NO_3)_2(Me_3PO)_2]$ there is less steric interaction between the ligands and the nitrato groups can approach closer to the cobalt (II) ion and bond in an asymmetric bidentate manner.

A similar structural interpretation can be applied to the copper(II) nitrato compounds for which molecular dimensions are available. Firstly, the group of compounds which formally contain unidentate nitrato groups, but with longer metal-oxygen bonds. (Table 2c).

Compound	Cu-O_1(Å)	N-O_1(Å)	Refs.
$[Cu(NO_3)(dach)_2]^+$	2.355(8)	1.258(11)	55
$[Cu(NO_3)(bipy)_2]^+$	2.30	-	56
$[Cu(NO_3)_2$(Meα-picolylamine$)_2]$	2.507(9)	1.257(14)	57
$[Cu(NO_3)_2$ (en$)_2]$	2.593(12)	1.258(2)	58
$[Cu(NO_3)_2$(NN^1-Me$_2$-en$)_2]$	2.520(5)	1.230(14)	59
$[Cu(NO_3)_2$(N-Me-en$)_2]$	no data	similar lattice dimensions	60
$[Cu(NO_3)_2$(N-2 hydroxyethyl[illegible]$)_2]$	no data		61
$[Cu(NO_3)_2$(1,3-$(NH_3)_2$-propane$)_2]$	2.51	1.255	

Table 2c

The copper-oxygen bonds are some 0.3-0.5Å, 16-20% longer than normal copper oxygen bonds. Such long axial bonds are a common feature of copper compounds due to the Jahn-Teller effect. However, the unidentate interaction of the nitrato group with the copper atom is correspondingly weaker, as shown by the small increase in the N-O_1 bond lengths over the free ion value. In the true unidentate compounds the N-O_1 bond lengths are much longer, of the order of 1.31Å.

Secondly, there is the group of compounds which are considered to contain unsymmetrically bidentate nitrato groups. (Table 2d).

	$Cu-O_1$(Å)	$N-O_1$	$Cu-O_2$	$N-O_2$	Refs.
$[Cu(NO_3)_2(\alpha\text{-picoline})_2]$	1.971(13)	1.27(2)	2.489(14)	1.20(2)	63
	2.026(16)	1.23(2)	2.307(13)	1.23(2)	
$[Cu(NO_3)_2(pyrazine)]$	2.010(4)	1.287(7)	2.490(5)	1.249(7)	64
$[Cu(NO_3)_2(H_2O)_2]0.5H_2O$	1.992(2)	1.281(2)	2.653(2)	1.238(2)	65,66
$[Cu(NO_3)_2(py)_2]_2$	2.035(6)	1.327(10)	2.618(8)	1.261(11)	67
$[Co(NO_3)_4]^{2-}$	2.11(2)	1.25(2)	2.54	1.20(3)	43
	2.03(2)	1.25(2)	2.36	1.21(3)	
$[Cu(NO_3)_2(py)_3]$	2·154(7)	1·261(10)	2·732(9)	1·248(13)	201

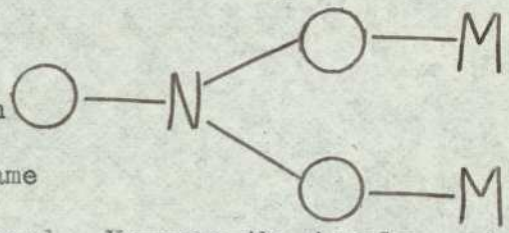
Table 2d

The metal-oxygen bond lengths fall into two groups. One group has a "normal" copper-oxygen bond length with a long $N-O_1$ bond length of about 1.28Å. The second group of Cu-O bond lengths is 0.3-0.6Å longer with correspondingly shorter nitrogen-oxygen bond lengths ($N-O_2$). Again this asymmetry is probably due to the Jahn-Teller effect, introducing a redistribution of the incompletely filled d-orbitals. This orbital asymmetry introduces a corresponding asymmetry into the nitrato group and this is probably the origin of the highly complex infra-red spectra associated with copper(II)-nitrate compounds.

2.1.5. Bridging Nitrato Groups

Bidentate ligand character is also realised in the NO_3 group acting as a bridge between two metal atoms. The majority of the compounds which have been studied involve co-ordination of the nitrato

group to copper(II) atoms. This mode is undoubtedly present in many more compounds.



The symmetry of the NO_3 group in an ideal arrangement should be the same as for a normal bidentate nitrato ligand. However the involvement of two separate metal atoms would cause a modification of the molecular motion of the group leading to the splitting of the fundamental bands in the vibrational spectrum.

Another form of bridging mode has recently been found in which only one oxygen atom of each nitrato group acts as the bridge between two metal atoms. In the compound $[Cu(py)_2(NO_3)_2](py)$[67] the oxygen atom bridges two copper(II) atoms. In the compound $Cu(NO_3)_2Hg.3H_2O$[68] the oxygen atom of the NO_3 group links a copper (II) atom and a mercury(II) atom. This mode of bridging is well established in other compounds in which the oxygen atom of pyridine-N-oxide acts as the bridge.

There is in addition a mode of unidentate bridging which is at present unique. In the compound $Cu_4(NO_3)_2(OH)_6$[69] one oxygen atom of the nitrate group is linked to three copper atoms, one being of normal length 2.18Å, and the other two are of the longer type, 2.35Å.

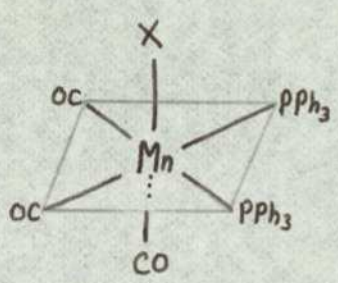
2.1.6. Several other possible modes of bonding have been suggested, but there has been no crystallographic evidence to support them. Among these are the tridentate nitrato group, and the nitrato group acting as a π-donor ligand, thus forming a "sandwich" type compound. This latter structure was proposed[70] to explain the volatility of $Cu(NO_3)_2$ and the low heat of vapo-risation (15.6K cals.mole^{-1}), which is of the same order as values for the carbonyls of metals of the chromium group and some metal cyclopentadienyl compounds e.g. ferrocene. This structure was suggested for the $Cu(NO_3)_2$ molecule in the vapour phase, but was found to be incompatible with subsequent electron diffraction studies[71]. These showed the molecule to contain two bidentate nitrato groups, although the orientation of the NO_3 groups relative to each other was not clearly established. These two suggested forms of bonding, the tridentate and the π-bonded structures are unlikely to exist for essentially the same reasons:

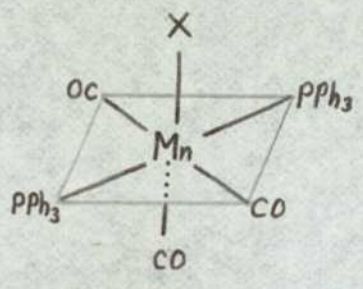
(a) The diameter of the NO_3 group is given variously as 3.2Å[72], 3.8Å[73,74], 4.3Å[75], and 4.62Å[76]. These figures indicate that the NO_3 group is much larger than the metal ions of the transition series (for the divalent metal ions Ti-Zn the diameter is of the order 1.80-1.40Å[77]). Hence, there would be poor orbital overlap, or at least the formation of long, weak M-O bonds.

(b) Whilst it might be possible for orbitals on the NO_3 group to overlap with suitable orbitals on the metal atom, it is unlikely that all three of the oxygen orbitals will be of suitable orientation. Only two of the NO_3 group molecular orbitals could overlap at any given time with d_{xy}, d_{xz}, d_{yz} orbitals, dz^2, $d_{x^2-y^2}$ orbital or s, p, or sp-hybrid

orbitals, because of the spatial distribution of these orbitals. In addition, it has been pointed[43,54] out that the NO_3 group has a short 'bite' resulting in distorted co-ordination environments. This is due to the short distance between the two oxygen atoms of the NO_3 group, which is about 2.00-2.20Å.[44,78,79]. (This last point is in contrast to point (a) above).

A more recent suggestion[80] is the possibility of bonding through the nitrogen atom of the NO_3 group in a manner analogous to the amines.





X = NO_3 group

yellow, CIS-isomer (O-bonded)

(i) CIS ⟶ trans: slow at room temp, rapid at 120°

(ii) Mn(I), diamagnetic, non-electrolyte prepared at low temp. (-8°)

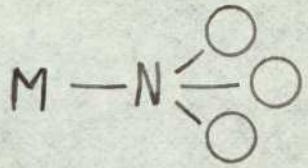
(iii) IR spectrum: 1465s, 1289s, 1008s, 803w (assigned by original authors to the NO_3 groups).

brown, trans-isomer (N-bonded)

(i) trans ⟶✗⟵ CIS-

(ii) Mn(1), diamagnetic, non-electrolyte thermally more stable-recrystallisable from hot nitromethane

(iii) 1547s, 1529s, 1254s, 821w



This mode of co-ordination was suggested to explain the differences in infra-red spectra between CIS- and trans- $[Mn(CO)_3(PPh_3)_2(NO_3)_2]$. Against this postulated structure one must raise several points. (1) The thermodynamic stability of the trans-isomer, with its nitrogen bonded nitrato group, is greater than that of the CIS-isomer, with its oxygen bonded nitrato group, as evidenced by the methods of preparation, reactivity and inter conversion (CIS→trans, trans↛CIS). In the infra-red spectrum the bands assigned to the NO_3 group occur at higher frequencies for the trans isomer, implying a stronger Mn-N interaction than for the Mn-O bond. This might lead one to expect other stable N-bonded nitrato compounds; only oxygen-bonded nitrato compounds are known at the present time.

(2) In all the structural studies of the NO_3 group there has been no evidence for a non-planar NO_3 group, other than some small deviation (of the order of 2-3°)[eg(25)] due to lattice forces. This implies that there is always sufficient π-bonding, delocalised over the group, to maintain a planar configuration. To form a pyramidal NO_3 group of C_{3v} point group symmetry would require a deviation of up to 19° from planarity. This would bring the oxygen atoms into closer proximity with each other since the ONO angles decrease from 120° to 109°. Any such change would be limited by the repulsion of the oxygen atoms leading to a larger bond angle and/or an increased nitrogen-oxygen bond length.

(3) One would expect an increase in the N-O bond length since there would be no electrons available on the nitrogen atom for π-bonding. The presence of N-O bonds of predominantly single-bond character would suggest infra-red bands at frequencies lower than those assigned to it. A band at 1550 cm^{-1} would be more characteristic of N-O bonds with largely double-bond character.

(4) Would the stereochemistry of this pyramidal NO_3 group still have p-orbitals on the nitrogen atom with an orientation suitable for overlap with p-orbitals on the oxygen atoms? No non-planar nitrogen-oxygen species are known at present.

Perhaps the differences in the infra-red spectrum can be ascribed to the strength of the interaction of the metal with the NO_3 group, assuming both isomers contain unidentate nitrato groups. For the *cis*-isomer with two bulky PPh_3 groups *cis* to each other, and a bent M-O-N bond, the metal and oxygen atoms are not able to interact closely, thus giving an infra-red band at 1465cm^{-1} (although this is a band of weak intensity). For the *trans* isomer, the arrangement of the two PPh_3 groups *trans* to each other on the same side of the molecule permits the nitrato group to approach closer to the manganese atom. Hence there would be a stronger manganese-oxygen interaction giving rise to infra-red bands for the nitrato group at about 1540cm^{-1}, which is then split by the low site symmetry or the inevitable distortion in the molecule to give two bands at 1547 and 1529cm^{-1}.

Holleck[81] suggested a similar structural change from a planar to a pyramidal nitrate structure in an interpretation of the phenomenon of catalysis of nitrate reduction at the dropping mercury electrode through polyvalent cations, such as lanthanum. Hollecks evidence for this change in shape is based on the optical findings of von Halban[82]. Katzin[83] has dismissed this argument by ascribing the variations in the electronic spectrum of aqueous nitrate solutions to shifts in the electronic orbitals without alteration of the planar distribution of the atoms.

2.2. Vibrational Spectra

2.21. The Nitrate Ion

The point group symmetry for the nitrate ion is D_{3h}, which is expected to give four fundamentals in the calculated vibrational spectrum. Of these three are infra-red active, three are Raman-active with only two coincidences (Table 2e). These spectral features have been confirmed by many investigations, However, the great sensitivity of the vibrational spectrum to the molecular environment of the NO_3 group shows that in many instances the point-group symmetry of the group is changed by the lattice to one of lower order. Thus, the infra-red spectrum shows perturbation of the nitrate ion due to lattice forces (crystal field) and also hydrogen bonding. An ionic nitrate is readily recognised in the infra-red because of the strong, broad band at about $1390cm^{-1}$ due to the degenerate symmetric and asymmetric NO_2-stretching modes.

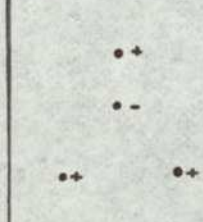
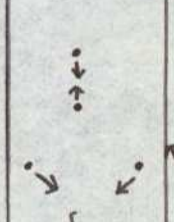
	$\nu_1(A_1')$	$\nu_2(A_2'')$	$\nu_3(E^1)$		$\nu_4(E^1)$	
						
			ν_s	ν_{as}	δ_s	δ_{as}
assignment	N-O stretch	out-of-plane bend	NO_2 stretching		NO_2-bending	
activity	Raman	Infra-red	Raman, Infra-red		Raman, Infra-red	
calculated frequency (cm^{-1})	1050	831	1390		720	

Table 2e: vibrational modes for the NO_3 group of D_{3h} point group symmetry[84].

Co-ordination of the NO_3 group in any of the modes mentioned above reduces the point group symmetry from D_{3h}. The correlation table is given in Table 2f[85].

Point Group	ν_1	ν_2	ν_3	ν_4
D_{3h}	$A_1'(R)$	A2"(I)	E'(I,R)	E'(I,R)
D_3	$A_1(R)$	$A_2(I)$	E(I,R)	E(I,R)
C_{2v}	$A_1(I,R)$	$B_1(I,R)$	$A_1(I,R)+B_2(I,R)$	$A_1(I,R)+B_2(I,R)$
Cs	$A'(I,R)$	$A'(I,R)$	$A'(I,R)+A(I,R)$	$A'(I,R)+A(I,R)$

Table 2f: correlation table for related point groups.

R = Raman active, I = infra-red active

2.2.2. Unidentate Nitrato Group

For a unidentate, bidentate or symmetrical bridging structure the symmetry of the NO_3-group is C_{2v}, but this may be modified by molecular or lattice distortions yielding a different, usually lower, site symmetry. The vibrational modes of the unidentate nitrato group are shown in Table 2g. No such table has been drawn up for the bidentate and bridging NO_3 groups because of differences of opinions about the assignment of frequencies and because of the mixing of fundamental vibrational modes.

Several normal co-ordinate analyses of the unidentate nitrato group have been carried out[86-90]. The agreement between them is quite close in their qualitative prediction of the effect of unidentate co-ordination of the NO_3 group on the infra-red spectrum. They all predict six bands and a similar kind of variation of band position, depending upon the strength of the metal-oxygen interaction. Topping[88]

and Hester and Britzinger[89] prefer not to assign the vibrational modes of the fundamentals in the way that Herzberg[86] and Addison[90] have, but merely record the character species of the bands. Table 2h shows that all are in agreement about the polarisation characters of the four highest bands, but Topping and Hester and Britzinger differ from others with regard to the character of the two lowest bands. This matter has not yet been confirmed experimentally, although the incomplete Raman work seems to support Hester et al. There are only a few transition-metal compounds with unidentate NO_3 groups for which both the structural and vibrational spectral data are available. But these, and those others for which unidentate character is assumed e.g. $[Mn(CO)_5(NO_3)]$, $[Co(NH_3)_5(NO_3)]^{2+}$, do not have complete sets of published data assigned to the nitrato group. The $\partial_4(E')$ fundamental of the nitrate ion is of weak intensity and decreases when the degeneracy is lifted to form two new fundamentals. Consequently, these two bands are not always easily identified. There is also an instrumental difficulty in that this pair of bands usually occurs in the range 700-780cm^{-1} which is near to the range limit for most of the instruments on which published work was carried out. There are also bands in this range due to the normal mulling agents used e,g.Nujol, HCB.

	Unidentate Nitrato Band Characters						Ref.
Addison	$\partial_4(B_1)$.	$\partial_1(A_1)$.	$\partial_2(A_1)$.	$\partial_6(B_2)$.	$\partial_3(A_1)$.	$\partial_5(B_1)$	87,90
Hester	B_2.	A_1.	A_1.	-	B_2.	A_1	89
Topping	B_2.	A_1.	A_1.	B_1.	B_2.	A_1.	88
Dehnicke	B_1.	A_1.	A_1.	B_2.	A_1.	B_1.	102

Table 2h.

Hester and Britzinger[89] have suggested that an accidental degeneracy of these fundamentals might occur due to the opposing forces of the polarisation of the NO_3 group and the effect of metal-oxygen bond formation. There is no experimental evidence for this at present. This suggestion is based upon the assumption of a linear Metal-Oxygen-NO_2 system, which is not borne out by the available crystallographic data for unidentate nitrato compounds. It is suggested that this system might be linear in aqueous solution where only one band is observed[89].

The order of the fundamentals could be determined by means of the observed polarisations of the Raman bands, which are six in number and coincident with the infra-red fundamentals. There is no published Raman data yet for known unidentate nitrato compounds, but Raman studies of aqueous solutions of several metal nitrates show that the order of the first four bands is in agreement with the suggested scheme. Only one other band is observed, but without polarisation data.[90]

Ferraro[91] has suggested that the degree of splitting of the E' modes of the nitrate ion could be used as a measure of the perturbation of the ion from D_{3h} point group symmetry, and hence as a criterion for the strength of the interaction of the metal atoms with the NO_3 groups in the molecule. Since the splitting of the more intense $\nu_3(E')$ mode is both greater and more easily observed than that of the less intense $\nu_4(E')$ fundamental, the former is measured as $\Delta\nu_3$. The suggested limits are $\Delta\nu = 0\ cm^{-1}$ for the alkali metal nitrates and $\Delta\nu = 385 cm^{-1}$ for CH_3-ONO_2. Thus for $X-O-NO_2$, where X = H,D,F, ,CH_3,O_2N the $\Delta\nu$ values are in the range 320-450 cm^{-1}. For the many transition-metal compounds with co-ordinated nitrato groups the splitting is in the range 85-250cm^{-1}.

with higher values being for metals in higher oxidation states. Whilst this empirical approach appears to have some validity it takes no account of the mode of co-ordination of the nitrato ligand, nor does it consider the nature of the fundamentals themselves, as will be discussed later.

Irish and Walrafen studied aqueous solutions of calcium nitrate and plotted the positions of the bands arising from the $\nu_3(E')$ mode of the nitrate ion as a function of concentration. This discussion implies a unidentate association of the NO_3 group and the calcium ions. They found that the lower band, $\nu_1(A_1)$, is little affected by changes in concentration, whereas the higher frequency band, $\nu_4(B_1)$, (See Table 2g) is much more sensitive. A similar, though lesser effect was noted for the pair of bands - $\nu_3(A_1)$ and $\nu_5(B_1)$ - arising from the $\nu_4(E')$ mode of the nitrate ion. The greater sensitivity of the $\nu_4(B_1)$ band to changes in the metal-oxygen bond and the distortion of the NO_3 group has been attributed to a mechanical effect in the molecule. An increase in the strength of the metal-oxygen bond has the effect of fixing the oxygen atom in space and is equivalent to an increase in weight at this position. Such an increase in weight is expected to influence the asymmetric vibration $\nu_4(B_1)$ more than the symmetric vibration $\nu_1(A_1)$, so that as the metal and the degree of covalency in the metal-oxygen bond change $\nu_4(B_1)$ will vary more than $\nu_1(A_1)$.

For the unidentate nitrato group the out-of-plane rocking vibration (ν_6) is expected to require less energy when the NO_3 group is bonded than when it is free. Hence, it is expected, and is observed at lower frequencies than for the free nitrate ion.

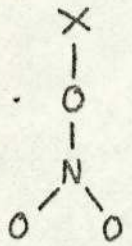
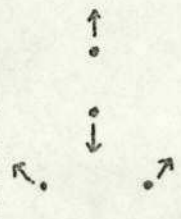
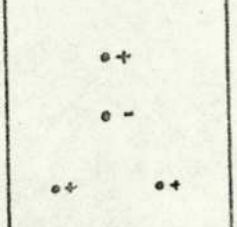
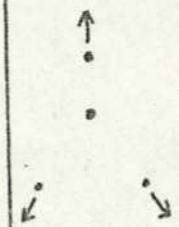
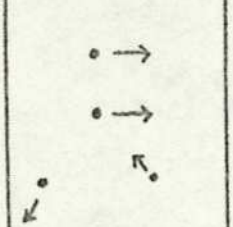
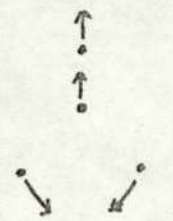
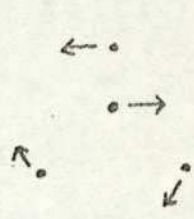
C_{2v}	$\nu_2(A_1)$	$\nu_6(B_2)$	$\nu_1(A_1)$	$\nu_4(B_1)$	$\nu_3(A_1)$	$\nu_5(B_1)$
						
Assignment	N-O stretch	out-of-plane rock	NO_2^- symmetric stretch	NO_2^- asymmetric stretch	NO_2^- symmetric bend	NO_2^- asymmetric bend
band position (cm^{-1})	1000±30	780-800	1230-1350	1480-1650	750	700 cm^{-1}
Raman band character	polarised	depolarised	polarised	depolarised	polarised	depolarised

Table 2g. Vibrational modes for the NO_3 group of C_{2v} symmetry[86,87]

	Unidentate Nitrato Band Character	Reference
Addison	$\nu_4(B_1).\nu_1(A_1).\nu_2(A_1).\nu_6(B_2).\nu_3(A_1).\nu_5(B_1)$	87,90
Hester	$B_2.\quad A_1.\quad A_1.\quad -\quad B_2.\quad A_1$	89
Topping	$B_2.\quad A_1.\quad A_1.\quad B_1.\quad B_2.\quad A_1$	88
Dehnicke	$B_1.\quad A_1.\quad A_1.\quad B_2.\quad A_1.\quad B_1$	102

Table 2h

	Bidentate Nitrato Band Character	Reference
Addison	$\nu_1(A_1).\nu_4(B_1).\nu_2(A_1).\nu_3(A_1).\nu_5(B_1).\nu_6(B_2)$	97
Hester	$A_1.\quad B_2.\quad A_1.\quad B_1.\quad A_1.\quad B_2.$	112
Topping	$\nu_1(A_1).\nu_4(B_2).\nu_2(A_1).\nu_6(B_1).\nu_3(A_1).\nu_5(B_2)$	88
Dehnicke	$A_1.\quad B_1.\quad A_1.$	109

Table 2i:

The N-O stretching vibration, $\nu_2(A_1)$, is now infra-red active and its appearance has been used to indicate the occurrence of a covalent nitrato group. However, this band is very sensitive to lattice forces and most workers consider the intensity of the band before deciding whether its appearance is due to distortion (giving a weak band) or a bonding interaction (giving a strong band). The displacement of this band to lower frequencies has been used by Gatehouse et al [93] as a measure of the strength of the metal-oxygen bond. The movement of this band is large only for simple molecules, X-O-NO_2, where X is a small group, or single atom. For metal compounds the variation is very small and this criterion has not been considered by later workers.

The above discussion is probably only relevant to unidentate nitrato groups. Most of the ideas were put forward before the versatility of NO_3 group as a ligand was realised, and have little or no validity when discussing the bidentate and bridging nitrato group.

2.2.3. The Bidentate Nitrato Group

The vibrational spectrum of the bidentate nitrato group has been the subject of much discussion. The ideal symmetry in this bonding mode is C_{2v} and would be expected to exhibit six coincidental infra-red and Raman fundamentals. There has been several attempts to predict and explain the spectra actually observed.

Fujita[94] observed that for carbonato complexes there appears to be a clear difference in the $\Delta(\nu_4 - \nu_1)$ value between unidentate and bidentate carbonato groups. Field and Hardy[95] suggested that

the same distinction could be applied to the iso-electronic nitrato group. However, they had little data available at this time, and subsequent studies have shown that nitrato spectra are more complex than carbonato spectra. The notion persists that bidentate nitrato compounds (simply) exhibit a greater splitting of the two highest bands than unidentate nitrato compounds, and that the two types are thus distinguishable. For reasons to be discussed later this is not so, although Curtis[96] claims to be able to differentiate between the two for his nickel(II) compounds. Practically, it has not proved valid to use the infra-red spectrum to identify bidentate nitrato compounds. Comparison of the spectra of known or reasonably-assumed unidentate and bidentate nitrato compounds shows many similarities, in terms of the positions of the highest bands and the wavenumber difference between the two bands of highest frequency.

Addison and Simpson[97] consider that whereas for the unidentate nitrato group the asymmetric-NO_2 stretching mode of character B_1 is the highest vibration, it is replaced by the N-O stretching mode of character A_1, in the bidentate case. It is to be expected from the structural changes that occur on bidentate co-ordination that the increased double-bond character of the terminal N-O bond, as it becomes shorter and stronger, will give rise to N-O-stretching modes at higher frequencies. Similarly, the other two N-O bonds in the group will exhibit stretching frequencies at lower values as the bond lengths become longer and weaker. These authors point to the high value for $\nu_{N=O}$ at 1696 cm^{-1} found in the vapour phase spectrum of nitrous acid H-O-N=O[98][99]. This high value can be compared with those of known bidentate nitrato compounds

e.g. $Ti(NO_3)_4$: 1628cm^{-1}(100) and 1635cm^{-1}(101)(infra-red), 1666cm^{-1}(101) (Raman); $Sn(NO_3)_4$: 1630cm^{-1}(97)(infra-red), 1657cm^{-1}(101)(Raman) and 1661cm^{-1}(102); $Co(NO_3)_3$: 1649, 1621cm^{-1}(103). Unfortunately, there are many more bidentate nitrato compounds which do not exhibit such high frequency bands. In addition there are compounds which undoubtedly possess bridging nitrato groups which exhibit bands at high frequencies e.g. $Be_4O(NO_3)_6$(95): 1620cm^{-1}(104); $NbO(NO_3)_3$: 1646cm^{-1}(106); $TaO(NO_3)_3$: 1614cm^{-1}(106). The most that can be said for this high frequency criterion is that it is indicative of a strong interaction between the metal and the NO_3 group.

In addition, the high value for $\nu_{N=O}$ found in nitrous acid is not found in transition-metal nitrito compounds. For $[Co(O-N=O)(NH_3)_5]Cl_2$ $\nu_{N=O}$=1468cm^{-1}(107), and for $[Ni(-O-N=O)_2(py)_4]$ $\nu_{N=O}$= 1360 cm^{-1}(108). Thus, the appearance of a high frequency band in transition metal nitrato compounds cannot be regarded exclusively as indicating a strong metal-bidentate nitrato interaction leading to a terminal N-O bond of predominantly double-bond character.

Reference to Table 2i shows that the stretching mode ν_{N-O} is labelled $\nu_2(A_1)$ for the unidentate group and $\nu_1(A_1)$ for the bidentate group. Thus, for the bidentate case the two fundamentals assigned to the asymmetric and symmetric stretching modes ν_{NO_2} are now the second and third bands in the spectrum. These two fundamentals are considered to arise for the degenerate $\nu_3(E')$ mode of the nitrate ion and the separation of these two bands has been suggested as a criterion of the covalent bonding strength of the NO_3 group in the unidentate case(91).

If the splitting of the $\nu_3(E')$ degeneracy is to be applied to the bidentate case then the difference between the second and third bands should be measured, and not the difference between the first two bands as in the unidentate case, and as suggested by Ferraro[91]. If it is still possible to assign specific vibrational modes to a given fundamental for the bidentate case then efforts to make a distinction between uni- and bidentate nitrato groups using the splitting criterion are futile. If such assignments are still valid, then the $\Delta(\nu_4 - \nu_2)$ value should be used. Unfortunately, experimental data indicates little variation in the position of ν_2(1000-1050cm^{-1}) for both uni- and bidentate nitrato compounds. Further, the bidentate nitrato compounds, which exhibit the greatest polarisation of the NO_3 group show a decreasing value for ν_4, in addition to the high frequency values for ν_1 (>1550 cm^{-1}). This latter variation suggests that there is some validity in considering the splitting of the two highest bands. No rationalisation of this paradoxical situation has yet been suggested.

