

X-ray Crystallographic Study of the Ruthenium Blue Complexes $[\text{Ru}_2\text{Cl}_3(\text{tacn})_2](\text{PF}_6)_2 \cdot 4\text{H}_2\text{O}$, $[\text{Ru}_2\text{Br}_3(\text{tacn})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$, and $[\text{Ru}_2\text{I}_3(\text{tacn})_2](\text{PF}_6)_2$: Steric Interactions and the Ru–Ru “Bond Length”

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X-ray crystal structures are reported for the following complexes: $[\text{Ru}_2\text{Cl}_3(\text{tacn})_2](\text{PF}_6)_2 \cdot 4\text{H}_2\text{O}$ (tacn = 1,4,7-triazacyclononane), monoclinic $P2_1/n$, $Z = 4$, $a = 14.418(8) \text{ \AA}$, $b = 11.577(3) \text{ \AA}$, $c = 18.471(1) \text{ \AA}$, $\beta = 91.08(5)^\circ$, $V = 3082 \text{ \AA}^3$, $R (R_w) = 0.039 (0.043)$ using 4067 unique data with $I > 2.5\sigma(I)$ at 293 K; $[\text{Ru}_2\text{Br}_3(\text{tacn})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$, monoclinic $P2_1/a$, $Z = 4$, $a = 13.638(4) \text{ \AA}$, $b = 12.283(4) \text{ \AA}$, $c = 18.679(6) \text{ \AA}$, $\beta = 109.19(2)^\circ$, $V = 3069.5 \text{ \AA}^3$, $R (R_w) = 0.052 (0.054)$ using 3668 unique data with $I > 2.5\sigma(I)$ at 293 K; $[\text{Ru}_2\text{I}_3(\text{tacn})_2](\text{PF}_6)_2$, cubic $P2_1/3$, $Z = 3$, $a = 14.03(4) \text{ \AA}$, $\beta = 90.0^\circ$, $V = 2763.1(1) \text{ \AA}^3$, $R (R_w) = 0.022 (0.025)$ using 896 unique data with $I > 2.5\sigma(I)$ at 293 K. All of the cations have cofacial bioctahedral geometries, although $[\text{Ru}_2\text{Cl}_3(\text{tacn})_2](\text{PF}_6)_2 \cdot 4\text{H}_2\text{O}$, $[\text{Ru}_2\text{Br}_3(\text{tacn})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$, and $[\text{Ru}_2\text{I}_3(\text{tacn})_2](\text{PF}_6)_2$ are not isomorphous. Average bond lengths and angles for the cofacial bioctahedral cores, $[\text{N}_3\text{Ru}(\mu\text{-X})_3\text{RuN}_3]^{2+}$, are compared to those for the analogous ammine complexes $[\text{Ru}_2\text{Cl}_3(\text{NH}_3)_6](\text{BPh}_4)_2$ and $[\text{Ru}_2\text{Br}_3(\text{NH}_3)_6](\text{ZnBr}_4)$. The Ru–Ru distances in the tacn complexes are longer than those in the equivalent ammine complexes, probably as a result of steric interactions.

Introduction

For many years there existed considerable speculation and uncertainty over the exact formula and structure of the ruthenium blue complexes.¹ In 1969, Lever and Powell² first isolated a blue solid from the reaction of hydrochloric acid with a warm solution of hexaammineruthenium(II) chloride. Subsequent analyses³ suggested that the complex was a mixed-valence Ru(III,II) species bridged by three halo ions, and interpretation of the infrared,⁴ electronic absorption,^{5,6} and resonance Raman⁷ spectra proceeded without definitive evidence from a crystal structure. The structures of $[\text{Ru}_2(\mu\text{-Cl})_3(\text{NH}_3)_6](\text{BPh}_4)_2$ (**1a**) and $[\text{Ru}_2(\mu\text{-Br})_3(\text{NH}_3)_6](\text{ZnBr}_4)$ (**2a**) have since been reported^{1,8} and both confirm the tris(μ -halo) geometry proposed from earlier measurements.³ In addition, the crystal structures show the complexes to have nearly perfect D_{3h} symmetry, consistent with a delocalized description of the mixed-valence electronic structure, as indicated by the interpretation of the electronic spectrum.⁶

The tridentate macrocycle 1,4,7-triazacyclononane (tacn), with 3-fold symmetry (Figure 1), has been synthesized and used extensively in inorganic and organic chemistry.⁹ Replacement of the six terminal ammine ligands in $[\text{Ru}_2\text{X}_3(\text{NH}_3)_6]^{2+}$ with two tacn ligands should yield complexes of the type $[\text{Ru}_2\text{X}_3(\text{tacn})_2]^{2+}$, with a cofacial bioctahedral geometry while retaining the 3-fold symmetry of the amine complex.

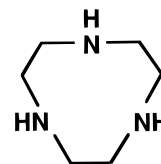


Figure 1. 1,4,7-Triazacyclononane (tacn).

