

# Linear-Type S-Bridged Triruthenium Complexes with Aliphatic Aminothiolate Ligands: Synthesis, Characterization, and Properties

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Treatment of  $[\text{RuCl}_2(\text{DMSO})_4]$  with 2-aminoethanethiol (Haet) in ethanol gave a dicationic triruthenium complex,  $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2]\text{Cl}_2$  (**1**) $\text{Cl}_2$ . Complex **1** was also obtained by treatment of  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  with excess Haet in water. When **1** $^{2+}$  was chromatographed on a cation-exchange column of SP-Sephadex C-25, meso ( $\Delta\Delta$ ) and racemic ( $\Delta\Delta/\Lambda\Lambda$ ) isomers of the corresponding tricationic complex,  $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2]^{3+}$  (**2**) $^{3+}$ , were eluted with aqueous  $\text{NaNO}_3$ . The racemic isomer of **2** $^{3+}$  was optically resolved into  $\Delta\Delta$  and  $\Lambda\Lambda$  isomers by using  $[\text{Sb}_2(\text{R},\text{R}-\text{tartrato})_2]^{2-}$  as a resolving agent. The molecular structures of  $\Delta\Delta$ - and  $\Delta\Delta/\Lambda\Lambda$ -**2** $(\text{NO}_3)_3$  were determined by X-ray crystallography. In these complexes, the central Ru atom is coordinated by six thiolato groups from two terminal *fac*-(S)- $[\text{Ru}(\text{aet})_3]$  units in an octahedral geometry, forming a linear-type S-bridged triruthenium structure. The spectroelectrochemical studies on the electronic absorption and CD spectra, together with the electrochemical studies, demonstrated that **1** $^{2+}$  and **2** $^{3+}$  are interconvertible with each other through a one-electron redox process, retaining the chirality of the triruthenium structure. Their electronic structures were investigated on the basis of EPR and magnetic susceptibility measurements, which indicated that **1** $^{2+}$  and **2** $^{3+}$  have spin ground states of  $S_1 = 0$  and  $S_1 = 1/2$ , respectively. The corresponding L-cysteinato complex,  $[\text{Ru}\{\text{Ru}(\text{L-cys-N,S})_3\}_2]^{3-}$ , which was formed from  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  and excess L-cysteine (L-H<sub>2</sub>cys) in water followed by air oxidation, is also presented.

## Introduction

2-Aminoethanethiolate (aet) is the most simple N,S-chelating ligand that has been used for the formation of various S-bridged polynuclear structures because of the strong Lewis basicity of its aliphatic thiolate group.<sup>1–3</sup> The first examples of aet polynuclear complexes with octahedral metal centers were reported by Jicha and Busch in 1962, who prepared  $[\text{Co}\{\text{Co}(\text{aet})_3\}_2]^{3+}$  and  $[\text{Ni}\{\text{Co}(\text{aet})_3\}_2]^{2+}$  by the reaction of *fac*-(S)- $[\text{Co}(\text{aet})_3]$  with  $\text{Co}^{\text{III}}$  or  $\text{Ni}^{\text{II}}$ , respectively.<sup>4</sup> The subsequent structural studies established that these complexes have a linear-type S-bridged trinuclear structure, in which the central  $\text{Co}^{\text{III}}$  or  $\text{Ni}^{\text{II}}$  ion is coordinated

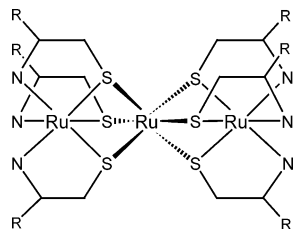
by six S atoms from two terminal *fac*-(S)- $[\text{Co}(\text{aet})_3]$  octahedral units.<sup>5</sup> The investigations of this class of complexes have been extended to include other metal ions such as  $\text{Fe}^{\text{III}}$  and  $\text{Ru}^{\text{III}}$  at the center and other *fac*-(S)- $[\text{M}(\text{aet})_3]$  ( $\text{M} = \text{Cr}^{\text{III}}$ ,  $\text{Rh}^{\text{III}}$ ,  $\text{Ir}^{\text{III}}$ ) units in the terminus of the trinuclear structure.<sup>6–8</sup> However, no report has appeared on the studies of S-bridged trinuclear complexes consisting of *fac*-(S)- $[\text{Ru}(\text{aet})_3]$  units,

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**Chart 1.** A Linear-Type S-Bridged Triruthenium Structure (R = H for aet and R = COO<sup>-</sup> for L-cys)



which are expected to exhibit intriguing redox and magnetic behavior, although a related linear-type triruthenium complex having a hexadentate-N<sub>3</sub>S<sub>3</sub> aromatic thiolate ligand, [Ru{Ru(L)}<sub>2</sub>]<sup>2+</sup> (L = 1,4,7-tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane), has been prepared by the reaction of [Ru(L)] with Ru<sup>II</sup>.<sup>9</sup>

Our continued interest in the stereochemical and electrochemical properties of S-bridged polynuclear complexes composed of *fac*-(S)-[M(aet)<sub>3</sub>] units<sup>10</sup> prompted us to prepare the mononuclear *fac*-(S)-[Ru(aet)<sub>3</sub>] that could be available as the starting complex for the construction of a variety of S-bridged polynuclear structures. In the course of this work, we found that the reactions of Ru<sup>III</sup> or Ru<sup>II</sup> with Haet led to the direct isolation of an S-bridged triruthenium complex having two *fac*-(S)-[Ru(aet)<sub>3</sub>] units, [Ru{Ru(aet)<sub>3</sub>]<sub>2</sub>]<sup>2+</sup>, which is easily oxidized to give the corresponding tricationic species, [Ru{Ru(aet)<sub>3</sub>]<sub>2</sub>]<sup>3+</sup>. In this paper, we report on the synthesis, characterization, and electrochemical and magnetic properties of these triruthenium complexes with six aet ligands (Chart 1), along with the crystal structures of meso (ΔΔ) and racemic (ΔΔ/ΛΛ) isomers of [Ru{Ru(aet)<sub>3</sub>]<sub>2</sub>]<sup>3+</sup>. The formation of an analogous triruthenium complex with L-cysteinate (L-cys) is also reported. The present results obtained for the basic triruthenium system would contribute significantly to our understanding not only of the coordination chemistry of S-bridged polynuclear complexes but also of the coordination chemistry of ruthenium complexes with thiolato donor groups,<sup>11</sup> which has been explored much less than that with other donor groups.

## Experimental Section

**Preparation of [Ru{Ru(aet)<sub>3</sub>]<sub>2</sub>]Cl<sub>2</sub> ([1]Cl<sub>2</sub>).** **Method A.** To a solution containing 1.00 g (2.06 mmol) of [RuCl<sub>2</sub>(DMSO)<sub>4</sub>]<sup>12</sup> in 200 mL of ethanol was added 0.48 g (6.22 mmol) of Haet. The mixture was refluxed in an oil bath for 3 h under a nitrogen atmosphere. The resulting dark brown solution was concentrated to dryness with a rotary evaporator. The residue was then dissolved in 10 mL of a 1 M NaCl aqueous solution, which was stored in a refrigerator for 1 day. The resulting dark green crystalline powder was collected by filtration, and was washed with a small amount of ethanol and diethyl ether. Yield: 0.10 g (17%). Anal. Calcd for [1]Cl<sub>2</sub>·2.5H<sub>2</sub>O: C, 16.45; H, 4.72; N, 9.59. Found: C, 16.42; H, 4.54; N, 9.54.

**Method B.** To a solution containing 1.00 g (3.82 mmol as Ru) of RuCl<sub>3</sub>·nH<sub>2</sub>O in 10 mL of water was added 1.47 g (19.1 mmol) of Haet. The mixture was refluxed in an oil bath for 5 h under a nitrogen atmosphere. The resulting dark brown solution was concentrated to dryness with a rotary evaporator. The residue was then dissolved in 10 mL of a NaCl aqueous solution, which was stored in a refrigerator for 1 day. The resulting dark green microcrystals were collected by filtration, and were washed with a small amount of ethanol and diethyl ether. Yield: 0.13 g (12%).

