Reinvestigation of the Crystal and Molecular Structures of Penta-amminenitrosylruthenium Trichloride Hydrate and *trans*-Tetra-amminehydroxonitrosylruthenium Dichloride

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The crystal and molecular structures of the title compounds have been reinvestigated and solved by Patterson and Fourier methods by use of diffractometer data. Crystals of $[Ru(NH_3)_5(NO)]Cl_3,H_2O$ are orthorhombic, space group $Pn2_1a$, a = 11·864(7), b = 6·878(5), c = 14·192(9) Å, Z = 4. The structure was refined by full-matrix methods to R 0·047 (971 observed reflections). The ruthenium ion is octahedrally co-ordinated by six nitrogen atoms, with Ru–NO 1·770(9), N–O 1·172(14), and $Ru-NH_3$ 2·017—2·133 Å. Because of correlation effects only two distances (*cis*-$Ru-NH_3$) are regarded as true measurements of the bond lengths. Crystals of *trans*-$[Ru(OH)(NH_3)_4(NO)]Cl_2$ are monoclinic, space group $C2/m$ (assumed), a = 11·422(3), b = 7·365(2), c = 11·157(3) Å, β = 109·09(2)°, Z = 4. Full-matrix refinement for 2398 observed reflections, gave R 0·031. The ruthenium ion is octahedrally co-ordinated with Ru–NO 1·735(3), $Ru-NH_3$ 2·099(3) and 2·106(3), Ru–OH, 1·961(3), N–O 1·159(5) Å, and Ru–N–O 173·8(3)°. The Ru–OH distance is shorter than expected from covalent radii considerations.

THE crystal structures of $[Ru(NH_3)_5(NO)]Cl_3,H_2O$, (I), and *trans*-$[Ru(OH)(NH_3)_4(NO)]Cl_2$, (II), were investigated previously by Khodashova [1] and by Parpiev and Bokii [2] respectively. We were interested in these structures because of our work on reactivity of metal-nitrosyls,[3-6] and felt they required re-investigation for several reasons. First in determinations of the structures [7,8] of $A_2[RuCl_5(NO)]$ ($A = K$ or NH_4) Veal and Hodgson found the axial Ru–Cl to be shorter than the equatorial Ru–Cl distances. Proceeding from an MO calculation for $[MnCl(CO)_5]$, which showed the Mn–Cl bond to be largely σ in character,[9] this shortening was suggested to be due to the success of Cl^- in competing with NO^+ for σ electrons. The short Ru–NO distance (compared to the sum of the covalent radii of Ru^{II} and NO) was due to the excellent π-acceptor capabilities of NO^+, leading to multiple bonding between Ru^{2+} and NO^+.† It was further suggested that similar mutually short axial distances would be found in other octahedral complexes with axial ligands, where one was largely a σ donor and the other largely a π acceptor. $[Ru(NH_3)_5(NO)]^{3+}$ provides an excellent test of this, since all donor atoms are nitrogen. The previous investigation gave Ru–NO 1·804, $Ru-NH_3$(axial) 2·19, and $Ru-NH_3$(equatorial) 2·00, 2·12, 2·09, and 2·14 Å.[1] This is in disagreement with Veal and Hodgson's suggestion, but is in agreement with the ready replacement of the axial-NH_3 in solution.[1]

Secondly, our investigations of metal nitrosyls show $[Ru(NH_3)_5(NO)]^{3+}$ is reactive toward nucleophiles.[3-5] Other complexes such as *trans*-$[Ru(OH)(NO_2)_4(NO)]^{2-}$ (whose structure is known [11]) are similarly reactive, whereas $[RuCl_5(NO)]^{2-}$ and *trans*-$[Ru(OH)(NH_3)_4(NO)]^{2+}$ are not.[12] We have explained this in terms of the electron density at the nitrosyl nitrogen, which can be crudely estimated by the NO stretching frequency and force constant,[12] but the reactivity should also be manifested in the structural parameters of the complexes.

Finally, the earlier investigation of (II) used projection data only and suggested an Ru–N–O bond angle of 150°.[2] This has unfortunately been cited as an example of a $Ru^{II}-NO^+$ complex with a bent Ru–N–O bond, though the conclusion was at best tentative.[13] Since Ru^{II} normally forms complexes with Ru–N–O linear (at least when only one NO is present),[14] the 150° seemed unlikely.

EXPERIMENTAL

(I) and (II) were prepared by literature methods,[15,16] and crystals obtained from aqueous solutions set aside at 5° for several days. Crystals were mounted in thin-walled glass tubes.

Crystal Data.—(I), $Cl_3H_{17}N_6O_2Ru$, M = 340·6, Orthorhombic, a = 11·864(7), b = 6·878(5), c = 14·192(9) Å, U = 1158·1 Å^3, D_c = 1·95, Z = 4, D_m (ref. 1) = 1·95. Zr-filtered Mo-K_α radiation, λ = 0·71069 Å, μ(Mo-K_α) = 19·9 cm^{-1}.

