

## Chapter 2. Incorporation of Chromium(III) Ion into S-Bridged Polynuclear Structures

### 2-1. Introduction

Chromium(III) complexes, which are the early transition metal complex, have been extensively investigated in connection with their stereochemical, spectrochemical, and magnetic features.<sup>1-14)</sup> While most of the chromium(III) complexes have contained 'hard' nitrogen and oxygen donor ligands such as aminoacidate<sup>1)</sup> and polyaminocarboxylate,<sup>2)</sup> studies on the chromium(III) complexes with 'soft' sulfur donor ligands have been relatively rare. This is attributed to the fact, for example, that the bridged donor atoms in the linear-type trinuclear chromium(III) complex with 2-hydroxyethanethiolate prefers the oxygen atoms to the sulfur atoms.<sup>3)</sup>

It has been recognized that the facial-type mononuclear trischelate complexes, *fac(S)*-[M(aet)<sub>3</sub>] (M = Co<sup>III</sup>, Rh<sup>III</sup>, and Ir<sup>III</sup>), function as tridentate ligands to metal ions such as M' = Fe<sup>III</sup> (d<sup>5</sup> electronic structure), Co<sup>III</sup> (d<sup>6</sup>), Co<sup>II</sup> (d<sup>7</sup>), and Ni<sup>II</sup> (d<sup>8</sup>), which prefer to take the octahedral coordination geometry, forming the linear-type S-bridged trinuclear complexes [M' {M(aet)<sub>3</sub>}<sub>2</sub>]<sup>n+</sup>.<sup>15-23)</sup> In these trinuclear complexes, the central metal atom M' forms an M'S<sub>6</sub> chromophore, and some properties of their complexes have been studied.

The chromium(III) ion, which is a d<sup>3</sup> type metal ion, also tends to take an octahedral coordination geometry. However, the S-bridged polynuclear chromium(III) complexes with soft sulfur donor ligand, which has the Cr<sup>III</sup>S<sub>6</sub> chromophore, have been little known in spite of interests in connection with their stereochemical, spectrochemical and magnetic features. The Cr-S bond cleavage reactions in [Cr<sup>III</sup>(L-cys-N,O,S)<sub>2</sub>]<sup>-</sup> have been widely recognized,<sup>4)</sup> in terms of strong affinity for oxygen atoms and relatively weak affinity for sulfur atoms. Since the chromium(III) ion has some properties different from the late transition metal ions as described previously, it is interesting to investigate whether *fac(S)*-[M(aet)<sub>3</sub>] complexes react with the chromium(III) ion to form the S-bridged polynuclear complexes having a Cr<sup>III</sup>S<sub>6</sub>

chromophore and what kinds of polynuclear complexes are formed by these reactions. Additionally, it is also anticipated forming of a novel polynuclear structure due to different reactivity of the chromium(III) ion.

In this chapter, I describe that the linear-type S-bridged trinuclear complexes,  $[\text{Cr}^{\text{III}}\{\text{M}(\text{aet})_3\}_2]^{3+}$  ( $\text{M} = \text{Ir}^{\text{III}}$  (1);  $\text{Rh}^{\text{III}}$  (2)), were prepared in order to elucidate the fundamental property of chromium(III) ion incorporated in the polynuclear structure. The obtained complexes were separated, and optically resolved into the possible isomers. These isomers for 1 and 2 were mainly characterized by using of absorption and CD spectroscopy, and the representative crystal structures of  $\Delta A$ - $[\text{Cr}^{\text{III}}\{\text{M}(\text{aet})_3\}_2]^{3+}$  (1a and 2a) were determined by the X-ray diffraction study. The stereochemical, spectrochemical, and electrochemical behavior for the present trinuclear complexes, which incorporate the chromium(III) ion, are discussed in comparison with those of the corresponding cobalt(III) complexes.<sup>15,16)</sup> The reactivity of the chromium(III) ion in these systems are also described.

## 2-2. Experimental

### 2-2-1. Materials

2-Aminoethanethiol (Haet) was purchased from Tokyo Kasei Kogyo Co., Inc.  $\text{IrCl}_3$  and  $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$  were purchased from Rare Metallic Co., Ltd. and N. E. Chemcat Co., Ltd., respectively.  $\text{Na}_2[\text{Sb}_2(\text{d-tart})_2] \cdot 5\text{H}_2\text{O}$  was prepared by the general procedure from  $\text{Na}(\text{d-H}_3\text{tart}) \cdot \text{H}_2\text{O}$  and  $\text{Sb}_2\text{O}_3$ .<sup>19)</sup> The other reagents were obtained from Wako Pure Chemical Ind., Co., Ltd. All chemicals were of reagent grade and were used without further purification.

### 2-2-2. Preparation and Resolution of Complexes

*fac(S)*- $[\text{Ir}(\text{aet})_3]$  This complex was prepared by a modified method of Konno et al.<sup>16)</sup> To a solution containing 8.36 g (209 mmol) of NaOH in 150 cm<sup>3</sup> of water was added 15.41 g (200 mmol) of Haet. To this was added 3.00 g (10.1 mmol) of  $\text{IrCl}_3$ . The mixture was stirred under

nitrogen atmosphere with gradually raising the temperature upto 110 - 115 °C for 45 min, and further stirred at 110 - 115 °C for 3 d. After cooling to room temperature, the resulting off-white precipitate was collected by filtration and washed with a large amount of water and methanol. To the rough powder was added 100 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> HCl solution, and insoluble dark gray materials were removed by filtration. The pale brown solution was neutralized with 6 mol dm<sup>-3</sup> NaOH solution. The resulting pale yellow-green precipitate was collected by filtration and washed with a large amount of water and methanol. Yield: 2.28 g (54 %).

*fac(S)*-[Rh(aet)<sub>3</sub>] This complex was prepared by a modified method of the literatures.<sup>25)</sup> A solution containing 7.61 g (98.6 mmol) of Haet in 40 cm<sup>3</sup> of water was added to a solution containing 3.95 g (98.8 mmol) of NaOH in 40 cm<sup>3</sup> of water. To this was added 2.46 g (9.56 mmol) of RhCl<sub>3</sub>·nH<sub>2</sub>O. The mixture was stirred under nitrogen atmosphere with gradually raising the temperature upto 95 - 100 °C for 30 min, and further stirred at 95 - 100 °C for 3.5 h. After cooling to room temperature, the resulting yellow precipitate was collected by filtration and washed with a large amount of water and methanol. Yield: 2.63 g (83 %).

*fac(S)*-[Co(aet)<sub>3</sub>] and *fac(S)*-[Cr(aet)<sub>3</sub>] These complexes were prepared by the methods described in the literatures.<sup>5,20)</sup>

[Cr{Ir(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup> (1) To a suspension containing 0.30 g (0.71 mmol) of *fac(S)*-[Ir(aet)<sub>3</sub>] in 7 cm<sup>3</sup> of water was added 2.00 g (5.00 mmol) of Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. The mixture was stirred at 60 °C for 10 min, whereupon it became a dark brown solution. The solution was stood at room temperature for 1 h. The resulting black plate crystals (1a(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O) were collected by filtration and washed with a small amount of acetone. Yield: 0.15 g (37 %). 1a(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O was recrystallized from warm water by adding a few drops of a saturated NaNO<sub>3</sub> solution, and one of the crystals was used for X-ray structural analysis. Found: C, 12.46; H, 3.82; N, 10.84; Cr, 4.32; Ir, 33.70 %. Calcd for [Cr{Ir(aet)<sub>3</sub>}<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O = C<sub>12</sub>H<sub>36</sub>N<sub>6</sub>O<sub>9</sub>N<sub>9</sub>S<sub>6</sub>CrIr<sub>2</sub>·3H<sub>2</sub>O: C, 12.71; H, 3.74; N, 11.12; Cr, 4.59; Ir, 33.92 %.

After removing  $1a(NO_3)_3 \cdot 3H_2O$  by filtration, to the filtrate was added ca.  $3 \text{ cm}^3$  of a saturated NaBr solution, followed by keeping in a refrigerator for 3 h. The resulting black needle crystals ( $1bBr_3 \cdot 1.5H_2O$ ) were collected by filtration and washed with a small amount of acetone. Yield: 0.12 g (29 %).  $1bBr_3 \cdot 1.5H_2O$  was recrystallized from warm water by adding a few drops of a saturated NaBr solution. Found: C, 12.52; H, 3.50; N, 7.26; Cr, 4.06; Ir, 33.81 %. Calcd for  $[Cr\{Ir(aet)_3\}_2]Br_3 \cdot 1.5H_2O = C_{12}H_{36}N_6S_6Br_3CrIr_2 \cdot 1.5H_2O$ : C, 12.42; H, 3.39; N, 7.24; Cr, 4.48; Ir, 33.14 %.

**1a** and **1b** were also separated by an SP-Sephadex C-25 column chromatography. Three bands, black (excess  $Cr^{3+}$ ), brown (**1a**), and brown (**1b**), were eluted in this order with using a  $0.3 \text{ mol dm}^{-3}$  NaCl aqueous solution. The brown eluate **1b** was charged again on the top of the SP-Sephadex C-25 column. Two bands,  $(-)^{CD}_{600}$ -**1b** and  $(+)^{CD}_{600}$ -**1b**, were partially separated by eluting with a  $0.1 \text{ mol dm}^{-3}$   $Na_2[Sb_2(d-tart)_2] \cdot 5H_2O$  aqueous solution. The pure  $(-)^{CD}_{600}$ -**1b** and  $(+)^{CD}_{600}$ -**1b** parts, which was found by the absorption and CD measurements, were eluted and fractionated with a  $0.3 \text{ mol dm}^{-3}$  NaCl solution. **1a** was not optically resolved by the same method. The  $\Delta\varepsilon$  values of each eluate containing the  $(-)^{CD}_{600}$ -**1b** and  $(+)^{CD}_{600}$ -**1b** isomers were evaluated on the basis of the absorption spectral data of  $1bBr_3 \cdot 1.5H_2O$ .

$[Cr\{Rh(aet)_3\}_2]^{3+}$  (**2**) To a suspension containing 0.30 g (0.91 mmol) of *fac(S)*- $[Rh(aet)_3]$  in  $10 \text{ cm}^3$  of water was added 2.00 g (5.00 mmol) of  $Cr(NO_3)_3 \cdot 9H_2O$ . The mixture was stirred at  $60 \text{ }^\circ\text{C}$  for 1 h, whereupon it became a dark brown solution. The solution was stood at room temperature for 1 h. The resulting black plate crystals ( $2a(NO_3)_3 \cdot 3H_2O$ ) were collected by filtration and washed with a small amount of acetone. Yield: 0.17 g (39 %).  $2a(NO_3)_3 \cdot 3H_2O$  was recrystallized from warm water by adding one drop of a saturated  $NaNO_3$  solution, and one of the crystals was used for X-ray structural analysis. Found: C, 14.82; H, 4.66; N, 12.88; Cr, 5.36; Rh, 21.49 %. Calcd for  $[Cr\{Rh(aet)_3\}_2](NO_3)_3 \cdot 3H_2O = C_{12}H_{36}O_9N_9S_6CrRh_2 \cdot 3H_2O$ : C, 15.10; H, 4.43; N, 13.20; Cr, 5.45; Rh, 21.56 %.

