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 $\nu$(Ru–OH), $\nu$(Ru–NO), and $\delta$(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 $\nu$(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 $\pi$ bonding are *a priori* greater in a mononitrosyl complex in which the other ligands are weakly $\pi$ 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 $\nu$(N–O) frequency of many pentacyanonitrosyl complexes shows that the ligand $NO^+$ is involved in $\pi$ bonding to an exceptional extent. This is demonstrated quantitatively by the calculation of the $\pi^*$(NO) character of the e(*xy,yz*) orbital.[16] However, M–NO $\pi$ 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 $\nu$(M–C) and $\delta$(M–CN) region of various pentacyanonitrosyl complexes are remarkably similar, considering the variation in $\nu$(N–O). It also accounts for the similarity, previously noted,[5] between $\nu$(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 $\pi$ 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 $\nu$(C–N) frequencies.

**Acknowledgment.**—Thanks are expressed to the Italian "Consiglio Nazionale delle Ricerche" for financial support.

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

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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# An Infrared Study of the Directive Influences by Ligands in Nitrosylruthenium Complexes[1]

BY E. E. MERCER, W. A. McALLISTER, AND J. R. DURIG

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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).

Sinitsyn and Zvyagintsev.[6] These workers reported the effect of various ligands on the N–O stretching frequency, which they assumed to be directly related to the strength of the Ru–N bond. To test the validity of this assumption, we have observed both the N–O and Ru–N stretching frequencies, as the ligands were varied in a systematic manner.

## Experimental Section

Infrared spectra were recorded from 4000 to 250 cm$^{-1}$ using a Perkin-Elmer Model 521 spectrophotometer. In the higher frequency range, the instrument was calibrated in the usual manner,[7] while the lower region was calibrated using atmospheric water vapor and the assignments of Randall, *et al.*[8] Samples were examined as Nujol mulls supported on CsBr plates or in KBr and CsBr disks. The far-infrared spectra from 350 to 50 cm$^{-1}$ were recorded on a Perkin-Elmer Model 301 spectrophotometer. This instrument was also calibrated with water vapor.[8] Both instruments were purged with dry nitrogen while the spectra were recorded. In the long-wave region all samples were examined in the solid state, suspended in polyethylene matrices. The polyethylene disks were prepared by pressing at 2000 psi and at 120° for 2 min a mixture of powdered polyethylene and the appropriate proportion of the crystalline compound (usually about 5% by weight). The resulting films were approximately 10 mils thick. All frequencies reported are expected to be accurate within 2 cm$^{-1}$ for sharp bands. Original tracings of the spectra or reproductions thereof are presented in Figures 1 and 2, and the frequencies of the observed bands are reported in Tables II–V.

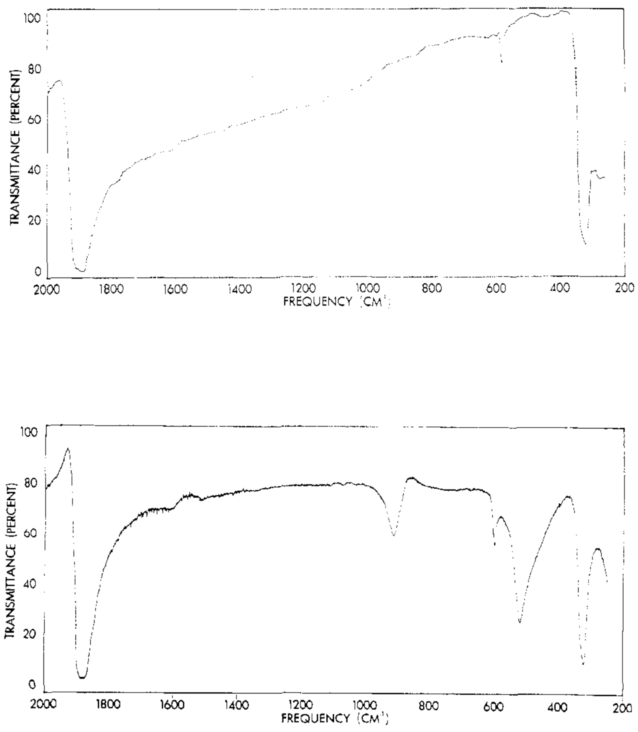

Figure 1.—Top curve, infrared absorption spectrum of K$_2$[RuNOCl$_5$]; lower curve, infrared absorption spectrum of Ag$_2$[RuNOCl$_4$OH].

