tions during the data collection. Of the 2275 unique reflections measured, 1762 having intensities larger than 3σ were considered to be observed. These were corrected for Lorentz and polarization effects but not for absorption, since the linear absorption coefficient was small (18.3 cm^{-1}). The range of transmission factors is 0.93–0.88.

An IBM 360-50 computer was used in all calculations,[26] and the function minimized in the least-squares refinement was $\Sigma w(|F_o| = |F_c|)^2$.[27]

Solution and Refinement of the Structure.—A three-dimensional map of the Patterson function was interpreted to give the locations of five heavy atoms, which were assumed to be a nickel and four sulfur atoms. After improving their coordinates by two cycles of least-squares refinement, an electron density map was calculated which indicated the positions of the remaining nonhydrogen atoms. Nine further cycles of least-squares refinement of positional and isotropic thermal parameters gave $R_1 = 0.116$ and $R_2 = 0.165$.[28]

At this point all atoms except carbon and nitrogen were allowed to vibrate anisotropically, and the effect of anomalous scattering of the nickel atom was included in the refinement. Five additional cycles of least-squares refinement reduced R_1 to 0.060 and R_2 to 0.089.

An electron density difference map computed at this stage had its largest peaks in locations expected for most of the hydrogen atoms.

All atoms were now included in the refinement,[29] and four further cycles reduced R_1 to 0.052.

The final weighted residue, R_2, is 0.071, and the standard deviation of an observation of unit weight, a rather large 2.4. The positional and thermal parameters are listed in Table I.[30] Tables II–V list derived parameters of interest.

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[26] The programs used were local modifications of Eiss' REDAT for data reduction, Zalkin's FORDAP for Patterson and electron density maps, Busing, Levy, and Martin's ORFLS for least-squares refinement, Johnson's ORTEP for drawings, and Wood's MGEOM for distances, angles, and planes.

[27] $w = 4F^2/L^2\sigma(I)$, where L is the reciprocal Lorentz–polarization correction and $\sigma(I) = [P + (t/20)^2B + (0.045I)^2]^{1/2}$. P is the peak intensity, t the scan time in seconds, and B the total background count.

[28] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$.

[29] The atomic scattering power of Ni was corrected for the real and imaginary part of the anomalous dispersion: J. A. Ibers in "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202, Table 3.3.1A. Scattering powers for Ni^+, F^-, and neutral S, N, C, and H were taken from D. H. Templeton, *ibid.*, p 202, Table 3.3.2B.

[30] A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1415. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL, CHAPEL HILL, NORTH CAROLINA 27514

The Crystal and Molecular Structure of Ammonium Pentachloronitrosylruthenate(II), $(NH_4)_2[Ru(NO)Cl_5]$

BY JACK T. VEAL AND DEREK J. HODGSON*

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The crystal and molecular structure of ammonium pentachloronitrosylruthenate(II), $(NH_4)_2[Ru(NO)Cl_5]$, has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in the space group D_4^2-$P2_12_12_1$ of the orthorhombic system with four molecules in a cell of dimensions $a = 10.534$ (3), $b = 13.441$ (5), and $c = 6.911$ (2) Å. The observed and calculated densities are 2.34 (2) and 2.337 g cm^{-3}, respectively. Least-squares refinement of the structure has yielded a final value for the conventional R factor (on F) of 0.022 for 1770 independent reflections having $F^2 > 2\sigma(F^2)$. The $[Ru(NO)Cl_5]^{2-}$ anion is a slightly distorted octahedron with the Ru–Cl bond trans to the nitrosyl group shorter then the cis Ru–Cl bonds; the trans bond distance is 2.357 (1) Å while the cis bonds range from 2.373 (1) to 2.379 (2) Å. The Ru–N–O group is approximately linear, with an Ru–N–O bond angle of 176.7 (5)° and Ru–N and N–O bond distances of 1.738 (2) and 1.131 (3) Å, respectively. These values suggest that the nitrosyl group is bonded as NO^+. The observation that the Ru–Cl bond trans to the nitrosyl is shorter than those cis to the nitrosyl is in apparent contradiction to reported conclusions based on infrared spectroscopic data.

