Inorg. Chem. **1996,** *35,* 3163−3172 **3163**

Syntheses and Crystal Structures of Ruthenium Complexes of 1,4,8,11-Tetraazacyclotetradecane, Tris(2-aminoethyl)amine (tren), and Bis(2-aminoethyl)(iminomethyl)amine. A Microporous Layered Structure Consisting of $\{[K(tren)]_2[RuCl_6]\}_n^{n-}$ and $\{(H_5O_2)_4[RuCl_6]\}_n^{n+}$

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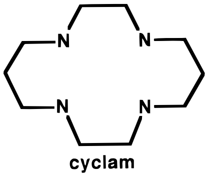
Received June 2, 1995[⊗]

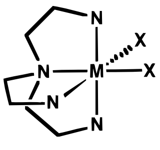
The second method for the synthesis of *cis*-$[Ru^{III}Cl_2(cyclam)]Cl$ (**1**) (cyclam = 1,4,8,11-tetraazacyclotetradecane), with use of *cis*-$Ru^{II}Cl_2(DMSO)_4$ (DMSO = dimethyl sulfoxide) as a starting complex, is reported together with the synthesis of $[Ru^{II}(cyclam)(bpy)](BF_4)_2\cdot H_2O$ (**2**) (bpy = 2,2′-bipyridine) from **1**. The syntheses of Ru complexes of tris(2-aminoethyl)amine (tren) are also reported. A reaction between $K_3[Ru^{III}(ox)_3]$ (ox = oxalate) and tren affords *fac*-$[Ru^{III}Cl_3(trenH)]Cl\cdot{}^1/_2H_2O$ (**3**) (trenH = bis(2-aminoethyl)(2-ammonioethyl)amine = monoprotonated tren) and $(H_5O_2)_2[K(tren)][Ru^{III}Cl_6]$ (**4**) as major products and gives *fac*-$[Ru^{III}Cl(ox)(trenH)]Cl\cdot{}^3/_2H_2O$ (**5**) in very low reproducibility. A reaction between **3** and bpy affords $[Ru^{II}(baia)(bpy)](BF_4)_2$ (**6**) (baia = bis(2-aminoethyl)-(iminomethyl)amine), in which tren undergoes a selective dehydrogenation into baia. The crystal structures of **2**−**6** have been determined by X-ray diffraction, and their structural features are discussed in detail. Crystallographic data are as follows: **2**, $RuF_8ON_6C_{20}B_2H_{34}$, monoclinic, space group $P2_1/c$ with $a = 12.448(3)$ Å, $b = 13.200(7)$ Å, $c = 17.973(4)$ Å, $\beta = 104.28(2)°$, $V = 2862(2)$ Å^3, and $Z = 4$; **3**, $RuCl_4O_{0.5}N_4C_6H_{20}$, monoclinic, space group $P2_1/a$ with $a = 13.731(2)$ Å, $b = 14.319(4)$ Å, $c = 13.949(2)$ Å, $\beta = 90.77(1)°$, $V = 2742(1)$ Å^3, and $Z = 8$; **4**, $RuKCl_6O_4N_4C_6H_{28}$, trigonal, space group $R\bar{3}$ with $a = 10.254(4)$, $c = 35.03(1)$ Å, $V = 3190(2)$ Å^3, and $Z = 6$; **5**, $RuCl_2O_{5.5}N_4C_8H_{22}$, triclinic, space group $P\bar{1}$ with $a = 10.336(2)$ Å, $b = 14.835(2)$ Å, $c = 10.234(1)$ Å, $\alpha = 90.28(1)°$, $\beta = 90.99(1)°$, $\gamma = 92.07(1)°$, $V = 1567.9(4)$ Å^3, and $Z = 4$; **6**, $RuF_8N_6C_{16}B_2H_{24}$, monoclinic, space group $P2_1/c$, $a = 10.779(2)$ Å, $b = 14.416(3)$ Å, $c = 14.190(2)$ Å, $\beta = 93.75(2)°$, $V = 2200.3(7)$ Å^3, and $Z = 4$. Compound **4** possesses a very unique layered structure made up of both anionic and cationic slabs, $\{[K(tren)]_2[Ru^{III}Cl_6]\}_n^{n-}$ and $\{(H_5O_2)_4[Ru^{III}Cl_6]\}_n^{n+}$ ($n = \infty$), in which both sheets $\{[K(tren)]_2\}_n^{2n+}$ and $\{(H_5O_2)_4\}_n^{4n+}$ offer cylindrical pores that are occupied with the $[Ru^{III}Cl_6]^{3-}$ anions. The presence of a C=N double bond of baia in **6** is judged from the C−N distance of 1.28(2) Å. It is suggested that the structural restraint enhanced by the attachment of alkylene chelates at the nitrogen donors of amines results in either the *mislocation* or *misdirection* of the donors, leading to the elongation of the Ru−N(amine) distances and to the weakening of their trans influence. Such structural strain is also discussed as related to the spectroscopic and electrochemical properties of the *cis*-$[Ru^{II}L_4(bpy)]^{2+}$ complexes ($L_4 = (NH_3)_4$, (ethylenediamine)$_2$, and cyclam).

Introduction

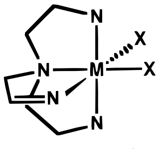
The ruthenium complexes having a general formula of either *cis*-$Ru^{II}Cl_2L_4$ or *cis*-$[Ru^{III}Cl_2L_4]^+$ ($L_4 = (NH_3)_4$,[1] (en)$_2$,[2] (bpy)$_2$,[3] and cyclam,[4] where en = ethylenediamine, bpy = 2,2′-bipyridine, and cyclam = 1,4,8,11-tetraazacyclotetradecane, **I**)



cyclam
I



[M(tren)X$_2$]
II



[M(baia)X$_2$]
III

have been widely used as useful precursors in a variety of inorganic syntheses. In our recent efforts to obtain bifunctional molecules containing more than two different metal centers, we initially tried to use *cis*-$[Ru^{III}Cl_2(cyclam)]Cl$ (**1**[4]) as a starting complex. However, we could not reproduce **1** in sufficient yield according to the method reported by Che et al.[4] Therefore we had to re-explore a better method for the preparation of compound **1** and are now able to report here on the second synthetic route for **1**.

As an alternative approach, we have also attempted to obtain an analogue of **1** by using "tren" (tris(2-aminoethyl)amine), instead of cyclam, as the ligand L_4. In contrast with the nature of cyclam being capable of forming both the cis[4] and trans[5] isomers, the ligand tren cannot help affording the cis isomer (**II**) when it occupies four of six octahedral coordination sites. The coordination chemistry of tren and the related multidentate amines have been extensively studied for the Rh(III)[6] and Co(III)[7] ions; however, no ruthenium complexes of tren have been reported so far. So we now report here on the first example of the syntheses and crystal structures of the ruthenium complexes containing tren and its dehydrogenated derivative,

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[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1996.

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S0020-1669(95)00688-4 CCC: 12.00 dollars

Table 1. Crystallographic Data of **2**−**6**

	2	**3**	**4**	**5**	**6**
formula	$RuF_8ON_6C_{20}B_2H_{34}$	$RuCl_4O_{0.5}N_4C_6H_{20}$	$RuKCl_6O_4N_4C_6H_{28}$	$RuCl_2O_{5.5}N_4C_8H_{22}$	$RuF_8N_6C_{16}B_2H_{24}$
fw	649.21	399.13	573.20	434.26	575.08
space group	$P2_1/c$ (No. 14)	$P2_1/a$ (No. 14)	$R\bar{3}$ (No. 148)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	12.448(3)	13.731(2)	10.254(4)	10.336(2)	10.779(2)
b, Å	13.200(7)	14.319(4)		14.835(2)	14.416(3)
c, Å	17.973(4)	13.949(2)	35.03(1)	10.234(1)	14.190(2)
α, deg				90.28(1)	
β, deg	104.28(2)	90.77(1)		90.99(1)	93.75(2)
γ, deg				92.07(1)	
V, Å^3; Z	2862(2); 4	2742(1); 8	3190(2); 6	1567.9(4); 4	2200.3(7); 4
ρ_{calcd}, g/cm^3	1.507	1.934	1.790	1.840	1.736
μ, cm^{-1}	6.24	19.04	17.03	13.67	7.97
R^a ($R_w{}^b$)	0.081 (0.071)	0.042 (0.039)	0.050 (0.046)	0.037 (0.031)	0.064 (0.049)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(F_o)$.

bis(2-aminoethyl)(iminomethyl)amine (baia, **III**). The selective dehydrogenation reaction of tren into baia observed in this study can be viewed as related to the previous works on the oxidation reactions of amines bound to Ru(III) into imines and nitriles.[8]

In addition, we show that a byproduct obtained in the synthesis of the ruthenium complex of tren possesses a very attractive two-dimensional layered structure. In this paper, special attention has also been paid to the structural strain around the N(L_4) donors derived from chelate rings, because of our question of how the *misdonation* (=*inappropriate donation*) of donors may affect the spectroscopic and electrochemical properties of the *cis*-$[Ru^{II}L_4(bpy)]^{2+}$ complexes (L_4 = $(NH_3)_4$, $(en)_2$, and cyclam).

Experimental Section

Syntheses. *cis*-$RuCl_2(DMSO)_4$[9] (DMSO = dimethyl sulfoxide) and $K_2[RuCl_5(H_2O)]$[10] were prepared according to the literature methods. A solution of $K_3[Ru(ox)_3]$ (ox = oxalate) was prepared according to the method reported by Che et al.[4]

***cis*-$[Ru^{III}Cl_2(cyclam)]Cl$ (1).** The new method developed in this work is as follows: A solution of *cis*-$RuCl_2(DMSO)_4$[9] (1 mmol) and cyclam (1 mmol) in ethanol (10 mL) was refluxed for 2 h followed by addition of concentrated HCl (10 mL). After bubbling with air for 20 min, the solution was refluxed for 3 h. Cooling of the solution to room temperature afforded a yellow powder, which was collected by filtration, washed with ethanol, and air-dried (yield: 65%). Anal. Calcd for $RuCl_3N_4C_{10}H_{24}$: C, 29.46; H, 5.93; N, 13.74. Found: C, 29.82; H, 6.02; N, 13.69.

$[Ru^{II}(cyclam)(bpy)](BF_4)_2 \cdot H_2O$ (2). A solution of **1** (0.2 mmol) and bpy (0.24 mmol) in ethanol (20 mL) was refluxed for 4 h followed by addition of an aqueous saturated $NaBF_4$ solution (0.1 mL). The solution was evaporated to a total volume of ca. 6 mL. The red microcrystals deposited were redissolved with heat, and the solution was filtered while it was hot. Standing of the filtrate at 5 °C overnight afforded the product as dark red prisms (yield: 70%). Anal. Calcd for $RuF_8ON_6C_{20}B_2H_{34}$: C, 37.00; H, 5.28; N, 12.95. Found: C, 36.67; H, 4.90; N, 12.47.