Our recent studies¹⁰ on the electronic spectroscopy of the three complexes $[\text{Ru}_2\text{Cl}_3(\text{tacn})_2]^{2+}$ (**3**), $[\text{Ru}_2\text{Br}_3(\text{tacn})_2]^{2+}$ (**4**), and $[\text{Ru}_2\text{I}_3(\text{tacn})_2]^{2+}$ (**5**) have shown that certain electronic transitions are very sensitive to the degree of metal–metal interaction. As well, differences in the resonance Raman (RR) spectra of complexes **1–5** were explained in terms of variations in both Ru–Ru distances and the steric interactions between bridging and terminal ligands.^{10,11} X-ray crystal structure analyses were carried out to provide the Ru–Ru distances for these complexes and also the interatomic distances necessary for assessing ligand steric effects.

A synthesis for the chloro complex $[\text{Ru}_2\text{Cl}_3(\text{tacn})_2](\text{PF}_6)_2 \cdot 4\text{H}_2\text{O}$ has been reported.¹² We now report the preparation and X-ray crystal structure analyses of all three complexes, $[\text{Ru}_2\text{Cl}_3(\text{tacn})_2](\text{PF}_6)_2 \cdot 4\text{H}_2\text{O}$ (**3a**), $[\text{Ru}_2\text{Br}_3(\text{tacn})_2](\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$ (**4a**), and $[\text{Ru}_2\text{I}_3(\text{tacn})_2](\text{PF}_6)_2$ (**5a**).

Experimental Section

$[\text{RuCl}(\text{dmsO})_2(\text{tacn})]\text{Cl}$ was prepared according to the published¹² procedure using $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Ventron, 0.77 g), 1,4,7-triazacyclononane (Aldrich, 0.50 g), and dimethyl sulfoxide (Merck, AR grade).

$[\text{RuCl}_3(\text{tacn})]$ was prepared from $[\text{RuCl}(\text{dmsO})_2(\text{tacn})]\text{Cl}$ and concentrated HCl (10 M, AnalaR, AR grade) according to the published¹² procedure. Anal. Calc for $\text{C}_9\text{H}_{15}\text{N}_3\text{Cl}_3\text{Ru}$: C, 21.4; H, 4.5; N, 12.5. Found: C, 20.7; H, 4.2; N, 11.9.

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Table 1. Crystal Data, Experimental Conditions, and Refinements for the Complexes

	[Ru ₂ Cl ₃ (tacn) ₂](PF ₆) ₂ ·4H ₂ O	[Ru ₂ Br ₃ (tacn) ₂](PF ₆) ₂ ·2H ₂ O	[Ru ₂ I ₃ (tacn) ₂](PF ₆) ₂
empirical formula	C ₁₂ H ₃₈ Cl ₃ F ₁₂ N ₆ O ₄ P ₂ Ru ₂	C ₁₂ H ₃₄ Br ₃ F ₁₂ N ₆ O ₂ P ₂ Ru ₂	C ₁₂ H ₃₀ I ₃ F ₁₂ N ₆ P ₂ Ru ₂
fw	928.90	1026.22	1131.19
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>3</i>
<i>a</i> , Å	14.418(8)	13.638(4)	14.030(4)
<i>b</i> , Å	11.577(3)	12.283(4)	
<i>c</i> , Å	18.471(1)	18.679(6)	
β, deg	91.08(5)	101.19(2)	
<i>V</i> , Å ³	3082	3069.5	2763.1(1)
<i>Z</i>	4	4	3
<i>D</i> _{calcd} , g cm ⁻³	2.002	2.221	2.048
temp, K	293	293	293
radiation (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
no. of reflns measd (<i>I</i> > 2.5σ(<i>I</i>))	6651	5867	2776
no. of reflns used	4067	3668	896
abs coeff, μ, cm ⁻¹	24.57	96.53	137.81
<i>R</i> (<i>F</i> _o) ^a	0.039	0.052	0.022
<i>R</i> _w ^b	0.043	0.054	0.025

$$^a R = \sum(|F_o| - |F_c|) / \sum|F_o|. \quad ^b R_w = [\sum(w|F_o| - |F_c|)^2 / \sum(w|F_o|^2)]^{1/2}.$$

[RuBr₃(tacn)] was prepared from [RuCl(dmsO)₂(tacn)]Cl according to the published¹² procedure using conc HBr (Merck, Ar grade) instead of HCl. Anal. Calc for C₆H₁₅N₃Br₃Ru: C, 15.3; H, 3.2; N, 8.9. Found: C, 15.2; H, 3.1; N, 8.6.

[RuI₃(tacn)] was prepared from [RuCl(dmsO)₂(tacn)]Cl similarly to the chloro and bromo complexes using conc HI (Merck, AR). The reaction mixture was refluxed for ~45 min, and a dark green solid was obtained. Anal. Calc for C₆H₁₅N₃I₃Ru: C, 11.8; H, 2.5; N, 6.9. Found: C, 11.8; H, 2.3; N, 6.5.

[Ru₂Cl₃(tacn)₂](PF₆)₂·4H₂O was prepared according to the published¹² procedure: [RuCl₃(tacn)] (110 mg) was refluxed in H₂O (20 mL) for 15 min, and the hot blue solution was filtered onto solid NaPF₆ (1.75 g) and subsequently cooled in ice. After ~45 min, the desired product had precipitated, leaving behind a green solution. The dark blue solid was filtered from solution, washed with diethyl ether, and air-dried (yields 31–75 mg, 11–27%). Anal. Calc for C₁₂H₃₈Cl₃F₁₂N₆O₄P₂Ru₂: C, 15.5; H, 4.1; N, 9.1; Cl, 11.5. Found: C, 15.2; H, 3.9; N, 9.2; Cl, 11.8.

