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Infrared Spectra and Bonding in Transition Metal Nitrosyl Complexes

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The infrared spectra of various metal–nitrosyl complexes have been recorded between 80 and 4000 cm^{-1}. The N–O stretching frequency shows large solid-state effects. The metal–nitric oxide vibrations in the complexes $[M(NO)X_5]^{n-}$ (M = Ru, Os, Ir and X = Cl, Br, I) and $[M(NO)(CN)_5]^{n-}$ (M = Cr, Mn, Fe) have been tentatively identified. The theory of metal–nitric oxide bonding is reviewed in the light of the metal–ligand vibrations.

Introduction

Infrared spectra have been widely used[1] to obtain information concerning metal to ligand $d\pi$–$p\pi$ bonding in complexes of the metals with the ligands CO, NO, and CN$^-$, but until far-infrared spectrophotometers became available most of this information has come from the study of only the ligand vibrations. We now report data concerning the low-frequency infrared-active fundamental vibrations in various nitric oxide complexes and reexamine the theory of bonding in the light of the infrared spectra measured in the range 80–4000 cm^{-1}.

Experimental Section

Most compounds were prepared by well-known methods.[2,3] The compound $Ag_2[Fe(NO)(CN)_5]$ was obtained by adding silver nitrate to an aqueous solution of the sodium salt. The other salts of $[Fe(NO)(CN)_5]^{2-}$ were obtained from the silver salt by reaction with the appropriate halide. The spectra were recorded on Perkin-Elmer spectrophotometers: Model 421 (4000–600 cm^{-1}), Model 21 with cesium bromide prism (660–375 cm^{-1}), and Model 301 (400–80 cm^{-1}). Nujol mulls supported on cesium bromide or polythene plates were employed, and in those cases where pressed potassium bromide or polythene disks were also used no differences were noted. Below 600 cm^{-1} reproducibility was *ca.* ±2 cm^{-1} and accuracy was probably ±3 cm^{-1}.

Results

The frequencies of the absorption bands are given in Tables I, II, and III. Some of the spectra obtained are illustrated in Figures 1 and 2. The spectrum of $Na_2[Fe(NO)(CN)_5]\cdot 2H_2O$ agrees with that published by Bor,[4] but not with that of Tosi and Danon.[5]

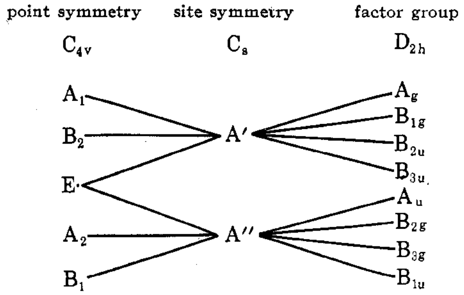
Discussion

All the compounds investigated are octahedral complexes of the form $[M(NO)L_5]^{n\pm}$ where the ligands L are not necessarily identical. The complex ions belong to the point group C_{4v}, the M–N bond being coincident with the C_4 (z) axis. In the molecular orbital treatment σ bonding occurs by combination of the metal s, p_x, p_y, p_z, $d_{x^2-y^2}$, and d_{z^2} orbitals with suitable ligand orbitals such as the N 2s orbital of the nitric oxide. The metal d_{xy} orbital is available for π bonding only in the xy plane and d_{xz},d_{yz} form a degenerate pair which can combine with the doubly degenerate π^* orbitals on nitric oxide, with the π acceptor orbitals of the ligand *trans* to NO and of the ligands along the x and y axes, respectively.[6]