For (I) $h0$—$2l$ Weissenberg photographs (Cu-K_α radiation)

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† Following the suggestion of Raynor,[10] these ruthenium complexes are referred to as being of ruthenium(II) and NO^+, though this nomenclature is incorrect according to IUPAC rules.

[1] T. S. Khodashova, *J. Struct. Chem.*, 1965, **6**, 678.

[2] N. A. Parpiev and G. B. Bokii, *Russ. J. Inorg. Chem.*, 1959, **4**, 1127.

[3] F. Bottomley and J. R. Crawford, *Chem. Comm.*, 1971, 200.

[4] F. Bottomley and J. R. Crawford, *J.C.S. Dalton*, 1972, 2145.

[5] F. Bottomley and J. R. Crawford, *J. Amer. Chem. Soc.*, 1972, **94**, 9092.

[6] F. Bottomley and S. B. Tong, *J.C.S. Dalton*, 1973, 217.

[7] J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, 1972, **11**, 1420.

[8] J. T. Veal and D. J. Hodgson, *Acta Cryst.*, 1972, **B28**, 3525.

[9] R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, 1970, **9**, 1053.

[10] J. B. Raynor, *Inorg. Chim. Acta*, 1972, **6**, 347.

[11] S. H. Simonsen and M. H. Mueller, *J. Inorg. Nuclear Chem.*, 1965, **27**, 309.

[12] F. Bottomley, W. V. F. Brooks, S. G. Clarkson, and S. B. Tong, *J.C.S. Chem. Comm.*, 1973, 919.

[13] T. S. Khodashova, M. A. Porai-Koshits, V. S. Sergienko, N. A. Parpiev, and G. B. Bokii, *J. Struct. Chem.*, 1972, **13**, 1024.

[14] For a review, see *e.g.* N. G. Connelly, *Inorg. Chim. Acta Rev.*, 1972, 47.

[15] J. N. Armor, H. A. Scheidegger, and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 5928.

[16] A. Werner, *Ber.*, 1907, **40**, 2714.

showed systematic absences in agreement with the space groups *Pnma* (D_{2h}^{16} No. 62) or *Pn*2$_1$*a* [non-standard setting of *Pna*2$_1$ (C_{2v}^{9}, No. 33)] found by Khodashova; the latter was shown to be correct from the subsequent successful refinement.

Crystal Data.—(II), $Cl_2H_{13}N_5O_2Ru$, M = 287·1, Monoclinic, a = 11·422(3), b = 7·365(2), c = 11·157(2) Å, β = 109·09(2)°, U = 886·9 Å^3, D_c = 2·15, Z = 4, D_m (by flotation in $CHCl_3$–$CHBr_3$) = 2·15. Mo-K_α Radiation, μ(Mo-K_α) = 22·85 cm^{-1}.

For (II), $h0$—$3l$ Weissenberg photographs (Cu-K_α radiation) could, at first sight, be indexed by use of the monoclinic *C* centred cell given by Parpiev and Bokii.[2] However, the weak $h0l$ (l odd) reflections found by them could not then be observed, even on much over-exposed photographs. From the higher-layer photographs the cell appeared centred on *B* as well as *C*. Therefore a new *C* centred cell was chosen, with systematic absences $hkl : h + k = 2n$. Possible space groups were C_2^3 (C_2^3, No. 5), *Cm* (C_s^3, No. 8), or *C*2/*m* (C_{2h}^3, No. 12), as before.[2]

Collection and Reduction of Intensity Data.—The crystal of (I) used for the intensity determination was a wedge-shaped chip (*ca.* 0·20 × 0·46 × 0·05 mm) cut from a long needle, and was mounted with the *b* axis *ca.* 12° mis-set from the ϕ axis of a Picker FACS 1 diffractometer.[17] The crystal of (II) was 0·15 × 0·36 × 0·28 mm, and was similarly mounted. Cell dimensions were determined from 12 accurately centred reflections with 2θ >40° for (I) and >52° for (II). For (I) a unique hkl data set was collected to 2θ 50° (1108 reflections) by the ω—2θ scan with instrumental settings as described before.[18] A similar technique (but with a 2° scan) with (II) gave 2568 hkl and $\bar{h}kl$ reflections to 2θ 75°. Three standard reflections were monitored every 15 reflections for (I) and every 50 reflections for (II), but no significant changes were observed.

Absorption, Lorentz, and polarization corrections [19] were then applied to the data [μR 66—80% for (I) and 63—78% for (II)]. Reflections with a net count <10 or <0·05 times the background count were considered unobserved, and not used in the structure refinements. All unobserved reflections had low $|F_c|$ in the final structure-factor calculation. The structure of (I) was solved from 971 observed structure amplitudes and of (II) from 2398.