Precipitation of crystalline [Ru₂Cl₃(tacn)₂](PF₆)₂·4H₂O was achieved by cooling the filtered reaction mixture slowly to room temperature (~1 h) and then to ~10 °C for 4–6 h (water bath). This procedure was repeated (with slight variations in cooling time) until crystals suitable for X-ray structure analysis were obtained. The dark-blue crystals were filtered from solution, washed with diethyl ether, and air-dried (yield < 1%).

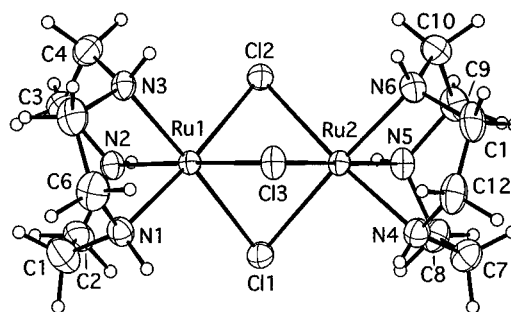
[Ru₂Br₃(tacn)₂](PF₆)₂·7H₂O. [RuBr₃(tacn)] (115 mg) was refluxed with Zn(Hg) in H₂O (20 mL) for 30 min under Ar. The blue solution was filtered hot (under Ar) onto solid NaPF₆ (~1.5 g) and cooled in ice. After ~40 min, a dark blue solid had precipitated. The product was filtered from solution, washed with diethyl ether, and air-dried. Although the synthesis was carried out under an inert atmosphere, the final product is not air-sensitive (yields 66–106 mg, 28–39%). Anal. Calc for C₁₂H₄₄Br₃F₁₂N₆O₇P₂Ru₂: C, 12.9; H, 4.05; N, 7.5; Br, 21.5. Found: C, 12.8; H, 4.0; N, 7.8; Br, 22.1.

[Ru₂Br₃(tacn)₂](PF₆)₂·2H₂O. Crystals of [Ru₂Br₃(tacn)₂](PF₆)₂·2H₂O were obtained as those for the chloro complex.

[Ru₂I₃(tacn)₂](PF₆)₂ was prepared similarly to the bromo complex except that [RuI₃(tacn)] (125 mg) was refluxed in H₂O for 30 min with Zn(Hg) and then for a further 30 min with the Zn(Hg) removed. The hot blue solution was filtered onto solid NaPF₆ (1.5 g) and cooled in an ice bath. A dark-blue solid precipitated immediately. The product was collected in air, washed with diethyl ether, and air-dried (yields 57–80 mg, 25–35%). Anal. Calc for C₁₂H₃₀F₁₂I₃N₆P₂Ru₂: C, 12.7; H, 2.7; I, 33.7. Found: C, 12.6; H, 2.9; N, 7.6; I, 33.8.

Single crystals of [Ru₂I₃(tacn)₂](PF₆)₂ were obtained in the same way as those for the chloro and bromo complexes.

The complexes [Ru₂X₃(tacn)₂]²⁺ (X = Cl, Br, or I) decompose in aqueous solution over a period of days to weeks.¹⁰ As such, they could not be left in aqueous solution for longer than 1 d, and all attempts to grow good crystals using recrystallization techniques were unsuccessful. The complexes are also unstable (for periods > week) in common

**Figure 2.** ORTEP drawing of the [Ru₂Cl₃(tacn)₂]²⁺ cation showing 30% probability thermal ellipsoids.

solvents such as acetone and methanol. As a result, crystals had to be obtained directly from the synthesis mixtures. The yields were decreased dramatically, but good crystals were obtained.

Crystallography. The crystals were mounted on glass fibers with epoxy resin. The data were collected and refined on an Enraf-Nonius structure CAD4-F diffractometer using graphite-monochromated Mo Kα radiation. Cell constants were determined by least-squares fits to the setting parameters of 25 independent reflections. Table 1 summarizes the relevant data for the crystal structure determinations.

Data were reduced, and Lorentz, polarization, and absorption corrections were applied using the Enraf-Nonius structure determination package (SDP).¹³ The structures were solved by direct methods using SHELX-86¹⁴ and refined by full-matrix least-squares analysis with SHELX-76.¹⁵ Hydrogen atoms were included at calculated sites (C–H, N–H 0.97 Å) with individual isotropic thermal parameters. All other atoms, except minor contributors to disordered groups, were refined anisotropically. Scattering factors and anomalous dispersion corrections for Ru were taken from ref 16; for all other atoms, the values supplied in SHELX-76¹⁵ were used. Drawings were produced using the program ORTEP.¹⁷

Results

The dications [Ru₂Cl₃(tacn)₂]²⁺ (**3**), [Ru₂Br₃(tacn)₂]²⁺ (**4**), and [Ru₂I₃(tacn)₂]²⁺ (**5**) have core structures consisting of two ruthenium ions bridged by three halo ions. Pseudooctahedral

