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Crystal and Molecular Structure of "Ruthenium Black"–Di-μ-amido-bis[tetraammineruthenium(III)] Chloride Tetrahydrate

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A black crystalline complex of stoichiometry $Ru_2N_{10}O_4H_{36}Cl_4$ has been isolated from an ammoniacal solution of Ru(III) chloride in the presence of air (ruthenium red solution). The crystal and molecular structure of this black complex, di-μ-amido-bis[tetraammineruthenium(III)] chloride tetrahydrate, $[(NH_3)_4Ru(NH_2)_2Ru(NH_3)_4]Cl_4 \cdot 4H_2O$, has been determined from three-dimensional X-ray data collected by counter techniques. The structure was refined by full-matrix least-squares methods. The refinement was carried out using 2114 nonzero reflections for which $F^2 > \sigma(F^2)$ and assuming anisotropic thermal motion for all nonhydrogen atoms. The least-squares refinement led to a final value of the conventional R factor (on F) of 0.036. The centrosymmetric cation $[(NH_3)_4Ru(NH_2)_2Ru(NH_3)_4]^{4+}$ features distorted octahedral Ru centers, two amido bridging groups, and a relatively short Ru-Ru distance of 2.625 (1) Å. The $Ru-NH_2-Ru$ bridging bond angle is acute [81.0 (1)°], suggesting Ru-Ru bonding interaction. The chloride ions and oxygen atoms of the water molecules occupy the "holes" in the crystal. Crystal data are as follows: monoclinic, space group $P2_1/n$; $a = 9.686$ (1) Å, $b = 9.872$ (1) Å, $c = 10.720$ (1) Å, $\beta = 95.69$ (3)° (temperature 22°); $Z = 2$; $d_{\text{calcd}} = 1.90$ g/cm^3.

Introduction

When ruthenium(III) chloride is allowed to stand in concentrated aqueous ammonia in the presence of air, dark red and brown compounds are formed.[2,3] These compounds are of considerable interest because they contain polynuclear, mixed-valence ruthenium complex cations.[2-8] The structure proposed[3-6] for the ruthenium red cation features a linear oxo-bridged sequence of the type $[(NH_3)_5Ru^{III}\text{-}O\text{-}Ru^{IV}(NH_3)_4\text{-}O\text{-}Ru^{III}(NH_3)_5]^{6+}$. The proposal is probably correct in view of the fact that a recent X-ray structural study[8] has established a linear Ru-O-Ru-O-Ru unit in the closely related ethylenediamine analog $[(NH_3)_5RuORu(en)_2ORu(NH_3)_5]Cl_6$.

Fletcher, who originally suggested the linear trinuclear cation structure for ruthenium red, also showed that ruthenium brown is a distinctly different species.[3] In addition to the red and brown compounds, we have isolated an insoluble black crystalline material in very small yield from ammoniacal solutions of ruthenium chloride. We present here the X-ray characterization of this new compound, which we will refer to as ruthenium black. Theoretical and experimental electronic structural studies of ruthenium black will be reported in subsequent papers.[9,10]

Experimental Section

Preparation of the Complex. The preparation of ruthenium black follows closely the original procedure of Fletcher[3] for the preparation of ruthenium red chloride. Commercial ruthenium chloride[11] was reduced to ruthenium(III) by refluxing for 2 hr with a small amount of ethanol. The liquid was concentrated by evaporation and an excess of concentrated ammonia (4 ml of 15 *M* NH_4OH/1 ml of concentrated solution) was added. The resulting solution was heated in air at about 90° for 2–3 hr with frequent additions of ammonia. The resulting solution was concentrated, filtered, and cooled to 0°, whereupon a brown solid crystallized out of solution. The solid was recrystallized three times from dilute NH_3 solution. A nearly saturated solution of the solid in dilute (~1 *M*) aqueous ammonia was allowed to stand overnight at 10° and a small yield of black crystals was obtained. The few black crystals were collected and washed with ethanol and diethyl ether, dried at 60° for several hours, and stored over Drierite. We will show that the crystals obtained by this procedure correspond to the formulation $[(NH_3)_4Ru(NH_2)_2Ru(NH_3)_4]Cl_4 \cdot 4H_2O$.[12]