***fac*-$[Ru^{III}Cl_3(trenH)]Cl \cdot {}^1/_2H_2O$ (3) (trenH = Bis(2-aminoethyl)-(2-ammonioethyl)amine), $(H_5O_2)_2[K(tren)][Ru^{III}Cl_6]$ (4), and *fac*-$[Ru^{III}Cl(ox)(trenH)]Cl \cdot {}^3/_2H_2O$ (5).** A solution of $K_2[RuCl_5(H_2O)]$[10] (1 mmol) and oxalic acid (3.38 mmol) in water (6 mL) was refluxed for 2.5 h followed by a neutralization with K_2CO_3. Further refluxing for 30 min gave a dark green solution containing $K_3[Ru(ox)_3]$.[4] A solution of tren in 1 M HCl (1.0 mmol/5.0 mL) was added dropwise to the former solution, under reflux, over 30 min. The solution was further refluxed for 3 h followed by addition of concentrated HCl (1.8 mL), during which the color of the solution turned red. Further refluxing for 2 h gave a dark green solution, which was left at 5 °C overnight. Reddish-brown prisms of **3** deposited at the bottom of the flask, and brown thin plates of **4** appeared on the surface of the solution. Without performing filtration, only the former crystals were collected by normal pipetting-out procedures, filtered, and dried in vacuo (yield: 10−20%). Anal. Calcd for $RuCl_4O_{0.5}N_4C_6H_{20}$: C, 18.06; H, 5,05; N, 14.04. Found: C, 17.83; H, 5.16; N, 13.84. After the complete removal of **3** from the reaction mixture, the crystals of **4** were collected by filtration (yield: 20−30%). Anal. Calcd for $RuKCl_6O_4N_4C_6H_{28}$: C, 12.57; H, 4.92; N, 9.77. Found: C, 12.61; H, 5.13; N, 9.68.

Brown cubes of $[Ru^{III}Cl(ox)(trenH)]Cl \cdot {}^3/_2H_2O$ (**5**) were accidentally isolated, about once in 10 times, during the optimization of the synthesis of **3**. However, the reproducibility of **5** was found to be extremely low, even though we pursued its optimized conditions by varying the amounts of both hydrochloric acid and oxalic acid. When we obtained this compound by chance, there were somehow no crystals of **3** codeposited, and therefore the sample of **5** obtained was pure enough to be analyzed without any treatment: Anal. Calcd for $RuCl_2O_{5.5}N_4C_8H_{22}$: C, 22.13; H, 5,11; N, 12.90. Found: C, 21.92; H, 5.10; N, 12.80.

$[Ru^{II}(baia)(bpy)](BF_4)_2$ (6). To 20 mL of ethanol were added **3** (0.2 mmol), bpy (0.24 mmol), and 2 mL of 0.1 M KOH. The same procedures as **2** afforded the product as dark red needles (yield: 60%). Anal. Calcd for $RuF_8N_6C_{16}B_2H_{24}$: C, 33.42; H, 4.21; N, 14.61. Found: C, 32.94; H, 4.01; N, 14.14. The assignment of ^1H NMR signals corresponding to the imino proton of baia is not successful due to the coexistence of H(bpy) signals in the same region.

X-ray Crystallography. Crystals obtained above were used without further treatment. Crystals were mounted on glass fibers. Diffraction data at 23 °C were measured on a Rigaku AFC-5S diffractometer using graphite monochromated Mo Kα (0.710 69 Å) radiation and the $\omega-2\theta$ scan technique (8 deg/min). Crystal data of **2**−**6** are listed in Table 1. All data sets were corrected for Lorentz and polarization effects and for absorption by employing ψ scans on several reflections with χ near 90°.[11] Metal atom positions were determined by direct methods (SAPI91[12] for **2** and **4**−**6** and SIR88[13] for **3**) and the remaining non-hydrogen atoms were located using both the DIRDIF[14] program and the difference Fourier techniques. Typically, all non-hydrogen atoms

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were refined anisotropically by full-matrix least squares. All hydrogen atoms, excluding those of water molecules, were located in their idealized positions (C−H = 0.95 and N−H = 0.87 Å), were included in the final refinements, and were not refined. Hydrogen atoms of water molecules were not located. Best-plane calculations were carried out using the BP70[15] program. Other calculations were all performed using the teXsan[16] software. Final positional and thermal parameters of **2**−**6** are offered as Supporting Information (Tables S4−S13).

Refinement for [Ru^{II}(cyclam)(bpy)](BF$_4$)$_2$·H$_2$O (2). Both of the B atoms were visible in the difference Fourier map but could not be refined. Therefore, all the atoms of each BF$_4^-$ ion were first refined isotropically under the rigid-group constraint with each atom having an equal temperature factor, and, at the final stage of the refinement, only the F atoms were refined anisotropically but all of the parameters of the B atoms were fixed.

Refinement for *fac*-[Ru^{III}Cl$_3$(trenH)]Cl·$^1/_2$H$_2$O (3). One of the two independent molecules shows disorder phenomena in which every ethylene moiety of trenH is disordered over two geometries. The occupancy value of each atom in each geometry was first refined independently and converged at a value close to $^1/_2$. Therefore, the occupancy value for each disordered site was finally taken to be 0.50. Hydrogen atoms on the disordered carbon atoms were not located.

Refinement for (H$_5$O$_2$)$_2$[K(tren)][Ru^{III}Cl$_6$] (4). When the O(1) atom locating on the 3-fold axis was normally refined anisotropically, it displayed an extraordinarily large thermal factor (U_{eq} = 0.164(6) Å^2) with the ellipsoid being largely elongated along the 3-fold axis. Therefore, we tried to resolve possible disordered structures hidden in this geometry. As a result, the O(1) atom was located over two sites (O(1A) and O(1B)) along the 3-fold axis, and their occupancy values were refined under the constraint of occupancy(O(1A)) + occupancy(O(1B)) = $^1/_3$. This treatment resulted in the effective diminution of both the temperature and the reliability factors.

Refinements for *fac*-[Ru^{III}Cl(ox)(trenH)]Cl·$^3/_2$H$_2$O (5) and [Ru^{II}(baia)(bpy)](BF$_4$)$_2$ (6). No special treatment was applied to each crystallography.

Measurements. UV−visible spectra were recorded on a Hitachi 340 spectrophotometer. Proton NMR spectra were acquired on a JEOL JNM-GX270 spectrometer. Cyclic voltammograms were measured on a Huso setup (HECS 321B and 311B), in which a Pt disk was employed as the working electrode.

EHMO Calculations. EHMO calculations were performed by using the ICON (QCMP011) program supplied from QCPE, Department of Chemistry, Indiana University, Bloomington, IN. The atomic parameters of Ru used are those in the literature.[17] Geometric parameters of [Ru^{II}(NH$_3$)$_4$(bpy)]$^{2+}$ and [Ru^{II}(en)$_2$(bpy)]$^{2+}$ have been constructed by using those of [Ru(NH$_3$)$_4$(glycinamido)](PF$_6$)[18] and [Ru(en)$_3$][ZnCl$_4$],[19] respectively, where those for the Ru(bpy) geometry has been extracted from the X-ray data of **2**. Geometric parameters for [Ru^{II}L$_4$(bpy)]$^{2+}$ (L$_4$ = cyclam, **2**, and baia, **6**) are those in the X-ray studies.

Results and Discussion

Syntheses. It was found that *cis*-[Ru^{III}Cl$_2$(cyclam)]Cl (**1**) can be prepared in good yield by employing *cis*-Ru^{II}Cl$_2$(DMSO)$_4$ (DMSO = dimethyl sulfoxide) as a starting material, although Che et al. previously prepared this complex from a solution of K$_3$[Ru(ox)$_3$] (ox = oxalate).[4] However, it is important to note here that the yield in the synthesis is quite sensitive to the quality of the starting material *cis*-Ru^{II}Cl$_2$(DMSO)$_4$. On the other hand, Che et al. also prepared [Ru^{II}(cyclam)(bpy)](PF$_6$)$_2$ by reacting complex **1** with a slight excess of bpy in water under Ar in the presence of amalgamated zinc.[4] In the present study, we prepared its tetrafluoroborate salt [Ru^{II}(cyclam)(bpy)](BF$_4$)$_2$·H$_2$O (**2**) by merely refluxing a solution of **1** and bpy in ethanol, in which the product deposited as quality single crystals that are suitable for the X-ray diffractometry.

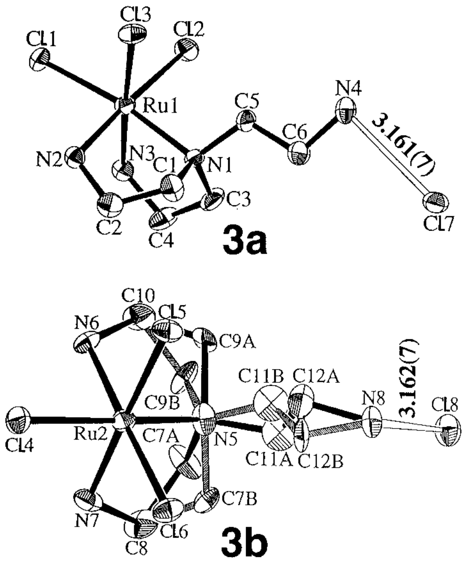

Figure 1. Structures of two independent *fac*-[Ru^{III}Cl$_3$(trenH)]Cl molecules in **3** (**3a** and **3b**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and a water molecule are omitted for clarity. Hydrogen bonds for N(ammonio group)···Cl are drawn with open lines.

On the other hand, with the aim of obtaining an analogue of **1** having tren instead of cyclam, *cis*-Ru^{II}Cl$_2$(DMSO)$_4$ was similarly reacted with tren under various reaction conditions, including those adopted in the synthesis of **1**, but all of the efforts resulted in vain. However, a reaction of K$_3$[Ru^{III}(ox)$_3$] with tren in the presence of hydrochloric acid afforded an unexpected complex *fac*-[Ru^{III}Cl$_3$(trenH)]Cl·$^1/_2$H$_2$O (**3**) (trenH = bis(2-aminoethyl)(2-ammonioethyl)amine), where trenH corresponds to the monoprotonated form of tren and its unprotonated diethylenetriamine moiety serves as a tridentate ligand in a facial manner. Thus the finally adopted synthetic method of **3** rather resembles that of **1** reported by Che et al. in that the starting material is K$_3$[Ru^{III}(ox)$_3$]. In the synthesis, reddish-brown prisms of **3** deposit at the bottom of the flask, and brown thin plates (**4**) simultaneously glow at the surface of the reaction mixture as a byproduct. To our astonishment, their crystal densities (1.934, **3**, and 1.790 g/cm^3, **4**; Table 1) are not significantly different from each other. This implies that the synthetic solution *fortunately* had a density between these two values, allowing us to separate the two products without any difficulty. On the basis of both the results of the elemental analysis and the X-ray diffractometry, the composition of the latter byproduct has been determined to be (H$_5$O$_2$)$_2$[K(tren)][Ru^{III}Cl$_6$] (**4**). In addition, as described in detail in the Experimental Section, *fac*-[Ru^{III}Cl(ox)(trenH)]Cl·$^3/_2$H$_2$O (**5**), which possesses an oxalate dianion instead of two of three chloride ions in **3**, was accidentally isolated; however, a reproducible method for the preparation of **5** remains unexplored.

