Crystal and Molecular Structure of Penta-amminenitroruthenium(II) Chloride Hydrate

By **F. Bottomley,** Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada

The crystal and molecular structure of the title compound has been determined from diffractometer data. The metal ion is octahedrally co-ordinated by six nitrogen atoms, with Ru–NO_2 1·906(5), Ru–NH_3(equatorial) 2·131(5) and 2·123(5), and Ru–NH_3(axial) 2·199(6) Å. The NO_2^- ligand [N–O 1·287(5) Å] is acting as a π-electron acceptor and shows a strong *trans*-effect. Crystals are orthorhombic, space group $Ccm2_1$, a = 19·805(5), b = 7·271(7), c = 7·011(3) Å, Z = 4. The structure was refined anisotropically by the block-diagonal approximation (57 parameters) to R 0·025 for 495 observed reflections.

IN the preceding paper [1] the preparation and properties of penta-amminenitroruthenium(II), $[Ru^{II}(NH_3)_5NO_2]^+$, were described. Other nitro-complexes of ruthenium(II) are formed similarly: pentacyanonitroruthenium(II), $[Ru^{II}(CN)_5NO_2]^{4-}$,[2] aniononitrobis-(2,2′-bipyridyl)ruthenium(II), $[Ru^{II}(bipy)_2NO_2X]$, and aniononitrobis-(*o*-phenanthroline)ruthenium(II), $[Ru^{II}(phen)_2NO_2X]$, (X = Cl, Br, or NO_2).[3,4] These complexes contain ligands capable of acting as π-electron acceptors. Ruthenium(II) complexes without π-electron acceptors are usually readily oxidized, and the stability of $[Ru^{II}(NH_3)_5NO_2]^+$ towards oxidation [1] indicated the nitro-ligand was acting as a π-electron acceptor.

Marked differences between $[Ru^{II}(NH_3)_5NO_2]^+$ and the formally similar penta-amminenitrocobalt(III), $[Co^{III}(NH_3)_5NO_2]^{2+}$, were found.[1] The latter complex has Co^{III}–NO_2 bond distances of 1·92 (dibromide salt [5]) or 1·91 Å (dichloride salt [6]), only 0·06 Å shorter than the mean Co^{III}–NH_3 distance in the $[Co^{III}(NH_3)_5NO_2]^{2+}$ ion,[5,6] and *ca.* 0·04 Å shorter than the Co^{III}–NH_3 distance in $[Co^{III}(NH_3)_6]I_3$.[7] Such a small difference between the Co^{III}–NO_2 and Co^{III}–NH_3 bond distances indicates little multiple bonding between cobalt(III)

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[1] F. Bottomley and J. R. Crawford, preceding paper.

[2] E. J. Baran and A. Müller, *Chem. Ber.*, 1969, **102**, 3915.

[3] T. J. Meyer, J. B. Godwin, and N. Winterton, *Chem. Comm.*, 1970, 872.

[4] J. B. Godwin and T. J. Meyer, *Inorg. Chem.*, 1971, **10**, 2150.

[5] F. A. Cotton and W. T. Edwards, *Acta Cryst.*, 1968, **B24**, 474.

[6] O. Börtin, *Acta Chem. Scand.*, 1968, **22**, 2890.

[7] N. E. Klime and J. A. Ibers, *Acta Cryst.*, 1969, **B25**, 1968.

and the nitrite ligand. Also, no *trans*-effect was found for the NO_2^- ligand in the cobalt complex.[5,6,8,9]

In order to provide evidence for multiple bonding between ruthenium(II) and nitrite, and to discover whether nitrite has a *trans*-effect in $[\mathrm{Ru^{II}(NH_3)_5NO_2}]^+$, the structure of $[\mathrm{Ru^{II}(NH_3)_5NO_2}]\mathrm{Cl,H_2O}$ has been determined and is reported here.