Structure Solution and Refinement.—(i) *Structure of* (I). The Patterson function was readily interpretable in terms of the Ru^{2+} and Cl^- positions given by Khodashova.[1] Three cycles of block-diagonal, isotropic, unit weighted refinement of the ruthenium and three chloride ions in space group *Pn*2$_1$*a* gave *R* 0·23. The quantity minimized throughout refinement was $\Sigma w(|F_o| - |F_c|)^2$. The scattering factor curve for Ru^{2+} was taken from ref. 20 and those for Cl^-, N, O, and H from ref. 21. The Ru^{2+} and Cl^- curves were corrected for both the real and imaginary parts of the anomalous dispersion.

A Fourier synthesis phased on these atoms revealed all other non-hydrogen atom positions, but was complicated either by false symmetry (due to the proximity of all heavy atoms to y = 1/4) or by genuine disorder such that the true space group would be *Pnma*. The effect of this was to produce two oxygen atom peaks (for the NO group) in the Fourier, one close to N(1) and the other to N(4) (see Figure 1 for the numbering scheme). Refinement was continued in *Pn*2$_1$*a* with the peak close to N(1) arbitrarily chosen as the oxygen of a nitrosyl group. Four cycles of isotropic, unit weighted, refinement of all non-hydrogen atoms gave *R* 0·075, and a difference Fourier synthesis showed no evidence of disorder in the NO oxygen atom. *Pn*2$_1$*a* is therefore confirmed as the correct space group. This difference synthesis also showed the necessity for anisotropic refinement of all atoms, and revealed the positions of the hydrogen atoms. Anisotropic refinement was therefore begun, using a weighting scheme of the form given before,[18] with P_1 = 25·0 and P_2 = 35·0. After several cycles the hydrogen atoms were introduced as fixed contributions to F_c. The positional parameters for the hydrogen atoms were calculated (but conforming to the difference Fourier) using the idealized values of 1·01 Å for N–H and 109·5° for Ru–N–H and H–N–H, and 0·95 Å for O–H and 109·5° for H–O–H. All hydrogen atoms were given isotropic thermal parameters of 5·0 Å^2 except those of the water of crystallization which were 7·0 Å^2. After several cycles of full-matrix refinement this model converged at *R* 0·047 and *R'* 0·058 {where $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$}. On the final cycle no shift was >0·5σ.

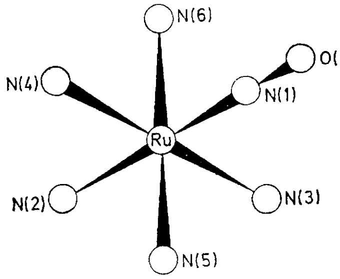

FIGURE 1 Numbering scheme for the $[Ru(NH_3)_5(NO)]^{3+}$ cation of (I)

A difference-Fourier synthesis had highest positive and lowest negative peaks of 0·65 and −0·56 eÅ^{-3}. An error analysis as a function of $|F_o|$, sin θ, and h, k, and l showed poor agreement for the very weakest reflections. Since these have a low weight this will not have significantly affected the final parameters. No other trends were found from the error analysis. The estimated standard deviation of an observation of unit weight was 1·41 electrons. Table 1 lists the parameters from the last cycle, with the hydrogen positions used given in Table 2. Observed and calculated structure factors for (I) and (II) are listed in Supplementary Publication No. 21011 (40 pp., 1 microfiche).*

(ii) *Structure of* (II). The ruthenium atom position was determined from a Patterson synthesis, and all other non-hydrogen atoms from a subsequent Fourier synthesis. Block-diagonal, unit weighted, refinement in *C*2/*m* and with anisotropic thermal parameters for all atoms proceeded smoothly to *R* 0·039. A difference synthesis revealed the hydrogen atom positions, which were then

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* For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[17] W. H. Zachariasen, *Acta Cryst.*, 1965, **18**, 705.

[18] F. Bottomley, *J.C.S. Dalton*, 1972, 2148.

[19] Programs used in this work were: the set by F. R. Ahmed, the National Research Council, Ottawa, Canada; ORFLS by W. R. Busing, H. A. Levy, and R. O. Martin, modified by D. Hall, University of Alberta, and further modified by P. Siew; CFIT, a programme for calculating atomic positions, W. V. F. Brooks.

[20] L. H. Thomas and K. Umeda, *J. Chem. Phys.*, 1957, **26**, 293.

[21] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

included as fixed contributions to F_c (B 3·5 Å^2) with geometry as before. Final refinement was by full-matrix, with the same weighting scheme as before (P_1 = 23·0, P_2 = 33·0), and converged to R 0·031, R' 0·041. All shifts were essentially zero on the last cycle. The highest positive and lowest negative peaks in the final difference synthesis were 1·03 and −1·2 eÅ^{-3}, the former near Ru^{2+} and the latter near a Cl$^-$. An error analysis again showed poor agreement for very weak reflections, but no other trends. The estimated standard deviation of an observation of unit weight was 1·54 electrons. Table 3 gives the parameters from the last cycle, and Table 4 the hydrogen atom positions. The atom numbering scheme is shown in Figure 2.