After removing  $2a(NO_3)_3 \cdot 3H_2O$  by filtration, to the filtrate was added ca.

5 cm<sup>3</sup> of a saturated NaBr solution, followed by keeping in a refrigerator for 1 d. The resulting black needle crystals (**2b**Br<sub>3</sub>·1.5H<sub>2</sub>O) were collected by filtration and washed with a small amount of acetone. Yield: 0.13 g (29 %). **2b**Br<sub>3</sub>·1.5H<sub>2</sub>O was recrystallized from warm water by adding one drop of a saturated NaBr solution. Found: C, 14.75; H, 4.01; N, 8.67; Cr, 5.12; Rh, 21.07 %. Calcd for [Cr{Rh(aet)<sub>3</sub>}<sub>2</sub>]Br<sub>3</sub>·1.5H<sub>2</sub>O = C<sub>12</sub>H<sub>36</sub>N<sub>6</sub>S<sub>6</sub>Br<sub>3</sub>CrRh<sub>2</sub>·1.5H<sub>2</sub>O: C, 14.69; H, 4.01; N, 8.56; Cr, 5.30; Rh, 20.97 %.

**2a** and **2b** were also separated by a column chromatographic treatment similar to that used for **1**. Three bands, black (excess Cr<sup>3+</sup>), orange (**2a**), and brown (**2b**), were eluted in this order with using a 0.3 mol dm<sup>-3</sup> NaCl aqueous solution. The brown eluate **2b** was charged again on the top of the SP-Sephadex C-25 column. Two bands, (-)<sub>600</sub><sup>CD</sup>-**2b** and (+)<sub>600</sub><sup>CD</sup>-**2b**, were separated by eluting with a 0.1 mol dm<sup>-3</sup> Na<sub>2</sub>[Sb<sub>2</sub>(d-tart)<sub>2</sub>]·5H<sub>2</sub>O aqueous solution. After two bands were completely separated, the (-)<sub>600</sub><sup>CD</sup>-**2b** and (+)<sub>600</sub><sup>CD</sup>-**2b** isomers were eluted with a 0.3 mol dm<sup>-3</sup> NaCl solution. **2a** was not optically resolved by the same method. The Δε values of each band of the (-)<sub>600</sub><sup>CD</sup>-**2b** and (+)<sub>600</sub><sup>CD</sup>-**2b** isomers were evaluated on the basis of the absorption spectral data of **2b**Br<sub>3</sub>·1.5H<sub>2</sub>O.

### 2-2-3. Measurements

The electronic absorption spectra were recorded with JASCO UVVIDEC-505, Ubest-55, and V-560 spectrophotometers. The CD spectra were recorded with a JASCO J-600 spectropolarimeter. All the measurements were carried out in aqueous solution at room temperature. The elemental analyses (C, H, N) were performed by the Analysis Center of the University of Tsukuba. The concentrations of Cr, Ir and Rh in the complexes were determined with a NIPPON Jarrell-Ash ICPA-575 ICP spectrophotometer. The diffuse reflectance spectra were recorded with a JASCO V-570 spectrophotometer. The molar conductances of the complexes were measured with a HORIBA conductivity meter DS-14 in aqueous solution at room temperature. The magnetic measurements were performed by using a

Sherwood Scientific apparatus at 23 °C. Diamagnetic corrections were obtained employing tabulated constants.<sup>26)</sup> Electrochemical measurements were performed by CV-1B apparatus (Biochemical Systems, Inc. (BSI)) using a glassy-carbon working electrode (BSI). An aqueous Ag/AgCl/NaCl (3 mol dm<sup>-3</sup>) electrode (BSI) and platinum wire were used as reference and auxiliary electrodes, respectively. The electrochemical experiments were conducted by the complex concentrations of 1.0 mmol dm<sup>-3</sup> in a 0.1 mol dm<sup>-3</sup> aqueous solution of Na<sub>2</sub>SO<sub>4</sub> as a supporting electrolyte. Molecular Mechanics calculations (MM2 program) were performed on a Power Macintosh computer with CAChe program.<sup>27)</sup>

The stability of the trinuclear complexes was monitored by the absorption spectral change. A solution containing 0.0013 g of **1a**(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O, 0.0013 g of **1b**Br<sub>3</sub>·1.5H<sub>2</sub>O or 0.0008 g of **2a**(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O in 8 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> HCl or water was prepared. Absorption spectra of the solution were measured at 40 °C or 25 °C on a JASCO Ubest-55 spectrophotometer equipped with a TAIYO COOLNIT CL-19.

#### 2-2-4. Crystallography

Single crystals of **1a**(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O and **2a**(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O were used for data collection on an Enraf Nonius CAD4 diffractometer with a graphite-monochromatized Mo *K*α (0.71073 Å) radiation. Unit cell parameters were determined by least-squares refinements of 25 reflections. Crystallographic data and experimental parameters are summarized in Table 2-1. The intensity data were collected by the  $\omega - 2\theta$  scan technique, and the scan rate varied from 1 to 5 ° min<sup>-1</sup> (on  $\omega$ ). The intensities were corrected for Lorentz and polarization. An empirical absorption correction based on a series of  $\psi$  scans was applied. The independent reflections with  $I_0 > 1.5 \sigma(I_0)$  were used for the structure determinations. The atomic positions of the Ir, Rh, Cr, and other non-hydrogen atoms were determined by the direct method (SIR92).<sup>28)</sup> The structures were refined by a full-matrix least-squares refinement on  $F$  of the positional parameters and the anisotropic thermal parameters of the non-hydrogen atoms in **1a**(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O or **2a**(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O. The hydrogen atoms

on the aet ligands were fixed by the geometrical and thermal constrains (C-H = N-H = 0.95 Å and  $U = 1.3U(C,N)$ ). All the calculations were performed on an Indigo II computer using the teXsan crystallographic software package.<sup>29)</sup> The final atomic coordinates for non-hydrogen atoms of **1a** and **2a** are given in Tables 2-2 and 2-3, respectively. The occupancy factors (Occ) for some atoms are also listed in Tables 2-2 and 2-3.

**Table 2-1.** Crystallographic Data for  $[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  (**1a**(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O) and  $[\text{Cr}\{\text{Rh}(\text{aet})_3\}_2](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  (**2a**(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O)

	<b>1a</b>	<b>2a</b>
Formula	C <sub>12</sub> H <sub>42</sub> N <sub>9</sub> O <sub>12</sub> S <sub>6</sub> CrIr <sub>2</sub>	C <sub>12</sub> H <sub>42</sub> N <sub>9</sub> O <sub>12</sub> S <sub>6</sub> CrRh <sub>2</sub>
Formula weight	1133.31	954.68
Cryst. dimems. / mm	0.18 x 0.12 x 0.08	0.25 x 0.18 x 0.09
Cryst. system	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
<i>a</i> / Å	8.904(2)	8.9088(7)
<i>b</i> / Å	8.942(2)	8.9347(7)
<i>c</i> / Å	12.136(2)	12.149(1)
$\alpha$ / °	70.69(2)	71.133(7)
$\beta$ / °	70.20(2)	70.228(5)
$\gamma$ / °	77.56(2)	77.680(6)
<i>V</i> / Å <sup>3</sup>	852.1(4)	855.3(1)
<i>Z</i>	1	1
<i>D</i> <sub>calcd</sub> / g cm <sup>-3</sup>	2.208	1.85
$\mu(\text{Mo } K\alpha)$ / cm <sup>-1</sup>	85.54	16.91
Transm. coeff.	0.7887 - 0.9983	0.8029 - 0.9989
Temp. / K	296	296
No. of measd reflens	3021	4990
No. of reflens for used	2783 ( $I_\theta > 1.5\sigma(I_\theta)$ )	3851 ( $I_\theta > 1.5\sigma(I_\theta)$ )
No. of parameters	232	250
Final <i>R</i>	0.032	0.039
Final <i>R</i> <sub>w</sub>	0.040	0.048
GOF	1.25	1.28

Table 2-2. Final Atomic Coordinates, Equivalent Isotropic Thermal Parameters ( $B_{\text{eq}} / \text{\AA}^2$ ),<sup>a)</sup> and Occupancy Factors (Occ) for Non-Hydrogen Atoms of  $[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  ( $1a(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ )

Atom	x	y	z	$B_{\text{eq}}$	Occ
Ir(1)	0.22384(3)	0.14426(3)	0.76807(2)	2.175(6)	
Cr(1)	0.0000	0.0000	1.0000	2.22(3)	1/2
S(1)	-0.0335(2)	0.2558(2)	0.8543(2)	2.67(3)	
S(2)	0.1194(2)	-0.0957(2)	0.8193(2)	2.59(3)	
S(3)	0.2680(2)	0.0598(2)	0.9590(2)	2.64(3)	
N(1)	0.2975(8)	0.3694(7)	0.7333(6)	3.5(1)	
N(2)	0.1716(8)	0.2001(8)	0.6013(5)	3.3(1)	
N(3)	0.4598(7)	0.0310(7)	0.7059(6)	3.2(1)	
C(1)	0.032(1)	0.4142(9)	0.8838(8)	3.9(2)	
C(2)	0.158(1)	0.4897(10)	0.7700(9)	4.5(2)	
C(3)	0.007(1)	-0.0267(10)	0.7066(7)	3.7(2)	
C(4)	0.1160(10)	0.062(1)	0.5868(7)	3.7(2)	
C(5)	0.4178(9)	-0.1088(9)	0.9279(7)	3.3(2)	
C(6)	0.5382(9)	-0.043(1)	0.8055(8)	3.9(2)	
N(4)	0.2580(9)	0.6589(10)	0.4460(7)	4.5(2)	
N(5)	0.500(2)	0.513(2)	0.095(3)	7.9(6)	1/2
O(1)	0.152(1)	0.581(1)	0.4648(8)	7.8(2)	
O(2)	0.247(2)	0.800(2)	0.423(2)	9.0(5)	2/3
O(3)	0.379(1)	0.584(2)	0.478(1)	6.8(3)	2/3
O(4)	0.322(4)	0.711(4)	0.322(3)	9.4(9)	1/3
O(5)	0.305(5)	0.729(5)	0.490(3)	9(1)	1/3
O(6)	0.407(2)	0.475(2)	0.052(2)	6.8(5)	1/2
O(7)	0.634(3)	0.536(3)	0.009(3)	9.4(8)	1/2
O(8)	0.455(2)	0.529(2)	0.197(1)	5.8(4)	1/2
O(1w)	0.186(2)	0.361(2)	0.311(2)	7.8(5)	1/2
O(2w)	0.4870(8)	0.2439(8)	0.4023(6)	5.3(2)	

a)  $B_{\text{eq}}$  denotes the equivalent isotropic temperature factors,  $B_{\text{eq}} = (8\pi^2/3)\sum\sum U_{ij}a_i^*a_j^*a_i \cdot a_j$



Table 2-3. Final Atomic Coordinates, Equivalent Isotropic Thermal Parameters ( $B_{\text{eq}} / \text{\AA}^2$ ),<sup>a)</sup> and Occupancy Factors (Occ) for Non-Hydrogen Atoms of  $[\text{Cr}\{\text{Rh}(\text{aet})_3\}_2](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  ( $2\text{a}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ )

Atom	x	y	z	$B_{\text{eq}}$	Occ
Rh(1)	0.22545(3)	0.14405(3)	0.76707(2)	2.334(4)	
Cr(1)	0.0000	0.0000	1.0000	2.34(1)	1/2
S(1)	-0.03120(9)	0.25264(9)	0.85463(7)	2.81(1)	
S(2)	0.12006(9)	-0.09482(9)	0.81968(6)	2.73(1)	
S(3)	0.26726(9)	0.06086(9)	0.95762(7)	2.81(1)	
N(1)	0.2955(3)	0.3694(3)	0.7337(2)	3.59(6)	
N(2)	0.1716(3)	0.1974(3)	0.6016(2)	3.27(5)	
N(3)	0.4609(3)	0.0320(3)	0.7058(2)	3.28(5)	
C(1)	0.0354(5)	0.4115(4)	0.8842(3)	4.09(7)	
C(2)	0.1601(5)	0.4880(4)	0.7704(4)	4.68(8)	
C(3)	0.0081(4)	-0.0260(4)	0.7078(3)	3.71(6)	
C(4)	0.1184(4)	0.0580(5)	0.5881(3)	4.02(7)	
C(5)	0.4176(4)	-0.1064(4)	0.9252(3)	3.58(6)	
C(6)	0.5387(4)	-0.0420(5)	0.8048(3)	3.98(7)	
N(4)	0.7441(4)	0.3424(4)	0.5541(3)	4.85(7)	
N(5)	0.493(1)	0.518(1)	0.123(2)	14.7(4)	1/2
O(1)	0.7570(8)	0.1992(7)	0.5829(7)	8.9(2)	2/3
O(2)	0.8552(6)	0.4052(8)	0.5416(7)	7.6(1)	2/3
O(3)	0.6231(6)	0.4162(7)	0.5213(4)	6.7(1)	2/3
O(4)	0.698(2)	0.270(2)	0.511(1)	8.8(3)	1/3
O(5)	0.688(2)	0.277(2)	0.679(1)	8.6(3)	1/3
O(6)	0.835(2)	0.443(1)	0.528(1)	11.6(3)	1/3
O(7)	0.615(1)	0.538(1)	0.023(1)	11.7(3)	1/2
O(8)	0.402(1)	0.4775(10)	0.0478(7)	7.3(2)	1/2
O(9)	0.428(1)	0.545(2)	0.1889(8)	6.5(2)	1/4
O(10)	0.470(1)	0.519(2)	0.2057(8)	6.8(2)	1/4
O(1w)	0.1906(10)	0.3602(8)	0.3082(6)	7.3(2)	1/2
O(2w)	0.5100(4)	-0.2456(4)	0.5973(3)	5.33(7)	

a)  $B_{\text{eq}}$  denotes the equivalent isotropic temperature factors,  $B_{\text{eq}} = (8\pi^2/3)\sum\sum U_{ij}a_i^*a_j^*a_i a_j$

## 2-3. Results and Discussion

### 2-3-1. X-Ray Crystal Structures

X-Ray structural analysis of **1a**(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O and **2a**(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O revealed the presence of discrete trivalent complex cation, nitrate anions, and water molecules. The total number of nitrate anions implies that the entire complex cations are trivalent. The perspective drawings of the entire complex cations **1a** and **2a** are given in Figures 2-1 and 2-2, respectively. The selected bond distances and angles are listed in Table 2-4. The complex cations **1a** and **2a** consist of two approximately octahedral *fac*(S)-[M(aet)<sub>3</sub>] (M = Ir<sup>III</sup> (**1a**); Rh<sup>III</sup> (**2a**)) units and one chromium atom. These are consistent with the plasma emission spectral analysis, which gave a value of Cr : M = 1 : 2. The three thiolato sulfur atoms in each *fac*(S)-[M(aet)<sub>3</sub>] unit coordinate to the central chromium atom, forming the Cr<sup>III</sup>S<sub>6</sub> chromophore. The crystallographic inversion center locates on the chromium atom and it requires that the three metals are aligned to be exactly linear with the two identical M-Cr distances. Thus, **1a** and **2a** are complete linear-type S-bridged MCr<sup>III</sup>M trinuclear structures, [Cr<sup>III</sup>{M(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup>.

The coordination geometry of the central chromium atom in [Cr{M(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup> is trigonally distorted from a regular octahedron, which has the acute S-Cr-S bite angles (average 84.36(6) ° for **1a**; 83.67(3) ° for **2a**) for the ligating *fac*(S)-[M(aet)<sub>3</sub>] unit. For the terminal *fac*(S)-[M(aet)<sub>3</sub>] units, the S<sub>3</sub> faces are compressed to give the acute S-M-S angles (average 88.45(6) ° for **1a**; 87.63(3) ° for **2a**), while the N<sub>3</sub> faces are expanded to give the obtuse N-M-N angles (average 95.1(2) ° for **1a**; 95.5(1) ° for **2a**). These angles seem to be affected by the sizes for the central and terminal metal ions.<sup>16-19)</sup> On the other hand, it is noted that the Ir-Cr distances (2.9096(3) Å) in **1a** are shorter by 0.023 Å than the corresponding Rh-Cr ones (2.9328(2) Å) in **2a**, although the Cr-S (average 2.421(2) Å) and Ir-S (average 2.330(2) Å) distances for **1a** are almost identical with the corresponding Cr-S (average 2.4110(8) Å) and Rh-S (average 2.3232(8) Å) ones for **2a**, respectively. This corresponds with the facts that the bridging Ir-S-Cr bite angles (average

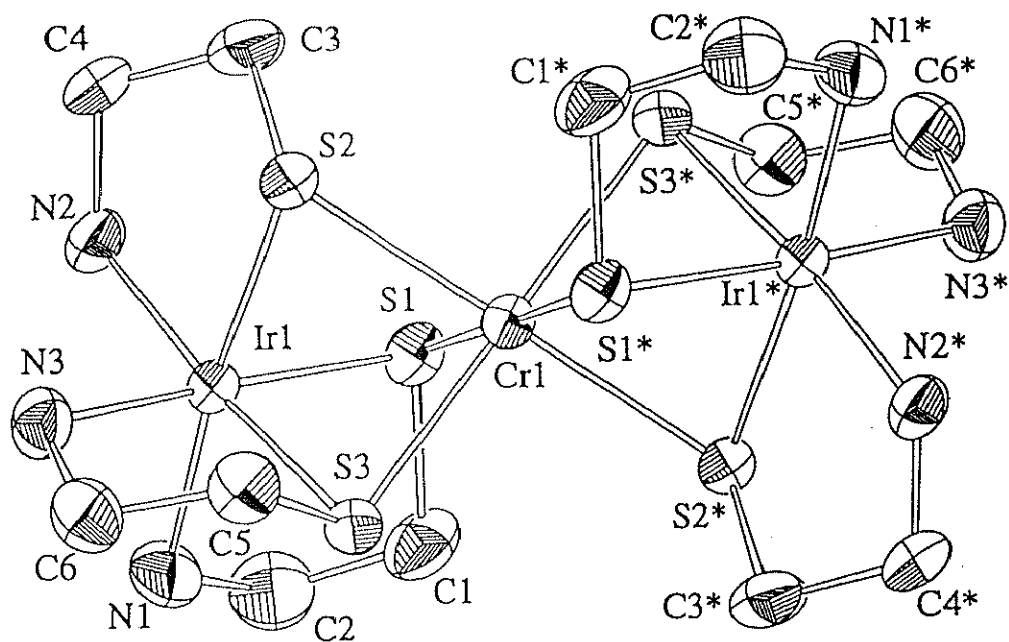


Figure 2-1. Perspective view of  $\Delta A$ -[Cr{Ir(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup> (1a) with the atomic labeling scheme.

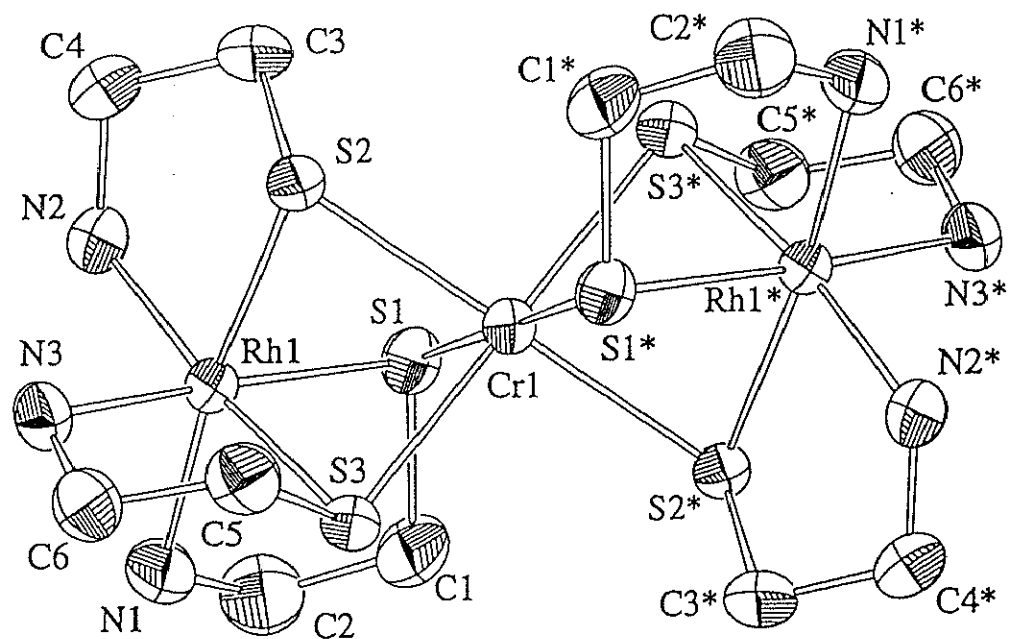


Figure 2-2. Perspective view of  $\Delta A$ -[Cr{Rh(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup> (2a) with the atomic labeling scheme.