Collection and Reduction of Intensity Data. The black crystals, obtained by the method described above, were many-faceted, and a major axis of the crystal was not apparent from its morphology. A series of 15° oscillation photographs was taken at random orientations of the crystal until a major axis was suggested by the appearance of distorted layer lines. The crystal was then aligned and a series of Weissenberg and precession photographs taken with Mo $K\bar{\alpha}$ and Cu $K\bar{\alpha}$ radiations indicated systematic absences of reflections $h0l$ with $h + l$ odd and $0k0$ with k odd. The crystals were assigned to the monoclinic system, space group $P2_1/n$.

Sixteen reflections ($2\theta > 40°$) were centered in the counter aperture by varying 2θ, ϕ, and χ in conjunction with the left–right and top–bottom balancing features of the variable receiving aperture. The cell constants and their standard deviations were determined by a least-squares refinement of the 2θ values for these 16 reflections. The results (Mo $K\bar{\alpha}$ radiation, λ 0.71069 Å) are $a = 9.686$ (1) Å, $b = 9.872$ (1) Å, $c = 10.720$ (1) Å, $\beta = 95.69$ (3)° (22°). The corresponding ϕ and χ values for the 16 reflections were used as input data for the orientation program operating under the CRYM crystallographic computing system. The independent intensity data set was collected from a single crystal at 22° using a Datex-automated General Electric diffractometer with an XRD-6 power supply. The crystal was mounted with its c axis approximately parallel to the ϕ axis of the diffractometer. The crystal was multifaceted but had spherical shape and did not measure more than 0.10 mm in diameter. The density was not measured but was calculated as 1.90 g/cm^3 assuming two formula weights per unit cell.

A total of 2326 independent reflections were collected by the θ–2θ scan technique in the range $4° \leqslant 2\theta$ (Mo $K\bar{\alpha}$) $\leqslant 55°$. A takeoff angle of 3° was used with the counter wide open. A check of several high-angle reflections indicated that our settings included the entire peak in the scan. The pulse height analyzer was set for approximately a 90% window centered on the Mo $K\alpha$ peak. A scan rate of 2°/min (in 2θ) was used with stationary-counter, stationary-crystal back-

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(12) An alternative recrystallization procedure was found to produce black crystals containing two ammonium chlorides in place of the four waters of hydration.[9] In this procedure, the concentrated solution of ruthenium red chloride was filtered through a very fine frit and concentrated ammonia solution was added to the filtrate until the ruthenium red solution was basic (pH 9–10). Evaporation of this solution, carefully protected from foreign particles, produced black crystals in somewhat larger yield than the original method. The cell constants for $[(NH_3)_4Ru(NH_2)_2Ru(NH_3)_4]Cl_4 \cdot 2NH_4Cl$ are very similar to those of the hydrated form of ruthenium black, and it is probable that the complex cation has the same structure in the two cases.