TABLE 1

Positional and thermal * parameters for (I)

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{22}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ru	0·22075(6)	0·25	0·10195(4)	41·0(4)	199(1)	24·5(3)	0	−0·4(6)	0
Cl(1)	0·3329(3)	0·7526(16)	0·2372(2)	170(4)	160(5)	37(1)	23(15)	−26(2)	2(10)
Cl(2)	0·3833(2)	0·2554(13)	0·4587(1)	42(1)	178(5)	31(1)	6(8)	1(1)	−19(7)
Cl(3)	0·0687(2)	0·2559(17)	0·3608(2)	37(1)	420(10)	34(1)	12(12)	7(1)	−15(11)
N(1)	0·1327(8)	0·4393(14)	0·1434(6)	48(6)	133(20)	40(5)	42(10)	7(5)	16(9)
N(2)	0·3289(9)	0·0507(15)	0·0499(7)	76(8)	159(23)	47(6)	47(13)	12(6)	18(10)
N(3)	0·3346(9)	0·4704(16)	0·0560(8)	68(8)	164(25)	63(6)	1(13)	1(6)	3(11)
N(4)	0·1140(8)	0·0366(16)	0·1472(7)	50(7)	231(28)	41(5)	−76(12)	9(5)	20(10)
N(5)	0·3075(6)	0·2449(43)	0·2309(5)	59(6)	300(28)	32(4)	−2(35)	−13(4)	55(24)
N(6)	0·1442(8)	0·2500(65)	−0·0309(6)	73(7)	380(35)	34(4)	3(43)	−16(4)	38(33)
O(1)	0·0653(8)	0·7268(16)	0·1712(7)	85(8)	252(24)	58(5)	59(13)	8(6)	−1(10)
O(2)	0·0873(11)	0·8410(49)	0·3803(7)	150(11)	418(67)	65(5)	−79(30)	−33(6)	43(22)

* The form of the thermal ellipsoid is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE 2

Positional parameters for the hydrogen atoms of (I)

Atom *	x	y	z
H(1)[O(2)]	0·040	0·841	0·380
H(2)[O(2)]	0·040	0·615	0·380
H(3)[N(2)]	0·367	−0·020	0·098
H(4)[N(2)]	0·381	0·115	0·003
H(5)[N(2)]	0·280	−0·048	0·009
H(6)[N(3)]	0·311	0·532	−0·001
H(7)[N(3)]	0·414	0·407	0·047
H(8)[N(3)]	0·345	0·571	0·110
H(9)[N(4)]	0·062	−0·002	0·097
H(10)[N(4)]	0·075	0·078	0·205
H(11)[N(4)]	0·164	−0·085	0·165
H(12)[N(5)]	0·254	0·303	0·283
H(13)[N(5)]	0·371	0·357	0·227
H(14)[N(5)]	0·339	0·128	0·247
H(15)[N(6)]	0·193	0·317	−0·077
H(16)[N(6)]	0·136	0·103	−0·052
H(17)[N(6)]	0·068	0·306	−0·027

* Atoms in square brackets are those to which the hydrogen is attached. For numbering scheme see Figure 1.

TABLE 3

Positional and thermal * parameters for (II)

Atom	x	y	z	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	β_{12}	$10^5\beta_{13}$	β_{23}
Ru	0·12396(2)	0·0	0·23893(2)	262(1)	542(4)	216(1)	0	48(1)	0
Cl(1)	0·41271(9)	0·0	0·13204(10)	464(7)	967(15)	529(8)	0	195(6)	0
Cl(2)	0·31220(9)	0·5	0·36201(10)	446(7)	1175(18)	511(8)	0	140(6)	0
				$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
N(1)	0·2762(3)	0·0	0·3400(3)	33(2)	89(5)	32(2)	0	4(2)	0
N(2)	0·1513(2)	0·1980(4)	0·1154(2)	51(2)	98(4)	40(2)	−3(2)	13(1)	17(2)
N(3)	0·0754(2)	0·2048(4)	0·3458(2)	59(2)	84(4)	42(2)	9(2)	18(2)	−13(2)
O(1)	0·3735(3)	0·0	0·4164(3)	34(2)	215(9)	50(3)	0	−8(2)	0
O(2)	−0·0499(2)	0·0	0·1295(3)	31(2)	113(5)	33(2)	0	5(1)	0

* The form of the thermal ellipsoid is given in Table 1.

Parpiev and Bokii reported (II) to be piezoelectric and, from optical measurements, to belong to the dihedral class of the monoclinic system. They therefore assumed space group $C2$.[2] A piezoelectric test on the crystals used in this work was negative. An E statistics test did not favour either the centric or non-centric cases. Because of the very low R it was felt no useful information would result from a non-centric refinement. $C2/m$ is therefore an assumed space group.

