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INFRARED SPECTRA AND BONDING IN METAL–NITROSYL COMPLEXES

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Infrared spectra have been widely used to obtain information concerning metal to ligand *dπ–pπ* bonding in metal complexes with the ligands CO, NO and CN^-, though most of this information has come from the examination of only the ligand vibrations[1]. This work was undertaken with the aim of studying the low frequency vibrations in various nitric oxide complexes, vibrations which may reflect more directly the state of the metal–ligand bonding.

The complexes studied were all of the form $[M(NO)L_5]^{n\pm}$. This complex ion belongs to the point group C_{4v}, the M–N bond being coincident with the $C_4(z)$ axis. A molecular orbital energy level scheme has been proposed[2] for this kind of ion. The M–N–O bonding may be described in valence bond terms as a resonance hybrid of the three forms

$$\begin{array}{ccccc} \mathrm{M-N{\equiv}O} & \leftrightarrow & \mathrm{M{=}N{=}O} & \leftrightarrow & \mathrm{M{\equiv}N-O} \\ \mathrm{(I)} & & \mathrm{(II)} & & \mathrm{(III)} \end{array}$$

However, the *M.O.* scheme makes it clear that form (II) has no physical significance in a linear M–N–O framework because of the degeneracy of the π^* acceptor orbitals.

The thirty-three normal modes of vibration of the ion $[M(NO)(XY)_5]^{n\pm}$ span the representations $8A_1+A_2+4B_1+2B_2+3E$ of which only the A_1 and E species are infrared active. The "group" vibrations are as follows:

N–O stretch	ν(N–O)	A_1
M–N stretch	ν(M–N)	A_1
X–Y stretch	ν(X–Y)	$2A_1 \quad +B_1 \quad +E$
M–X stretch	ν(M–X)	$2A_1 \quad +B_1 \quad +E$
M–NO rock	δ(M–NO)	E
M–XY rock	δ(M–XY)	$A_1+A_2+B_1+B_2+3E$
X–M–X(N) deformation	δ(X–M–X)	$A_1 \quad +B_1+B_2+3E$

The eighteen normal modes of vibration of the ions $[M(NO)X_5]^{n\pm}$ are entirely analogous.

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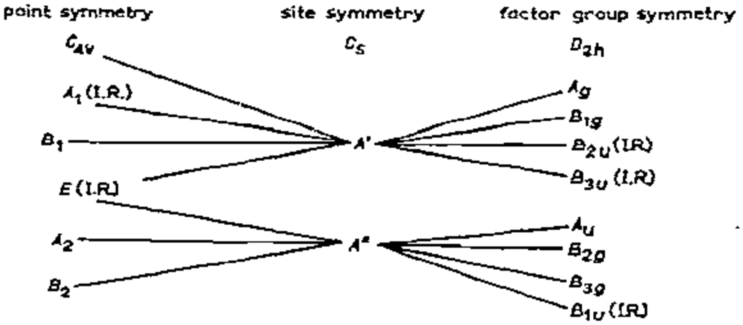
High frequency region (above 1500 cm^{-1})

In the spectrum of $Na_2[Fe(NO)(CN)_5]2H_2O$ seven C–N stretching bands are observed under high resolution conditions[3]. As this number is larger than the number of cyano groups in the complex ion, there must be intermolecular coupling of vibrations between different complex ions. The crystal structure of this compound is known[4], and the correlation table can be drawn up as follows:



This correlation table indicates that 9 C–N stretching bands are expected in the factor group symmetry. The same factor group applies[5] to the compound $K_2[Ru(NO)Cl_5]$ so that the correlation table indicates that the A_1 ν(N–O) mode should split into two ($B_{2u}+B_{3u}$). Two bands were observed at 1900 and 1890 cm^{-1} whereas previously only a single N–O stretching band had been reported[2]. In fact two bands were observed in a large number of complexes of the type $A_2[Ru(NO)X_5]$, single bands being found only for A = (Et_4N), X = Cl, Br. It was also noted that ν(N–O) is considerably (*ca.* 80 cm^{-1}) lower in the tetraethylammonium salts than in the potassium salts.

Clearly the electronic structure of the polar NO group is greatly influenced by the electric field generated by its surroundings. The frequency shifts imply that electrons in the NO group are attracted more towards the oxygen atom in the higher field generated by the K^+ ion. The effect of replacing K^+ by Cs^+ is also to reduce ν(N–O). This may be due to the smaller charge/size ratio of Cs^+ or to a general expansion of the crystal lattice. The ν(M–X) frequencies are also influenced by the cation and this in turn may affect ν(N–O).

Low frequency region

ν(M–X) and δ(X–M–X) in the ruthenium, osmium and iridium pentahalonitrosyl complexes are easily assigned by comparison with other halo-complexes, and also for internal consistency[6]. Three Ru–X stretching bands were found, as expected, in $Cs_2[Ru(NO)I_5]$ and all the bromo-complexes, but only two bands were found in the chloro-complexes. This kind of anomalous intensity behaviour has been observed in other complexes[7] (*e.g.* $[ReCl_6]^{2-}$) and it makes the process of assignment very difficult. ν(Ru–N) and δ(Ru–NO) are assigned to the two bands found at *ca.* 600 cm^{-1}. In gaseous $Co(NO)(CO)_3$ an ^{15}N substitution experiment led to the firm assignment[8] of these two modes at 565 cm^{-1} and 594 cm^{-1}, these frequencies to be compared with 573 cm^{-1} and 609 cm^{-1} found in $(Et_4N)_2$-$[Ru(NO)Br_5]$. Further evidence in favour of this assignment may be drawn from the solid state effects. For example the intensity relationship of the two bands in $(Et_4N)_2[Ru(NO)Cl_5]$ is the inverse of that found in $K_2[Ru(NO)Cl_5]$. Since ν(N–O) shows no splitting in the tetraethylammonium salt there is a strong implication that the two bands at *ca.* 600 cm^{-1} do not arise by any solid state splitting mechanism, but do represent two fundamental vibrations.