The 33 normal modes of vibration of the ion $[M(NO)(XY)_5]^{n\pm}$ span the representations $8A_1 + A_2 + 4B_1 + 2B_2 + 9E$, of which only the A_1 and E species are infrared active. The "group" vibrations are divided into symmetry species as follows. ν(N–O) (N–O stretch) and ν(M–N) (M–N stretch), A_1; ν(X–Y) (X–Y stretch) and ν(M–X) (M–X stretch), $2A_1 + B_1 + E$; δ(M–NO) (M–NO rock), E; δ(M–XY) (M–XY rock), $A_1 + A_2 + B_1 + B_2 + 3E$; δ(X–M–X(N)) (X–M–X(N) deformation), $A_1 + B_1 + B_2 + 3E$. The 18 normal modes of vibration of the ions $[M(NO)X_5]^{n-}$ are entirely analogous with the exception of the ν(X–Y) and δ(M–XY), which, of course, are absent in these complexes.

High-Frequency Region (above 1500 Cm^{-1}).—The compound $Na_2[Fe(NO)(CN_5)]\cdot 2H_2O$ crystallizes with the space group $D_{2h}{}^{12}$-Pnmn, the complex ions lying on planes of symmetry.[7] The number of vibrations expected of the complex ions in the crystalline state can therefore be calculated by means of the correlations shown in Chart I. The B_{1u}, B_{2u}, and B_{3u} species are infrared active.

CHART I



Thus, eight C–N stretching modes should be active in the crystal. Six well-resolved bands are observed and a seventh is detectable (Figure 1). We therefore

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[1] J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 32 (1958).

[2] G. Brauer, "Handbook of Preparative Inorganic Chemistry," Academic Press, New York, N. Y., 1963; Gmelin, "Handbuch der Anorganischen Chemie," Teil 63 (ruthenium), Teil 66 (osmium), Teil 67 (iridium), Verlag Chemie, Berlin.

[3] L. Malatesta and M. Angoletta, *Angew. Chem. Intern. Ed. Engl.*, **2**, 155 (1963).

[4] G. Bor, *J. Inorg. Nucl. Chem.*, **17**, 174 (1961).

[5] L. Tosi and J. Danon, *Inorg. Chem.*, **3**, 150 (1964).

[6] H. B. Gray, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3404 (1962); H. B. Gray, P. T. Manoharan, J. Pearlman, and R. F. Riley, *Chem. Commun.*, 62 (1965).

[7] P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963).

TABLE I

FREQUENCIES (CM^{-1}) AND INTENSITIES OF ABSORPTION BANDS IN PENTACYANONITROSYL COMPLEXES

Compound	C–N str region	N–O str	M–N str, M–NO rock	M–C str, M–CN rock	Bending and lattice modes
$Na_2[Fe(NO)(CN)_5] \cdot 2H_2O$	2170 m, 2160 m, 2158 m, 2142 s, 2125 vw, 2109 vw, 2098 vw	1935 vs	658 m, 647 m	515 w,[a] 497 w, 466 w, 430 sh, 422 s, 416 s, 318 m	189 s, 145 m, 138 s, 117 m, 91 m
$Cs_2[Fe(NO)(CN)_5]$	2149 w, 2140 s, 2133 sh	1929 vs, 1910 s	663 m, 658 m, 651 w	500 w, 454 w, 430 sh, 417 s, 406 s, 391 sh, 318 m	139 s
$[(CH_3)_4N]_2[Fe(NO)(CN)_5]$	2147 w, 2138 s, 2133 s	1908 vs, 1883 s	660 m, 656 m	498 w, 465 sh, 455 m,[a] 405 s, 385 w, 317 w	141 s, 91 s
$[(C_2H_5)_4N]_2[Fe(NO)(CN)_5] \cdot H_2O$	2162 m, 2156 m, 2150 m, 2142 s	1880 vs, 1845 sh	662 m, 653 w	540 m,[a] 500 m, 469 w, 463 w, 424 w, 405 s, 389 w, 319 m	149 s, 79s
$K_3[Mn(NO)(CN)_5]$	2130 w, 2101 s, 2060 w	1700 s	655 m	487 m, 454 m, 448 m, 405 s, 367 s, 327 w, 314 w	174 s, 130 s
$K_3[Cr(NO)(CN)_5]$	2120 s, 2073 vw	1630 vs	616 m	428 s, 397 s, 346 s, 305 w, 291 w	169 s, 126 s
$[(CH_3)_4N]_3[Cr(NO)(CN)_5]$	2110 s, 2067 vw	1625 vs	607 m	460 w,[a] 427 s, 388 s, 347 s, 327 w, 303 w	161 s, 101 s

[a] Band not arising from vibrations of the complex ion. Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder.