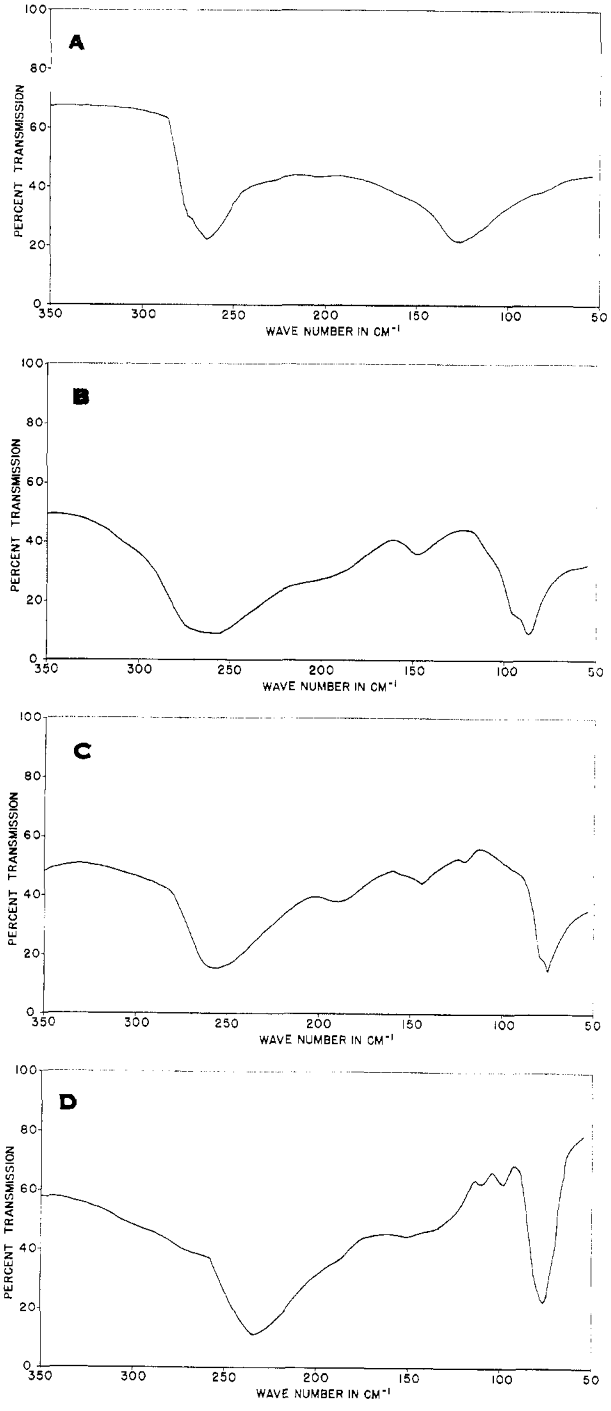

Figure 2.—A, Far-infrared spectrum of [RuNO(NH$_3$)$_4$OH]Cl$_2$; B, far-infrared spectrum of [RuNO(NH$_3$)$_4$OH]Br$_2$; C, far-infrared spectrum of [RuNO(NH$_3$)$_4$OH]I$_2$; D, far-infrared spectrum of [RuNO(ND$_3$)$_4$OD]I$_2$.

**Preparations of Compounds.**—*trans*-[RuNO(NH$_3$)$_4$OH]X$_2$ (X = Cl, Br, I) compounds were prepared by dissolving the appropriate ammonium pentahalonitrosylruthenate in concentrated aqueous ammonia and evaporating the solution to a small volume. The compounds were recrystallized from concentrated ammonia.

*trans*-[RuNO(NH$_3$)$_4$]X$_2$ compounds were made by recrystallizing the [RuNO(NH$_3$)$_4$OH]X$_2$ compounds from dilute solutions of the respective hydrohalic acid.

[RuNO(NH$_3$)$_5$]Cl$_3$ was prepared by the method of Gleu and Büddecker.[9]

Na$_2$[RuNO(NO$_2$)$_4$OH]·2H$_2$O was made by the addition of a

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[6] N. M. Sinitsyn and O. E. Zvyagintsev, *Dokl. Akad. Nauk SSSR*, **145**, 109 (1962).

[7] "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworth Inc., Washington, D. C., 1961.

[8] H. M. Randall, D. M. Dennison, N. Ginsburg, and L. R. Weber, *Phys. Rev.*, **52**, 160 (1937).

[9] K. Gleu and I. Büddecker, *Z. Anorg. Allgem. Chem.*, **268**, 208 (1952).

