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Linear-Type S-Bridged Trinuclear Complexes with Ru^{III} Ion and Octahedral $\text{fac}(\text{S})$ - $[\text{M}(\text{aet})_3]$ Units ($\text{M} = \text{Rh}^{\text{III}}, \text{Ir}^{\text{III}}$; $\text{aet} = 2$ -Aminoethethiolate)

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Linear-Type S-Bridged Trinuclear Complexes with Ru^{III} Ion and Octahedral $fac(S)-[M(aet)_3]$ Units ($M = Rh^{III}, Ir^{III}$; $aet = 2$ -Aminoethethiolate)

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*The reactions of $fac(S)-[M(aet)_3]$ ($M = Rh^{III}, Ir^{III}$; $aet = 2$ -aminoethanethiolate) with $RuCl_3 \cdot 3H_2O$ in water gave trinuclear complexes, $\Delta\Delta$ -, $\Delta\Delta/\Delta\Delta$ - $[Ru\{Rh(aet)_3\}_2]^{3+}$ (**1a**, **1b**) and $\Delta\Delta$ -, $\Delta\Delta/\Delta\Delta$ - $[Ru\{Ir(aet)_3\}_2]^{3+}$ (**2a**, **2b**). The crystal structure of **2a**(NO_3)₃ $\cdot 3H_2O$ revealed that the central Ru^{III} ion is coordinated by six S atoms from two $fac(S)-[Ir(aet)_3]$ units in an octahedral geometry, forming a linear-type S-bridged trinuclear structure. It was found that the UV-Visible (UV-Vis) spectral patterns of all complexes depend upon the terminal $fac(S)-[M(aet)_3]$ units. In the electro- and spectroelectrochemistry of these complexes, the Ir trinuclear complex showed a reversible $[Ru\{Ir(aet)_3\}_2]^{3+/4+}$ redox process.*

Keywords: crystal structure; ruthenium(III); spectroelectrochemistry; sulfur-bridged; trinuclear complexes

INTRODUCTION

It has been recognized that mononuclear complexes, $fac(S)-[M(aet)_3]$ ($M = Rh^{III}, Ir^{III}$), act as good sulfur-donor ligands [1]. In particular they react with many first-, second-, and third-row transition metal ions to form S-bridged trinuclear complexes $[M'\{M(aet)_3\}_2]^{n+}$ ($M' = V^{III}, Cr^{III}, Fe^{III}, Co^{II,III}, Ni^{II}, Mo^{III,IV}, Re^{III}$; $M = Rh^{III}, Ir^{III}$; $n = 2-4$) [2]. These complexes indicated unique reactivity, electrochemistry, and stereochemistry, depending highly upon the central metal ions and the metal ions in the terminal building blocks. Recently

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stereochemical and spectrochemical properties of the complexes involving heavy transition metal ions such as the $\text{Rh}^{\text{III}}(5d^6)$ ion have also been reported [3]. These complexes, as expected, were relatively stable and inactive. In this work, the Ru^{III} ion with $5d^5$ electronic configuration preceding the Rh^{III} ion has been incorporated into the S-bridged polynuclear structures to obtain complexes that are relatively less stable and more reactive than Rh^{III} complexes.

The oxidation states of Ru vary from $-II$ to $+VIII$, and the most common states are $II-IV$. For the oxidation states $II-IV$ there is great complexity because many complexes can undergo reversible reduction and oxidation reactions to give species with the same structure but a different charge. It is therefore more useful to consider the chemistry according to the ligands present [4]. It is worthwhile to incorporate the Ru^{III} ion in S-bridged polynuclear structures and to investigate the changes in stereochemical, spectrochemical, and electrochemical properties. Moreover this work also contributed to complete the series of S-bridged trinuclear complexes.