Another empirical approach, to the bidentate case has been made by Dehnicke[109] who made a comparison with the spectra of bidentate carbonato compounds. He considers the structural changes in the NO_3 group on co-ordination and discusses the effect upon the stretching frequencies. The free N-O bond of the bidentate nitrato group approaches double bond character and he thus compares it to the nitric oxide molecule. The latter has a band at 1877cm^{-1}[110] and $Co(NO_3)_2 N_2O_4$[109] has a band at 1807cm^{-1}, assigned as ν N-O. This comparison is not justified because nitric oxide is a free molecule and has a bond order greater than two, whereas the nitrogen-oxygen bond in the bidentate nitrato group has a bond order of 1.5-2.0. Also, in our experience, bands in this position

are weak and this band at 1807cm^{-1} is undoubtedly a combination and not a fundamental. The symmetric stretching frequency, ν_{NO_2}, is considered to be lowered further than in the unidentate case of methyl nitrate and Dehnicke identifies a band at 742cm^{-1} for $Co(NO_3)_2 N_2O_4$. In methyl nitrate[111] this band is assigned to the ν_{N-O} and such low values are only found in simple molecules and not in transition metal nitrato compounds where they are found around 1000cm^{-1}. Apart from this, the order and character of the bands is similar to other authors for bidentate nitrato groups. However, Dehnickes' assignments and his inability to account for all of the observed bands makes this approach unacceptable. Dehnicke does not appear to have used this in his subsequent work[102].

Topping[88] has carried out a normal co-ordinate analysis of the bidentate nitrato group in a manner analogous to his analysis of the unidentate group. He is able to compute an approximate force field capable of reproducing the known spectrum of the bidentate nitrato compound $Rb[UO_2(NO_3)_2]$ and also the observed isotopic shifts. The orders and characters of the bands are shown in Table 2i. Topping advances the reservations that his model will overestimate the nitrogen-oxygen stretching force constant, partly due to neglect of the two metal-oxygen force constants and partly due to the simplicity of the model, which considers only one NO_3 group bonded to the metal. Although Topping considers his set of force constants to be physically reasonable there is little practical difference between the unidentate and bidentate models. The only difference between the two types lies in the order of the bands as shown by their characters.

	Bidentate Nitrato Band Characters	Ref.
Addison	$\partial_1(A_1).\partial_4(B_1).\partial_2(A_1).\partial_3(A_1).\partial_5(B_1).\partial_6(B_2)$	97
Hester	$A_1.\quad B_2.\quad A_1.\quad B_1.\quad A_1.\quad B_2.$	112
Topping	$\partial_1(A_1).\partial_4(B_2).\partial_2(A_1).\partial_6(B_1).\partial_3(A_1).\partial_5(B_2)$	88
Dehnicke	$A_1.\quad B_1.\quad A_1.$	109

Table 2i

The normal co-ordinate analysis of Hester and Grossman[112] does take the metal-oxygen force constants into consideration. Using a series of procedures similar to those for the unidentate analysis they obtained a set of data giving a band variation diagram similar to that for the unidentate case[89]. The method of varying the N-O stretching force constants to imitate the structural changes in the bidentate group again ignores changes in the bond angles. The calculations indicate significantly higher metal-oxygen stretching frequences for the bidentate case. This is rather similar to saying that there is a stronger metal-oxygen bonding interaction giving rise to a greater splitting of the degenerate (E') modes of the nitrate ion. They consider that although their calculations fail to reproduce the high frequencies observed for some bidentate nitrato compounds these could be obtained by increasing the terminal nitrogen-oxygen stretching force constants i.e. these compounds must contain highly polarised NO_3 groups.

Although their diagrams of the variation of group frequencies with changing force constant imply that the new frequencies are derived from those of nitrate ion, Hester and Grossman point out that this is actually

not justified. Eigenvector calculations show that it is misleading to assign a particular vibrational mode to a particular fundamental band. Rather, each mode is in fact a complex admixture of several types of molecular motion. This coupling appears to be particularly important for the bidentate case because the formation of a ring adds extra deformation modes to those already present. In addition there are high metal-oxygen stretching frequencies which couple to the ONO angle deformation motions. Some help in assigning the stretching modes might be forthcoming from observation of isotopic shifts. The only published examples involve uranyl compounds[113] where substitution of N^{15} for N^{14} causes the three highest bands (stretching frequencies) to shift to lower frequencies. In addition, the band assigned to the out-of-plane rocking mode in the unidentate nitrate group and in the nitrate ion also shifts to a lower frequency.

Addison et al[101], following the conclusions of Hester and Grossman[112], attempted to assign the infra-red and Raman spectra of several bidentate nitrato compounds of known structure, with reference to their molecular symmetry. Whilst this is fundamentally more correct it was not found possible to assign all of the observed bands.

Thus, at present there is no ready criterion by which the ligand character of the NO_3 group can be determined from the infra-red spectrum alone.

2.2.4. Raman Spectra

Although the authors mentioned above do not agree entirely about the order of the six bands expected in the ideal spectrum of the bidentate

nitrato group, it is possible to differentiate between them by considering the band character. All agree that the order of the first three bands for the unidentate case is B_1, A_1, A_1, which differs from the agreed order for the bidentate case A_1, B_1, A_1. Thus it should be possible to differentiate between uni- and bi-dentate nitrato compounds by observing the polarisation characters of the first three bands - the A-modes being polarised, and the B-modes being depolarised. The Raman studies that have been published agree with these orders,[101][111][114-123] and thus we do find a criterion for distinguishing between unidentate and bidentate nitrato compounds. This technique is not without its difficulties and will be discussed later.

The lower three bands in the Raman spectrum are also a point of difference between Addison et al and Hester et al. For the unidentate case Addison[97] et al suggest the order B_2, A_1, B_1, whilst Hester et al[89], and Topping[88] suggest B_1, B_2, A_1. The very limited Raman data[111] available[114-117] from solution spectra suggests that the order of Addison[97] et al is the correct one. However, for bidentate nitrato compounds there is a conflict between published data. Ferraro, Cristallini and Fox[120] support the order of Addison of A_1, B_1, A_1, A_1, B_1, B_2, whilst the work of several different authors[121-123] supports the band order of Topping and of Hester: A_1, B_2, A_1, B_1, A_1, B_2.

It would appear that Raman spectroscopy holds the key to the study of nitrato compounds. In addition to the band positions, and the depolarisation ratios of the bands, Addison[27] has indicated another possible distinction between uni- and bi-dentate nitrato compounds arising from the Raman spectra. It has been noted that the sequence of relative intensities of the three highest Raman shifts is different for

the two bonding modes - for unidentate nitrato compounds the second band is the most intense, whilst for bidentate nitrato compounds the first band is the most intense.

It is to be hoped that with the advent of laser sources and photo electric recorders that much more Raman work will be carried out to illuminate these problems.

2.2.5 The perfect bridging nitrato group has the same point group symmetry as the uni- and bi-dentate nitrato groups and would be expected to exhibit six coincident infra-red and Raman fundamentals. No study has been made of bridging nitrato groups, although there are expected to be structural differences between this mode and the uni- and bidentate modes. Nearly all of the bridging nitrato compounds characterised at present involve copper(II) compounds. The others are $[Ni(NO_3)_2(H_2O)_2]$[124] and $[Zn(NO_3)_2(H_2O)_2]$[125]. There is no simple pattern in the infra-red spectra, and no Raman data at all, and indeed these infra-red spectra are marked by their complexity. The suggestion[126] that the occurrence of bands above 1570cm^{-1} is indicative of bridging nitrato groups, has not been borne out by subsequent work. The copper(II) nitrato system is a very complex one and would merit a review of its own.

2.3. Spectral Difficulties and Practical Problems

The foregoing discussion of the structure and expected spectra of the possible bonding modes of the NO_3 group is an attempt to codify and rationalise a much confused section of the chemical literature. Some of the source of confusion and the practical difficulties standing in the way of clear interpretation of the spectroscopic data will now be reviewed.

Originally the nitrato group was regarded as a unidentate ligand because of the simple molecules such as nitric acid[127], methyl nitrate[128] and fluorine nitrate[128] which had been structurally examined. This was then applied to the nitrato compounds of metals and the spectra assigned as unidentate compounds. Hence the simple splitting scale of Ferraro[91] using alkali metal nitrates with $\Delta\nu = 0$ and methyl nitrate with $\Delta\nu = 385$ cm^{-1} as the reference points on the scale. Discussions at this time appeared to have precluded bidentate nitrato groups even though an early X-ray study[129] indicated its existence, and only much later was it recognised as being an important bonding mode. At the present time it would appear that the bidentate nitrato group is the most common form of co-ordinated NO_3 group, the unidentate group being found in a very few molecules.

Prior to 1955 the NO_3 group had not been considered as a ligand and consequently its presence in a molecule was ignored. For the next ten years the published work assigned all nitrate spectra as a unidentate ligand. Much of this work requires re-interpretation or cautious handling. Only when other data is available can the stereochemistry of the molecule be decided. Such information is often derived from conductivity measurements or electronic spectra with little regard for the effect of the solvent. Solvation can occur by substituting the NO_3 group by a solvent molcule or by the solvent molecule adding on to the central metal atom, thus changing the co-ordination number and geometry of the molecule. Such an addition may also involve the NO_3^- group changing its mode of co-ordination e.g. from bi- to unidentate, from co-ordinated to ionic. Such changes would thus produce misleading data.

Another hazard encountered is the technique of preparing the spectral sample as a potassium bromide disc. Often exchange takes place and the co-ordinated NO_3 group is changed to a nitrate ion. In addition some reactive nitrates react with the mulling[97,100,103] agents and the sodium chloride or potassium bromide windows. In earlier papers hygroscopic compounds were studied without taking precautions to prevent hydration. There are also many examples of the nitrato bands being obscured by those of other ligands present in the molecule and by the bands due to the mulling agent.

A more intractable and fundamental problem is the appearance of extra bands, usually evident as the splitting of recognisable bands, in the infra-red spectra of solids. Such band splitting can be ascribed to several factors:

(i) The grouping is part of a larger molecular arrangement, thus restricting its freedom of movement. The molecule also belongs to an infinite array of molecules all held in regular positions in a crystal lattice. The site symmetry of the group and of the molecule as a whole is often less than perfect because of the restrictions of space and the crystal lattice. This lowering of the site symmetry allows the fundamental bands to split into otherwise forbidden sub-bands of lesser intensity. The actual number of bands depends upon the symmetry of the site.

(ii) The coupling of motions within a molecule can yield combination bands, though usually of much less intensity than the fundamentals.

(iii) The coupling of motions between molecules within a unit cell or factor group can lead to a lowering of the factor group symmetry, giving rise to band splitting. Hydrogen-bonding is one type of molecular coupling.

(iv) The coupling of internal vibrational modes with external or lattice modes can also give rise to additional weak bands.

(v) Band splitting can also arise when crystallographically non-equivalent nitrate groups are present in the same unit cell[63].

However, a complete vibrational analysis requires a complete set of spectral data, i.e. single-crystal infra-red and Raman spectra, together with the band polarisation data and some knowledge of the space group of the crystal. In the absence of such data only an approximate analysis can be attempted.

The effect of site symmetry is probably the single most important factor. At the present time only a few papers have attempted the formidable problem of relating the point group and site symmetries, and none of these involve the NO_3 group. The effects of hydrogen bonding have been discussed, and related to the infra-red spectrum.[28,130] Workers in the field of aqueous solutions and melts have been discussing the sources of the band splitting for the nitrate ion for some years. The suggestions have included restriction of free-rotation[131,132] (leading to a lowering of the symmetry), ion-pair interaction with metal cations[133,134], solvation[135,136], and "outer-sphere complexes"[137] e.g. $M^+ - H_2O - NO_3^-$. Some recent work[137] has suggested that solvation by means of hydrogen bonding is an important factor. It is clear that in aqueous solutions the water molecules exert a strong influence on the structure of the nitrate group through hydrogen bonding, and this is reflected in the vibrational spectrum. From electrochemical studies of the structure of water Good[138] observed that nitrate ions destroy the structure of water to a significantly greater degree than the chloride ions. This is probably due to the hydrogen bonding interaction between water molecules and nitrate ions.

Another source of extra bands is the presence of different nitrato groups in the same molecule. Examples are known of ionic and unidentate[55], unidentate and bidentate[25,26], unidentate and bidentate bridge[24][66], bidentate and unidentate bridge[67]. All of these examples involve Copper(II) compounds. In addition it is known that dinitrato copper(II) in the solid state is a mixture of two isomers, α-and β-forms[139]. This

is further complicated, at least in the case of dinitrato copper(II), because the infra-red spectrum, particularly in the range 500-200cm^{-1}, varies according to the method of preparation, the temperature of sublimation and the nature of the cold-finger[140].

Yet another possible source of extra bands is the unsymmetrical co-ordination of the nitrato group,[24,43,44,63,141] giving different metal-oxygen and nitrogen-oxygen bond lengths. The influence of this asymmetry on the vibrational spectrum has not yet been discussed in the literature.

The introduction of the laser-Raman spectrometer has presented a new set of problems which limit the usefulness of this valuable spectroscopic method. The technique involves the scattering of the incident beam at right angles to the incident-beam-direction. Since less than 10% of the incident beam is scattered coherently in this manner the intensity of the incident beam is very important. This technique has become more widely used with the introduction of the high-intensity laser beam as the radiation source, with the consequent increase in the intensity of the scattered beam. The increased intensity of the incident beam, however, often causes decomposition due to thermolytic and/or photolytic processes. In addition, many compounds become fluorescent under these conditions and the light given out interferes with the Raman spectrum. A further technical problem involves the colour of the sample which sometimes interferes with the colour of the laser beam. This problem can be circumvented by using a laser beam of a different colour. Prior to the advent of the laser source Raman studies were limited to colourless samples, or coloured

samples at high dilution. The laser source provides the flexibility of varying the wavelength of the exciting radiation. Thus, the He-Nelaser emits at 6328Å compared to the 4358Å line obtained from the mercury arc lamps previously used. Other coloured sources available are the A_r^+-ion (4880, 5145Å), the K_r^+-ion (5682,6471Å), and the mixed A_r^+/K_r^+-laser. Variation of the exciting wavelength can reduce or even eliminate the problems of fluorescence and photodecomposition referred to earlier.

One of the great advantages of Raman spectroscopy is the possibility of studying single-crystal spectra. However, the vibrations of the crystal are related to the molecular symmetry and the crystal symmetry. Thus, a complete spectral analysis requires the determination of the spectrum along the three crystal axes, together with the polarisation data. For each of the thirty-two point groups to which all crystalline solids belong, group theory predicts the possible vibrations and the way in which they are polarised. At the present time, however, there is very little published literature relating the crystalline space groups, the molecular point groups and the vibrations and their polarisation tensors which would enable this technique to be more widely used and the data to be correctly interpreted.

Thus, there are many possible sources of difficulty which contribute to the problem of spectroscopically identifying the NO_3 group in its various modes of bonding.

2.4 The Scope of This Research

The work was undertaken in order to try and draw up a set of criteria which would be relevant to any discussion of nitrate spectra and to test several of the criteria previously suggested. It was considered that if a related series of compounds could be established in which the character of the NO_3 group was known, or could be confidently assumed, then perhaps a set of criteria could be obtained, at least for a given metal. The related series is $[M^{II}(H_2O)_6](NO_3)_2$; $[M(NO_3)_2(H_2O)_4]$; $[M(NO_3)_2(H_2O)_2]$; $[M(NO_3)_2]$.

It was also decided to examine the use of the far infra-red region (200-500cm^{-1}) as a source of useful data. In addition there was a general and qualitative interest in the use of liquid dinitrogen pentoxide as a reagent and solvent.

EXPERIMENTAL

3. EXPERIMENTAL

3.1.1. Preparations were carried out using A.R. grade commercial samples (from Hopkin and Williams):- $[Ni(H_2O)_6](NO_3)_2$; $[Co(H_2O)_6](NO_3)_2$; $[Mn(H_2O)_4(NO_3)_2]$; these are referred to subsequently as the precursors. They were treated in the following ways:

(i) The precursor was dehydrated by pumping on the vacuum-line (≈ 0.1mm Hg) at room temperature ⟶ $[M(NO_3)_2(H_2O)y]$

(ii) Standing crushed crystals over silica gel in a vacuum desiccator for several weeks at room temperature ⟶ $[M(NO_3)_2(H_2O)x]$

(iii) Standing crushed crystals over P_2O_5 powder in a vacuum desiccator for several weeks at room temperature ⟶ $[M(NO_3)_2(H_2O)z]$

(iv) The crushed crystals were treated with excess liquid N_2O_4. The solution was shaken to ensure complete mixing and was then reduced to dryness on the vacuum line. The solid thus produced was then heated under vacuum to remove any adhering N_2O_4 ⟶ $[M(NO_3)_2(H_2O)v]$.

(v) The crushed crystals were treated with an excess of liquid N_2O_5. After shaking to ensure complete mixing the solution was reduced to dryness on the vacuum line and heated ⟶ $[M(NO_3)_2(H_2O)T]$

(vi) The solid from (v) was always a hydrate and was treated with a second excess of liquid N_2O_5. The solution was shaken, reduced to dryness, heated and examined ⟶ $[M(NO_3)_2]n$.

3.1.2. The liquid N_2O_4 was obtained from a cylinder (Air Products Ltd). The liquid N_2O_5 reagent was freshly prepared each time by the dehydration of fuming nitric acid (A.R. grade: specific gravity = 1.5) over powdered phosphorus pentoxide. $2HNO_3 \longrightarrow N_2O_5 + H_2O$

The apparatus used is shown in figure 3.1.

APPARATUS FOR THE PREPARATION OF LIQUID DINITROGEN PENTOXIDE

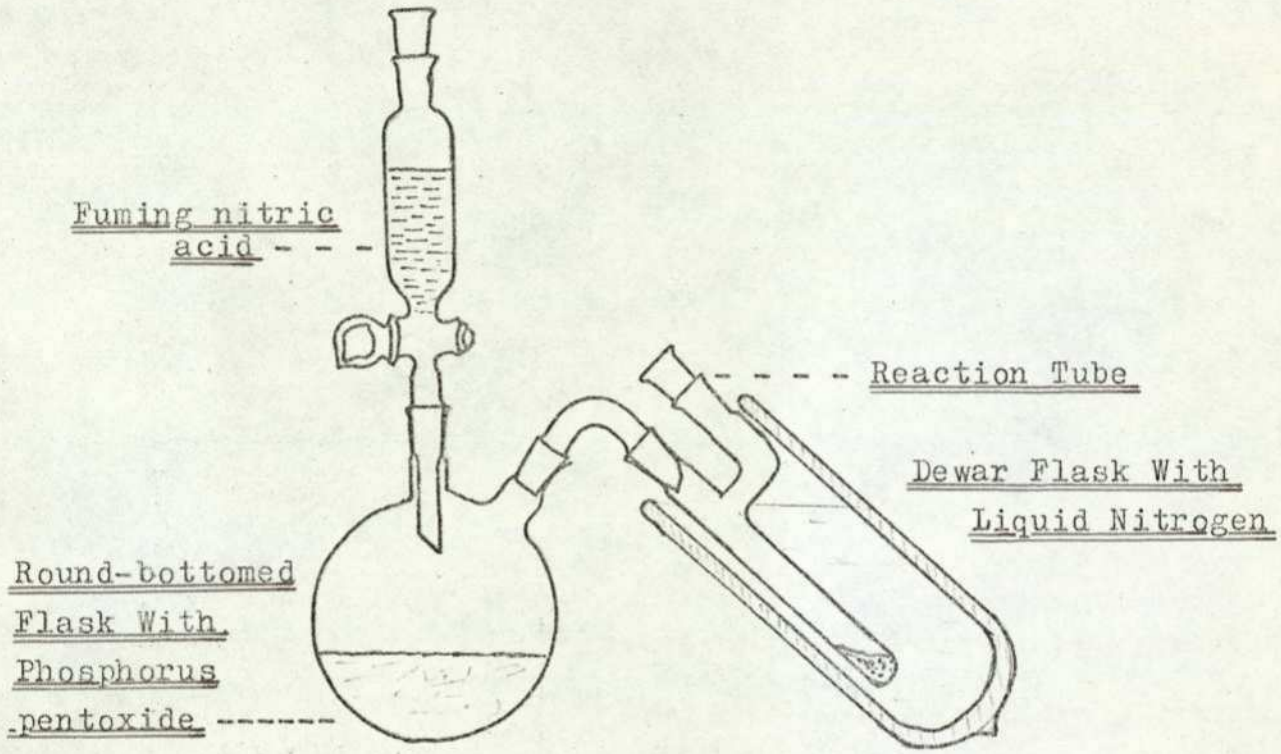


Figure 3.1.

Fuming nitric acid was allowed to drip onto phosphorus pentoxide. The initial clouds of brown fumes flush moist air out of the apparatus and the reaction tube containing the hydrated nitrate to be reacted. The side-tube was then stoppered and a Dewar flask of liquid nitrogen placed around it. This fulfills the dual purpose of trapping the N_2O_5 in the reaction-tube, and also creating a partial vacuum which causes more N_2O_5 vapour to enter from the reaction flask to equalise the pressure.

Continued addition of the fuming nitric acid ensures a steady production of N_2O_5. It is necessary to agitate the flask occasionally to break up the syrupy layer which forms over the surface of the phosphorus pentoxide powder after reaction with the nitric acid. No heating is necessary, except at the beginning, as the dehydration is highly exothermic. The N_2O_5, with a boiling point of $45^{\circ}C$, condenses in the cold region at the top of the side-arm and runs down in the reaction tube where it solidifies. In our apparatus there was a tendency for the liquid N_2O_5 to run back into the reaction flask. This was counteracted by tilting the whole apparatus to make the reaction tube more vertical. Also a current of warm air was applied to the side-arm so that condensation of the N_2O_5 only took place on the cooler part at the top of the reaction tube.

The quantity of N_2O_5 reagent prepared by this method is of the order of $20cm^3$. Care must be taken not to use too large a volume of reactants, or too high a reaction temperature because of the danger of the contents of the reaction flask bubbling over into the reaction tube.

Since the chemicals involved in the preparation and the products are dangerous materials protective clothing is essential (coat, neoprene rubber gloves and face visor). All manipulations were carried out in a well ventilated fume cupboard. In addition, all the glass joints in the apparatus were sheathed in PTFE sleeves, because both apiezon and silicone greases are attacked by fuming nitric acid and by N_2O_5.

The liquid N_2O_5 reagent prepared by this method is probably not pure and undoubtedly contains some anhydrous nitric acid. Pure N_2O_5 melts at 30°C, whilst a crystalline adduct $N_2O_5.2HNO_3$ [142] has been reported with a melting point of 5°C. Our solid product melts at room temperature (≈ 15-20°C). A more rigorous preparation of N_2O_5 requires the passage of ozonised oxygen, to oxidise the remaining nitric acid [143] N_2O_5 is thought to decompose to N_2O_4 and oxygen. Dehnicke [109] found that the reaction of N_2O_5 with anhydrous metal chlorides yielded N_2O_4 adducts of the anhydrous metal nitrates. This remarkable, almost quantitative conversion of N_2O_5 to N_2O_4 was not observed in this work. All the compounds obtained by reaction with N_2O_5 were dissolved in water and the solutions examined in the ultra-violet range for bands assignable to the nitrite ion. None were ever observed. The NO_2^- band at 354mμ is about three and a half times more intense than the NO_3^- band at 302mμ, and is clearly observable in concentrations of 0.01M, even in the presence of a ten-fold excess of nitrate ions. Thus, if any N_2O_4 would have been present its presence would have been observed.

When the N_2O_5 preparation reaction was complete the reaction tube was detached and stoppered, care being taken to prevent the entry of moist air by the use of dry nitrogen gas. The reaction tube was allowed to stand upright in the liquid nitrogen for a short time and then the coolant was removed. As the reaction tube warmed up to room temperature the solid, white N_2O_5 melted and fell onto the hydrated nitrate compound at the bottom of the reaction tube. When all of the reagent had melted, the mixture was shaken mechanically to produce a homogeneous solution. These solutions were intensely coloured and appeared to be stable for several days.

The reaction tube was then transferred to the vacuum line and the solutions were reduced to dryness. The vacuum-line, figure 3.2 was first purged with dry nitrogen gas. The vacuum was produced by the use of an Edwards High Vacuum two-stage rotary vacuum pump, assisted by two liquid nitrogen traps, performing the dual function of trapping the volatilised solution from the reaction-tube, and reducing the pressure in the system. The pressure in the apparatus was measured with a Pirani guage attached to the first section of the vacuum-line. Usual pressures recorded were of the order 10^{-2}-10^{-3} Torr.

When the samples required heating on the vacuum-line an electrically-heated tube furnace was raised into position around the reaction tube. The temperature was controlled by a variac potentiometer and measured by a calibrated thermocouple.

When the reaction tube was removed from the vacuum-line it was first filled with dry nitrogen gas, removed, stoppered and transferred to a dry-box. All dehydrated compounds were stored in a dry-box, which was flushed with dry nitrogen gas and further dehydrated with fresh phosphorus pentoxide powder. The dryness of the box was monitored with a calibrated

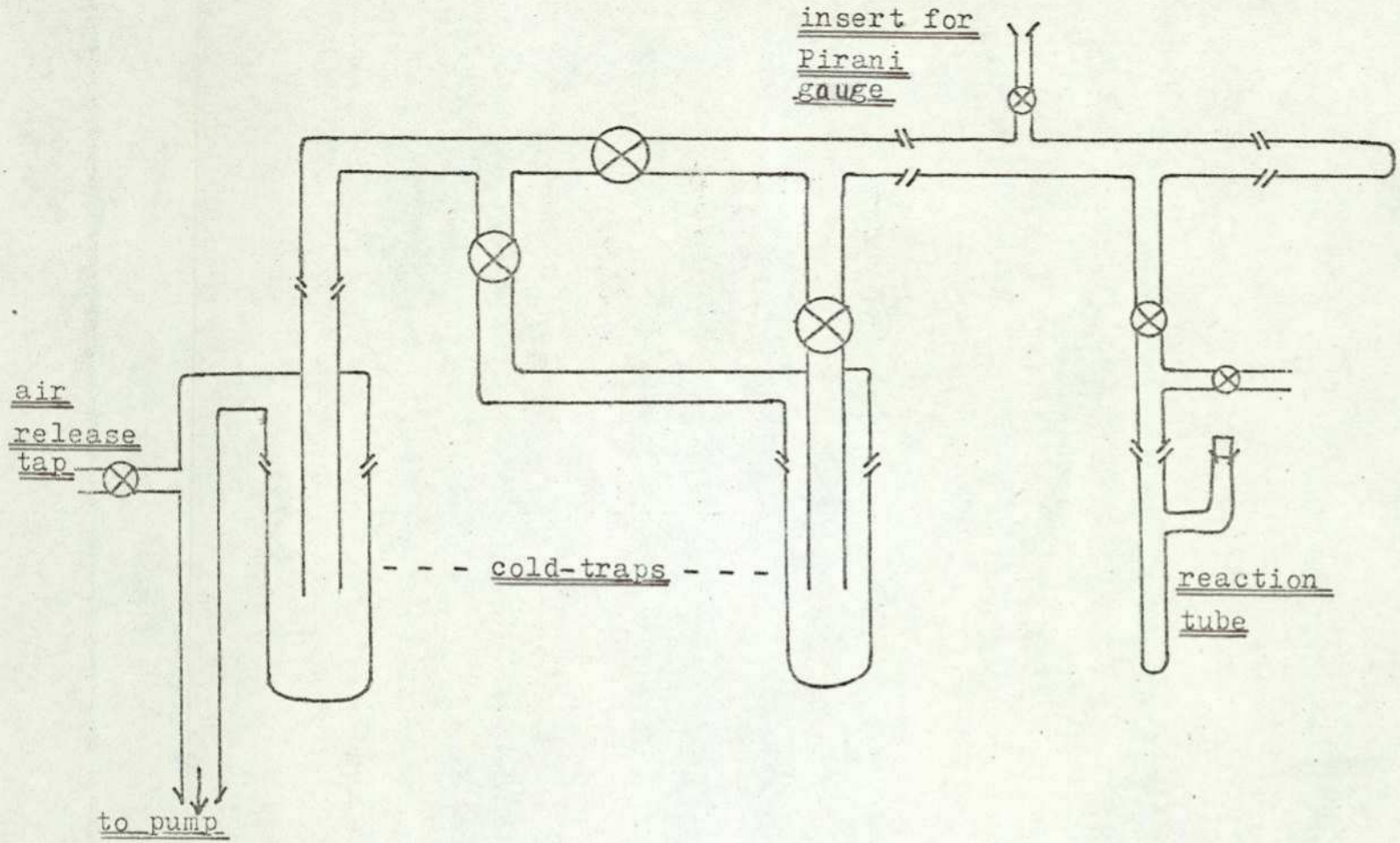


Figure 3.2.: Vacuum-Line Apparatus

hair-hygrometer. All transfers of samples and manipulations with the dehydrated nitrato compounds took place in the dry-box.