TABLE I

ANALYSES

| | N, % | | Halogen, % | | Ru, % | |
|---|---|---|---|---|---|---|
| | Calcd | Found | Calcd | Found | Calcd | Found |
| $[RuNO(NH_3)_4OH]Cl_2$ | 24.16 | 24.27 | 24.45 | 24.28 | | |
| $[RuNO(NH_3)_4OH]Br_2$ | 18.49 | 18.42 | 42.17 | 42.27 | | |
| $[RuNO(NH_3)_4OH]I_2$ | 14.81 | 14.73 | 53.67 | 53.53 | | |
| $[RuNO(NH_3)_4Cl]Cl_2$ | 22.71 | 22.43 | 34.48 | 33.89 | | |
| $[RuNO(NH_3)_4Br]Br_2$ | 15.85 | 15.87 | 54.26 | 54.28 | | |
| $[RuNO(NH_3)_4I]I_2$ | 12.02 | 11.47 | 65.32 | 52.44[a] | 17.3 | 17.3 |
| $[RuNO(NH_3)_5]Cl_3$ | 25.83 | 25.84 | 32.68 | 32.51 | | |
| $Na_2RuNO(NO_2)_4OH \cdot 2H_2O$ | 16.88 | 15.32 | | | 18.4 | 18.4 |
| $Ag_2RuNO(NO_2)_4OH$ | 12.78 | 11.16 | | | 24.3 | 23.6 |
| $Ag_2RuNOCl_4OH$ | 2.77 | 2.94 | 28.05 | 27.93 | | |

[a] Iodide analyses on Ru complexes containing coordinated iodide are invariably low.

TABLE II

INFRARED SPECTRA OF SILVER HYDROXOTETRACHLORONITROSYLRUTHENATE[a]

| $Ag_2[RuNOCl_4OH]$ | $Ag_2[RuNOCl_4OD]$[b] | Assignment |
|---|---|---|
| 3730 vvw | | |
| 3500 w | | O–H str |
| | 2582 w | O–D str |
| 1883 s | 1880 s | N–O str |
| | 1873 sh, w | N–O str |
| 1600 vvw | | $H_2O$ bending |
| | 1200 vvw | $D_2O$ bending |
| 914 m | | Ru–O–H bending |
| | 700 m | Ru–O–D bending |
| 600 w | 585 m | Ru–NO str |
| 590 sh, vvw | | Impurity? |
| 519 s | | Ru–OH str |
| | 497 m | Ru–OD str |
| 470 sh, vvw | | ? |
| | 370 vvw | ? |
| 358 sh, vvw | 355 vvw | Ru–NO bending |
| 330 sh, vw | 326 sh, vvw | Combination 230 + 100 |
| 321 s | 318 s | Ru–Cl str |
| 230 w | | Ru–OH bending |
| 175 b, vw | | $RuCl_4$ in-plane bending |
| 131 w | | $RuCl_4$ out-of-plane bending |
| 116 w | | Lattice vib |
| 102 w | | Lattice vib |
| 87 w | | Lattice vib |

[a] Abbreviations used: s, strong; m, medium; w, weak; v, very; sh, shoulder. [b] The spectrum below 250 cm$^{-1}$ for this molecule was not recorded.

slight excess of sodium nitrite to a warm (*ca.* 80°) solution of ruthenium chloride (38.60% Ru) obtained from Engelhard Industries. Upon cooling, large crystals of the desired compound were obtained and were recrystallized from water.

$Ag_2[RuNO(NO_2)_4OH]$ is slightly soluble and was made by addition of a solution of silver nitrate to a freshly prepared solution of $Na_2[RuNO(NO_2)_4OH] \cdot 2H_2O$.

$Ag_2[RuNOCl_4OH]$ was prepared as follows. A dilute solution of $K_2RuNOCl_5$ in water was heated for 45 min at 80°. Fractional precipitation with silver nitrate formed $Ag_2RuNOCl_5$, AgCl, and $Ag_2RuNOCl_4(OH)$, in that order. The final fraction was washed with water, ethanol, and ether, and was dried under vacuum. The X-ray powder pattern of this material was the same as that prepared by Mercer, Campbell, and Wallace.[10]

The deuterium-substituted compounds were made from the normal hydrogen compounds by precipitation from $D_2O$. $K_2RuNOCl_5$ containing nitrogen-15 was prepared by contacting an aqueous solution of $K_2RuCl_5(H_2O)$ with gaseous $^{15}NO$ for several hours. The salt was precipitated from solution by evaporation of the solvent. Other nitrogen-15 compounds which were made from this salt by simple ligand-exchange reactions were $[RuNO(NH_3)_4OH]Cl_2$ and $Na_2RuNO(NO_2)_4OH \cdot 2H_2O$. The chloro and ammine complexes showed 95% $N^{15}$ substitution while the $NO_2$ complex contained approximately 50% $N^{15}O$. In all of the infrared spectra obtained on these $^{15}N$ compounds only the N–O and the Ru–NO absorption bands showed any significant isotopic shift.