EXPERIMENTAL

Preparation

$\Delta\Delta$ - and $\Delta\Delta/\Delta\Delta$ - $[\text{Ru}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$ (**1a** and **1b**)

To a dark red solution containing 0.13 g (0.5 mmol) of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in 15 cm^3 of H_2O was added 0.33 g (1.0 mmol) of *fas*(*S*)- $[\text{Rh}(\text{aet})_3]$ [5]. The mixture was stirred at 40°C for 1 h, cooled to room temperature, and filtered. Saturated NaBr solution was added to the dark greenish-brown filtrate and kept in a refrigerator. The greenish-brown powder was isolated as *meso* isomer (**1a**). Yield: 0.042 g (7%). Anal. found: C, 12.30; H, 4.43; N, 6.92%. Calcd. for $[\text{Ru}\{\text{Rh}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_3\}_2]\text{Br}_3 \cdot 8\text{H}_2\text{O}$: C, 12.56; H, 4.56; N, 7.32%. UV-Vis absorption maxima $[\sigma_{\text{max}}/10^3\text{ cm}^{-1}(\log \epsilon/\text{mol}^{-1}\text{ dm}^3\text{ cm}^{-1})]$: 14.05 (3.58), 31.23 (1.1 sh), 44.52 (5.1 sh), 51.02 (6.9 sh). Reflectance maxima $[\sigma_{\text{max}}/10^3\text{ cm}^{-1}]$: 13.91, 29.51, 40.16, 49.14. Molar conductivity $[\Lambda_{\text{m}}/\text{S cm}^2\text{ mol}^{-1}]$: 344. The filtrate obtained by isolating the *meso* isomer was kept again in refrigerator after the addition of saturated NaClO_4 solution, where upon greenish-brown powder of *racemic* (*rac*) isomer was obtained (**1b**). Yield: 0.10 g (18%). Anal. found: C, 12.82; H, 4.23; N, 7.28%. Calcd. for $[\text{Ru}\{\text{Rh}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_3\}_2](\text{ClO}_4)_3 \cdot 5\cdot 5\text{H}_2\text{O}$: C, 12.51; H, 4.23; N, 7.28%. UV-Vis absorption maxima $[\sigma_{\text{max}}/10^3\text{ cm}^{-1}(\log \epsilon/\text{mol}^{-1}\text{ dm}^3\text{ cm}^{-1})]$: 14.14 (1.95), 30.23 (1.3 sh), 44.32 (4.1 sh), 50.81 (6.37). Reflectance maxima $[\sigma_{\text{max}}/10^3\text{ cm}^{-1}]$: 14.15, 29.72, 39.84, 49.75. Molar conductivity $[\Lambda_{\text{m}}/\text{S cm}^2\text{ mol}^{-1}]$: 404.

$\Delta\Delta$ - and $\Delta\Delta/\Delta\Delta$ -[Ru{Ir(aet)₃}₂]³⁺ (2a** and **2b**)**

To a dark red solution containing 0.13 g (0.5 mmol) of RuCl₃·3H₂O in 30 cm³ of H₂O was added 0.42 g (1.0 mmol) of *fas*(S)-[Ir(aet)₃] [**2b**,f]. The mixture was stirred at 40°C for 1 h, cooled to room temperature, and filtered. Saturated NaNO₃ solution was added to the very dark green filtrate and kept in a refrigerator. The reddish-orange crystals were isolated and were found to be a dinuclear Ir complex with a disulfide bond [6]. The filtrate was again treated with saturated NaNO₃ solution and kept in a refrigerator for a few days, whereupon dark green crystals of *meso* isomer were obtained (**2a**). Yield: 0.03 g (10%). Anal. found: C, 11.93; H, 3.86; N, 10.22%. Calcd. for [Ru{Ir(NH₂CH₂CH₂S)₃}₂](NO₃)₃·5.5H₂O: C, 11.82; H, 3.88; N, 10.33%. UV-Vis absorption maxima [$\sigma_{\max}/10^3 \text{ cm}^{-1}(\log \epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$]: 13.76 (4.10), 17.87 (2.12), 23.67 (1.27), 31.07 (5.41), 40.32 (8.97), 51.02 (6.55). Reflectance maxima [$\sigma_{\max}/10^3 \text{ cm}^{-1}$]: 13.71, 17.71, 22.91, 30.39, 39.76, 47.39. Molar conductivity [$\Lambda_{\text{m}}/\text{S cm}^2 \text{ mol}^{-1}$]: 347. The filtrate obtained by isolating the *meso* isomer was kept in a refrigerator after the addition of saturated NaClO₄ solution, whereupon green powder of *rac* isomer was obtained (**2b**). Yield: 0.12 g (19%). Anal. found: C, 10.79; H, 3.17; N, 7.73%. Calcd. for [Ru{Ir(NH₂CH₂CH₂S)₃}₂](NO₃(ClO₄)₂·3H₂O: C, 11.46; H, 3.36; N, 7.79%. UV-Vis absorption maxima [$\sigma_{\max}/10^3 \text{ cm}^{-1}(\log \epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$]: 13.73 (2.82), 18.23 (7.83), 24.13 (3.10), 31.25 (1.05), 40.16 (1.9 sh), 51.30 (1.3 sh). Reflectance maxima [$\sigma_{\max}/10^3 \text{ cm}^{-1}$]: 13.75, 17.68, 22.98, 29.76, 39.84, 47.17. Molar conductivity [$\Lambda_{\text{m}}/\text{S cm}^2 \text{ mol}^{-1}$]: 392. Dark green prismatic crystals of **2a**(NO₃)₃·3H₂O suitable for X-ray crystallography were obtained by adding a few drops of saturated NaNO₃ solution to the filtrate after the isolation of the dinuclear Ir complex with a disulfide bond and keeping it in a refrigerator for a few days.