3.2. Analysis:

3.2.1. (a) Nitrate:

The compounds were weighed out into stoppered weighing bottles and then dissolved in distilled water. The nitrate ion was precipitated as nitron nitrate using the method described by Vogel[144]. The nitron reagent was prepared by dissolving 5g of nitron in 50cm^3 of 5% acetic acid and then stored in an amber bottle. The reagent was prepared freshly for each batch of analyses. The nitrate solution was then acidified with 1cm^3 of glacial acetic acid, heated until nearly boiling and 10cm^3 of the nitron reagent was added. After stirring, the solution was allowed to stand and was then cooled for at least two hours in ice, very often it was left overnight. The pink precipitate was then filtered on through a weighed, dried sintered crucible (porosity 4), washed successively with a cold saturated solution of nitron nitrate and ice cold water and then oven-dried at 105°. The precipitate was weighed as nitron nitrate, $C_{20}H_{16}N_4 \cdot HNO_3$ using the factor 16.519 derived from the molecular weights of the compounds, and not the apparently empirical factor 16.70 recommended by Hopkins and Williams[145].

Some of the dehydrated compounds reacted with the moisture in the air during the process of dissolving the compounds in water, thus giving rise to a loss of nitrate as brown fumes of nitrogen dioxide. This loss was prevented by weighing out the compounds into gelatine capsules which were dissolved under the surface of the hot acidified water. Analysis of dry A.R. grade potassium nitrate using these gelatine capsules showed that the capsules do not interfere with the nitron nitrate precipitation.

3.2.2. (b) Metals:

Weighed samples were dissolved in distilled water, the solutions made up to 100cm^3, and 10cm^3 aliquots were then titrated against standardised 0.01M EDTA solutions.

(i) Nickel:(146)

Some solid murexide indicater was added to the 10cm^3 aliquot and the purple solution was diluted to about 100cm^3. The solution was then made alkaline with ammonia (pH 10) until the solution became yellow. This solution was then titrated with 0.01M EDTA solution until the colour change yellow to purple was observed. The end-point has to be approached slowly because of the slow rate of co-ordination of the nickel ions by the EDTA.

(ii) Cobalt:(147)

A few drops of Xylenol Orange indicator were added to the 10cm^3 aliquot and several drops of bench dilute sulphuric acid until the colour of the solution changed from red to yellow. The solution was then diluted to about 50cm^3 and powdered hexammine was added until the red colour of the solution had been restored (pH 6). After warming the solution to about 40°C it was titrated with 0.01M EDTA solution until the colour change red to yellow was observed.

(iii) Manganese:(148)

The 10cm^3 aliquot was diluted to about 50cm^3 and one drop of 0.88 ammonia solution, 6cm^3 of 2.5% potassium cyanide solution, and 0.2g of ascorbic acid and 2cm^3 of pH 10 buffer solution were added. Several drops of Eriochrome Black T indicator were then added and the solution was titrated with 0.01M EDTA solution until the colour change red to blue was observed.

3.3. Spectra

3.3.1. (i) Infra-red: the range 3,650-350cm^{-1} was investigated with the Unicam SP100 spectrometer. Samples were mulled with Nujol and with hexachlorobutadiene (HCB), both of which were stood over 3A molecular sieve, stored and handled in the dry box. Silver chloride windows (0.1cm thick) were used to minimise dry reactions.

The range 500-200cm^{-1} was investigated with the Grubb-Parsons-DM4 spectrometer. Samples were mulled with Nujol and placed between polythene windows (0.1cm). This instrument has an infra-red beam which produces temperatures of some 45°, and many samples were melted by the heat of the beam and the cell compartment, which is not insulated from the Globar source. For the Manganese compounds a cooled cell was designed, based on a prototype by a colleague (A.W.Atkinson).

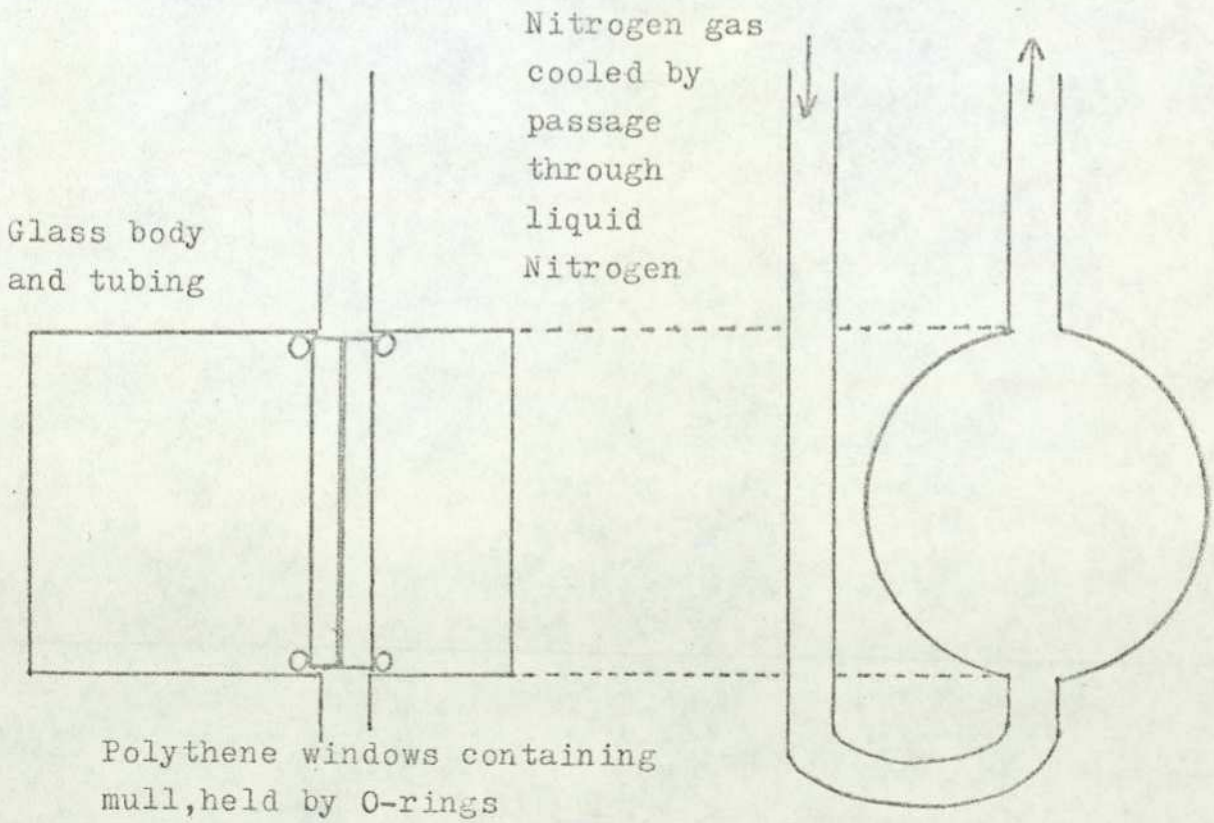


Figure :3.3

The ends of the cell are covered with thin polythene, to prevent the cool gas from escaping. By this means samples could be cooled and their spectra recorded. Some increase in band intensity was observed on cooling the samples.

3.3.2. (ii) Electronic Spectra: samples were dissolved in distilled water and the solution spectrum recorded using the Perkin-Elmer 137 spectrophotometer. This was carried out mainly to determine whether any nitrite was present. None was ever observed.

Solid state reflectance spectra were recorded using the Coleman-Hitachi spectrophotometer fitted with a reflectance attachment. This was used to determine the environment of the metal atom in its solid compounds.

3.4. Magnetic Susceptibility:

Measurements were made at room temperature using a Gouy balance, used in the usual manner. The tube was 0.1cm diameter and 7.4cm in length.

Diamagnetic corrections for the NO_3 groups and H_2O molecules were taken from Figgis and Lewis[149] for NO_3 = 18.9 x10^{-6} : for H_2O 13 x 10^{-6} cgs. units.

4. RESULTS

4.1.1 Nickel

The $Ni(NO_3)_2$ - H_2O system has been studied before. Sieverts and Schreiner[150] investigated the binary phase system and noted the temperature ranges of each hydrated form of Nickel (II) nitrate. They also investigated the ternary system $Ni(NO_3)_2$-HNO_3-H_2O.

4.1.2 $[Ni(H_2O)_6](NO_3)_2$:

Sieverts and Schrieners general method was to construct the phase diagram for the binary system $Ni(NO_3)_2$ - H_2O[150]. They then recrystallised the desired compound in the temperature range indicated by the phase diagram. This was found to be a very slow and not always reliable method giving solids with non-stoichiometric amounts of water. The method was thus not pursued as a preparative route to this compound.

Weigel[154] et al conducted a thermo-gravimetric study of the pyrolysis of this compound to NiO. They reported the tetra-aquo (45°-80°C) and di-aquo (80°-120°) compounds to be stable intermediates. Thereafter, above 145°, decomposition to the basic nitrate - $Ni(NO_3)_2 . 2Ni(OH)_2$- occurs, and above 200° the oxide, NiO is formed.

Whilst the above experience was found to be correct, that as water was removed from the system, so the melting point increased, neither this nor the method of Sieverts and Schreiner presented themselves as methods of preparing the intermediates.

The dark-green hygroscopic crystals of the hexa-aquo compound have been shown to be triclinic[151-153], and not monoclinic[77] as was reported elsewhere.

The molecular structure has been determined by Braibanti[153] et al who found an array of $[Ni(H_2O)_6]^{2+}$ cations and nitrate anions held together by a network of hydrogen bonds. The cations themselves are only approximately octahedral being deformed to an orthorhombic bipyramid. The six Ni-OH_2 bonds are all of different length ranging from 2.021Å to 2.095Å, and the bond angles about the central nickel ion range from 85.8° to 93.2°. This deformation of the structure is due to the formation of hydrogen-bonding interactions by the water molecules which are all different both in direction and in strength.

In addition, the two nitrate groups are crystallographically independent, and whilst they are both planar they do deviate significantly from trigonal symmetry. The significance of this deviation of symmetry in relation to the infra-red spectrum will be discussed later (Section 4.1.6).

4.1.3 $Ni(NO_3)_2(H_2O)_4$

The crystal structure of this compound has been determined by Weigel et al.[18] The nickel atom is octahedrally co-ordinated by four water molecules and two unidentate nitrato groups in positions CIS- to each other. The nitrato groups show evidence of slight distortion due to hydrogen-bonding in the crystal lattice.

The attempts to prepare this compound are summed up below.

$[Ni(H_2O)_6](NO_3)_2$ $\xrightarrow[6\ hrs./r.temp]{vac\text{-}line/10^{-2}mm}$ $Ni(NO_3)_2(H_2O)y$

$\xrightarrow[2\ weeks/r.temp]{silica\ gel}$ $Ni(NO_3)_2(H_2O)x$

$\xrightarrow[2\ weeks/r.temp]{P_2O_5}$ $Ni(NO_3)_2(H_2O)z$

$\xrightarrow{N_2O_4}$ $Ni(NO_3)_2(H_2O)w$ $\xrightarrow{N_2O_4}$ $Ni(NO_3)_2(H_2O)vi$ $\xrightarrow{N_2O_4 + heat}$ $Ni(NO_3)_2(H_2O)v2$

all preparations were carried out at atmospheric pressure unless otherwise stated.

This latter method using liquid N_2O_4 was first used by Addison and Chapman[155]. Weigel et al crystallised the compound from a saturated solution of acidified Nickel(II) nitrate solution, utilising the phase diagrams of Sieverts and Schreiner.

The analytical data for the compounds prepared is compiled in Table 4.1.c.

	%Ni	$\%NO_3$	$\%H_2O$	Ratio
$Ni(NO_3)_2(H_2O)_4$ calc.	23.04	48.67	28.19	1:2:4
$Ni(NO_3)_2(H_2O)$w	21.43	44.99	33.58	1:2:5.1
$Ni(NO_3)_2(H_2O)$vi	21.99	46.53	31.48	1:2:4.5
$Ni(NO_3)_2(H_2O)$v2	22.75	48.00	29.25	1:2:4.2
$Ni(NO_3)_2(H_2O)$x	23.28	48.43	28.29	1:1.97:3.96
$Ni(NO_3)_2(H_2O)$y	22.65	46.34	31.01	1:1.94:4.46
$Ni(NO_3)_2(H_2O)_z$	23.32	49.60	27.68	1:1.99:3.86

The analytical data indicates that the tetra-aquo compound is produced by dehydration over silica gel and P_2O_5 and by the use of liquid N_2O_4. In all cases the deliquescent dark-green crystals of the hexa-aquo compound are converted to a light green powder of higher melting point.

The nickel(II) ion has an electron configuration of d^8. For this ion in an octahedral ligand field there are three spin-allowed d-d transitions, giving three absorption bands with low molar absorbances ($\varepsilon \simeq 10$). These are observed (Table 4.1.c), together with the splitting of the middle band, ν_2, which is due to spin-orbit coupling which mixes the $^3T_{1g}(F)$ and ^1Eg energy levels[203].* In addition, the spin—forbidden transition[184], $^3A_{2g} \rightarrow {}^1Eg$ appears weakly, indicating slight distortion of the octahedral environment of the nickel(II) ion. This distortion is confirmed by the structural study of the compound[18].

* Ballhausen[182] ascribes the splitting to the wide spread of the spin-orbit components of $^3T_{1g}(F)$, leaving an energy "gap" which is not bridged by vibronic coupling.

The table of collected data (Table 4.1.c) shows that the electronic spectrum is closely similar to that of the hexa-aquo Nickel (II) ion, and is also green in colour, as found for nickel-oxygen systems.

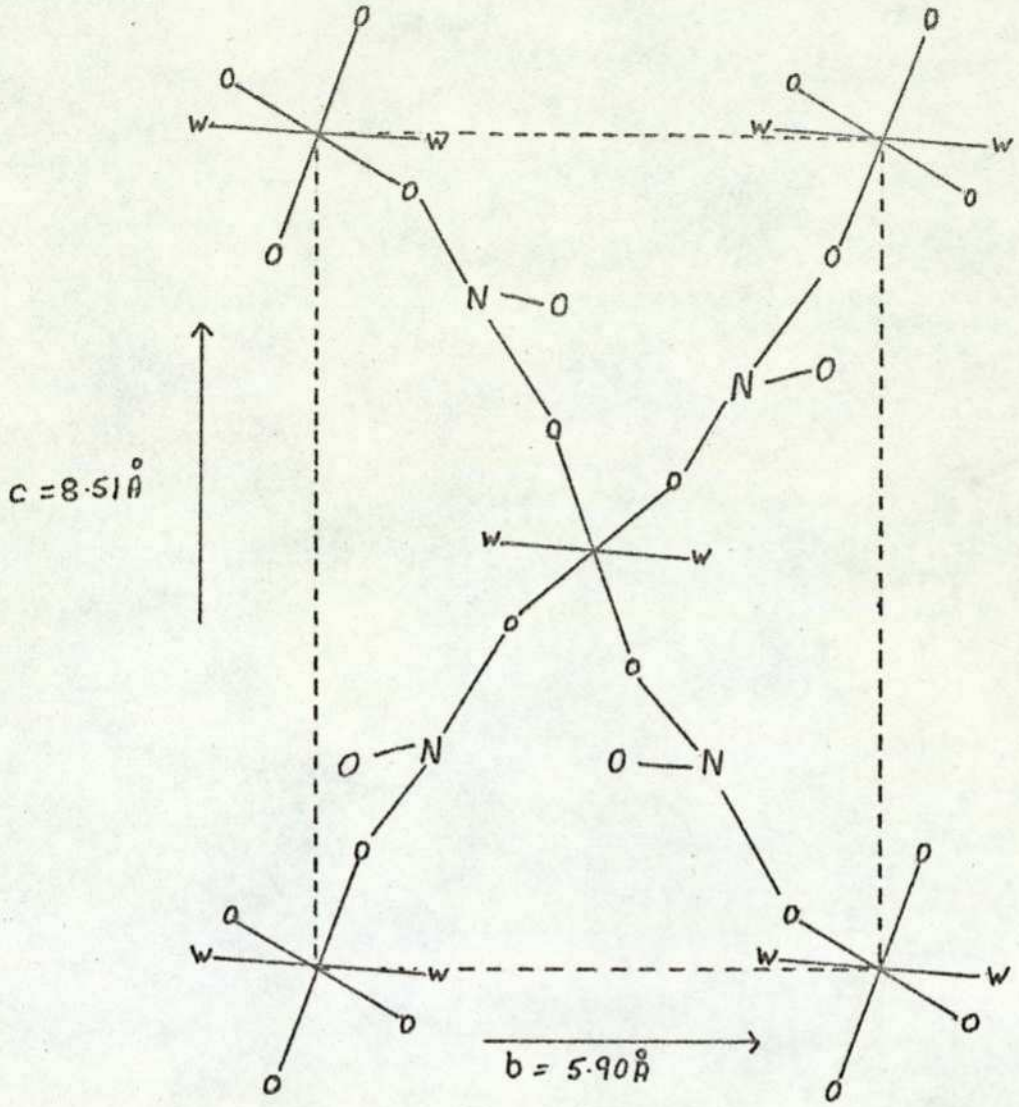
The octahedral environment of the Nickel (II) ion gives rise to a paramagnetic ion with two unpaired electrons. The spin-only magnetic moment is 2.83 BM, whilst the observed magnetic moment for this compound is 2.87 ± 0.04 BM (at 22.5°C). This indicates that there is only a small deviation from octahedral co-ordination of the nickel(II) ion in the tetra-aquo compound.[204]

4.1.4 $Ni(NO_3)_2(H_2O)_2$:

This compound has been previously prepared by Hathaway[156] who added anhydrous nitric acid to the anhydrous metal chloride. Shortly after this a low-temperature magnetic susceptibility study of the solid was reported by Berger and Friedberg[124], who used the unpublished structural data of Baughman and Jeffrey. These latter workers prepared their crystals by the method of Sieverts and Schreiner, which involves the recrystallisation of an acidified aqueous solution of nickel(II) nitrate in the temperature range >85°C. They interpreted the structure of the monoclinic crystals as a polymeric system with bridging nitrato groups with transwater molecules. The only molecular dimensions given are the nickel-oxygen bond lengths. See Table 4.1.f.

Berger and Friedberg found that their magnetic data fitted in with this structure. The low temperature molar susceptibilities of the hexa- and tetra-aquo compounds are practically identical to each other suggesting similar structures, but they are very different from the di-aquo compound.

The di-aquo compound was prepared by adding an excess of liquid N_2O_5 to crushed crystals of the hexa-aquo compound using the method described earlier (3.1.2). The dark-green solution yields a light-green solid on removal of the solvent. This compound is lighter in colour than the tetra-aquo compound, and has a higher melting point. The analytical data are shown in Table 4.1.b.



projection of the unit cell on bc plane

Ni^{2+} ions form a face-centred pattern

$[Ni(NO_3)_2(H_2O)_2]$ after Boughman and Jeffrey (124)

Table 4.1.b

	% Ni	% NO_3	% H_2O difference	Ratio
$Ni(NO_3)_2(H_2O)T$	27.12	56.32	16.56	1:1.97:1.99
$Ni(NO_3)_2(H_2O)_2$ calculated	26.85	56.67	16.48	1:2.0:2.0

The electronic spectrum of the diaquo compound is very similar to that of the tetra-aquo compound, and is closely similar to that reported by Hathaway[157] for the diaquo compound (Table 4.1.c) The spectrum indicates a distorted octahedral environment for the nickel(II) ion. In particular, the splitting of ν_2 is more pronounced and the band is broader, suggesting greater distortion of the octahedral environment of the nickel(II) ion.

The magnetic moment was found to be 3.04 $\pm$ 0.04 BM (22.5°C). Hathaway[157] reports a value of 3.34 BM. These values imply an orbital contribution to the magnetic moment. Since no orbital contribution is expected for the d^8 configuration in an octahedral field, the existence of such a contribution implies that the octahedral environment is distorted.[204]

The electronic spectral data is collected in Table 4.1.c.

Table 4.1.c.

	$\nu_1(^3T_{2g} \leftarrow {}^3A_{2g})$	$\nu_2(^3T_{1g} \leftarrow {}^3A_{2g})$	$\nu_3(^3T_{1g}(p) \leftarrow {}^3A_{2g})$	$(^1E_g \leftarrow {}^3A_{2g})$	$(^1T_{1g} \leftarrow {}^3A_{2g})$	Nitrate
$[Ni(H_2O)_6]^{2+}$ soln.(158)	1176	724.6 doublet	395.3	657.9	454.5	
" (solid)	1160 vbr.	700ss,720doublet	386 br.	660w		228sh,248(2), 292(5)
$Ni(NO_3)_2(H_2O)v_2$ (solid)	1200(±40)br.	710,740doublet	394	660m	410-420sh	223,252(2), 285(5)
$Ni(NO_3)_2(H_2O)_2$ (solid)	1140(±20)	720,740 doublet	400(4)	680m	480sh	227,225(3), 290-310br
" (157) (solid)	1170s	740-660vbr	398s	(740-660vbr)	470sh	285•7sh
$[Ni(NO_3)_2]n$ (solid)	970sh	780	416br	700m		223,260(4)-290vbr
$Ni(NO_3)_2/N_2O_5$ (soln.)	960sh	780	416(8)vs	680(10)sbr		
$[Ni(NO_3)_3]^-$ (166) (DMS soln)	≈ 1250	775.2	420.0	710.2		

i) all values ate in mμ
i) figures in brackets indicate band half-widths

4.1.5 $[Ni(NO_3)_2]_n$:

This compound was prepared by the reaction of liquid N_2O_5 with the di-aquo compound using the method described in 3.1.2. The intense dark-green solution yielded a lime-green powder on removing the solvent under vacuum. This solid evolved brown fumes on standing, even in an atmosphere of dry nitrogen gas in a dry-box. Analysis confirmed that there was an excess of nitrate present arising from an N_2O_5 molecular addition compound. Heating the solid to 70°/ 0.05mm Hg pressure removed some of this N_2O_5, and raising the temperature to 100° for several hours removed even more. Heating for about 15 hrs at this temperature and pressure yielded the yellow-green, free-flowing powder of the anhydrous nitrato compound.

$$Ni(NO_3)_2.N_2O_5 \xrightarrow[4\ hrs]{70°/0.05mm} 78.82\%NO_3 \xrightarrow[2\ hrs]{100°/0.05mm} 70.47\%NO_3 \xrightarrow{15\ hrs} 67.41\%NO_3$$

	% Ni	% NO_3
$Ni(NO_3)_2$	31.18	67.41
$Ni(NO_3)_2$ calc.	32.14	67.86

Table 4.1.d.

Heating at higher temperatures, above 125°, under vacuum, produced no volatile metal products, and instead decomposition takes place.

The anhydrous compound is soluble in donor solvents such as water, ethyl acetate, methyl cyanide, nitromethane and ether, but insoluble in chloroform, carbontetrachloride and benzene. It is soluble in liquid N_2O_5.

The electronic spectrum is very similar to that of the other compounds and is assigned on the basis of a distorted octahedral environment for the nickel atom (Table 4.1.c.) It is noticeable that the bands are broader for this compound than for any of the other nickel compounds, and without any fine structure. This broadening is typical of polymeric substances.

The anhydrous compound was found to have a magnetic moment of 2.99BM at room temperature[159], and to obey the Curie-Weiss Law over the temperature range 77°-290°K. Johnson found a value of 2.86BM[160] for this compound. The small orbital contribution to the magnetic moment indicates an octahedral environment which is only slightly distorted. This will be discussed further in relation to the infra-red spectrum.

This method of preparation was used by Guntz and Martin[161], who obtained a yellow powder which decomposed above 105°.

Johnson[160] used liquid N_2O_4 in the presence of an electron-donating solvent. Nickel metal is not attacked under these conditions, but anhydrous nickel(II) chloride reacts vigorously with a suspension of nickel in liquid N_2O_4 and ethyl acetate. The suggested reaction scheme is:

$$NiCl_2 + 2N_2O_4 \longrightarrow Ni(NO_3)_2 + 2NOCl$$

$$2NOCl + Ni \longrightarrow NiCl_2 + 2NO$$

$$2NO + N_2O_4 \longrightarrow 2N_2O_3 \qquad \text{(green solution)}$$

$$Ni(NO_3)_2 + N_2O_4 \longrightarrow Ni(NO_3)_2.N_2O_4 \xrightarrow{130^\circ/10^{-2}\,mm} Ni(NO_3)_2$$

The product is a pale green solid with a magnetic moment of 2.86BM.

Addison and Ward[162] obtained a flocculent pale green powder by the reaction of liquid N_2O_5 with anhydrous nickel(II) chloride or diaquo dinitrato nickel (II). Their study of the compound suggests that it is a high-spin Nickel (III) compound with a magnetic moment of 4.52 ± 0.028 B.M. and they formulated it as $NO_2^+[Ni^{III}(NO_3)_4]^-$.

No evidence for such a compound was found in any of our many preparations of the anhydrous compound. One intermediate which was isolated and examined showed evidence for the formulation $NO_2^+[Ni(NO_3)_3]^-$ with a normal Nickel (II) - value for the magnetic moment and a band at 2380 cm^{-1} assigned to NO_2^+[163-165]. The species $[Ni(NO_3)_3]^-$ [166] has been recognised in molten dimethyl sulphone having a similar electronic spectrum (Table 4.1.c) showing the three main bands and a spin—forbidden band at 710.2mμ.

Some time after the completion of this work another investigation of this system was published which queried this unusual oxidation Ni(II)→ Ni(III). Kimber and James[167] repeated the procedure of Addison and Ward and obtained a non-stoichiometric adduct with a magnetic moment of 2.87B.M. They formulated their adduct as $Ni(NO_3)_2\ \frac{1}{2}N_2O_5$ or $NO^+[Ni_2(NO_3)_5]^-$ mainly because of the strong band in the infra-red at 2255 cm^{-1} assigned to NO^+. The compound is polymeric and reactive. They explain the reactivity of the compound as the solvent breakdown of the polymeric network yielding NO_2 gas and acidic solutions which are capable of oxidising potassium iodide solutions.

This experience is similar to our own, except that Kimber and James only removed the excess N_2O_5 under vacuum at room temperature, whilst our preparation removed adhering N_2O_5 by heating to about 100°C under vacuum.

4.1.6. Infra-Red Spectra:

The spectral data for all the nickel(II) compounds is collected in Table 4.1.e. (P63)

All the compounds exhibit a large number of bands. In all cases more bands are observed than would be expected assuming the simple concept of the isolated NO_3 group, as discussed in the introduction. (P36)

The tabulated data shows a change from the compounds of high symmetry - $[Ni(H_2O)_6](NO_3)_2$ with a relatively simple spectrum, through the intermediates with many bands, to the anhydrous compound where a relatively simple pattern is again observed. The simple variation of the bands in the 1250-1450 cm^{-1} region found by Curtis and Curtis[96] is not apparent in this system. This is possibly due to the smaller water ligand in this system allowing a greater rearrangement of all the ligands co-ordinated to the nickel atom on changing from one compound to another; Curtis and Curtis used ethylenediamine complexes.