**Table 2-4.** Selected Bond Distances (Å) and Angles (°) for  $[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$  and  $[\text{Cr}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$

$[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$ (1a)		$[\text{Cr}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$ (2a)	
Ir(1)-Cr(1)	2.9096(3)	Rh(1)-Cr(1)	2.9328(2)
Ir(1)-S(1)	2.328(2)	Rh(1)-S(1)	2.3186(8)
Ir(1)-S(2)	2.332(2)	Rh(1)-S(2)	2.3264(8)
Ir(1)-S(3)	2.330(2)	Rh(1)-S(3)	2.3245(8)
Ir(1)-N(1)	2.117(6)	Rh(1)-N(1)	2.109(3)
Ir(1)-N(2)	2.106(6)	Rh(1)-N(2)	2.106(3)
Ir(1)-N(3)	2.127(6)	Rh(1)-N(3)	2.118(3)
Cr(1)-S(1)	2.416(2)	Cr(1)-S(1)	2.4037(7)
Cr(1)-S(2)	2.438(2)	Cr(1)-S(2)	2.4268(7)
Cr(1)-S(3)	2.408(2)	Cr(1)-S(3)	2.4024(8)
S(1)-Ir(1)-S(2)	88.40(6)	S(1)-Rh(1)-S(2)	87.48(3)
S(1)-Ir(1)-S(3)	89.24(6)	S(1)-Rh(1)-S(3)	88.47(3)
S(1)-Ir(1)-N(1)	86.2(2)	S(1)-Rh(1)-N(1)	85.95(8)
S(1)-Ir(1)-N(2)	89.9(2)	S(1)-Rh(1)-N(2)	89.94(8)
S(1)-Ir(1)-N(3)	174.7(2)	S(1)-Rh(1)-N(3)	174.02(7)
S(2)-Ir(1)-S(3)	87.70(6)	S(2)-Rh(1)-S(3)	86.93(3)
S(2)-Ir(1)-N(1)	174.4(2)	S(2)-Rh(1)-N(1)	173.21(7)
S(2)-Ir(1)-N(2)	86.5(2)	S(2)-Rh(1)-N(2)	86.59(8)
S(2)-Ir(1)-N(3)	90.1(2)	S(2)-Rh(1)-N(3)	90.76(8)
S(3)-Ir(1)-N(1)	90.8(2)	S(3)-Rh(1)-N(1)	91.16(8)
S(3)-Ir(1)-N(2)	174.2(2)	S(3)-Rh(1)-N(2)	173.39(8)
S(3)-Ir(1)-N(3)	85.7(2)	S(3)-Rh(1)-N(3)	85.73(8)
N(1)-Ir(1)-N(2)	94.9(2)	N(1)-Rh(1)-N(2)	95.1(1)
N(1)-Ir(1)-N(3)	95.2(2)	N(1)-Rh(1)-N(3)	95.6(1)
N(2)-Ir(1)-N(3)	95.1(2)	N(2)-Rh(1)-N(3)	95.7(1)
S(1)-Cr(1)-S(1)*	180.0	S(1)-Cr(1)-S(1)*	180.0
S(1)-Cr(1)-S(2)	84.05(6)	S(1)-Cr(1)-S(2)	83.34(2)
S(1)-Cr(1)-S(2)*	95.95(6)	S(1)-Cr(1)-S(2)*	96.66(2)
S(1)-Cr(1)-S(3)	85.42(6)	S(1)-Cr(1)-S(3)	84.74(3)
S(1)-Cr(1)-S(3)*	94.58(6)	S(1)-Cr(1)-S(3)*	95.26(3)
S(2)-Cr(1)-S(2)*	180.0	S(2)-Cr(1)-S(2)*	180.0
S(2)-Cr(1)-S(3)	83.61(6)	S(2)-Cr(1)-S(3)	82.98(3)
S(2)-Cr(1)-S(3)*	96.39(6)	S(2)-Cr(1)-S(3)*	97.02(3)
S(3)-Cr(1)-S(3)*	180.0	S(3)-Cr(1)-S(3)*	180.0
Ir(1)-S(1)-Cr(1)	75.63(5)	Rh(1)-S(1)-Cr(1)	76.76(2)
Ir(1)-S(2)-Cr(1)	75.14(5)	Rh(1)-S(2)-Cr(1)	76.16(2)
Ir(1)-S(3)-Cr(1)	75.76(5)	Rh(1)-S(3)-Cr(1)	76.68(2)

75.51(5) °) are more acute than the corresponding Rh-S-Cr ones (average 76.53(2) °).

The overall structure of **1a** is fairly similar to that of the corresponding  $[\text{Co}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$ .<sup>16)</sup> However, the Cr-S distance (average 2.421(2) Å) is ca. 0.12 Å longer than the corresponding Co-S distance (average 2.297(2) Å). This fact is in agreement with the results that the Cr-S distances of  $[\text{Cr}(\text{C}_2\text{H}_5\text{SCS}_2)_3]$  (average 2.400(1) Å) and  $[\text{Ni}\{\text{Cr}(\text{aet})_3\}_2]^{2+}$  (average 2.370(2) Å) are ca. 0.12 Å longer than the Co-S distances of  $[\text{Co}(\text{C}_2\text{H}_5\text{SCS}_2)_3]$  (average 2.272(1) Å) and  $[\text{Ni}\{\text{Co}(\text{aet})_3\}_2]^{2+}$  (average 2.253(1) Å), respectively,<sup>5,6,18)</sup> reflecting the larger size of the  $\text{Cr}^{\text{III}}\text{S}_6$  chromophore than that of the  $\text{Co}^{\text{III}}\text{S}_6$  chromophore. Further, the Cr-S distances of  $[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$  (average 2.421(2) Å) and  $[\text{Cr}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$  (average 2.4110(8) Å) are ca. 0.04 Å longer than those of  $[\text{Ni}\{\text{Cr}(\text{aet})_3\}_2]^{2+}$  (average 2.370(2) Å),<sup>5)</sup> in which the chromium atoms locate in the terminal *fac(S)*- $[\text{Cr}(\text{aet})_3]$  units. The chromium atoms in  $[\text{Cr}\{\text{M}(\text{aet})_3\}_2]^{3+}$  has the  $\text{Cr}^{\text{III}}\text{S}_6$  chromophore and six coordinated sulfur atoms are, of course, *trans* to other sulfur atoms. While, the chromium atoms in  $[\text{Ni}\{\text{Cr}(\text{aet})_3\}_2]^{2+}$  has  $\text{Cr}^{\text{III}}\text{N}_3\text{S}_3$  chromophore and three coordinated sulfur atoms are mutually *cis* position. This means that the Cr-S distances, which occupy the *trans* position to the sulfur atoms, are longer than those to the other nitrogen or oxygen atoms. A similar trend was also observed: the Cr-S distances that occupy the *trans* position to the sulfur atoms are 2.400(1) Å in  $[\text{Cr}(\text{C}_2\text{H}_5\text{SCS}_2)_3]$ ,<sup>6)</sup> 2.416(1) Å in *trans(S)*- $[\text{Cr}(\text{L-cys-N,O,S})_3]$ ,<sup>7)</sup> 2.389(5) Å in *trans(S)*- $[\text{Cr}(\text{aet})_2(\text{en})]^+$ ,<sup>8)</sup> and 2.396(7) Å in  $[\text{Cr}(\text{C}_2\text{O}_2\text{S}_2)_3(\text{NiL})_3]^{3+}$  (L = racemi-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane).<sup>9)</sup> On the other hand, the Cr-S distances occupied the *trans* position to the nitrogen or oxygen atoms are 2.337(2) Å in  $[\text{Cr}(\text{SCH}_2\text{CH}_2\text{COO})(\text{en})_2]^+$ <sup>10)</sup> and 2.332(2) Å in  $[\text{Cr}(\text{L-his})(\text{D-pen})]$  (L-his = L-histidinate, D-pen = D-penicillamate),<sup>11)</sup> and 2.364(5) Å in  $[\text{Cr}\{\text{Cr}(\text{SCH}_2\text{CH}_2\text{O})_3\}_2]^{3+}$ .<sup>3)</sup> Accordingly, the Cr-S bond lengthening of  $[\text{Cr}\{\text{M}(\text{aet})_3\}_2]^{3+}$  compared with  $[\text{Ni}\{\text{Cr}(\text{aet})_3\}_2]^{2+}$  would be due to the sulfur *trans* influence.

Considering the absolute configurations ( $\Delta$  and  $\Lambda$ ) due to the skew pair of the chelate rings of the two terminal *fac(S)*- $[\text{M}(\text{aet})_3]$  (M =  $\text{Ir}^{\text{III}}$  and  $\text{Rh}^{\text{III}}$ ) units, three isomers ( $\Delta\Delta$ ,  $\Lambda\Lambda$ , and  $\Delta\Lambda$ ) are possible for the present trinuclear

complexes,  $[\text{Cr}\{\text{M}(\text{aet})_3\}_2]^{3+}$ . The  $\Delta\Delta$  and  $\Lambda\Lambda$  isomers are a pair of enantiomers, which combine to form a racemic compound. The  $\Delta\Lambda$  isomer is a meso compound. The space group  $P\bar{1}$  and  $Z = 1$  clearly indicates that **1a** and **2a** are the meso isomer containing the  $\Delta$ - and  $\Lambda$ -*fac(S)*- $[\text{M}(\text{aet})_3]$  units, as shown in Figures 2-1 and 2-2. This is consistent with the fact that **1a** and **2a** were not optically resolved. Three aet chelate rings have a distinct *gauche* form with the  $\lambda$  conformation for the  $\Delta$ -*fac(S)*- $[\text{M}(\text{aet})_3]$  unit and the  $\delta$  conformation for the  $\Lambda$  unit. Therefore, all the bridging sulfur atoms are fixed to the *R* configuration for the  $\Delta$ -*fac(S)*- $[\text{M}(\text{aet})_3]$  unit and the *S* configuration for the  $\Lambda$  unit. In addition, the stereochemical behavior is also consistent with that observed in the corresponding trinuclear complexes, which were reported previously.<sup>16-19)</sup>

### 2-3-2. Characterization

The electronic absorption and CD spectra of **1a**,  $(-)^{\text{CD}}_{600}$ -**1b**, **2a** and  $(-)^{\text{CD}}_{600}$ -**2b** are shown in Figures 2-3 and 2-4, together with corresponding trinuclear complexes,  $\Delta\Delta$ - $[\text{Co}\{\text{M}(\text{aet})_3\}_2]^{3+}$ . The diffuse reflectance data as well as absorption and CD spectral data are summarized in Table 2-5. The absorption spectrum of **1b** is quite similar to that of  $\Delta\Lambda$ - $[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$  (**1a**), whose structure was determined by X-ray crystal analysis, over the whole region (Figure 2-3). Similarly, the absorption spectrum of **2b** agrees well with that of  $\Delta\Lambda$ - $[\text{Cr}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$  (**2a**), although the intensity of the bands at 16 and 25  $\times 10^3 \text{ cm}^{-1}$  for **2b** differs slightly from those for **2a** (Figure 2-4). The elemental analytical data for **1b** and **2b** as well as those for **1a** and **2a** are in good agreement with the proposed formula,  $[\text{Cr}\{\text{M}(\text{aet})_3\}_2]^{3+}$  ( $\text{M} = \text{Ir}^{\text{III}}$  (**1**) and  $\text{Rh}^{\text{III}}$  (**2**)). The plasma emission spectral analyses for **1b** and **2b** also indicate that the ratio of Cr : M is 1 : 2. Furthermore, **1b** and **2b** were optically resolved into the  $(-)^{\text{CD}}_{600}$  and  $(+)^{\text{CD}}_{600}$  isomers, which exhibit the enantiomeric CD spectra to each other, by using the column chromatographic method, while **1a** and **2a** were not optically resolved. Accordingly, these facts indicate that **1b** and **2b** are also the geometrical isomers of the trinuclear complexes, that is, **1b** or **2b** is the racemate, *rac*- ( $\Delta\Delta$ - and  $\Lambda\Lambda$ -)