Introduction

The nature of the bonding in transition metal–nitrosyl complexes has been the subject of much recent work,[1–11] and it has been concluded that the nitrosyl moiety bonds as NO^+ to Ru(II) and other d^6 systems. NO^+ is an extremely efficient π-acceptor ligand[12] and, like the isoelectronic CO and CN^- species, is a very strong trans-labilizing ligand in square-planar four-coordinate complexes.

Recently reported molecular orbital calculations for the complexes $Mn(CO)_5X$, where X = Cl, Br, or I, have shown[13] that the Mn–X bond is entirely σ in nature and that the Mn–C bond trans to the halogen, while having much more π overlap, has slightly less σ overlap than the Mn–C bonds cis to the halogen—*i.e.*, that the halogen successfully competes with the carbonyl for σ-electron density. If it were also true that in complexes of the type $M(CO)X_5$ or $M(NO)X_5$ the M–X bonds are almost entirely σ in character and that the halogen competes successfully with the carbonyl or nitrosyl group for σ-electron density, then one would predict that the M–X bond trans to the carbonyl or nitrosyl would be stonger and shorter

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than the M–X bonds cis to the π-acceptor ligand. This suggestion is in direct contradiction with the findings of Durig, *et al.*,[14] who concluded from vibrational spectroscopy that in ions of the type $[Ru(NO)X_5]^{2-}$ the Ru–X bond trans to the nitrosyl is weaker than the bonds cis to the nitrosyl.

The crystal structure of $K_2[Ru(NO)Cl_5]$ has been reported by Khodashova and Bokii,[15] but the abnormally long N–O bond length of 1.25 Å caused us to doubt the precision of this early analysis, and recent work on the same complex in our laboratory has shown that the space group was incorrectly assigned as *Pnma* by the earlier workers and should be assigned as $P2_12_12_1$.[16] In an attempt to resolve the apparent difference between the molecular orbital calculations and the spectral data and also to continue our studies on the bonding of metal nitrosyls, we have undertaken a complete three-dimensional structural investigation of the ammonium salt of this anion, $(NH_4)_2[Ru(NO)Cl_5]$.

Experimental Section

The dark red compound was prepared by recrystallizing 1 g of $K_2Ru(NO)Cl_5$ from 30 ml of 3 *M* NH_4Cl solution. The mixture was allowed to stand at room temperature for 7 days, after which period a crop of dark red distorted octahedral crystals was filtered and air-dried.

On the basis of Weissenberg and precession photographs the crystals were assigned to the orthorhombic system. The observed systematic absences are $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd which strongly suggests that the space group is $D_4{}^2$-$P2_12_12_1$. The $0kl$ reflections with $k + l$ odd and the $hk0$ reflections with h odd are all weak but are not absent; thus, the space group is not $D_{2h}{}^{15}$-$Pnma$, as has been reported[15] for the potassium salt. The lattice constants, obtained by the least-squares procedure described previously,[17] are $a = 10.534$ (3), $b = 13.441$ (5), and $c = 6.911$ (2) Å. A density of 2.337 g cm^{-3} calculated for four formula units in the cell agrees with the value of 2.34 (2) g cm^{-3} obtained by flotation in diiodomethane–1,2-dibromoethane solution. Hence, no crystallographic symmetry need be imposed on monomeric species in the cell.