Optical Resolution of **1b and **2b****

1b and **2b** were optically resolved by a modified fractional precipitation method [2e]. Optical resolution by column chromatography was not successful, as most of the complexes were decomposed and remained at the top of the column. Therefore, it was found that the fractional precipitation method is better than column chromatography in this case. A solution containing 0.1 mmol of Na₂[Sb₂(*R,R*-tartrato)₂]·5H₂O in 1.5 cm³ of H₂O was added to a solution containing 0.1 mmol of *rac* isomer (**1b**, **2b**) in 2.5 cm³ of H₂O and the mixture was stirred at 40°C for 1.5 h. Greenish-brown powder appeared immediately. This powder (0.05 g) was added to a solution containing 2.0 g of NaNO₃ in 5.0 cm³ of H₂O and then kept in a refrigerator. Greenish-brown powder appeared, which was isolated. The circular dichromism

(CD) spectra of this powder showed negative circular dichromism (CD) band around 357 nm (**1b**) and around 329 nm (**2b**). The $\Delta\epsilon$ values for $(-)^{\text{CD}}_{357}\text{-1b}$ and $(-)^{\text{CD}}_{329}\text{-2b}$ were calculated from the ϵ values of the respective *rac* isomers in UV-Vis absorption spectra. CD extrema [$\sigma_{\text{max}}/10^3 \text{ cm}^{-1}(\Delta\epsilon/\text{mol}^{-1}\text{dm}^3 \text{ cm}^{-1})$]: $(-)^{\text{CD}}_{357}\text{-1b}$; 15.6 (−2.13), 22.98 (+0.18), 30.58 (−1.17). $(-)^{\text{CD}}_{329}\text{-2b}$; 22.98 (+0.93), 30.49 (−2.45), 35.84 (+0.02), 39.22 (+2.55), 44.64 (+11.38).

Measurements

The elemental analysis (C, H, and N) was performed by the Chemical Analysis Center of the University of Tsukuba. The concentrations of Ru, Rh, and Ir in the complexes were determined with a NIPPON Jarell-Ash ICPA-575 spectrophotometer. The IR and far-IR spectra were recorded on a JASCO FT/IR-550 spectrometer using KBr disks in the range of 4000–400 cm^{-1} and Nujol mulls between polyethylene plates in the range of 650–100 cm^{-1} . The UV-Vis absorption spectra were recorded with a JASCO V-560 spectrophotometer and the CD spectra were recorded with a JASCO J-600 spectropolarimeter in aqueous solution. The diffuse reflectance spectra were recorded by a JASCO V-570 spectrophotometer equipped with an integrating sphere apparatus JASCO ISN-470. The molar conductance of the complexes was measured with a HORIBA conductivity meter DS-14 in aqueous solution. The magnetic measurements were performed by using a Sherwood Scientific MSB-AUTO susceptibility balance. The diamagnetism was taken into account by using Pascal's constants. Electrochemical measurements were performed by a CV-50W voltammetry analyzer, Bioanalytical systems, Inc. (BAS), using a platinum-working electrode (BAS, Pt). Spectroelectrochemical measurements were performed by a JASCO CT-10TP multichannel spectrophotometer and a CV-1B voltammetry analyzer (BAS) using a thin-layer quartz cell with a platinum mesh-working electrode [7]. In both electrochemical and spectroelectrochemical experiments, an aqueous $\text{Ag}/\text{AgCl}/\text{NaCl}$ [3 mol dm^{-3} (M)] (BAS, RE-1B) and platinum wire were used as reference and auxiliary electrodes, and the experiments were conducted by the complex concentrations of 0.001 M in 0.1 M aqueous solution of Na_2SO_4 as a supporting electrolyte. All the measurements were carried out at room temperature.