Assignments:

(i) All the hydrates show the usual bands due to the presence of co-ordinated water molecules - that is: broad bands in the 3300-3600 cm^{-1} region due to ν O-H, and usually two bands in the 1600-1680 cm^{-1} region due to the δ O-H mode. In the hexa- and tetra-aquo compounds these bands are all broad due to extensive hydrogen-bonding. In the diaquo-compound these bands are fewer and sharper. They are totally absent in the anhydrous compound.

In addition, there are bands due to the Ni-OH_2 vibration in 500-700 cm^{-1} (νas) and 400-450cm^{-1} (νs) regions. These are also absent in the anhydrous compound.

(ii) For the hexa-aquo compound the simple ionic nitrate pattern is not observed. The appearance of the forbidden band at 1060cm^{-1} and the lifting of the degeneracies of the two E′-modes indicates that the local site symmetry of the NO_3^- ion has been reduced, probably to C_{2v}, as shown by the X-ray analysis of this compound[153].

(iii) The other aquo-compounds show a similar set of bands: 1470, 1310(40), 1040 cm^{-1}(N-O stretching modes).

805(10), 760cm^{-1} (ONO-bending modes) (The spectrum of the tetra-aquo compound is similar to that reported)[130,155].

(iv) The weak bands in the 2000-2500 cm^{-1} region can be assigned to combination modes.

(v) Bands in the 1300(40)cm^{-1} and 1475(20)cm^{-1} regions are all broad and are undoubtedly broad envelopes of several bands, which are only sometimes partially resolved. This fine structure is a consequence of the various factors discussed above (Section 2.3). Only a single crystal study using both infra-red and Raman techniques would resolve the fine structure.

(vi) There are bands in the 1760-1790 cm^{-1} and 2000-2500 cm^{-1} regions which are present in all the spectra and which disappear on complete dehydration. These are combination modes.

Thus, no simple pattern emerges from the 3600-500 cm^{-1} region to give any guidance concerning the nature of the bonding of the nitrato group.

The data for the 500-200cm^{-1} region is collected in Table 4.1.e. and figs 4.1 and 4.2. The spectra and figures indicate that in this region each compound has a distinctive spectrum.

(i) The hexa-aquo compound shows no specific absorption in this region. Although the high temperature of the beam usually caused melting of the compound, cooling the mull produced no better spectra. This broad absorption is typical of this and other fully hydrated compounds.

(ii) The tetra-aquo compounds vary considerably in the pattern of the bands, although the actual band positions are closely similar in all the compounds. The "wetter" compounds 'w' and 'y' give the least specific patterns. The clearest patterns are shown by compounds 'V$_2$' and 'Z' which correspond the most closely to $[Ni(NO_3)_2(H_2O)_4]$. These two actually differ in the number of bands appearing in the spectrum. The reason for the difference could be due to the different methods of preparation. Thus, dehydration over P_2O_5 produces a compound in which the two nitrato groups are trans to each other. a chromophore MO_4Y_2 with This molecule would have a point group symmetry of D_{4h} giving five infra-red active vibrations. Dehydration with liquid N_2O_4 produces a compound in which the nitrato groups are CIS- to each other, as found by Weigel et al. This molecule would have the lower symmetry of the C_{2v} point group, giving thirteen infra-red active vibrations. (See figure 4.1). On standing the nujol mull for about 24 hrs. the more complex infra-red pattern was observed to change to the simpler pattern. This seems to imply a lattice rearrangement of the CIS- to the trans-dinitrato structure.

(a) All show a broad band centred on 440 cm^{-1}, assignable to a ν_{Ni-OH_2} vibration. The broadening is probably due to the presence of four co-ordinated water molecules, all of which are extensively hydrogen bonded. This changes to a sharper band at 405cm^{-1} in the diaquo-compound, and disappears on further dehydration.

(b) The pattern of the remaining bands becomes simpler on passing from the tetra- to the di-aquo compound. This latter compound has three bands at 305,250 (10), and 225-230 cm^{-1}.

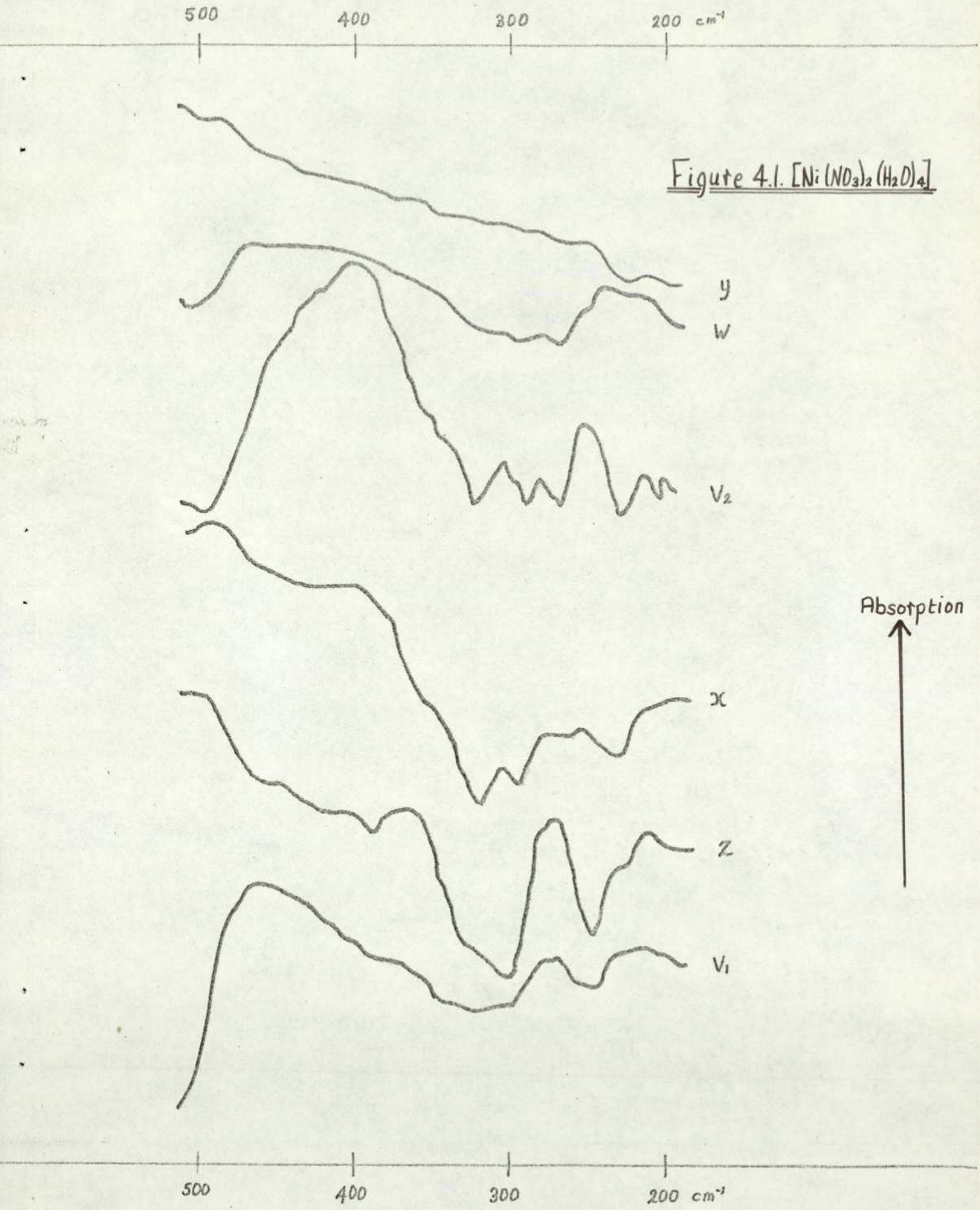


Figure 4.1. $[Ni(NO_3)_2(H_2O)_4]$

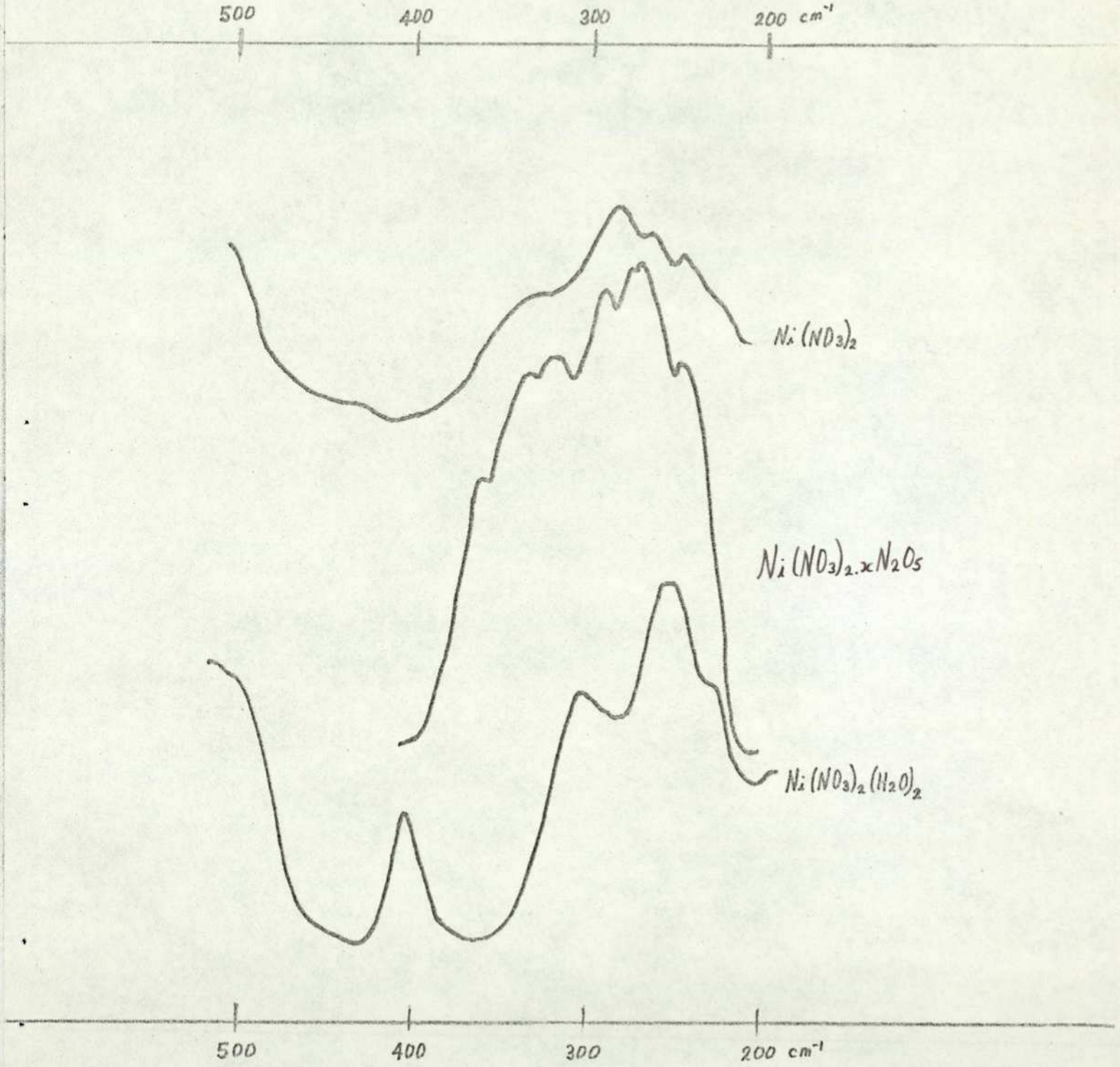

500
400
300
200 cm⁻¹
Ni(NO3)2
Ni(NO3)2.xN2O5
Ni(NO3)2(H2O)2
500
400
300
200 cm⁻¹

Figure 4.2.

Table 4.1.e.

Assignment	$[Ni(OH_2)_6](NO_3)_2$	$[Ni(NO_3)_2(H_2O)_3]$ "W"	$Ni(NO_3)_2(H_2O)_{4.5}$ "V_1"	$Ni(NO_3)_2(H_2O)_4$ "V_2"	$Ni(NO_3)_2(H_2O)_4$ "X"	$Ni(NO_3)_2(H_2O)_4$ "Z"	$Ni(NO_3)_2(H_2O)_2$	$Ni(NO_3)_2$
Ni-Onitrate stretching and bending modes		235(20)br 280-285mw 325	250-255w	215 mm 255ms(split) 280ms 305ms	210br.sh 250-255m 275-280m 305(5)brs	210 230 270ss 305	225-230sh 250(5)m.s 305 m.s	220w 240m 260m 280s 325 wbr
Ni-OH_2 stretching modes	416mm	425 vbr 460(20)vbr	435(20)br w	405(40)vbrs 440(30)br.s	405(15)br.s 440(20)br.w 470 wsh	440(10)sh	405s.s	
Ni-OH_2 wag and rock	620-685brs	560(20)vbr	510-615vbr.w 655-700br.w	600(20)br.m 680(20)br.m	615(30)br.m	590(10)w	665(30)br	
δ nitrate(a)	760ss	770shw	750mm	760m	770mm	760w	765sm	740sh 780sw
δ nitrate(b)	807s	835(10)w	810m.s. 870(10)sh	810m.s 875mm	815sm 870m	820(10)m	810s.s	805s.s 850vw
∂ nitrate (c)	1025sh 1060s	1040m 1060sh	1040ss	1040ss	1045sm	1045ss	1060ss	1020sh 1050m
∂ nitrate(d)	1310(20)br	1280sh 1315(10)brs	1250sh 1310(20)brs	1250shm 1310(10)brs 1370m	1260sh 1310(20)brs	1270sh 1315(10) 1390(10)m	1260sh 1310(20)brs 1340sh	1260brsh 1310sm 1340sh
∂ nitrate(e)	1470(20)br	1470brm		1480(10)bm	1490(30)brs	1475(20)ms	1475(10)brs	1470
δ O-Hwater	1625sm	1620sh 1650 1670(10) m	1620shs 1645s	1615m) 1640m)	1630(10)ms 1675mm	1640ms 1685mm	1630ms	1540 1560
combination (a)+(c)	1790	1760(10)w	1760sh	1760w	1760m	1760m	1790m	
overtone 2 x (c)	2075	2080w	2070(10)w	2060vw	2065m	2070vw	2035vw 2110vw	
combination (d) +(c)			2380w	2320w) 2350)	2350w.s	2300vw 2350vw	2350mw	
combination (e) +(c)		2435(20)brw	2440w 2500s	2500sh		2500w	2515	
∂ O-H(symmetric)		3200 vbr	3200-3300br	3210(20)brs	3200 vbr	3290vbr	3490	
∂ O-H(asymmetric)		3600	3400-3500	3410(20)brs	3600	3460vbr	3535	

Note (i) all values are wave numbers (cm^{-1})

(ii) figure in brackets indicate half-band widths

(iii) letters after the figure indicate (a) band shape: s = sharp, m = medium, br = broad

(b) band intensity: s = strong, m = medium, w = weak, sh= shoulder

The latter two bands are broad and overlap considerably. If the molecule consisted of two trans-bidentate nitrato groups and two trans water molecules then the five-band pattern for D_{4h} symmetry would be expected. Baughman and Jeffrey[124] indicate that the molecule is composed of four oxygen atoms from four different bridging bidentate nitrato groups and two oxygen atoms from two trans water molecules. Thus, the basic molecular symmetry is D_{4h} and the expected fivebands are observed.(Table4.1.f and figure 4.2.)

Table 4.1.f.

	Ni-OH_2(Å)	Ni-OH_2(cm^{-1})	Ni-O (Å)	Ni-Onitrate(cm^{-1})
$[Ni(H_2O)_6]^{2+}$	2.094[158]	405(645(wag)[169]	-	-
$[Ni(H_2O)_6](NO_3)_2$	2.086,2.070 2.033[153]	416		
$[Ni(H_2O)_4(NO_3)_2]$	trans:2.085[18] CIS:2.046	405[580br(wag)]	2.065[18]	305,280,255(5),215
$[Ni(H_2O)_2(NO_3)_2]$	trans:2.06[124]	405(685)(wag)	2.06,2.11[124]	305,250(5),230-225
$[Ni(NO_3)_2]$				325,280,260,240,220

(c) The anhydrous compound exhibits a rather different pattern of overlapping bands in the range 340-240 cm^{-1}, suggesting a mixture of modified modes. Such broadening and overlapping of bands is typical of polymeric substances and the anhydrous dinitrato nickel(II) probably possesses bridging bidentate nitrato groups. The bridging function of the nitrato probably involves at least two of the three oxygen atoms in the group. This mode of bonding allows a relaxation of the strain on the NO_3 groups bond angles, with the result that the symmetry of the group becomes more regular. This is reflected in the more simple infra-red pattern and the lower intensity of the band at 1050cm^{-1}. In addition, the environment of the central nickel(II) ion becomes less distorted, as shown by the small orbital contribution to the magnetic moment (Section 4.1.5.), and by the more symmetric, although broader, bands in the electronic spectrum.

Bands have been observed in the 350-250cm^{-1} range by other workers[170-173] for nitrato compounds of Nickel(II), although these compounds also contain bulky N-bonded organic ligands. Kimber and James[167] also observed a broad band at 300 cm^{-1} in the N_2O_5 adduct.

4.2.1. Cobalt

The cobalt (II) nitrate - H_2O system has previously been studied by Weigel[174] et al who found evidence for tetra, di- and mono-aquo compounds, using thermogravimetric methods. Prior to this Katzin and Ferraro[175] reported evidence for the tetra, tri- and di-aquo compounds in the system $Co(NO_3)_2$-H_2O-acetone and later prepared them[176].

4.2.2 $[Co(H_2O)_6](NO_3)_2$:

The brownish-red crystals are hygroscopic and become salmon-pink in colour when cooled with liquid nitrogen.

Jayaraman[177] reports that the crystals are monoclinic (space group C2/c) with four molecules per unit cell. The detailed crystal structure has not been reported, but intuition and the infra-red spectrum indicate a structure consisting of an array of hexa-aquo cobalt(II) and nitrate ions held together by hydrogen bonding. The infra-red spectrum indicates that there is little distortion of the nitrate ion, the forbidden A_1' mode appearing only weakly.

4.2.3 $Co(NO_3)_2(H_2O)_4$:

The crystal structure of this compound has not been reported. As with the analogous nickel compounds several methods were used to prepare this compound, as outlined below:

$[Co(H_2O)_6](NO_3)_2$ — 2 x liquid N_2O_4, solid heated to 40° → $[Co(NO_3)_2(H_2O)v]$

silica gel/3 weeks/room temp → $[Co(NO_3)_2(H_2O)x]$

vacuum dehydration/10^{-2}mm Hg, 6 hrs/room temp → $[Co(NO_3)_2(H_2O)y]$

P_2O_5/1 week/room temp → $[Co(NO_3)_2(H_2O)_z]$

(All reactions were carried out at normal pressure unless otherwise shown).

The table of analytical data, Table 4.2.a, indicates that the first three methods were successful, the method of dehydration over silica gel probably requires a longer time for complete dehydration. Dehydration over P_2O_5 was very effective and gave a product nearer to a tri-aquo compound. Katzin and Ferraro[176] dehydrated the hexahydrate by melting it and removing the excess water under vacuum.

Table 4.2.a

	% Co	% NO_3	% H_2O	Ratio
$Co(NO_3)_2(H_2O)_4$ calc.	23.11	48.63	28.26	1:2:4
$Co(NO_3)_2(H_2O)v$	23.17	48.12	28.71	1:1.97:4.05
$Co(NO_3)_2(H_2O)x$	22.75	47.79	29.46	1:2.00:4.24
$Co(NO_3)_2(H_2O)y$	23.32	48.30	28.30	1:1.97:3.97
$Co(NO_3)_2(H_2O)_z$	25.50	52.40	22.10	1:1.95:2.84
$Co(NO_3)_2(H_2O)_3$ calc.	24.87	52.33	22.80	1:2:3

The electronic spectrum of the tetra-aquo compound is assigned on the basis of octahedral co-ordination of the cobalt(II) ion (Table 4.2.c.). The cobalt (II) ion, with a d^7 electron configuration in an octahedral ligand field is expected to exhibit three spin-allowed d-d transitions. Jorgensen[158] has assigned these bands as shown in the diagram below. This scheme has been followed by some other workers[178,179]. Cotton[180,181], however, following Ballhausen[182] suggests a different assignment of the three bands, and this scheme is followed by many other workers[183,184].

Jorgensen[158]:

ν_1: $^4T_{1g}(F) \rightarrow {}^4T_{2g}$: 1266mμ ($\epsilon$=1.30)

ν_2: $\rightarrow {}^4A_{2g}$: 625mμ (ϵ=0.35)

ν_3: $\rightarrow {}^4T_{1g}(P)$: 513mμ ($\epsilon$=4.8); 481mμ ($\epsilon$=3.65) sh

Cotton[180]:

ν_1: $^4T_{1g}(F) \rightarrow {}^4T_{2g}$: 1266mμ

ν_2: $\rightarrow {}^4T_{1g}(P)$: 625mμ, 513mμ

ν_3: $\rightarrow {}^4A_{2g}$:

(the data quoted is for $[Co(H_2O)_6]^{2+}$ in aqueous solution)

Thus, in Cotton's scheme, ν_3 is very close to ν_2, frequently being overlapped and even obscured by the more intense transition. It should be noted that the intensities here are very relative because ν_2 has a molar absorbance of only about 5 in aqueous solution and ν_3 is expected to be about 10^{-2} weaker than this.

In the tetra-aquo compound a shoulder is observed on the high-frequency side of the main band. This is attributed by Jorgensen to a transition and by Cotton to spin-orbit coupling in the $^4T_{1g}$ (P) state of the ν_2 transition.

Thus, the tetra-aquo compound is essentially octahedral about the central cobalt(II) ion. The tri-aquo compound, whilst showing the same spectral features has a more distorted band shape with the shoulder at 508 mμ appearing more clearly. This seems to indicate a slightly more distorted octahedral environment. It is difficult to decide exactly what chemical entity is present in this compound. Perhaps it is better described as an array of aquated cobalt(II) and nitrate ions from which water molecules have been removed. As this process continues the NO_3 groups enter the co-ordination sphere of the cobalt (II) ions. The tri-hydrate could thus represent an intermediate between the unidentate nitrato tetra-aquo compound and the bidentate bridging nitrato di-aquo compound. The asymmetry of such a compound is reflected in the electronic spectrum and in the infra-red spectrum which shows many bands, all of which are split because of the low site symmetry of the nitrato groups in such a bonding situation. Possibly the tri-hydrate is an equimolar mixture of the tetra- and di-hydrate compounds giving an averaged set of analysis data.

4.2.4 $[Co(NO_3)_2(H_2O)_2]$:

The crystal structure of the diaquo compound has not yet been determined. However, it has been prepared by Katzin and Ferraro[176], who melted the hexahydrate and removed the excess water under vacuum, and by Hathaway[156] et al who added anhydrous nitric acid to the anhydrous metal chloride.

Our preparation involved the addition of the liquid N_2O_5 reagent to the hexa-aquo compound, in the manner described earlier (Section 3.1.2).

	%Co	$\%NO_3$	$\%H_2O$
4I	23.72	52.48	
4II	26.24	55.53	18.23
$Co(NO_3)_2(H_2O)_2$ calc.	26.91	56.63	16.46

Table 4.2.b

The hexa-aquo compound dissolved to give a purple solution or suspension whichwas reduced on the vacuum-line to a light-purple solid (4I). This solid was heated to about 50° under vacuum, and the resulting salmon-pink solid (4II) was found by analysis to be the di-aquo compound. Table 4.2.b.

The electronic spectrum of the diaquo compound is very similar to that reported by Hathaway[157] (Table 4.2.c). It is also very similar to that of the tetra-aquo compound, indicating that the essentially octahedral environment of the cobalt (II) ion has been preserved. The main band, due to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition is, however, broader than in the other compounds - about 180 mμ compared to 140-150mμ - and a new shoulder appears on the high-frequency side of this transition. If this diaquo compound is similar in structure to the diaquo nickel (II) compound then the bridging nitrato groups would introduce a greater degree of distortion into the octahedral environment of the cobalt (II) ion. This is the probable source of the extra shoulder.

Hathaway[157] reports a magnetic moment of 4.73BM for this compound. As discussed earlier (Section 2.1.4) such a value indicates a large orbital contribution to the 'spin-only' magnetic moment, and possibly also the presence of an orbital triplet ground state. However, taken together with the electronic spectrum this supports the assignment of a distorted octahedral environment for the cobalt(II) ion in this compound.

4.2.5 $[Co(NO_3)_2]_n$:

Addition of excess of the liquid N_2O_5 reagent to the di-aquo compound under the conditions described earlier (3.1.2) produced an intensely coloured deep-violet solution. This was reduced on the vacuum-line to a deep-violet coloured solid (4III). This solid evolved brown fumes on standing, and the analysis suggests that this is an adduct of dinitrato cobalt(II), possibly $Co(NO_3)_2.\frac{1}{2}N_2O_5$ (%Co = 25%, $\%NO_3$ = 78.9%)

Table 4.2.c

	$\nu_1(^4T_{1g}(F)\rightarrow{}^4T_{2g})$	$\nu_2(^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$	$\nu_3(^4T_{1g}(F)\rightarrow{}^4A_{2g})$	Nitrate
$(Co(H_2O)_6)^{2+}$ soln.(158)	1235.0m	625.0vw, 515.0s		
$(Co(H_2O)_6)(NO_3)_2$ solid	1140 br	540	460	221-226sh,230,250,292-302
$(Co(NO_3)_2(H_2O)_4)$ solid	1160(40)	510	480,460	230(4),260(5),280-300
$(Co(NO_3)_2(H_2O)_3)$ solid	1160(40)	508	486,460	229,265(5),290-310
$(Co(NO_3)_2(H_2O)_2)$ solid	1160-1240	590-560br.sh 510	482s,460sh	230(4),260-280 (268 max)
$(Co(NO_3)_2(H_2O)_2)$ (157) solid	1190s	550.2sh 500sh	483.3s,460sh	270.3
$(Co(NO_3)_2)n$ solid	1160-1250	700sh 534	476sh	230(4),260-300vb

assignment according to Cotton(180)

$(Co(H_2O)_6)^{2+}$ soln.(158)	1235.0m	625.0vw	515.0s	
$(Co(H_2O)_6)(NO_3)_2$ solid	1140 br	540	460	221-226sh,230,250,292-302
$(Co(NO_3)_2(H_2O)x)x=4$	1160(40)	510	480,460	230(4),260(5),280-300
$(Co(NO_3)_2(H_2O)z)z=3$	1160(40)	508	486,460	229,265(5),290-310
$(Co(NO_3)_2(H_2O)_2)$	1160-1240	590-560brsh 510	482s,460sh	230(4),260-280(268max)
$(Co(NO_3)_2(H_2O)_2)$ (157)	1190s	550.2sh 500sh	483.3s,460sh	270.3
$(Co(NO_3)_2)n$	1160-1260	700sh 534	476sh	230(4),260-300vb

assignment according to Jorgensen(158)

	% Co	% NO_3
4III	26.65	77.92
4 IV	31.12	67.52
$Co(NO_3)_2$ calc.	32.21	67.79

Table 4.2.d

Heating the intermediate 4 III to $80^\circ/10^{-2}$mm pressure yielded the slightly lighter purple solid, 4 IV, which is the anhydrous compound.

Addison and Sutton[185] obtained the same compound by heating the N_2O_4 adduct at 120° in vacuo for several hours. Dehnicke and Strähle[109] heated the adduct at 45° under vacuum (10^{-4}mm) and then at 120° for 4-6 hours. At 160° the anhydrous nitrate began to decompose and this process was completed by heating at 250° for 8 hours.