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Table 2. Selected Average Bond Lengths (Å) of the Bioctahedral Complexes

complex	Ru···Ru	Ru—X	Ru—N	complex	Ru···Ru	Ru—X	Ru—N
[Ru ₂ Cl ₃ (tacn) ₂](PF ₆) ₂ ·4H ₂ O	2.830(1)	2.401(7)	2.068(4)	[Ru ₂ Cl ₃ (NH ₃) ₆](BPh ₄) ₂ ^a	2.753(4)	2.395(15)	2.111(8)
[Ru ₂ Br ₃ (tacn) ₂](PF ₆) ₂ ·2H ₂ O	2.924(1)	2.534(12)	2.073(3)	[Ru ₂ Br ₃ (NH ₃) ₆](ZnBr ₄) ^a	2.852(4)	2.528(22)	2.084(31)
[Ru ₂ I ₃ (tacn) ₂](PF ₆) ₂	3.068(2)	2.700(1)	2.101(4)				

^a Average bond lengths for [Ru₂Cl₃(NH₃)₆](BPh₄)₂ and [Ru₂Br₃(NH₃)₆](ZnBr₄) were calculated from data in reference 8 and 1, respectively. Estimated standard deviations (esd's) in structure parameters, occurring in the least significant figure, are given in parentheses. Esd's for Ru—X and Ru—N bond lengths are statistical and esd's for the Ru—Ru distances are experimental standard deviations.

Table 3. Selected Average Bond Angles (deg) of the Bioctahedral Complexes

complex	Ru—X—Ru	X—Ru—X	N—Ru—N	N—Ru—X
[Ru ₂ Cl ₃ (tacn) ₂](PF ₆) ₂ ·4H ₂ O	72.2(2)	88.8(14)	81.9(2)	94.6(10)
[Ru ₂ Br ₃ (tacn) ₂](PF ₆) ₂ ·2H ₂ O	70.5(4)	90.0(9)	81.8(2)	94.0(10)
[Ru ₂ I ₃ (tacn) ₂](PF ₆) ₂	69.3(1)	90.9(2)	81.3(4)	94.0(18)
[Ru ₂ Cl ₃ (NH ₃) ₆](BPh ₄) ₂ ^a	70.2(5)	90.2(12)	90.9(9)	89.5(12)
[Ru ₂ Br ₃ (NH ₃) ₆](ZnBr ₄) ^a	68.7(6)	91.2(35)	90.0(10)	89.4(21)

^a Average bond angles for [Ru₂Cl₃(NH₃)₆](BPh₄)₂ and [Ru₂Br₃(NH₃)₆](ZnBr₄) were calculated from data in refs 8 and 1, respectively. Estimated standard deviations (esd's) in structure parameters, occurring in the least significant figure, are given in parentheses. Esd's are statistical standard deviations.

Table 4. Ru—N(amine) Distances for Various Ru(II), Ru(II,III), and Ru(III) Complexes