Ruthenium analyses for the nitro complexes were made spectrophotometrically by the method of Gortsema[11] as modified by Mercer, *et al.*,[10] using the absorbance at 385 m$\mu$ with a molar extinction coefficient of 930 l. mole$^{-1}$ cm$^{-1}$. Ruthenium analysis for $[RuNO(NH_3)_4I]I_2$ was accomplished by hydrogen reduction of the complex to ruthenium metal. All other analyses were made by Alfred Bernhardt and all analyses are presented in Table I.

## Band Assignments

In work reported earlier[5] the Ru–NO stretching fundamental was found in the range 585–553 cm$^{-1}$ for a series of pentahalonitrosylruthenate complexes. Similarly, the Ru–Cl, Ru–Br, and Ru–I stretching vibrations were found in the ranges 328–282, 255–219, and 213–172 cm$^{-1}$, respectively.[5] Using these data along with the well-characterized assignments for the vibrations falling above 1000 cm$^{-1}$, it is possible to assign most of the normal modes of the complexes studied herein. These assignments are summarized in Tables II–V and are discussed below.

From a comparison of the spectrum of $Ag_2[RuNOCl_4OH]$ with that for $K_2[RuNOCl_5]$ (see Figure 1), it is apparent that the bands at 914 and 519 cm$^{-1}$ arise from the Ru–OH moiety. Deuteration of the hydroxo complex resulted in shifts to 700 and 497 cm$^{-1}$, respectively. The higher frequency band is therefore assigned to the RuOH bending in accord with Scargill.[12] Although the shift of 22 cm$^{-1}$ for the lower frequency band is slightly larger than that expected for the Ru–OD stretching, it seems most reasonable to assign this band to that motion with possibly a slight interaction with the OH torsion. The Ru–NO stretching vibration is assigned to the band at 600 cm$^{-1}$ and the weak band at 358 cm$^{-1}$ is assigned to the Ru–NO bending mode in agreement with our previous assignments.[5] The $RuCl_4$ in-plane bending and out-of-plane bending vibrations are assigned to the bands at 175 and 135 cm$^{-1}$. The assignment of these two vibrations is based on the vibrational spectra of some tetrahalo complexes

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(10) E. E. Mercer, W. M. Campbell, Jr., and R. M. Wallace, *Inorg. Chem.*, **3**, 1018 (1964).

(11) F. P. Gortsema, Ph.D. Thesis, Purdue University, 1959.

(12) D. Scargill, *J. Chem. Soc.*, 4440 (1961).

### TABLE III

### INFRARED SPECTRA OF COMPOUNDS CONTAINING HYDROXOTETRANITRONITROSYLRUTHENATE ION

### $M_2[RuNO(NO_2)_4OH]$

| M = Na[a] | | M = Ag | | Assignment |
|---|---|---|---|---|
| 3770 w | (3900 w)[b] | 3740 vw | | |
| 3607 m | | | | |
| 3520 sh, m | (2604 s) | 3525 m | (2520 m)[b] | $\nu$(OH)[d] |
| 3500 s | | | | |
| 2713 w | (2722 w) | 2700 vw | | |
| 2650 w | (2658 w) | 2642 vw | | |
| 1893 vs | (1900 s) | 1883 vs | (1890 vs) | $\nu$(NO) |
| 1615 s | | | | $\delta(H_2O)$ |
| 1430 vs | (1420 s) | 1425 vs | (1440 sh, m) | $\nu_a(NO_2)$ |
| 1398 sh, w, 1381 sh, vw | | 1400 vs | (1398 vs) | $\nu_a(NO_2)$ |
| 1350 sh, vw | (1362 sh, w) | 1335 vw | (1365 m) | $\nu_s(NO_2)$ |
| 1330 vs | (1332 s) | 1330 vs | (1315 vs) | $\nu_s(NO_2)$ |
| 1270 sh, w | | 1318 sh, w | | |
| 1120 sh, vw | (1105 vw) | 1110 vw | (1170 vw) | |
| 995 s | (721 m) | 955 m | (730 m) | $\delta$(OH) |
| 837 sh, m | (839 sh, w) | 835 m | (835 s) | $\delta(NO_2)$ |
| 828 s | (830 s) | 825 vs | (832 sh, w) | $\delta(NO_2)$ |
| | | 820 sh, m | (822 m) | |
| 638 m | (631 sh, m) | 625 m | (630 m) | $\nu$(Ru–NO) |
| 608 m | (612 m) | 620 sh, vw | (618 sh, w) | $\delta_w(NO_2)$ |
| 588 w | 571 sh, w) | 583 sh, w | (572 sh, w) | $\nu$(Ru–OH) |
| 560 s | (550 m) | 574 m | (551 m) | $\delta_w(NO_2)$ |
| | (545 sh, vvw) | | (539 sh, vw) | |
| 490 vb, s[c] | (480 w) | 470 vw | (470 sh, vw) | $\nu(Ru–NO_2)$ |
| | (400 w) | 400 w | (423 w) | |
| 360 b, m | | 343 sh, vw | | |
| 317 s | (318 s) | 325 m | (315) | $\delta(NO_2–Ru–NO_2)$ |
| 301 s | | 309 s | | |
| 285 s | | 279 m | | |
| 263 sh, w | | | | |
| 159 m | | 120 b, m | (120 b) | Lattice |