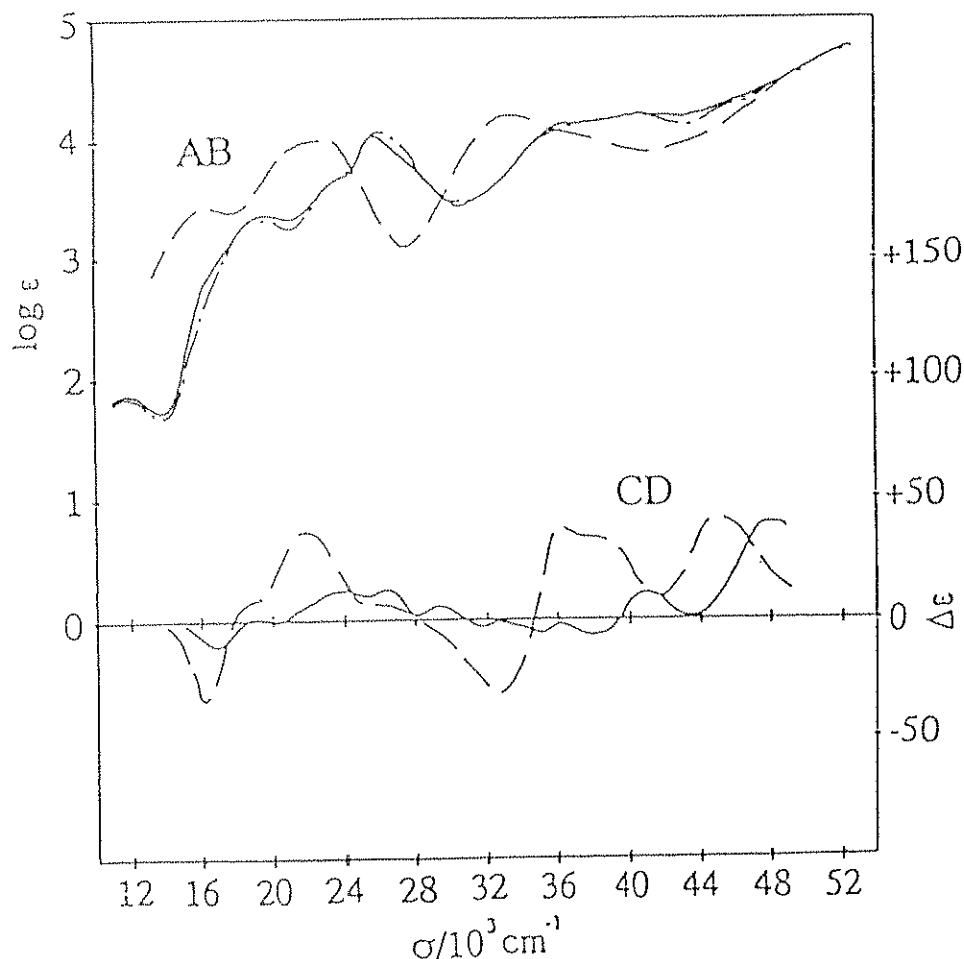


Figure 2-3. Electronic absorption and CD spectra of  $[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$  ( $\Delta A$ -1a;  $-\cdot-$ ) and  $(\overset{\text{CD}}{-})_{600}\Delta A$ -1b;  $-\text{---}$ ), and  $\Delta A$ - $[\text{Co}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$  ( $-\text{---}$ ).

$[\text{Cr}\{\text{M}(\text{aet})_3\}_2]^{3+}$ . The characteristic intense bands of the diffuse reflectance spectra of **1a** and **2a** are observed at the similar region to the bands of absorption spectra in water (Table 2-5). It indicates that the structures of **1a** and **2a** in solid state retain the trinuclear structure in solution. This is compatible with the observed molar conductivity in water of  $350 \text{ S cm}^2 \text{ mol}^{-1}$  for **1a** and  $352 \text{ S cm}^2 \text{ mol}^{-1}$  for **2a**, which are in agreement with those of the 1 : 3 electrolytes,  $\Delta A$ - $[\text{Co}\{\text{Co}(\text{aet})_3\}_2]^{3+}$  ( $373 \text{ S cm}^2 \text{ mol}^{-1}$ ).<sup>30)</sup> The results are also supported by the facts that the molar conductivity in water and the magnetic moments at 296 K of **1b** and **2b** in solid state are in good agreement with those of **1a** and **2a**, respectively (Table 2-6).

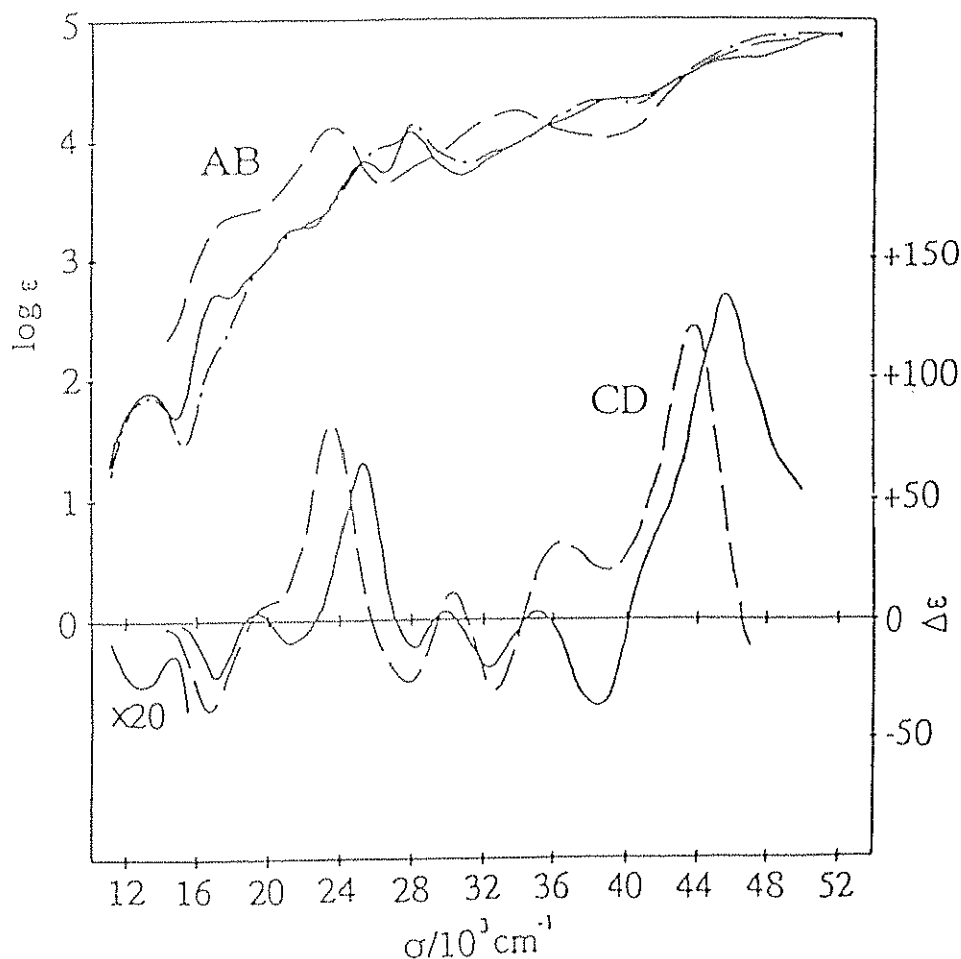


Figure 2-4. Electronic absorption and CD spectra of  $\Delta A$ -[Cr{Rh(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup> ( $\Delta A$ -2a; — · —) and ((-)<sub>600</sub><sup>CD</sup>- $\Delta A$ -2b; ———), and  $\Delta A$ -[Co{Rh(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup> (-----).

The absorption spectra of (-)<sub>600</sub><sup>CD</sup>-[Cr{M(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup> (M = Ir<sup>III</sup> (1b) or Rh<sup>III</sup> (2b)) and  $\Delta A$ -[Co{M(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup> resemble each other (Figures 2-3 and 2-4), although the absorption bands of (-)<sub>600</sub><sup>CD</sup>-1b or (-)<sub>600</sub><sup>CD</sup>-2b commonly shift to higher energy than those of  $\Delta A$ -[Co{M(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup>.<sup>15,16)</sup> The most intense band in the UV region for [Cr{Ir(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup> (1: > ca. 40 × 10<sup>3</sup> cm<sup>-1</sup>) or [Cr{Rh(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup> (2: > ca. 38 × 10<sup>3</sup> cm<sup>-1</sup>) corresponds well to the sulfur-to-iridium or the sulfur-to-rhodium charge transfer band as observed in previous complexes, respectively, which involve *fac*(S)-[M(aet)<sub>3</sub>] units.<sup>15-17,31)</sup> The characteristic intense bands in the visible and near-ultraviolet regions of the corresponding complexes [Co{M(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup> are assigned as arising from the central Co<sup>III</sup>S<sub>6</sub> chromophore, taking account of the absorption spectral



Table 2-5. Electronic Absorption, Diffuse Reflectance, and CD Spectral Data of  $[\text{Cr}\{\text{M}(\text{aet})_3\}_2]^{3+}$

Complexes	Absorption maxima $\sigma / 10^3 \text{ cm}^{-1}$ ( $\log \epsilon / \text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ )	Reflectance maxima $\sigma / 10^3 \text{ cm}^{-1}$	CD extrema $\sigma / 10^3 \text{ cm}^{-1}$ ( $\Delta\epsilon / \text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ )
$\Delta\Delta$ - $[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$ (1a)	11.78 (1.75)	19.2	
	16.3 (2.6sh <sup>a)</sup> )	23.9	
	19.61 (3.31)	25.7	
	23.9 (3.7sh)		
	25.97 (4.02)		
	27.8 (3.8sh)		
	37.5 (4.1sh)		
$(-)^{\text{CD}}_{600}$ - $\Delta\Delta$ - $[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$ $((-)^{\text{CD}}_{600}$ - $\Delta\Delta$ -1b)	40.98 (4.13)		
	50.00 (4.71)		
	11.99 (1.84)		16.81 (-11.2)
	16.6 (2.8sh)		18.90 (+0.2)
	19.80 (3.36)		19.84 (-0.3)
	23.7 (3.6sh)		23.75 (+11.5)
	25.84 (4.00)		26.60 (+8.9)
	28.6 (3.8sh)		29.24 (+5.3)
	36.5 (4.1sh)		31.55 (-1.6)
	41.32 (4.23)		34.84 (-4.1)
$\Delta\Delta$ - $[\text{Co}\{\text{Ir}(\text{aet})_3\}_2]^{3+ \text{ b)}$	50.00 (4.86)		38.02 (-8.7)
			40.82 (+8.0)
			48.54 (+49.8)
	16.29 (3.41)		16.18 (-33.65)
	21.1 (3.9sh)		19.0 (+8.4sh)
	22.88 (3.98)		21.88 (+36.95)
	33.33 (4.17)		25.97 (+7.01)
$\Delta\Delta$ - $[\text{Cr}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$ (2a)	51.81 (4.72)		32.57 (-31.32)
			36.23 (+37.46)
			39.2 (+28.2sh)
			45.25 (+40.69)
	13.09 (1.89)	18.9sh	
	17.5 (2.3sh)	21.5sh	
	22.0 (3.3sh)	26.0	
26.53 (3.93)	27.6		
28.01 (4.12)			
38.91 (4.32)			
49.75 (4.85)			

Table 2-5. Continued.