**Preparation of ΔΔ-[Ru{Ru(aet)<sub>3</sub>]<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub> ([2a](NO<sub>3</sub>)<sub>3</sub>) and ΔΔ/ΛΛ-[Ru{Ru(aet)<sub>3</sub>]<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub> ([2b](NO<sub>3</sub>)<sub>3</sub>).** An aqueous solution of [1]Cl<sub>2</sub>·2.5H<sub>2</sub>O (0.10 g) was charged on the top of an SP-Sephadex C-25 column (Na<sup>+</sup> form, 3 cm × 40 cm). After the column had been washed with water, the adsorbed band was developed with a 0.5 M aqueous solution of NaNO<sub>3</sub>. Two green bands, [2a]<sup>3+</sup> and [2b]<sup>3+</sup> ([2a]<sup>3+</sup>: [2b]<sup>3+</sup> ≈ 1:1), the absorption spectra of which are distinct from the spectrum of [1]<sup>2+</sup>, were eluted in this order. Each of the [2a]<sup>3+</sup> and [2b]<sup>3+</sup> eluates was concentrated to a small volume with a rotary evaporator, and a large amount of methanol was added to it. After the deposited NaNO<sub>3</sub> was filtered off, the filtrate was again concentrated to a small volume, and was then stored in a refrigerator for several days. The resulting dark green crystalline solid was collected by filtration. Yield for [2a]-(NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O: 0.04 g. Anal. Calcd for [2a](NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O: C, 14.95; H, 3.97; N, 13.08. Found: C, 14.75; H, 3.81; N, 12.98. Yield for [2b](NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O: 0.04 g. Anal. Calcd for [2b](NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O: C, 14.95; H, 3.97; N, 13.08. Found: C, 14.83; H, 3.80; N, 13.06.

Dark green crystals of [2a](NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O and [2b](NO<sub>3</sub>)<sub>3</sub>·3.5H<sub>2</sub>O suitable for X-ray analyses were obtained by recrystallization from a small amount of water at room temperature.

**Optical Resolution of [2b]<sup>3+</sup>.** **Method A.** An aqueous solution of [2b](NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O (0.04 g) was chromatographed on an SP-Sephadex C-25 column (Na<sup>+</sup> form, 2 cm × 30 cm), using a 0.25 M aqueous solution of Na<sub>2</sub>[Sb<sub>2</sub>(R,R-tartrato)<sub>2</sub>]·5H<sub>2</sub>O as an eluent. When the adsorbed band was circulated three times in the same column, it was significantly broadened, but was not clearly separated into two bands. The broadened band was fractionally eluted with

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a 0.5 M aqueous solution of NaCl. Each fraction was concentrated to a small volume with a rotary evaporator, which was used for the spectral measurements. It was found from the absorption and CD spectral measurements that several earlier and later fractions contained dominantly the (+)<sub>460</sub><sup>CD</sup> and (-)<sub>460</sub><sup>CD</sup> isomers of [2b]<sup>3+</sup>, respectively, which showed CD curves enantiomeric to each other. Complex [2a]<sup>3+</sup> was not optically resolved by the same column chromatographic method.

**Method B.** To a solution containing [2b](NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O (0.07 g, 0.07 mmol) in 15 mL of water was added a solution containing Na<sub>2</sub>[Sb<sub>2</sub>(R,R-tartrato)<sub>2</sub>]·5H<sub>2</sub>O (0.07 g, 0.11 mmol) in 5 mL of water. The mixture was allowed to stand in a refrigerator for 3 days, and the resulting dark green powder was collected by filtration. This powder was then suspended in 2 mL of a saturated NaNO<sub>3</sub> aqueous solution, which was then stirred at room temperature for 1 h. The dark green powder thus obtained was collected by filtration, and was recrystallized from a small amount of water by adding a saturated NaNO<sub>3</sub> aqueous solution. It was found from the absorption and CD spectral measurements that this product contained dominantly the (-)<sub>460</sub><sup>CD</sup> isomer of [2b]<sup>3+</sup>.

**Reaction of RuCl<sub>3</sub>·nH<sub>2</sub>O with L-Cysteine.** To a solution containing 1.00 g (3.82 mmol as Ru) of RuCl<sub>3</sub>·nH<sub>2</sub>O in 100 mL of water was added 3.20 g (26.4 mmol) of L-cysteine (L-H<sub>2</sub>cys) dissolved in 23 mL of a 1 M KOH aqueous solution. The mixture was refluxed in an oil bath for 3 h under a nitrogen atmosphere. The resulting dark brown reaction solution was chromatographed on a QAE-Sephadex A-25 column (Na<sup>+</sup> form, 4 cm × 88 cm). After the column had been swept with a 0.2 M aqueous solution of KCl, three green bands, **3a**, **3b**, and **3c** (**3a**:**3b**:**3c** ≈ 1:2:1), were eluted with a 0.5 M aqueous solution of KCl in this order. Although **3b** and **3c** showed absorption spectra similar to that of [1]<sup>2+</sup>, the spectral feature of **3a** corresponded to that of a mixture of [1]<sup>2+</sup> and [2]<sup>3+</sup>. Air was then bubbled through each of the **3a**, **3b**, and **3c** eluates (26 h for **3a**, 36 h for **3b**, and 60 h for **3c**) to be converted into **4a**, **4b**, and **4c**, respectively, which showed absorption spectra very similar to that of [2]<sup>3+</sup>. Attempts to isolate solid samples from the **4a**, **4b**, and **4c** solutions were unsuccessful, and their spectroscopic data were obtained only qualitatively.

**Measurements.** The electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer, and the CD spectra on a JASCO J-700 spectrophotometer at room temperature. The elemental analyses (C, H, N) were performed at Osaka University. Molar conductivities of the complexes were measured with a Horiba DS-12 conductivity meter at room temperature. X-Band EPR spectra were recorded on a JEOL EPR spectrometer JM-FE1 at 77 K and room temperature (298 K). The g values were calibrated precisely with a Mn<sup>2+</sup> marker, which was used as a reference. Variable-temperature magnetic susceptibility measurements were made using a SQUID magnetometer MPMS 5S (Quantum Design) at 1 T. The diamagnetic correction was determined from Pascal's constants. Voltammetric studies were performed by a CV-600A apparatus (BAS) using a glassy-carbon working electrode (3 mm φ), an aqueous Ag/AgCl/NaCl (3 M) reference electrode, and a Pt-wire auxiliary electrode. Electrochemical experiments were conducted at 25 °C in water with 0.1 M Na<sub>2</sub>SO<sub>4</sub> as a supporting electrolyte and complex concentrations of 1.0 mM. Spectroelectrochemical studies were performed by a CV-600A apparatus (BAS) using a thin-layer quartz cell (0.5 mm light path length) with a Pt-mesh (100 mesh) working electrode, an aqueous Ag/AgCl/NaCl (3 M) reference electrode, and a Pt-wire auxiliary electrode. Spectroelectrochemical experiments were conducted at 25 °C in water with 0.1 M Na<sub>2</sub>SO<sub>4</sub> as a supporting electrolyte and complex concentrations of 1.0 mM.

**Table 1.** Crystallographic Data of ΔΛ-[Ru{Ru(aet)<sub>3</sub>}]<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub> ([2a](NO<sub>3</sub>)<sub>3</sub>) and ΔΔ/ΛΛ-[Ru{Ru(aet)<sub>3</sub>}]<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub> ([2b](NO<sub>3</sub>)<sub>3</sub>)