Finally, in order to evaluate the usefulness of compound **3** as a precursor in other inorganic syntheses and to obtain a complex having a "*cis*-Ru(tren)" moiety, a reaction of complex **3** with 1 equiv of bpy was conducted as the simplest model for the reaction of complex **3**. However, the reaction gave another unexpected complex [Ru^{II}(baia)(bpy)](BF$_4$)$_2$ (**6**), in which one of the primary amines in the tren ligand had undergone an oxidative dehydrogenation to give the ligand baia. Such oxidation reactions of amines coordinated to Ru(III) have been well-investigated, so far, for several Ru(III) complexes.[8] It is

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Table 2. Selected Interatomic Distances (Å) and Angles (deg) for *fac*-[Ru^{III}Cl$_3$(trenH)]Cl·$^1/_2$H$_2$O (**3**)

Ru(1)−Cl(1)	2.378(2)	Ru(1)−Cl(2)	2.381(2)
Ru(1)−Cl(3)	2.387(2)	Ru(1)−N(1)	2.126(6)
Ru(1)−N(2)	2.081(6)	Ru(1)−N(3)	2.081(6)
Ru(2)−Cl(4)	2.364(2)	Ru(2)−Cl(5)	2.392(2)
Ru(2)−Cl(6)	2.383(2)	Ru(2)−N(5)	2.145(6)
Ru(2)−N(6)	2.087(6)	Ru(2)−N(7)	2.085(6)
N(1)−C(1)	1.502(10)	N(1)−C(3)	1.514(10)
N(1)−C(5)	1.499(9)	N(2)−C(2)	1.485(10)
N(3)−C(4)	1.469(10)	N(4)−C(6)	1.476(9)
C(1)−C(2)	1.47(1)	C(3)−C(4)	1.47(1)
C(5)−C(6)	1.484(10)	N(7)−C(8)	1.486(10)
N(6)−C(10)	1.480(10)	N(5)−C(7A)	1.47(2)
N(5)−C(7B)	1.64(2)	N(5)−C(9A)	1.63(2)
N(5)−C(9B)	1.46(2)	N(5)−C(11A)	1.55(2)
N(5)−C(11B)	1.43(3)	N(8)−C(12B)	1.43(2)
N(8)−C(12A)	1.47(3)	C(7A)−C(8)	1.55(2)
C(7B)−C(8)	1.38(2)	C(9A)−C(10)	1.38(2)
C(9B)−C(10)	1.54(2)	C(11A)−C(12A)	1.51(4)
C(11B)−C(12B)	1.51(4)		

Cl(1)−Ru(1)−Cl(2)	90.98(7)	Cl(1)−Ru(1)−Cl(3)	91.49(8)
Cl(1)−Ru(1)−N(1)	172.0(2)	Cl(1)−Ru(1)−N(2)	91.8(2)
Cl(1)−Ru(1)−N(3)	91.7(2)	Cl(2)−Ru(1)−Cl(3)	92.25(8)
Cl(2)−Ru(1)−N(1)	94.7(2)	Cl(2)−Ru(1)−N(2)	177.2(2)
Cl(2)−Ru(1)−N(3)	87.7(2)	Cl(3)−Ru(1)−N(1)	94.0(2)
Cl(2)−Ru(1)−N(3)	87.7(2)	Cl(3)−Ru(1)−N(1)	94.0(2)
Cl(3)−Ru(1)−N(2)	88.5(2)	Cl(3)−Ru(1)−N(3)	176.9(2)
N(1)−Ru(1)−N(2)	82.5(2)	N(1)−Ru(1)−N(3)	82.9(2)
N(2)−Ru(1)−N(3)	91.5(2)	Cl(4)−Ru(2)−Cl(5)	90.61(8)
Cl(4)−Ru(2)−Cl(6)	91.62(8)	Cl(4)−Ru(2)−N(5)	168.3(2)
Cl(4)−Ru(2)−N(6)	90.3(2)	Cl(4)−Ru(2)−N(7)	91.4(2)
Cl(5)−Ru(2)−Cl(6)	94.37(7)	Cl(5)−Ru(2)−N(5)	96.6(2)
Cl(5)−Ru(2)−N(6)	85.7(2)	Cl(5)−Ru(2)−N(7)	177.9(2)
Cl(6)−Ru(2)−N(5)	97.0(2)	Cl(6)−Ru(2)−N(6)	178.0(2)
Cl(6)−Ru(2)−N(7)	84.9(2)	N(5)−Ru(2)−N(6)	81.1(3)
N(5)−Ru(2)−N(7)	81.5(3)	N(6)−Ru(2)−N(7)	95.0(2)
Ru(1)−N(1)−C(1)	107.4(5)	Ru(1)−N(1)−C(3)	106.8(5)
Ru(1)−N(1)−C(5)	111.1(4)	Ru(1)−N(2)−C(2)	111.8(5)
Ru(1)−N(3)−C(4)	112.4(5)	Ru(2)−N(5)−C(7B)	102.0(7)
Ru(2)−N(5)−C(7A)	109.8(7)	Ru(2)−N(5)−C(9B)	109.8(7)
Ru(2)−N(5)−C(9A)	102.6(7)	Ru(2)−N(5)−C(11B)	117.7(10)
Ru(2)−N(5)−C(11A)	22(1)	Ru(2)−N(6)−C(10)	112.8(5)
Ru(2)−N(7)−C(8)	112.8(5)		

Possible Hydrogen Bonds

Cl(4)−N(4)	3.314(7)	Cl(7)−N(4)	3.161(7)
Cl(7)−N(7)	3.264(7)	Cl(8)−N(8)	3.162(7)
Cl(8)−N(3)[a]	3.193(6)	Cl(8)−N(2)[a]	3.296(7)
Cl(1)−N(8)[b]	3.248(6)	Cl(7)−N(8)[c]	3.293(7)
Cl(3)−N(4)[d]	3.179(7)	Cl(4)−N(2)[d]	3.383(7)
Cl(2)−N(8)[e]	3.317(7)	Cl(5)−N(4)[e]	3.221(7)
O(1)−N(4)[e]	2.991(9)	Cl(6)−N(8)[f]	3.386(7)
Cl(8)−O(1)[g]	3.070(7)		

[a−g] Symmetry operations: (a) $-1 + x, y, 1 + z$; (b) $1 + x, y, -1 + z$; (c) $-^3/_2 - x, -^1/_2 + y, 2 - z$; (d) $-1 - x, 1 - y, 1 - z$; (e) $-1 - x, 1 - y, 2 - z$; (f) $-2 - x, 1 - y, 2 - z$; (g) $-^1/_2 + x, ^1/_2 - y, z$.

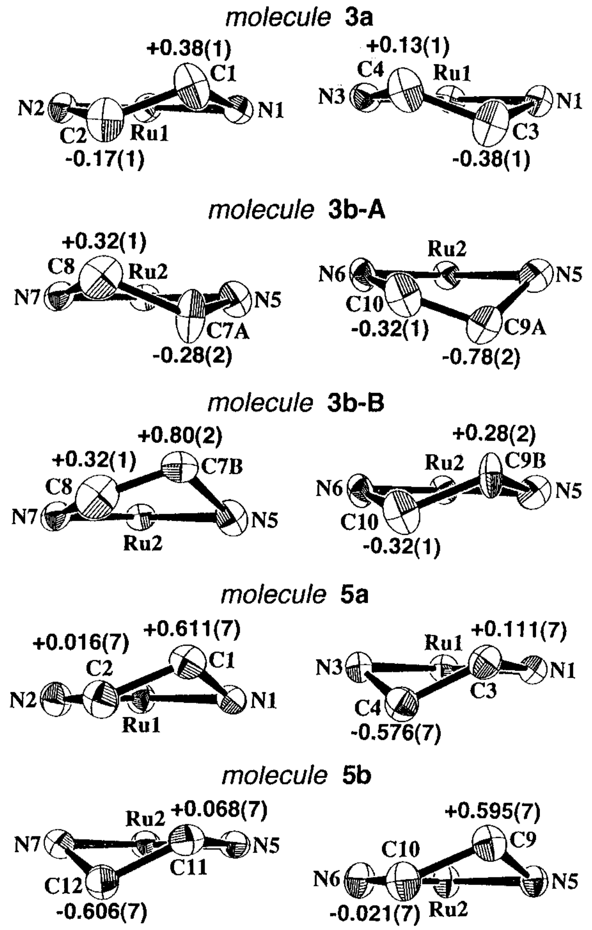


Figure 2. Views parallel to the N−Ru−N planes for the five-membered chelate rings involved in **3** and **5**, where values are shifts (Å) of C atoms from the corresponding N−Ru−N plane (see also Table 3).

now believed that Ru(III) complexes disproportionate into the Ru(II) and Ru(IV) species and the dehydrogenation of amines occurs *via* the intermediate Ru(IV) species.[8e]

Structure of *fac*-[Ru^{III}Cl$_3$(trenH)]Cl·$^1/_2$H$_2$O (3). Compound **3** contains two independent *fac*-[Ru^{III}Cl$_3$(trenH)]Cl molecules in the asymmetric unit (**3a** and **3b** in Figure 1). Selected interatomic distances and angles for **3** are summarized in Table 2. Note that all of the C−N distances (1.43(2)−1.48(1) Å) possess a single-bond character, which reconfirms that no C=N double bond is formed during the synthesis of **3**. On the bases of both the oxidation state of Ru and the total charge of the complex, the uncoordinated primary amine in each molecule is judged to be in the protonated form ($-NH_3^+$). These ammonio groups are hydrogen bonded to the neighboring chloride counterions (N(4)−Cl(7) = 3.161(7) and N(8)−Cl(8) = 3.162(7) Å). As summarized in Table 2, both the coordinated and the chloride counterions are further associated with either the amino or ammonio groups of the neighboring cations, giving a three-dimensional hydrogen bonding network (N($-NH_2$ or $-NH_3^+$)−Cl = 3.179(7)−3.386(7) Å; see Table 2). Although **3a** and **3b** are chemically identical, they exhibit a distinct structural difference in the chelating ethylene geometries, which must be relevant to the difference of their packing environments. Although molecule **3a** does not possess any disorder problem, every ethylene moiety in **3b** is disordered over two geometries (**A** and **B**), where the two disordered structures have been judged to have an equal population and therefore the occupancy values of all of the disordered atoms have been taken to be 0.50. Molecule **3a** almost satisfies C_s symmetry, while both **3b-A** and **-B** possess no imposed symmetry (Figure 1). The reason why only **3b** possesses disordered structures may be that molecule **3b** has more space around the ethylene unit than has molecule **3a**.

Views for the chelating geometries found in **3** and **5** are shown in Figure 2, and the results of best-plane calculations for these geometries, together with those for **1**, **2**, and **6**, are summarized in Table 3. They show that most of the five-membered chelate rings tend to form a so-called *envelope* conformation. A pure *gauche* conformation is only found in molecules **3b-A** and **-B**. Each five-membered chelate ring in **3a** has an intermediate structure between envelope and gauche conformations (gauche−envelope). In either molecule **3b-A** or **-B**, one chelate ring has a gauche conformation and the other has an envelope conformation.