DISCUSSION

Description of the Structures.—As expected, hydrogen bonding links the cation, Cl$^-$, and, where present, water of crystallization. Tables 5 and 6 list the important hydrogen bonds (the distances are dependent on the assumed NH_3 and H_2O geometry). In both structures all NH_3 ligands are linked to Cl$^-$ by at least one hydrogen bond. In (I) (for which a diagram of the unit cell is given in ref. 1) there is strong hydrogen bonding between the *trans*-NH_3 and the water of crystallization, but the latter is only weakly bonded to Cl$^-$. This is shown also by the i.r. spectrum, in which the NH_3 vibrations are broadened by hydrogen bonding whereas the OH stretching vibration is quite sharp.[22] There is no significant interaction between the water and the oxygen of the NO. In (I), ν(NO) is split into two bands, but only one is observed for its solution, or the anhydrous

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[22] F. Bottomley and S. G. Clarkson, unpublished results.

form,[22] and this may therefore be due to the environment of NO with respect to Cl^-. In (II) the *trans*-OH forms a strong hydrogen bond to a Cl^-. In addition there is a hydrogen bond from NH_3, *via* H(3)[N(2)], of one cation to OH^- of an adjacent cation. Thus the cations form a zig-zag chain, with Cl^- surrounding it. This is illustrated in ref. 2 (the changes in c and β do not affect the gross structure). An unusually close-packed structure results, as is shown by the high density (D_m 2·15); similar complexes have densities near 1·8.[18,23]

TABLE 4

Positional parameters for the hydrogen atoms of (II)

Atom *	x	y	z
H(1)[O(2)]	−0·1049	0·0	0·2145
H(2)[N(2)]	0·2377	0·1860	0·1099
H(3)[N(2)]	0·0880	0·1828	0·0286
H(4)[N(2)]	0·1423	0·3235	0·1492
H(5)[N(3)]	0·0735	0·3262	0·3022
H(6)[N(3)]	−0·0068	0·1782	0·3544
H(7)[N(3)]	0·1412	0·2109	0·4332

* Atoms in square brackets are those to which the hydrogen atom is attached. For numbering scheme see Figure 2.

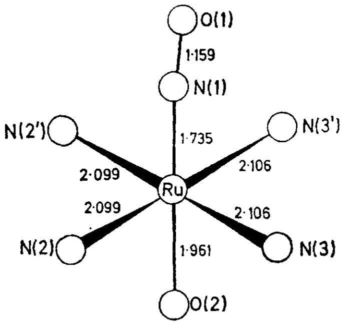

FIGURE 2 Numbering scheme for the $[Ru(OH)(NH_3)_4(NO)]^{2+}$ cation of (II)

TABLE 5

Hydrogen bond distances (Å) in (I)

Bond A · · · H–B	A–B	A · · · H
O(2) · · · H(4)–N(2)	2·87	1·94
Cl(1) · · · H(3)–N(2)	3·36	2·55
Cl(2) · · · H(5)–N(2)	3·48	2·47
Cl(1) · · · H(8)–N(3)	3·30	2·20
Cl(3) · · · H(7)–N(3)	3·36	2·48
Cl(2) · · · H(9)–N(4)	3·30	2·66
Cl(1) · · · H(11)–N(4)	3·49	2·51
Cl(1) · · · H(14)–N(5)	3·48	2·59
Cl(3) · · · H(13)–N(5)	3·36	2·75
Cl(2) · · · H(17)–N(6)	3·38	2·42
Cl(1) · · · H(15)–N(6)	3·30	2·69
Cl(3) · · · H(1)–O(2)	3·66	2·89
Cl(1) · · · H(2)–O(2)	3·45	3·11

TABLE 6

Hydrogen bond distances (Å) in (II)

Bond A · · · H–B	A–B	A · · · H
O(2) · · · H(3)–N(2)	2·77	2·15
Cl(1) · · · H(1)–O(2)	3·45	2·15
Cl(1) · · · H(2)–N(2)	3·49	2·45
Cl(1) · · · H(4)–N(2)	3·49	2·79
Cl(1) · · · H(5)–N(3)	3·28	2·47
Cl(2) · · · H(6)–N(3)	3·42	2·47
Cl(2) · · · H(7)–N(3)	3·42	2·67

The *trans*-$[Ru(OH)(NH_3)_4NO]^{2+}$ cation has strict crystallographically imposed C_s symmetry, the plane bisecting the N(2)–Ru–N(2′) and N(3)–Ru–N(3′) angles. Consideration of intramolecular distances, angles, and a selection of mean planes (Tables 7 and 8) shows the only significant deviation from idealized C_{4v} symmetry is the Ru–N–O angle of 173·8(3)°. The equatorial NH_3 groups are displaced 0·12 Å towards NO^+.

TABLE 7

Intramolecular geometry in the cation of (II)

(*a*) Distances (Å)

Ru–N(1)	1·735(3)	Ru–O(2)	1·961(3)
Ru–N(2)	2·099(3)	N(1)–O(1)	1·159(5)
Ru–N(3)	2·106(3)		

(*b*) Angles (deg.)