TABLE II

FREQUENCIES (CM^{-1}) AND INTENSITIES OF ABSORPTION BANDS IN PENTAHALONITROSYL COMPLEXES[a]

Compound	N–O str	Ru–NO str, Ru–NO rock	M–X str	Deformation modes	Lattice vibrations
$K_2[Ru(NO)Cl_5]$	1912 vs, 1897 vs	604 vw, 587 w	334 vs, 288 w	190 sh, 181 w	143 vw, 96 vs
$Rb_2[Ru(NO)Cl_5]$		602 vw, 588 w	330 vs, 284 w	184 sh, 178 w	107 vw, 80 vs
$Cs_2[Ru(NO)Cl_5]$	1873 vs, 1863 vs	599 sh, 589 w	322 vs, 279 vw	178 w	<70
$[(C_2H_5)_4N]_2[Ru(NO)Cl_5]$	1830 vs	613 w, 588 w	315 vs, 281 w	168 w	<70
$K_2[Ru(NO)Br_5]$	1880 vs, 1865 vs	605 vw, 573 m	257 vs, 221 m, 185 vw, 181 vw	128 vw, 111 vw	81 s
$Rb_2[Ru(NO)Br_5]$		606 vw, 578 m	255 vs, 220 w, 180 vw	125 vw, 108 vw	70 s
$Cs_2[Ru(NO)Br_5]$		599 vw, 578 w	251 vs, 222 m, 176 w	123 w, 106 vw	<70
$[(CH_3)_4N]_2[Ru(NO)Br_5]$	1840 sh, 1821 vs	610 w, 577 w	247 vs, 217 m, 175 w	121 w	75 m
$[(C_2H_5)_4N]_2[Ru(NO)Br_5]$	1832 vs	609 w, 573 w	245 vs, 222 w, 178 vw		<70
$K_2[Ru(NO)I_5]$	1840 vs	598 vw, 573 vw, 552 w	214 s, 172 w		105 vs
$Cs_2[Ru(NO)I_5]$		598 sh, 581 vw, 559 w	210 s, 169 w, 128 vw		<70
$[(C_2H_5)_4N]_2[Ru(NO)I_5]$		605 vw, 578 vw, 559 w	208 s, 172 w		<70
$K_2[Os(NO)Cl_5]$	1865 vs	617 vw, 593 w	320 vs, 294 w	196 w, 173 w	
$K_2[Os(NO)Br_5]$		623 vw, 585 w	230 s, 217 w		
$K[Ir(NO)Br_5]$	1973 s, 1955 vs	552 w, 534 vw	236 m, 225 m		

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder.

conclude that C–N stretching vibrations of different complex ions within the unit cell are coupled together despite the large distances between cyano groups. Other spectra illustrated in Figure 1 show that the pattern of splitting of ν(C–N) in $[Fe(NO)(CN)_5]^{2-}$ depends strongly on the nature of the cation. It may be noted that the greatest splitting occurs in the hydrated compounds, although in $Na_2[Fe(NO)(CN)_5] \cdot 2H_2O$ the intermolecular distances were considered too large for hydrogen bonding to exist.[7]

The compound $K_2[Ru(NO)Cl_5]$ crystallizes in the space group D_{2h}^{16}-Pnma.[8] As the site symmetry is C_s, Chart I also applies to this compound. The N–O stretching vibrations span the representations $A_g + B_{1g} + B_{2u} + B_{3u}$ and two infrared bands are indeed observed (Table II), indicating that the vibrations of the NO groups in different complex ions are also coupled together in spite of the groups' large separation of at least 5 A. Splitting of ν(N–O) was also noted in other compounds.