Turning our attention to the coordination sphere, we see that all of the Ru−Cl distances (Table 2) are much longer than the

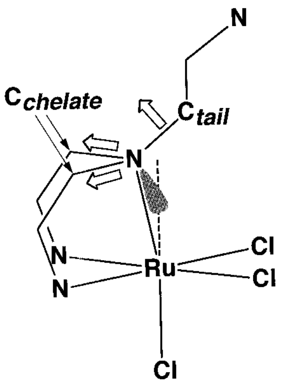
Table 3. Structural Features of Five- and Six-Membered Chelate Rings in **1**−**3**, **5**, and **6**[a]

complex	N1−Ru−N2	C1 (shift,[b] Å)	C2 (shift,[b] Å)	C3 (shift,[b] Å)	conformation
1[c]	N(3)Ru(1)N(2)	C(5) (−0.205(7))	C(4) (+0.493(6))		gauche−envelope
	N(4)Ru(1)N(1)	C(9) (−0.508(8))	C(10) (+0.196(8))		gauche−envelope
	N(2)Ru(1)N(1)	C(3) (+0.886(6))	C(2) (+0.560(8))	C(1) (+0.871(8))	chair
	N(4)Ru(1)N(3)	C(8) (+0.844(9))	C(7) (+0.598(9))	C(6) (+0.864(9))	chair
2	N(3)Ru(1)N(2)	C(5) (+0.01(3))	C(4) (−0.51(3))		envelope
	N(4)Ru(1)N(1)	C(9) (+0.47(3))	C(10) (−0.08(4))		envelope
	N(2)Ru(1)N(1)	C(3) (−0.69(4))	C(2) (−0.39(4))	C(1) (−0.79(4))	chair
	N(4)Ru(1)N(3)	C(8) (−0.66(3))	C(7) (−0.47(3))	C(6) (−0.90(3))	chair
3a	N(2)Ru(1)N(1)	C(2) (−0.17(1))	C(1) (+0.38(1))		gauche−envelope
	N(3)Ru(1)N(1)	C(4) (+0.13(1))	C(3) (−0.38(1))		gauche−envelope
3b-A	N(7)Ru(2)N(5)	C(8) (+0.32(1))	C(7A) (−0.28(2))		gauche
	N(6)Ru(2)N(5)	C(10) (−0.32(1))	C(9A) (−0.78(2))		envelope
3b-B	N(7)Ru(2)N(5)	C(8) (+0.32(1))	C(7B) (+0.80(2))		envelope
	N(6)Ru(2)N(5)	C(10) (−0.32(1))	C(9B) (+0.28(2))		gauche
5a	N(2)Ru(1)N(1)	C(2) (+0.016(7))	C(1) (+0.611(7))		envelope
	N(3)Ru(1)N(1)	C(4) (−0.576(7))	C(3) (+0.111(7))		envelope
5b	N(7)Ru(2)N(5)	C(12) (−0.606(7))	C(11) (+0.068(7))		envelope
	N(6)Ru(2)N(5)	C(10) (−0.021(7))	C(9) (+0.595(7))		envelope
6	N(3)Ru(1)N(1)	C(4) (−0.01(2))	C(3) (+0.62(2))		envelope
	N(2)Ru(1)N(1)	C(2) (+0.03(2))	C(1) (−0.62(2))		envelope
	N(4)Ru(1)N(1)	C(6) (−0.08(3))	C(5) (+0.00(2))		planar

[a] Chelating units in five- and six-membered rings are defined as N1−C1−C2−N2 and N1−C1−C2−C3−N2, respectively. [b] The values, obtained in the best-plane calculations using BP70, are shifts of C1−C3 atoms out of their individual N1−Ru−N2 planes, where the positive direction is taken to be in the *z* direction when the Ru → N1 and Ru → N2 vectors are assumed to be in the *x* and *y* directions, respectively. [c] Geometric parameters of **1** are those in ref 4.

value of $Ru^{IV}-Cl = 2.318(2)$ Å reported for $K_2[Ru^{IV}Cl_6]$[20] and are comparable to the values of $Ru^{III}-Cl = 2.372(2)-2.384(2)$ Å reported for $[Al(H_2O)_6][Ru^{III}Cl_6]\cdot 4H_2O$[21] and to the values of $Ru^{III}-Cl = 2.369(1)-2.373(1)$ Å reported for $[Ru^{III}Cl_2(cyclam)]Cl$ (**1**).[4] The Ru−N distances (Table 2) are comparable to those observed in $[Ru^{III}(en)_3]^{3+}$ (2.11 Å),[22] $[Ru^{III}(NH_3)_6]^{3+}$ (2.104 Å),[23] and $[Ru^{III}Cl_2(cyclam)]^+$ (**1**) (2.104(3)−2.117(3) Å).[4] The important feature is that the Ru−Cl distance trans to the tertiary amine (2.378(2) Å for **3a** and 2.364(2) Å for **3b**) is obviously shorter than those trans to the primary amines (2.381(2)−2.387(2) Å for **3a** and 2.383(2)−2.392(2) Å for **3b**). Moreover, the $Ru-N_{tert}$ distance (2.126(6) Å for **3a** and 2.145(6) Å for **3b**) is clearly longer than the $Ru-N_{prim}$ distances (2.081(2) Å for **3a** and 2.085(6)−2.087(6) Å for **3b**) (hereafter N_{tert} and N_{prim} denote nitrogen atoms of tertiary and primary amines, respectively). These facts indicate that, in the trenH ligand, the tertiary amine is somehow weaker in trans influence than the primary amines, despite that the trans influence is expected to increase in the order of $NH_3 < NH_2R\ (=N_{prim}) < NHR_2 < NR_3\ (=N_{tert})$ (R is an alkyl substituent), which corresponds to the sequence of their basicities.[24] The coordination angles involving the N_{tert} atom, $N_{tert}-Ru-X$ (X = N and Cl), show an exceptional deviation from the ideal angle (90 or 180°) (see Table 2); i.e., both molecules **3a** and **3b** have a distorted octahedron in which the nitrogen atom of tertiary amine is displaced out of the ideal octahedral coordination sites (Scheme 1).

Scheme 1



Furthermore, the $Ru-N_{tert}-C_{tail}$ angle (111.1(4)° for **3a**, 122(1) for **3b-A**, and 118(1)° for **3b-B**) is by 2−10° larger than the $Ru-N_{tert}-C_{chelate}$ angles (106.8(5)−107.4(5)° for **3a**, 102.6(7)−109.8(7)° for **3b-A**, and 102.0(7)−109.8(7)° for **3b-B**), indicating that the lone pair on the tertiary amine is not appropriately bound to the ruthenium ion, as illustrated in Scheme 1. In every feature mentioned above, the extent of strain around the N_{tert} atom is found to be larger in molecule **3b** than in molecule **3a** (for example, compare both the $Ru-N_{tert}$ distances and the $Ru-N_{tert}-C_{tail}$ angles between **3a** and **3b**).

In conclusion, the $Ru-N_{tert}$ bond has a relatively poor σ-overlap due to the large strain enhanced by the two chelate rings, leading both to the longer coordination distance and to the weaker σ-trans influence. It is assumed from Scheme 1 that the coordination of the fourth nitrogen donor of the ligand tren toward the Ru ion is not favored due to the *mislocation* of the N_{tert} atom. In contrast with this, the Co(III) ion is known to form stable complexes with tren and the related polyamines without having such a large strain around the N_{tert} atom.[7] This is relevant to the difference in the M−N(amine) distance between the Ru(III) and Co(III) ions. For instance, the $Co^{III}-N(amine)$ distances in $[Co^{III}(Metren)(NH_3)Cl](ZnCl_4)$ (Metren = 2-(methylamino)-2′,2″-diaminotriethylamine) are reported to be in the range of 1.935(9)−1.981(5) Å,[7a] which are distinctively shorter than those of Ru(III) observed (see Table 2). Perhaps, we may have to realize that the tren ligand is an essentially inappropriate ligand for the complexation of the Ru ion, having a longer bonding radius than the Co(III) ion.

Structure of *fac*-$[Ru^{III}Cl(ox)(trenH)]Cl\cdot{}^3/_2H_2O$ (5). Selected interatomic distances and angles for **5** are summarized

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(20) Deloume, J.-P.; Faure, R.; Thomas-David, G. *Acta Crystallogr.* **1979**, *B35*, 558, and references cited therein.
(21) Hopkins, T. E.; Zalkin, A.; Templeton, D. H.; Adamson, M. G. *Inorg. Chem.* **1969**, *8*, 2421.
(22) Peresie, H. J.; Stanko, J. A. *J. Chem. Soc. D* **1970**, 1674.
(23) Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 2304.
(24) For example, the pK_a values of amines in water at 25 °C are 9.24 (NH_3), 10.63 (ethylamine), 10.93 (diethylamine), and 10.72 (triethylamine). Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum Press: New York, London 1974−1977; Vol. 1−3.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for *fac*-$[Ru^{III}Cl(ox)(trenH)]Cl\cdot{}^3/_2H_2O$ (**5**)

Ru(1)−Cl(1)	2.349(1)	Ru(1)−O(1)	2.056(3)
Ru(1)−O(2)	2.061(3)	Ru(1)−N(1)	2.124(4)
Ru(1)−N(2)	2.086(4)	Ru(1)−N(3)	2.079(4)
Ru(2)−Cl(2)	2.360(1)	Ru(2)−O(5)	2.069(3)
Ru(2)−O(6)	2.047(3)	Ru(2)−N(5)	2.112(4)
Ru(2)−N(6)	2.091(4)	Ru(2)−N(7)	2.077(4)
O(1)−C(7)	1.286(5)	O(2)−C(8)	1.281(5)
O(3)−C(7)	1.219(5)	O(4)−C(8)	1.230(5)
O(5)−C(15)	1.281(5)	O(6)−C(16)	1.269(5)
O(7)−C(15)	1.229(5)	O(8)−C(16)	1.225(5)
N(1)−C(1)	1.499(5)	N(1)−C(3)	1.512(6)
N(1)−C(5)	1.487(5)	N(2)−C(2)	1.488(6)
N(3)−C(4)	1.479(6)	N(4)−C(6)	1.462(6)
N(5)−C(9)	1.504(5)	N(5)−C(11)	1.499(6)
N(5)−C(13)	1.496(5)	N(6)−C(10)	1.488(6)
N(7)−C(12)	1.477(6)	N(8)−C(14)	1.475(6)
C(1)−C(2)	1.506(6)	C(3)−C(4)	1.496(6)
C(5)−C(6)	1.528(6)	C(7)−C(8)	1.566(6)
C(9)−C(10)	1.509(6)	C(11)−C(12)	1.500(6)
C(13)−C(14)	1.521(6)	C(15)−C(16)	1.572(6)