Table I. Positional and Thermal Parameters of the Heavy Atoms[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	4701 (0.2)	4351 (0.2)	6008 (0.2)	35 (0.2)	40 (0.2)	31 (0.2)	0.3 (0.5)	13 (0.3)	3 (0.4)
N(1)	5656 (3)	6141 (3)	5834 (2)	50 (3)	41 (3)	38 (2)	−1 (4)	13 (4)	−11 (4)
N(2)	4949 (3)	4594 (3)	8007 (2)	71 (3)	65 (4)	39 (2)	−8 (5)	16 (4)	−4 (4)
N(3)	2728 (3)	5291 (3)	6056 (3)	53 (3)	56 (3)	46 (2)	−8 (4)	22 (4)	−0.5 (4)
N(4)	6619 (3)	3274 (3)	6241 (3)	56 (3)	54 (3)	52 (2)	−21 (5)	19 (4)	−9 (4)
N(5)	3694 (3)	2488 (3)	6390 (3)	59 (3)	55 (3)	56 (2)	−13 (5)	15 (4)	11 (4)
Cl(1)	5860 (1)	956 (1)	8510 (1)	65 (1)	106 (1)	73 (1)	−5 (2)	−12 (1)	−57 (2)
Cl(2)	1723 (1)	3690 (1)	8684 (1)	99 (1)	71 (1)	66 (1)	−13 (2)	56 (1)	23 (1)
O(1)	8068 (4)	4327 (4)	8987 (3)	125 (4)	109 (4)	85 (3)	32 (7)	22 (5)	15 (5)
O(2)	4874 (5)	7501 (5)	8934 (5)	219 (6)	107 (4)	118 (3)	22 (8)	−9 (8)	46 (6)

[a] The atom-labeling scheme (Ru and N) is given in Figure 2. Positional and thermal parameters have been multiplied by 10^4. The estimated standard deviations in the least significant figure(s) as derived from the inverse matrix of the final least-squares refinement cycle are given in parentheses in Tables I and II. The temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{33}kl)]$.

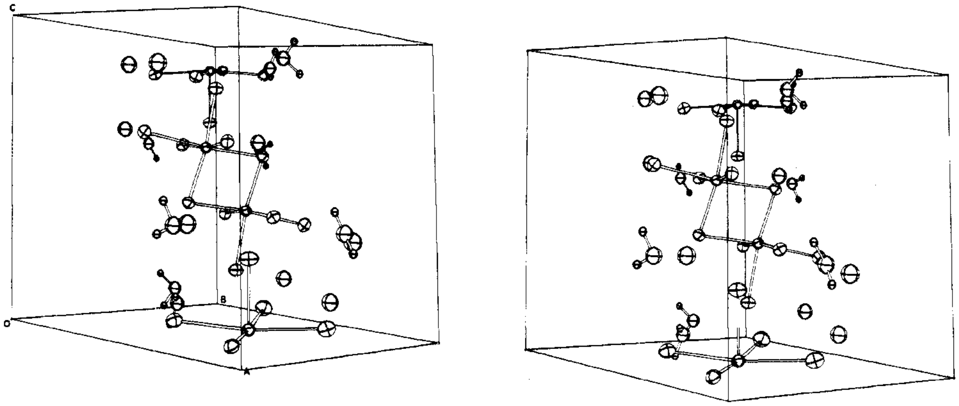

Figure 1. A stereoscopic view of the packing in a unit cell of $[(NH_3)_4Ru(NH_2)_2Ru(NH_3)_4]Cl_4\cdot 4H_2O$. Hydrogen atoms on the cation have been omitted. The 40% probability ellipsoids are shown here and in Figure 2.

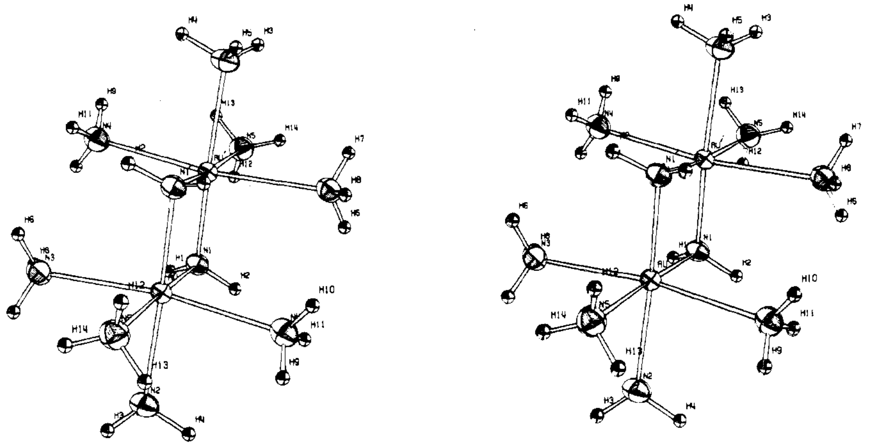

Figure 2. A stereoscopic view of the binuclear cation $[(NH_3)_4Ru(NH_2)_2Ru(NH_3)_4]^{4+}$.