complex	Ru—N(amine), Å	ref	complex	Ru—N(amine), Å	ref
[Ru ^{II} (NH ₃) ₆] ₂	2.144(4)	35	[Ru ^{III} (NH ₃) ₆](BF ₄) ₃	2.104(4)	35
[Ru ^{II} (NH ₃) ₆] ₂ Cl ₂	2.137(7)	36			
[Ru ^{II} (en) ₃](ZnCl ₄) ^a	2.131(3)	37	[Ru ^{III} (en) ₃] ₂ Cl ₃ ·H ₂ O ^a	2.11(3)	38
[Ru ^{II} (Mesar)](CF ₃ SO ₃) ₃ ^b	2.105(10)	39	[Ru ^{III} (sar)](CF ₃ SO ₃) ₃ ^b	2.097(8)	39
[Ru ^{II} (NH ₃) ₅ (pz)](BF ₄) ₂ ^c	2.153(9) cis 2.166(7) trans	}40	[Ru ^{III} (NH ₃) ₅ (pz)](CF ₃ SO ₃) ₃ ·H ₂ O ^c	2.106(6) cis 2.125(8) trans	}40
[Ru ^{II} (NH ₃) ₅ (Mepz)]I ₃ ^d	2.129(8) cis 2.17(1) trans		}41	[Ru ^{III} (NH ₃) ₅ (Mepz)](tos) ₄ ·5H ₂ O ^d	
[Ru ^{II} (NH ₃) ₅ (dmsO)](PF ₆) ₂ ^e	2.169(5) cis 2.209(8) trans	}42		[Ru ^{III} (NH ₃) ₅ (his)]Cl ₃ ·H ₂ O ^f	2.08(2) cis 2.12(9) trans
[Ru ^{II} (NH ₃) ₅ NO ₂]Cl·H ₂ O	2.127(5) cis 2.199(6) trans		}44	[Ru ^{III} (NH ₃) ₅ (NO)]Cl ₃ ·H ₂ O	2.09(4) cis 2.017(11) trans
[Ru ^{II} Cl(NH ₃) ₄ (SO ₂)]Cl	2.127(6) cis	}46		[Ru ^{III} (OH)(NH ₃) ₄ (NO)]Cl ₂	2.103(4) all cis
<i>cis</i> -[Ru ^{II} (NH ₃) ₄ (isn) ₂](ClO ₄) ₂ ^g	2.143(7) cis 2.167(11) trans		}47	<i>cis</i> -[Ru ^{III} (NH ₃) ₄ (isn) ₂](ClO ₄) ₃ ·H ₂ O ^g	2.118(9) cis 2.13(2) trans
[Ru ^{II} (en) ₂ (N ₃)(N ₂)](PF ₆) ^a	2.125(19)	48		<i>cis</i> -[Ru(en) ₂ (OH ₂)Cl](CF ₃ SO ₃) ₂ ·H ₂ O ^a	2.10(2)
[Ru ^{II} (NH ₃) ₅ N ₂]Cl ₂	2.10(1) av ^h	50	[Ru ^{III} (NH ₃) ₅ Cl]Cl ₂	2.096(4) cis 2.108(4) trans	}51
[(NH ₃) ₃ Ru ^{II/2} (pz)Ru ^{II/2} (NH ₃) ₅]Br _{10/3} Cl _{5/3} ·4H ₂ O ^c	2.11(1) cis 2.127(7) trans	}52	[(NH ₃) ₄ Ru ^{III} (NH ₂) ₂ Ru ^{III} (NH ₃) ₄]Cl ₄ ·4H ₂ O	2.137(3) NH ₃ 2.02(1) NH ₂	
[(NH ₃) ₃ Ru ^{II} N ₂ Ru ^{II} (NH ₃) ₅](BF ₄) ₄	2.12 cis ⁱ 2.140(6) trans		}54	[Ru ^{III} (NH ₃) ₅ (2,3-Cl ₂ pcyd)](SO ₄)·C ₂ H ₅ OH ^j	2.12(2) cis 2.105(11) trans
				[Ru ^{III} (NH ₃) ₃ Cl ₂ (caffeine)]Cl·H ₂ O	2.10(3)
			[Ru ^{III} Cl ₃ (NH ₃) ₃]	2.112(10)	57
			<i>cis</i> -[Ru ^{III} (cyclam)Cl ₂]Cl ^k	2.115(3) cis 2.105(3) trans	}58
			<i>trans</i> -[Ru ^{III} (cyclam)Cl ₂]Br ^k	2.083(3)	

^a en = ethylenediamine. ^b sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane. Mesar = 1-methyl derivative of sar. ^c pz = pyrazine. ^d Mepz⁺ = *N*-methylpyrazinium, tos = *p*-toluenesulfonate. ^e dmsO = dimethyl sulfoxide. ^f his = histidine. ^g isn = isonicotinamide. ^h Only the average value is given in ref 50. ⁱ Average value given in ref 54 with no standard deviation. ^j 2,3-Cl₂pcyd = 2,3-dichlorophenylcyanamide. ^k cyclam = 1,4,8,11-tetraazacyclotetradecane = [14]aneN₄.

coordination at each ruthenium is completed by a facially-coordinated tacn ligand. Cations **1–3** have cofacial bioctahedral geometries, and overall, the [N₃Ru(μ-X₃)RuN₃]²⁺ cores show little deviation from D_{3h} symmetry. Figure 2 shows the structure of cation **3**; the structures of cations **4** and **5** in crystals of **4a** and **5a** are very similar and, as such, are not shown here.

Average bond lengths and angles for cations **3–5** are listed in Tables 2 and 3. Average bond lengths and angles for cations **1** and **2** have been calculated from the published¹ data and are also listed in Tables 2 and 3. Complete lists of bond distances, bond angles, anisotropic thermal parameters, hydrogen atomic coordinates with isotropic thermal parameters, and fractional atomic coordinates are deposited as Supporting Information.

The average Ru—N bond length for [Ru₂Cl₃(tacn)₂]²⁺ (2.068(4) Å) is much shorter than the average Ru—N bond length for [Ru₂Cl₃(NH₃)₆]²⁺ (2.111(8) Å). Even the Ru—N bond length

for [Ru₂Br₃(tacn)₂]²⁺ (2.073(3) Å) is significantly shorter than that expected for a Ru(II_{1/2})—N bond and is, in fact, shorter than any of the Ru(III)—N bond lengths listed in Table 4. By contrast, the Ru—Cl distances in the two chloro complexes, **1** and **3**, are the same within the statistical limits. Likewise, the Ru—Br distances in **2** and **4** are the same, within statistical limits. As expected, when the bridging halide is varied from Cl to Br to I, the Ru—X distances increase: the average Ru—Br bond length (2.534(12) Å) in **4** is approximately 0.13 Å longer than the equivalent distance in the chloro complex (**3**). Correspondingly, the average Ru—I bond length (2.700(1) Å) in **5** is ca. 0.17 Å longer than the equivalent distance in the bromo complex (**4**). These changes accord well with the trends in Ru—X bond lengths in Table 5 and the increasing ionic radii in the series Cl, Br, and I (1.81, 1.95, and 2.16 Å, respectively).¹⁸