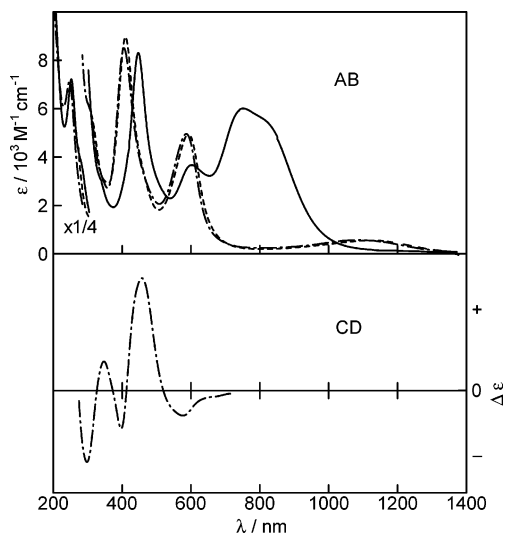
|                                          | [2a](NO <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O                                        | [2b](NO <sub>3</sub> ) <sub>3</sub> ·3.5H <sub>2</sub> O                                        |
|------------------------------------------|-----------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|
| formula                                  | C <sub>12</sub> H <sub>44</sub> N <sub>9</sub> O <sub>13</sub> Ru <sub>3</sub> S <sub>6</sub> | C <sub>12</sub> H <sub>43</sub> N <sub>9</sub> O <sub>12.5</sub> Ru <sub>3</sub> S <sub>6</sub> |
| fw                                       | 1018.13                                                                                       | 1009.12                                                                                         |
| space group                              | P1̄ (No. 2)                                                                                   | P1̄ (No. 2)                                                                                     |
| a (Å)                                    | 9.11(2)                                                                                       | 11.48(2)                                                                                        |
| b (Å)                                    | 9.07(2)                                                                                       | 12.40(2)                                                                                        |
| c (Å)                                    | 12.14(2)                                                                                      | 13.22(1)                                                                                        |
| α (deg)                                  | 70.3(2)                                                                                       | 68.77(5)                                                                                        |
| β (deg)                                  | 68.3(2)                                                                                       | 69.73(5)                                                                                        |
| γ (deg)                                  | 77.8(2)                                                                                       | 71.59(3)                                                                                        |
| V (Å <sup>3</sup> )                      | 873(3)                                                                                        | 1606(3)                                                                                         |
| Z                                        | 1                                                                                             | 2                                                                                               |
| T (K)                                    | 200                                                                                           | 200                                                                                             |
| radiation λ (Å)                          | 0.71075                                                                                       | 0.71075                                                                                         |
| ρ <sub>calcd</sub> (g cm <sup>-3</sup> ) | 1.936                                                                                         | 2.087                                                                                           |
| μ Mo Kα (mm <sup>-1</sup> )              | 1.703                                                                                         | 1.850                                                                                           |
| R (I > 2σ(I))                            | 0.031                                                                                         | 0.052                                                                                           |
| R <sub>w</sub> (all data)                | 0.079                                                                                         | 0.178                                                                                           |

**X-ray Structural Determinations.** Single-crystal X-ray diffraction experiments for [2a](NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O and [2b](NO<sub>3</sub>)<sub>3</sub>·3.5H<sub>2</sub>O were performed on a Rigaku RAXIS RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation at 200 K. Crystallographic data are summarized in Table 1. Unit-cell parameters were determined by a least-squares refinement. The intensity data were collected by the ω scan mode up to 2θ<sub>max</sub> = 55.0°. An empirical absorption correction was applied. The 3213 and 5748 independent reflections with I > 2σ(I) of the measured 8261 and 14 941 reflections were considered to be observed values, and were used for the structure determination. The structures were solved by direct methods using SHELXL-97 and Patterson methods using PATTY in DIRDIF99, respectively. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. All hydrogen atoms except those of water molecules were placed at calculated positions, but were not refined. In [2a](NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O, one nitrate anion was disordered, and appeared as two fragments that are superposed on each other. The two sets of disordered oxygen atoms (O1–O3 and O4–O6) of this nitrate anion were refined with site occupancy factors of 0.75 and 0.25. In addition, the site occupancy factors of nitrogen and oxygen atoms (N5, O7–O9) of the other nitrate anion, besides two water oxygen atoms (O11, O12), were fixed to 0.5. In [2b](NO<sub>3</sub>)<sub>3</sub>·3.5H<sub>2</sub>O, nitrogen and oxygen atoms of three nitrate anions (N9–N11, O4–O15), besides water oxygen atoms (O16, O18–O21), were refined with a site occupancy factor of 0.5. All calculations were performed using the CrystalStructure software package.<sup>13</sup>

## Results and Discussion

**Synthesis and Characterization.** The reaction of [Ru<sup>II</sup>-Cl<sub>2</sub>(DMSO)<sub>4</sub>] with 3 molar equiv of 2-aminoethanethiol (Haet) in ethanol under reflux gave a dark brown solution, from which a dark green crystalline solid ([1]Cl<sub>2</sub>) was isolated. Complex [1]Cl<sub>2</sub> was also obtained by reacting RuCl<sub>3</sub>·nH<sub>2</sub>O with excess Haet in water. In the latter reaction, the formation of [1]Cl<sub>2</sub> was not observed on using 3 molar equiv of Haet, indicating that Haet serves not only as a ligating agent but also as a reducing agent for Ru<sup>III</sup>. No other desirable products were isolated from the reaction mixture in both of the reactions. The elemental analytical data of [1]Cl<sub>2</sub> are in agreement with the formula for [Ru<sub>3</sub>-

(13) CrystalStructure analysis package; Rigaku MSC: Kent, U.K., 2004.



**Figure 1.** Absorption and CD spectra of  $[1]^{2+}$  (—),  $[2a]^{3+}$  (---), and  $(+ )_{460}^{CD}\Delta\Delta\text{-}[2b]^{3+}$  (-·-) in  $\text{H}_2\text{O}$ . The scale of CD is arbitrary.

(aet) $_6$ ]Cl $_2$  rather than with that for the expected mononuclear  $[\text{Ru}(\text{aet})_3]$ . The molar conductivity of  $[1]\text{Cl}_2$  in water is  $247 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ , which is close to those values in 1:2 electrolytes, such as  $[\text{Pd}\{\text{Co}(\text{aet})_3\}_2]\text{Cl}_2$  ( $234 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) and  $[\text{Ni}\{\text{Rh}(\text{aet})_3\}_2](\text{NO}_3)_2$  ( $235 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ).<sup>7c,10b</sup> As shown in Figure 1, the electronic absorption spectrum of  $[1]^{2+}$  in water is characterized by three intense visible bands at 447, 603, and 752 nm (Table S1).<sup>14</sup> Three similar intense absorption bands have been observed for a linear-type S-bridged triruthenium complex with hexadentate- $\text{N}_3\text{S}_3$  thiolate ligands,  $[\text{Ru}\{\text{Ru}(\text{L})\}_2]^{2+}$  ( $\text{L} = 1,4,7\text{-tris}(4\text{-tert-butyl-2-mercaptobenzyl})\text{-}1,4,7\text{-triazacyclononane}$ ), in which two  $[\text{Ru}(\text{L})]$  units are linked by a central Ru atom through six sulfur bridges.<sup>9</sup> On the basis of these results, we assigned  $[1]^{2+}$  as an S-bridged triruthenium complex consisting of two *fac*-(*S*)- $[\text{Ru}(\text{aet})_3]$  units,  $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2]^{2+}$ , the structure of which is analogous to that of  $[\text{Ru}\{\text{Ru}(\text{L})\}_2]^{2+}$ .

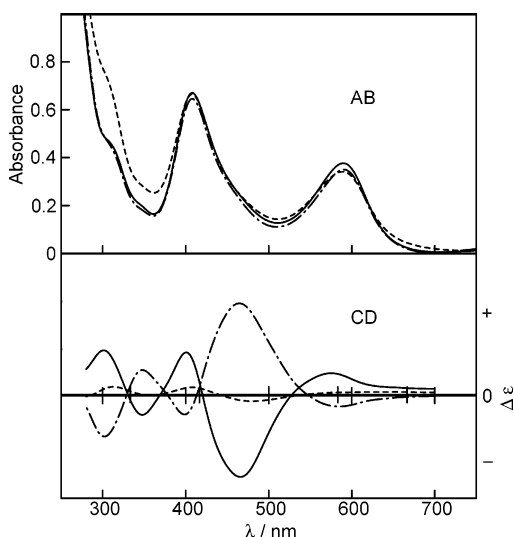
When an aqueous solution of  $[1]^{2+}$  was chromatographed on a cation-exchange column of SP-Sephadex C-25, two green bands,  $[2a]^{3+}$  and  $[2b]^{3+}$ , were eluted with a 0.5 M  $\text{NaNO}_3$  aqueous solution. From the two eluates, complexes  $[2a]^{3+}$  and  $[2b]^{3+}$  were successfully isolated as the nitrate salt. The absorption spectra of  $[2a]^{3+}$  and  $[2b]^{3+}$  are essentially the same, suggestive of the isomeric ( $\Delta\Delta$  vs  $\Delta\Delta/\Delta\Lambda$ ) relationship. Notably, their absorption spectra differ significantly from the spectrum of  $[1]^{2+}$ , giving only two intense bands (409 and 592 nm for  $[2a]^{3+}$  and 405 and 587 nm for  $[2b]^{3+}$ ) in the visible region (Figure 1 and Table S1). This spectral feature corresponds well with that of the tricationic  $[\text{Ru}\{\text{Ru}(\text{L})\}_2]^{3+}$ , which has been generated from the dicationic  $[\text{Ru}\{\text{Ru}(\text{L})\}_2]^{2+}$  by the electrochemical oxidation.<sup>9</sup> The elemental analytical data of  $[2a](\text{NO}_3)_3$  and  $[2b](\text{NO}_3)_3$  are consistent with the formula of  $[\text{Ru}_3(\text{aet})_6](\text{NO}_3)_3$ , and their molar conductivities in water ( $350 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  for  $[2a](\text{NO}_3)_3$ ,  $354 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  for  $[2b](\text{NO}_3)_3$ ) are compatible with those of the 1:3 electrolytes.<sup>8</sup> The linear-