The interpretation of the spectra of the complex ions $[Fe(NO)(CN)_5]^{2-}$, $[Mn(NO)(CN)_5]^{3-}$ and $[Cr(NO)(CN)_5]^{3-}$ in the low frequency region was not attempted in detail due to the difficulty of distinguishing between δ(M–CN) and ν(M–C). It was noted however, that previous assignments[9] for $Na_2[Fe(NO)(CN)_5]$-$2H_2O$ were in error as bands at 515 cm^{-1} and 540 cm^{-1} must be ascribed to water molecule vibrations. The remaining bands between 300 and 500 cm^{-1} were collectively assigned to ν(M–C) and δ(M–CN) since the known frequencies for these vibrations in comparable molecules are usually within these limits. Bands found in the region 600–650 cm^{-1} were thus ascribed to ν(M–N) and δ(M–NO)—a doublet in the nitroprusside ion and a single band in the chromium and manganese complexes. In the latter cases it must be concluded that one band is particularly weak, or that ν(M–N) and δ(M–NO) are accidentally degenerate. Either way it is unlikely that the frequency difference between the two vibrations is greater than 30 cm^{-1} since it is not so in all the other nitrosyl complexes studied.

Conclusions

The value of 500–600 cm^{-1} for ν(M–N) is much higher than the values of ν(M–C) in carbonyl and cyano complexes (339 cm^{-1} in $[Cr(CN)_6]^{3-}$ to 441 cm^{-1} in $Cr(CO)_6$). This result confirms what has long been suspected, namely that nitric oxide is a more powerful π-bonding ligand, though it must be added that there is more opportunity for π-bonding in a mononitrosyl complex: in an octahedral carbonyl the three T_{2g} orbitals are shared equally among six ligands whereas in the nitrosyl the d_{xz}, d_{yz} pair is available for π-bonding to the NO alone.

It is interesting to note that when ν(N–O) is shifted by a solid state effect, there is little or no shift in ν(M–N) and δ(M–NO). This would imply that the solid state shifts (and perhaps solvent shifts[10]) arise mainly from differences in the N–O σ-bonding. Also, although there is a difference of over 150 cm^{-1} in ν(N–O) between $[Cr, Mn(NO)(CN)_5]^{3-}$ and $[Fe(NO)(CN)_5]^{2-}$ there is not much difference in the metal–ligand frequencies and again this can be taken to imply that ν(N–O) is more influenced by the effects of σ-bonding than of π-bonding. The dis-

TABLE I

SOME INFRARED FREQUENCIES IN NITROSYL COMPLEXES

Complexes	*ν(N–O) stretch*	*ν(M–N) stretch* *δ(M–NO) rock*	*ν(M–X) stretch*	*Deformation*	*Lattice vibrations*
$K_2[Ru(NO)Cl_5]$	1912 (9)** 1897 (10)	604 (1) 587 (3)	337 (10) 284 (4)	190 (4) 181 (4)	94 (9)
$Cs_2[Ru(NO)Cl_5]$	1873 (10) 1863 (10)	599 (1)* 589 (3)	322 (10) 279 (2)	178 (2)	<70
$[(C_2H_5)_4N]_2[Ru(NO)Cl_5]$	1830 (10)	613 (4) 588 (3)	315 (10) 281 (3)	168 (2)	<70
$K_2[Ru(NO)Br_5]$	1880 (10) 1865 (10)	605 (1) 573 (4)	257 (10) 221 (4) 185 (2) 181 (2)	128 (1)	81 (7)
$[(C_2H_5)_4N]_2[Ru(NO)Br_5]$	1832 (10)	609 (3) 573 (4)	245 (10) 222 (4) 178 (2)	123 (3)	70
$K_2[Ru(NO)I_5]$	1840 (10)	598 (1) 573 (1) 552 (3)	214 (8) 172 (3)	( )	105 (10)
$K_2[Os(NO)Cl_5]$	1865 (10) 1855 (10)	617 (1) 593 (3)	320 (10) 294 (3)	196 (3) 173 (3)	
$K_2[Ir(NO)Br_5]$	1974 (8) 1951 (10)	552 (3) 534 (1)	236 (5) 225 (5)		
$Na_2[Fe(NO)(CN)_5]2H_2O$	1935 (10)	658 (5) 647 (3)			
$[(CH_3)_4N][Fe(NO)(CN)_5]$	1908 (10) 1883 (3)	656 (5) 652 (3)			
$K_3[Cr(NO)(CN)_5]$	1638 (10)	616 (3)			
$K_3[Mn(NO)(CN)_5]$	1700 (10)	655 (4)			

* Shoulder.

** Intensity on arbitrary scale increasing from 0–10.

cussion given at the conference concerning the possibility that the results might be rationalised in terms of NO^- rather than NO^+ being the ligand, was based on E.S.R. evidence[11] for the non-linearity of the M–N–O framework in $[Cr(NO)(CN)_5]^{3+}$. The E.S.R. results have since been seriously questioned[12], and hence the NO^- hypothesis is untenable in these compounds.

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