X-Ray Crystallography

The intensity data of $2\mathbf{a}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ were collected on a Rigaku AFC-7S four-circle diffractometer with graphite-monochromatized Mo K α

radiation ($\lambda = 0.71069 \text{ \AA}$) by the $\omega - 2\theta$ scan technique up to 55° at 296 K. $\text{C}_{12}\text{H}_{42}\text{Ir}_2\text{N}_9\text{O}_{12}\text{RuS}_6$ (formula weight = 1182.39) crystallized in the triclinic space group $P1$ (No. 2) with $a = 8.944$ (2), $b = 12.105$ (2), $c = 8.912$ (2) \AA , $\alpha = 110.17$ (1), $\beta = 102.44$ (2), $\gamma = 70.69$ (2)°, $V = 849.1$ (3) \AA^3 , $Z = 1$, and $D_c = 2.312 \text{ g cm}^{-3}$. Of 3914 unique reflections measured, 3496 [$>1.5\sigma(I_0)$] were used in refinement ($R = 0.038$, $R_w = 0.053$, and $\text{GOF} = 1.02$). The positions of most nonhydrogen atoms were determined by a direct method (SIR 92) [8] and some remaining atoms positions were found by successive difference Fourier techniques [9]. The structures were refined by full-matrix least-square techniques using anisotropic thermal parameters for nonhydrogen atoms. All the hydrogen atoms except those of water molecules were included in calculated positions [$\text{C}-\text{H} = \text{N}-\text{H} = 0.95 \text{ \AA}$ and $U(\text{H}) = 1.2U(\text{C}, \text{N})$]. All of the calculations were performed using the *teXsan* crystallographic software package [10]. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 236247.

RESULTS AND DISCUSSION

The reactions of *fac*(S)-[M(aet)₃] ($\text{M} = \text{Rh}^{\text{III}}$, Ir^{III}) with $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in water at 40°C in the molar ratio of 2:1 gave a mixture of *meso* (**1a**, **2a**) and *rac* (**1b**, **2b**) isomers of the trinuclear complexes. After the *meso* isomer was filtered off, the *rac* isomer was obtained from the filtrate. Column chromatography of the reaction mixture showed several bands including both the isomers. Each *meso* and *rac* isomer that was isolated by the addition of appropriate anions was checked for purity by using SP-Sephadex C-25 column (Na^+ form). Only a single band was found in each case when the isomer solution was eluted with 0.5 mol dm^{-3} (M) NaCl aqueous solution. The dinuclear Ir complex $[\text{Ir}_2(\text{aet})_4(\text{cysta})]^{2+}$ (*cysta* = cystamine) was obtained as the first product because of relatively low solubility [6]. The plasma emission analysis indicated that the complexes contain M and Ru in 2:1 ratio. The molar conductivities in water gave the values expected for 1:3 electrolytes $[\text{M}'\{\text{M}(\text{aet})_3\}_2]^{3+}$ (323–420 $\text{S cm}^2 \text{ mol}^{-1}$) [2b, 2h–j, 3]. These results indicate that **1a**, **1b**, **2a**, and **2b** are S-bridged trinuclear complexes $[\text{Ru}\{\text{M}(\text{aet})_3\}_2]^{3+}$.

X-ray structural analysis of **2a** revealed the presence of a discrete complex cation, three nitrate anions, and three water molecules. The total site occupancy factor of the nitrate anions implies that the entire complex cation **2a** is trivalent. A perspective drawing of the entire complex cation for **2a** is given in Figure 1, showing that it consists of two approximately octahedral *fac*(S)-[Ir(aet)₃] units