Addison and Sutton give a figure of 270° for the decomposition temperature. Our compound began to decompose at about 120° under vacuum and the rate accelerated as the temperature was raised to 180°, no doubt catalysed by the oxide formed in the initial decomposition. Guntz and Martin[161] obtained the pale pink compound by a similar method and report a decomposition temperature of 100°.

The electronic spectrum of the anhydrous compound is very similar to those of the other cobalt (II) compounds and is assigned on the basis of octahedral co-ordination of the cobalt(II) ion (Table 4.2.c). The spectrum is very similar to that reported by Addison and Sutton[185]. The broad band centred on 534 mμ is more symmetrical than those observed for the other compounds. Addison and Sutton observed the solution spectra for this compound, and the molar absorbance values are found to be relatively low (10-80) varying according to the solvent. As discussed earlier (Section 2.1.4) many nitrato cobalt (II) compounds show much higher values, and thus the lower values observed for this compound underline the smaller distortion of the octahedral environment of the cobalt (II) ion.

The magnetic moment was found to be 4.63 ± 0.04BM (at 22.5°C). Both Dehnicke[109] and Addison[185] report a value of 4.85BM. These values indicate a large orbital contribution to the magnetic moment and probably the existence of an orbital triplet ground state. These values are also similar to the magnetic moment of the diaquo-compound indicating, together with the electronic spectrum an approximately similar environment for the cobalt(II) ion in these compounds.

Although no adducts of anhydrous dinitrato cobalt(II) with N_2O_5 have yet been characterised two adducts with N_2O_4 have been reported. Dehnicke and Strähle[109] obtained $Co(NO_3)_2.N_2O_4$ by adding liquid N_2O_5 to anhydrous $CoCl_2$ suspended in carbon tetrachloride.

$$CoCl_2 + 2N_2O_5 \longrightarrow Co(NO_3)_2.N_2O_4 + Cl_2$$

This suggests the reaction sequence:

$$2N_2O_5 \rightleftharpoons 2NO_3^- + 2NO_2^+$$

$$CoCl_2 + 2NO_2^+ \longrightarrow Co^{2+} + Cl_2 + 2NO_2$$

$$Co^{2+} + 2NO_3^- \longrightarrow Co(NO_3)_2 \qquad 2NO_2 \rightleftharpoons N_2O_4$$

$$Co(NO_3)_2 + N_2O_4 \longrightarrow Co(NO_3)_2.N_2O_4$$

The same product was obtained by adding $Cl.NO_3$ to anhydrous $CoCl_2$

$$CoCl_2 + 4Cl.NO_3 \longrightarrow Co(NO_3)_2.N_2O_4 + 3Cl_2 + O_2$$

suggesting the reaction sequences:

$$2ClNO_3 \longrightarrow 2Cl^+ + NO_3^- \qquad 2ClNO_3 \longrightarrow 2OCl^- + 2NO_2^+$$

$$CoCl_2 + 2NO_3^- \longrightarrow Co(NO_3)_2 + 2Cl^- \qquad 2Cl^- + 2NO_2^+ \longrightarrow Cl_2 + 2NO_2$$

$$2NO_2 \rightleftharpoons N_2O_4 \qquad Co(NO_3)_2 + N_2O_4 \longrightarrow Co(NO_3)_2.N_2O_4$$

$$2OCl^- + 2Cl^+ \longrightarrow O_2 + 2Cl_2$$

Addison and Sutton[185] prepared the adduct $Co(NO_3)_2.2N_2O_4$ by dissolving cobalt metal in a solution of liquid N_2O_4 in ethyl acetate. The adduct crystallised as red-purple crystals on the addition of further N_2O_4. When this adduct was heated at $50°/10^{-3}$mm for several hours, followed by trituration under liquid N_2O_4, the 1:1 adduct was formed as a pink solid. The 1:1 adduct cannot be converted to the 1:2 adduct by immersion in liquid N_2O_4. The 1:2 adduct was also obtained by reacting liquid N_2O_4 with dicobalt octacarbonyl. $Co_2(CO)_8$

4.2.6 Infra-Red Spectra:

The data are collected in Table 4.2.e. The general remarks discussed in relation to the Ni(II) spectra, concerning the large number of bands observed and the band splitting and broadening, are equally relevant here.

(a)(i) All the hydrates exhibit two very broad bands in the 3200-3600 cm^{-1} range, assigned to the asymmetric and symmetric ν O-H modes. Similarly there are bands in the 1600-1680cm^{-1} range assigned to the δ O-H mode. In the hexa-aquo compound there is one broad band in this range, about 100 cm^{-1} in breadth, which is probably an envelope of the motions of the six water molecules, further broadened by hydrogen-bonding. In the tetra-aquo compounds there are two bands in the range, the lower one, at 1640cm^{-1}, frequently being split or broadened. In the diaquo compound this simplifies to a single band .

(ii) In all the hydrates there are broad absorptions in the ranges 500-550cm^{-1} and 600-680cm^{-1} which are usually ascribed to "rocking" and "wagging" modes of the co-ordinated water molecules.

(iii) In the range 200-500cm^{-1} the hexahydrate yields only a very broad unstructured absorption, whilst the tetra-hydrates exhibit two broad bands at 400 and 450cm^{-1}. The di-aquo compound has one sharp band at 390cm^{-1}, with a weaker one at 470cm^{-1}.

All of these bands are absent in the anhydrous compound.

(b) The absorptions assignable to the nitrato group are numerous.

(i) The hexa-aquo compound has the simplest spectrum, but is also the poorest in quality because of the difficulty in mulling the hygroscopic crystals. Some lifting of the degeneracies is observable, indicating a slight lowering of the high symmetry of the nitrate ion (D_{3h}).

(ii) The tetra-aquo compounds show all the bands expected of compounds containing co-ordinated nitrato groups, including overtone and combination bands. The spectrum is very similar to that reported by Addison and Chapman[155]. The analysis data, infra-red spectrum and comparison with the nickel(II) analogue suggest that the compounds contain unidentate nitrato groups arranged in positions trans to each other in the octahedron of co-ordinated atoms around the cobalt atom. Such an arrangement, of D_{4h} point symmetry, would yield an (expected) far infra-red spectrum of five bands. The trihydrate, z, which is of lower symmetry has a near infra-red spectrum almost identical to that of the tetra-aquo compounds, but more bands in the far infra-red, most of which are split (Fig. 43).

(iii) The diaquo compound exhibits a near infra-red spectrum similar to that of the tetra-aquo compounds. The data is similar to that of Ferraro and Walker[188], and Hathaway[157] et al, except that the latter observed a band at 1540-1560cm^{-1} not observed by either ourselves or Ferraro and Walker.

The far infra-red spectrum is more simple with two bands at 390 and 470cm^{-1} assignable to νCo-OH_2 and two at 210 and 310cm^{-1} assignable to νCo-O vibrations; these latter bands are undoubtedly envelopes of several bands, possibly of the motions of the co-ordinated nitrato groups. The spectrum bears little resemblance to that of neutron-scatter study by Rush, Ferraro and Walker[187] but is similar to the far infra-red spectrum of Ferraro and Walker[186].

(iv) The anhydrous compound probably contains bridging nitrato groups and the consequences for the NO_3 group are that the overall distortion of the group is reduced, leading to a simpler symmetry pattern/higher symmetry group. This is evidenced by the reduced intensity of the fundamental band at 1050 cm^{-1}, which is often used to indicate how far the NO_3 group has deviated from D_{3h} symmetry. Addison and Gatehouse[188] did not observe this band at all and assumed the compound to be ionic.

This, however, is not borne out by the remainder of the infra-red spectrum which exhibits the numerous bands typical of co-ordinate nitrato groups and bands assignable to the interaction of the cobalt atom with the oxygen atoms of the nitrato groups. This is supported by band shifts in the electronic spectrum which indicate interaction between the cobalt ion and the nitrato groups. This is observed both in the nitrate spectrum and in the cobalt (II) spectrum. Further the reactivity of the compound, in particular the nitrogen dioxide fumes produced on exposure to moist air, indicates that there is probably a linkage between the metal and the nitrato group leading to the reduction of the nitrato group to nitrogen dioxide.

There is a large measure of agreement between our spectrum and those of Addison and Gatehouse[188], and Dehnicke and Strähle[109], Ferraro and Walker[186] and James and Kimber[189]. It should be noted, however, that the interpretation of Dehnicke and Strähle is not acceptable (Section 2.2.3) but their data can be interpreted on a basis of a different model as discussed earlier (Section 2.2.3).

The far infra-red spectrum is different from those of all the other cobalt(II) compounds examined in having no bands between 325cm^{-1} and 700cm^{-1} due to the absence of water from the compound. The three bands with peaks at

225,260s and 325m cm^{-1} merge together at their bases in a manner typical of mixed vibrations and frequently observed in the infra-red and electronic spectra of polymeric substances (Figure 4.4). Ferraro and Walker observed bands at 217sh, 271s, 316w.sh, whilst James and Kimber observed a broad band at 270cm^{-1}. Other workers[170-173] have observed bands in the 250-280 and 300-340 cm^{-1} ranges for nitrato complexes.

Comparison of the far infra-red spectrum of the di-aquo compound with the nickel analogue suggests a similar structure of bridging nitrato groups and trans-water molecules. The polymeric character of the diaquo compounds is reflected in the analogous chloride $[Co(H_2O)_2Cl_2]_n$[190] in which the metal atoms are linked through the anions and the water molecules occupy the remaining two positions in the octahedron about the cobalt atom. As found in the nickel-nitrate system, the Co-OH_2 bond length shortens from 2.12Å[191] to 2.04Å on passing from $[Co(H_2O)_6]Cl_2$ to $[Co(H_2O)_2Cl_2]$.

The far infra-red spectrum of the anhydrous dinitrato cobalt(II) is similar to that of the nickel compound (compare figs 4.2 and 4.4). There is also a marked simplification in the near infra-red spectrum indicating a smaller distortion of the symmetry of the NO_3 group. This is supported by the symmetric shape of the main band in the electronic spectrum which indicates a more symmetric environment for the cobalt(II) ion. This could be achieved by the nitrato groups acting as bridging ligands, thus reducing the bond angle strain for both the cobalt(II) ion and the nitrato groups. This is similar to the nickel compound, and suggests that the NO_3 group is bonded to two, and possibly three, different metal atoms. The simple character of the spectrum, indicates the presence of symmetrical bridging nitrato groups in an infinite 3 dimensional array of metal atoms.

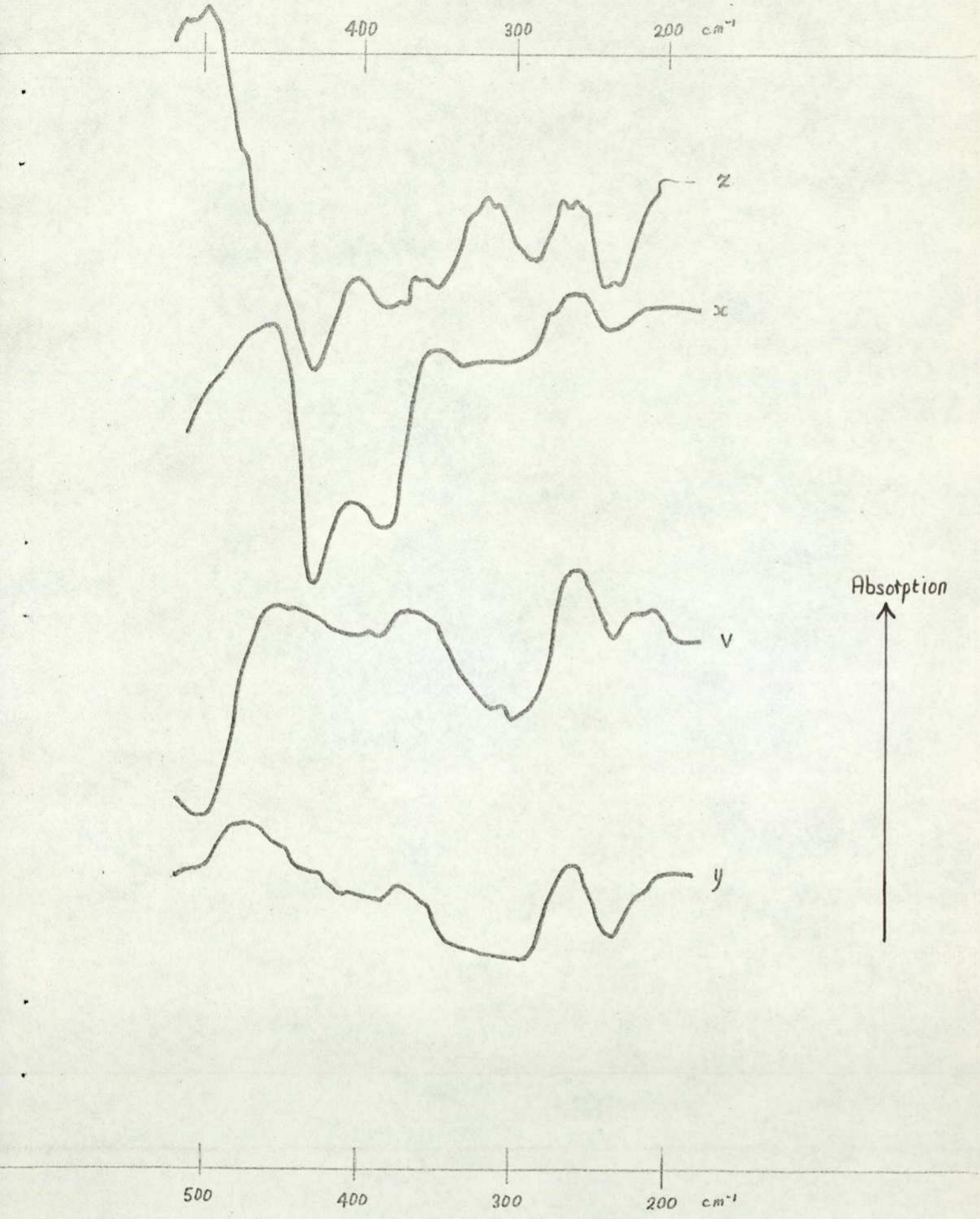


Figure 4.3. $[Co(NO_3)_2(H_2O)_4]$

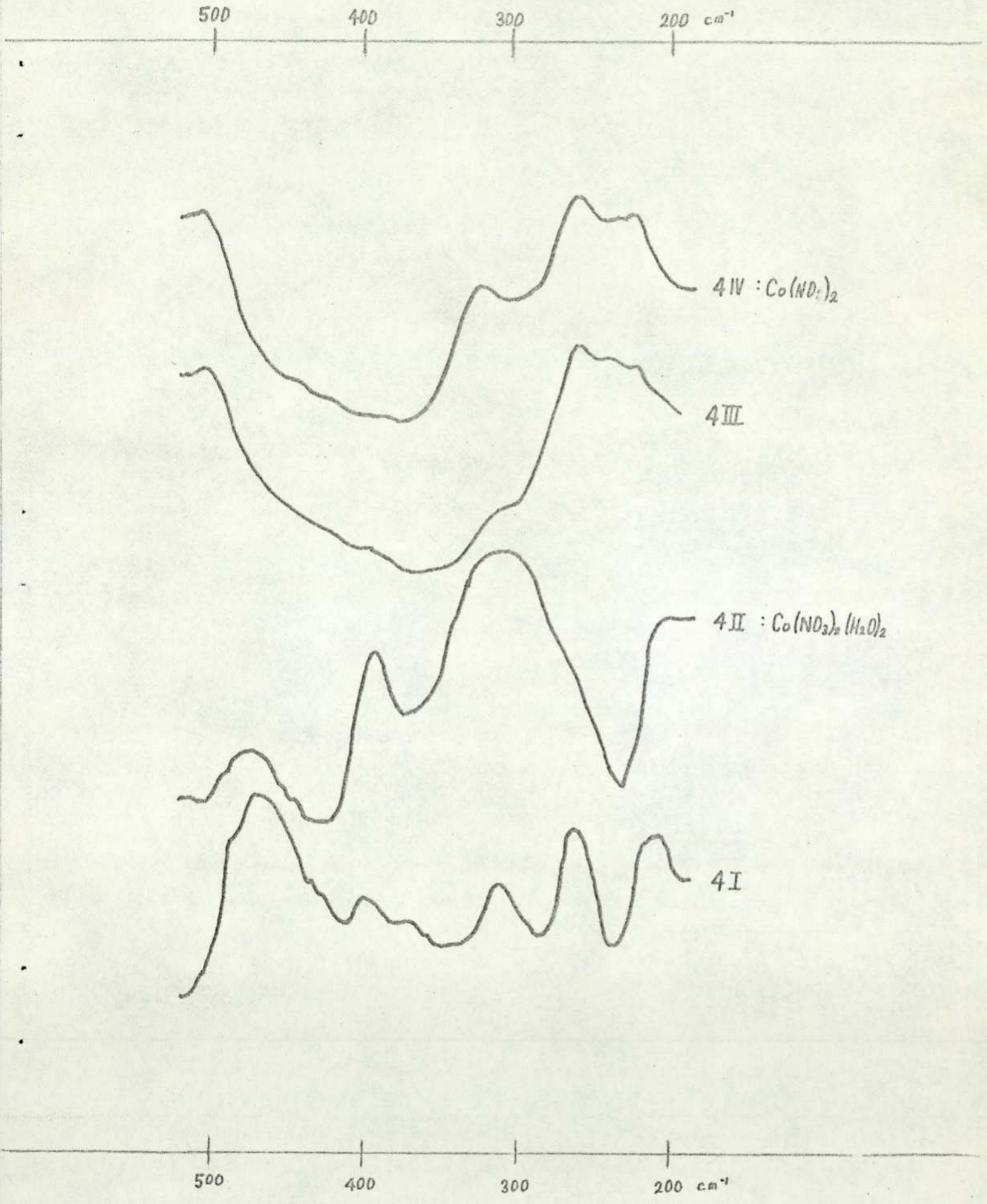

500
400
300
200 cm⁻¹
4IV : Co(NO₃)₂
4III
4II : Co(NO₃)₂ (H₂O)₂
4I
500
400
300
200 cm⁻¹

Figure 4.4.

Table 4.2.e

Assignment	$Co(NO_3)_2(H_2O)_4$ 'x'	$Co(NO_3)_2(H_2O)_4$ 'y'	$Co(NO_3)_2(H_2O)_3$ 'z'	$Co(NO_3)_2(H_2O)_4$ 'v'	4I	4II $Co(NO_3)_2(H_2O)_2$	4III	4IV $Co(NO_3)_2$
Co-Onitrate stretching and bending modes	220w 265(10)brs 315(10)brw 345(10)brm	215brw 260(10)brs 315brvw (355w (375brm	210) 220) brm 235w 250) 257) brm 267) 295w 308) 315) br 327) 355m	212) 222) brm 260(5)ms 310w 355) 365(10)br)	210(10)brs split 260ss 310(10)brm 355sh 365) w 375)	210brs 260sh 310(25)Vbrs 350sh	220) 240) brs 260) 305brm	220ss 235w 260ms 325mm
Co-OH$_2$ stretching modes	400(10)brm 430(10)sh 455(10)vbrs	405(5)w	393) 405) brm 445sh) 460sh) 470sh)	395w Vbr 450(30) s	400(10)brm 425sh) 435sh) 450sh) 470brs)	390ss 445sh 440(15)bm		450(5)sh
Co-OH$_2$ wag and rocking modes	535(20)brm 610-680brs	530(20)br 615(20)) 685(10)) br 615(30)vbr	520(20)br	505) 535) brm 610(40) vbrs	525(15)br 580-630br	510-540brsh 570-690vbrs		
δ nitrate (a)	760ms	760mm	750mm	750mm	760m	760ms	765) 780) split	760sw 770rsm
δ nitrate (b)	820ms	820ss	815sm	820ss	815sm	812ss	795) 805) s	795) 800) sm
ν nitrate (c)	1045ss	1045ss	1040ss	1040ss	1045ss	1055ss	1025(5)m	1050(10)wm
ν nitrate (d)	1320(15)brs 1360sh	1320(10)br 1350sh	1320(10)brs 1345sh	1315(10)) 1355sh) br	1215wsh 1310(10)sm 1350sh	1250(15)br 1320(10)mm 1340sh	1250mm 1300(10)sm 1380sh	1210sh 1310mb 1350sh
ν nitrate (e)	1485(20)vbrs	1490vbrs			1460(10)bm	1450(15)brs	1450(10)m	1430mm
δ O-H symmetric water	1625sh) 1640mm)	1640ms	1625sm	1625) 1635) brs	1640(10)mm	1635(10)sm		
ν asymmetric	1685mm	1685mr	1675mm	1680mm	1680(10)n		1675mm	
Combination (a) + (c)	1760sw	1765sw	1765w	1760sw	1770w	1770sw	1740mm	1820vw
Overtone 2 x (c)	2070w	2080ww	2070vw	2070vw	2050vw	1805w		2030vvw
Combination ? + (c)	2275ww						2265mw	2270vw
Combination (d) + (c)	2350sm	2350sw	2355vw	2355w				
Combination (e) + (c)	2490(10)m	2480vw	2500vw					
ν O-H Symmetric	3200 3550 vbrs	3250(25)brs 3450(35)brs	3445(25)vbrs	3250(40)vbrs 3460(40)vbrs	3190(50) 3390(50)	3180(20)w 3450(20)brs	3170(20)w 3450(100)vbr	
Asymmetric	3550		3530br			3520(10)brs	3525	

Note: (i) all values are wavenumbers cm^{-1}/

(ii) figures in brackets indicate band half-widths

(iii) letters after the figures indicate (a) bandshape: s=sharp, m=medium, br=broad

(b) band intensity: s=strong, m=medium, sh=shoulder

4.3.1 Manganese:

The $Mn(NO_3)_2$ - H_2O system has been studied by several workers[174,192,193] who found evidence for stable hydrates. Ewing[192,193] et al presented evidence for the hexa, tetra, di- and mono-hydrates of manganese(II) nitrate in the ternary phase system: $Mn(NO_3)_2$-HNO_3-H_2O, and in the binary phase system $Mn(NO_3)_2$ - H_2O. Weigel et al[174] confirmed this.

4.3.2 $[Mn(H_2O)_6](NO_3)_2$:

This compound was prepared by Weigel[174] by evaporation of an aqueous solution of the nitrate at ambient temperature. The material is very hygroscopic and has a melting point of 25.8°. We did not obtain the hexa-aquo compound and all available samples were found to be either a mass of wet crystals or syrupy solutions. The precursor used for all subsequent work was a new bottle from Hopkin and Williams Limited. This was found by analysis to be a 'wet' tetra-aquo Manganese(II) nitrate.

4.3.3 $Mn(NO_3)_2(H_2O)_4$:

The excess water was removed by dehydration at room temperature over silica gel in a vacuum desiccator for three weeks giving $[Mn(NO_3)_2(H_2O)x]$. Table 4.3.a. Dehydration on a vacuum-line at 27°/0.5mm for 7 hrs. removed more water yielding a trihydrate $[Mn(NO_3)_2(H_2O)y]$. Table 4.3.a.(P.81).

The electronic spectrum, Table 4.3.b shows that the environment of the manganese atom is essential octahedral. There are no spin-allowed d-d transitions for the manganese(II) ion in an octahedral environment and the appearance of even weak bands indicates distortion of this environment. As the table shows very weak bands are observed, the strongest at about 400mμ, with very low molar absorbances of the order of $\varepsilon = 0.4$.

Changes in the electronic spectrum of the NO_3^- ion in t-butanol in the presence of Mn^{2+} have been observed by Katzin[83] who attributed it to interaction of the metal with the nitrate ion. An ^{14}N-nmr study of an aqueous solution of manganese nitrate showed a very large negative shift with a broad line width, indicating strong interaction between the metal and NO_3^- ions in the solution. Solutions of similar concentration of iron, cobalt, nickel and chromium showed no shift at all[194].

4.3.4 $Mn(NO_3)_2(H_2O)_2$

Standing crushed crystals of the pale pink precursor in a desiccator over P_2O_5 for three weeks at room temperature produced the pale yellow di-aquo compound. $[Mn(NO_3)_2(H_2O)_z]$. The attempt to dehydrate the precursor tetra-aquo compound with liquid N_2O_4 met with little success. This produced a hard, white solid which turned to a sticky yellow mass in excess of the reagent. This material was not suitable for analysis or spectroscopic investigation, even after trying to dry it on the vacuum line. Hathaway[156] prepared the dihydrate by treating the anhydrous metal chloride with anhydrous nitric acid and found a magnetic moment of 6.00B.M.[157].

The high-spin manganese(II) ion, with a d^5 electron configuration, is expected to have a spin-free magnetic moment of 5.92B.M. in an octahedral ligand field. Such an ion would not be expected to have an orbital contribution to the magnetic moment. Selwood[195] quotes a range of 5.2-6.0B.M. for the magnetically isolated manganese(II) ion in an octahedral environment. The value reported by Hathaway is close to that expected for the manganese(II) ion in a regular octahedral environment.

The reaction of the liquid N_2O_5 reagent with the precursor tetra-aquo compound gave a complex mixture of products. The addition of a small quantity ($\approx 10cm^3$) of the N_2O_5 reagent produced a whitish solid under a yellow-orange liquid layer. When this was reduced to dryness the sticky solid, $[Mn(NO_3)_2(H_2O)_n]$ analysed as the monohydrate (Table 4.3.a). When this solid was heated to 70° under vacuum (10^{-2} mm Hg) the dry, hygroscopic white solid had less water $[Mn(NO_3)_2(H_2O)T2]$, (Table 4.3.a). The monohydrate was prepared by Guntz and Martin[161] by dehydration of a concentrated nitric acid solution of manganese(II) nitrate over P_2O_5.

When an excess of liquid N_2O_5 reagent was used the solution became black and quite viscous on standing. The addition of more N_2O_5 reagent had no effect. However, the addition of fuming nitric acid removed the viscosity and the black colouration, leaving a homogeneous orange-coloured solution. This solution yielded a hydrated nitrate. It was not found possible to extract this black material and it appeared to be a colloidal suspension, the solution passing unchanged through a No.4 sintered filter. When the black solution was pumped to dryness on the vacuum-line it yielded a sticky brown mass of imprecise composition, which melted at about 45°C. The black colour seems to imply oxidation Mn(II) → Mn(IV) by the nitric acid, but no precipitate was obtained, and the change appears to be easily reversed, which is unusual for manganese dioxide.

4.3.5 $Mn(NO_3)_2$:

Guntz and Martin[161] obtained the anhydrous nitrate by adding the liquid N_2O_5 reagent to the monohydrate. Excess reagent was removed by standing the resulting solution over a mixture of anhydrous calcium oxide and phosphorus pentoxide. The small, colourless crystals produced by this method begin to decompose at 160° (atmospheric pressure). Dehnicke and Strähle[109]

reacted anhydrous manganese(II) chloride with liquid N_2O_5 and $Cl.NO_3$. They obtained a non-stoichiometric N_2O_4 adduct of manganese(II) nitrate which gave off fumes of nitrogen dioxide. This adduct was decomposed by heating it to 90°/8 hrs/10^{-4}mm, to yield the colourless anhydrous nitrate. They found the magnetic moment to be 5.48B.M. Hathaway[156] obtained the same adduct by dissolving manganese metal in a solution of N_2O_4 in ethyl acetate. The yellow adduct was decomposed by heating at 90° under vacuum. Kilner[196] reports a magnetic moment of 5.72B.M. for the anhydrous compound. These magnetic moments which are lower than the spin-only value, are difficult to interpret structurally, except to note that they are within the range quoted by Selwood[195] for the manganese(II) ion in an octahedral environment.