ground counts of 30-sec duration taken at each end of the scan. A symmetric scan range of between 2 and 3.4° was adjusted to account for α_1-α_2 splitting.

Throughout the data collection the intensity of a reference reflection, 340, was measured every 20 reflections. During the approximately 10 days of 24-hr operation, the arcs of the goniometer had to be readjusted twice. Eight hundred and seventy-eight reflections were measured twice and the weights averaged in the initial processing of the data. There were no signs of crystal decomposition in the X-ray beam.

The values for the observed intensities, I_{obsd}, were derived from the scalar counts using the formula

$$I_{\text{obsd}} = S - \frac{B_1 + B_2}{2}\left(\frac{t}{30}\right)$$

where S is the scan count, B_1 and B_2 are the two background counts, and t is the scan time in seconds. Negative values of I_{obsd} calculated from this formula were set equal to zero. The standard deviation for each reflection was calculated using

$$\sigma^2(I_{\text{obsd}}) = S + \frac{B_1 + B_2}{2}\left(\frac{t}{30}\right)^2 + (0.02S)^2$$

The last term in this equation is an empirical term (Busing and Levy[13]) which presumably allows for errors not due to counting statistics. The standard deviations calculated in this way were the basis for the weights used in the least-squares refinement. The intensities and their standard deviations were corrected for Lorentz and polarization effects but not for absorption.[14] The linear absorption coefficient (Mo Kα) for this compound is 19.8 cm^{-1}. The data were put on an approximately absolute scale with a Wilson plot.[15] The result of a tabulation of E statistics[16] and of an application of the zero-moment

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

(14) Neglect of absorption effects could have led to errors in the relative values of the structure factors amounting to about 3% in an extreme case.

(15) A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

(16) I. L. Karl, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, **19**, 713 (1965).

test of Howells, Phillips, and Rogers[17] suggested a centric space group in accord with our assignment, $P2_1/n$. Of the 2326 reflections collected, 2114 obeyed the condition $F^2 > \sigma(F^2)$ and were used in subsequent calculations.

Elucidation and Refinement of the Structure

Heavy-atom methods were applied to solve the structure. The positions of the ruthenium and chlorine atoms were readily determined from a three-dimensional Patterson function calculation. The remaining nonhydrogen atoms were located in a Fourier map with the exception of one oxygen atom which became apparent in a difference Fourier map. Two cycles of full-matrix, least-squares refinement of the coordinates and an anisotropic temperature factor for the ruthenium atoms and isotropic temperature factors for the chlorine atoms reduced the R index ($R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$) to 0.061.

At this point difference maps were calculated in the planes where the hydrogen atoms of the NH_3 groups were expected, assuming a tetrahedral environment around each nitrogen atom. All of the ammonia hydrogens were apparent and were included in subsequent calculations. The hydrogen atoms of the water molecules were located from difference maps calculated in the regions around the oxygen atoms. Each hydrogen atom was assigned an isotropic temperature factor one unit higher than the value of the last refined isotropic temperature factor for the atom to which the hydrogen was attached.

In subsequent least-squares cycles, 163 parameters were adjusted; these included a scale factor, positional parameters of all of the 28 atoms, anisotropic temperature factors for the nonhydrogen atoms, and isotropic temperature factors for the hydrogen atoms. The 163 parameters were apportioned among two complete matrices due to storage limitations of the computer.

