Contribution from the School of Chemistry and Department of Theoretical Chemistry,
University of Sydney, Sydney, NSW 2006, Australia

Crystal and Molecular Structure of the Mixed-Valence Ruthenium Dimer Tris(μ-bromo)bis(triammineruthenium)(2+) Tetrabromozincate(II), $[(NH_3)_3RuBr_3Ru(NH_3)_3](ZnBr_4)$

James K. Beattie,* Patricia Del Favero, Trevor W. Hambley, and Noel S. Hush

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The structure of the title compound has been found by single-crystal X-ray analysis to contain a triple bromo bridge between two triammineruthenium end groups (space group $P2_1/m$; a = 9.019 (2) Å, b = 10.283 (2) Å, c = 10.109 (3) Å; β = 95.30 (2)°; Z = 2). The structure was refined to a conventional R value of 0.054 by using 792 significant reflections. The cation lies on a mirror plane that contains the two ruthenium atoms, which are not crystallographically equivalent. There are small differences between the average bond lengths of the two ruthenium coordination spheres. These can be attributed to differences in hydrogen bonding in the crystal lattice and do not imply that the complex is valence localized. The Ru–Ru distance is 2.852 (4) Å, and the average Ru–Br–Ru angle is 68.5°, suggesting a weak Ru–Ru interaction.

Introduction

There has been considerable speculation and uncertainty over the nature of the ruthenium "blue" complexes formed by the action of hydrohalic acids on ruthenium(II) ammine complexes.[1] Bottomley and Tong[2] suggested that the intense blue color arises from a mixed-valence diruthenium(II,III) complex. They isolated salts that were formulated as $[Ru_2(NH_3)_6X_4H_2O]X$, where X = Cl^- or Br^-, and interpreted their chemical and physical evidence as consistent only with a monohalo-bridged dimer.

Mercer and Gray[3] formulated the chloro complex as $[Ru_2(NH_3)_6Cl_3]^{2+}$. Their evidence included isolation of a number of different salts, including $[Ru_2(NH_3)_6Cl_3][MCl_4]$, where M = Zn(II), Cd(II), and Hg(II). On the basis of the oxidative decomposition of the complex to *cis*-$[Ru(NH_3)_3Cl_3]$,[4] they suggested that the mixed-valence complex contains a tris(μ-chloro) bridge.

Attempts to prepare single crystals of these complexes suitable for an X-ray crystal structure determination have, until recently, been unsuccessful. Consequently, the interpretation of the physical and chemical properties of these complexes has proceeded without the definitive evidence of a crystal structure. Interpretation of the infrared,[5] electronic absorption,[6] and resonance Raman spectra[7] were all consistent with a trihalo-bridged structure. Analysis of the electronic spectrum[6] was only consistent with a delocalized mixed-valence description of the oxidation states.

We now report the structure of the bromo analogue of the Mercer and Gray tetrachlorozincate compound. Independently, the structure of the tetraphenylborate salt of the chloro-bridged complex has just been communicated.[8] Both confirm the tris(μ-halo) geometry proposed from other measurements.

Experimental Section

Synthesis. Tris(μ-bromo)bis(triammineruthenium)(2+) bromide was prepared by the method of Bottomley and Tong.[2] Crystals of $[Ru_2(NH_3)_6Br_3](ZnBr_4)$ were prepared by dissolution of approximately 0.002 g of $[Ru_2(NH_3)_6Br_3]Br_2$ in a deoxygenated solution of 0.01 g of $ZnBr_2$ in 1 mL of H_2O. The solution was left to evaporate slowly by passing a stream of Ar over the surface. Before all of the solution had evaporated, crystals had formed that could be easily isolated. We were unable to form suitable crystals of the analogous $[Ru_2(NH_3)_6Cl_3](ZnCl_4)$.

Crystallography. The crystals used were extemely thin. Lattice parameters were determined by a least-squares fit to the setting angles of 25 independent reflections. Crystal data and data collection parameters are listed in Table I. Data were collected on a Enraf-Nonius CAD4F four-circle diffractometer, employing graphite-monochromated Mo Kα radiation.