N(1)–Ru–O(2)	178·2(1)	N(2)–Ru–N(3)	89·9(1)
N(1)–Ru–N(2)	95·4(1)	N(2)–Ru–N(2′)	88·0(1)
N(1)–Ru–N(3)	91·5(1)	N(3)–Ru–N(3′)	91·5(1)
O(2)–Ru–N(2)	85·9(1)	Ru–N(1)–O(1)	173·8(3)
O(2)–Ru–N(3)	87·2(1)		

TABLE 8

Equations * of weighted mean planes and, in square brackets, distances (Å) of atoms from the plane for the cation of (II)

Plane (1)

Ru, N(2), N(2′), N(3), N(3′)	$-0{\cdot}8190X - 0{\cdot}5738Z = -1{\cdot}8887$

[Ru −0·002(0), N(2) 0·120(3), N(3) 0·124(3)]

Plane (2)

Ru, N(1), N(2), N(3′), O(2)	$0{\cdot}4232X - 0{\cdot}7074Y - 0{\cdot}5661Z = -1{\cdot}1958$

[Ru 0(0), N(1) −0·023(2), N(2) 0·029(3), N(3′) 0·029(3), O(2) −0·018(2)]

* X, Y, and Z are orthogonal co-ordinates in Å, related to the crystallographic axes by: $X = ax - c\cos\beta$, $Y = by$, and $Z = c\sin\beta$.

For $[Ru(NH_3)_5(NO)]^{3+}$, on which no crystallographic symmetry is imposed, consideration of distances, angles, and mean planes (Tables 9 and 10) shows distortions from idealized C_{4v} symmetry to be severe, apparently in the equatorial Ru–N distances, the angles all being acceptably close to 90°.

Unequal distances for chemically equivalent bonds have been observed before,[24-26] but can be explained in terms of thermal motion,[27] crystal decomposition,[26] or other large systematic errors. In the present case there was no similar explanation even after examination

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[23] F. Bottomley and S. C. Nyburg, *Acta Cryst.*, 1968, **B24**, 1289.

[24] M. Black, R. H. B. Mais, and P. G. Owston, *Acta Cryst.*, 1969, **B25**, 1753.

[25] M. A. Spinnler and L. N. Becka, *J. Chem. Soc.* (*A*), 1967, 1194.

[26] B. R. Davis and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 2768.

[27] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1964, **17**, 142.

of all possible sources of error. However, the correlation matrix from the refinement revealed correlations up to 0·9 between the parameters of N(1) and N(4) and of N(2) and N(3). These atoms appear related by a pseudo-mirror-plane through Ru, N(5), and N(6) (see Figure 1). The correlated atoms are chemically non-equivalent, and this is presumed to be the reason for the observed variation in the equatorial distances. There is little correlation between the parameters of N(5) and N(6), and the distances involving these atoms are similar [2·100(8) and 2·093(9) Å] and essentially identical to those in (II) [2·099(3) and 2·106(3) Å].

TABLE 9

Intramolecular geometry in (I)

(*a*) Distances (Å)

Ru–N(1)	1·770(9)	Ru–N(5)	2·100(8)
Ru–N(2)	2·017(11)	Ru–N(6)	2·093(9)
Ru–N(3)	2·133(11)	N(1)–O(1)	1·172(14)
Ru–N(4)	2·042(11)		

(*b*) Angles (°)

N(1)–Ru–N(2)	175·4(4)	N(2)–Ru–N(6)	86·3(8)
N(1)–Ru–N(3)	87·3(4)	N(3)–Ru–N(4)	179·0(4)
N(1)–Ru–N(4)	93·3(4)	N(3)–Ru–N(5)	86·7(6)
N(1)–Ru–N(5)	89·1(6)	N(3)–Ru–N(6)	90·6(8)
N(1)–Ru–N(6)	93·2(8)	N(4)–Ru–N(5)	92·6(6)
N(2)–Ru–N(3)	88·2(4)	N(4)–Ru–N(6)	90·1(8)
N(2)–Ru–N(4)	91·2(4)	N(5)–Ru–N(6)	176·4(9)
N(2)–Ru–N(5)	91·2(6)	Ru–N(1)–O(1)	172·8(9)

TABLE 10

Equations * of weighted mean planes and, in square brackets, distances (Å) of atoms from the plane of the cation of (I)

Plane (1): Ru, N(1)—(4)
$-0{\cdot}4698X + 0{\cdot}0287Y - 0{\cdot}8823Z = -2{\cdot}4577$
[Ru 0·000(1), N(1) 0·007(9), N(2) 0·008(10), N(3) −0·016(12), N(4) −0·013(10)]

Plane (2): Ru, N(1), N(2), N(5), N(6)
$0{\cdot}6174X + 0{\cdot}7065Y - 0{\cdot}3458Z = 2{\cdot}3320$
[Ru 0(0), N(1) 0·072(9), N(2) 0·081(11), N(5) 0·033(21), N(6) 0·069(32)]

Plane (3): Ru, N(3)—(6)
$0{\cdot}6367X - 0{\cdot}6986Y - 0{\cdot}3265Z = -0{\cdot}0060$
[Ru 0(0), N(3) 0·014(11), N(4) 0·012(10), N(5) 0·026(21), N(6) 0·058(32)]

* *X*, *Y*, and *Z* are orthogonal co-ordinates in Å related to the crystallographic axes by: $X = ax$, $Y = by$, and $Z = cz$.