Cl(1)−Ru(1)−O(1)	88.72(10)	Cl(1)−Ru(1)−O(2)	90.52(9)
Cl(1)−Ru(1)−N(1)	96.1(1)	Cl(1)−Ru(1)−N(2)	87.6(1)
Cl(1)−Ru(1)−N(3)	175.8(1)	O(1)−Ru(1)−O(2)	81.5(1)
O(1)−Ru(1)−N(1)	175.0(1)	O(1)−Ru(1)−N(2)	96.9(1)
O(1)−Ru(1)−N(3)	92.7(1)	O(2)−Ru(1)−N(1)	99.6(1)
O(2)−Ru(1)−N(2)	177.6(1)	O(2)−Ru(1)−N(3)	85.8(1)
N(1)−Ru(1)−N(2)	82.1(1)	N(1)−Ru(1)−N(3)	82.5(1)
N(2)−Ru(1)−N(3)	96.1(1)	Cl(2)−Ru(2)−O(5)	88.36(10)
Cl(2)−Ru(2)−O(6)	92.20(10)	Cl(2)−Ru(2)−N(5)	95.4(1)
Cl(2)−Ru(2)−N(6)	87.0(1)	Cl(2)−Ru(2)−N(7)	176.2(1)
O(5)−Ru(2)−O(6)	81.9(1)	O(5)−Ru(2)−N(5)	176.2(1)
O(5)−Ru(2)−N(6)	98.0(1)	O(5)−Ru(2)−N(7)	93.7(1)
O(6)−Ru(2)−N(5)	97.5(1)	O(6)−Ru(2)−N(6)	179.2(1)
O(6)−Ru(2)−N(7)	85.0(1)	N(5)−Ru(2)−N(6)	82.7(1)
N(5)−Ru(2)−N(7)	82.5(1)	N(6)−Ru(2)−N(7)	95.8(1)
Ru(1)−O(1)−C(7)	13.3(3)	Ru(1)−O(2)−C(8)	113.2(3)
Ru(2)−O(5)−C(15)	111.7(3)	Ru(2)−O(6)−C(16)	113.5(3)
Ru(1)−N(1)−C(1)	106.1(3)	Ru(1)−N(1)−C(3)	107.7(3)
Ru(1)−N(1)−C(5)	111.4(3)	Ru(1)−N(2)−C(2)	112.0(3)
Ru(1)−N(3)−C(4)	107.6(3)	Ru(2)−N(5)−C(9)	106.0(3)
Ru(2)−N(5)−C(11)	108.2(3)	Ru(2)−N(5)−C(13)	110.2(3)
Ru(2)−N(6)−C(10)	111.1(3)	Ru(2)−N(7)−C(12)	107.2(3)

Possible Hydrogen Bonds

Cl(3)−N(8)	3.195(5)	Cl(4)−N(4)	3.183(5)
O(2)−O(9)	2.973(6)	O(9)−O(10)	2.703(6)
O(10)−N(4)	2.762(6)	O(11)−N(8)	2.823(6)
Cl(4)−N(7)[a]	3.247(4)	Cl(4)−N(3)[a]	3.265(4)
Cl(4)−N(2)[a]	3.313(4)	Cl(4)−N(6)[a]	3.333(4)
O(3)−O(10)[b]	2.819(5)	O(7)−O(11)[c]	2.781(5)
Cl(4)−N(8)[d]	3.309(4)	Cl(3)−O(11)[e]	3.260(4)
O(8)−N(8)[e]	3.041(6)	Cl(3)−O(9)[f]	3.000(5)
O(1)−N(2)[f]	3.187(5)	O(3)−N(3)[g]	3.130(5)
O(4)−N(3)[g]	3.041(5)	O(4)−N(4)[h]	2.974(6)
O(5)−N(6)[i]	3.178(5)	O(8)−N(7)[j]	2.905(5)

[a−j] Symmetry operations: (a) 1 + *x*, *y*, *z*; (b) −1 + *x*, *y*, *z*; (c) *x*, *y*, −1 + *z*; (d) 1 + *x*, *y*, −1 + *z*; (e) −*x*, −*y*, 2 − *z*; (f) 1 − *x*, 1 − *y*, 1 − *z*; (g) 1 − *x*, 1 − *y*, −*z*; (h) 2 − *x*, 1 − *y*, −*z*; (i) 1 − *x*, −*y*, 1 − *z*; (j) −*x*, −*y*, 1 − *z*.

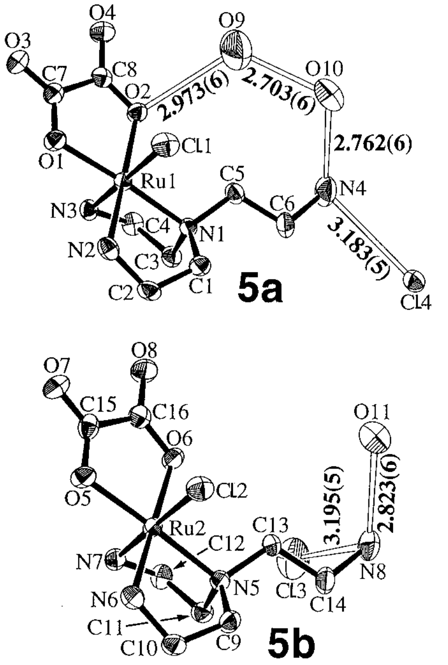

Figure 3. Structures of two independent *fac*-$[Ru^{III}Cl(ox)(trenH)]Cl$ molecules in **5** (**5a** and **5b**), including the neighboring hydrogen-bonded water molecules. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. Hydrogen bonds are drawn with open lines.

in Table 4. The asymmetric unit of **5**, similarly, contains two independent *fac*-$[Ru^{III}Cl(ox)(trenH)]Cl$ molecules (**5a** and **5b** shown in Figure 3). In this case, there is no disorder problem. As shown in Figure 3, the peripheral ammonio groups are not only hydrogen bonded to the neighboring chloride counterions but also associated with water molecules contained as crystal solvents. In **5a**, an eight-membered metallocycle is formed in association with a hydrogen-bonded pair of water molecules, "$(H_2O)_2$". The hydrogen bond distance within this pair (O(9)−O(10) = 2.703(6) Å) is somewhat short as a hydrogen bond for normal water molecules (2.76 Å)[25] but is too long to be regarded as a bond within an "$H_5O_2^+$" ion (O···O = 2.42−2.59 Å).[26] Therefore it is not likely that the proton on this complex cation locates at the midpoint of O(9) and O(10). One approvable explanation is that the proton is fundamentally attached to the N(4) atom but resides between the N(4) and O(10) atoms so that the $(H_2O)_2$ unit can slightly bear the nature of $H_5O_2^+$. The Ru−Cl distances (2.349(1) Å for **5a** and 2.360(1) Å for **5b**) are slightly shorter than those found in compound **3** but are still comparable to the reported Ru^{III}−Cl distances exemplified above. The $Ru-N_{prim}$ and $-N_{tert}$ distances are all very similar to those discussed above for **3**. Furthermore, the $Ru-N_{tert}-C$ angles ($Ru-N_{tert}-C_{tail}$ = 110.2(3)−111.4(3)° and $Ru-N_{tert}-C_{chelate}$ = 106.0(3)−108.2(3)°) have the same features as those observed for **3**. The remarkable difference in the trenH geometry may be found in the conformations around the ethylene moieties. As given in Figure 2 and Table 3, all of the five-membered chelate rings have an envelope conformation. In each molecule, the oxalate ion has a planar geometry and the two nitrogen atoms trans to the O(ox) atoms as well as the Ru ion almost locate on the same plane, where the nine-atom root mean square deviation obtained in the best-plane calculation was 0.047 Å for **5a** and 0.039 Å for **5b**. All of the C−N distances (1.462(6)−1.512(6) Å) can be regarded as single bonds. Crystal packing is again electrostatically stabilized with an extensive hydrogen bonding network (see Table 4), as observed in complex **3**.

Structure of $(H_5O_2)_2[K(tren)][Ru^{III}Cl_6]$ (4). Selected interatomic distances and angles for **4** are summarized in Table 5. All of the molecules (K^+, tren, H_3O^+, H_2O, and $Ru^{III}Cl_6^{3-}$) are fused, forming a three-dimensional network *via* electrostatic interactions. However, the interactions are strong in the crystallographic *a* and *b* directions and are not so strong along the *c*-axis. As a result, the unit cell of **4** adopts a very interesting quasi-two-dimensional layered framework. As shown in Figure

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(25) Lundgren, J.-O.; Olovsson, I. *J. Chem. Phys.* **1968**, *49*, 1068.

(26) (a) Olovsson, I. *J. Chem. Phys.* **1968**, *49*, 1063, and references cited therein. (b) Faggiani, R.; Lippert, B.; Lock, C. J. *Inorg. Chem.* **1980**, *19*, 295. (c) Faggiani, R.; Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 1111.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for $(H_5O_2)_2[K(tren)][Ru^{III}Cl_6]$ (**4**)

Ru(1)−Cl(1)	2.374(3)	Ru(2)−Cl(2)	2.367(2)
K(1)−N(1)	3.09(1)	K(1)−N(2)^a	3.204(7)
O(1A)−O(1B)	1.25(5)	O(1A)−O(2)	2.725(9)
O(1B)−O(2)	2.64(1)	O(2)−O(2)^b	2.76(1)
N(1)−C(1)	1.508(7)	N(2)−C(2)	1.475(8)
C(1)−C(2)	1.520(9)		
Cl(1)−Ru(1)−Cl(1)^c	89.31(7)	Cl(1)−Ru(1)−Cl(1)^d	180.0
Cl(1)−Ru(1)−Cl(1)^e	90.69(7)	Cl(2)−Ru(2)−Cl(2)^f	88.74(9)
Cl(2)−Ru(2)−Cl(2)^g	91.25(9)	Cl(2)−Ru(2)−Cl(2)^h	180.0
N(1)−K(1)−N(2)^a	117.8(1)	N(2)^a−K(1)−N(2)^i	100.1(2)
O(2)−O(1A)−O(2)^j	111.6(4)	O(2)−O(1B)−O(2)^j	117.3(7)
O(1B)−O(1A)−O(2)	72.7(4)	O(1A)−O(1B)−O(2)	80(1)
O(1A)−O(2)−O(1B)	26(1)	O(1A)−O(2)−O(2)^b	105.4(4)
O(1B)−O(2)−O(2)^b	90.2(8)	K(1)−N(1)−C(1)	108.9(5)
C(1)−N(1)−C(1)^c	110.1(5)	K(1)^a−N(2)−C(2)	100.2(4)
N(1)−C(1)−C(2)	110.6(6)	N(2)−C(2)−C(1)	110.8(6)
	Possible Hydrogen Bonds		
Cl(1)−O(2)	3.140(6)	Cl(1)−N(2)^k	3.275(6)
Cl(1)−N(2)^l	3.339(6)	Cl(2)−N(2)^j	3.234(7)
O(2)−N(2)^m	3.086(9)		

$^{a-m}$ Symmetry operations: (a) $^2/_3 - x$, $^1/_3 - y$, $^1/_3 - z$; (b) $-x$, $-1 - y$, $-z$; (c) $-y$, $x - y$, z; (d) $-x$, $-y$, $-z$; (e) y, $x + y$, $-z$; (f) $^2/_3 + y$, $^1/_3 - x + y$, $^1/_3 - z$; (g) $1 - x + y$, $-x$, z; (h) $^2/_3 - x$, $-^2/_3 - y$, $^1/_3 - z$; (i) $-^1/_3 + y$, $^1/_3 - x + y$, $^1/_3 - z$; (j) $-y$, $-1 + x - y$, z; (k) $^1/_3 - y$, $-^1/_3 + x - y$, $-^1/_3 + z$; (l) $-^2/_3 + x$, $-^1/_3 + y$, $-^1/_3 + z$; (m) $-^1/_3 + x - y$, $-^2/_3 + x$, $^1/_3 - z$.