All calculations were carried out on an IBM 370-155 computer using subprograms operating under the CRYM crystallographic computing system.[18] The quantity minimized throughout the least-squares refinement was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Atomic form factors for Ru, Cl, O, and N were taken from Hanson, Herman, Lea, and Skillman,[19] the value for Ru being reduced by 1.37 electrons to take account of the real part of anomalous dispersion.[20] $\Delta f''$ was ignored. The atomic form factor used for hydrogen was that calculated by Stewart, Davidson, and Simpson.[21]

In the final cycle of refinement no heavy-atom parameter shifted by as much as 0.2 esd. The final R index for 2114 reflections above σ was 0.036 and the goodness of fit, $[\Sigma w(F_o^2 - F_c^2)^2/(m - s)]^{1/2}$, where m is the number of reflections and s the number of refinable parameters, was 1.02. On a final difference Fourier synthesis the highest peak was 0.34 e/Å^3 as compared with the value 0.6 e/Å^3 for a typical hydrogen atom in this structure. The final parameters for the heavy atoms and for the hydrogen atoms are given in Tables I and II, respectively. The values of the observed and calculated structure factors (in e × 10) are available.[22]

The estimated standard deviations in the positions of the ruthenium atoms are approximately 0.0002 Å, those for the chloride ions are approximately 0.001 Å, and those for the bridging and nonbridging nitrogens range from 0.002 to 0.003 Å. The estimated standard deviations in the positions of the oxygen atoms of the waters of hydration are all about 0.005 Å.

Table II. Positional and Thermal Parameters of the Hydrogen Atoms[a]

Atom	x	y	z	B, Å^2
H(1) (N(1))	533 (3)	676 (3)	602 (3)	1.3 (6)
H(2)	649 (4)	620 (4)	612 (3)	4.0 (8)
H(3) (N(2))	433 (4)	415 (4)	838 (4)	4.6 (9)
H(4)	575 (4)	426 (4)	835 (4)	4.0 (8)
H(5)	501 (4)	535 (4)	824 (3)	2.7 (8)
H(6) (N(3))	220 (4)	511 (4)	542 (4)	3.6 (8)
H(7)	243 (4)	498 (4)	673 (3)	3.3 (8)
H(8)	273 (4)	615 (4)	608 (3)	1.6 (6)
H(9) (N(4))	660 (4)	274 (4)	686 (4)	3.4 (8)
H(10)	679 (4)	274 (4)	565 (4)	3.8 (8)
H(11)	717 (4)	376 (4)	642 (4)	3.8 (8)
H(12) (N(5))	358 (4)	209 (4)	580 (4)	3.7 (8)
H(13)	420 (4)	195 (4)	694 (4)	4.5 (9)
H(14)	301 (4)	260 (4)	666 (4)	4.1 (9)
H(15) (O(1))	852 (5)	459 (5)	852 (4)	5.9 (11)
H(16)	812 (5)	483 (5)	957 (4)	6.3 (11)
H(17) (O(2))	462 (7)	785 (9)	868 (8)	9.7 (15)
H(18)	485 (5)	784 (5)	957 (4)	4.3 (9)

[a] The positional parameters have been multiplied by 10^3. Hydrogen atoms are bonded to the atom given in parentheses. No designation indicates bonding to the atom in parentheses immediately above the hydrogen.

Discussion

The X-ray study establishes the formulation $[(NH_3)_4Ru(NH_2)_2Ru(NH_3)_4]Cl_4 \cdot 4H_2O$ for ruthenium black. Interatomic distances and angles are given in Table III and a stereoscopic representation of the unit cell contents is given in Figure 1. The two Ru^{3+} ions in the centrosymmetric complex cation are bridged by two amido groups, with four ammonia molecules completing a distorted octahedral geometry at each metal site (Figure 2).