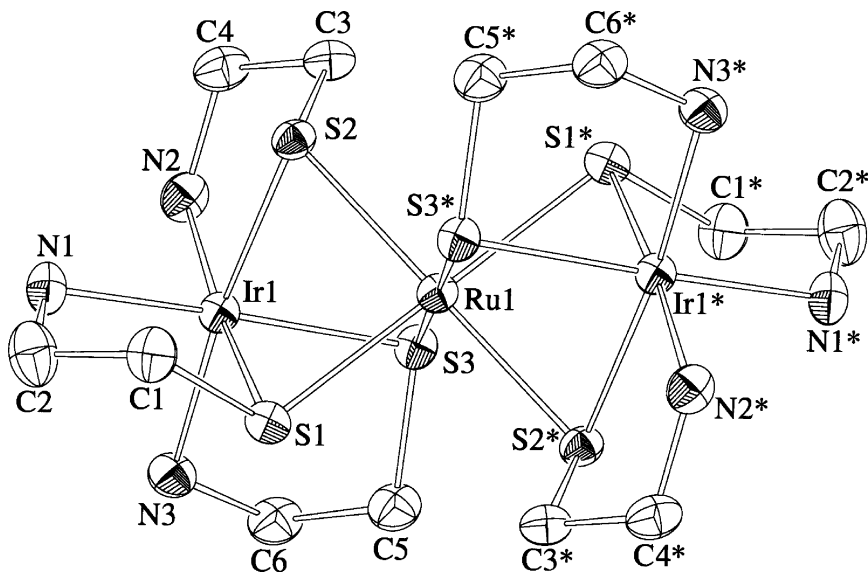


FIGURE 1 Perspective view of $\Delta\Lambda$ - $[\text{Ru}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$ (**2a**) complex cation with the atomic labeling scheme. Selected bond distances (Å) and angles (°): Ir1...Ru1, 2.8850 (3); Ir1–S1, 2.325 (2); Ir1–S2, 2.326 (2); Ir1–S3, 2.330 (2); Ir1–N1, 2.112 (6); Ir1–N2, 2.122 (7); Ir1–N3, 2.129 (6); Ru1–S1, 2.379 (2); Ru1–S2, 2.382 (2); Ru1–S3, 2.404 (2); S1–Ir1–S2, 88.61 (6); S1–Ir1–S3, 87.76 (6); S2–Ir1–S3, 87.20 (6); N1–Ir1–N2, 95.0 (3); N1–Ir1–N3, 95.1 (3); N2–Ir1–N3, 95.0 (3); S1–Ru1–S2, 86.07 (6); S1–Ru1–S3, 84.85 (6); S2–Ru1–S3, 84.28 (6); Ir1–S1–Ru1, 75.66 (5); Ir1–S2–Ru1, 75.58 (5); Ir1–S3–Ru1, 75.09 (5).

and one Ru^{III} ion. The central Ru^{III} ion is coordinated by six S atoms of the terminal *fac*(S)- $[\text{Ir}(\text{aet})_3]$ units and situated in an octahedral environment with $\text{Ru}^{\text{III}}\text{S}_6$ chromophore to form the linear-type trinuclear structure $[\text{Ru}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$. Considering the absolute configurations (Δ and Λ) of the *fac*(S)- $[\text{Ir}(\text{aet})_3]$ units, **2a** is $\Delta\Lambda$ (*meso*) isomer with an inversion center located on the Ru atom. The aet chelate rings have a distinct *gauche* form with the λ conformation for the Δ -*fac*(S)- $[\text{Ir}(\text{aet})_3]$ unit and the δ conformation for the Λ unit. Therefore, all of the bridging sulfur atoms are fixed to the *R* configuration for the Δ -*fac*(S)- $[\text{Ir}(\text{aet})_3]$ unit and the *S* configuration for the Λ unit. The Ru–S distances [average 2.388 (2) Å] in **2a** are similar to the corresponding Rh–S distances [average 2.380 (2) Å] in $\Delta\Lambda$ - $[\text{Rh}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$ [3]. The bond distances associated with the aet ligands, *fac*(S)- $[\text{Ir}(\text{aet})_3]$ [average Ir–S = 2.327 (2), Ir–N = 2.121 (7), S–C = 1.821 (9), C–C = 1.520 (1), and C–N = 1.493 (1) Å] in **2a** are