Table 5. Ru–Cl Distances for Various Ru(II), Ru(II,III), and Ru(III) Complexes

complex	Ru–Cl, Å	ref
[Ru ^{II} Cl(NH ₃) ₄ (SO ₂)]Cl	2.415(3)	46
<i>cis</i> -[Ru ^{II} (bpy) ₂ Cl ₂]·3.5H ₂ O ^a	2.426(1)	60
<i>trans</i> -[Ru ^{II} Cl ₂ (dmsO) ₄] ^b	2.402(2)	61
<i>cis</i> -[Ru ^{II} Cl ₂ (dmsO) ₄] ^b	2.423(2)	61
[NMe ₂ H ₂][<i>fac</i> -Ru ^{II} Cl ₃ (dmsO) ₃] ^b	2.426(13)	62
<i>cis</i> -[Ru ^{II} Br ₂ (dmsO) ₄] ^b	2.563(1)	61
[NEt ₄][<i>fac</i> -Ru ^{II} Br ₃ (dmsO) ₃] ^b	2.559(12)	63
[(C ₂ H ₅) ₄ N] ₂ [H ₇ O ₃ ⁺] ₂ [Cl ₃ Ru ^{III} Cl ₃ Ru ^{II} Cl ₃ Ru ^{III} Cl ₃]	2.376(13) (μ -Cl) ₃	64
	2.369(3) terminal	
Cs ₃ [Ru ₂ III ₂ Cl ₉]	2.391(4) (μ -Cl) ₃	22
	2.332(4) terminal	
[emim] ₃ [Ru ₂ III ₂ Br ₉] ^c	2.512(11) (μ -Br) ₃	21
	2.505(14) terminal	
[Ru ^{III} (NH ₃) ₅ Cl]Cl ₂	2.34(5)	51
[Ru ^{III} Cl ₃ (NH ₃) ₃]	2.377(11)	57
Cs ₂ [Ru ^{III} Cl ₅ (OH ₂) ₂]	2.353(4) <i>cis</i>	65
	2.311(8) <i>trans</i>	
<i>cis</i> -[Ru ^{III} (bpy) ₂ Cl ₂]Cl·2H ₂ O ^a	2.325(4)	60
<i>cis</i> -[Ru ^{III} (en) ₂ (OH ₂)Cl](CF ₃ SO ₃) ₂ ·H ₂ O ^d	2.323(1)	49
<i>cis</i> -[Ru ^{III} (cyclam)Cl ₂]Cl ^e	2.371(3)	58
<i>trans</i> -[Ru ^{III} (cyclam)Cl ₂]Br ^e	2.343(1)	59
Ru ₃ (μ -H)(μ -Br)(CO) ₁₀	2.566(7)	66
Ru ₃ (μ -H)(μ -I)(CO) ₉	2.685(8)	66
Ru ₃ (μ -I) ₂ (CO) ₁₀	2.768(8)	66
[(DAD)Ru(CO) ₂ I ₂] ^f	2.708(1)	67

^a bpy = bipyridine. ^b dmsO = dimethyl sulfoxide. ^c emim = 1-ethyl-3-methylimidazolium. ^d en = ethylenediamine. ^e cyclam = 1,4,8,11-tetraazacyclotetradecane = [14]aneN₄. ^f DAD = *p*-tolyl–N=CMe–CMe=N–*p*-tolyl (a diaza diene).

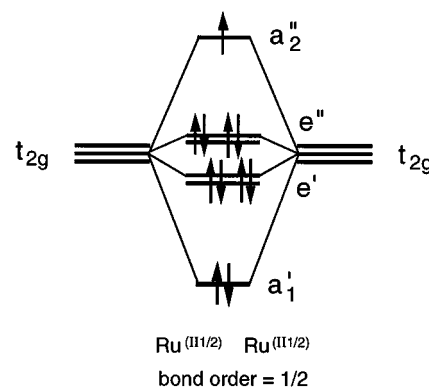
When the bridging halide is changed from Cl to Br to I, the Ru–Ru distance increases also: the average Ru–Ru distances (Å) for the chloro, bromo, and iodo complexes are respectively 2.830(1), 2.924(1), and 3.068(2) Å. In fact, for every case in which bromides and chlorides of the same metal dimer have been studied,^{19–22} the metal–metal distance for the bromide complex is longer. This is to be expected because longer Ru–X bond lengths will, necessarily, give rise to larger Ru–Ru separations unless there is a large compensating change in the Ru–X–Ru bond angle. For this series of complexes, the increase in Ru–Ru distance is moderated by a slight reduction of the Ru–X–Ru bond angle as the bridging halide goes from Cl to Br to I.

From the bond lengths listed in Table 2, the N₃RuX₃RuN₃ cores of these complexes can be compared to with those of the equivalent ammine complexes. For both the chloro and bromo cases, the Ru–Ru distances are longer in the tacn complex than in the ammine complex, while the Ru–N distances are shorter in the tacn complex. The Ru–X distances are not significantly different. The increased Ru–Ru distance is, therefore, a direct result of the larger Ru–X–Ru angles in the tacn complexes (Table 3).