Our assignment of the bridging atoms as nitrogens rather than as oxygens was made chiefly on the basis of a difference Fourier synthesis calculated in the plane perpendicular to the Ru-Ru line and having the bridging atom as its center, *i.e.*, the plane in which tetrahedral hydrogens, if any, are constrained to lie. The synthesis clearly showed the presence of two electron density peaks corresponding to hydrogen atoms. Moreover, the anisotropic temperature factors for oxygen are unusually large for a bridging atom.[23] Analytical and physical data are also consistent with our assignment of amido bridging groups.[9]

Perhaps the most interesting feature of the structure is the very small $Ru-NH_2-Ru$ bridging bond angle (and the related, relatively short Ru-Ru distance) in the complex cation. Dahl, *et al.*,[24] have discussed M-B-M bond angle compression as a measure of the degree of metal-metal bonding in M_2B_2 systems, where B is a bridging atom. Molecular parameters indicate that in M_2B_2 systems without metal-metal bonding interaction the B-M-B angles generally are considerably less

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(17) E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Crystallogr.*, 3, 210 (1950).

(18) CRYM is an integrated series of crystallographic routines written by Dr. R. E. Marsh and coworkers at the California Institute of Technology. D. J. Duchamp, American Crystallographic Association Meeting, Bozeman, Mont., 1964, Paper B-14, p 29.

(19) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

(20) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

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

(22) A listing of observed and calculated 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. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2153.

(23) $\beta_{11} = 0.008277$, $\beta_{22} = 0.007953$, $\beta_{33} = 0.005289$, $\beta_{12} = 0.001733$, $\beta_{13} = 0.002193$, $\beta_{23} = 0.000718$.

(24) L. F. Dahl, E. Rodulfo de Gil, and R. D. Feltham, *J. Amer. Chem. Soc.*, 91, 1653 (1969).

Table III. Intramolecular Distances (Å) and Angles (Deg)[a]

Atoms	Distances	Atoms	Angles
Ru-Ru′	2.625 (1)	Ru-N(1)-Ru′	81.0 (1)
Ru-N(1)	2.011 (4)	N(1)-Ru-N(5)	174.2 (2)
Ru-N(1)′	2.029 (4)	N(1)′-Ru-N(2)	171.8 (2)
Ru-N(2)	2.146 (3)	N(3)-Ru-N(4)	170.8 (2)
Ru-N(3)	2.130 (4)	N(1)-Ru-N(1)′	99.0 (1)
Ru-N(4)	2.133 (4)	N(1)-Ru-N(2)	89.3 (2)
Ru-N(5)	2.140 (4)	N(1)-Ru-N(3)	92.4 (2)
N(1)-N(1)′	3.072 (7)	N(1)-Ru-N(4)	92.6 (2)
Ru-O(1)	4.333 (3)[b]	N(1)′-Ru-N(3)	93.5 (2)
Ru-O(2)	4.409 (4)[b]	N(1)′-Ru-N(4)	93.3 (2)
Ru-Cl(1)	4.369 (3)[b]	N(1)′-Ru-N(5)	86.8 (2)
Ru-Cl(2)	4.315 (3)[b]	N(2)-Ru-N(3)	86.5 (2)
N(1)-H(1)	0.73 (6)[c]	N(2)-Ru-N(4)	85.9 (2)
N(1)-H(2)	0.84 (7)[c]	N(2)-Ru-N(5)	85.0 (2)
O(1)-H(15)	0.74 (7)	N(3)-Ru-N(5)	86.7 (2)
O(1)-H(16)	0.79 (8)	N(4)-Ru-N(5)	87.6 (2)
O(2)-H(17)	0.50 (7)	H(1)-N(1)-H(2)	106 (3)
O(2)-H(18)	0.76 (7)	H(15)-O(1)-H(16)	109 (3)
		H(17)-O(2)-H(18)	97 (5)