The structure was solved by direct methods using SHELX-76.[9] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at calculated sites (N–H, 0.91 Å) with a group isotropic thermal parameter. Full-matrix least-squares refinement converged with all shifts less than 0.12σ. The final R value is slightly high and is a

Table I. Crystal Data

cryst system	monoclinic
space group	$P2_1/m$
a, Å	9.019 (2)
b, Å	10.283 (2)
c, Å	10.109 (3)
β, deg	95.30 (2)
V, Å^3	933.6
D_{calcd}, g cm^{-3}	3.304
empirical formula	$Br_7H_{18}N_6Ru_2Zn$
fw	929.03
Z	2
F(000), electrons	846
abs coeff, cm^{-1}	175.66
habit	plates
dimens, mm	0.06 × 0.22 × 0.002
faces	±1,0,0; 0,±1,0; 0,0,±1
abs cor	numerical integration
transmissn factor range	0.96–0.51
temp, K	294
diffractometer	Enraf-Nonius CAD4-F, four circle
radiation	Mo Kα; λ = 0.71069 Å
monochromator	graphite
scan mode	ω
2θ range, deg	2.0–46.0
reflcns measd	1473
hkl ranges	−9 to +9, 0 to 11, 0 to 11
nonequiv reflcns	1230
merging R	0.030
no. of reflcns used ($I > 2.5\sigma(I)$)	792
no. of variables	98
R	0.054
R_w	0.051
weighting constants: k, g ($w = k/(\sigma^2F_o + gF_o^2)$)	1.37, 0.00048
shift/esd	0.2σ
residual extrema in final difference map, eÅ^{-3}	±1.5

Table II. Positional Parameters (×10^4)

	x	y	z	B_{eq}, Å^2
Ru(1)	6637 (2)	2500	11058 (3)	1.69
Ru(2)	8083 (3)	2500	8665 (3)	1.89
Br(1)	5244 (4)	2500	8753 (4)	2.52
Br(2)	8237 (3)	683 (2)	10344 (2)	3.13
N(1)	5248 (20)	3912 (18)	11748 (19)	2.73
N(2)	7896 (35)	2500	12829 (30)	3.40
N(3)	10408 (29)	2500	8746 (30)	2.96
N(4)	7951 (19)	3938 (19)	7162 (19)	2.96
Zn(1)	7392 (4)	7500	5072 (4)	3.17
Br(3)	4751 (5)	7500	5022 (5)	7.83
Br(4)	8210 (4)	7500	7461 (4)	2.98
Br(5)	8251 (4)	5653 (3)	3962 (3)	5.20

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* To whom correspondence should be addressed at the School of Chemistry.

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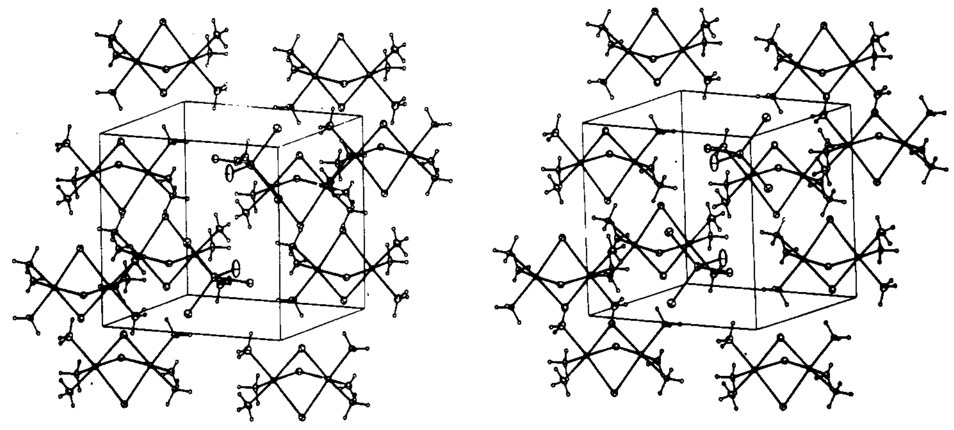

Figure 1. Stereoview of the unit cell of $[(NH_3)_3RuBr_3Ru(NH_3)_3](ZnBr_4)$. Thermal ellipsoids shown have 50% probability.