approximately the same as those [average Ir–S = 2.325 (2), Ir–N = 2.129 (9), S–C = 1.825 (10), C–C = 1.501 (2), and C–N = 1.488 (2) Å] in Rh^{III} complex. However, Ru···Ir distances [2.8850 (3) Å], S–Ir–S [average 87.85 (6)°], and Ru–S–Ir [average 75.44 (5)°] angles are significantly different from those of the Rh^{III} complex, i.e., Rh···Ir [average 3.0194 (3) Å], S–Ir–S [average 84.45 (9)°], and Ru–S–Ir [average 79.84 (7)°]. As reported earlier, according to the electronic configuration, the structure of the central metal ion could be divided into two categories, with symmetrical and an asymmetrical arrangements of electrons [3]. The values of Ru···Ir distances and S–Ir–S, and Ru–S–Ir angles imply that the present Ru^{III} complexes that have d⁵ electronic configurations can be considered as the end of the range of the category with asymmetrical arrangements of electrons. The cubic field term for the ground state in this case is ²T_{2g} and the effective magnetic moment (1.82 μ_B) of Ru^{III} ion in the present complex at 296 K also supports a low spin state (S = 1/2). The Ru···Ir distance as expected for the category was less than 2.9 Å but S–Ir–S angles are somewhat acute (<90°) and Ru–S–Ir angles are slightly obtuse (>75°). The Ru^{III}–S_{thiolato} distances [average 2.388 (2) Å] in the present complex are somewhat longer than the Ru^{III}–S_{thiolato} distances [2.3065 (1), 2.319 (2) Å] in [Ru(H₂edta)(μ-SPh)]₂ and [Cp^{*}RuCl(μ-SPh)]₂ (edta = ethylenediaminetetraacetate, Cp^{*} = pentamethylcyclopentadienyl, SPh = phenylsulfide) [11]. However, it was noted that the average Ru^{III}–S distances [2.388 (2) Å] are little shorter than the M'–S distances [average 2.439 (4), 2.421 (2), 2.458 (7) Å] in the corresponding trinuclear complexes [M' {Ir(aet)₃}]₂ⁿ⁺ (M' = V^{III}, Cr^{III}, Mo^{IV}; n = 3, 4) [2a, b, h], reflecting the smaller size of Ru^{III}S₆ chromophore as compared to those of the M'S₆ chromophores. The O atoms of the nitrate anions and the water molecules in **2a**(NO₃)₃·3H₂O seem to participate in hydrogen bonding [for example, O(2)···O(11) = 2.86 (3), O(2)···O(10) = 2.98 (2), O(6)···O(11) = 2.96 (4) Å].

The overall IR and far-IR spectral patterns of *meso* and *rac* isomers (**1a** and **1b**, **2a** and **2b**) are quite similar to each other, reflecting the structural similarity between the isomers. Moreover, this is a typical pattern found in trinuclear complexes [M' {M(aet)₃}]₂ⁿ⁺ [2a, 2h–j, 3].

The characteristic intense bands of the diffuse reflectance spectra of **1a**, **1b**, **2a**, and **2b** were observed approximately at a similar region to the bands of absorption spectra in water. This indicates that the complexes in solid state retain the trinuclear structure in solution. The absorption spectral patterns of **1a** and **1b** or **2a** and **2b** are similar to each other over the whole region, although the intensity of bands is slightly different for each of the two isomers. The Ir^{III}Ru^{III}Ir^{III}

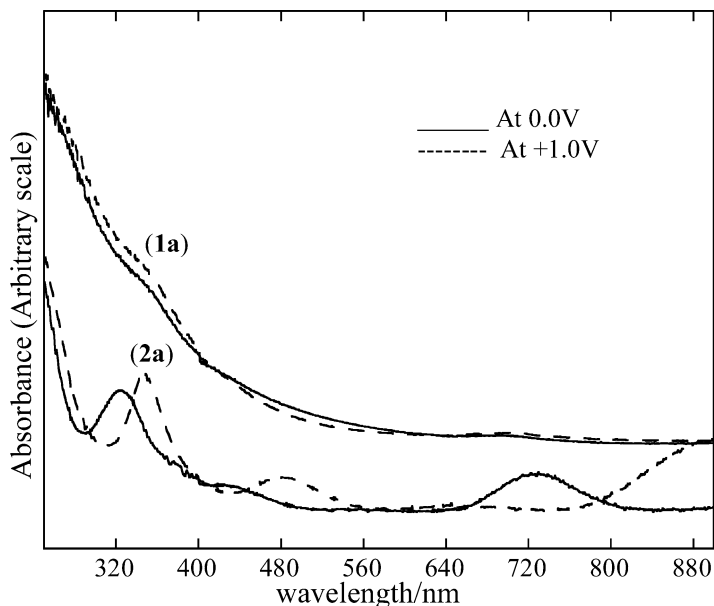


FIGURE 2 UV-Vis absorption spectra of $\Delta\Delta$ -[Ru{Rh(aet)₃}₂]³⁺ (**1a**) and $\Delta\Delta$ -[Ru{Ir(aet)₃}₂]³⁺ (**2a**) obtained during spectroelectrochemical experiments. Applied potentials *vs.* Ag/AgCl: original (—) and at +1.0V for 5 min (---).