[a] The sodium salt contains two waters of hydration. [b] Frequencies of the bands in parentheses are for the deuterium compounds. [c] The 490 $cm^{-1}$ band also includes $H_2O$ librational mode. [d] Abbreviations used: b, broad; s, strong; m, medium; w, weak; v, very; sh, shoulder; $\nu$, stretching; $\delta$, bending; $\rho_r$, rocking mode; $\delta_w$, wagging mode.

### TABLE IV

### INFRARED SPECTRA OF *trans*-HYDROXOTETRAAMMINENITROSYLRUTHENIUM SALTS

### $[RuNO(NH_3)_4OH]X_2$[a]

| X = Cl | X = Br | X = I | | Band assignments |
|---|---|---|---|---|
| 3655 w | 3645 w | 3650 vw | (2665 w)[b] | $\nu(H_2O)$[c] |
| 3465 m | 3482 m | 3500 m | (2560 m) | $\nu$(OH) |
| 3250 s | 3218 s | 3225 s | (2400 s) | $\nu(NH_3)$ |
| 3080 b, s | 3100 b, s | 3120 s | (2260 s) | $\nu(NH_3)$ |
| 1834 s | 1840 s | 1840 s | (1830 s) | $\nu$(NO) |
| 1600 sh, vw | 1600 vw | 1610 w | | $\delta(H_2O)$ |
| | 1570 sh, w | 1592 sh, w | (1200 w) | $\delta(NH_3)$ |
| 1525 m | 1525 m | 1540 m | (1130 m) | $\delta(NH_3)$ |
| 1400 sh, vw | | 1397 vw | | |
| 1320 m | 1329 m | 1325 m | (1008 sh, w) | $\delta(NH_3)$ |
| 1290 s | 1292 s | 1292 s | (990 s) | $\delta(NH_3)$ |
| 1272 sh, w | | | | |
| 1120 vw | | 1115 vw | | |
| 965 m | 950 m | 945 m | (743 m) | $\delta$(Ru–O–D) |
| | | 838 sh, w | (673 sh, w) | |
| 848 s | 827 s | 828 s | (660 s) | $\rho_r(NH_3)$ |
| 750 sh, vw | | | | |
| 628 s | 624 s | 624 s | (621 s) | $\nu$(Ru–NO) |
| 591 sh, m | 589 m | 589 sh, m | (567 sh, w) | |
| 565 s | 565 s | 567 s | (540 s) | $\nu$(Ru–OH) |
| 495 sh, vw | 495 sh, vw | 497 sh, vw | (460 sh) | $\nu(Ru–NH_3)$ |
| 473 s | 468 s | 469 s | (444 s) | $\nu(Ru–NH_3)$ |
| 395 sh, vw | 395 sh, vw | 398 sh, vw | | $\delta$(Ru–NO) |
| 370 sh, vw | 360 sh, vw | | | |
| 305 sh, vw | 300 sh, vw | 302 sh, vw | (285 sh, vw) | |
| 285 sh, vw | 275 sh, vw | 280 sh, vw | | |
| 267 s | 261 s | 258 s | (235 b, s) | (N–Ru–N) |
| | 197 b, w | 190 w | | |
| | 147 w | 144 w | (145 b, w) | |
| | | | (110 w) | |
| 126 s | 86 s | 75 s | (75 s) | Lattice mode |

[a] Several weak bands in the 2000–2600-$cm^{-1}$ range have not been listed because they are undoubtedly overtone or combination bands. [b] Frequencies of the bands in parentheses are for the deuterium compound $[RuNO(ND_3)_4OD]I_2$. [c] Abbreviations used: same as Table III.