EXPERIMENTAL

Crystals of $[\mathrm{Ru^{II}(NH_3)_5NO_2}]\mathrm{X,H_2O}$ (X = Cl or Br) were grown as described in ref. 1. They formed approximately parallelepipeds, elongated along *c*, but were not well formed and many were twinned. Great difficulty was experienced in obtaining data from the crystals, two major problems being encountered. First, once removed from their mother liquor the crystals became amorphous quite rapidly (*ca.* 2 days). This was not decomposition, as was shown by their i.r. spectrum which was unchanged over a period of several months, although after this period the crystals were completely opaque and crumbled on contact. The observation that the more rigorously a crystal was dried the more rapidly it become amorphous indicated that loss of water of crystallization was responsible for breakdown of the crystal. The problem of variable water of crystallization in these compounds was referred to before.[1] Attempts to mount crystals in their mother liquor were not successful since decomposition occurred unless the temperature was <5 °C. Secondly, the crystals attacked the Lindemann glass used to contain them (probably because of their highly alkaline nature), becoming dark brown over a period of a few days. Crystals coated with Shellac immediately after air drying were reasonably stable over the period necessary for data collection, and the crystal used for the structure determination was treated in this way. Weissenberg photographs taken after data collection showed a few diffuse streaks, which may have been due to decomposition or breakdown of the crystal.

Collection and Reduction of Intensity Data.—Initial work was performed on the bromide salt with Mo-K_α radiation. *hk*0—2 Weissenberg, *h*0—1*l* and 0—3*kl* precession photographs showed Laue symmetry *mmm* and systematic absences *hkl*: $h + k = 2n + 1$, 0*kl*: $l = 2n$. The possible space groups were therefore *Ccmm* (D^{17}_{2h}, No. 63), *Cc*2*m* (C^{16}_{2v}, 40), and *Ccm*2_1 (C^{12}_{2v}, 36), these being non-standard settings of *Cmcm*, *Ama*2, and *Cmc*2_1 respectively.

Crystal Data. $[\mathrm{Ru^{II}(NH_3)_5NO_2}]\mathrm{Br,H_2O}$, $M = 330{\cdot}2$, Orthorhombic, $a = 20{\cdot}27$, $b = 7{\cdot}31$, $c = 7{\cdot}15$ Å, $D_c = 2{\cdot}07$, $Z = 4$, D_m (by flotation) = 2·06. Space group *Ccmm*, *Cc*2*m*, or *Ccm*2_1.

A unique data set (202 observed reflections, $2\theta < 40°$) were collected from this crystal, when the problem of the attack on Lindemann glass was discovered. The net count of the standard reflection decreased by 55% in the 12 h required to collect the data. Since such a decrease in intensity indicated the data would be of inferior quality no further use was made of this data, the experience gained being applied to the chloride salt. Weissenberg photographs showed this was isomorphous and probably isostructural with the bromide.

Crystal data. $[\mathrm{Ru^{II}(NH_3)_5NO_2}]\mathrm{Cl,H_2O}$, $M = 285{\cdot}7$, Orthorhombic, $a = 19{\cdot}805(5)$, $b = 7{\cdot}271(7)$, $c = 7{\cdot}011(3)$ Å,† $U = 1009{\cdot}6$ Å^3, $D_m = 1{\cdot}83$, $Z = 4$, $D_c = 1{\cdot}85$. Space group: *Ccmm*, *Cc*2*m*, or *Ccm*2_1 (structure refinement, *vide infra*, indicates *Ccm*2_1 is correct). Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; $\mu(\text{Mo-}K_\alpha) = 17{\cdot}2$ cm^{-1}.

A crystal 0·12 × 0·2 × 0·34 mm was coated with Shellac, fixed to a glass rod and mounted on a Picker FACS 1 computer controlled diffractometer with the *c* axis *ca.* 1° mis-set from the diffractometer ϕ axis.[10] Cell dimensions were determined with Mo-K_α radiation from 6 accurately centred reflections with $2\theta > 40°$. Three forms, *hkl*, $h\bar{k}l$, and $\bar{h}\bar{k}l$ of the data were collected by the ω—2θ scan technique with zirconium filtered Mo-K_α radiation to 2θ 50° using the following instrumental settings: 1·5° scan corrected for $K_{\alpha1}$–$K_{\alpha2}$ dispersion; scan rate 1° min^{-1} in 2θ; stationary 20 s background counts on either side of the peak were used to correct for background; attenuators to reduce the count by a factor of *ca.* 3 were automatically inserted when the count reached 1×10^4 s^{-1}; the pulse-height analyser was set for *ca.* 97% of the Mo-K_α window; the take-off angle was *ca.* 1·0°. The 910 reflection was measured after every 15 reflections as standard. Its net count was found to decrease approximately 6% over the period of measurement, and allowance for this decrease was made during data processing.