type S-bridged triruthenium structure in  $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2]^{3+}$ , in which two *fac*-(*S*)- $[\text{Ru}(\text{aet})_3]$  units are linked by an octahedral Ru atom, was established by single-crystal X-ray crystallography for both  $[2a](\text{NO}_3)_3$  and  $[2b](\text{NO}_3)_3$  (vide infra). Thus, it is seen that the dicationic  $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2]^{2+}$  ( $[1]^{2+}$ ) is subject to air oxidation, forming the tricationic  $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2]^{3+}$  ( $[2]^{3+}$ ) in the course of the column chromatographic procedure. Consistent with this, the absorption spectrum of  $[1]^{2+}$  in water under an aerobic condition was found to change to the spectrum of  $[2]^{3+}$  after 24 h, showing several isosbestic points in the visible region (Figure S1). In addition, it was recognized that the oxidation of  $[1]^{2+}$  with  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  in water affords  $[2]^{3+}$ , which is reverted back to  $[1]^{2+}$  by the reduction with Zn powder in water. No significant absorption spectral change was noticed for  $[2]^{3+}$  in water for at least 24 h, indicating that the tricationic  $[\text{Ru}_3(\text{aet})_6]^{3+}$  species with aet ligands is fairly stable in solution. Here, it should be noted that only the dicationic species ( $[\text{Ru}\{\text{Ru}(\text{L})\}_2]^{2+}$ ) is able to be isolated for the analogous triruthenium complex composed of  $[\text{Ru}(\text{L})]$  units,<sup>9</sup> which is rationalized by its high  $[\text{Ru}_3(\text{L})_2]^{2+/3+}$  redox potential (vide infra).

With respect to the chiral configurations ( $\Delta$  and  $\Lambda$ ) of each *fac*-(*S*)- $[\text{Ru}(\text{aet})_3]$  unit, meso ( $\Delta\Lambda$ ) and racemic ( $\Delta\Delta/\Delta\Lambda$ ) isomers<sup>1,5</sup> are possible for  $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2]^{3+}$ . X-ray analysis indicated that  $[2a]^{3+}$  and  $[2b]^{3+}$  are the meso and racemic isomers, respectively (vide infra). This is compatible with the fact that  $[2b]^{3+}$  was optically resolved into a pair of enantiomers, whereas  $[2a]^{3+}$  was not optically resolved. It has been shown that for all the tricationic S-bridged trinuclear complexes with aet ligands so far isolated,  $[\text{M}\{\text{M}(\text{aet})_3\}_2]^{3+}$ , the  $\Delta\Delta$  isomer is commonly eluted with  $[\text{Sb}_2(\text{R,R-tartrato})_2]^{2-}$  earlier than the  $\Delta\Lambda$  isomer in the SP-Sephadex C-25 column chromatography.<sup>7,8</sup> This indicates that chiral discrimination of this class of complexes by  $[\text{Sb}_2(\text{R,R-tartrato})_2]^{2-}$  is independent of the kind of trivalent transition-metal ions incorporated in the trinuclear structure. Thus, the  $(+ )_{460}^{CD}$  and  $(- )_{460}^{CD}$  isomers of  $[2b]^{3+}$ , which were eluted earlier and later, respectively, in the SP-Sephadex C-25 column, could be assigned to have the  $\Delta\Delta$  and  $\Delta\Lambda$  configurations, respectively.

To investigate the formation of an analogous S-bridged triruthenium structure with use of other aliphatic aminothioliolate-type ligands, we reacted  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  with excess L-cysteine (L-H $_2$ cys) in water. When a dark brown reaction solution was chromatographed on an anion-exchange column of QAE-Sephadex A-25, three green bands, **3a**, **3b**, and **3c**, were eluted with a 0.5 M KCl aqueous solution. The absorption spectra of the **3b** and **3c** eluates resembled that of  $[1]^{2+}$  (Figure S2), rather than that of  $[2]^{3+}$ , whereas the spectrum of **3a** corresponded with that of a mixture of  $[1]^{2+}$  and  $[2]^{3+}$ . Air was then bubbled through each of the **3a**, **3b**, and **3c** eluates, which produced **4a**, **4b**, and **4c**, respectively. As shown in Figure 2, the absorption spectral curves of **4a**, **4b**, and **4c** are very similar to those of  $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2]^{3+}$  ( $[2]^{3+}$ ), suggesting that these products are three isomers

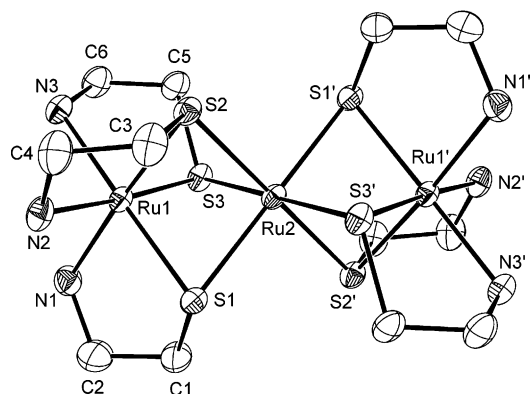
(14) The extinction coefficients of these visible bands are commonly greater than  $10^3 \text{M}^{-1} \text{cm}^{-1}$ , indicating that these bands are dominated by Ru-to-S and/or S-to-Ru charge-transfer transitions.



**Figure 2.** Absorption and CD spectra of **4a** (—), **4b** (---), and **4c** (-·-). The scales of absorption and CD are arbitrary.

( $\Delta_{LLL}\Delta_{LLL}$ ,  $\Lambda_{LLL}\Lambda_{LLL}$ , and  $\Delta_{LLL}\Lambda_{LLL}$ )<sup>15</sup> of the corresponding triruthenium complex with L-cys ligands,  $[\text{Ru}\{\text{Ru}(\text{L-cys-}N,S)_3\}_2]^{3-}$ . Given that this assignment is correct, the CD spectral behavior of two of the three products would be similar to that of  $\Delta\Delta$ - or  $\Lambda\Lambda$ - $[\text{2}]^{3+}$ , whereas the remaining product shows a much weaker CD. Indeed, the CD spectral patterns of **4a** and **4c** correspond well with those of  $\Lambda\Lambda$ - $[\text{2}]^{3+}$  and  $\Delta\Delta$ - $[\text{2}]^{3+}$ , respectively, whereas the CD spectrum of **4b** is rather weak in intensity over the whole region (Figure 2). Accordingly, we assign **4a**, **4b**, and **4c** to the  $\Lambda_{LLL}\Lambda_{LLL}$ ,  $\Delta_{LLL}\Lambda_{LLL}$ , and  $\Delta_{LLL}\Delta_{LLL}$  isomers of  $[\text{Ru}\{\text{Ru}(\text{L-cys-}N,S)_3\}_2]^{3-}$ , respectively, the structure of which is analogous to that of  $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2]^{3+}$ . Unfortunately, none of the pure solid samples were isolated from the eluates, because of the high solubility of products in water and the contamination of the large amount of KCl used for an eluent. It may be worth mentioning that the L-cys triruthenium species is more resistant to air oxidation than  $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2]^{2+}$  (**1**)<sup>2+</sup>, as indicated by the fact that the eluates of **3a**, **3b**, and **3c** still contained the reduced form ( $[\text{Ru}\{\text{Ru}(\text{L-cys-}N,S)_3\}_2]^{4-}$ ). The presence of six free carboxylate groups in the L-cys triruthenium structure, which hinders the approach of oxygen molecules to ruthenium centers, may be responsible for this result.