In the compounds $A_2[Ru(NO)X_5]$, no splitting of ν(N–O) was observed for A = $[(C_2H_5)_4N]$, X = Cl, Br. It was also noted that ν(N–O) is considerably lower in the tetraethylammonium salts than in the potassium salts. Similar differences were observed in

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(8) T. S. Khodashova and G. B. Bokii, *Zh. Strukt. Khim.*, **1**, 151 (1960).

TABLE III

FREQUENCIES (CM^{-1}) AND INTENSITIES OF ABSORPTION BANDS IN VARIOUS METAL–NITROSYL COMPLEXES

	$[Ru(NO)(NH_3)_4OH]Cl_2$	$[Ru(NO)(NH_3)_4OH]Br_2$	$[Ru(NO)(NH_3)_4OH]I_2$	$[Ru(NO)(NH_3)_4Cl]Cl_2$
O–H str	3470 m	3498 m	3510 m	
N–H str	3250 s	3250 s	3250 s	3250 s
N–H str	3120 s	3140 s	3130 s	3150 s
N–O str	1837 vs	1840 vs	1850 vs	1880 vs
N–O str				1874 sh
N–O str				1835 sh
NH_3 def	1550 m	1570 m	1570 m	1550 m
NH_3 def	1320 w	1328 m	1330 w	1303 s
NH_3 def	1290 s	1300 sh	1300 m	
NH_3 def	1279 w	1295 s		
NH_3 def		1283 sh		
Ru–OH rock	970 w	960 w	930 w	
Ru–NH_3 rock	850 m	845 s	840 m	855 m
Ru–NH_3 rock			820 m	
Ru–OH str	633 m	626 m	625 w	
Ru–NO str,	598 w	591 w	590 vw	610 w
Ru–NO rock	570 m	566 m	568 w	568 vw
Ru–NH_3 str	500 w	497 vw	497 vw	483 w
Ru–NH_3 str	478 m	469 m	462 w	
Ru–Cl str				326 vs
Deformation	325 sh	264 vs	*a*	272 vs
Deformation	271 vs	204 sh		210 sh
Deformation	218 sh			
Lattice vibr	130 s	112 sh	*a*	136 vs
Lattice vibr		89 s		124 vs

	$K_2[Ru(NO)(NO_2)_4OH]$	$K_2[Os(NO)(NO_2)_4OH]$
O–H str	3530 m	3500 m
N–O str	1879 vs	1829 s
NO_2 str	1400 vw	1398 vw
NO_2 str	1350 sh	1341 sh
NO_2 str	1340 sh	1330 m
NO_2 str	1330 m	1297 w
NO_2 str	1317 vw	
M–OH rock	957 m	965 m
NO_2 sciss	834 w	835 w
NO_2 sciss	828 s	828 s
NO_2 sciss	820 w	822 w
M–OH str, NO_2 wag	628 m	645 w
		624 m
M–NO str, M–NO rock	586 w	613 m
	578 w	606 m
	568 sh	559 vw
M–NO_2 rock, M–NO_2 str, deformations	347 m	461 vw
	331 s	357 vw
	303 vs	341 w
	286 vs	307 m
	273 s	299 sh
	237 sh	291 s
	192 m	278 vs
		259 w
		245 vw
		176 m
		165 m
Lattice vibr	132 m	128 m
		92 m

[a] Not investigated. Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder.

salts of $[Fe(NO)(CN)_5]^{2-}$, and solvent shifts of ν(N–O) have been also reported.[9] Clearly the electronic structure of the polar NO group is greatly influenced by the electric field generated by its surroundings. The frequency shifts observed imply that the electrons of the NO group are attracted more toward the oxygen atom in the higher field generated by the K$^+$ ions. 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. ν(M–X) frequencies are also influenced by the cation (see tables), and this in turn may affect