Complexes	Absorption maxima $\sigma / 10^3 \text{ cm}^{-1}$ ( $\log \epsilon / \text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ )	Reflectance maxima $\sigma / 10^3 \text{ cm}^{-1}$	CD extrema $\sigma / 10^3 \text{ cm}^{-1}$ ( $\Delta\epsilon / \text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ )
$(-)^{CD}_{600}\text{-}\Delta\Delta\text{-}[\text{Cr}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$	13.19 (1.90)		13.07 (-1.4)
	17.21 (2.71)		17.09 (-24.1)
$((-)^{CD}_{600}\text{-}\Delta\Delta\text{-}2\text{b})$	21.9 (3.3sh)		19.38 (+3.5)
	25.38 (3.81)		21.23 (-9.3)
	28.01 (4.07)		25.25 (+65.6)
	39.53 (4.34)		28.17 (-11.7)
	46.5 (4.7sh)		29.85 (+3.7)
			32.26 (-20.0)
			35.09 (+3.1)
			38.46 (-36.7)
			45.66 (+112.5)
$\Delta\Delta\text{-}[\text{Co}\{\text{Rh}(\text{aet})_3\}_2]^{3+ \text{ c)}$	18.7 (3.4sh)		16.86 (-37.3)
	23.56 (4.11)		20.3 (+5.1sh)
	28.7 (3.9sh)		23.69 (+81.4)
	33.61 (4.26)		27.93 (-27.0)
	49.38 (4.80)		30.31 (+10.9)
			32.68 (-30.0)
			36.63 (+32.1)
			43.86 (+117.4)

a) sh denotes a shoulder. b) Ref. 16. c) Ref. 15.

Table 2-6. Molar Conductivity ( $\Lambda_m / \text{S cm}^2 \text{ mol}^{-1}$ )<sup>a)</sup> and Magnetic Moments ( $\mu_{\text{eff}} / \text{B.M.}$ )<sup>b)</sup> of  $[\text{Cr}\{\text{M}(\text{aet})_3\}_2]^{3+}$ 

	$\Lambda_m$	$\mu_{\text{eff}}$
$\Delta\Delta\text{-}[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$ (1a)	355	3.77
$\Delta\Delta\Delta\Delta\text{-}[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$ (1b)	369	3.76
$\Delta\Delta\text{-}[\text{Cr}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$ (2a)	352	3.95
$\Delta\Delta\Delta\Delta\text{-}[\text{Cr}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$ (2b)	377	3.87

a) in water. b) at 296 K.

behavior of the *fac(S)*-[M(aet)<sub>3</sub>] units in the corresponding region.<sup>15,16)</sup> Therefore, it is assumed that the characteristic intense bands in the visible and near-ultraviolet regions ( $12 - 30 \times 10^3 \text{ cm}^{-1}$ ) of  $[\text{Cr}\{\text{M}(\text{aet})_3\}_2]^{3+}$  depend on the  $\text{Cr}^{\text{III}}\text{S}_6$  chromophore, as in the case of the  $\text{Co}^{\text{III}}\text{S}_6$  chromophore. Since the terminal  $\text{IrN}_3\text{S}_3$  chromophores show less absorption band in the visible region than the terminal  $\text{RhN}_3\text{S}_3$  ones,<sup>16)</sup> the similarity of spectral behavior between the  $\text{Cr}^{\text{III}}\text{S}_6$  chromophore and the  $\text{Co}^{\text{III}}\text{S}_6$  one is displayed more clearly in the iridium complexes. In this region of  $12 - 30 \times 10^3 \text{ cm}^{-1}$ , it is noticed that the absorption bands for  $[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$  are located at lower energy than those for  $[\text{Cr}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$ . A similar blue-shift was also observed for  $[\text{Co}\{\text{M}(\text{aet})_3\}_2]^{3+}$ .<sup>15,16)</sup> Accordingly, these facts seem to reflect that the thiolato sulfur atoms in *fac(S)*-[Ir(aet)<sub>3</sub>] possess an electron donating ability weaker than those in *fac(S)*-[Rh(aet)<sub>3</sub>]. This is supported by the X-ray crystal analysis that the Cr-S bond distances in  $[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$  are longer than those of  $[\text{Cr}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$ .

The CD spectral behavior of  $(-)\text{}_{600}^{\text{CD}}\text{-2b}$  is in agreement with that of  $\Delta\Delta$ -[Co{Rh(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup> over the whole region, considering the absorption spectral shift. Accordingly, it seems to be assigned that  $(-)\text{}_{600}^{\text{CD}}\text{-2b}$  and  $(+)\text{}_{600}^{\text{CD}}\text{-2b}$  are  $\Delta\Delta$ - and  $\Lambda\Lambda$ -[Cr{Ir(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup>, respectively. It will be also assigned similarly that  $(-)\text{}_{600}^{\text{CD}}\text{-1b}$  and  $(+)\text{}_{600}^{\text{CD}}\text{-1b}$  are  $\Delta\Delta$ - and  $\Lambda\Lambda$ -[Cr{Ir(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup>, respectively, by comparing with corresponding  $\Delta\Delta$ -[Co{Ir(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup> complex.

### 2-3-3. Formation and Reactivity

In the synthetic investigation of the iridium complexes, 'black' IrCl<sub>3</sub> has been used as a starting material.<sup>32)</sup> In this work, I used 'green' IrCl<sub>3</sub> because of relative reasonable price. The 'green' IrCl<sub>3</sub> produced a rough *fac(S)*-[Ir(aet)<sub>3</sub>]. Since dark gray contaminants were insoluble in acid, the rough off-white powder could be purified by using acid and base.

The reaction of *fac(S)*-[M(aet)<sub>3</sub>] (M = Ir<sup>III</sup> and Rh<sup>III</sup>) with a large excess of chromium(III) nitrate in water at 60 °C gave *meso*- and *rac*-[Cr{M(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup>. The trinuclear MCr<sup>III</sup>M complexes, in which the chromium(III) ion is bound by the six S donor atoms and incorporated in the

S-bridged polynuclear structure, were hardly formed by the reaction using an equivalent amount of chromium(III) nitrate or by the reaction at room temperature. These are in contrast to the fact that the corresponding complexes,  $[\text{Co}\{\text{M}(\text{aet})_3\}_2]^{3+}$ , were formed by the reaction of *fac(S)*- $[\text{M}(\text{aet})_3]$  with an equivalent amount of  $[\text{Co}^{\text{III}}\text{Cl}(\text{NH}_3)_5]^{2+}$  or cobalt(II) ion at room temperature.<sup>15,16)</sup> In chromium(III) complexes with L-cysteinate (L-cys),  $[\text{Cr}(\text{L-cys-}N,O,S)_2]^{3+}$ <sup>4,7,12)</sup> and  $[\text{Cr}(\text{L-Hcys-}N,O)_3]^{13)}$  have been obtained but  $[\text{Cr}(\text{L-Hcys-}N,S)_3]$  has not. These are significantly different from those for the iridium(III), rhodium(III) and cobalt(III) complexes with L-cysteinate, in which  $[\text{M}(\text{L-Hcys-}N,S)_3]$  is easily formed.<sup>15,16,33)</sup> Moreover, the central chromium(III) ion in the trinuclear complex  $[\text{Cr}\{\text{Cr}(\text{SCH}_2\text{CH}_2\text{O})_3\}_2]^{3+}$ , in which the terminal units have both of the facial(O) or facial(S) coordination sites, has been bridged by the alkoxide oxygen atoms.<sup>3)</sup> Accordingly, it seems to be indicated that the difficulty concerning the formation of the  $\text{MCr}^{\text{III}}\text{M}$  trinuclear complexes should be due to the weak affinity of the chromium(III) ion toward the sulfur atoms, since the chromium(III) complexes prefer an O coordination mode to an S one. Some studies on the polynuclear chromium(III) complexes containing the coordinated sulfur atom have been reported.<sup>3,5,9)</sup> However, this is the first case where chromium(III) ion binds to the coordinated sulfur atoms of the thiolato complexes, such as *fac(S)*- $[\text{M}(\text{aet})_3]$ , and is incorporated in the S-bridged polynuclear structure.

In the present reaction, both *meso*- and *rac*- $[\text{Cr}\{\text{M}(\text{aet})_3\}_2]^{3+}$  were obtained. The formation ratio of isomers was ca. 1 : 1 from column chromatography. The calculated structural energies (MM2 program) for *meso*- and *rac*- $[\text{Cr}\{\text{M}(\text{aet})_3\}_2]^{3+}$  were summarized in Table 2-7. This little

Table 2-7. Structural Energy Calculations ( $E / \text{kJ mol}^{-1}$ ) of  $[\text{Cr}\{\text{M}(\text{aet})_3\}_2]^{3+}$

	Ir complexes	Rh complexes
$\Delta\Delta$ -isomer	-425.0	-442.8
$\Delta\Delta\Delta$ -isomer	-426.4	-444.2

difference of structural stability between *meso*- and *rac*-isomers supports the 1 : 1 formation ratio. The geometrical isomerization in solution, which is due to intermolecular exchange, has been recognized in trinuclear MM'M (M' = Co<sup>III</sup> and Ni<sup>II</sup>) complexes.<sup>15-17)</sup> In the present MCr<sup>III</sup>M complexes, the geometrical isomerization is not observed by absorption spectral change and column chromatography, and only decomposition was observed (*vide infra*). When each isomer of the MCr<sup>III</sup>M trinuclear complexes under an excess amount of the chromium(III) ion was stirred for a few hours in warm water (70 °C), both the *meso* and *racemic* isomers were found by a column chromatographic method. It suggests that the treating with an excess chromium(III) ion is required for these isomerization reactions.

The reactions of chromium(III) ion with *fac(S)*-[M(aet)<sub>3</sub>] also cause side reactions due to the difficulty of the formation of the Cr-S bonds. Moreover, the reactivity is highly dependent on the ratio of reactants and the reaction temperature. It is noticed that this difference of reactivity between the iridium complex and the rhodium complex was observed well. In the case of the synthesis of the Rh<sup>III</sup>Cr<sup>III</sup>Rh<sup>III</sup> complexes, a spread band was observed when the reaction mixture was separated by the cation exchange column chromatography. The ratio of the spread band increased and the trinuclear complexes were not obtained, when the reaction temperature was too high (ca. > 70 °C). On the other hand, in the case of the synthesis of the Ir<sup>III</sup>Cr<sup>III</sup>Ir<sup>III</sup> complexes, a new orange band (3) appeared. In the cation exchange column chromatography, the adsorbed band of the complex 3 was eluted with a 0.15 mol dm<sup>-3</sup> NaCl aqueous solution, while those of Cr<sup>3+</sup>, 1a, and 1b were not eluted by this eluent. These suggest that 3 is mono- or divalent complex cation. However, the plasma emission spectral analyses indicated that the complex 3 contains only iridium atom as a metal. Moreover, treatment of 3 with base in water gave starting mononuclear complex, *fac(S)*-[Ir(aet)<sub>3</sub>]. It is likely to occur oxidation of the mononuclear complexes by acid as a side reaction in this system. Further, although the Cr-S bond cleavage as well as oxidation is apt to occur in acid condition, I had to handle the reaction under acidic conditions because the neutralization caused the precipitation of chromium(III) hydroxide. This oxidized complex 3 is assigned to the

dinuclear complex with a bridging disulfide bond,  $[\text{Ir}_2(\text{aet})_4(\text{cysta})]^{2+}$ , by its absorption spectral behavior (chapter 3). Since the oxidation proceeds steadily with time and the  $[\text{Ir}_2(\text{aet})_4(\text{cysta})]^{2+}$  complex crystallizes earlier than  $\text{Ir}^{\text{III}}\text{Cr}^{\text{III}}\text{Ir}^{\text{III}}$  complexes in the method of fractional precipitation, isolation of both of *meso* and *rac*  $\text{Ir}^{\text{III}}\text{Cr}^{\text{III}}\text{Ir}^{\text{III}}$  complexes is not easy. From such properties of chromium(III) ion preventing from forming the trinuclear complexes by plural factors, speedy and careful procedure is required especially in the synthesis of the  $\text{Ir}^{\text{III}}\text{Cr}^{\text{III}}\text{Ir}^{\text{III}}$  complexes. For the corresponding  $\text{Rh}^{\text{III}}\text{Cr}^{\text{III}}\text{Rh}^{\text{III}}$  complexes, in which *fac(S)*- $[\text{Rh}(\text{aet})_3]$  is oxidized more hardly than *fac(S)*- $[\text{Ir}(\text{aet})_3]$ , a similar reaction would not form a dinuclear complex with a bridging disulfide bond. Probably, the Rh-S bonds are partially snapped. It is considered that these facts are due to the difference between the redox property of the thiolato sulfur atoms of *fac(S)*- $[\text{Ir}(\text{aet})_3]$  and that of *fac(S)*- $[\text{Rh}(\text{aet})_3]$ .