Compound	% Mn	% NO_3	Formulation
Precursor	21.27 (21.89)	48.19 (49.40)	$Mn(NO_3)_2(H_2O)_4$
$Mn(NO_3)_2(H_2O)x$	21.52	48.25	$Mn(NO_3)_2(H_2O)_4$
$Mn(NO_3)_2(H_2O)y$	23.67 (23.57)	52.95 (53.22)	$Mn(NO_3)_2(H_2O)_3$
$Mn(NO_3)_2(H_2O)z$	25.67 (25.55)	57.79 (57.68)	$Mn(NO_3)_2(H_2O)_2$
$Mn(NO_3)_2(H_2O)T_1$	27.16 (27.89)	63.87 (62.96)	$Mn(NO_3)_2(H_2O)$
$Mn(NO_3)_2(H_2O)T_2$	29.89 (30.70)	66.80 (69.30)	$Mn(NO_3)_2(H_2O)0.3$

Table 4.3.a (figures in brackets are the calculated % for that hydrate)

Table 4.3.b

	$^4T_{1g}(G)\leftarrow$	$^4T_{2g}(G)\leftarrow$	$^4A_{1g}(G)+E_g(G)\leftarrow$	$^4T_{2g}(D)\leftarrow$	Nitrate
$[Mn(H_2O)_6]^{2+}$ (197) (a.q.soln)	530.0	432.5	400.6, 395.6sh	357.4	
$Mn(NO_3)_2(H_2O)_4$ (acetone)	-	-	406 -	-	
$Mn(NO_3)_2(H_2O)x$ solid	540(10) vw,br	440(10) vw,br	404m, 398sh	360w.sh	225, 260br, 290-310
$Mn(NO_3)_2(H_2O)T$ solid	500(10) vw,br	424vw	405m	360vw.sh	225, 260br, 270-310
*$[Mn(NO_3)_4]^{2-}$ (45) solid	530sh	450sh	410		

[Ground State is $^6A_{1g}(S)$]

*Footnote: included only becauses it contains bidentate nitrato groups and is the only nitrate manganese(II) compound to have been studied structurally[202].

4.3.6 Infra-red spectra:

The hydrate data is collected in table 4.3.c. The quality of the recorded spectra was influenced by the nature of the samples. The sticky character of many of the compounds prevented the preparation of fine mulls. In addition, the low melting points of the compounds caused difficulties because of the high temperature of the far infra-red beam.

The compounds all show bands due to the presence of co-ordinated water molecules:

(a) two broad bands in the 3200-3600cm^{-1} range due to the asymmetric and symmetric νO-H modes.

(b) bands in the 1620-1680cm^{-1} range due to the δ O-H mode.

(c) broad but weak, unstructured bands in the 500-700cm^{-1} range assigned to the 'rocking' and 'wagging' modes of the co-ordinated water molecules.

(d) envelopes of bands in the 280-320cm^{-1} and 400-500cm^{-1} ranges assigned to the νmetal-OH_2 stretching modes. Nakagawa[169] has observed ν_{Mn-OH_2} at 395cm^{-1} and ρw at 560cm^{-1} in $[Mn(H_2O)_6]^{2+}$.

All of these bands change from broad to sharp bands with a clearer structure as water is progressively removed from the compounds. This is shown by the bands at 1620-1680cm^{-1} which change from two overlapping bands in the tetra-aquo compound to a single band at 1635cm^{-1} in the mono-aquo compound. It is more marked in the lower range where the water bands change from strong broad bands to weak bands at the same position, whilst the adjacent νmetal-O(nitrate) bands at 200-250cm^{-1} remain unchanged.

The bands due to the co-ordinated nitrato group are found in their usual positions together with the usual overtone and combination modes.

Although the anhydrous nitrato compound was not obtained, the trend in the far infra-red spectrum shows that the metal-oxygen stretching frequencies are found in the 200-230cm^{-1} range, in agreement with Ferraro and Walker[186] who report bands at 231, 199sh, 138ms, 96wsh, in the anhydrous compound. There is very little other data published with which to make a comparison, Nuttall[170] reports bands in the 253-258cm^{-1} range and $Mn^{II}O$ has a band at 250cm^{-1}[198].

It is to be expected that the lower hydrates are polymeric. Again, perhaps, comparison can be made with analogous chlorides. α-$Mn(H_2O)_4Cl_2$[199] has been shown to be monomeric, with CIS-chloro ligands, which is structurally similar to $Ni(NO_3)_2(H_2O)_4$[18]. The diaquo compound[200] is polymeric with chlorobridges and trans-water molecules similar to $Ni(NO_3)_2(H_2O)_2$[124]. There is a similar shortening of the manganese-water bond, from 2.215Å to 2.150Å on passing from the tetra-aquo to the diaquo compound. As more water is removed from the molecule the co-ordination sphere around the manganese atom is occupied more fully by the remaining ligands. Hence, one would expect the anhydrous dinitrato manganese(II) to be polymeric. It is not volatile, perhaps indicating a complex polymeric solid state structure.

Table 4.3.c

Precursor	$Mn(NO_3)_2(H_2O)_4$ 'x'	$Mn(NO_3)_2(H_2O)_2$ 'z'	$Mn(NO_3)_2(H_2O)^1_{T_1}$	$Mn(NO_3)_2(H_2O)^{9.3}_{T_2}$	CCl_4 extract	Assignment
215(10) 230(10) br 270w	215(10) 230(10) br 270w	210-215split m 230(5)w 260-265m	205) 230) s.br 255)	225(5)sh 240m) 250(5)m) 285sh	208) 235) s.br 245)	Mn-Onitrate stretching and bending mode
285sh) 295sh)	285sh) 295sh)	285w 300w)	280sh.m 305sh			
320(15)br)	320(15)brs)	310w)	325br.w	330m) 345)	315-345br	
350m.sh 430) 445) brs 465sh)	350m.sh 430) 445) brs 465sh)	375-400sh. 425-435sh 455(20)brvw	395(10)w 430(10)w	385sh) 400-405m)	375-445vbrw 470-510vbrw	Mn-OH_2 stretching modes
		525(10)brvw 580vvw	507(5)) 525(10)) w			Mn-OH_2 wagging
600(100)vbr			630(20)vw			Mn-OH_2 rocking
750	740sm	750sm	740m	755sm	760ss	δ nitrate(a)
820) 840) brm	815mm	815sm	805sm	805sm	810ss	δ nitrate(b)
1050(10)ms	1040(10)mm	1030wsh 1055ss	1025sm	1025sm	1030ms	ν nitrate(c)
1265brm 1310sh	(1310)	1305brs	1310brs			ν nitrate(d)
1410(25)	1470(10)brs	1475(20)	1455(15)brm	1470(20)brm		ν nitrate(e)
1490sh	1550(10)sh	1550sh		1560mm	1560brs	ν nitrate(f)
1630-1680	1620mm 1660mm	1635)) 1640)) brm 1670)	1635	1640mm	1605sh 1640mm	δ O-H water
1760brm	1705sh 1770sw	1785sm	1785mw	1730mw 1780mw	1730sh 1775mw	combination (a) + (c)
			1815mw	1820mw	1820mw	combination (b)+(c)
2070(10)brw	2080mw	2050brvw	2030			overtone 2 x (c)
2205 2290mw	2350mm	2350mw	2330w	2300brw	2290mvw	combination (d) + (c)
2370mw 2450mw	2500brw			2450	2440mw	combination (e) + (c)
2490shw 3100 | vbrw 3600	3300 | vbrw 3600	3200 | vbrw 3600	3470 | brm 3570	3460vbrm 3540vbrm	3460(50)brs	ν O-Hwater (symmetric) ν O-H water (asymmetric)

Note (i) all values are wavenumbers (cm^{-1})

(ii) figures in brackets are the band half-widths

(iii) letters after the figures indicate (a) bandshape: s = sharp, m = medium, br=broad

(b) band intensity: s = strong, m = medium, w = weak,

sh = shoulder

CONCLUDING DISCUSSION

The series of compounds $[M(H_2O)_6](NO_3)_2$, $[M(NO_3)_2(H_2O)_4]$ $[M(NO_3)_2(H_2O)_2]$, $[M(NO_3)_2]$, where M=Mn(II), Co(II), Ni(II), was successfully prepared, except for the manganese series when the first and last compounds were not obtained. The object of preparing this series was to obtain a related group of compounds in which the NO_3 group varied from ionic to unidentate to bidentate to bridging. This was somewhat thwarted by the discovery that the diaquo compounds contain bridging nitrato groups and not bidentate nitrato groups. This suggests that the bridging modes are more common than has hitherto been supposed, and they deserve some attention. They are present in most of the known copper(II) compounds, probably all of the non-volatile anhydrous metal nitrates and possibly in the solid-state of some of the volatile anhydrous metal nitrates.

From the preparative aspect the solvent, liquid N_2O_5, was found to be a very effective dehydrating and nitrating agent. It is free of the problem of adduct formation, except in a very few cases, but which is more frequently found with liquid N_2O_4. The method of using hydrated compounds as precursors has the advantage of not requiring organic solvents, which tend to co-ordinate strongly to the metal, and the hydrates contain easily substituted water molecules. However, it is difficult to use this solvent with easily oxidised species because it is a powerful oxidising medium.

Ferraro's splitting criterion is not easily applied to our spectra. As pointed out in section 2.2.2 this criterion is strictly only applicable to unidentate nitrato compounds. Also the polarising power of the three metals is closely similar $\left[\frac{\text{charge}}{\text{ionic radius}} = 2.56(Ni^{II}),\ 2.44(Co^{II}),\ 2.20(Mn^{II})\right]$

and little differences should be expected in the spectra. For the tetra-aquo compounds, with unidentate nitrato groups, little difference is observed between them, even though the polarising power of the manganese(II) ion is less than that of the other two. In fact there is little difference between the band positions in any of the aquo compounds, thus emphasising the problem of using this region of the infra-red for structural analysis. As for the high-frequency band criterion for bridging modes, no such bands are found in the cobalt compounds, only the anhydrous nickel compound has a band above 1500cm^{-1}, and all of the manganese compounds show bands at about 1550cm^{-1}. If the frequency of the bands is a criterion of the distorting effect of the metal ion then it is surprising that the least polarising of the three metals should give the highest frequencies.

The far infra-red region is more informative. Here the order of the metal-water and metal-nitrato bands is the expected one: Ni≈Co>Mn. Also, as water molecules are removed from the compounds the spectra become more simple, indicating a more symmetric environment for the central metal atom. Toppings'[88] criterion of two stretching frequencies is probably justified, but it is difficult to assign them unambiguously. Also, the symmetry about the central metal atom has to be considered, as well as the actual structure of the nitrato group. Since it is considered that none of our compounds contain bidentate nitrato groups to a single metal atom, this cannot be discussed further. Nuttall[170-172] et al feel that for bidentate nitrato compounds Toppings criterion is correct.

There are the additional features of band splitting and band overlap. Since the anhydrous compounds are probably polymeric there will be a modification of the vibrations of the NO_3 bridging units. The far infra-red range does, however, provide a great deal of information about the nature of the metal-ligand interaction. The strength of the metal-oxygen bond seems to be remarkably constant for a given metal, as indicated by the position of the main metal-oxygen bands. There is undoubtedly a mechanism for decreasing any bond-angle strain so that a stable bonding interaction is

maintained. This is probably one of the driving forces behind the change to bridging ligand character on dehydration rather than to the strained bidentate ligand with a small bond angle ($\approx 105^{\circ}$-115° instead of 120°) and a short co-ordinating "bite".

The above discussion is strictly relevant only to metal-oxygen systems and it is doubtful if it can be applied to systems where other types of ligand are present, unless it is possible to distinguish clearly between the metal-ligand and metal-oxygen bands. Organic ligands are difficult to distinguish because of the large number of weak modes observed in the far infra-red in addition to the metal-ligand modes. Probably the only true method is to examine isotopically substituted compounds.

The infra-red region cannot be used in isolation. Magnetic, electronic and Raman spectral data must be used in conjunction in order to determine the molecular structure of nitrato compounds. The small amount of Raman literature already available indicates that it has much to contribute to this subject.

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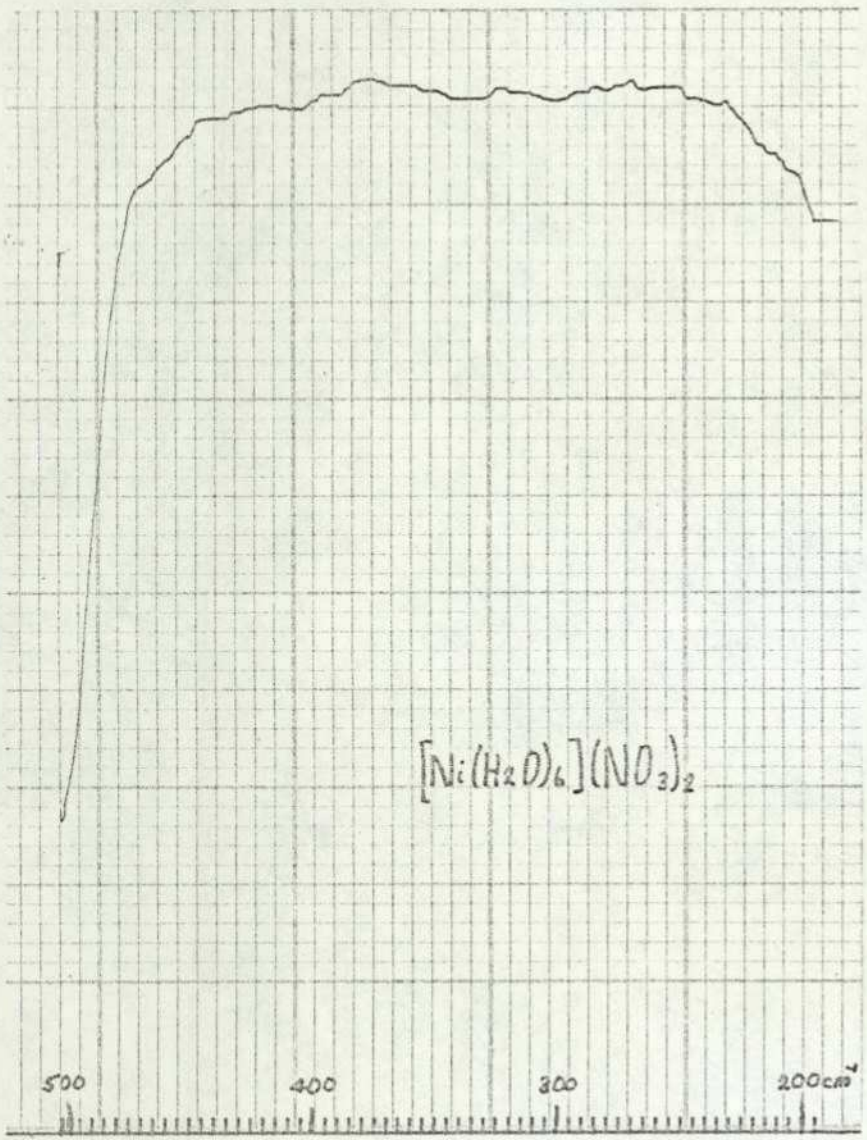
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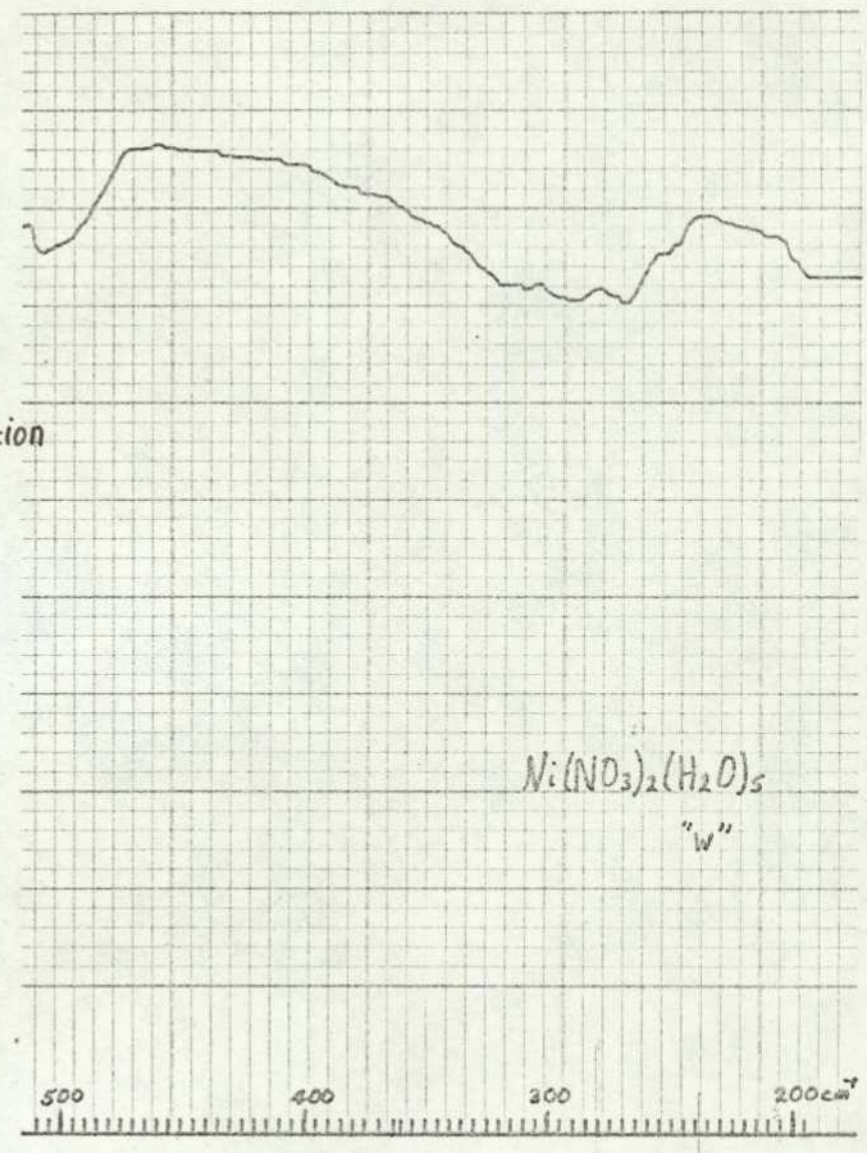
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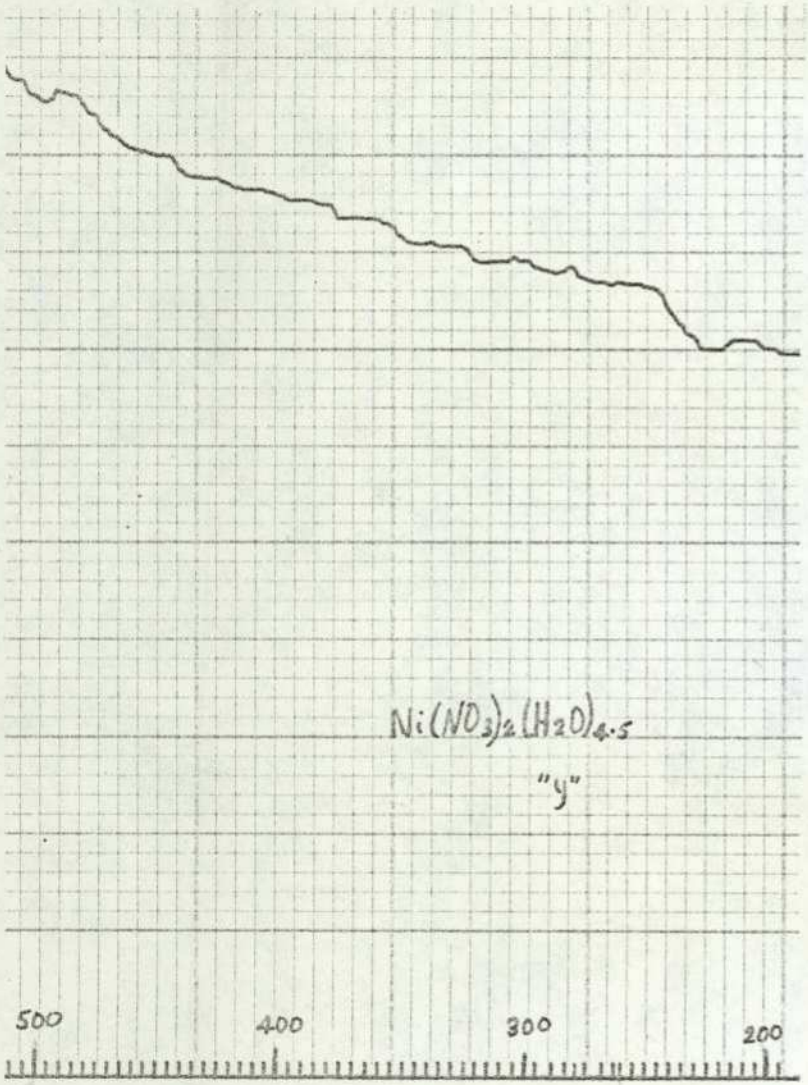
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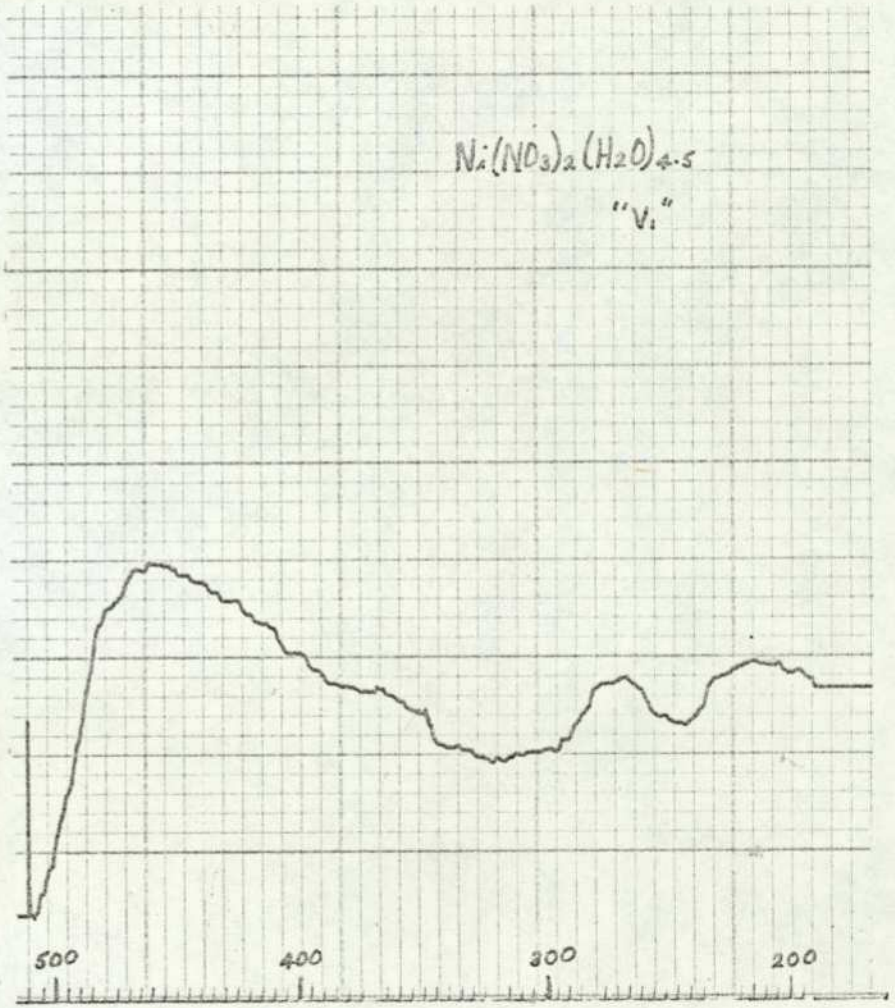
APPENDIX: INFRA-RED SPECTRA