The data were averaged to give the *hkl* form using a procedure whereby the average was taken only if the equation $[\mathrm{N}(1) - \mathrm{N}(2)]/[\mathrm{T}(1) - \mathrm{T}(2)] \leqslant 1{\cdot}96$ was satisfied [where N and T are net and total counts for measurements (1) and (2) respectively].[11] Otherwise the measurement with the higher net count was accepted. Only 24 of 532 reflections were not averaged in all forms, all 24 having a very high count. Of the 532 reflections, 37 had a net count either <10 or <0·05 times the background count. These were considered unobserved and not used in the structure refinement. When the structure determination was completed all 37 were found to have a small $|F_c|$. These reflections are asterisked in the final list of structure factors. Lorentz and polarization corrections were applied.

Because the crystal was not well formed and was coated with Shellac determination of its faces was not possible and hence an appropriate absorption correction could not be made. An approximate calculation based on the crystal treated as a cylinder showed the transmission factors did not vary appreciably.

Structure Solution and Refinement.—The Patterson function could not be interpreted in space group *Cc*2*m* because the short *b* and *c* axes gave chemically unreasonable interatomic distances. Solutions for the ruthenium and chloride ions were found, with difficulty, in *Ccm*2_1 and *Ccmm*. The structure was refined in *Ccm*2_1. Two cycles of block-diagonal refinement with unit weighting and isotropic thermal parameters for ruthenium and chloride ions gave *R* 0·23. The function minimized throughout the refinement was $\Sigma w(|F_o| - |F_c|)^2$. The scattering factors for ruthenium were taken from ref. 12 and those

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† Throughout this paper figures in parentheses are estimated standard deviations relating to the least significant figure.

[8] J. Halpern, R. A. Palmer, and L. M. Blakely, *J. Amer. Chem. Soc.*, 1966, **88**, 2877.

[9] D. R. Lewellyn, C. J. O'Connor, and A. L. Odell, *J. Chem. Soc.*, 1964, 196.

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

[11] All calculations in this work were by the set of programmes written by F. R. Ahmed and his associates at the National Research Council, Ottawa, Canada.

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

for chlorine, nitrogen, oxygen, and hydrogen from ref. 13. Ruthenium and chlorine were corrected for anomalous dispersion.

TABLE 1

Comparison of dimensions in centrosymmetric (*Ccmm*) and non-centrosymmetric (*Ccm*2_1) space groups (hydrogen atoms omitted from refinement)

Dimension	*Ccm*2_1	*Ccmm*
Ru–N(1)	1·915(8) Å	1·915(7) Å
Ru–N(2)	2·209(9)	2·202(8)
Ru–N(3)	2·139(8)	2·133(4)
Ru–N(4)	2·125(8)	
N(1)–O(1)	1·282(7)	1·276(7)
Ru–N(1)–O(1)	122·9(1·5)°	123·1(3)°
O–N–O	114·1(1·7)	113·9(4)

A Fourier synthesis revealed all other non-hydrogen atom positions, and inclusion of these reduced *R* to 0·13 without refinement. Three cycles of isotropic refinement with unit weights gave *R* 0·082 and a difference-Fourier synthesis revealed the necessity for anisotropic thermal parameters for the ruthenium and chloride ions. A weighting scheme of the form $\sqrt{w} = 1/\{1 + [|F_o| - P_2/P_1]^4\}^{\frac{1}{2}}$, where $P_2 = |F_o|_{\text{average}}$ and $P_1 = (|F_o|_{\text{average}} - 10)$ was introduced and 6 cycles of refinement reduced *R* to 0·035. A difference-Fourier synthesis showed all atoms required anisotropic thermal parameters and revealed the hydrogen atom positions. At this stage consideration was given to the fact that *Ccm*2_1 is a polar space group and the problem of the absolute configuration arises. Therefore, two parallel series of refinements were made (hydrogen atoms excluded). In both refinements all atoms were assigned anisotropic thermal parameters, but in one the *hkl* form of the data was used, in the other $\bar{h}\bar{k}\bar{l}$.[14] The *hkl* refinement converged at *R* 0·030 after 4 cycles, the $\bar{h}\bar{k}\bar{l}$ at 0·032 after 5. The *hkl* data was therefore accepted. The reduction of 0·005 in *R* after introduction of anisotropic thermal parameters for all atoms is significant at better than the 0·005 confidence level.[15]