In *meso*- and *rac*- $[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$ , they are fairly stable in water at room temperature, and their absorption spectra change only a little with time. However, the more the temperature or acidity increases, the greater does the degree of the changes with time become. The spectral changes in solution for the present trinuclear complexes were investigated. The representative absorption spectral change of *meso*- $[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$  (**1a**) is shown in Figure 2-5. The spectral changes involve mainly decrease of intense band, which are assigned as arising from the central  $\text{Cr}^{\text{III}}\text{S}_6$  chromophore. The absorption spectrum became almost constant within 24 h. This absorption curve, which has a peak at ca. 345 nm, is similar to that of **3**. Plots of relative absorbance of the intense band (**1a**, 385.0 nm; **1b**, 388.0 nm; and **2a**, 357.6 nm) versus time are given in Figure 2-6. It is shown that the rate of decrease of intense bands depends on temperature and acidity. Little difference between *meso* and *rac* isomers is also observed. On the other hand, it is indicated that the  $\text{Rh}^{\text{III}}\text{Cr}^{\text{III}}\text{Rh}^{\text{III}}$  complexes are more stable in solution than the  $\text{Ir}^{\text{III}}\text{Cr}^{\text{III}}\text{Ir}^{\text{III}}$  complexes, although they cannot be compare with each other simply because of difference of their spectral pattern. These decreases of intense bands can be regarded as the decomposition reaction, which may be due to cleavage of the Cr-S bonds.

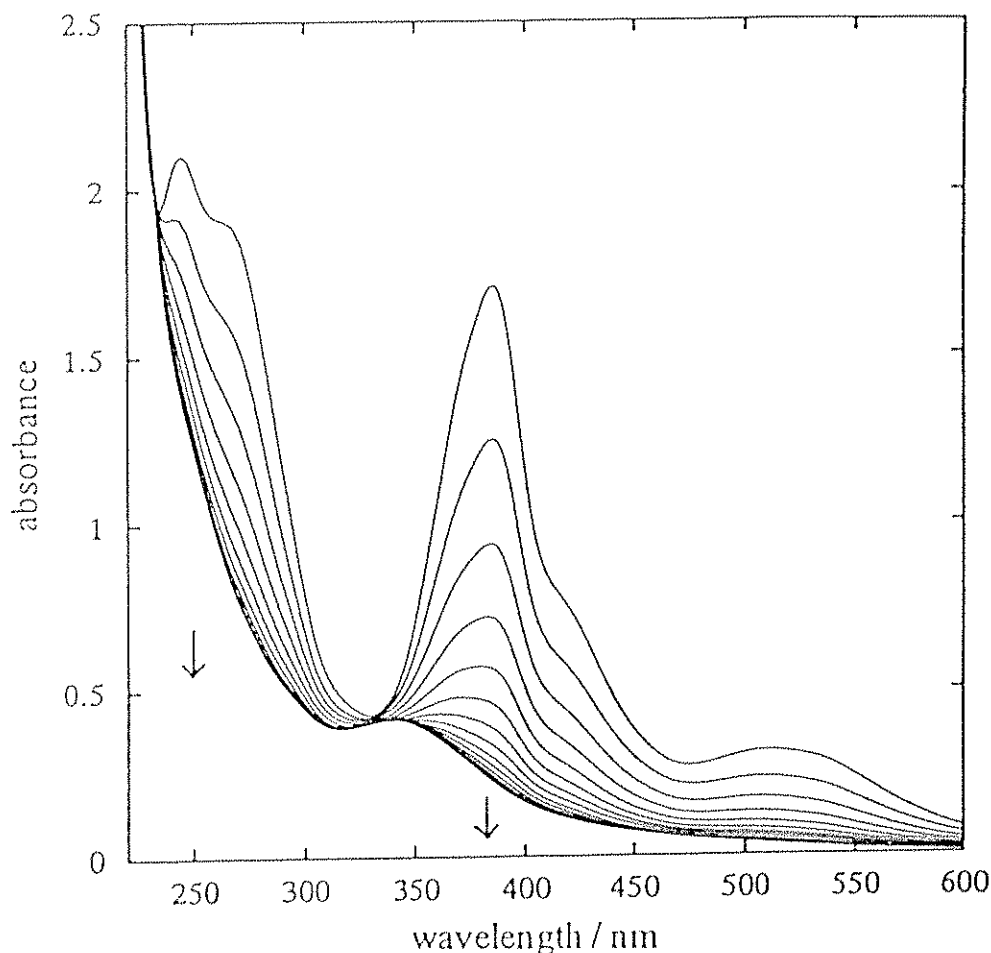


Figure 2-5. Absorption spectral change for *meso*-[Cr{Ir(aet)<sub>3</sub>]<sub>2</sub>]<sup>3+</sup> (1a) in 1 mol dm<sup>-3</sup> HCl at 40 °C; the curves show the spectra measured at 2 h intervals.

In the optical resolution for the method of column chromatography, it took a lot of time to separate the band of *rac*-[Cr{Rh(aet)<sub>3</sub>]<sub>2</sub>]<sup>3+</sup> into two bands. However, optical resolution of *rac*-[Cr{Ir(aet)<sub>3</sub>]<sub>2</sub>]<sup>3+</sup> is more difficult than that of *rac*-[Cr{Rh(aet)<sub>3</sub>]<sub>2</sub>]<sup>3+</sup>. During the column chromatography, the [Cr{Ir(aet)<sub>3</sub>]<sub>2</sub>]<sup>3+</sup> complex is decomposed before the band of the racemic isomer is separated clearly into two bands. While, in the method of fractional precipitation, [Sb<sub>2</sub>(d-tart)<sub>2</sub>]<sup>2-</sup> salt of the [Cr{Ir(aet)<sub>3</sub>]<sub>2</sub>]<sup>3+</sup> complex is decomposed in the solution and could not be recrystallized. This behavior suggests that the [Sb<sub>2</sub>(d-tart)<sub>2</sub>]<sup>2-</sup> salt of the [Cr{Ir(aet)<sub>3</sub>]<sub>2</sub>]<sup>3+</sup> is unstable in water, and the speedy procedure is required in the optical resolution. Accordingly,

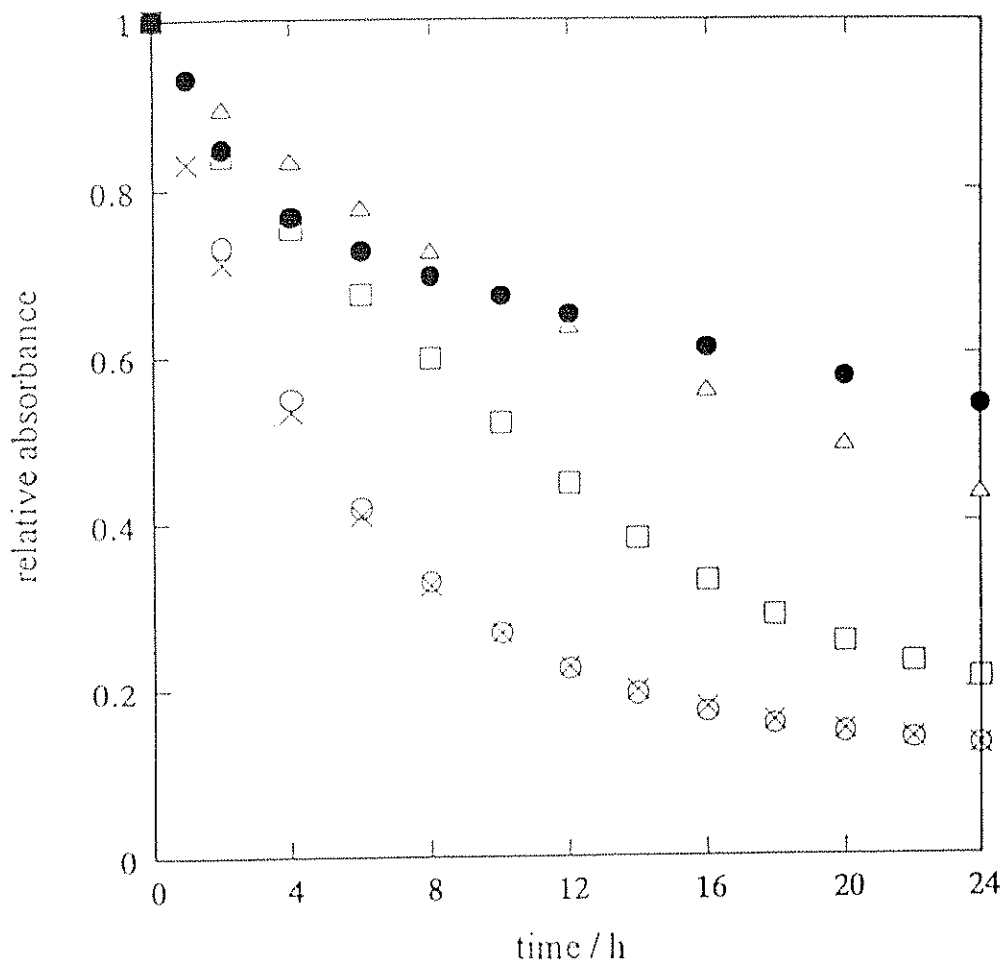


Figure 2-6. Time dependence of relative absorbance for  $[\text{Cr}\{\text{M}(\text{aet})_3\}_2]^{3+}$ ; M = Ir, *meso* isomer (**1a**), at 40 °C, in 1 mol dm<sup>-3</sup> HCl (○); M = Ir, *meso* isomer (**1a**), at 40 °C, in H<sub>2</sub>O (□); M = Ir, *meso* isomer (**1a**), at 25 °C, in 1 mol dm<sup>-3</sup> HCl (△); M = Ir, *rac* isomer (**1b**), at 40 °C, in 1 mol dm<sup>-3</sup> HCl (×); M = Rh, *meso* isomer (**2a**), at 40 °C, in 1 mol dm<sup>-3</sup> HCl (●). Concentration of samples is 0.14 (**1a** and **1b**) and 0.11 (**2a**) mmol dm<sup>-3</sup>.

it is not clear whether this *rac*- $[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$  complex is completely resolved. These results significantly different from the case of the  $\text{MCo}^{\text{III}}\text{M}$  complexes.