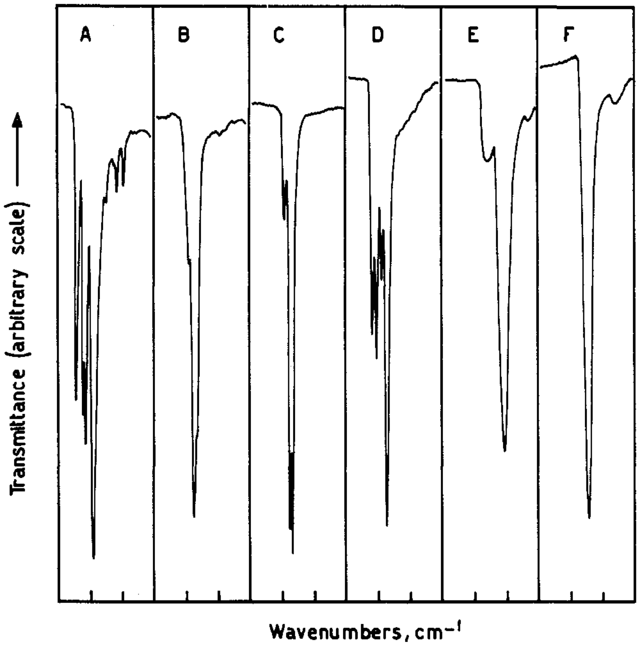

Figure 1.—Spectra (2200–2050 cm^{-1}) of (A) $Na_2[Fe(NO)(CN)_5]\cdot 2H_2O$, (B) $Cs_2[Fe(NO)(CN)_5]$, (C) $[(CH_3)_4N]_2[Fe(NO)(CN)_5]$, (D) $[(C_2H_5)_4N]_2[Fe(NO)(CN)_5]\cdot H_2O$, (E) $K_3[Mn(NO)(CN)_5]$, and (F) $K_3[Cr(NO)(CN)_5]$.

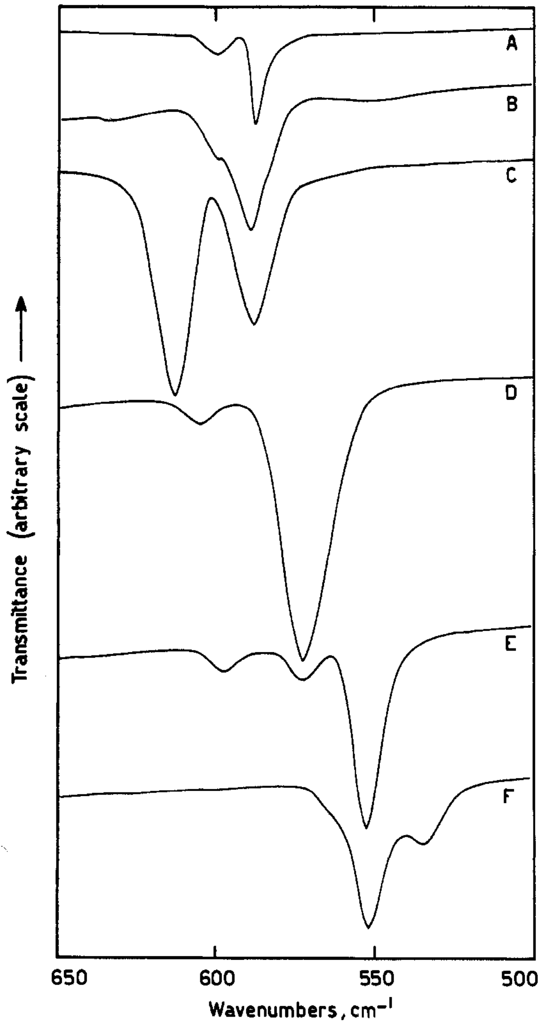

Figure 2.—ν(M–N) and δ(M–NO) in (A) $K_2[Ru(NO)Cl_5]$, (B) $Cs_2[Ru(NO)Cl_5]$, (C) $[(C_2H_5)_4N]_2[Ru(NO)Cl_5]$, (D) $K_2[Ru(NO)Br_5]$, (E) $K_2[Ru(NO)I_5]$, and (F) $K[Ir(NO)Br_5]$.