Because of the high correlation the only distances in $[Ru(NH_3)_5(NO)]^{3+}$ useful for comparison purposes are Ru–N(5) and Ru–N(6). We could not therefore test Veal and Hodgson's suggestion as to the *trans*-influence of NO^+, nor compare Ru–NO and N–O distances in (I) and (II). It can only be stated that ready replacement of the axial-NH_3 in $[Ru(NH_3)_5(NO)]^{3+}$ does not require this distance to be longer than the equatorial distances. The replacement reactions always involve alkaline solutions, although the initial product(s) of these reactions are not always isolated.[4,28-30] We find $[Ru(NH_3)_5(NO)]^{3+}$ is essentially unaffected by acid,[22] but in alkaline solution $[Ru(NH_3)_5(NO)]^{3+}$ is in equilibrium with $[Ru(NH_3)_5(NO_2)]^+$.[4] In the latter there is a marked lengthening of the axial-NH_3 [2·199(6) Å *vs.* mean equatorial distance of 2·127(5) Å [18]]. Hence substitution can take place *via* $[Ru(NH_3)_5NO_2]^+$ {alkaline solutions of $[Ru(NH_3)_5(NO)]^{3+}$ irreversibly form *trans*-$[RuOH(NH_3)_4(NO)]^{2+}$ (ref. 4)}. A kinetic *trans*-effect of NO^+ seems less likely because of the unreactivity of $[Ru(NH_3)_5(NO)]^{3+}$ towards acids. Initial replacement of a *cis*-NH_3 followed by isomerisation cannot be completely discounted either.

The mean Ru–N(eq) distance in (II) is $2{\cdot}102_5$ Å, and the mean of Ru–N(5) and Ru–N(6) in (I) is $2{\cdot}096_5$ Å. These may be compared to 2·144(5) in $[Ru(NH_3)_6]I_2$,[31] and mean Ru–N(eq) 2·124(15) in $[\{Ru(NH_3)_5\}_2N_2][BF_4]_2,2H_2O$,[32] and 2·127(5) Å in $[Ru(NH_3)_5(NO)_2]Cl,H_2O$.[18] The Ru–N(eq) shortening in the last-named two, when compared to that in $[Ru(NH_3)_6]I_2$, is ascribed to withdrawal of electrons from Ru^{2+} by d_π–π^* (N_2 or NO_2^-) bonding.[18,32] Assuming electron withdrawal increases with the π-acceptor capability of the ligand, the distances determined here indicate NO^+ to be a better π-acceptor than N_2 or NO_2^-. This is in agreement with a recent i.r. study of $[RuCl(das)_2(AB)]^{n+}$ [das = *o*-phenylenebisdimethylarsine, AB = N_2, CO (n = 1), or NO^+ (n = 2)], where the π-acceptor capability is: $NO^+ > CO > N_2$.[33] Further evidence for the high π-acceptor capability of NO^+ comes from the Ru–NO distance [1·735(3) Å] in (II), which is compared with other Ru^{II}–N multiple bonded distances in Table 11. Ru–NO distances are *ca.* 0·15 Å shorter than Ru–N_2 or Ru–NO_2, which are in turn *ca.* 0·2 Å shorter than the σ-bonded NH_3 discussed earlier. Assuming the decrease in the Ru–N distance

TABLE 11

Multiple bonded Ru–N distances (Å) in some ruthenium complexes

$[Ru(OH)(NH_3)_4(NO)]Cl_2$ (II)	1·735(3) [a]
$[\{Ru(NH_3)_5\}_2N_2][BF_4]_4,2H_2O$	1·928(6) [b]
trans-$[RuN_3(en)_2N_2]PF_6$	1·894(9) [c]
$[Ru(NH_3)_5(NO_2)]Cl,H_2O$	1·906(5) [d]
$K_2[RuCl_5(NO)]$	1·747(6) [e]
$[NH_4]_2[RuCl_5(NO)]$	1·738(2) [f]
$Na_2[Ru(OH)(NO_2)_4(NO)]$	1·748(4) [g]

[a] This work. [b] Ref. 32. [c] Ref. 26. [d] Ref. 18. [e] Ref. 8. [f] Ref. 7. [g] Ref. 11.

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[28] A. F. Schreiner, S. W. Lin, P. J. Hauser, E. A. Hopcus, D. J. Hamm, and J. D. Gunter, *Inorg. Chem.*, 1972, **11**, 880.