Attempts to prepare the corresponding trinuclear  $\text{Co}^{\text{III}}\text{Cr}^{\text{III}}\text{Co}^{\text{III}}$  complex by the reaction of the chromium(III) ion with *fac(S)*- $[\text{Co}(\text{aet})_3]$  were not successful. In this reaction, before chromium(III) ion binds to thiolato sulfur atom of *fac(S)*- $[\text{Co}(\text{aet})_3]$ , the  $[\text{Co}\{\text{Co}(\text{aet})_3\}_2]^{3+}$  complexes<sup>19-22)</sup> are formed. It was previously reported that the reactions of not only chromium(III) ion but

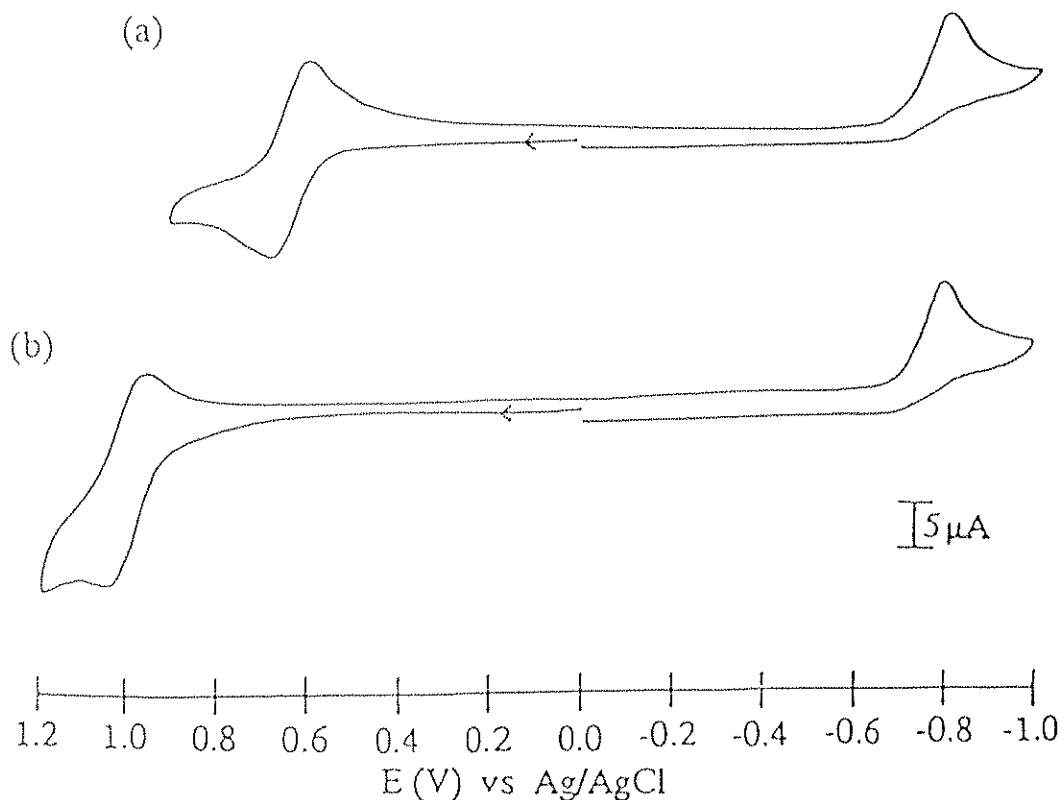


also  $\text{Ce}^{4+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{VO}^{2+}$  with *fac(S)*- $[\text{Co}(\text{aet})_3]$  resulted in the isolation of the homometallic  $[\text{Co}\{\text{Co}(\text{aet})_3\}_2]^{3+}$  rather than the heterometallic  $[\text{M}\{\text{Co}(\text{aet})_3\}_2]^{3+}$ .<sup>21)</sup> It was also reported that the oxidation reaction of *fac(S)*- $[\text{Co}(\text{aet})_3]$  by acid results in the isolation of the  $[\text{Co}\{\text{Co}(\text{aet})_3\}_2]^{3+}$ . Attempts to prepare the corresponding trinuclear  $\text{Cr}^{\text{III}}\text{Cr}^{\text{III}}\text{Cr}^{\text{III}}$  complex by the reaction of the chromium(III) ion with *fac(S)*- $[\text{Cr}(\text{aet})_3]$  were also not successful. In this reaction, before chromium(III) ion binds to thiolato sulfur atom of *fac(S)*- $[\text{Cr}(\text{aet})_3]$ , Cr-S bond may be cleaved due to acidic condition.

#### 2-3-4. Electrochemical Property

Electrochemical studies were performed for *meso*- $[\text{Cr}^{\text{III}}\{\text{M}(\text{aet})_3\}_2]^{3+}$  ( $\text{M} = \text{Ir}^{\text{III}}$  (1),  $\text{Rh}^{\text{III}}$  (2)) in 0.1 mol dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub> aqueous solution. The cyclic voltammograms are shown in Figure 2-7, and their data are summarized in Table 2-8. As shown in Figure 2-7, the cyclic voltammograms at a glassy-carbon electrode for both **1a** and **2a** display a reversible redox couple at a positive potential region and an irreversible reduction wave at a negative region. It seems to be indicated that the reversible redox couple ( $E^{0'} = + 0.64$  V;  $E_{\text{pa}} = + 0.68$  V;  $E_{\text{pc}} = + 0.60$  V) for the  $\text{Ir}^{\text{III}}\text{Cr}^{\text{III}}\text{Ir}^{\text{III}}$  complex (**1a**) would involve the terminal Ir(IV)/Ir(III) redox process, because a similar redox couple appeared at almost a similar positive region to the  $\text{Ir}^{\text{III}}\text{Co}^{\text{III}}\text{Ir}^{\text{III}}$  complex ( $E^{0'} = + 0.73$  V). However, the chromium(III) complex appears at 0.09 V more negative than the cobalt(III) complex.<sup>16)</sup> Similarly, the reversible redox couple ( $E^{0'} = + 1.01$  V;  $E_{\text{pa}} = + 1.05$  V;  $E_{\text{pc}} = + 0.97$  V) for the  $\text{Rh}^{\text{III}}\text{Cr}^{\text{III}}\text{Rh}^{\text{III}}$  complex (**2a**) involves the terminal Rh(IV)/Rh(III) redox process, because a similar redox couple appeared at almost the same positive region as that of the  $\text{Rh}^{\text{III}}\text{Co}^{\text{III}}\text{Rh}^{\text{III}}$  complex ( $E^{0'} = + 1.01$  V).<sup>16)</sup> Therefore, the  $\text{Ir}^{\text{III}}\text{Cr}^{\text{III}}\text{Ir}^{\text{III}}$  complex is generally oxidized more easily than the  $\text{Rh}^{\text{III}}\text{Cr}^{\text{III}}\text{Rh}^{\text{III}}$  complex, as it is observed in the  $\text{MCo}^{\text{III}}\text{M}$  complexes.

The irreversible reduction waves ( $E_{\text{pc}} = - 0.85$  V) for  $[\text{Cr}^{\text{III}}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$  appear at almost the same potential as that for the  $\text{Rh}^{\text{III}}\text{Cr}^{\text{III}}\text{Rh}^{\text{III}}$  complex ( $E_{\text{pc}} = - 0.86$  V). Since it has been known that both of the Ir(III)/Ir(II) and Rh(III)/Rh(II) redox processes do not occur in the potential region from + 1.1



**Figure 2-7.** Cyclic voltammograms of  $\Delta A$ - $[\text{Cr}\{\text{M}(\text{aet})_3\}_2]^{3+}$ ; (a)  $\text{M} = \text{Ir}$  and (b)  $\text{M} = \text{Rh}$ ; scan rate  $100 \text{ mV s}^{-1}$ ; in  $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$  aqueous solution.

**Table 2-8.** Electrochemical Data ( $E^{0'} = (E_{pa} + E_{pc})/2$  in V vs. Ag/AgCl) of Trinuclear Complexes,  $[\text{M}'\{\text{M}(\text{aet})_3\}_2]^{3+}$

Complex	$\text{M}^{\text{IV/III}}\text{M}^{\text{III}}\text{M}^{\text{III}}$	$\text{M}^{\text{III}}\text{M}^{\text{III/II}}\text{M}^{\text{III}}$
$[\text{Cr}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$ ( <b>1a</b> )	+0.64	-0.85 <sup>b)</sup>
$[\text{Cr}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$ ( <b>2a</b> )	+1.01	-0.86 <sup>b)</sup>
$[\text{Co}\{\text{Ir}(\text{aet})_3\}_2]^{3+}$ <sup>a)</sup>	+0.73	-0.23
$[\text{Co}\{\text{Rh}(\text{aet})_3\}_2]^{3+}$ <sup>a)</sup>	+1.01	-0.36

a) *rac*-isomer; at  $22 \text{ }^\circ\text{C}$  in water ( $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ ) at a glassy-carbon electrode with scan rate  $100 \text{ mV s}^{-1}$  (ref. 16).

b) Irreversible reduction process  $E_{pc}$ .

to  $-1.1 \text{ V}$  for the  $\text{Ir}^{\text{III}}\text{Co}^{\text{III}}\text{Ir}^{\text{III}}$  and  $\text{Rh}^{\text{III}}\text{Co}^{\text{III}}\text{Rh}^{\text{III}}$  complexes,<sup>16)</sup> the irreversible reduction waves probably are the central Cr(III)/Cr(II) reduction process and

are implied by the decomposition of the complexes. The additional irreversible oxidation waves ( $E_{pa} = + 0.21$  V for 1a and + 0.49 V for 2a) are not observed unless going through the reduction scans.<sup>30)</sup> This suggests that the trinuclear complexes are decomposed by the reduction process and the created species with the metal ions might be oxidized by the oxidation process. On the other hand, the Co(III)/Co(II) redox couple ( $E^0 = - 0.23$  V) for the Ir<sup>III</sup>Co<sup>III</sup>Ir<sup>III</sup> complex appears at 0.13 V more positive than that ( $E^0 = - 0.36$  V) for the Rh<sup>III</sup>Co<sup>III</sup>Rh<sup>III</sup> complex, indicating that the central cobalt(III) ion is made easier to reduce by the terminal *fac(S)*-[Ir(aet)<sub>3</sub>] units than the *fac(S)*-[Rh(aet)<sub>3</sub>] units.<sup>16)</sup> Accordingly, the electrochemical behavior of the central chromium(III) ion in the MCr<sup>III</sup>M complexes is significantly different from that of the cobalt(III) ion in the MCo<sup>III</sup>M ones, that is, it seems to be indicated that the central chromium(III) ion in the MCr<sup>III</sup>M complex is hardly reduced and the trinuclear structure no longer exists when it is reduced. This means that in the trinuclear MM'M (M = Ir<sup>III</sup>, Rh<sup>III</sup>; M' = Cr<sup>III</sup>, Co<sup>III</sup>) complexes, the Ir-S bonds are stronger than Rh-S bonds and Co-S bonds are stronger than Cr-S bonds, as indicated by their stereochemical and spectrochemical behavior. Therefore, the present electrochemical results also suggest that the M-S bond strengths are the factor of the electrochemical differences of these complexes.

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