Discussion

A bonding scheme for the interaction of the d orbitals in a cofacial bioctahedron of *D*_{3h} symmetry has been described in several papers^{6,23–25} and is illustrated in Scheme 1. Complexes of the type [L₃Ru(μ -X)₃RuL₃]²⁺ (L = neutral ligand, X = halide) have a total of 11 4d electrons, and so a single vacancy

Scheme 1



exists in the σ^* orbital, giving them a formal Ru–Ru bond order of $1/2$. For the ammine complexes, **1** and **2**, both vibrational and electronic spectroscopic studies^{4,6,7,26} indicated that the odd electron is delocalized over the two rutheniums. As such, the symmetrical cofacial bioctahedral geometries determined by X-ray crystallography for [Ru₂(μ -X)₃(NH₃)₆]²⁺ (X = Cl, Br)^{1,8} and [Ru₂(μ -X)₃(tacn)₂]²⁺ (X = Cl, Br, I) accord well with the delocalized electronic structure proposed previously.

Comparison of the structures reported here (**3–5**) with structures of the closely related complexes (**1** and **2**) gives an indication of the factors determining the Ru–Ru distances. For the same bridging halide, the Ru–Ru distance is longer in the tacn complexes than in the ammine complexes. As well, for all of the complexes **1–5**, there is an increase in Ru–Ru distance as the bridging halide goes from Cl to Br to I, although the latter increase is moderated by a slight reduction of the Ru–X–Ru bond angle. While a reduction in the Ru–X–Ru bond angle was interpreted previously¹ as indicating the existence of a metal–metal “bond” between the two Ru atoms for complex **2**, it is more likely that this decrease is a steric effect arising

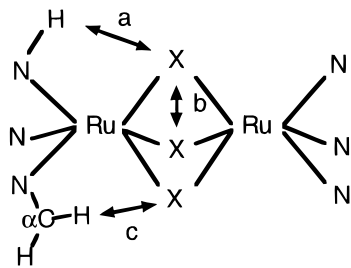
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Table 6. Closest Contacts between Atoms in the Dimers^a

complex	a, Å	b, Å	c, Å
[Ru ₂ Cl ₃ (tacn) ₂] ²⁺	3.10	3.32	2.82
[Ru ₂ Br ₃ (tacn) ₂] ²⁺	3.19	3.56	2.90
[Ru ₂ I ₃ (tacn) ₂] ²⁺	2.95	3.85	3.05

^aVan der Waals Radii (Å):³¹ H, 1.20; Cl, 1.76; Br, 1.85; I, 1.98.

**Figure 3.** Closest contacts between atoms in the [Ru₂X₃(tacn)₂]²⁺ complexes.

from the increased repulsive interaction between the larger bridging halides. Certainly, for the tacn complexes, **3–5**, the intramolecular X...X distances are much shorter than twice the van der Waals radii of X (Table 6 and Figure 3).

The related Ru^{III}₂ nonahalide dimers Cs₃[Ru₂Cl₉] and Cs₃[Ru₂Br₉] have Ru–Ru distances of 2.725(3) Å²² and 2.86 Å,²⁷ respectively, and both complexes have a formal bond order of 1. The mixed-valence dimers, **1–5**, also have three halide bridges but have formal bond orders of only 1/2. If metal–metal bonding plays a significant role in determining Ru–Ru distance in these (μ-X)₃ cofacial bioctahedral dimers, then Ru–Ru distances should be smallest in the dimers with the highest bond order. The Ru–Ru distances for the nonahalide complexes are shorter than those for the corresponding tacn complexes, **3** and **4**. However, the Ru–Ru distances for the ammine complexes, **1** and **2** (2.753(4) and 2.852(4) Å, respectively), are almost the same as those in the nonahalide dimers. Thus, it is evident that metal–metal bonding does not play a dominant role in determining the Ru–Ru distance in these cofacial bioctahedral dimers and, as such, the magnitude of the Ru–Ru distances in **3–5** cannot be used to confirm or refute the existence of a metal–metal bond.

The subject of metal–metal bonding in cofacial bioctahedral dimers has been of interest for many years,^{23,28–30} and it is well understood that there are many factors determining the geometries of the dimers and the metal–metal separations. These factors include direct metal–metal bonding, the nature of the bridging ligands, and the geometrical preference of the monomer fragment.²³ We have demonstrated that direct metal–metal bonding does not play a dominant role in determining the overall geometry of the ruthenium blue complexes, **1–5**. However, from the structural data presented in this work, it is apparent that steric interactions, particularly those between the bridging and terminal ligands, do play a significant role in determining the Ru–Ru distance and the overall geometry of complexes **3–5**.

With increasing size of the bridging halide (Cl < Br < I), there is increased repulsive interaction between the halides in the bridge, giving rise to a decrease in the Ru–X–Ru angle down the series Cl, Br, I. As a consequence of this, and also of the increased van der Waals radii of the halides, the close

proximity of the halides to the hydrogens on the tacn ligands becomes important. Due to the internal steric requirements of the tacn ligand, the average N–Ru–N angle is significantly smaller in the [Ru₂X₃(tacn)₂]²⁺ complexes (~82°) than in the [Ru₂X₃(NH₃)₆]²⁺ complexes (~90°). This has the effect of moving the tacn amine hydrogens further from the halides, and as such, the hydrogen-bonding interactions¹ between the amine hydrogens (N–H) and the bridging ligands (X) should be greater in the ammine complexes, **1** and **2**, than in the tacn complexes, **3–5**. However, in **3–5**, the closest intramolecular contacts are not between N–H and X; there are closer contacts between hydrogens on the α-carbon in tacn (C–H) and X. Unlike the attractive hydrogen-bonding interaction between N–H and X, that between C–H and X is repulsive. For all of the complexes **3–5** (Table 6 and Figure 3), the distance between C–H and X is significantly shorter than the sum of their van der Waals radii.³¹ As such, there must be appreciable steric hindrance from the tacn ligand as a result of the repulsive interaction between C–H and X.