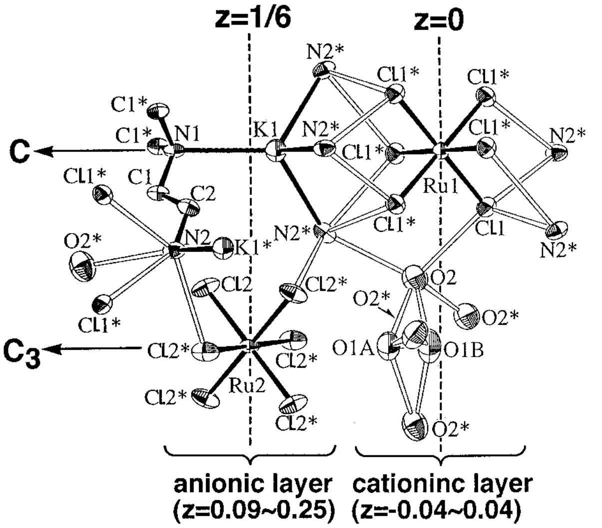

Figure 4. ORTEP view, perpendicular to the *c*-axis, of **4** in the asymmetric unit, together with the atoms in the nearest neighbor (asterisked atoms). Hydrogen bonds are drawn with open lines. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.

4, the ruthenium ions are located at inversion centers and two crystallographic 3-fold axes pass through the N(1)K(1)Ru(1) and Ru(2)O(1A)O(1B) atoms, respectively. The crystal is made up of two types of layers that alternate along the *c*-axis (Figure 4); one is an anionic $\{[K(tren)]_2[Ru^{III}Cl_6]\}_n{}^{n-}$ slab (Figure 5a), and the other is a cationic $\{(H_5O_2)_4[Ru^{III}Cl_6]\}_n{}^{n+}$ slab (Figure 5b) ($n = \infty$). The most important features of these 2-D sheets are that they can be regarded as microporous layers in which the pores are occupied with $[Ru^{III}Cl_6]^{3-}$ molecules. The Ru−Cl distances in the two independent $[Ru^{III}Cl_6]^{3-}$ molecules (Ru(1)−Cl(1) = 2.374(3) and Ru(2)−Cl(2) = 2.367(2) Å) are clearly longer than that of Ru^{IV}−Cl = 2.318(2) Å reported for $K_2[Ru^{IV}Cl_6]$[20] and are consistent with those of Ru^{III}−Cl = 2.372(2)−2.384(2) Å reported for $[Al(H_2O)_6][Ru^{III}Cl_6]\cdot 4H_2O$.[21] Therefore, the oxidation level of each Ru ion is reasonably determined as +3.0.

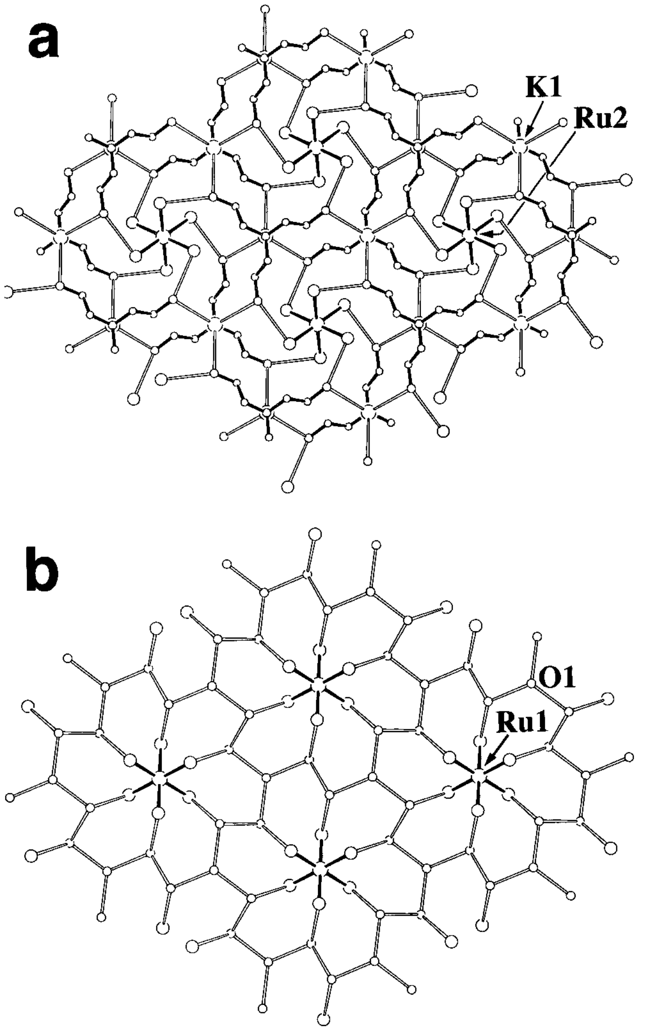

Figure 5. Views along the c-axis of (a) $\{[K(tren)]_2[Ru^{III}Cl_6]\}_n{}^{n-}$ ($z = {}^1/_6 \pm 0.08$) and (b) $\{(H_5O_2)_4[Ru^{III}Cl_6]\}_n{}^{n+}$ ($z = 0 \pm 0.04$) ($n = \infty$), where atoms are drawn with ideal spheres for clarity. Hydrogen and K−N bonds are drawn with open lines.

In $\{[K(tren)]_2[Ru^{III}Cl_6]\}_n{}^{n-}$ (Figure 5a), each potassium ion is tetrahedrally surrounded by nitrogen atoms of four different tren molecules (K(1)···N(1) = 3.09(1) and K(1)···N(2)^a = 3.204(7) Å) (Figure 4). All of the four nitrogen donors of tren interact with a neighboring potassium ion and are thereby regarded as unprotonated amines, which means that the tren ligand is neutral. The 2-D sheet $\{[K(tren)]\}_n{}^{n+}$ adopts a bilayer structure, and large cylindrical cavities are present that have a diameter of approximately 7.4 Å and a depth of 4.6 Å. Each cavity consists of two 24-membered rings and is occupied by an $[Ru^{III}Cl_6]^{3-}$ ion with six hydrogen bonds formed between the primary amines of tren and the chloride atoms bound to Ru(III) (Cl(2)···N(2)^j = 3.234(7) Å) (Figure 5a).

In $\{(H_5O_2)_4[Ru^{III}Cl_6]\}_n{}^{n+}$ (Figure 5b), oxygen atoms form beautiful 18-membered cyclic arrays with moderately strong hydrogen bonds, O(1A)···O(2) = 2.725(9), O(1B)···O(2) = 2.64(1), and O(2)···O(2)^b = 2.76(1) Å. The O(1A)···O(2) and O(1B)···O(2) distances are obviously shorter than those for the normal hydrogen bonds between neutral water molecules (O···O = 2.76 Å).[25] From the total charge balance, the trigonal pyramidal tetrahydrate (O(1A)O(2)O(2)*O(2)* or O(1B)O(2)O(2)*O(2)*) must involve two protons and should be expressed with "$H_{10}O_4{}^{2+}$". An H_3O^+ ion is known to serve as a better hydrogen donor than normal water molecules,[25] and H_3O^+ ions found in $H_5O_2{}^+$,[26] $H_7O_3{}^+$,[25] and $H_9O_4{}^+$ [25] are reported to form hydrogen bonds in the range of O···O = 2.42−2.59 Å.

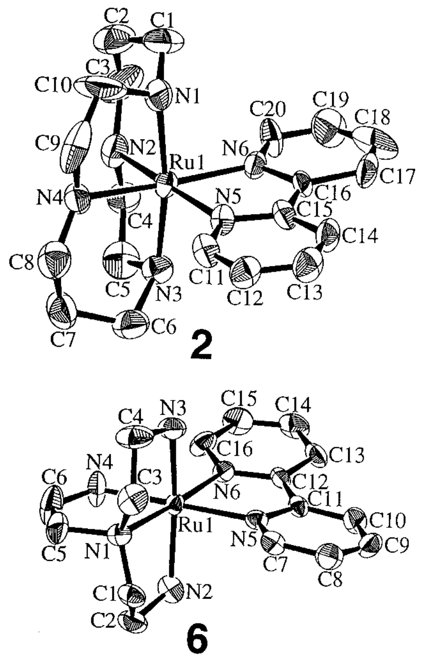

Figure 6. Structures of $[Ru^{II}(cyclam)(bpy)]^{2+}$ in **2** (top) and $[Ru^{II}(baia)(bpy)]^{2+}$ in **6** (bottom). Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

Table 6. Selected Interatomic Distances (Å) and Angles (deg) for $[Ru^{II}(cyclam)(bpy)](BF_4)_2{\cdot}H_2O$ (**2**)

Ru(1)−N(1)	2.08(2)	Ru(1)−N(2)	2.12(2)
Ru(1)−N(3)	2.07(2)	Ru(1)−N(4)	2.11(1)
Ru(1)−N(5)	2.10(1)	Ru(1)−N(6)	2.06(1)
N(1)−C(1)	1.45(2)	N(1)−C(10)	1.40(3)
N(2)−C(3)	1.47(2)	N(2)−C(4)	1.50(2)
N(3)−C(5)	1.52(2)	N(3)−C(6)	1.53(2)
N(4)−C(8)	1.43(2)	N(4)−C(9)	1.51(2)
N(5)−C(11)	1.37(2)	N(5)−C(15)	1.33(2)
N(6)−C(16)	1.35(2)	N(6)−C(20)	1.36(2)
C(1)−C(2)	1.50(3)	C(2)−C(3)	1.38(3)
C(4)−C(5)	1.40(2)	C(6)−C(7)	1.56(2)
C(7)−C(8)	1.47(3)	C(9)−C(10)	1.41(3)
C(11)−C(12)	1.34(2)	C(12)−C(13)	1.35(2)
C(13)−C(14)	1.37(2)	C(14)−C(15)	1.38(2)
C(15)−C(16)	1.48(2)	C(16)−C(17)	1.46(2)
C(17)−C(18)	1.40(3)	C(18)−C(19)	1.27(3)
C(19)−C(20)	1.32(3)		
N(1)−Ru(1)−N(2)	90.2(7)	N(1)−Ru(1)−N(3)	170.0(6)
N(1)−Ru(1)−N(4)	82.4(6)	N(1)−Ru(1)−N(5)	92.7(6)
N(1)−Ru(1)−N(6)	92.4(6)	N(2)−Ru(1)−N(3)	81.7(6)
N(2)−Ru(1)−N(4)	87.1(6)	N(2)−Ru(1)−N(5)	174.9(6)
N(2)−Ru(1)−N(6)	97.7(6)	N(3)−Ru(1)−N(4)	91.2(6)
N(3)−Ru(1)−N(5)	95.8(6)	N(3)−Ru(1)−N(6)	94.5(5)
N(4)−Ru(1)−N(5)	97.4(6)	N(4)−Ru(1)−N(6)	173.0(7)
N(5)−Ru(1)−N(6)	78.1(6)	Ru(1)−N(1)−C(1)	116(1)
Ru(1)−N(1)−C(10)	111(1)	Ru(1)−N(2)−C(3)	119(1)
Ru(1)−N(2)−C(4)	107(1)	Ru(1)−N(3)−C(5)	111(1)
Ru(1)−N(3)−C(6)	115(1)	Ru(1)−N(4)−C(8)	122(1)
Ru(1)−N(4)−C(9)	103(1)	Ru(1)−N(5)−C(11)	130(1)
Ru(1)−N(5)−C(15)	116(1)	Ru(1)−N(6)−C(16)	115(1)
Ru(1)−N(6)−C(20)	127(1)		
	Possible Hydrogen Bonds		
F(2)−N(1)	3.04(2)	F(5)−N(4)	3.06(2)
F(5)−N(2)	3.24(2)	F(7)−N(3)[a]	3.02(2)
F(7)−N(6)[a]	3.21(2)		

[a] Symmetry operation: $x, {}^1/_2 - y, {}^1/_2 + z$.