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[9] W. Beck and K. Lottes, *Z. Naturforsch.*, **19b**, 987 (1964); M. B. Fairey and R. J. Irving, *Spectrochim. Acta*, **20**, 1757 (1964).

ν(N–O). The solid-state shifts and splitting of ν(N–O) are presumably both the consequences of a large change in the bond dipole moment of the NO group during its vibrations and hence a sensitivity to the external electric field.

Low-Frequency Region. (a) **Ruthenium Complexes.**—The following bands are expected in this region, in order of increasing frequency: lattice vibrations, δ(X–Ru–X(N)), ν(Ru–X), ν(Ru–N), and δ-(Ru–NO).

The lattice vibrations are easily identified in most cases by comparing the spectra of different salts of the same complex ion, since the change of counterion causes little alteration to the spectra except for the lattice vibrations.

ν(Ru–X) and δ(X–Ru–X(N)) are assigned by analogy with other halo complexes[10] and also for internal consistency. 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. Woodward and Ware[11] have also found anomalous intensity behavior in the Raman spectra of $[ReCl_6]^{2-}$ and $[ReBr_6]^{2-}$.

The band at *ca.* 180 cm^{-1} in $K_2[Ru(NO)Br_5]$ shows signs of being a doublet, but it does not do so in the other salts. This leads to the probable assignment of this band to the ν(Ru–Br) doubly degenerate mode. Comparison of the spectrum of $K_2[Ru(NO)Cl_5]$ with that of *trans*-$[Ru(NO)(NH_3)_4Cl]Cl_2$ makes it likely that the band at 337 cm^{-1} in the former is largely associated with vibrations of the Ru–Cl bond *trans* to the NO group. We therefore have a provisional assignment of ν(Ru–Br) in $[(C_2H_5)_4N]_2[Ru(NO)Br_5]$: A_1 (*trans*), 245 cm^{-1}; A_1 (*xy* plane), 222 cm^{-1}; E, 178 cm^{-1}.

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 N^{15} substitution experiment[12] led to the firm assignment of these two modes to bands at 565 and 594 cm^{-1}, frequencies to be compared with 573 and 609 cm^{-1} found in $[(C_2H_5)_4N]_2[Ru(NO)Br_5]$. Further evidence in favor of the assignment may be drawn from the solid-state effects illustrated in Figure 2. The three bands found in $[Ru(NO)I_5]^{2-}$ probably correspond to the E mode, split by solid-state interactions, and the A_1 mode. For $[Ru(NO)Cl_5]^{2-}$ the N–O stretching region provides clear evidence that solid-state interactions are weakest in the tetraethylammonium salt. In this salt the relative intensities of the two bands become inverted from the pattern more commonly found in the ruthenium complexes. These observations suggest that the two bands found at *ca.* 600 cm^{-1} do represent the fundamental vibrations ν(Ru–N) and δ(Ru–NO) and do not represent ν(Ru–N), split by solid-state interactions, as has been recently suggested.[13]