Refinement in *Ccmm* was tried also at this stage. With the parameters from the second *hkl* cycle as starting point this refinement converged at *R* 0·032 in 4 cycles. The difference in *R* between the two space groups favours the non-centric *Ccm*2_1 at the 0·005 confidence level.[15] A number of other points were considered in choosing the space group. First, a difference was found between the *hkl* and $\bar{h}\bar{k}\bar{l}$ refinements, which would not be observed if the structure was centrosymmetric. Secondly, the difference synthesis in *Ccm*2_1 which located the hydrogen atoms showed no evidence of disorder in their position. The hydrogen atoms attached to N(2) must be disordered in *Ccmm*. However, the standard deviations of *z* are relatively large for those atoms having a fixed *z* in *Ccmm*. The bond lengths derived from the two refinements are given in Table 1, and do not differ significantly.

TABLE 2

Positional and thermal parameters * for $[Ru^{II}(NH_3)_5(NO_2)]Cl,H_2O$

Atom	*x*	*y*	*z*	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{23}$	$10^5\beta_{13}$	$10^5\beta_{12}$
Ru	0·12169(2)	0·0	0·0	98(1)	1158(8)	922(8)	0	−138(19)	0
Cl	0·24712(7)	0·5	0·0026(11)	140(3)	161(3)	130(3)	0	167(9)	0
				$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{23}$	$10^4\beta_{13}$	$10^4\beta_{12}$
N(1)	0·0255(3)	0·0	−0·0103(29)	11(1)	131(10)	64(21)	0	−36(15)	0
N(2)	0·2326(3)	0·0	−0·0129(35)	10(1)	200(14)	141(31)	0	−51(18)	0
N(3)	0·1245(2)	0·2080(7)	0·2140(7)	13(1)	150(10)	114(9)	12(17)	15(6)	−25(6)
N(4)	0·1238(2)	0·1974(7)	−0·2230(7)	19(1)	130(9)	111(9)	64(16)	19(6)	−3(6)
O(1)	−0·0101(2)	0·1478(5)	−0·0085(20)	13(1)	139(1)	158(13)	1(38)	1(11)	25(4)
O(2)	0·0474(4)	0·5	−0·0136(53)	29(2)	137(12)	555(59)	0	105(34)	0

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

The hydrogen atoms were introduced in space group *Ccm*2_1. The difference-Fourier synthesis showed the mirror plane at $y = 0$ was a mirror plane of the N(2) ammine group, which had normal geometry. The hydrogen atoms of this group were therefore placed in calculated positions (N–H 0·90 Å, Ru–N–H and H–N–H 109·5°). The positions of the hydrogen atoms attached to O(2), N(3), and N(4) were taken from the difference-Fourier synthesis. Refinement converged in 6 cycles to a final *R* of 0·025. On the final cycle no shift was $> 0{\cdot}16\sigma$. A difference-Fourier synthesis had as its highest peak one of 0·75 eÅ^{-3} *ca.* 1 Å from the ruthenium ion and was otherwise featureless. An error analysis indicated relatively poor agreement for the 5 reflections with $F_o > 200$, but did not indicate the necessity for absorption or extinction corrections, nor any unexpected trends.