complexes showed well-defined bands as compared to the Rh^{III}Ru^{III} Rh^{III} complexes. All complexes exhibit d-d transition and ligand to metal charge-transfer (LMCT) bands as observed in the previous complexes that have *fac*(S)-[M(aet)₃] units (M = Rh^{III}, Ir^{III}) [2,3]. (–)₃₅₇^{CD}-**1b** and (–)₃₂₉^{CD}-**2b**, which were optically resolved by the fractional precipitation method, are in agreement with those of the $\Delta\Delta$ -[M′{M(aet)₃}₂]³⁺ (M′ = Re^{III}, Rh^{III}; M = Rh^{III}, Ir^{III}) [2i,3] over the whole region, although the bands in Ir^{III}Ru^{III}Ir^{III} complex **2b** (especially in the higher energy region) are shifted to higher energy than those of Ir^{III}M′/Ir^{III} complexes. Accordingly it can be assigned that the (–)₃₅₇^{CD}-**1b** and (–)₃₂₉^{CD}-**2b** isomers are $\Delta\Delta$ -[Ru{M(aet)₃}₂]³⁺ (M = Rh^{III}, Ir^{III}). The UV-Vis absorption and CD spectra showed no significant changes with time for several hours. This shows the stability of the trinuclear structure including absolute configurations even under aerobic condition, therefore retaining the oxidation state.

Electrochemical studies showed no apparent redox waves in the case of Rh^{III}Ru^{III}Rh^{III} isomers **1a** and **1b** in the region of –1.0 to +1.0 V. In the case of Ir^{III}Ru^{III}Ir^{III} isomers **2a** and **2b**, on the other

hand, each of the voltammogram at platinum electrode displayed almost reversible redox couples at $E^{ol} = +0.24$ V (**2a**) and $+0.25$ V (**2b**) with peak–peak separation 0.05 V in a positive potential region (*vs.* Ag/AgCl). Therefore the complexes retain their trinuclear structure during the redox process. Further it was found that the redox potentials are independent on the absolute configuration of the terminal *fac*(S)-[Ir(aet)₃] units. To confirm the reversibility of the redox processes, the spectroelectrochemical experiments were carried out. Absorption spectral changes of the representative isomers **1a** and **2a** in visible region were observed (Figure 2). It was found that in the case of **1a** the absorption spectra do not change much even at higher potential and increased time duration. This coincides with Rh^{III}Re^{III}Rh^{III} and MRh^{III}M complexes (M = Rh^{III}, Ir^{III}) [2i,3]. The spectra were recorded before electrolysis, at +1.0 V and at 0 V. The Rh^{III}Ru^{III}Rh^{III} complexes are not easily oxidized whereas absorption spectra of Ir^{III}Ru^{III}Ir^{III} complexes changed on applying a potential of +1.0 V. The characteristic bands below 600 nm showed significant changes and shifted upon electrochemical oxidation. On the other hand, the band around 720 nm disappeared at +1.0 V; this can be assigned to the Ru^{III}S₆ chromophore. When the potential was back to 0 V, the original spectrum was obtained, which shows that the process is reversible. The exact origin of the difference of the redox potentials depending upon Rh^{III} and Ir^{III} is not clear yet; therefore, we can conclude that the wave of cyclic voltammogram for **2a** and **2b** is due to the one-electron [Ru{Ir(aet)₃}₂]^{3+/4+} redox process, may be with delocalization of electrons between metal ions. The present Ir^{III}Ru^{III}Ir^{III} complexes like Ir^{III}Re^{III}Ir^{III} complexes [2j] are more easily oxidized than the corresponding complexes, [M' {Ir(aet)₃}₂]³⁺ (M' = Cr^{III}, Co^{III}) [2b,f].

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