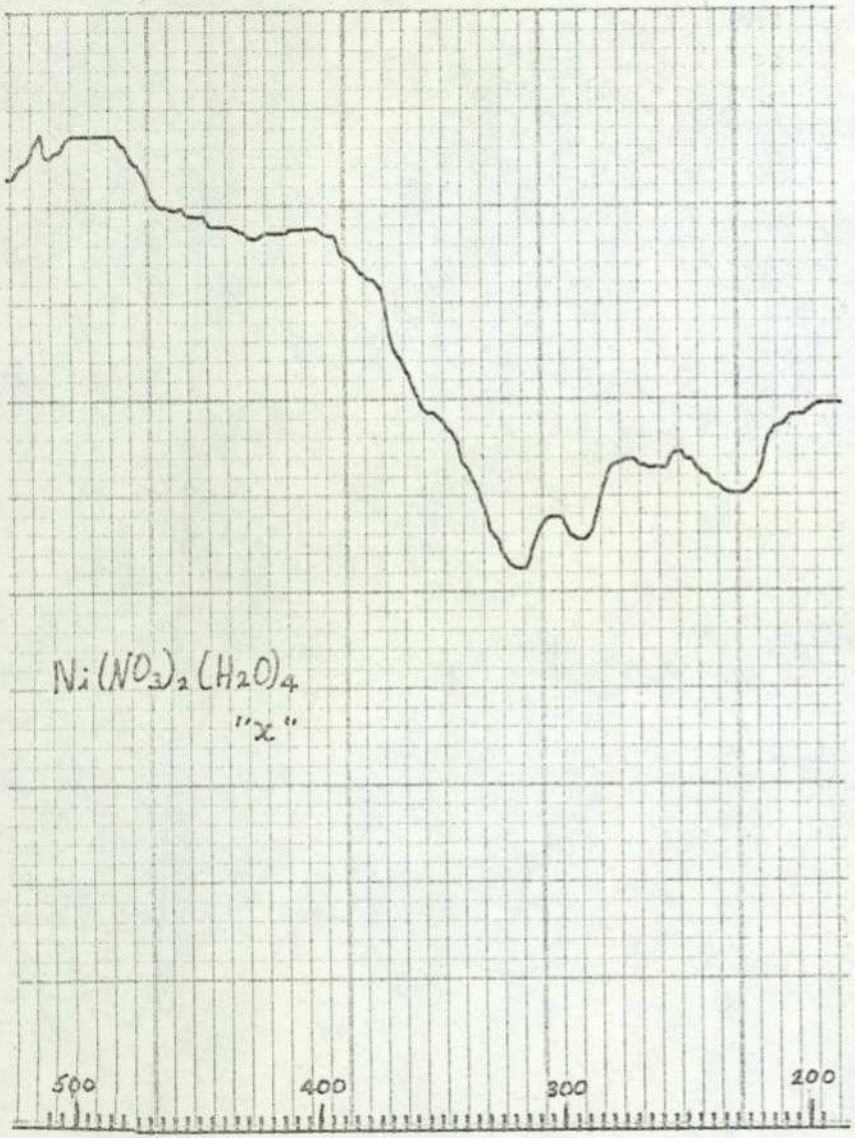

[Ni(H2O)6](NO3)2
500
400
300
200cm-1

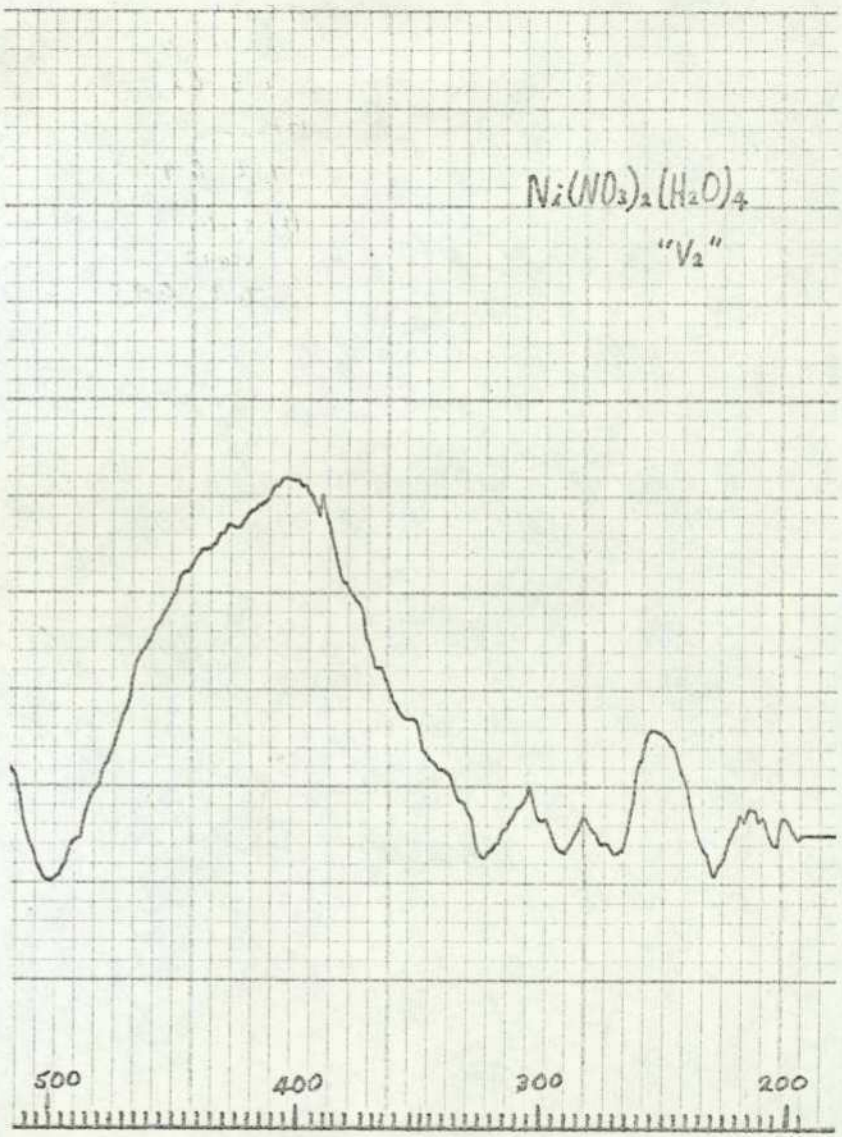
Absorption

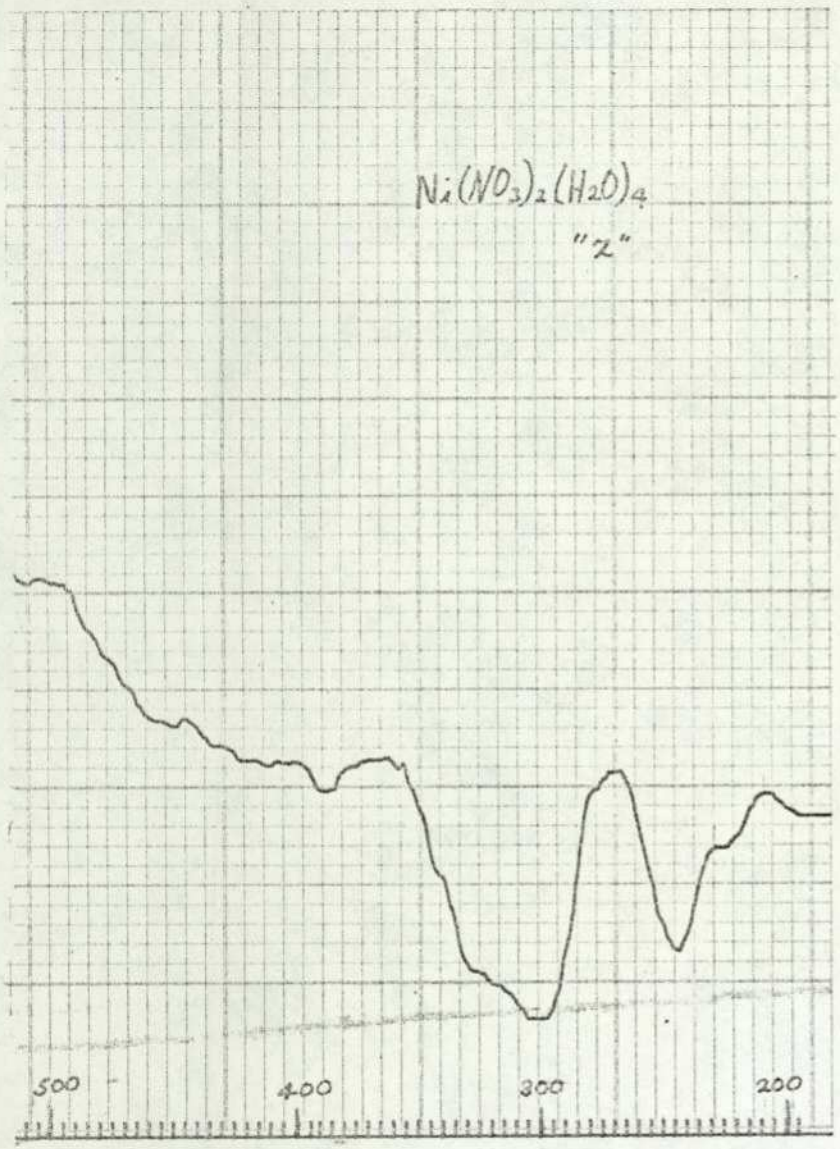

Ni(NO3)2(H2O)5
"W"
500
400
300
200cm-1

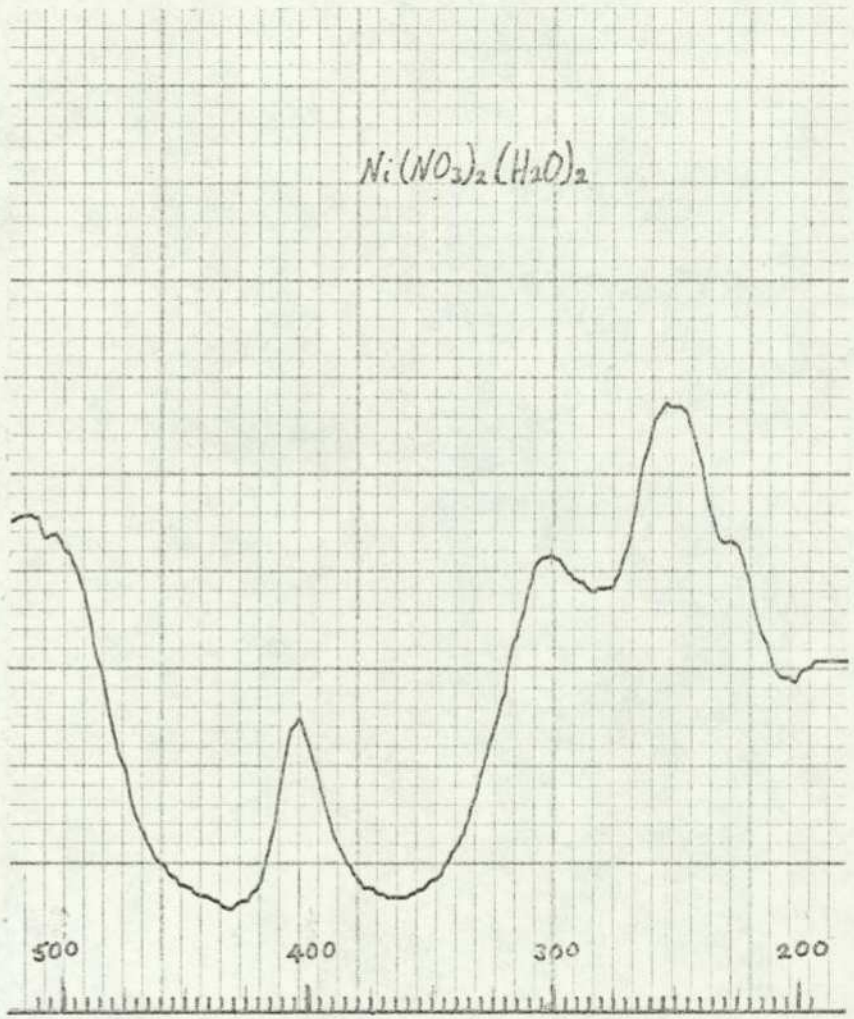

Ni(NO3)2(H2O)4.5
"y"
500
400
300
200

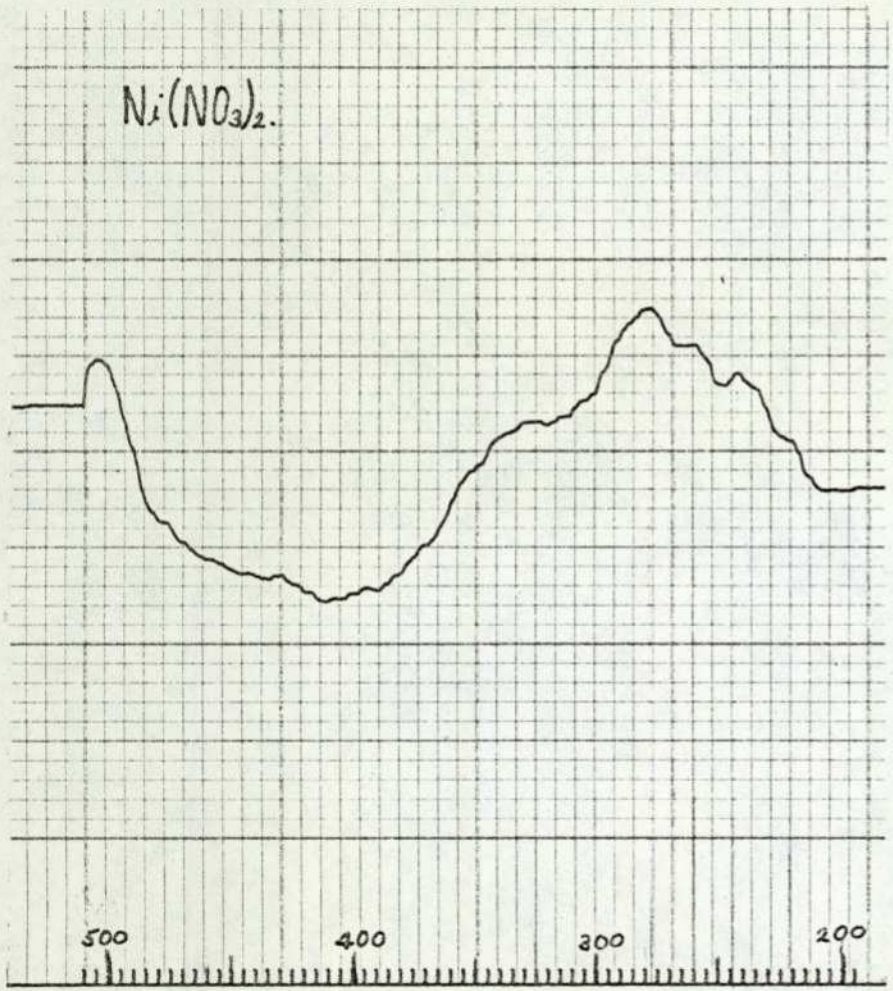

Ni(NO3)2(H2O)4.5
"v1"
500
400
300
200

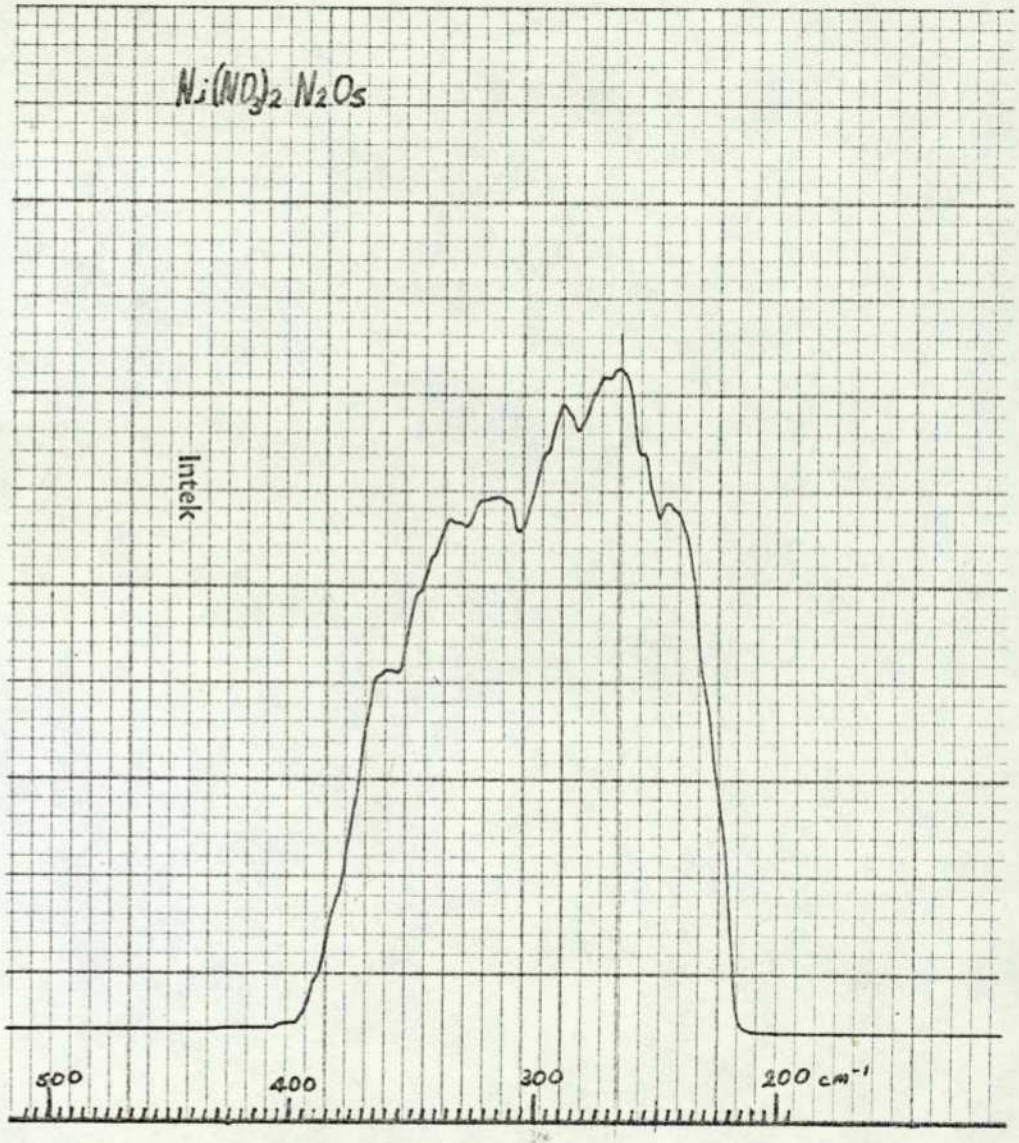

$Ni(NO_3)_2(H_2O)_4$
"x"
500
400
300
200

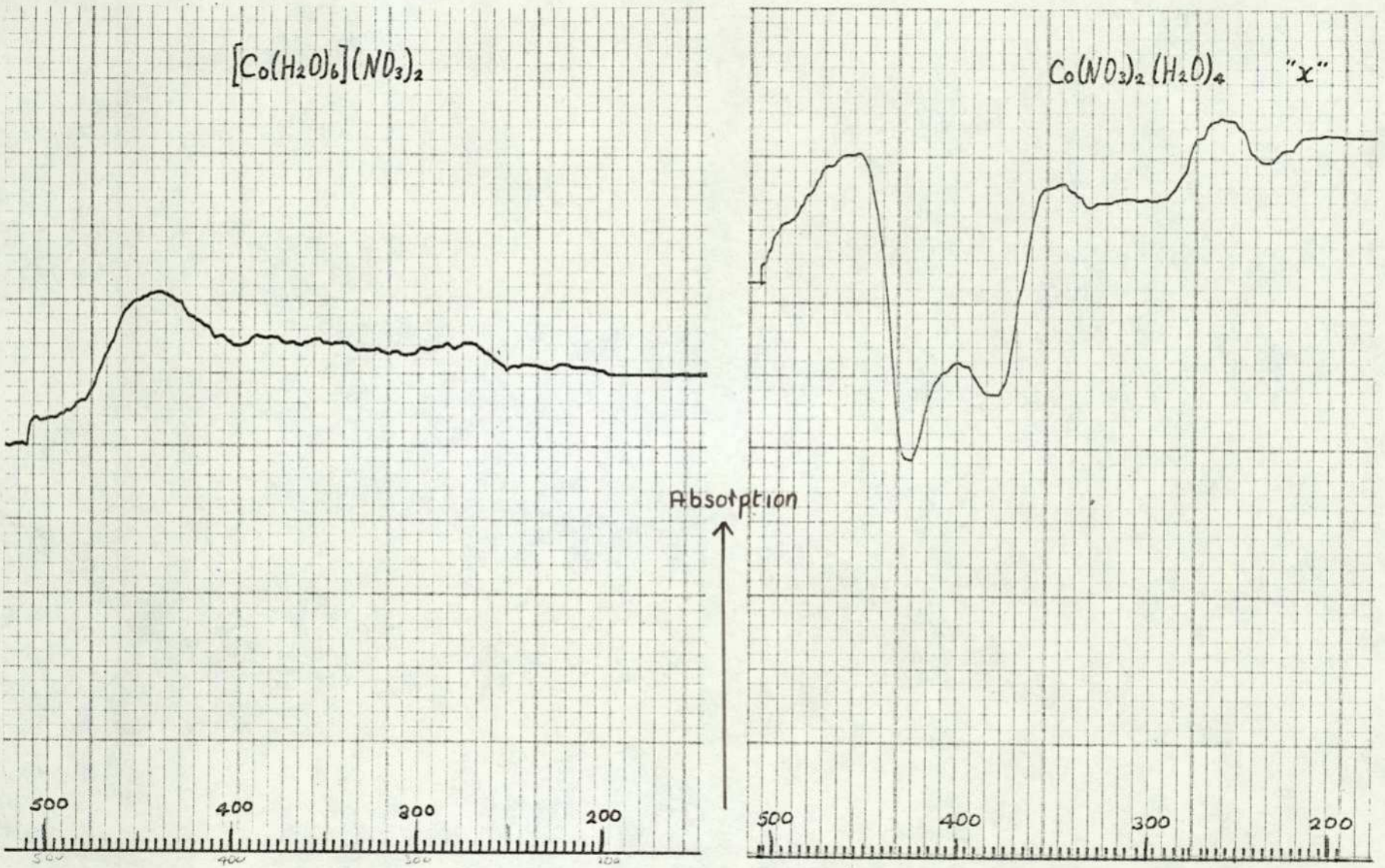

$Ni(NO_3)_2(H_2O)_4$
"V_2"
500
400
300
200

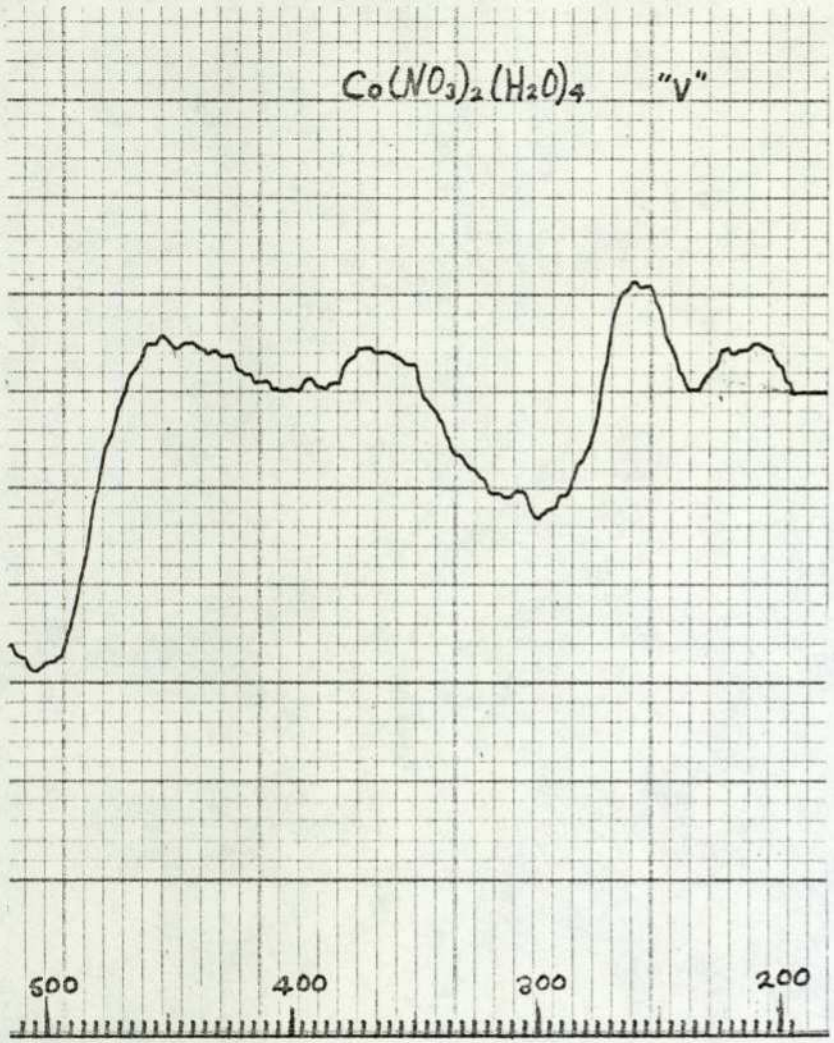

$Ni(NO_3)_2(H_2O)_4$
"2"
500
400
300
200

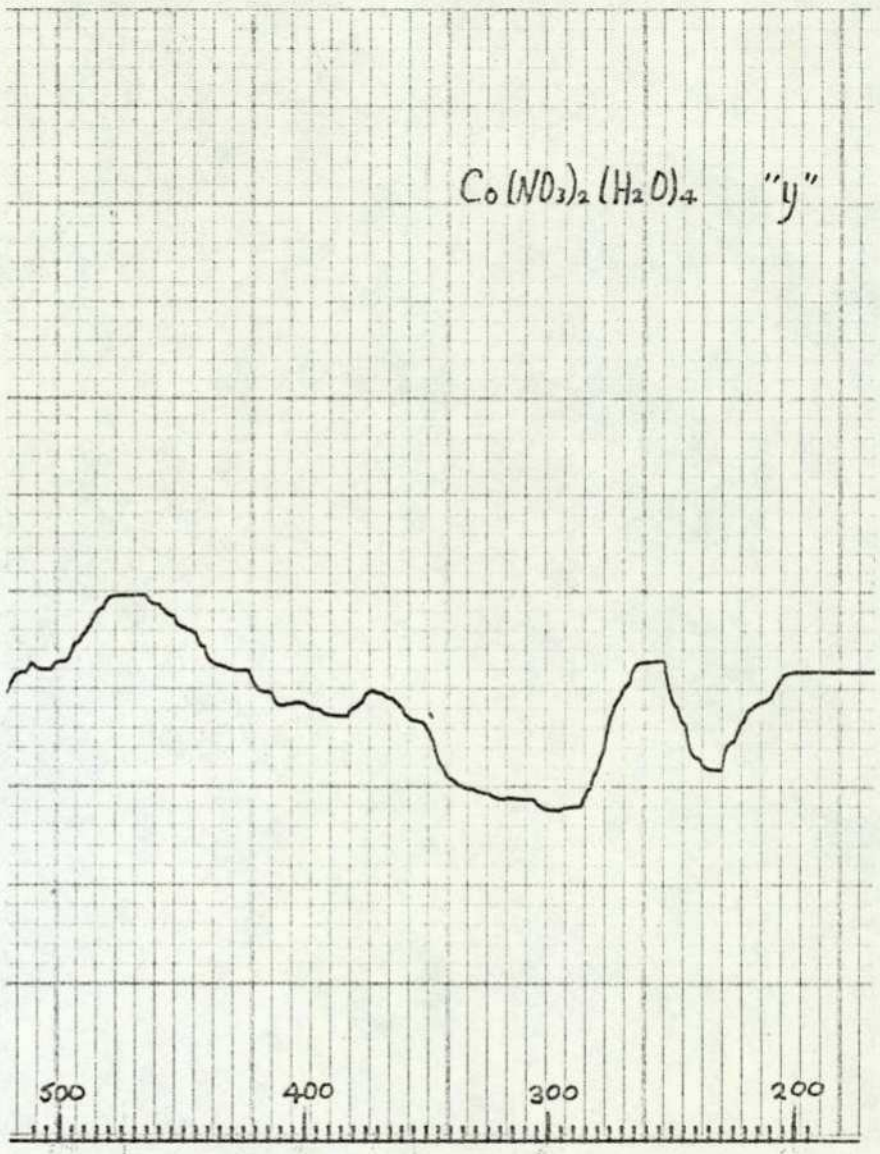

$Ni(NO_3)_2(H_2O)_2$
500
400
300
200

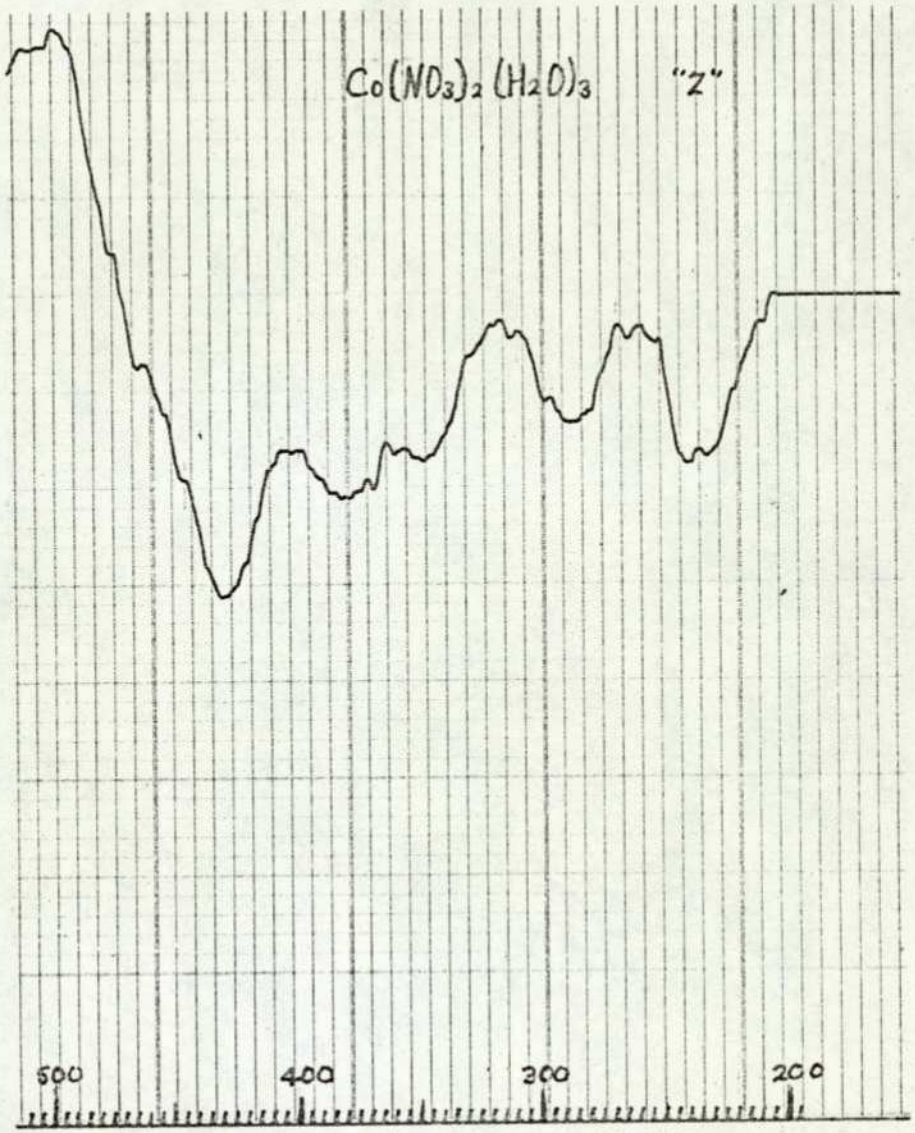

$Ni(NO_3)_2$.
500
400
300
200

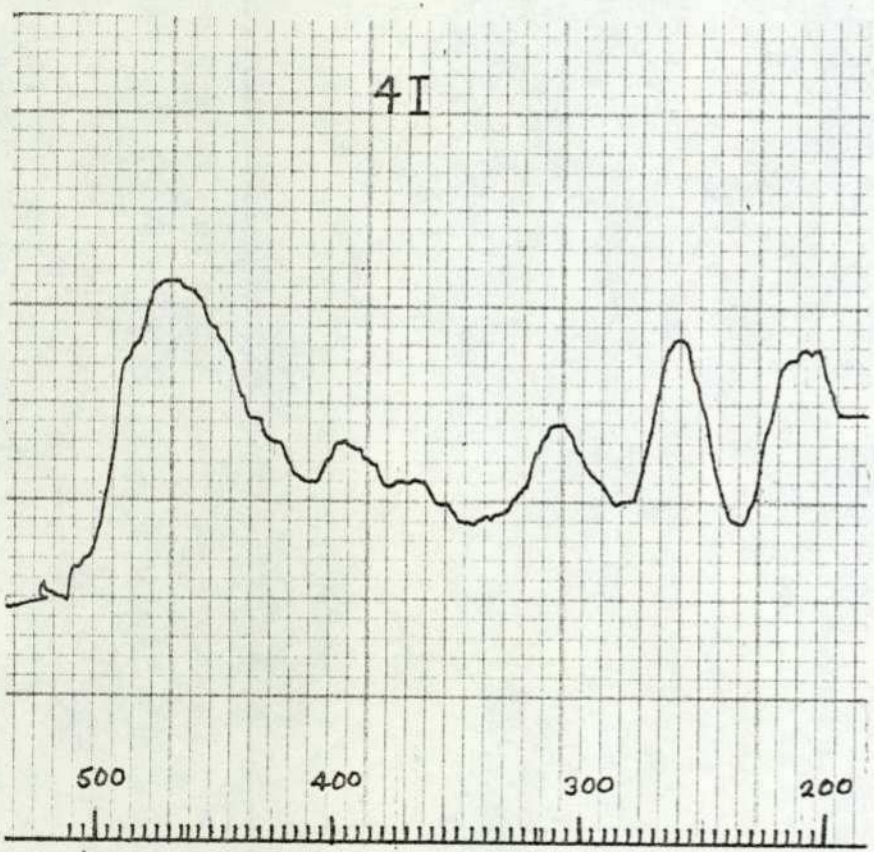

$Ni(NO_3)_2\ N_2O_5$
Intek
500
400
300
200 cm⁻¹

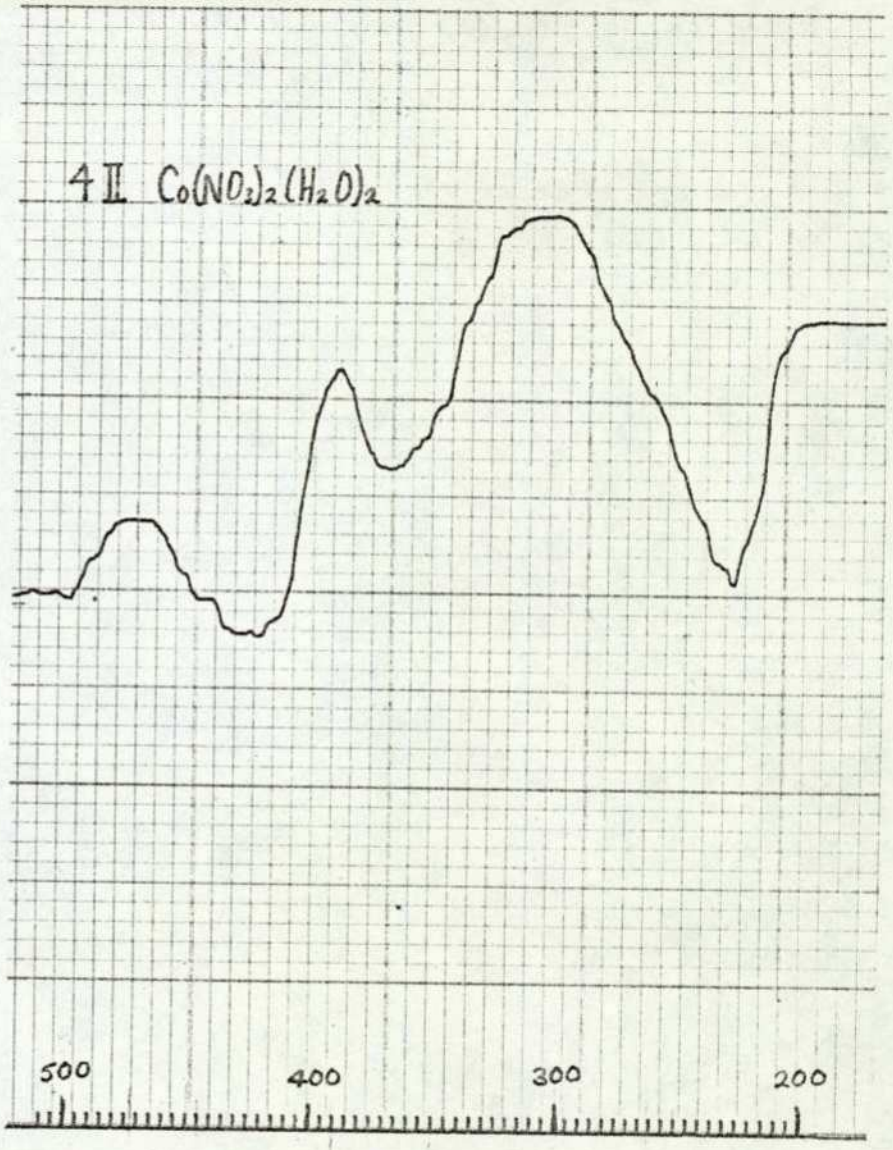