The parameters obtained from the last cycle are given in Table 2, together with their estimated standard deviations derived from the inverse matrix. Table 3 gives the hydrogen atom positions used in the refinement. Observed and calculated structure factors are listed in Supplementary Publication No. 20440 (8 pp., 1 microfiche).†

TABLE 3

Positional parameters for the hydrogen atoms

Atom	*x*	*y*	*z*	B_{iso}
H(1) [N(2)] *	0·248	0·0	−0·134	3·5
H(2) [N(2)]	0·248	0·101	0·048	3·5
H(3) [O(2)]	0·020	0·393	−0·009	3·5
H(4) [N(3)]	0·160	0·189	0·294	3·5
H(5) [N(3)]	0·083	0·203	0·280	3·5
H(6) [N(3)]	0·129	0·306	0·150	3·5
H(7) [N(4)]	0·133	0·309	0·175	3·5
H(8) [N(4)]	0·154	0·175	−0·305	3·5
H(9) [N(4)]	0·083	0·188	−0·275	3·5

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

From Table 2 it is seen that the thermal parameters of O(2) (the oxygen atom of the water of crystallization) are much larger than for the other atoms (the isotropic thermal parameter was approximately twice the values

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† For details of Supplementary Publications, see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

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

[14] J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, 1964, **17**, 781.

[15] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

for the other atoms). It appeared from this, and other evidence,[1] the formula of the compound was $[Ru^{II}(NH_3)_5NO_2]Cl,xH_2O)$ ($x < 1$). No attempt was made to vary the site occupancy of O(2), since it seemed the introduction of this parameter would not provide any worthwhile value of x.

DISCUSSION

Description of the Structure.—The structure consists of $[Ru^{II}(NH_3)_5NO_2]^+$ ions connected to H_2O and Cl^- by hydrogen bonds. The contents of the unit cell are shown in Figure 1. Table 4 lists distances between atoms which may be involved in hydrogen bonding. The positions of the hydrogen atoms H(3)—(9) are not accurate, being obtained from the difference-Fourier synthesis, but taken in conjunction with i.r. evidence[1] they allow some discussion of the hydrogen bonding. By the criteria of ref. 16 reasonably strong hydrogen bonding exists between the nitrite ligand [O(1)] and the water of crystallization [O(2)] [involving H(3); Figure 1] and between the *trans*-ammonia ligand [N(2)] and the chloride ion [involving H(1)]. Weaker hydrogen bonds connect the equatorial ammonia ligands [N(3) and N(4)] to Cl^- [*via* H(4) and H(8)] and to the water of crystallization [*via* H(6) and H(7)]. In addition weak intramolecular hydrogen bonds connect the equatorial NH_3 ligands to the NO_2^- ligand *via* H(5) and H(9). The O(1) · · · H(3)–O(2) hydrogen bond is manifested by the broad H_2O vibrations in the i.r. spectrum, and the NH_3 vibrations also show evidence of hydrogen bonding.[1]