**Crystal Structures of  $\Delta\Delta$ - $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2](\text{NO}_3)_3$  (**2a**)- $(\text{NO}_3)_3$  and  $\Delta\Delta/\Lambda\Lambda$ - $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2](\text{NO}_3)_3$  (**2b**)- $(\text{NO}_3)_3$ .** X-ray structural analysis of **2a**( $\text{NO}_3$ )<sub>3</sub>·4H<sub>2</sub>O revealed the presence of a discrete complex cation, nitrate anions, and water molecules. The total site occupancy factor of the nitrate anions implies that the entire complex cation is trivalent. A perspective drawing of entire complex cation **2a**<sup>3+</sup> is shown in Figure 3, and its selected bond distances and angles are listed in Table 2. The complex cation consists of two terminal *fac*-(S)- $[\text{Ru}(\text{aet})_3]$  units and one central Ru atom. The three thiolato S atoms of each *fac*-(S)- $[\text{Ru}(\text{aet})_3]$  unit coordinate



**Figure 3.** Perspective view of **2a**<sup>3+</sup> with the atomic labeling scheme. Ellipsoids represent the 50% level of probability. Hydrogen atoms are omitted for clarity.

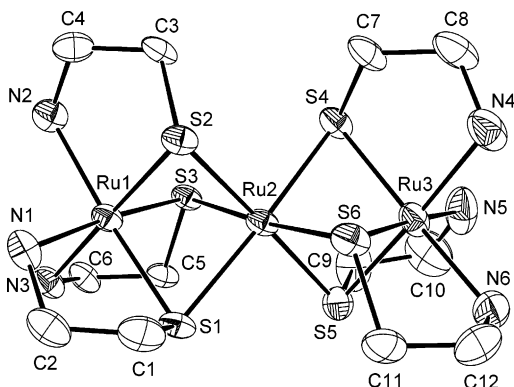
**Table 2.** Selected Bond Distances (Å) and Angles (deg) of  $\Delta\Delta$ - $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2](\text{NO}_3)_3$  (**2a**)- $(\text{NO}_3)_3$

| Distances |          |           |           |
|-----------|----------|-----------|-----------|
| Ru1···Ru2 | 2.757(7) | Ru1–N2    | 2.176(4)  |
| Ru1–S1    | 2.344(5) | Ru1–N3    | 2.203(6)  |
| Ru1–S2    | 2.341(6) | Ru2–S1    | 2.402(6)  |
| Ru1–S3    | 2.346(4) | Ru2–S2    | 2.417(4)  |
| Ru1–N1    | 2.172(6) | Ru2–S3    | 2.415(5)  |
| Angles    |          |           |           |
| S1–Ru1–S2 | 91.0(2)  | S1–Ru1–N3 | 177.04(8) |
| S2–Ru1–S3 | 90.2(2)  | S2–Ru1–N1 | 175.85(9) |
| S3–Ru1–S1 | 92.9(2)  | S3–Ru1–N2 | 175.40(9) |
| S1–Ru1–N1 | 84.9(2)  | S1–Ru2–S2 | 92.2(2)   |
| S2–Ru1–N2 | 85.4(2)  | S2–Ru2–S3 | 93.2(2)   |
| S3–Ru1–N3 | 84.2(2)  | S3–Ru2–S1 | 89.8(2)   |

to the central Ru atom, forming a linear-type S-bridged triruthenium structure in  $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2]^{3+}$ . In **2a**<sup>3+</sup>, the Ru–S bond distances of the two terminal *fac*-(S)- $[\text{Ru}(\text{aet})_3]$  units (with an average of 2.344(6) Å) are appreciably shorter than those around the central Ru atoms (average of 2.411(6) Å). This implies that the bridging thiolato groups bind with the terminal Ru center more strongly than they do with the central Ru center, forming a relatively rigid *fac*-(S)- $[\text{Ru}(\text{aet})_3]$  unit. The coordination geometry of the central Ru atom is very close to that of the regular octahedron, having trans S–Ru–S angles of 180° and bite S–Ru–S angles of ca. 90° (average of 91.7(2)°). The terminal *fac*-(S)- $[\text{Ru}(\text{aet})_3]$  units are also octahedral with the averaged S–Ru–S angle of 91.4(2)°, although the N–Ru–N angles (average of 94.2(2)°) slightly deviate from 90°, giving the expanded N<sub>3</sub> faces. It has been shown that the S–Ru–S angles in the related diruthenium(III) complexes with bridging aromatic thiolate ligands,  $[\text{Ru}_2(\text{H}_2\text{edta})_2(\mu\text{-SC}_6\text{H}_5)_2]$  (103.2(6)°) and  $[\text{Ru}_2(\mu\text{-pyS})_3(\text{pyS})_2]^+$  (average of 107.7(1)°), significantly deviate from 90° to form distorted Ru<sup>III</sup> octahedrons.<sup>16</sup> The Ru–Ru distance in **2a**<sup>3+</sup> (2.757(7) Å) is just between those in  $[\text{Ru}_2(\text{H}_2\text{edta})_2(\mu\text{-SC}_6\text{H}_5)_2]$  (2.866(1) Å) and  $[\text{Ru}_2(\mu\text{-pyS})_3(\text{pyS})_2]^+$  (2.693(1) Å), in which a Ru<sup>III</sup>–Ru<sup>III</sup> single bond exists, whereas the averaged Ru–S bond distance (2.378(6) Å) in **2a**<sup>3+</sup> is longer than the corresponding distances in  $[\text{Ru}_2(\text{H}_2\text{edta})_2(\mu\text{-SC}_6\text{H}_5)_2]$  (average of 2.307(2) Å) and  $[\text{Ru}_2$ -

(15) (a) Konno, T.; Aizawa, S.; Okamoto, K.; Hidaka, J. *Chem. Lett.* **1985**, 1017. (b) Okamoto, K.; Aizawa, S.; Konno, T.; Einaga, H.; Hidaka, J. *Bull. Chem. Soc. Jpn.* **1986**, 59, 3859. (c) Aizawa, S.; Okamoto, K.; Einaga, H.; Hidaka, J. *Bull. Chem. Soc. Jpn.* **1988**, 61, 1601.

(16) (a) Cameron, B. R.; Bridger, G. J.; Maresca, K. P.; Zubieta, J. *Inorg. Chem.* **2000**, 39, 3928. (b) Sokolov, M.; Sasaki, Y.; Umakoshi, K. *Inorg. Chem. Commun.* **2001**, 4, 142.



**Figure 4.** Perspective view of  $[2b]^{3+}$  with the atomic labeling scheme. The  $\Delta\Delta$  isomer is selected. Ellipsoids represent the 50% level of probability. Hydrogen atoms are omitted for clarity.

$(\mu\text{-pyS})_3(\text{pyS})_2]^+$  (average of 2.308(3) Å). The Ru–N bond distances of each *fac*-(S)-[Ru(aet)<sub>3</sub>] unit in  $[2a]^{3+}$  (average of 2.184(6) Å) are slightly longer than those in  $[\text{Ru}(\text{en})_3]^{3+}$  (average of 2.11(2) Å) and *cis*-[RuCl(H<sub>2</sub>O)(en)]<sup>2+</sup> (average of 2.099(2) Å),<sup>17</sup> presumably because of the trans influence due to thiolato donor atoms. The two *fac*-(S)-[Ru(aet)<sub>3</sub>] units in  $[2a]^{3+}$  have the  $\Delta$  and  $\Lambda$  chiral configurations, which give the meso form ( $\Delta\Lambda$ - $[2]^{3+}$ ), as evidenced by an inversion center located on the central Ru atom. The bridging S atoms in the  $\Delta$ - and  $\Lambda$ -*fac*-(S)-[Ru(aet)<sub>3</sub>] units are regulated to have the *R* and *S* configurations, respectively, with all aet chelate rings being fixed to a distinct gauche form of the *lel* conformation ( $\lambda$  for the  $\Delta$  unit and  $\delta$  for the  $\Lambda$  unit).