### TABLE V

### INFRARED SPECTRA OF *trans*-SUBSTITUTED COMPLEXES OF TETRAAMMINENITROSYLRUTHENIUM HALIDES

### $[RuNO(NH_3)_4X]X_2$[a]

| X = Cl | X = Br | X = I | X = $NH_3$[b] | Band assignment |
|---|---|---|---|---|
| 3630 w | 3620 vw | | 3690 vw | $\nu(H_2O)$[c] |
| 3260 s | 3190 vb, s | 3200 sh, s | 3210 sh, w | $\nu(NH_3)$ |
| 3160 sh, s | | 3110 s | 3100 s | $\nu(NH_3)$ |
| | | | 1922 sh, w | |
| 1880 s | 1870 s | 1862 s | 1903 s | $\nu$(NO) |
| | | | 1865 sh, w | |
| 1595 sh, vw | 1585 sh, w | 1585 sh, w | 1620 w | $\delta(NH_3)$ |
| 1560 b, m | 1530 m | 1525 m | 1540 m | $\delta(NH_3)$ |
| | 1414 w | 1390 w | 1358 w | |
| | | | 1324 sh, m | |
| 1300 s | 1300 s | 1290 s | 1303 s | $\delta(NH_3)$ |
| 858 m | 845 s | 825 s | 845 s | $\rho_r(NH_3)$ |
| | 795 sh, vw | 788 sh, vw | | |
| 608 m | 591 m | 572 m | 602 s | $\nu$(Ru–NO) |
| 483 m | 472 m | 466 m | 474 m | $\nu(Ru–NH_3)$ |
| | | | 445 vw | $\nu(Ru–NH_3)$ |
| | 298 vw | 390 sh, vw | 395 vw | $\delta$(Ru–NO) |
| 328 m | 222 s | 173 m | | $\nu$(Ru–X) |
| 270 s | 264 vw | 255 m | 270 b, m | $\delta(H_3N–Ru–NH_3)$ |
| | 193, 176 vw | | | |
| | 157, 142 vw | | | |
| 139 s | 113 s | 80 w | | $\delta$(Ru–X) |
| | 125 sh, vw | 97 vw | | |
| 117 m | 92 s | | 127 vb, m | Lattice mode |
| | 80, 74 vw | | | |
| 66 w | | 58 w | | Lattice mode |

[a] Several weak bands above 2000 $cm^{-1}$ which were obviously overtone or combination bands were omitted from the table. [b] The formula of this compound is $[RuNO(NH_3)_5]Cl_3$. [c] Abbreviations used: same as Table III.

of palladium(II).[13] The band at 230 $cm^{-1}$ is close to the expected frequency of both the Ru–OH bending and the O–H torsional vibrations. The torsion is expected to give rise to a weak infrared band and the band is thus assigned to the Ru–OH bending. The bands at 116, 102, and 87 $cm^{-1}$ are all assigned as lattice vibrations.

The infrared spectra of sodium and silver *trans*-hydroxytetranitronitrosylruthenate are considerably more complicated than those of the complexes containing simpler ligands. The discussion of the fundamentals is limited to the observed bands for the sodium salt, but the assignments for the silver salt follow directly from these. The $NO_2$ antisymmetric stretching vibration at 1430 $cm^{-1}$ appears to be doubled. Similar behavior is also found for the $NO_2$ symmetric stretching vibration at 1330 $cm^{-1}$. These fundamentals also have additional bands which appear as shoulders on the main absorption band. It is possible some of this structure arises from combination bands, but in most of the compounds it appears that the $NO_2$ groups interact with one another and cause considerable splitting in this region of the spectra. The $NO_2$ deformation was assigned to bands in the 830-$cm^{-1}$ range. Again the additional bands probably result from interactions of the $NO_2$ groups. The assignment of the band at 995 $cm^{-1}$ to the Ru–O–H bending was verified by deuterium substitution.

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(13) J. R. During, B. R. Mitchell, C. H. Perry, D. P. Athans, and E. F. Young, *Spectrochim. Acta*, in press.

The 550–650 cm$^{-1}$ range is expected to contain four fundamentals. The isotopic shift of 17 cm$^{-1}$ produced upon introduction of $^{15}$NO showed clearly that the 638-cm$^{-1}$ band arises from the Ru–NO stretching. The $NO_2$ wagging vibration has been shown by Nakamoto, *et al.*,[14] to occur in the 600-cm$^{-1}$ region as two bands for the $[Pt(NO_2)_4]^{2-}$ ion. The band located at 608 cm$^{-1}$ in the spectrum of $Na_2[RuNO(N_2O)_4OH]\cdot 2H_2O$ did not shift in any of the isotopic studies, and it is assigned to the $NO_2$ wagging mode. The Ru–OH stretching frequency was assigned to the band at 588 cm$^{-1}$ which shifted to 571 cm$^{-1}$ on deuteration. Recrystallization of this salt from an ammonium chloride solution of pH 4 resulted in a yellow solid which we believe to be an impure sample of $Na_2[RuNO(NO_2)_4Cl]$, based on the changes observed in the infrared spectrum. The band at 588 cm$^{-1}$ decreased considerably in intensity in the spectrum of this sample, which tends to substantiate our assignment.