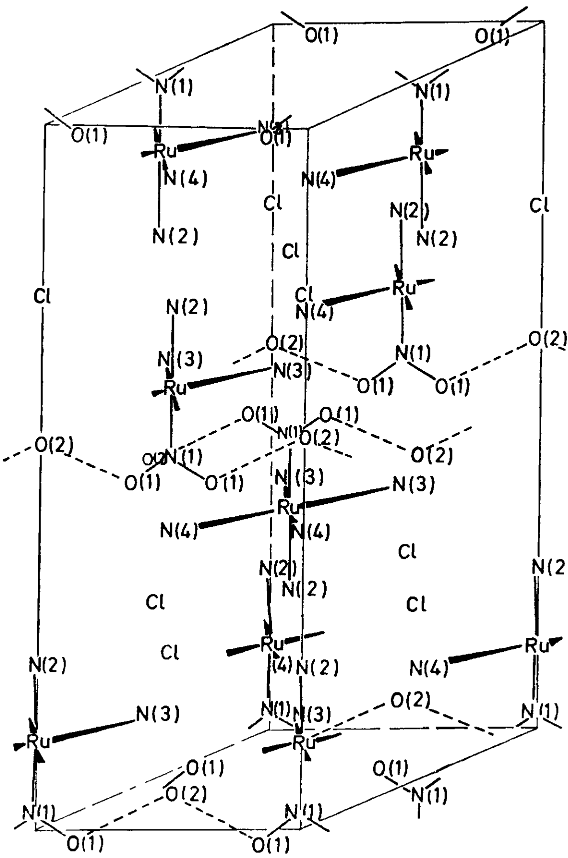

FIGURE 1 The unit cell of $[Ru^{II}(NH_3)_5NO_2]Cl,H_2O$

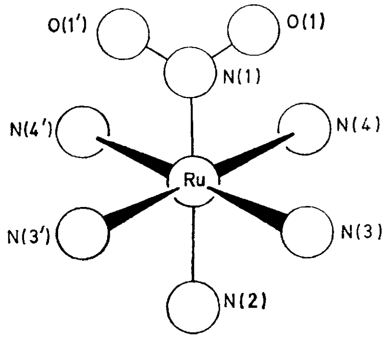

FIGURE 2 A diagram of the cation showing the numbering system used

The geometry of the cation and the atom numbering system used is shown in Figure 2, and the bond distances and angles in Tables 5 and 6. The dimensions are uncorrected. The cation has strict C_s crystallographic symmetry, the plane passing through N(1),Ru,-N(2) and bisecting the O(1)–N(1)–O(1′), N(3)–Ru–N(3′), and N(4)–Ru–N(4′) angles. Weighted mean planes (Table 7) show deviations from idealized C_{2v} symmetry are small, consisting of rotation of N(2) and N(3′) by an average of 2·65° with respect to N(1) and N(4). The centric *Ccmm* structure has crystallographic C_{2v} symmetry of the non-hydrogen atoms.

TABLE 4

Hydrogen bonding in $[Ru^{II}(NH_3)_5(NO_2)]Cl,H_2O$

Bond A · · · H–B	Distance A–B (Å)	Distance A · · · H (Å)
O(1) · · · H(3)–O(2)	2·80	1·9
O(1) · · · H(4)–N(3)	3·02	3·3
O(1) · · · H(5)–N(3)	3·02	2·1
O(1) · · · H(6)–N(3)	3·02	3·2
O(1) · · · H(7)–N(4)	3·03	3·6
O(1) · · · H(8)–N(4)	3·03	3·2
O(1) · · · H(9)–N(4)	3·03	2·2
O(2) · · · H(4)–N(3)	3·06	3·8
O(2) · · · H(5)–N(3)	3·06	3·1
O(2) · · · H(6)–N(3)	3·06	2·4
O(2) · · · H(7)–N(4)	3·05	2·5
O(2) · · · H(8)–N(4)	3·05	3·8
O(2) · · · H(9)–N(4)	3·05	3·0
Cl^- · · · H(1)–N(2)	3·42	2·5
Cl^- · · · H(2)–N(2)	3·42	2·9
Cl^- · · · H(4)–N(3)	3·58	2·7
Cl^- · · · H(5)–N(3)	3·58	3·9
Cl^- · · · H(6)–N(3)	3·50	2·9
Cl^- · · · H(7)–N(4)	3·50	2·9
Cl^- · · · H(8)–N(4)	3·50	2·7
Cl^- · · · H(9)–N(4)	3·50	3·9

TABLE 5

Intermolecular distances (Å) in the $[Ru^{II}(NH_3)_5(NO_2)]^+$ cation

Ru–N(1)	1·906(5)	Ru–N(4)	2·123(5)
Ru–N(2)	2·199(6)	N(1)–O(1)	1·287(5)
Ru–N(3)	2·131(5)		

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[16] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' Benjamin, New York, 1968.