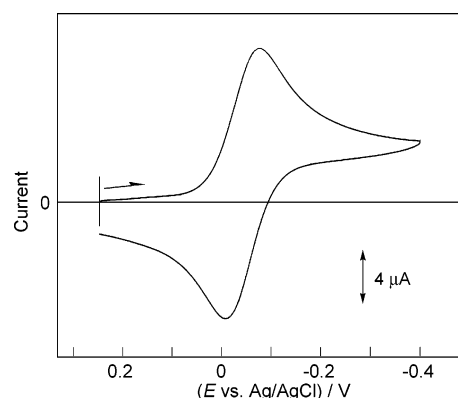
X-ray analysis for  $[2b](\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  indicated that the complex cation  $[2b]^{3+}$  also has an S-bridged triruthenium structure in  $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2]^{3+}$ , in which the central Ru atom is coordinated by six S atoms from two octahedral *fac*-(S)-[Ru(aet)<sub>3</sub>] units (Figure 4). However, the two *fac*-(S)-[Ru(aet)<sub>3</sub>] units in  $[2b]^{3+}$  have the same chiral configuration, which gives the racemic form ( $\Delta\Delta/\Lambda\Lambda$ - $[2]^{3+}$ ). The chiral behavior of the bridging S atoms and the aet chelate rings in  $[2b]^{3+}$  are the same as that found in  $[2a]^{3+}$  ( $\Delta\Lambda$ - $[2]^{3+}$ ). Although the bond angles around the three Ru atoms in  $[2b]^{3+}$  are very similar to the corresponding angles in  $[2a]^{3+}$  (Table 3), the Ru–S bond distances in  $[2b]^{3+}$  (average  $\text{Ru}_{\text{terminal}}\text{-S} = 2.308(3)$  Å,  $\text{Ru}_{\text{central}}\text{-S} = 2.368(3)$  Å) are ca. 0.04 Å shorter than the corresponding distances in  $[2a]^{3+}$  (average  $\text{Ru}_{\text{terminal}}\text{-S} = 2.344(6)$  Å,  $\text{Ru}_{\text{central}}\text{-S} = 2.411(6)$  Å), leading to slightly shorter Ru···Ru distances (average of 2.708(3) Å) in  $[2b]^{3+}$  relative to those in  $[2a]^{3+}$  (2.757(7) Å). This can be explained by the steric congestion between the aet chelate rings of the two terminal *fac*-(S)-[Ru(aet)<sub>3</sub>] units in the  $\Delta\Lambda$  isomer, which appears to be greater than that in the  $\Delta\Delta/\Lambda\Lambda$  isomer. It is interesting to note that not only the terminal Ru–S bond distances (average 2.308(3) Å) but also the central Ru–S distances in  $\Delta\Delta/\Lambda\Lambda$ - $[2]^{3+}$  (average of 2.368(3) Å) are comparable with those found in the related dicationic  $\Delta\Delta/\Lambda\Lambda$ -[Ru{Ru(L)}<sub>2</sub>]<sup>2+</sup> (average  $\text{Ru}_{\text{terminal}}\text{-S} = 2.321(5)$  Å,  $\text{Ru}_{\text{central}}\text{-S} = 2.391(5)$  Å),<sup>9</sup> despite

**Table 3.** Selected Bond Distances (Å) and Angles (deg) of  $\Delta\Delta/\Lambda\Lambda$ -[Ru{Ru(aet)<sub>3</sub>]<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub> ( $[2b](\text{NO}_3)_3$ )

| Distances |          |           |           |
|-----------|----------|-----------|-----------|
| Ru1···Ru2 | 2.734(3) | Ru2–S3    | 2.391(2)  |
| Ru2···Ru3 | 2.681(3) | Ru2–S4    | 2.353(3)  |
| Ru1–S1    | 2.313(3) | Ru2–S5    | 2.355(3)  |
| Ru1–S2    | 2.304(3) | Ru2–S6    | 2.377(2)  |
| Ru1–S3    | 2.310(3) | Ru3–S4    | 2.307(3)  |
| Ru1–N1    | 2.134(6) | Ru3–S5    | 2.305(3)  |
| Ru1–N2    | 2.148(6) | Ru3–S6    | 2.308(3)  |
| Ru1–N3    | 2.160(6) | Ru3–N4    | 2.154(8)  |
| Ru2–S1    | 2.365(3) | Ru3–N5    | 2.128(8)  |
| Ru2–S2    | 2.369(3) | Ru3–N6    | 2.128(7)  |
| Angles    |          |           |           |
| S1–Ru1–S2 | 89.7(1)  | S6–Ru3–S4 | 92.00(9)  |
| S2–Ru1–S3 | 92.39(8) | S4–Ru3–N4 | 84.7(2)   |
| S3–Ru1–S1 | 90.82(9) | S5–Ru3–N5 | 85.0(3)   |
| S1–Ru1–N1 | 85.1(2)  | S6–Ru3–N6 | 84.9(2)   |
| S2–Ru1–N2 | 85.0(2)  | S4–Ru3–N6 | 175.7(2)  |
| S3–Ru1–N3 | 84.9(2)  | S5–Ru3–N4 | 177.0(2)  |
| S1–Ru1–N2 | 174.7(2) | S6–Ru3–N5 | 175.5(3)  |
| S2–Ru1–N3 | 177.3(2) | S4–Ru2–S5 | 92.2(2)   |
| S3–Ru1–N1 | 175.0(2) | S5–Ru2–S6 | 93.2(9)   |
| S1–Ru2–S2 | 86.9(2)  | S6–Ru2–S4 | 89.17(8)  |
| S2–Ru2–S3 | 88.80(8) | S1–Ru2–S4 | 174.76(6) |
| S3–Ru2–S1 | 87.63(8) | S2–Ru2–S5 | 175.39(6) |
| S4–Ru3–S5 | 92.3(2)  | S3–Ru2–S6 | 175.46(6) |
| S5–Ru3–S6 | 90.66(9) |           |           |

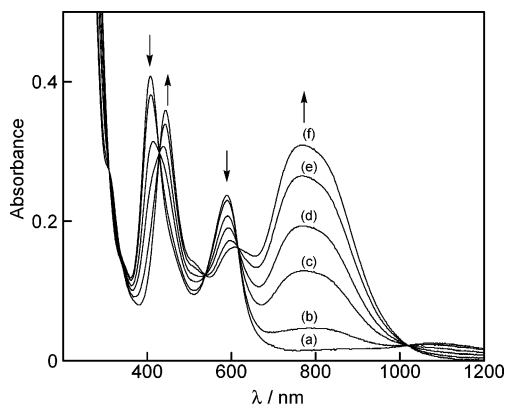
the difference in oxidation state of the triruthenium structure ( $\text{Ru}_3^{9+}$  for  $[2]^{3+}$  vs  $\text{Ru}_3^{8+}$  for  $[\text{Ru}\{\text{Ru}(\text{L})\}_2]^{2+}$ ) and the difference in the thiolato groups bridging three metal centers (aliphatic thiolato for  $[2]^{3+}$  vs aromatic thiolato for  $[\text{Ru}\{\text{Ru}(\text{L})\}_2]^{2+}$ ).

**Electrochemistry and Spectroelectrochemistry of  $[\text{Ru}\{\text{Ru}(\text{aet})_3\}_2]^{2+/3+}$ .** Electrochemical properties were studied by cyclic voltammetry at a grassy-carbon electrode in aqueous solutions containing 0.1 M  $\text{Na}_2\text{SO}_4$  as the supporting electrolyte. When the potential was held at 0.0 V, a cathodic electrolysis occurred for  $\Delta\Lambda$ - $[2]^{3+}$  ( $[2a]^{3+}$ ) and  $\Delta\Delta/\Lambda\Lambda$ - $[2]^{3+}$  ( $[2b]^{3+}$ ), whereas no significant electrolysis occurred at +0.2 V. This implies that the isolated  $\Delta\Lambda$ - and  $\Delta\Delta/\Lambda\Lambda$ - $[2]^{3+}$  exist in the oxidized form ( $\text{Ru}_3^{9+}$ ), consistent with the X-ray analytical results. The cyclic voltammogram for each of  $\Delta\Lambda$ - and  $\Delta\Delta/\Lambda\Lambda$ - $[2]^{3+}$  displays only one redox couple between +0.2 and –0.2 V (Figure 5), and no other redox process is observed in the potential region +1.1 to –1.1 V (vs Ag/AgCl). The peak currents are proportional to the square root of the scan rates, and the ratio of anodic to cathodic peak



**Figure 5.** Cyclic voltammogram of  $\Delta\Lambda$ - $[2]^{3+}$  ( $[2a]^{3+}$ ) in 0.1 M  $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$  with a scan rate of 0.1 V s<sup>-1</sup>.