Although the distance of O(1B)···O(2) = 2.64(1) Å is slightly longer than these values, it could be regarded as a hydrogen bond of an H_3O^+ ion. However, the distance of O(1A)···O(2) = 2.725(9) Å is too long as a bond for H_3O^+. The occupancy values of O(1A) and O(1B) were refined and converged at values of 0.237(31) and 0.096(31), respectively. There still remains a possibility that these two values should be given as $^2/_9$ and $^1/_9$, respectively, with a certain regularity. However we could not solve this problem due to the lack of further information. Nevertheless we believe that this polymeric water layer is fundamentally composed of $H_5O_2^+$ units, with inevitable disorder problems. Similar to the layer $\{[K(tren)]_2[Ru^{III}Cl_6]\}_n{}^{n-}$, an $[Ru^{III}Cl_6]^{3-}$ ion occupies the cavity of each cyclic water array with six hydrogen bonds formed between the chloride atoms and the oxygen atoms (Cl(1)−O(2) = 3.140(6) Å) (Figure 5b), in which the cavity has a diameter of 8.4 Å and a depth of 1.6 Å.

Although we have accidentally encountered this unique framework, such layered structures have attracted considerable interest in recent years in the studies of crystal engineering, molecular recognition, molecular ferromagnets, and supramolecular chemistry.[27]

Structures of $[Ru^{II}(cyclam)(bpy)](BF_4)_2{\cdot}H_2O$ (2) and $[Ru^{II}(baia)(bpy)](BF_4)_2$ (6). The ORTEP views of the complex cations in **2** and **6** are shown in Figure 6. Selected interatomic distances and angles for **2** and **6** are given in Tables 6 and 7, respectively. All of the C−N(1−4) distances in the Ru(cyclam) geometry in **2** (1.43(2)−1.53(2) Å) have a single-bond character. As summarized in Table 3, the six-membered chelate rings containing propylenediamine units in **2** have a *chair* conformation and are quite similar to those found in **1**. The conformations around the ethylene units are slightly different between **1** and **2**; the five-membered chelate rings in **1** have an intermediate structure between envelope and gauche conformations (gauche−envelope), while both of those in **2** possess an envelope conformation. As discussed above for the Ru(trenH) system, it is worth examining the Ru−N−C angles to understand the strain around the coordinated nitrogen donors. The Ru−N−C angles in the Ru(cyclam) unit can be classified into three groups, $Ru{-}N{-}C_{ethyl}$, $Ru{-}N{-}C_{propyl}$, and Ru−N−H, where C_{ethyl} and C_{propyl} are defined as carbon atoms on ethylene and propylene units, respectively. Although the Ru−N−H angle is not observable in the X-ray diffractometry, the strain around the N(cyclam) atoms can be evaluated from the rest of the angles. In complex **1**, the $Ru{-}N{-}C_{ethyl}$ angles (106.6(3)−108.6(2)°)[4] are by 8−11° smaller than the $Ru{-}N{-}C_{propyl}$ angles (116.4(3)−117.4(3)°),[4] indicating that the strain around the four nitrogen donors of cyclam is as large as those observed for the N_{tert} atoms in **3** and **5**. The deviation of the Ru−N−C angle from the ideal angle of 109.47° is greater in the $Ru{-}N{-}C_{propyl}$ angles than in the $Ru{-}N{-}C_{ethyl}$ angles. This fact indicates that the strain induced by the propylenediamine chelate is larger than that induced by the ethylenediamine chelate, which is consistent with the well-known fact that the five-membered chelate rings are more stable than the six-membered one in the alkylenediamine-chelate systems. What is seen in **2** is very similar to the tendency mentioned above for **1**; the $Ru{-}N{-}C_{ethyl}$ angles (103(1)−111(1)°) are by 4−19° smaller than the $Ru{-}N{-}C_{propyl}$ angles (115(1)−122(1)°). These observations reveal that, in both **1** and **2**, there is significant strain around the N(cyclam) atoms and therefore the cyclam ligand does not appear to be appropriately bound to the Ru ion, as observed for the N_{tert} atoms in **3** and **5**. As was previously observed for **1**,[4] the helicity of

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(27) (a) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989. (b) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304. (c) Goodgame, D. M. L.; Menzer, S.; Smith, A. M.; Williams, D. J. *Inorg. Chem.* **1994**, *33*, 6409. (d) Farrell, R. P; Hambley, T. W.; Lay, P. A. *Inorg. Chem.* **1995**, *34*, 757. (e) Braga, D.; Grepioni, F.; Byrne, J. J.; Wolf, A. *Chem. Soc., Chem. Commun.* **1995**, 1023. (f) Biradha, K.; Edwards, R. E.; Foulds, G. J.; Robinson, W. T.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1995**, 1705.

Table 7. Selected Interatomic Distances (Å) and Angles (deg) for $[Ru^{II}(baia)(bpy)](BF_4)_2$ (**6**)

Ru(1)−N(1)	2.119(10)	Ru(1)−N(2)	2.10(1)
Ru(1)−N(3)	2.11(1)	Ru(1)−N(4)	2.05(1)
Ru(1)−N(5)	2.10(1)	Ru(1)−N(6)	2.046(9)
N(1)−C(1)	1.47(2)	N(1)−C(3)	1.49(2)
N(1)−C(5)	1.51(2)	N(2)−C(2)	1.49(1)
N(3)−C(4)	1.49(2)	N(4)−C(6)	1.28(2)
N(5)−C(7)	1.33(1)	N(5)−C(11)	1.37(1)
N(6)−C(12)	1.36(1)	N(6)−C(16)	1.34(1)
C(1)−C(2)	1.51(2)	C(3)−C(4)	1.52(2)
C(5)−C(6)	1.46(2)	C(7)−C(8)	1.40(2)
C(8)−C(9)	1.35(2)	C(9)−C(10)	1.34(2)
C(10)−C(11)	1.41(2)	C(11)−C(12)	1.44(2)
C(12)−C(13)	1.38(2)	C(13)−C(14)	1.38(2)
C(14)−C(15)	1.34(2)	C(15)−C(16)	1.38(2)
N(1)−Ru(1)−N(2)	82.3(4)	N(1)−Ru(1)−N(3)	83.1(4)
N(1)−Ru(1)−N(4)	78.3(4)	N(1)−Ru(1)−N(5)	105.3(4)
N(1)−Ru(1)−N(6)	176.4(5)	N(2)−Ru(1)−N(3)	164.2(4)
N(2)−Ru(1)−N(4)	90.7(5)	N(2)−Ru(1)−N(5)	88.2(4)
N(2)−Ru(1)−N(6)	99.2(4)	N(3)−Ru(1)−N(4)	92.2(5)
N(3)−Ru(1)−N(5)	89.8(4)	N(3)−Ru(1)−N(6)	95.7(4)
N(4)−Ru(1)−N(5)	176.1(4)	N(4)−Ru(1)−N(6)	98.4(4)
N(5)−Ru(1)−N(6)	78.1(4)	Ru(1)−N(1)−C(1)	106.0(8)
Ru(1)−N(1)−C(3)	105.2(8)	Ru(1)−N(1)−C(5)	112.7(9)
Ru(1)−N(2)−C(2)	109.7(8)	Ru(1)−N(3)−C(4)	109.3(9)
Ru(1)−N(4)−C(6)	119(1)	Ru(1)−N(5)−C(7)	129.5(9)
Ru(1)−N(5)−C(11)	114.2(8)	Ru(1)−N(6)−C(12)	116.5(9)
Ru(1)−N(6)−C(16)	124.3(9)		
Possible Hydrogen Bonds			
F(5)−N(4)[a]	3.06(2)	F(2)−N(2)[b]	3.35(2)
F(3)−N(2)[b]	3.26(2)	F(2)−N(3)[c]	3.35(2)
F(4)−N(3)[c]	3.28(2)		

[a−c] Symmetry operations: (a) $1 - x$, $^1/_2 + y$, $^1/_2 - z$; (b) $1 - x$, $-y$, $-z$; (c) x, $^1/_2 - y$, $-^1/_2 + z$.

the four nitrogen centers of cyclam in **2** are either RRRR or SSSS (definition of R and S is in the literature[28]), and, of course, the unit cell can be regarded as a racemic mixture of these optical isomers. The ligand bpy has a planar geometry, where the 12-atom root mean square deviation was 0.021 Å.

On the other hand, one of the C−N distances in the Ru(baia) unit in **6** (C(6)−N(4) = 1.28(2) Å) clearly possesses a double-bond character, where the remaining C−N(1−3) distances in the L_4 geometry are in the range of 1.47(2)−1.51(2) Å. The Ru(1)−N(4) distance (2.05(1) Å) is significantly shorter than the Ru(1)−N(1−3) distances, indicating that there is an effective π back-bonding nature involved in the Ru(1)−N(4) bond. Thus only the primary amine trans to the N(bpy) atom has undergone an oxidative dehydrogenation, resulting in the formation of the imino group of baia. The distance of C(5)−C(6) = 1.46(2) Å in the iminomethyl unit is much shorter than those in the ethylene units (C(1)−C(2) = 1.51(2) and C(3)−C(4) = 1.52(2) Å), and the five-membered chelate ring consisting of the Ru(1), N(1), C(5), C(6), and N(4) atoms is almost planar (see Table 3), suggesting that the sp^2 hybridized nature is, to some extent, delocalized over this metallocycle. Both of the two five-membered chelate rings for the ethylene units possess an envelope conformation (Table 3). The two pyridyl rings of bpy in **6** themselves are planar, but they are twisted about the central C(11)−C(12) axis at an angle of 7.7(5)°, where the six-atom root mean square deviations in the best-plane calculations for N(5)C(7−11) and N(6)C(12−16) were 0.007 and 0.013 Å, respectively.

It was previously pointed out by Bernhard and Sargeson[8e] that, in the dehydrogenation of the ethylenediamine unit bound to Ru(III), an introduction of one imino group leads to the enhancement of a second oxidation in the same unit due to the stabilization effect of the conjugation in the five-membered chelate ring. This must also be viewed as related to the very rapid character in the dehydrogenation of an amine ligand in $[Ru^{III}(bpy)_2(ampy)]^{3+}$ (ampy = 2-(aminomethyl)pyridine).[8d] For the selectivity observed in the dehydrogenation of tren into baia, one intriguing possibility deduced from these reports may be that the conjugation in the Ru(bpy) unit indirectly induces a selective dehydrogenation of the amine trans to the bpy ligand. However, the answer for this question is not straightforward, for there may be some steric driving force for the formation of baia. For example, the diethylenetriamine part of tren attached in a mer fashion (see **II** in Introduction) is clearly poorer in flexibility compared to the central ethylenediamine unit which undergoes a selective oxidation. Such a steric difference is another factor which must be taken into consideration.