Diffraction data were collected at 22° with the wavelength assumed as λ(Mo Kα_1) 0.7093 Å using a Picker four-circle automatic diffractometer. An elongated octahedral crystal was selected for data collection. The four trapezoidal faces parallel to the needle axis were (101), $(\bar{1}01)$, $(10\bar{1})$, and $(\bar{1}0\bar{1})$, and the four triangular faces at the ends of the needle were assigned as $(\bar{1}10)$, (110), $(1\bar{1}0)$, and $(\bar{1}\bar{1}0)$. The separations of the faces were as follows: $(\bar{1}0\bar{1})$ to (101), 0.020 cm; $(\bar{1}01)$ to $(10\bar{1})$, 0.027 cm; $(\bar{1}\bar{1}0)$ to (110), 0.060 cm; $(\bar{1}10)$ to $(1\bar{1}0)$, 0.060. The crystal was mounted on a glass fiber roughly parallel to the *b* axis and in this orientation intensity data were collected. The mosaicity of the crystal was examined by means of the narrow-source, open-counter ω-scan technique.[18] The width at half-height for a typical strong reflection was 0.10°, which is in the range we consider to be acceptable, and the peaks were symmetric and single. Twelve reflections, accurately centered through a narrow vertical slit at a takeoff angle of 1.0°, formed the basis for the least-squares refinement which was effected using the logic documented by Busing and Levy[19] on the PDP-8/L computer. Intensity data were collected at a takeoff angle of 1.4°; at this angle the peak intensity for a typical strong reflection was about 90% of the maximum value as a function of takeoff angle. The counter aperture was 4.0 mm high by 4.0 mm wide and was positioned 32 cm from the crystal. The data were collected by the θ–2θ scan technique at a scan rate of 1.0°/min. Allowance was made for the presence of both Kα_1 and Kα_2 radiations, the scan range for each reflection being from 0.65° below the calculated Kα_1 peak position to 0.65° above the calculated Kα_2 peak position. Stationary-counter stationary-crystal background counts of 10 sec were taken at each end of the scan. The diffracted beam was filtered through a 1.5-mil Nb foil. Cu-foil attenuators giving attenuator factors of approximately 2.3 were inserted automatically when the intensity of the diffracted beam exceeded about 7000 cps during the scan; these attenuator factors were determined by the method previously described.[20] The pulse height analyzer was set for approximately a 90% window centered on the Mo Kα peak.

A unique data set having $2\theta < 65°$ was gathered; a total of 2050 independent intensities were recorded. The intensities of three standard reflections were measured after every 100 reflections and showed only the deviation from the mean predicted from counting statistics. There were very few data above background at values of $2\theta > 65°$. Only one form (*hkl*) of the data was gathered. Data processing was carried out as described by Corfield, *et al.*,[21] using our program DATPROC, the value of p in the expression

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_h + B_l) + (pI)^2]^{1/2}$$

being assigned as 0.040. This term is used to prevent extremely high weight being given to very large reflections.[22] The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects and for absorption factors. The absorption coefficient for this compound for Mo Kα radiation is 28.65 cm^{-1}, and for the sample chosen the transmission coefficients evaluated by numerical integration[23] were found to range from 0.521 to 0.575. Of the 2050 independent reflections, 1770 were greater than twice their estimated standard deviations.

Solution and Refinement of Structure

All least-squares refinements in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. In all calculations of F_c the atomic scattering factors for Ru were taken from Cromer and Waber,[24] that for H from Stewart, Davidson, and Simpson,[25] and those for Cl and N from the tabulation of Ibers.[26] The effects of anomalous dispersion were included in calculations of F_c,[27] the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulation of Cromer.[28] The 1721 independent intensities which were greater than 3 times their estimated standard deviations were used for the initial refinement of the structure, and the 1770 independent intensities which were greater than 2 times their estimated standard deviations were used for the final refinement.

The position of the Ru atom was determined from a three-dimensional Patterson function. Two cycles of least-squares refinement on the Ru positions using a variable isotropic thermal parameter were run, yielding values for the usual agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R_2 (or weighted R factor) $= (\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2)^{1/2}$ of 0.540 and 0.686, respectively.

The remaining nonhydrogen atoms were located in subsequent difference Fourier maps, and least-squares refinement of these atoms with isotropic thermal parameters yielded values of 0.104 and 0.166 for R_1 and R_2. Three further cycles on the 1770 independent intensities which were greater than twice their estimated standard deviations in which the atoms were assigned variable anisotropic thermal parameters were run, the resulting values of R_1 and R_2 being 0.030 and 0.041. Since only one form (*hkl*) of the data had been collected, two cycles of least-squares refinement were run in which (*hkl*) was replaced by $(\bar{h}\bar{k}\bar{l})$; this is equivalent to changing the positions (x, y, z) of all atoms to $(\bar{x}, \bar{y}, \bar{z})$. As anticipated,

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[22] W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

[23] In addition to various local programs, the programs for the IBM 360/75 used in this analysis were local modifications of Hamilton's GONO9 absorption correction program, Ibers' NUCLS least-squares program, Busing, Levy, and Martin's ORFFE function and error program, Zalkin's FORDAP Fourier program, and Johnson's ORTEP plotting program.

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[25] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[26] J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, Table 3.31A.