(b) **Pentacyanonitrosyl Complexes.**—Our spectrum of $Na_2[Fe(NO)(CN)_5]\cdot 2H_2O$ agrees well with that of Miller, *et al.*[14] (though our resolution is better), but not with that of Tosi and Danon.[5] A comparison of the hydrated salts with the anhydrous cesium and tetramethylammonium salts shows that the bands at 515 or 540 cm^{-1} must be ascribed to the effect of the hydrate water molecules. In order to make a rough assignment of the remaining bands we assume that ν(M–C) and δ(M–CN) will be similar in compounds where ν(C–N) is similar and compare the spectrum of $[Fe(NO)(CN)_5]^{2-}$ with that of $[Fe(CN)_6]^{3-}$ and $[M(NO)(CN)_5]^{3-}$ with $[M(CN)_6]^{3-}$ (M = Mn, Cr). It is found that for each ν(M–C) and δ(M–CN) band in the hexacyano complex there exists a strong band of similar frequency in the nitrosyl complex. The use of this analogy is strengthened by the observation that the bands in $[Fe(NO)(CN)_5]^{2-}$ found between 300 and 500 cm^{-1} fall within the complete range of frequencies, including those not active in the infrared, found in $[Co(CN)_6]^{3-}$,[15] apart from the band at 318 cm^{-1}.

It is not possible, on the basis of the present data alone, to make a more detailed assignment of ν(M–C) and δ(M–CN). On the basis of the qualitative assignment, however, the bands found at *ca.* 660 cm^{-1} must be ascribed to ν(M–N) and δ(M–NO). In $[Fe(NO)(CN)_5]^{2-}$ the relative intensity of the two bands in this region varies, as did the corresponding bands in $[Ru(NO)X_5]^{2-}$, according to cation. In the chromium and manganese compounds only one band is found, so it must be concluded that the other is particularly weak, or accidentally degenerate. Regardless of any precise assignment in this region ν(M–N) can be given the value of *ca.* $\nu_{obsd} \pm 30$ cm^{-1} since this is the largest frequency difference found in the ruthenium compounds and in $Co(NO)(CO)_3$.

(c) **Other Compounds.**—The spectra of $K_2[Os(NO)Cl_5]$ and $K_2[Os(NO)Br_5)$ are very similar to those of the corresponding ruthenium compounds. In $K[Ir(NO)Br_5]$, however, the intensity pattern at *ca.* 560 cm^{-1} is different.

Some data for compounds of the type $[Ru(NO)(NH_3)_4L]X_2$ and $K_2[M(NO)(NO_2)_4OH]$ are given in Table III, together with a set of self-consistent assignments. The spectra of the ammine complexes are less complex than expected for a molecule of C_{4v} symmetry except for the M–N stretching frequencies. The deformation frequencies, of which three (E) are expected, are presumably all contained within the very broad envelope of the band at *ca.* 270 cm^{-1}. Fairey and Irving[13] have also published data on some of these compounds, and their experimental results are in entire agreement with ours. They were unable to make more than a tentative assignment of the

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[10] R. J. H. Clark and T. M. Dunn, *J. Chem. Soc.*, 1198 (1963); D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerrat, *ibid.*, 2189 (1963); D. M. Adams and H. A. Gebbie, *Spectrochim. Acta*, **19**, 925 (1963); A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964).

[11] L. A. Woodward and M. J. Ware, *Spectrochim. Acta*, **20**, 711 (1964).

[12] R. S. McDowell, W. D. Horrocks, and J. Yates, *J. Chem. Phys.*, **34**, 530 (1961).

[13] M. B. Fairey and R. J. Irving, *Spectrochim. Acta*, **22**, 359 (1966).

[14] F. A. Miller, C. L. Carlson, F. F. Bentley, and W. H. Jones, *ibid.*, **16**, 165 (1960).

[15] L. H. Jones, *J. Chem. Phys.*, **36**, 1209 (1962).

bands between 565 and 635 cm^{-1}. We suggest that the three bands found in this region in the compounds $[Ru(NH_3)_4(NO)(OH)]X_2$ should be assigned to ν(Ru–OH), ν(Ru–NO), and δ(Ru–NO), but neither the deuteration data[13] nor correlations with other compounds permit us to make a more precise assignment.

Bonding in Nitrosyl Complexes.—The large changes in the spectra found to result from solid-state interactions make the problem of interpretation a difficult one. Small differences in ν(N–O) from one compound to another may have virtually no significance with regard to the metal–ligand bonding.