Table III. Bond Lengths (Å)

Ru(2)–Ru(1)	2.852 (4)	N(3)–Ru(2)	2.092 (27)
N(1)–Ru(1)	2.080 (17)	N(4)–Ru(2)	2.115 (19)
N(2)–Ru(1)	2.020 (33)		
Br(1)–Ru(1)	2.543 (4)	Br(3)–Zn(1)	2.377 (6)
Br(2)–Ru(1)	2.507 (3)	Br(4)–Zn(1)	2.458 (6)
Br(1)–Ru(2)	2.570 (4)	Br(5)–Zn(1)	2.372 (4)
Br(2)–Ru(2)	2.520 (3)		

Table IV. Bond Angles (deg)

N(1)–Ru(1)–Ru(2)	128.4 (5)	Br(1)–Ru(1)–Ru(2)	56.6 (1)
N(1)–Ru(1)–Br(1)	92.6 (6)	Br(1)–Ru(2)–Ru(1)	55.7 (1)
N(1)–Ru(1)–Br(2)	175.7 (5)	Br(2)–Ru(1)–Ru(2)	55.6 (1)
N(1)–Ru(1)–N(1)	88.6 (10)	Br(2)–Ru(2)–Ru(1)	55.2 (1)
N(2)–Ru(1)–Ru(2)	119.1 (8)	Br(2)–Ru(1)–Br(1)	89.2 (1)
N(2)–Ru(1)–Br(1)	175.6 (8)	Br(2)–Ru(1)–Br(2)	96.4 (1)
N(2)–Ru(1)–Br(2)	87.9 (5)	Br(2)–Ru(2)–Br(1)	88.3 (1)
N(2)–Ru(1)–N(1)	90.5 (8)	Br(2)–Ru(2)–Br(2)	95.7 (1)
N(3)–Ru(2)–Ru(1)	120.2 (8)	Br(4)–Zn(1)–Br(3)	103.3 (2)
N(3)–Ru(2)–Br(1)	175.8 (8)	Br(5)–Zn(1)–Br(3)	111.1 (1)
N(3)–Ru(2)–Br(2)	88.9 (6)	Br(5)–Zn(1)–Br(4)	112.5 (1)
N(4)–Ru(2)–Ru(1)	127.5 (5)	Br(5)–Zn(1)–Br(5)	106.3 (2)
N(4)–Ru(2)–Br(1)	92.0 (5)	Ru(2)–Br(1)–Ru(1)	67.8 (1)
N(4)–Ru(2)–Br(2)	176.5 (6)	Ru(2)–Br(2)–Ru(1)	69.1 (1)
N(4)–Ru(2)–N(3)	91.0 (7)		
N(4)–Ru(2)–N(4)	88.6 (11)		

consequence of the unfavorable crystal morphology.

Positional parameters are listed in Table II and bond lengths and angles in Tables III and IV, respectively. Anisotropic thermal parameters (Table SI), hydrogen atom parameters (Table SII), and observed and calculated structure factors are available as supplementary material.

Programs used were SUSCAD[10] for data reduction, ABSORB[10] for absorption corrections, SHELX 76[9] for refinement, and ORTEP[11] for plotting. Scattering factors and anomalous dispersion terms were taken from ref 12.

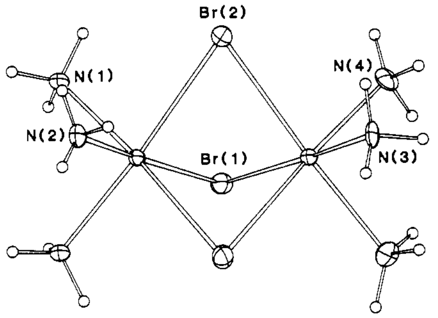

Figure 2. View of the $[(NH_3)_3RuBr_3Ru(NH_3)_3]^{2+}$ cation with atom numbering.