[29] K. Gleu and I. Bueddecker, *Z. anorg. Chem.*, 1952, **268**, 202.

[30] N. M. Sinitsyn and O. E. Zvyagintsev, *Doklady Akad. Nauk. S.S.S.R., Ser. khim.*, 1962, **145**, 109.

[31] H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 2304.

[32] I. M. Treitel, M. T. Flood, R. E. Marsh, and H. B. Gray, *J. Amer. Chem. Soc.*, 1969, **91**, 6512.

[33] M. S. Quinby and R. D. Feltham, *Inorg. Chem.*, 1972, **11**, 2648.

to be due to π-bonding, it is clear that NO^+ is the most effective π-bonding ligand, and N_2 and NO_2^- are about equal, at least when bonded to Ru^{II}. Differences in the Ru–NO distances for the nitrosyl complexes are small. Because of their different charges, and without an accurate Ru–NO distance for $[Ru(NH_3)_5(NO)]^{3+}$, it is not possible to relate the Ru–NO distance to reactivity.

The N–O distance of 1·159(5) Å in (II) is in the range generally observed for NO^+ in ruthenium complexes, 1·11—1·20 Å.[7,8,11,14] It is somewhat longer than in $K_2[RuCl_5NO]$ 1·112(7),[8] $[NH_4]_2[RuCl_5NO]$ 1·131(3),[7] or *trans*-$Na_2[Ru(OH)(NO_2)_4(NO)]$, 1·127(7) Å,[11] and (II) does have the lowest ν(NO) and *F*(N–O) of these complexes.[12] There appears to be some correlation between reactivity and N–O bond length.

The Ru–N–O angle [173·8(3)°] is reasonably close to 180° and the previous conclusion [2] of a markedly bent Ru–N–O moiety is not substantiated. For a C_{4v} complex there is every theoretical reason to expect a strictly linear Ru–N–O,[34,35] but there is, as yet, insufficient accurate structural data for metal nitrosyls to establish whether the slight bending is significant for the bonding scheme. Certainly the angle is one of the lowest of those observed so far for NO^+ complexes.[7,8,11,14]

From calculations involving the covalent radii of Ru^{II} and O, Ru–OH is 1·99—2·10 Å. In (II) the distance [1·961(3) Å] is shorter than expected, and close to that [1·950(2) Å] in *trans*-$Na_2[Ru(OH)(NO_2)_4(NO)]$,[11] in agreement with Veal and Hodgson's suggestion.[7,8] This effect seems confined to NO^+. In $[Os(NH_3)_5N_2]^{2+}$ (as noted previously [7,8]) all Os–NH_3 distances are equal.[36] In $[\{Ru(NH_3)_5\}_2N_2]^{4+}$ the axial Ru–NH_3 distance is 0·02 Å longer than the mean equatorial Ru–NH_3.[32] In *trans*-$[RuCl_4(H_2O)(CO)]^{2-}$ the Ru–OH_2 distance may be as much as 0·09 Å longer than expected.[37] However, in addition to the short axial distances in $[RuCl_5(NO)]^{2+}$, *trans*-$[Ru(OH)(NH_3)_4NO]^{2+}$, and *trans*-$[Ru(OH)(NO_2)_4(NO)]^{2-}$, $[OsCl_2(Ph_3P)_2(HgCl)NO]$ has a *trans*-Cl distance of 2·37(2) Å but a *cis*-Cl distance of 2·42(2) Å.[38] There is much evidence that the π-electron acceptor capabilities of NO^+, CO, and N_2 fall in the order $NO^+ > CO > N_2$, and the σ-electron donor capabilities $NO^+ \leqslant N_2 < CO$.[33,39-43] It seems that only the very powerful π-acceptor and very weak σ-donor NO^+ produces mutually short axial distances.

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[34] J. H. Enemark, *Inorg. Chem.*, 1971, **10**, 1952.

[35] S. F. A. Kettle, *Inorg. Chem.*, 1965, **4**, 1661.

[36] J. E. Fergusson, J. L. Love, and W. T. Robinson, *Inorg. Chem.*, 1972, **11**, 1662.

[37] J. A. Stanko and S. Chaipayungpundhu, *J. Amer. Chem. Soc.*, 1970, **92**, 5580.

[38] G. A. Bentley, K. A. Laing, W. R. Roper, and J. M. Waters, *Chem. Comm.*, 1970, 998.

[39] K. F. Purcell, *Inorg. Chim. Acta*, 1969, **3**, 540.

[40] J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1969, 2841.

[41] D. J. Darensbourg and C. L. Hyde, *Inorg. Chem.*, 1971, **10**, 431.

[42] P. K. Maples, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1971, **10**, 765.

[43] G. M. Bancroft, R. E. B. Garrod, A. G. Maddock, M. J. Mays, and B. E. Prater, *J. Amer. Chem. Soc.*, 1972, **94**, 647.