[27] J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

[28] D. T. Cromer, *ibid.*, **18**, 17 (1965).

TABLE I

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $[(NH_4)_2RuNOCl_5]$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	0.00044 (5)	0.14161 (1)	0.17408 (2)	0.00339 (2)	0.00247 (1)	0.00848 (4)	0.00042 (3)	0.00030 (6)	0.00015 (1)
N (of NO)	0.0000 (5)	0.2394 (1)	0.0096 (3)	0.0033 (1)	0.0029 (1)	0.0100 (3)	0.0007 (4)	0.0009 (7)	−0.0003 (1)
O	0.0040 (6)	0.3006 (2)	−0.1026 (3)	0.0059 (2)	0.0040 (1)	0.0153 (4)	−0.0001 (4)	0.0003 (7)	0.0028 (2)
Cl1	0.5022 (3)	0.4761 (1)	0.0818 (1)	0.0069 (1)	0.0038 (1)	0.0108 (1)	−0.0003 (2)	0.0001 (2)	−0.0014 (1)
Cl2	−0.2248 (1)	0.1399 (1)	0.1850 (2)	0.0034 (1)	0.0035 (1)	0.0186 (3)	0.0002 (1)	0.0003 (2)	0.0008 (2)
Cl3	0.2261 (1)	0.1374 (1)	0.1767 (2)	0.0039 (1)	0.0051 (1)	0.0141 (3)	0.0001 (1)	0.0007 (1)	0.0003 (2)
Cl4	−0.0004 (2)	0.2472 (1)	0.4501 (1)	0.0068 (1)	0.0036 (1)	0.0127 (1)	−0.0002 (2)	0.0016 (2)	−0.0019 (1)
Cl5	−0.0004 (2)	0.0055 (1)	0.3891 (1)	0.0062 (1)	0.0033 (1)	0.0120 (1)	0.0008 (1)	0.0000 (2)	0.0015 (1)

Group[b]	x_c	y_c	z_c	δ	ϵ	η	B(group)
NH_4A	0.2492 (4)	0.3911 (4)	0.3325 (9)	−3.077 (42)	−3.341 (44)	2.852 (42)	3.38 (12)
NH_4B	−0.2522 (3)	0.3895 (4)	0.3363 (8)	2.115 (48)	−2.667 (38)	−0.495 (46)	2.77 (10)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] x_c, y_c, and z_c are the fractional coordinates of the rigid-group centers. The angles δ, ϵ, and η (in radians) have been defined previously.[3]

since $P2_12_12_1$ is not a polar space group[29,30] and since the structure is so nearly centrosymmetric, this change did not cause any significant change in the atomic parameters or in the agreement factors R_1 and R_2.

A difference Fourier synthesis computed at this stage showed no peaks higher than 0.81 e Å^{-3}, with all peaks higher than 0.40 e Å^{-3} in the vicinity of the cation nitrogen atoms; the peak height of a typical nitrogen atom in this analysis was about 12 e Å^{-3}.

The ammonium hydrogen atoms were included in the calculation by refining the $[NH_4^+]$ cation as a rigid group, with the N–H bond lengths assigned the value of 0.90 Å and the group restricted to tetrahedral geometry; the initial positions of the H atoms were derived from the difference Fourier synthesis. Two cycles of least-squares refinement, in which these groups were assigned variable isotropic thermal parameters, were computed; these calculations yielded values for R_1 and R_2 of 0.029 and 0.038, respectively. At this point an examination of the data revealed that all of the strong low-angle data were systematically too weak, indicating that the data were subject to secondary extinction. A correction of the form described by Zachariasen[31] was made. After four cycles of least-squares refinement, using all intensities greater than twice their estimated standard deviations, no parameter experienced a shift as great as 10% of its estimated standard deviation, which indicated the refinement had converged. The values of R_1 and R_2 were 0.022 and 0.032, respectively, and the final value of the extinction coefficient was 1.79 (8) × 10^{-7}.