Table V. Close Intermolecular Contacts (Å)[a]

	N···Br	H···Br
N(1)–H(1C)···Br(3)^{i}	3.57	2.80
N(2)–H(2A)···Br(3)^{i}	3.37	3.06
N(4)–H(4C)···Br(3)^{ii}	3.46	2.62
N(4)–H(4B)···Br(4)	3.68	2.90
N(1)–H(1A)···Br(4)^{i}	3.60	2.90
N(2)–H(2B)···Br(4)^{iii}	3.56	2.41
N(2)–H(2A)···Br(5)^{iv}	3.45	2.65
N(3)–H(3A)···Br(5)^{iv}	3.63	2.96
N(4)–H(4A)···Br(5)^{iv}	3.73	2.85
N(3)–H(3A)···Br(5)^{v}	3.63	3.12
N(2)–H(2B)···Br(5)^{vi}	3.45	3.50
N(1)–H(1B)···Br(1)^{i}	3.74	2.93
N(3)–H(3B)···Br(2)^{vii}	3.58	2.71

[a] Symmetry elements: (i) $1 - x, 1 - y, 2 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $2 - x, 1 - y, 2 - z$; (iv) $2 - x, 1 - y, 1 - z$; (v) $2 - x, y - {}^1/_2, 1 - z$; (vi) $x, {}^3/_2 - y, {}^1/_2 + z$; (vii) $2 - x, {}^1/_2 + y, 2 - z$.

Results and Discussion

The structure consists of a $[Ru_2(NH_3)_6Br_3]^{2+}$ cation and a $[ZnBr_4]^{2-}$ anion, each lying on a crystallographic mirror plane (Figure I). There are numerous hydrogen bonds between the bromine atoms of the anion and the ammine ligands of the cation. There are also two hydrogen bonds between the bromine atoms of the cation and the ammine ligands of an adjacent cation.

The cation consists of two $Ru(NH_3)_3$ units connected by three bromine bridging atoms (Figure 2), as was found in the analogous chlorine complex.[8] Atoms Ru(1), Ru(2), Br(1), N(2), and N(3) lie in the mirror plane. Overall, the complex shows only small deviations from D_{3h} symmetry. The average ruthenium–ligand bond lengths about Ru(1) are shorter than those about Ru(2), but the difference is not statistically significant, given the variation in the individual bond lengths and the rather large standard deviation in the Ru–N distances. Furthermore, hydrogen bonding of the ammine protons at either end of the molecule is asymmetric, as is observed from examination of the close intermolecular contacts given in Table V. Three of the four shortest intermolecular contacts and three of the four shortest hydrogen bonds occur at the Ru(1) end of the molecule. The observed deviations from D_{3h} symmetry can therefore be ascribed to lattice forces. There is no evidence, then, from the crystal structure to suggest other than a static, delocalized description of the mixed-valence

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electronic structure, as indicated by the interpretation of the electronic spectrum.[6]

The average Ru-Br bond length (2.53 (3) Å) is, as expected, about 0.12 Å longer than the equivalent distance in the chlorine complex.[8] This leads to an increase in the Ru-Ru distance [2.852 (4) Å, cf. 2.753 (4) Å]. The increase is moderated by a slight closing in the Ru-Br-Ru angle (average 68.5°, cf. 70.2°) suggesting the presence of a Ru-Ru interaction. The average Ru-N distance (2.08 (4) Å) is smaller than that found in the chlorine complex (2.11 Å),[8] but the precision of both determinations is low so the difference is not significant.