Discussion. It has previously been shown by Che et al.[4] that the transition energy (E_{abs} (eV)) for the lowest energy MLCT band of the *cis*-$[Ru^{II}L_4(bpy)]^{2+}$ complex increases in the order of $L_4 = (NH_3)_4 < (en)_2 <$ cyclam (Table 8), in which the observed blue shift in the MLCT band has been explained in terms of the *solvation effect*. They have suggested that the extent of solvation decreases *as the number of alkyl substituents in L_4 increases* and is much greater in the MLCT excited state than in the ground state due to the larger polarity of the molecule in the charge-transferred state, so that a less hydrophobic (=more solvated) compound has a smaller energy gap for the MLCT transition. Very important examples relating to this *alkyl substituent-dependence* have been shown by Curtis et al.;[30] they showed that the hydrogen-bonding type of *solvent donor−solute acceptor interactions* via the N−H groups of amines (e.g., Ru−N−H···OH_2) greatly affect the electron density at the Ru ion, $E_{1/2}(Ru^{II/III})$, and E_{abs}.

It is well-known that the transition energy for the MLCT band, E_{abs}, shows a linear dependence on the difference in redox potentials between the first metal-based oxidation and the first ligand-based reduction, $\Delta E_{1/2}$ ($E_{1/2}(Ru^{II/III}) - E_{1/2}$(ligand/ligand$^-$)),[31−33] even though Che et al. did not pay much attention to the correlation. However, our fitting experiment performed using their results reveals that a plot of E_{abs} vs $E_{1/2}(Ru^{II/III})$ for the three *cis*-$[Ru^{II}L_4(bpy)]^{2+}$ complexes ($L_4 = (NH_3)_4$, $(en)_2$, and cyclam; Table 8) affords a *straight* line:

$$E_{abs} = 0.564E_{1/2}(Ru^{II/III}) + 2.223$$

with a correlation coefficient of 0.999. In the calculation, $E_{1/2}(Ru^{II/III})$ has been adopted instead of $\Delta E_{1/2}$, since $E_{1/2}(bpy/bpy^-)$ remains unknown for each complex. However, it is quite reasonable to assume that $E_{1/2}(bpy/bpy^-)$ is little affected by the variation of L_4. This assumption is strongly supported by the results of Curtis;[30] it was observed for $[Ru^{II}(NH_3)_5(L)]^{3+}$ (L = 4-cyano-*N*-methylpyridinium) that $E_{1/2}(Ru^{II/III})$ exhibits a dramatic solvent dependence but $E_{1/2}(L/L^-)$ is almost unaffected by the change of solvent, in which the change in the extent of

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Table 8. MLCT Bands, Redox Potentials, Distortion in RuL_4, and EHMO Energy Levels of *cis*-$[Ru^{II}L_4(bpy)]^{2+}$

L_4	MLCT band λ, nm (log ϵ)	$E_{1/2}(Ru^{II/III})$[a] (V vs SCE)	$\Delta\theta(N-Ru-N)_{av}$[b] (deg)	$\Delta\theta(Ru-N-C)_{av}$[c] (deg)	energy level (eV) HOMO[d]	energy level (eV) LUMO[e]
$(NH_3)_4$	522 (3.24)[f]	0.269[g]	0.9[j]	0[j]	−10.858	−9.539
$(en)_2$	513 (3.53)[f]	0.349[f]	4.6[k]	1.5[k]	−10.848	−9.535
cyclam	504 (3.66)[f]	0.409[f]	4.2	5.8	−10.822	−9.521
baia	495 (3.64)[h]	0.650[i]	6.2	2.1	−10.808	−9.587

[a] The values reported in volts vs NHE are converted into values vs SCE using SCE = 0.241 V vs NHE. [b] The average value of six $\Delta\theta$(N−Ru−N) angles within the RuL_4 geometry is defined as $\Delta\theta(N-Ru-N)_{av}$, where $\Delta\theta(N-Ru-N) = |\theta(N-Ru-N)_{obsd} - \theta(N-Ru-N)_{ideal}|/n$ ($n = 1$ for $\theta(N-Ru-N)_{ideal} = 90°$ and $n = 2$ for $\theta(N-Ru-N)_{ideal} = 180°$). [c] The average value for all the possible $\Delta\theta$(Ru−N−C) values in RuL_4 is defined as $\Delta\theta(Ru-N-C)_{av}$, where $\Delta\theta(Ru-N-C) = |\theta(Ru-N-C)_{obsd} - \theta(Ru-N-C)_{ideal}|$ ($\theta(Ru-N-C)_{ideal} = 109.47$ and 120° for single and double C−N bonds, respectively). [d] $d\pi$(Ru). [e] π^*(bpy). [f] Reference 4. [g] Reference 29. [h] Measured in H_2O at room temperature. [i] Measured in an acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate in Ar at room temperature. [j] Geometric parameters used are those in ref 18. [k] Geometric parameters used are those in ref 19. The Ru−N−C angles are 106.6(4) and 109.2(5)° for one chelate and 106.9(4) and 109.3(5)° for the other.

solvation around the NH_3 groups has the same meaning with the variation of L_4 in $[Ru^{II}L_4(bpy)]^{2+}$. Although the slope obtained above is not larger than 1 expected for the MLCT processes,[33b] the linear nature of the plot indicates that the same $d\pi-\pi^*$ MLCT orbitals are involved in both the optical and electrochemical processes.

Considering the results of Curtis, no doubt the solvation effect would play an important role in the dramatic *alkyl-substituent dependence of both* E_{abs} *and* $E_{1/2}(Ru^{II/III})$ mentioned above. Moreover, the results of EHMO calculations performed on these compounds (Table 8) reveal that the energy levels of the HOMO and LUMO are not much affected by the variation of L_4, suggesting that the electronic structures of them may not be greatly affected by the structural change in the RuL_4 geometry. Nevertheless, the present X-ray studies provide a proposal that the steric restraint around the $N(L_4)$ donors, which increases as the number of chelate rings is increased, may partly contribute to the tendency observed above, since the misdonation of donors induced by such a structural strain is expected to result in a decrease in the net donicity of the ligand, leading to an increase in both E_{abs} and $E_{1/2}(Ru^{II/III})$. The extent of misdonation of donors can be evaluated with use of both the $\Delta\theta(N-Ru-N)_{av}$ and $\Delta\theta(Ru-N-C)_{av}$ terms defined in Table 8. The former corresponds to the extent of mislocation of donors from O_h, while the latter corresponds to the extent of misdirection of a lone pair from its ideal binding direction, which is equal to the N → Ru direction. Although the $\Delta\theta(N-Ru-N)_{av}$ value for $L_4 = (en)_2$ is very similar to that for L_4 = cyclam, the $\Delta\theta(Ru-N-C)_{av}$ value is greatly increased with an introduction of two propylene chelates when L_4 is changed from $(en)_2$ to cyclam (the value of $\Delta\theta(Ru-N-C)_{av} = 4.7°$ calculated for **1** is comparably large as that of **2**). Indeed, the Ru^{III}−Cl distances observed for **1** (2.369(1)−2.373(1) Å)[4] are as short as those trans to the N_{tert} atoms in **3** (2.364(2)−2.378(2) Å), indicating that the N(cyclam) atoms have also failed in achieving their ideal binding states. Even in $L_4 = (en)_2$, a meaningful strain is found for the Ru−N−C angles, the details of which are given in footnote *k* to Table 8. This also implies that the ethylenediamine unit is *too short* for the appropriate chelation of the Ru ion. Additionally, although the pK_a value increases in the order of $NH_3 < NH_2R < NHR_2 < NR_3$ (R is an alkyl substituent),[24] the observed sequence of $E_{1/2}(Ru^{II/III})$ is rather in the reverse manner to what can be expected from the change in the basicity of ligands, indicating that this factor is rather irrelevant to the *alkyl-substituent dependence* focused here.

Although the properties of **6** should not be directly compared with those of **2** and other complexes, the $\Delta\theta(N-Ru-N)_{av}$ values given in Table 8 show that the extent of distortion from O_h in **6** is the largest of all but the energy levels of the HOMO and LUMO calculated for **6** are quite similar to those of other complexes. In spite of the greatest mislocation of the $N(L_4)$ donors, the misdirection of donors (the $\Delta\theta(Ru-N-C)_{av}$ value) in **6** is not so large compared with that of **2**. However, as expected, the $\Delta\theta$(Ru−N−C) values around the N_{tert} atom in **6** are as large as those for **3** and **5** (Table 7). Due to the existence of an extra π back-bonding achieved with the imino group of baia formed in the selective dehydrogenation of tren, the effective charge on Ru(II) in **6** must be increased and therefore the MLCT band of **6** is observed at highest energy (Table 8).

Concluding Remarks

We have presented a new synthetic route for the Ru(cyclam) complexes and reported on the synthesis of the first ruthenium complex of a tridentate trenH ligand in a facial manner, *fac*-$[Ru^{III}Cl_3(trenH)]Cl$. It is also confirmed that this complex can be readily transformed into a complex $[Ru^{II}(baia)L_2]^{2+}$ containing a tetradentate baia ligand. In the synthesis of *fac*-$[Ru^{III}Cl_3(trenH)]Cl$, we have encountered a byproduct having a very interesting microporous layered structure. One interesting approach to utilize this unique framework would be to replace the $[Ru^{III}Cl_6]^{3-}$ ions encapsulated in the micropores with some other ions or molecules. Through the detailed examinations into the steric strain generated by the chelate rings, it is suggested that, in some cases, undesirable weakening of coordination bonds may occur with an introduction of chelate systems because of the *misdonation effect*, even though the apparent stability of complexes may be increased owing to the *chelate effect*. The exceptionally long $Ru-N_{tert}$ distance and the weak σ-trans influence of the N_{tert} atom recognized in the X-ray analyses of **3** and **5** are good examples showing that the mislocation and misdirection of donors in polyamine complexes having chelate systems are not trivial phenomena but might be important factors giving subtle but effective changes in the electronic structures at the metal centers.

Acknowledgment. This work was financially supported by Grants-in-Aid for Scientific Research (No. 04854061 and 05854065) from the Ministry of Education, Science, and Culture of Japan. We thank Professor Shigenobu Yano and Ms. Yasuko Yamada (Nara Women's University, Japan) for their useful discussions about the synthesis of compound **1**.

Supporting Information Available: Tables of crystal and data collection parameters, atomic coordinates, hydrogen atom coordinates, anisotropic thermal parameters, and interatomic distances and angles for **2**−**6** and a figure of E_{abs} vs $E_{1/2}(Ru^{II/III})$ for *cis*-$[Ru^{II}L_4(bpy)]^{2+}$ (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from ACS or downloaded by subscribers from the Internet; see any current masthead page for ordering information and internet access instructions.

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