The positional and thermal parameters derived from the last least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Table I. The calculated positional parameters for the atoms of the rigid groups are given in Table II and the mean-square amplitudes of vibration are given in Table III. A table of observed and calculated structure factors is available.[32]

TABLE II

DERIVED PARAMETERS FOR ATOMS OF NH_4^+ GROUPS

Atom	x	y	z
NA1[a]	0.2492 (4)	0.3911 (4)	0.3325 (9)
HA1	0.3312 (11)	0.3914 (28)	0.3689 (53)
HA2	0.2168 (33)	0.4527 (13)	0.3446 (57)
HA3	0.2056 (34)	0.3488 (24)	0.4074 (47)
HA4	0.2433 (33)	0.3713 (28)	0.2089 (20)
NB1[a]	−0.2523 (3)	0.3895 (4)	0.3363 (8)
HB1	−0.3070 (30)	0.4324 (29)	0.2813 (49)
HB2	−0.1727 (13)	0.4043 (30)	0.2985 (48)
HB3	−0.2715 (44)	0.3273 (14)	0.3001 (50)
HB4	−0.2579 (33)	0.3941 (25)	0.4654 (10)

[a] Atoms with an A designation belong to group NH_4A, and those with B belong to group NH_4B.

Description of the Structure

The structure consists of $[Ru(NO)Cl_5]^{2-}$ anions which are well separated from ammonium cations. There is no evidence of any interaction between the chlorine atoms of the anion and the hydrogen atoms of the cation, there being no Cl···H contact shorter than 2.5 Å. The geometry of, and bond distances in, the anion are shown in Figure 1. The coordination polyhedron around ruthenium is a distorted octahedron, with the average equatorial Ru–Cl bond length of 2.376 (2) Å being significantly longer than the axial Ru–Cl bond length of 2.357 (1) Å. The bond angles around ruthenium are shown in Table IV. The Ru–N

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(30) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **8**, 326 (1969).

(31) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963); *Acta Crystallogr., Sect. A*, **24**, 212 (1968).

(32) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1420. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE III
MEAN-SQUARE AMPLITUDES OF VIBRATION (Å²)

Atom	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	0.0190	0.0225	0.0205	0.0029	0.0011	0.0007
N (of NO)	0.0187	0.0268	0.0241	0.0046	0.0031	−0.0013
O	0.0331	0.0362	0.0369	−0.0009	0.0009	0.0130
Cl1	0.0389	0.0351	0.0260	−0.0019	0.0005	−0.0067
Cl2	0.0189	0.0315	0.0449	0.0012	0.0010	0.0036
Cl3	0.0207	0.0468	0.0340	0.0005	0.0026	0.0014
Cl4	0.0383	0.0332	0.0307	−0.0011	0.0057	−0.0087
Cl5	0.0348	0.0298	0.0289	0.0060	0.0000	0.0071

[a] The expression for the anisotropic thermal ellipsoid is $\exp\{-[2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]\}$.

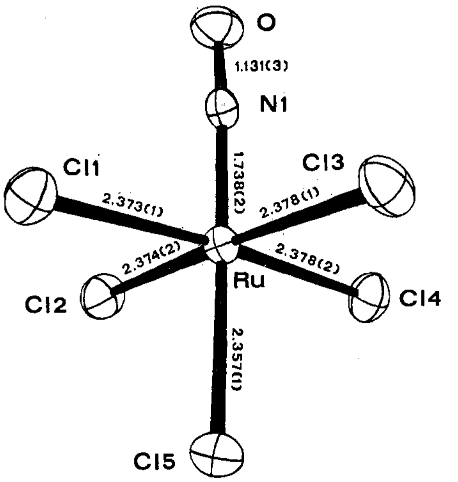

Figure 1.—View of the $[Ru(NO)Cl_5]^{2-}$ ion in $(NH_4)_2[Ru(NO)Cl_5]$. The thermal ellipsoids are drawn at the 50% probability level.