As the size of the bridging halide is increased, the repulsive interaction between C–H and X becomes greater. Increasing the Ru–X–Ru angles, which would increase the separation of C–H and X, would minimize this repulsive interaction. However, the intramolecular X...X distances are much shorter than twice the van der Waals radii of X (Table 6 and Figure 3). The overall result is that the Ru–X–Ru angles are slightly larger in the tacn complexes, **3** and **4**, than in the equivalent ammine complexes, **1** and **2**.

For a given halide, there are no significant differences between the average Ru–X distances for the ammine and the tacn complexes: the average Ru–X distance is ~2.40 Å for both of the chloro complexes, **1** and **3**, and ~2.53 Å for both of the bromo complexes, **2** and **4**. On the other hand, the Ru–Ru distances in the tacn complexes are significantly longer than those in the corresponding ammine complexes. The latter observation can be attributed directly to the steric interaction between C–H and X, discussed above. It is the larger Ru–X–Ru bond angles that give rise to the longer Ru–Ru distances observed in the tacn complexes compared to the analogous ammine complexes.

The average Ru–N bond lengths for the chloro and bromo tacn complexes, **3** and **4**, are 2.068 and 2.073 Å, respectively. These bond lengths are significantly shorter than most other reported Ru(II)–N and Ru(III)–N amine bonds lengths (Table 4) and, as such, are much shorter than expected for a ruthenium(II^{1/2}) amine complex. We have already shown that the steric requirements of the tacn ligand affect greatly the Ru–Ru distances and the N–Ru–N angles (82°) in complexes **3–5**. In view of this, it is reasonable to assume that the short Ru–N bond lengths in complexes **3–5** are also a result of the steric constraints imposed by the tacn ligand. The only other similar ruthenium complex containing such short Ru–N bond lengths and acute N–Ru–N angles (81°) is the analogous tacn complex [Ru₂(μ-OH)₂(μ-OH)(tacn)₂][I₃H₂O].¹²

Conclusions

The X-ray crystal structures of [Ru₂Cl₃(tacn)₂]²⁺, [Ru₂Br₃(tacn)₂]²⁺, and [Ru₂I₃(tacn)₂]²⁺ have provided valuable information about the effects of steric interactions on the geometry of these complexes. The structures show, quite clearly, that the tridentate tacn ligands are more sterically demanding than the unidentate NH₃ ligands. The average N–Ru–N angle in each of the tacn complexes, **3–5** (~82°), is significantly smaller than

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that in the ammine complexes, **1** and **2** ($\sim 90^\circ$), and despite this, there is considerable steric hindrance between the hydrogens on the α -carbon of tacn and the halide bridge—particularly for the bromo and iodo complexes. The steric requirements imposed by the tacn ligands lead to an increase in the Ru—X—Ru angle which, in turn, increases the Ru—Ru distances in the tacn complexes compared to the corresponding NH_3 complexes. It is also apparent that the short Ru—N bond lengths may be due, in part, to the steric demands of the tacn ligands.

There have been several structures published of trichloro-bridged $\text{Ru}^{\text{II } 1/2}\text{—Ru}^{\text{II } 1/2}$ species^{8,32–34} and only one structure of a tribromo-bridged $\text{Ru}^{\text{II } 1/2}\text{—Ru}^{\text{II } 1/2}$ species.¹ However, this

appears to be the first structure report of a mixed-valence $\text{Ru}^{\text{II } 1/2}\text{—Ru}^{\text{II } 1/2}$ dimer with a triiodo bridge. Structural information, of the type described here, has been invaluable in the interpretation of the electronic and resonance Raman (RR) spectroscopies¹⁰ of $[\text{Ru}_2\text{Cl}_3(\text{tacn})_2]^{2+}$, $[\text{Ru}_2\text{Br}_3(\text{tacn})_2]^{2+}$, and $[\text{Ru}_2\text{I}_3(\text{tacn})_2]^{2+}$. As well, it has proven to be extremely useful in understanding the electrochemical behavior¹⁰ of these complexes—the electrochemistry and the electronic and RR spectroscopies of the ruthenium blues are currently being investigated, the results of which will be published in the near future.

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Supporting Information Available: Listings of crystal data and structure refinement parameters, non-hydrogen fractional atomic coordinates and anisotropic thermal parameters, hydrogen positional and isotropic thermal parameters, bond distances, and bond angles for each of the three crystal structures, ORTEP drawings of compounds **4** and **5**, and a packing diagram of the unit cell of compound **3** (16 pages). Ordering information is given on any current masthead page.

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