The band occurring at 560 cm$^{-1}$ was not affected significantly by the isotopic substitutions or by the partial replacement of the hydroxide ligand by chloride. The most reasonable assignment of the 560-cm$^{-1}$ band would be to another component of the Ru–$NO_2$ wagging mode. The weak band at 480 cm$^{-1}$ in the deuterium compound is assigned to the metal–$NO_2$ stretching vibration.[14] This band is apparently masked by the very broad band at 490 cm$^{-1}$ in the normal hydrogen compound. The band at 400 cm$^{-1}$ is assigned to the Ru–NO bending vibration in accord with the assignment given this vibrational mode for the other compounds of this series. Of the remaining bands, those at 490 and 263 cm$^{-1}$ may be assigned as librations of the waters of crystallization, since they disappear when the salt is dehydrated. The bands at 317 and 305 cm$^{-1}$ are attributed to the $O_2N$–Ru–$NO_2$ bending modes, and the 159-cm$^{-1}$ absorption is probably a lattice mode. The above assignments are summarized in Table III for the sodium and silver salts of both the normal and deuterium complexes.

The band assignments for the series of compounds $[RuNO(NH_3)_4X]Y_n$ (X = $NH_3$, OH, Cl, Br, I; Y = halide; $n$ = 2 or 3, depending on the charge of X) may be made easily by analogy to the spectra discussed above. These assignments are summarized in Tables IV and V. A few comments on some of the features of these spectra are warranted. The Ru–NO stretching vibration ranges in frequency from 628 to 572 cm$^{-1}$. The assignment was verified for the $[RuNO(NH_3)_4OH]X_2$ complexes by the substitution of $^{15}$NO, which showed a shift of 16 cm$^{-1}$. The Ru–$NH_3$ stretching vibrations ranged in frequency from 483 to 466 cm$^{-1}$ with the exception of the band at 445 cm$^{-1}$, which results from the motion of the $NH_3$ group in the *trans* position. The assignment of this vibration was verified by deuterium substitution. The shoulders at 495 cm$^{-1}$ in the spectra for the $[RuNO(NH_3)_4OH]X_2$ complexes are probably the result of coupling of molecules in the unit cell or less restrictive selection rules because of site symmetry. A similar band appears on the low-frequency side of the Ru–NO stretching fundamental, and we have assigned it as a combination band. The bands in the 260-cm$^{-1}$ region are confidently assigned to the Ru–$NH_3$ bending vibrations. The corresponding vibrations of the $Pd(NH_3)_4^{2+}$ ion have been assigned to approximately the same frequency.[12] The assignment of the lattice modes in these compounds is supported by the observation of the expected shifts as the mass of the anion is changed (see Figure 2). It is interesting to note that in the pentaammine salt, all of the Ru–$NH_3$ bending modes are apparently accidentally degenerate. Several very weak bands in the low-frequency region of the spectra could not be unequivocally assigned, but they are probably combination bands. The bands at 590 cm$^{-1}$ in the *trans*-hydroxotetraamminenitrosylruthenium complexes have been tentatively assigned to a combination band.

## Discussion

The correlation of infrared stretching frequencies with the *trans*-labilizing effect of ligands in metal coordination compounds has been the subject of a number of recent publications.[6,15–17] In cases where square-planar complexes were involved in the studies, the results indicated that bond polarization and $\pi$ interactions are of importance in most cases. There are very few cases in which a proven *trans* effect has been observed in octahedral complexes. It has been found that the NO group in nitrosylruthenium does have a very strong labilizing effect on the group in the *trans* position. In our previous work[5] on the compounds containing the ions $RuNOX_5^{2-}$ (where X = Cl, Br, I, or CN), the Ru–X stretching vibration for the group *trans* to the NO occurred at a frequency 30–40 cm$^{-1}$ lower than the corresponding group in the *cis* position, thus indicating that a bond-weakening mechanism is important in the labilizing influence of the nitrosyl.