TABLE IV
SELECTED INTRAMOLECULAR DISTANCES AND ANGLES

Intramolecular distance, Å		Angle, deg	
Ru–Cl1	2.373 (1)	Ru–N–O	176.7 (5)
Ru–Cl2	2.374 (2)	N–Ru–Cl1	91.0 (1)
Ru–Cl3	2.378 (2)	N–Ru–Cl2	91.5 (2)
Ru–Cl4	2.378 (1)	N–Ru–Cl3	91.5 (2)
Ru–Cl5	2.357 (1)	N–Ru–Cl4	94.2 (1)
Ru–N1	1.738 (2)	N–Ru–Cl5	178.2 (4)
N–O	1.131 (3)	Cl5–Ru–Cl1	87.3 (1)
		Cl5–Ru–Cl2	88.2 (1)
		Cl5–Ru–Cl3	87.6 (1)
		Cl5–Ru–Cl4	88.9 (1)
		Cl1–Ru–Cl2	91.4 (1)
		Cl1–Ru–Cl3	174.8 (1)
		Cl1–Ru–Cl4	89.0 (1)
		Cl2–Ru–Cl3	88.6 (1)
		Cl2–Ru–Cl4	177.0 (1)
		Cl3–Ru–Cl4	90.7 (1)

and N–O bond lengths of 1.738 (2) and 1.131 (3) Å, respectively, are in good agreement with the values of 1.748 (4) and 1.127 (7) Å found[33] in $[Ru(NO)(OH)(NO_2)_4]^{2+}$, but the N–O bond length is much shorter than the value of 1.25 Å reported for $K_2[Ru(NO)Cl_5]$ by Khodashova and Bokii.[15] The near linearity of the Ru–N–O linkage (176.7 (5)°) is strongly indicative of the nitrosyl moiety's bonding as NO^+, and the N–O bond length of 1.131 (3) Å falls within the range found[2] for such systems. Moreover the Ru–N distance is similar to the value of 1.738 (16) Å found[34] for the $Ru–NO^+$ moiety in $[Ru(NO^+)(NO^-)Cl(PPh_3)_2]^+$ but quite different from the value of 1.859 (16) Å found[34] for the $Ru–NO^-$ fragment in the same ion.

The dominant feature of this structure is the relative shortening of the Ru–Cl bond trans to the nitrosyl as compared to the cis Ru–Cl bonds, which is an apparent contradiction of the trans effect rule usually applied in systems containing groups trans to coordinated CO, NO^+, and N_2. Extensive studies on the nature of NO^+ bonding in metal complexes, along with the isoelectronic N_2 and CO systems, have been reported in the literature.[35–40] The accepted bonding scheme involves considerable π donation from the metal to the nitrosyl group, using the metal d_{xz} and d_{yz} orbitals. The trans effect is usually discussed in terms of competition for these electrons by the groups trans to each other; *i.e.*, the bond to the better π acceptor is strengthened relative to the bond trans to it.

Recent work reported by Fenske and DeKock[13] on the bonding in $Mn(CO)_5L$ (L = H, Cl, Br, I) has provided calculations which take into account not only the M–C–O bonding but also the nature of the ligand trans to the CO group, and these authors have postulated an overall bonding scheme which can also be applied to the $[Ru(NO)Cl_5]^{2-}$ system. Fenske and DeKock demonstrated that in $Mn(CO)_5X$ the carbonyl groups which are cis to the halide have slightly stronger σ bonding than the carbonyl trans to the halide, although this axial carbonyl has much stronger π bonding than do the equatorial ligands. Their work also shows that there is no π character in the Mn–X bond. If it is also true in complexes of the type $M(CO)X_5$ or $M(NO)X_5$ that the M–X bonds are purely σ in character, one predicts that the M–X bond trans to the carbonyl or nitrosyl will be stronger than the equatorial bonds since in $Mn(CO)_5X$ the halogen competes successfully with the carbonyl for σ electrons. This conclusion is borne out by our observation that the axial Ru–Cl bond length of 2.357 (1) Å is shorter than the equatorial values in $[Ru(NO)Cl_5]^{2-}$. This finding is probably consistent with the observation[41] that there is no significant difference between the axial and equatorial osmium–ammine separations in $[Os(N_2)(NH_3)_5]^{2+}$ despite the great π-acceptor ability of the N_2 ligand. Moreover, it is in no way inconsistent with the recent report[11] that the axial cobalt–ammine distance in $[Co(NH_3)_5NO]^{2+}$ is much longer than the equatorial distances, since in the cobalt complex the nitrosyl moiety

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is present as NO^-, and NO^- is a strong σ-donor ligand which competes favorably with NH_3 for σ electrons. This cobalt case is analogous to the situation in $[Cr(CN)_5NO]^{3-}$,[42] where the axial cyanide is more weakly bound than the equatorial cyanide. In the cobalt example, the two ligands are both competing for σ electrons, and NO^- is stronger than NH_3, while in the chromium case the two ligands are competing for π electrons, and NO^+ is apparently stronger than CN^-. In the present ruthenium case, however, the π-acceptor NO^+ ligand does not compete with the σ donor Cl^- ligand, and so both axial bonds (Ru–N and Ru–Cl) are strengthened.