$[Co(H_2O)_6](NO_3)_2$
$Co(NO_3)_2(H_2O)_4$ "x"
Absorption
500
400
300
200
500
400
300
200

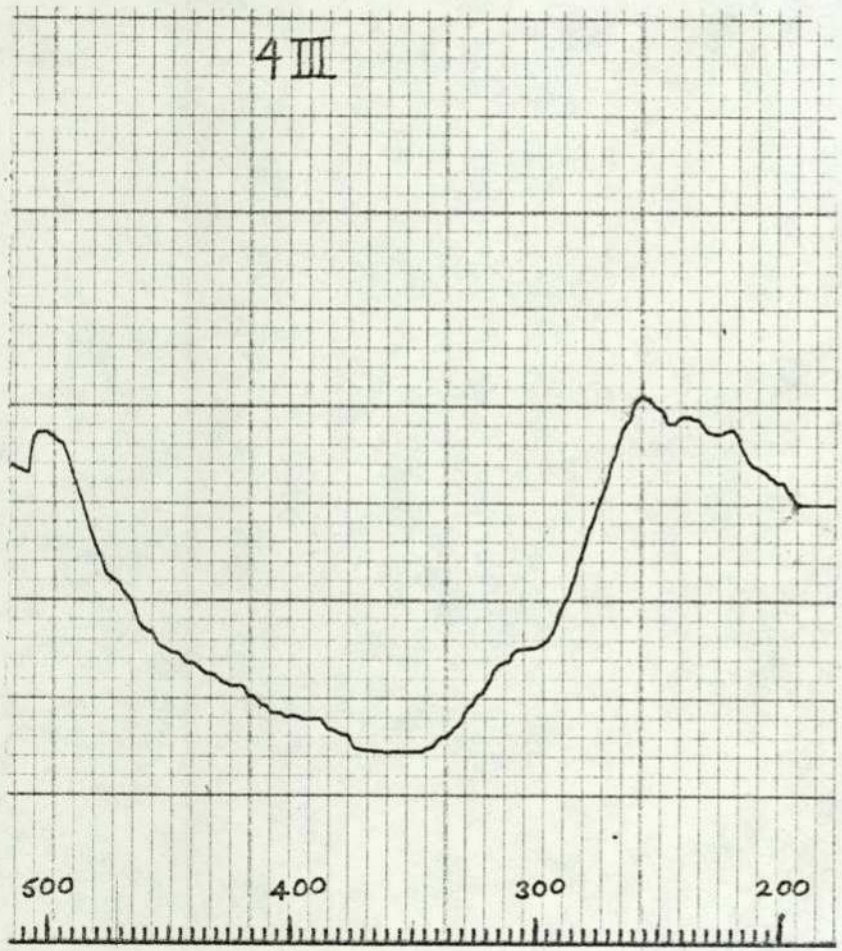

$Co(NO_3)_2(H_2O)_4$ "V"
500
400
300
200

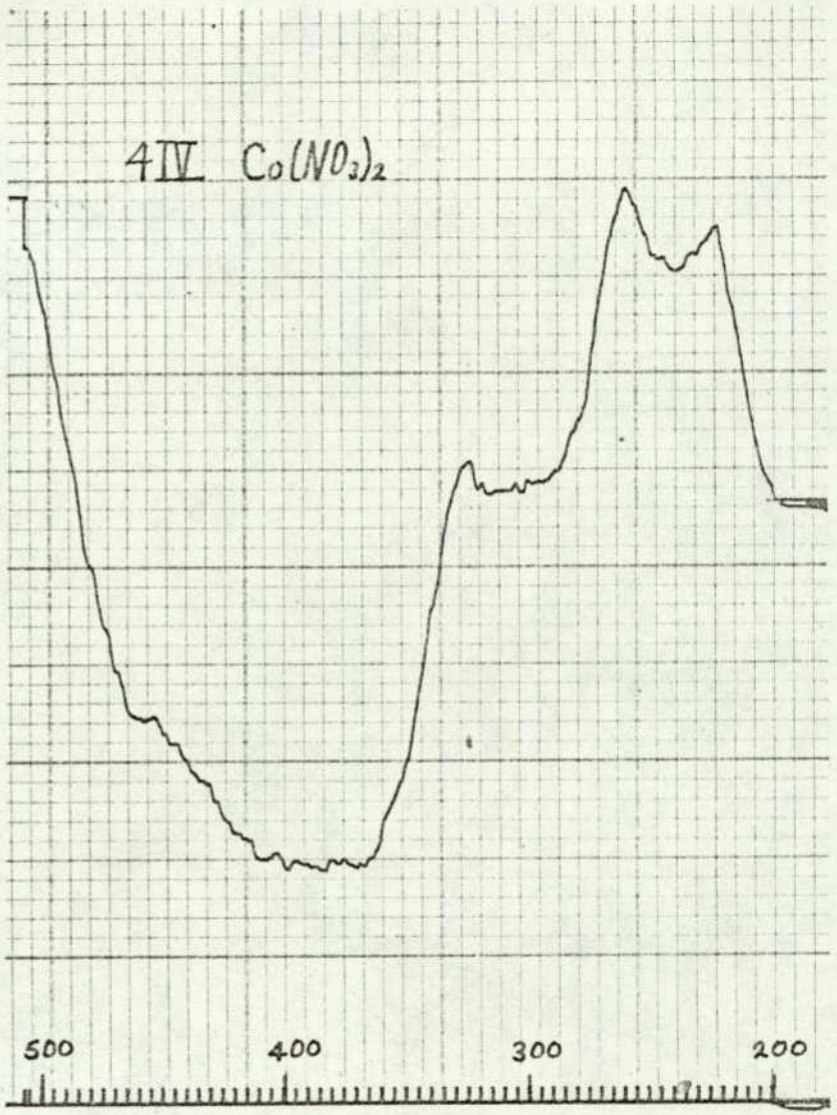

$Co(NO_3)_2(H_2O)_4$ "y"
500
400
300
200

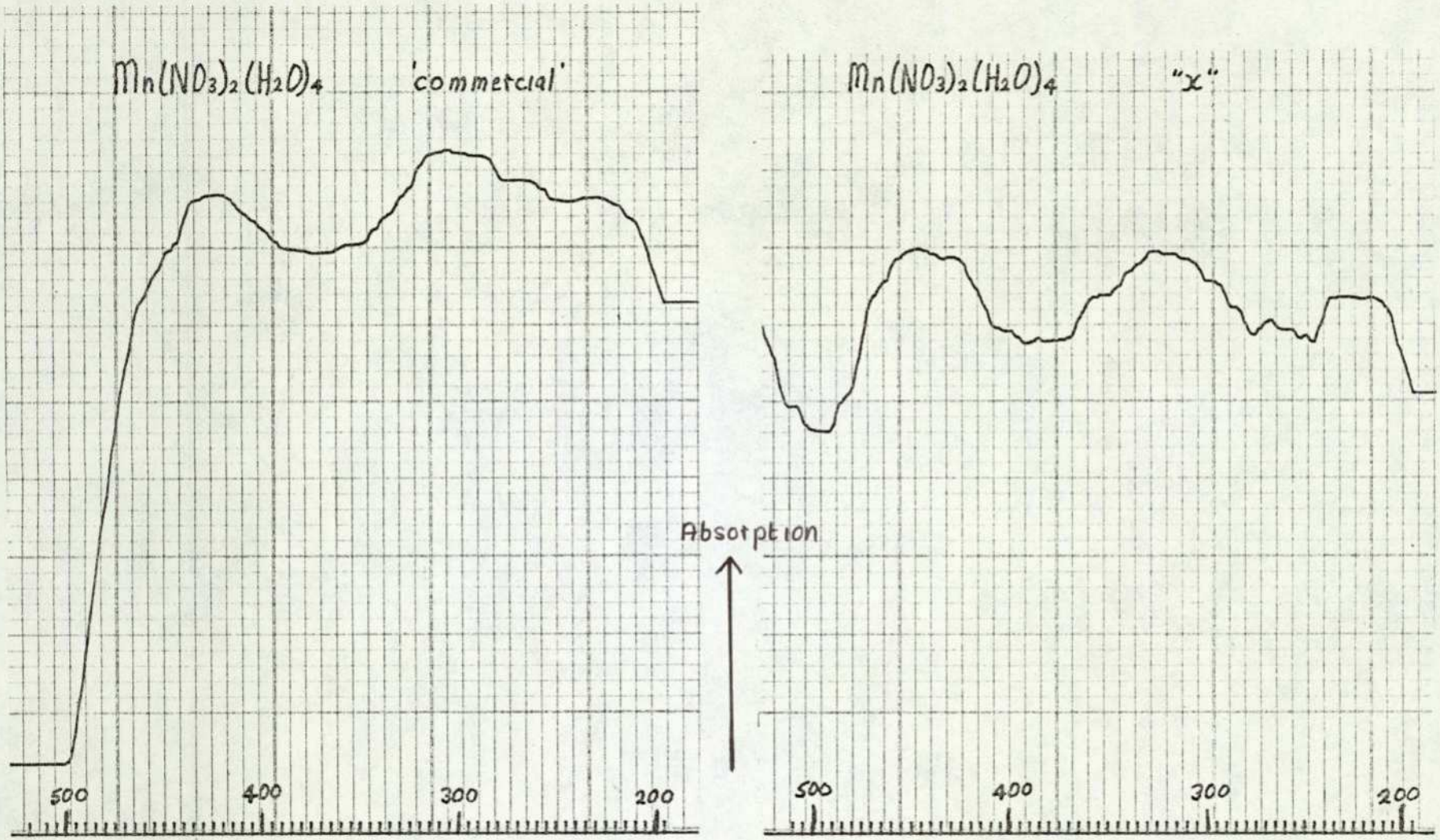

$Co(NO_3)_2(H_2O)_3$ "Z"
500
400
300
200

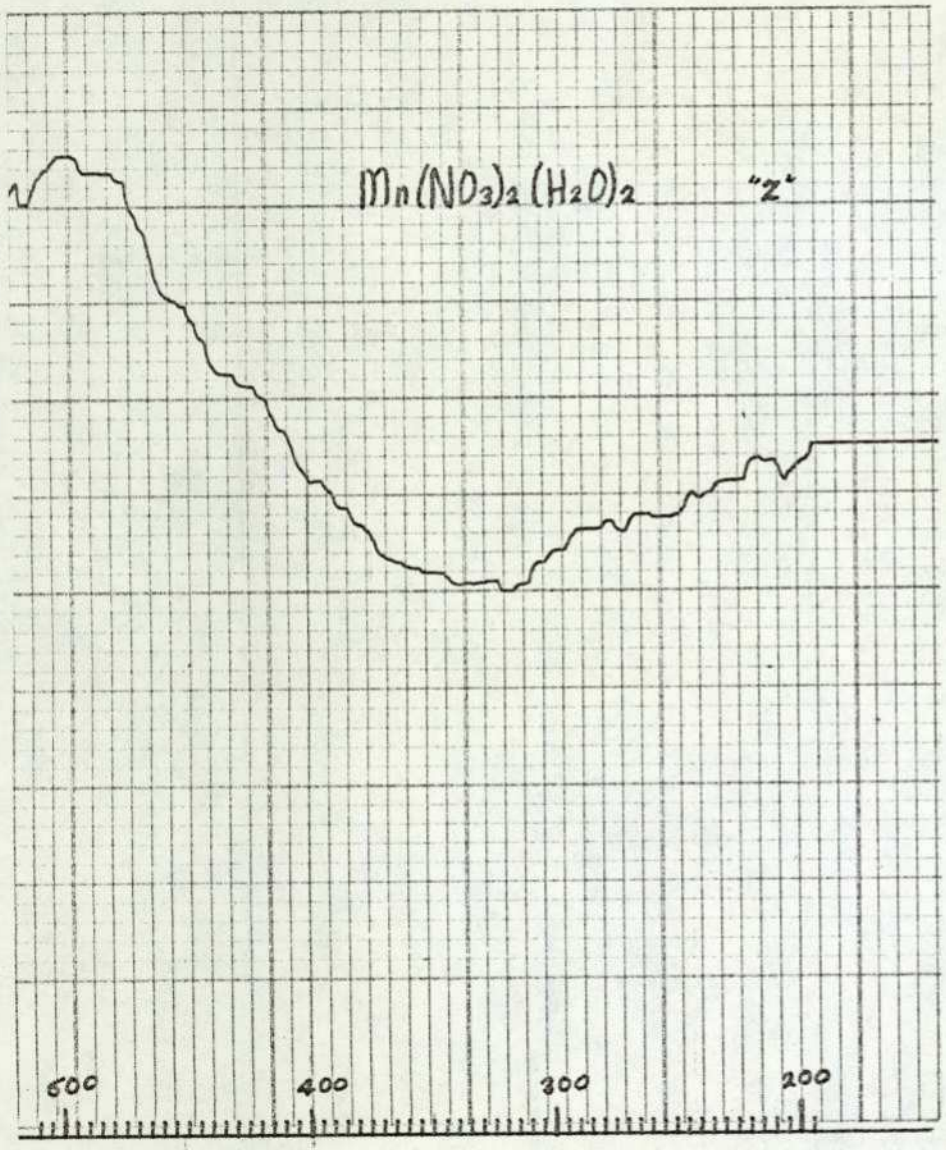

4I
500
400
300
200

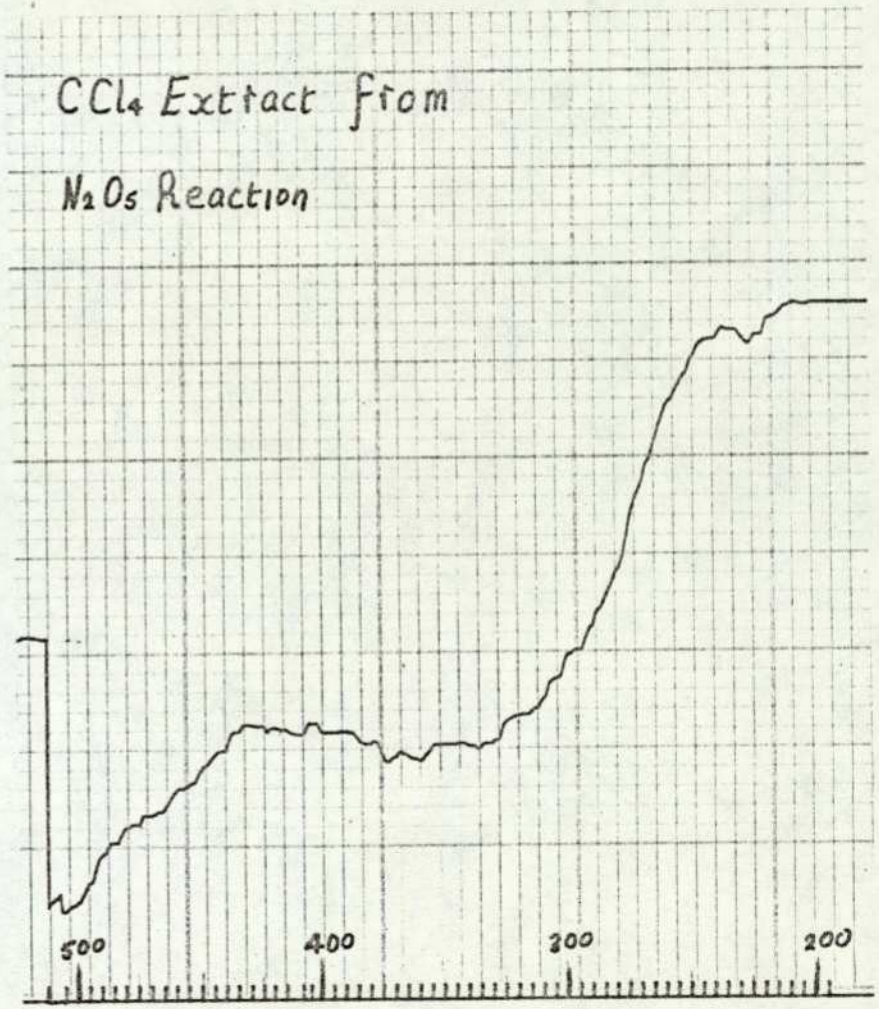

4II $Co(NO_3)_2(H_2O)_2$
500
400
300
200

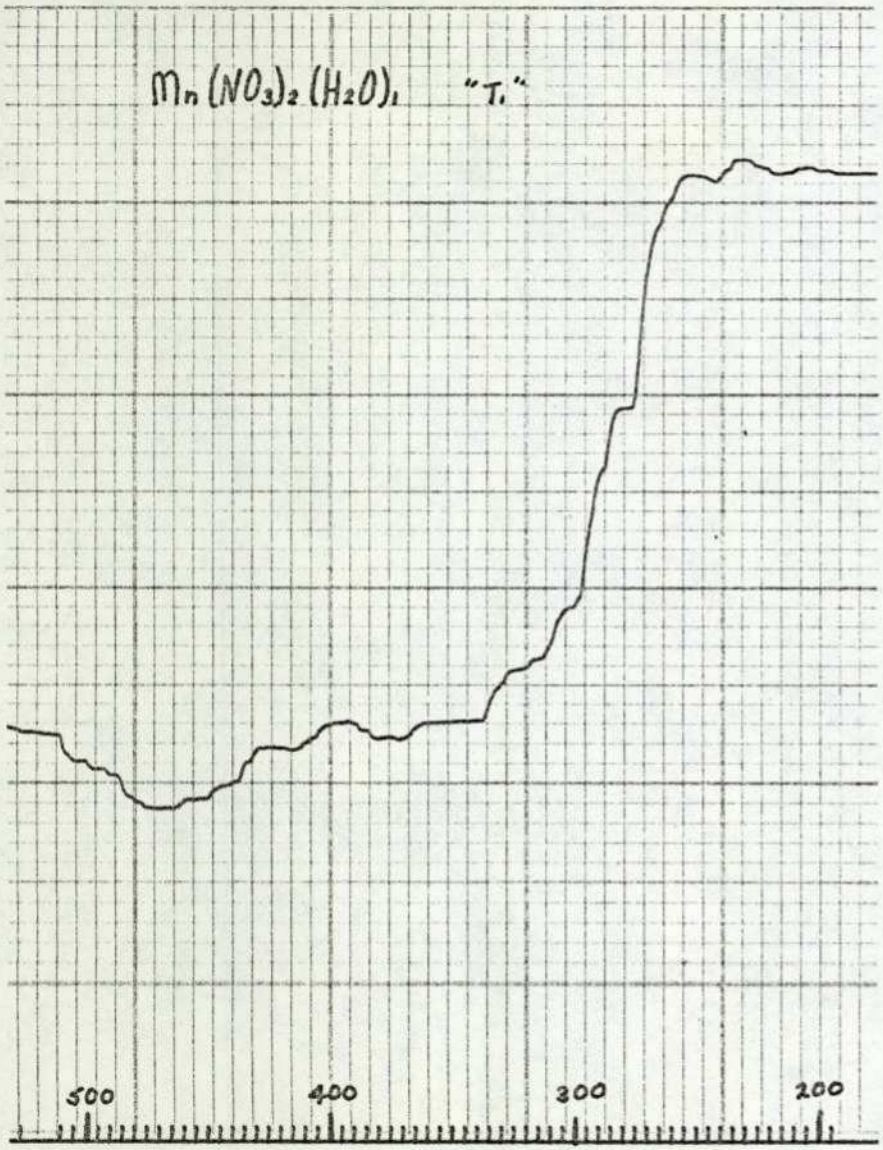

4 III
500
400
300
200

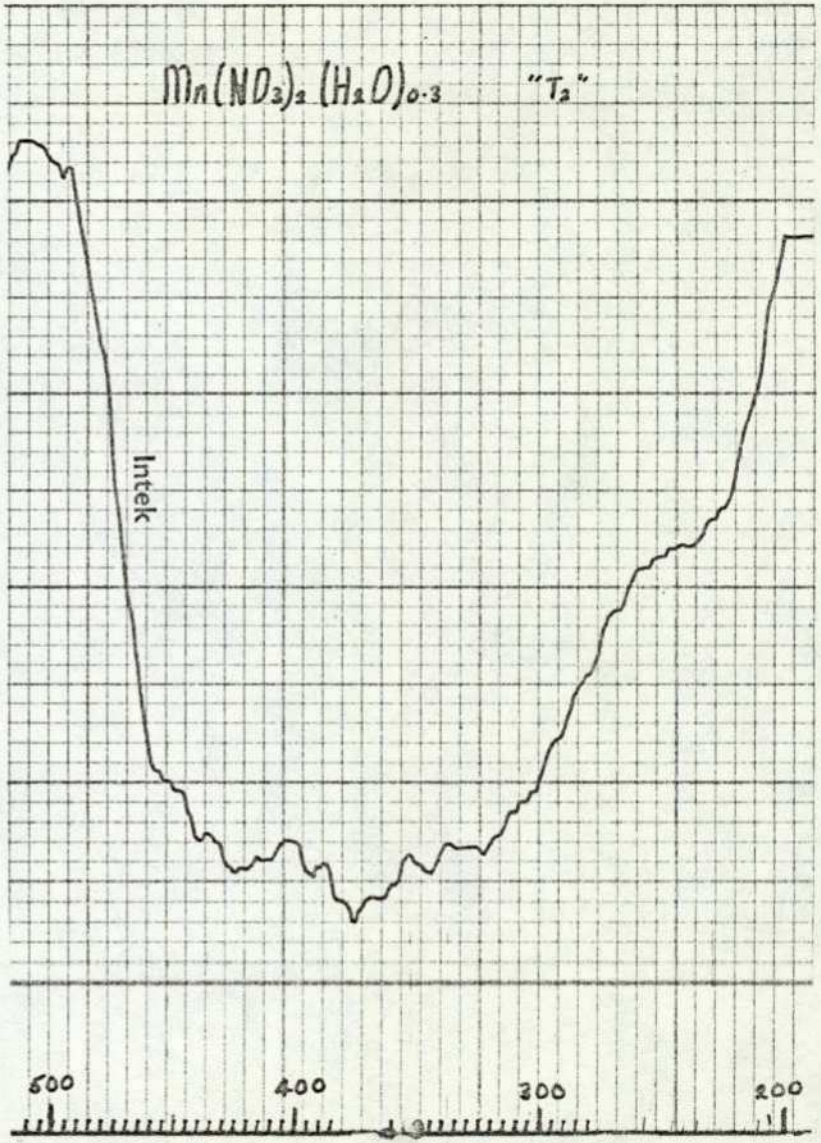

4 IV Co(NO3)2
500
400
300
200


$Mn(NO_3)_2(H_2O)_4$ 'commetcial'
$Mn(NO_3)_2(H_2O)_4$ "x"
Absorption
500
400
300
200
500
400
300
200


$Mn(NO_3)_2(H_2O)_2$ "Z"
500
400
300
200


CCl_4 Extract From
N_2O_5 Reaction
500
400
300
200


$Mn(NO_3)_2(H_2O)_1$ "T_1"
500
400
300
200


$Mn(NO_3)_2(H_2O)_{0.3}$ "T_2"
Intek
500
400
300
200