The metal–nitrogen stretching frequencies are very high compared with metal–carbon stretching frequencies in carbonyl and cyano complexes. On the other hand, the opportunities for π bonding are *a priori* greater in a mononitrosyl complex in which the other ligands are weakly π bonding. The nitric oxide interacts strongly with the d_{xz},d_{yz} pair, reducing the availability of these electrons to the other ligands. The situation is not like that obtaining in an octahedral carbonyl complex where the three T_{2g} d orbitals are shared equally among six ligands.

The very low ν(N–O) frequency of many pentacyanonitrosyl complexes shows that the ligand NO^+ is involved in π bonding to an exceptional extent. This is demonstrated quantitatively by the calculation of the π^*(NO) character of the e(xy,yz) orbital.[16] However, M–NO π bonding has very little effect on the bonding between M and the other ligands since orbitals of quite different energy (and perhaps symmetry) are involved. This accounts for the fact that the infrared spectra in the ν(M–C) and δ(M–CN) region of various pentacyanonitrosyl complexes are remarkably similar, considering the variation in ν(N–O). It also accounts for the similarity, previously noted,[5] between ν(C–N) in the complexes $[Fe^{II}(NO^+)(CN)_5]^{2-}$ and $[Fe^{III}(CN)_6]^{3-}$; there is an analogous similarity between $[Cr^{I}(NO^+)(CN)_5]^{3-}$ and $[Cr^{III}(CN_6]^{3-}$ and the corresponding manganese compounds. One result of extensive π bonding to NO^+ is that the effective electrical charge on the central metal atom is nearly the same as in the hexacyano complexes of the metal in a higher oxidation state, and this largely determines the ν(C–N) frequencies.

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[16] P. T. Manoharan and H. B. Gray, *Chem. Commun.*, 324 (1965).

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An Infrared Study of the Directive Influences by Ligands in Nitrosylruthenium Complexes[1]

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The infrared spectra of several complexes of nitrosylruthenium have been recorded from 4000 to 50 cm^{-1} and assignments of the bands to the fundamental vibrational modes have been made. A study of the frequency of the ligands in both the *cis* and *trans* positions is interpreted in terms of a *cis*- and *trans*-labilizing influence. The *trans* series formed was: $I^- > Br^- > NH_3 \geq Cl^- > OH^- > CN^-$. While the influence of *cis* ligands was less than that of the *trans*, it is much too large to ignore in these complexes as has been done in square-planar complexes. The following fundamental vibrational frequencies have been assigned: Ru–NO stretching at 638–572 cm^{-1}; Ru–NO_2 stretching at 480–470 cm^{-1}; Ru–NH_3 stretching at 497–445 cm^{-1}; Ru–OH stretching at 588–519 cm^{-1}. Suggested assignments for the low-frequency bending modes are also presented.

Introduction

In octahedral complexes of transition metal ions, very little is known about the influence which different coordinated groups have on the bond strength and the lability of other ligands present in the complex. Such influences have been well studied in square-planar complexes of platinum and other metals and are best interpreted by a *trans* effect.[2–4] Our present infrared study was initiated in an attempt to discover whether such a *trans* effect is dominant in octahedral complexes or if *cis* groups also have large effects upon metal–ligand bonds. For this purpose we have chosen to study a number of nitrosylruthenium complexes by infrared spectroscopy.

In our previous paper[5] on some nitrosylruthenium complexes, a review of earlier infrared studies on this series of compounds was presented. One study of particular pertinence to our present report is that of

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[1] Presented at the Southeast–Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 2–4, 1965.

[2] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 171.

[3] F. Cotton and R. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 552.

[4] F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

[5] J. R. Durig, W. A. McAllister, J. N. Willis, Jr., and E. E. Mercer, *Spectrochim. Acta*, **22**, 1091 (1966).