This conclusion is supported by the structural data reported[33] for $[Ru(NO)(OH)(NO_2)_4]^{2+}$. Using Pauling's[43] value of 0.99 Å for the covalent radius of chlorine and our average equatorial Ru–Cl bond length of 2.376 Å we deduce an effective octahedral covalent radius for Ru(II) in these systems of 1.39 Å, which is in fair agreement with the value of 1.33 Å reported by Pauling.[43] A similar calculation, using the average $Ru–NO_2$ bond distance[33] in $[Ru(NO)(OH)(NO_2)_4]^{2+}$ of 2.079 Å and a covalent radius[43] for nitrogen of 0.70 Å, leads to a value of 1.38 Å. Using either of these two calculated radii and a covalent radius for oxygen of 0.66 Å,[43] one predicts that the Ru–O bond length should be approximately 2.04 Å. Hence, the axial Ru–O bond length[33] of 1.950 Å in $[Ru(NO)(OH)(NO_2)_4]^{2-}$ is much shorter than the calculated value; this is again a consequence of the successful competition of the σ-donor hydroxide ligand for σ electrons, in an exactly analogous manner to that found here for the axial Ru–Cl bond in $[Ru(NO)Cl_5]^{2-}$. We would anticipate similar results in other octahedral complexes in which one axial ligand is a π acceptor and the other is a σ donor.

The structural data are evidently in contradiction to the spectral data, which have been interpreted[14] as indicating that the axial Ru–Cl bond is weaker (and, presumably, longer) than the equatorial bonds. We assume that a reexamination of the spectral data, especially if Raman data become available to supplement the infrared data, will lead to the conclusion that the axial Ru–Cl bond is indeed stronger than the equatorial bonds.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PORTLAND STATE UNIVERSITY, PORTLAND, OREGON 97207

Reaction of Catechol with Colloidal Silica and Silicic Acid in Aqueous Ammonia

BY DENNIS W. BARNUM

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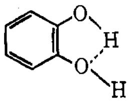
Reaction of catechol with silicic acid or colloidal silica in 8–15 *M* aqueous ammonium hydroxide gives large colorless crystals of a silicon–catechol complex that contains ammonia of crystallization. The ammonia can be removed at room temperature giving a product that analyzes for $(NH_4)_2[Si(C_6H_4O_2)_3] \cdot H_2O$. This compound has been studied by ir, nmr, X-ray powder diffraction, and its chemical behavior. The "water of crystallization" is probably present as an Si–OH group and a phenolic hydrogen. Removal of this "water" is difficult but can be accomplished in some cases. Other complexes have been prepared containing acetone, ethanol, dimethyl sulfoxide, or a fourth mole of catechol. A complex previously reported by other workers to contain 2 g-atoms of silicon/7 mol of catechol is actually the ethanol solvate $(NH_4)_2[Si(C_6H_4O_2)_3] \cdot xH_2O \cdot C_2H_5OH$ where $x = 3$ or 4.

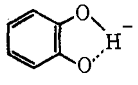
Introduction

Silicon forms very few coordination complexes with organic molecules and those that are known are generally unstable in the presence of water. An outstanding exception is catechol and other aromatic *vic*-diols which in aqueous basic solutions react with silica gel, colloidal silica, and even finely divided quartz to form coordination complexes of silicon.[1,2] Although these complexes have been investigated previously,[3-7] modern spectrometric methods have not been applied. In this investigation difficulty was encountered in repeating reported preparations and much of the previous work has been found to require modification.

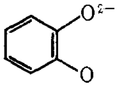
Rosenheim, *et al.*,[1] first reported the reaction of an aqueous solution of catechol with freshly precipitated silica in the presence of a base. They prepared $(NH_4)_2[Si(cat)_3] \cdot 9H_2O$[8] and several other salts of the $Si(cat)_3^{2-}$



H_2cat



$Hcat^-$



cat^{2-}

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