[a] The values in parentheses are estimated standard deviations as obtained from the least-squares refinement process *via* the inverse matrix. [b] These are the closest Ru-X (X = O, Cl) distances. [c] The 14 N-H distances have a mean value of 0.82 (2) Å.

than 90° and the M-B-M angles greater than 90°, whereas in metal-metal bonded complexes, the M-B-M angle is often acute. The observed M-B-M and B-M-B angles of 81.0 (1) and 99.0 (1)°, respectively, in the ruthenium black cation are therefore consistent with the presence of Ru-Ru bonding. The relatively short Ru-Ru distance of 2.625 (1) Å leads to significant nonbonded repulsions between N(3)-N(4)′ and N(3)-N(4) (2.963 (7) Å), resulting in an N(3)-Ru-N(4) angle of 170.8 (2)° (Figure 2).

The mean Ru-N distance in the ruthenium black cation is 2.112 (25) Å. The Ru-NH$_2$ distances (2.011 (4), 2.029 (4) Å) are approximately 0.1 Å shorter than those for Ru-NH$_3$, however, most likely due in part to the Ru-Ru bonding. The mean Ru-NH$_3$ distance in the cation is 2.137 (3) Å, which may be compared with the Ru-N distances of 2.104 (4) and 2.144 (4) Å in [Ru(NH$_3$)$_6$][BF$_4$]$_3$ and [Ru(NH$_3$)$_6$]I$_2$, respectively.[25] The fact that the Ru-NH$_3$ distances in ruthenium black approach in value those observed in the Ru(II) reference compound indicates that the effective charge on each of the ruthenium atoms is much less than 3+, due to electron donation from the amido groups.

Table IV. Short Contacts of Nonhydrogen Cation and Water Atoms with Surrounding Atoms[a]

Atoms	Distance, Å	Angle, deg
N(2)-H(4) · · · O(1)	3.11	155
N(2)-H(5) · · · O(2)	3.04	172
N(4)-H(9) · · · O(1)	3.30	103
N(4)-H(11) · · · O(1)	3.30	122
N(5)-H(13) · · · Cl(1)	3.30	167
O(1)-H(16) · · · Cl(2)(a)	3.16	179
O(2)-H(17) · · · Cl(2)(b)	3.28	148
O(2)-H(18) · · · Cl(1)(a)	3.29	165

[a] Heavy-atom distances are given. Symmetry code: no letter, coordinates given in Tables I and II; (a) $1-x$, $1-y$, $2-z$; (b) $^1/_2-x$, $^1/_2+y$, $^3/_2-z$.

Bond distances and angles within the amido and ammine ligands appear normal. The 14 N-H distances have a mean value of 0.82 (2) Å and the maximum deviation from the tetrahedral angle of 109° for the bond angles around the nitrogen atoms, *i.e.*, the Ru-N-H(x) angles, excluding N(1), is 6°. The Ru-N(1)-H(1), H(2) angles are 118 and 120°, respectively.

The chloride ions and water molecules form a network of atoms occupying the "holes" of the crystal (Figure 1), and the short heavy-atom contacts involving these atoms are listed in Table IV. Although some of the entries may be ascribed to hydrogen bonding, we note that the NH$_2$ bridging group is not involved in such interaction.

The ellipsoids of thermal motion for the heavy atoms of the cation are shown in Figures 1 and 2. The hydrogen, oxygen, and chlorine atoms in Figure 1 and the hydrogen atoms in Figure 2 have been given arbitrary radii. The rms amplitudes for the cation atoms along the principal directions range from 0.12 to 0.18 Å, with the smallest and most isotropic movement associated with the Ru atoms. The largest thermal vibrations in the structure are displayed by the water molecules and chloride ions with rms amplitudes up to 0.33 Å. No attempt was made to correct the bond lengths for the effects of thermal motion.

Registry No. [(NH$_3$)$_4$Ru(NH$_2$)$_2$Ru(NH$_3$)$_4$]Cl$_4$ · 4H$_2$O, 40548-28-5.

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