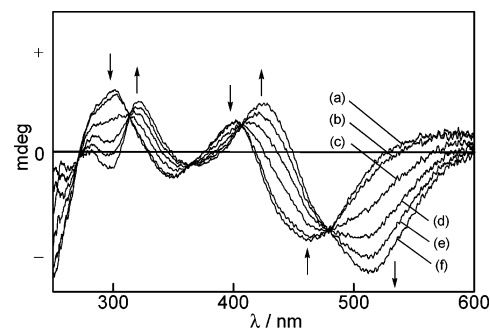
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**Figure 6.** Sequential absorption spectra obtained during an OTTLE spectropotentiostatic experiment on 1.0 mM  $\Delta\Delta/\Lambda\Lambda$ -[2]<sup>3+</sup> (**[2b]**)<sup>3+</sup> in 0.1 M Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O at the following applied potentials: (a) +200, (b) +50, (c) 0, (d) -25, (e) -50, and (f) -200 mV (vs Ag/AgCl).

currents is nearly unity. At a scan rate of 100 mV s<sup>-1</sup>, the observed peak separation ( $E_{pc} - E_{pa}$ ) is 60 mV for each redox couple. These results establish that the redox process observed for each of  $\Delta\Lambda$ - and  $\Delta\Delta/\Lambda\Lambda$ -[2]<sup>3+</sup> is of a reversible, one-electron nature.<sup>18</sup> The  $E_{1/2}$  value for  $\Delta\Delta/\Lambda\Lambda$ -[2]<sup>3+</sup> (0.00 V) is 40 mV more positive than that for  $\Delta\Lambda$ -[2]<sup>3+</sup> (-0.04 V), indicating that the meso isomer is oxidized more easily than the racemic isomer. This may be related to the larger Ru···Ru separation in  $\Delta\Lambda$ -[2]<sup>3+</sup> relative to that in  $\Delta\Delta/\Lambda\Lambda$ -[2]<sup>3+</sup> because of the steric demand. As expected, the cyclic voltammogram of [1]<sup>2+</sup> is essentially the same as that of  $\Delta\Lambda$ - or  $\Delta\Delta/\Lambda\Lambda$ -[2]<sup>3+</sup>, giving a redox couple at  $E_{1/2} = -0.02$  V. However, the peak separation ( $E_{pc} - E_{pa} = 80$  mV) for [1]<sup>2+</sup> is slightly larger, which is understood by the coexistence of the meso and racemic isomers. From this voltammogram, together with the anodic electrolysis that occurred at 0.0 V, the isolated [1]<sup>2+</sup> is confirmed to be the reduced form (Ru<sub>3</sub><sup>8+</sup>) of [2]<sup>3+</sup>. It should be noted that this redox potential is much more negative than that for [Ru{Ru(L)}<sub>2</sub>]<sup>2+</sup> (L = 1,4,7-tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane) ( $E_{1/2} = +0.61$  V vs Ag/AgNO<sub>3</sub> in CH<sub>3</sub>CN), which has been isolated only as the reduced form.<sup>9</sup> This is compatible with the expected electron-donating ability of the aliphatic thiolato donors in [1]<sup>2+</sup>, which is greater than that of the aromatic thiolato donors in [Ru{Ru(L)}<sub>2</sub>]<sup>2+</sup>.

Spectroelectrochemical experiments for  $\Delta\Delta/\Lambda\Lambda$ -[2]<sup>3+</sup> were carried out using an optically transparent thin-layer electrode (OTTLE) cell, to establish the reversible redox process between [1]<sup>2+</sup> and [2]<sup>3+</sup>. Figure 6 shows the absorption spectra that were recorded during a potentiostatic reduction for  $\Delta\Delta/\Lambda\Lambda$ -[2]<sup>3+</sup>. When the potential is decreased from +0.20 V, the absorption spectrum of  $\Delta\Delta/\Lambda\Lambda$ -[2]<sup>3+</sup> gradually changes, with an appearance of the broad band at ca. 800 nm, and the final spectrum recorded at -0.20 V is identical to that of [1]<sup>2+</sup>. The isosbestic points are maintained at 309, 429, 537, 615, and 1018 nm during the spectral change, and a Nernst plot<sup>19</sup> of  $E_{app}$  vs log([Ox]/[Red]) for



**Figure 7.** Sequential CD spectra obtained during an OTTLE spectropotentiostatic experiment on 1.0 mM  $\Delta\Delta$ -[2]<sup>3+</sup> in 0.1 M Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O at the following applied potentials: (a) +200, (b) +50, (c) 0, (d) -25, (e) -50, and (f) -200 mV (vs Ag/AgCl).

the data at 407 nm is nearly linear and yields  $E_{1/2} = 0.01$  V and  $n = 0.95$ . In addition, the increase of the potential from -0.20 to +0.20 V recovered the original absorption spectrum for  $\Delta\Delta/\Lambda\Lambda$ -[2]<sup>3+</sup>. These results clearly indicate that [1]<sup>2+</sup> and [2]<sup>3+</sup> are electrochemically interconvertible with each other, retaining the linear-type S-bridged triruthenium structure.

The CD spectral change due to the potentiostatic reduction was also recorded for the optically active  $\Delta\Delta$ -[2]<sup>3+</sup> using an OTTLE cell under the same conditions. As illustrated in Figure 7, the CD spectrum of  $\Delta\Delta$ -[2]<sup>3+</sup> gradually changes on decreasing the potential from +0.20 to -0.20 V, parallel with the absorption spectral change. Several isodichroic points are observed (270, 314, 364, 407, and 478 nm) during the CD spectral change. The overall CD pattern of the spectrum recorded at -0.20 V resembles that of the original  $\Delta\Delta$ -[2]<sup>3+</sup> spectrum, but a marked red-shift is noticed for each CD band. When the potential reverted to +0.20 V, the original CD spectrum was regained. From these observations, it is obvious that the CD spectrum recorded at -0.20 V represents the CD for the dicationic  $\Delta\Delta$ -[1]<sup>2+</sup> and that the two *fac*-(S)-[Ru(aet)<sub>3</sub>] units in the triruthenium structure are stable toward isomerization, at least in the course of the spectroelectrochemical experiments. This is in contrast to the fact that the corresponding tricobalt complex with aet ligands, [Co{Co(aet)<sub>3</sub>}]<sup>3+</sup>, loses its optical activity during the one-electron reduction process, although its S-bridged trinuclear structure is retained.<sup>20</sup>

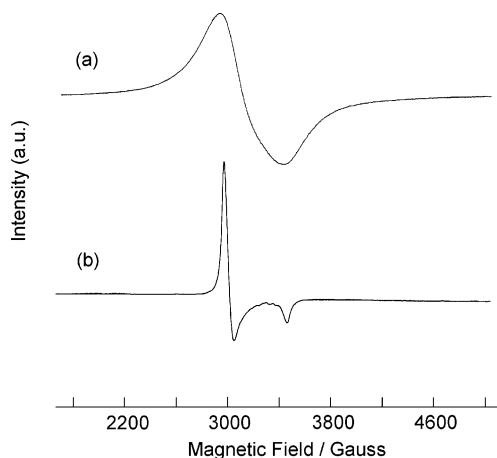
**EPR and Magnetic Studies of [Ru{Ru(aet)<sub>3</sub>}]<sub>2</sub><sup>2+/3+</sup>.** Complex [1]Cl<sub>2</sub> is EPR silent at room temperature (298 K) and at low temperature (77 K) in the solid state, and the diamagnetic nature of [1]Cl<sub>2</sub> was confirmed by its magnetic susceptibility measurement. On the other hand, the X-band EPR spectrum of  $\Delta\Lambda$ -[2](NO<sub>3</sub>)<sub>3</sub> (**[2a]**(NO<sub>3</sub>)<sub>3</sub>) at room temperature in the solid state gives a broad signal centered at  $g_{iso} = 2.140$  (Figure 8).<sup>21</sup> At 77 K,  $\Delta\Lambda$ -[2](NO<sub>3</sub>)<sub>3</sub> shows an axial spectrum with distinct  $g_{\perp}$  and  $g_{\parallel}$  signals of 2.190 and 1.892, respectively ( $g_{av} = 2.091$ ). Almost the same EPR

(18) The observed peak currents for each redox couple were very similar to those for the [Fe(CN)<sub>6</sub>]<sup>2+</sup>/[Fe(CN)<sub>6</sub>]<sup>3+</sup> couple under the same experimental conditions, supporting the one-electron nature.