This appears to be the first structure report of a mixed-valence Ru^{II}-Ru^{III} dimer with a tribromo bridge. There have been several structures published over the last few years of Ru^{II}-Ru^{III} dimers with trichloro bridges.[8,13-15] In addition, there are many known trihalo-bridged Ru^{II}-Ru^{II} compounds with phosphine and arsine ligands.[16] The structures of these and of other related compounds which have been determined, however, all appear to be of the trichloro species.[16-19] The only structural characterization of a dimer with a tribromo bridge appears to be that of the Ru^{III}-Ru^{III} dimer $[Ru_2Br_9]^{3-}$ determined by powder diffraction.[20] Mixed-valence states of this species have been generated electrochemically,[21] but do not appear to have been structurally characterized.

Finally, although the tris(μ-halo) dimeric structure appears to be common for ruthenium complexes, other possibilities must be considered. Bino and Cotton[22] have described a linear, trinuclear Ru^{III}-Ru^{II}-Ru^{III} complex with two tris(μ-chloro) bridges, $[Ru_3Cl_{12}]^{4-}$. And the tris(ethylenediamine)ruthenium(II) ion can react with hydrohalic acids to form intense blue species.[23] Because of the bidentate nature of the ethylenediamine ligand, these are unlikely to be structurally analogous to the compound described in this article. Further work on such compounds would be desirable in view of the biological activity of the chloro-bridged compound.[24,25]

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Registry No. $[Ru_2(NH_3)_6Br_3](ZnBr_4)$, 114094-47-2; $[Ru_2(NH_3)_6Br_3]Br_2$, 58320-17-5.

Supplementary Material Available: Tables SI and SII, listing thermal parameters and the restrained hydrogen positional and thermal parameters (1 page); a table of calculated and observed structure factors (5 pages). Ordering information is given on any current masthead page.

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Contribution from the Chemistry Division,
Argonne National Laboratory, Argonne, Illinois 60439

Oxygen-17 NMR of Seven-Valent Neptunium in Aqueous Solution[1]

Evan H. Appelman,* Arthur G. Kostka, and James C. Sullivan

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Alkaline solutions of seven-valent neptunium in water enriched in oxygen-17 show a ^{17}O NMR resonance about 1470 ppm downfield from the solvent resonance. Measurement of relative areas indicates that the Np(VII) oxygen resonance contains about four oxygen atoms per Np atom. This result is interpreted in terms of the six-coordinated Np(VII) anion $NpO_4(OH)_2^{3-}$, in which four oxygen atoms are present in a square plane around the Np and are responsible for the observed resonance. The two hydroxyl groups are located further from the Np at the vertices of a tetragonal bipyramid and presumably exchange too rapidly with solvent oxygen for their ^{17}O resonance to be seen. The Np(VII) oxygen resonance has a line width that increases with temperature and is around 400 Hz at 25 °C. The temperature dependence of the line width can be accounted for by a process of oxygen exchange between the Np(VII) species and the solvent, with a pseudo-first-order rate constant of about 10^3 s^{-1} at 25 °C. No Np(VI) oxygen resonance was observed in alkaline solution, probably because the Np(VI) oxygens exchange too rapidly with the solvent.

Introduction

Although Np(VII) has been known since 1967, considerable doubt still remains regarding the form in which it exists in aqueous solutions. Potentiometric measurements have shown the electrode potential of the Np(VI)-Np(VII) couple to increase as (RT/F) log $[H^+]^2$ in acid solution[2] and to decrease as (RT/F) log $[OH^-]^2$ in base.[3,4] Since the form of Np(VI) in acid solution has been established to be NpO_2^{2+}, this implies that the Np(VII) species in acid has a charge of +1. The nature of Np(VI) in alkaline solution has not been well established, because of its low solubility. The authors of the potentiometric studies assumed it to be NpO_4^{2-} or $NpO_2(OH)_4^{2-}$, and they therefore concluded that the Np(VII) species in base had a charge of −3.

In any case, these measurements do not establish the actual coordination number of the Np(VII) species. The conventional wisdom seems to be that Np(VII) exists in the form NpO_3^+ in acid and in the form $NpO_4(OH)_2^{3-}$ in base.[5] The latter conclusion is supported by the observation that salts containing six-coordinated Np(VII) can be isolated from alkaline solution.[6-8]

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