Bond lengths in the cation. The equatorial Ru–NH_3 distances [2·123(5) and 2·131(5) Å] are essentially equal and the mean value (2·127 Å) may be compared to that [2·144(5) Å] in $[Ru^{II}(NH_3)_6]I_2$ [17] and to the mean [2·124(15) Å] of the Ru–NH_3(equatorial) distances in $[(NH_3)_5Ru^{II}N_2\,Ru^{II}(NH_3)_5](BF_4)_4,2H_2O$.[18] The difference in the Ru^{II}–NH_3 bond distances for the last two complexes has been ascribed to partial withdrawal of electrons from the ruthenium by d_π–$N_{2\pi^*}$ bonding in the dinitrogen complex.[17,18] Presumably a similar effect is operating in the present case. Evidence for multiple bonding between the ruthenium and the NO_2^- ligand is given by the short Ru–N(1) distance [1·906(5) Å]. $[Ru^{II}(NH_3)_5(NO)]Cl_3,H_2O$ was reported to have Ru–N(O) 1·80(1) Å.[19] Better comparison can probably be made with the more accurate values for Ru^{II}–N_2 in $[(NH_3)_5Ru^{II}N_2Ru^{II}(NH_3)_5](BF_4)_4,2H_2O$ 1·928(6),[18] and Ru^{II}–N_2 in $[Ru^{II}(en)_2N_2N_3]PF_6$ 1·894(9) Å,[20] both of which complexes show Ru–N_2 multiple bonding.

TABLE 6

Intramolecular angles (°) in the $[Ru^{II}(NH_3)_5(NO_2)]^+$ cation

N(1)–Ru–N(2)	175·5(5)	N(3)–Ru–N(3′)	90·4(2)
N(1)–Ru–N(3)	93·0(4)	N(3)–Ru–N(4′)	176·2(2)
N(1)–Ru–N(4)	89·5(4)	N(4)–Ru–N(4′)	85·1(2)
N(2)–Ru–N(3)	90·2(4)	Ru–N(1)–O(1)	123·3(9)
N(2)–Ru–N(4)	87·1(4)	O(1)–N(1)–O(1′)	113·2(1·0)
N(3)–Ru–N(4)	92·2(2)		

TABLE 7

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

Plane (1):

Ru, N(1), N(2), O(1), O(1′) $0{\cdot}0181X + 0{\cdot}0Y - 0{\cdot}9998Z = 0{\cdot}0436$

[Ru − 0·0001(0), N(1) 0·038(20), N(2) 0·130(24), O(1) 0·012(14)]

Plane (2):

Ru, N(1), O(1), O(1′) $0{\cdot}0245X + 0{\cdot}0Y - 0{\cdot}9997Z = 0{\cdot}0589$

[Ru 0·0000(0), N(1) 0·025(20), O(1) − 0·004(14), N(2) 0·144(24)]

Plane (3):

Ru, N(3), N(3′), N(4), N(4′) $1{\cdot}0000X + 0{\cdot}0Y - 0{\cdot}0047Z = 2{\cdot}4105$

[Ru − 0·0004(4), N(3) 0·049(4), N(4) 0·049(5)]

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

The Ru^{II}–N(2) distance (the *trans*-NH_3) of 2·199(6) Å is significantly (0·07 Å) longer than the mean Ru–NH_3-(equatorial), or the Ru–NH_3 distance in $[Ru^{II}(NH_3)_6]I_2$,[17] and indicates the strong *trans*-effect of NO_2^- in the complex. This is in contrast to $[Co^{III}(NH_3)_5(NO_2)]^{2+}$. Although the Co^{III}–NO_2 bond [1·921(21);[5] 1·912(14) Å [6]] is *ca.* 0·06 Å shorter than the Co^{III}–NH_3 distances there is no significant difference between the axial and equatorial Co^{III}–NH_3 distances [Co–N(axial): 1·976(19) [5] and 1·977(16);[6] Co–N(equatorial): 1·985(15) and 1·972(15),[5] and 1·956(7) and 1·957(8) Å [6]] and no *trans*-effect was observed.[8,9]

The NO_2^- ligand has N–O 1·287(5) Å and O–N–O 113·2(1·0)°. These may be compared with values for NO_2^- in $NaNO_2$: N–O 1·236(14) Å, O–N–O 115·3(1·7)°.[21] In $[Co^{III}(NH_3)_5(NO_2)]^{2+}$ the N–O values are reported to be 1·161(22) [5] and 1·230(11) Å, and the O–N–O angles 113·9(1·9) [5] and 120·8(1·4)° [6] (the value for the latter angle is surprising in view of the angle in NO_2^-, that found in ref. 5 and the present work). The distance found in the present work is longer than either of those reported for the cobalt complex, again reflecting multiple bonding of ruthenium(II) to the ligand *via* d_π–$NO_{2\pi^*}$ interaction.

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