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(21) The EPR spectra of **[2a]**(NO<sub>3</sub>)<sub>3</sub> and **[2b]**(NO<sub>3</sub>)<sub>3</sub> in water/ethylene glycol (1:1) at 77 K were essentially the same as those in the solid state ( $g_{\perp} = 2.189$ ,  $g_{\parallel} = 1.886$ , and  $g_{av} = 2.088$  for **[2a]**(NO<sub>3</sub>)<sub>3</sub>,  $g_{\perp} = 2.185$ ,  $g_{\parallel} = 1.895$ , and  $g_{av} = 2.088$  for **[2b]**(NO<sub>3</sub>)<sub>3</sub>). See the Supporting Information (Figure S3).



**Figure 8.** X-Band EPR spectra of **[2a]**(NO<sub>3</sub>)<sub>3</sub> (a) at 298 K and (b) at 77 K in the solid state.

spectrum was observed for  $\Delta\Delta/\Lambda\Lambda$ -**[2]**(NO<sub>3</sub>)<sub>3</sub> (**[2b]**(NO<sub>3</sub>)<sub>3</sub>) under the same conditions ( $g_{\perp} = 2.190$ ,  $g_{\parallel} = 1.894$ , and  $g_{av} = 2.091$  at 77 K), indicating that the electronic structures of  $\Delta\Lambda$ - and  $\Delta\Delta/\Lambda\Lambda$ -**[2]**<sup>3+</sup> are identical, as expected. The overall EPR spectral features and the averaged  $g$  values for  $\Delta\Lambda$ - and  $\Delta\Delta/\Lambda\Lambda$ -**[2]**<sup>3+</sup> correspond well with those reported for a related linear-type S-bridged Fe<sup>III</sup>Ru<sup>III</sup>Fe<sup>III</sup> complex, [Ru{Fe(L)}<sub>2</sub>]<sup>3+</sup> ( $g_{\perp} = 2.31$ ,  $g_{\parallel} = 1.86$ , and  $g_{av} = 2.16$  in CH<sub>3</sub>-CN solution at 10 K),<sup>22</sup> which possesses a spin ground state of  $S_t = 1/2$ . Thus,  $\Delta\Lambda$ - and  $\Delta\Delta/\Lambda\Lambda$ -**[2]**<sup>3+</sup> are also assigned to a spin ground state of  $S_t = 1/2$ . Temperature-dependent magnetic susceptibility was measured for the solid sample of  $\Delta\Lambda$ -**[2]**<sup>3+</sup> in the temperature range 2–300 K (Figure S4). Compatible with the  $S_t = 1/2$  ground state assigned from the EPR spectrum, the  $\mu_B$  values of 1.90  $\mu_B$  at 300 K and 1.71  $\mu_B$  at 50 K for  $\Delta\Lambda$ -**[2]**<sup>3+</sup> are very close to the expected value of 1.81  $\mu_B$  for  $S = 1/2$  with a  $g$  value of 2.091, although the  $\mu_B$  values decrease rapidly at low temperature, presumably due in part to the presence of an intermolecular antiferromagnetic interaction.

With respect to the charge balance, we can best describe the formal oxidation states of three Ru atoms in **[1]**<sup>2+</sup> ([Ru<sub>3</sub>(aet)<sub>6</sub>]<sup>2+</sup>) and **[2]**<sup>3+</sup> ([Ru<sub>3</sub>(aet)<sub>6</sub>]<sup>3+</sup>) as Ru<sup>III</sup>Ru<sup>II</sup>Ru<sup>III</sup> (Ru<sub>3</sub><sup>8+</sup>) and Ru<sup>III</sup>Ru<sup>III</sup>Ru<sup>III</sup> (Ru<sub>3</sub><sup>9+</sup>), respectively, and thus the observed electronic ground states for **[1]**<sup>2+</sup> ( $S_t = 0$ ) and **[2]**<sup>3+</sup> ( $S_t = 1/2$ ) are indicative of the presence of a very strong antiferromagnetic coupling ( $J < -400$  cm<sup>-1</sup>) between two Ru<sup>III</sup> ions. The electronic ground states for these complexes could be explained by a simple MO description that involves a direct overlap of magnetic orbitals. It has been shown that in the linear-type trinuclear system involving a direct metal–metal interaction, the overlap of metal  $t_{2g}$  orbitals having lobes along the 3-fold symmetry axis affords three-center molecular orbitals, a bonding  $\sigma_b$ , a nonbonding  $\sigma_n$ , and an antibonding  $\sigma_a$ .<sup>23</sup> In **[1]**<sup>2+</sup> (Ru<sub>3</sub><sup>8+</sup>), there are four electrons that occupy these molecular orbitals to give a  $(\sigma_b)^2(\sigma_n)^2$  configuration with a formal Ru–Ru bond order of 0.5, leading to a diamagnetic  $S_t = 0$  ground state. On the other

hand, **[2]**<sup>3+</sup> (Ru<sub>3</sub><sup>9+</sup>) has three electrons, giving a  $(\sigma_b)^2(\sigma_n)^1$  configuration with a formal Ru–Ru bond order of 0.5, yielding an  $S_t = 1/2$  ground state. The same MO picture has been used to rationalize the electronic structures of [Ru{Ru(L)}<sub>2</sub>]<sup>2+</sup> ( $S_t = 0$ ) and [Fe{Ru(L)}<sub>2</sub>]<sup>3+</sup> ( $S_t = 1/2$ ),<sup>9,22</sup> which are isoelectronic with **[1]**<sup>2+</sup> and **[2]**<sup>3+</sup>, respectively. In the Ru<sub>3</sub><sup>8+</sup> and Ru<sub>3</sub><sup>9+</sup> species with a formal Ru–Ru bond order of 0.5 so far reported, the Ru–Ru distances are in a range of 2.78–2.91 Å.<sup>9,23,24</sup> The Ru–Ru distances in  $\Delta\Lambda$ -**[2]**<sup>3+</sup> (2.757(7) Å) and  $\Delta\Delta/\Lambda\Lambda$ -**[2]**<sup>3+</sup> (average of 2.708(3) Å) are at the shortest of this range, and thus are compatible with the presence of a direct Ru–Ru bonding interaction with a formal bond order of 0.5, which is essential for the generation of a spin ground state of  $S_t = 1/2$ . Analogously, **[1]**<sup>2+</sup> would also contain a direct Ru–Ru bonding interaction with a formal bond order of 0.5, taking into account its  $S_t = 0$  ground state, although X-ray structural analysis for **[1]**<sup>2+</sup> has not been done.

## Conclusion

In this study, the linear-type S-bridged triruthenium species bearing aliphatic aminothiolate ligands were directly formed by treating [RuCl<sub>2</sub>(DMSO)<sub>4</sub>] or RuCl<sub>3</sub> with 2-aminoethanethiolate (Haet) or L-cysteinate (L-cys). The isolation of both the dicationic form (**[1]**<sup>2+</sup> with a  $S_t = 0$  state) and its oxidized tricationic form (**[2]**<sup>3+</sup> with a  $S_t = 1/2$  ground state) for the aet complexes under ambient conditions is worth mentioning, thanks to the electron-donating ability of the aliphatic thiolato groups that leads to the Ru<sub>3</sub><sup>8+/9+</sup> redox potential of ca. 0.0 V. The oxidized form (**[2]**<sup>3+</sup>) was successfully separated and optically resolved, which enabled us to reveal the stability of this triruthenium species in the course of the redox process, together with the difference in the absorption and CD spectral profiles of the Ru<sub>3</sub><sup>8+</sup> and Ru<sub>3</sub><sup>9+</sup> forms, by means of the spectroelectrochemical techniques.

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**Supporting Information Available:** X-ray crystallographic files, in CIF format, for the structure determinations of **[2a]**(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O and **[2b]**(NO<sub>3</sub>)<sub>3</sub>·3.5H<sub>2</sub>O, a table of the absorption and CD spectral data of **[1]**<sup>2+</sup>, **[2a]**<sup>3+</sup>, and  $\Delta\Delta$ -**[2b]**<sup>3+</sup> (Table S1), figures of the absorption spectral change with time of **[1]**<sup>2+</sup> (Figure S1), absorption spectra of the **3a**, **3b**, and **3c** eluates (Figure S2), EPR spectra of **[2a]**(NO<sub>3</sub>)<sub>3</sub> in water/ethylene glycol (Figure S3), and plot of  $\mu_{eff}$  vs  $T$  of **[2a]**(NO<sub>3</sub>)<sub>3</sub> (Figure S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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