Sinitsyn and Zvyagintsev[6] have correlated the N–O stretching frequency with the *trans*-directing influence of the X group in the series $[RuNO(NH_3)_4X]^{n+}$, on the assumption that the Ru–N stretching frequency parallels that of the N–O. In Table VI we have summarized the pertinent absorption frequencies for the same series of compounds. The *trans*-directing influence based on the Ru–NO stretching frequency is I > Br > $NH_3$ > Cl > OH > CN. With the exception of cyanide, this order is quite close to the order found for the platinum(II) complexes. The rather anomalous position in this series of the cyanide ion, which should be a strong *trans* director, may arise from the strong competition between the nitrosyl and cyanide for $\pi$-bond formation. An alternative explanation is the presence of fairly strong coupling between the Ru–CN and Ru–NO stretching vibrations. Further, the compound used is not strictly comparable because the *cis*

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Table VI

*trans* Effect on the Nitrosyl Frequencies

| Complex | Ru–NO, cm$^{-1}$ | N–O, cm$^{-1}$ |
|---|---|---|
| $K_2RuNO(CN)_5$ | 634 | 1920 |
| $[RuNO(NH_3)_4OH]Cl_2$ | 628 | 1834 |
| $[RuNO(NH_3)_4Cl]Cl_2$ | 608 | 1880 |
| $[RuNO(NH_3)_4NH_3]Cl_3$ | 602 | 1903 |
| $[RuNO(NH_3)_4Br]Br_2$ | 591 | 1870 |
| $[RuNO(NH_3)_4I]I_2$ | 572 | 1862 |

ligands in this complex are not the same. The very high frequency observed for the Ru–NO stretching vibration in the hydroxo compound must be interpreted with caution because of the coupling found in the deuterium substitution studies. Even taking the coupling of the vibrations into account, it appears that the OH group is a weaker *trans* director than the next lowest member of the series.

The possibility that the observed shift in the frequency of the Ru–NO stretching vibration arises solely from a mass coupling effect was considered. This postulate was rejected for several reasons. The position of the pentaammine complex in this series is inconsistent with the above explanation. Furthermore, consideration of the relative frequencies of the Ru–$NH_3$ stretching vibrations in the *cis* and *trans* positions indicates that the NO group is exerting a very strong labilizing influence on the *trans* ligand. This same effect was also observed in our earlier work on the pentahalonitrosylruthenates.[5] The greater lability of the group *trans* to the NO is well established on the basis of chemical evidence. For example, only the *trans*-hydroxotetrachloronitrosylruthenate is produced from the hydrolysis of the pentachloro salt. Therefore, it seems reasonable that a reciprocal effect should be observed in the Ru–NO bond strength changing the lability of that group. Because of the inertness of the Ru–NO bond it is not possible to observe this change in lability by chemical reactivity. For these reasons as well as the wide variation in the frequency of the Ru–NO stretching vibration, we feel that a mass coupling effect is not adequate to explain the data.

In octahedral complexes, a *cis* effect might be anticipated, particularly when metal d–$\pi$ orbitals are important in determining the labile group. A comparison of the *trans*-hydroxynitrosylruthenium complexes having different *cis* groups is presented in Table VII. The lack of correlation between the Ru–NO or Ru–OH frequencies and the N–O stretching vibration is immediately obvious. A second fact to be noted is the very large effect which the *cis* ligands produce in all of these stretching frequencies. While this influence is less than that observed for *trans* ligands, it is much too large to be ignored completely as has been done in square-planar complexes.

Table VII

*cis* Effect on the Nitrosyl Frequencies

| Complex | Ru–OH, cm$^{-}$ | Ru–NO, cm$^{-1}$ | N–O, cm$^{-1}$ |
|---|---|---|---|
| $Na_2RuNO(NO_2)_4OH \cdot 2H_2O$ | 588 | 638 | 1893 |
| $[RuNO(NH_3)_4OH]Cl_2$ | 565 | 628 | 1834 |
| $Ag_2RuNOCl_4OH$ | 519 | 600 | 1883 |

The general order of the shift of the Ru–N stretching vibration for the *cis* compounds could be accounted for quite readily on the basis of $\pi$ interactions only. However, a wider range of *cis* ligands would have to be investigated to state that the polarization effects may be neglected. The variation of the Ru–O stretching frequency in this series is difficult to rationalize by either polarization or $\pi$ interactions. The large shift of the Ru–OH stretching frequency may be qualitatively accounted for by assuming the *trans* effect of the NO group decreases drastically as the $\pi$ contribution to the Ru–N bond increases. This would be consistent with the expected change in polarizability of the central metal atom. However, the magnitude of the observed shifts seems entirely too large to be caused solely by this interaction. A second possible cause of this shift could be changes in the coupling of the Ru–O stretching vibration with the OH torsion. The magnitude of such changes in coupling would be very difficult, if not impossible to predict.

Extreme care must be taken in formulating general rules from the *cis* effect observed here since the Ru–N bond in nitrosylruthenium is known to have a great deal of $\pi$ character. Thus, the large *cis* effect observed for these complexes may be reduced considerably when tested on ligands such as $NH_3$, where the bonding by $\pi$ electrons is not possible.

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