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Preparation and Resolution of Bis[tris(2-aminoethaneselenolato)-cobalt(III)-μ-Se, μ-Se′, μ-Se″]cobalt(III) Complex

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Synopsis. The title *Se*-bridged complex, $[\mathrm{Co^{III}\{Co^{III}(aese)_3\}_2}]^{3+}$ (aese=2-aminoethaneselenolate), was newly prepared by the reaction of *fac*-$[\mathrm{Co(aese)_3}]$ with $\mathrm{Co^{2+}}$ and separated into three isomers, *ΔΔ*, *ΔΛ*, and *ΛΛ*, by the ion-exchange chromatographic method. The isomers were characterized from their absorption, CD, and ^{13}C NMR spectra.

Thiolate ligands tend to form polynuclear metal complexes with μ-thiolato structure and several trinuclear cobalt(III) complexes with 2-aminoethanethiolate (aet) and L-cysteinate (L-cys) have been investigated.[1–12] This tendency is also expected for the selenolate ligand such as 2-aminoethaneselenolate (aese). However, up to now no study has appeared on the *Se*-bridged polynuclear cobalt(III) complexes. This note describes the preparation and resolution of the *Se*-bridged tricobalt(III) complex with 2-aminoethaneselenolate $[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$ (Fig. 1). The isomers obtained are characterized from their absorption, CD, and ^{13}C NMR spectra in comparison with those of the corresponding tricobalt(III) complexes with 2-aminoethanethiolate, $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$.[3,4,9] The redox properties of $[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$ and $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$ are also reported.

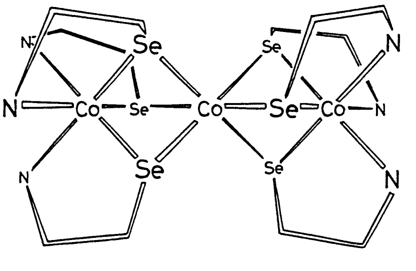

Fig. 1. The *ΛΛ* isomer of $[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$.

Experimental

Preparation and Resolution of Complexes. 1) *fac*-$[\mathrm{Co(aese)_3}]$: To a deoxygenated solution containing 0.7 g (18.2 mmol) of $\mathrm{NaBH_4}$ in 45 cm^3 of water were successively added with stirring a deoxygenated solution containing 3.0 g (9.1 mmol) of $\mathrm{(NH_2CH_2CH_2Se\text{-})_2 \cdot 2HCl \cdot 0.5H_2O}$[13] in 70 cm^3 of water and a deoxygenated solution containing 2.2 g (6.1 mmol) of $\mathrm{Na_3[Co(CO_3)_3] \cdot 3H_2O}$ in 45 cm^3 of water. The mixture was continuously stirred at 60 °C for 5 h under nitrogen atmosphere. The resultant deep green complex was collected by filtration and washed with ethanol and ether. This complex is sparingly soluble in water. Found: C, 16.84; H, 4.24; N, 9.82%. Calcd for $[\mathrm{Co(aese)_3}]=\mathrm{C_6H_{18}N_3Se_3Co}$: C, 16.83; H, 4.21; N, 9.69%.

2) *meso*-$[\mathrm{Co\{Co(aese)_3\}_2}]\mathrm{I_3}$ and *rac*-$[\mathrm{Co\{Co(aese)_3\}_2}]\mathrm{Cl_3 \cdot 1.5H_2O \cdot NaCl}$: To a suspension of 1.8 g (4.2 mmol) of *fac*-$[\mathrm{Co(aese)_3}]$ in 30 cm^3 of water was added a solution containing 0.5 g (2.1 mmol) of $\mathrm{CoCl_2 \cdot 6H_2O}$ in 10 cm^3 of water. The mixture was stirred at 40 °C for 1 h, whereupon the color of the solution became deep brownish green. Addition of a large amount of ethanol to the reaction solution in an ice bath yielded a deep green precipitate of $[\mathrm{Co\{Co(aese)_3\}_2}]\mathrm{Cl_3}$, which was collected by filtration.

One gram of $[\mathrm{Co\{Co(aese)_3\}_2}]\mathrm{Cl_3}$ was dissolved in a small amount of water and poured onto a column of SP-Sephadex C-25 ($\mathrm{Na^+}$ form, 5.5 cm×45 cm). After the column had been swept with water, the adsorbed band was eluted with a 0.2 mol dm^{-3} aqueous solution of NaCl. A circulating-chromatographic technique was employed for the separation of the isomers. After circulating the eluate in the same column twice, two dark green bands, A-1 and A-2, were eluted in that order. It was found, from the result of the optical resolution procedure, that the A-1 and A-2 eluates contained *meso*- and *rac*-$[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$, respectively. Each eluate was concentrated to a small volume with a rotary evaporator below 25 °C. On cooling the concentrated eluate in a refrigerator overnight, crystals of the A-2 isomer appeared and were collected by filtration. This isomer was recrystallized twice from water by adding ethanol in an ice bath. The crystals of the A-1 isomer were obtained as an iodide salt by adding a large amount of saturated NaI solution to the concentrated eluate. These aese tricobalt(III) isomers are unstable in aqueous solution in comparison with the aet tricobalt(III) ones. Found for A-1: C, 11.03; H, 2.78; N, 6.30%. Calcd for $[\mathrm{Co\{Co(aese)_3\}_2}]\mathrm{I_3}=\mathrm{C_{12}H_{36}N_6I_3Se_6Co_3}$: C, 11.12; H, 2.80; N, 6.49%. Found for A-2: C, 13.11; H, 3.59; N, 7.64%. Calcd for $[\mathrm{Co\{Co(aese)_3\}_2}]\mathrm{Cl_3 \cdot 1.5H_2O \cdot NaCl}=\mathrm{C_{12}H_{39}N_6O_{1.5}NaCl_4Se_6Co_3}$: C, 13.02; H, 3.55; N, 7.59%.

3) Optical Resolution of $[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$: The A-2 isomer was optically resolved by column chromatography, while the A-1 isomer could not be resolved. An aqueous solution of the A-2 isomer (0.2 g) was charged on the top of an SP-Sephadex C-25 column ($\mathrm{Na^+}$ form, 4 cm×85 cm). Two bands were separated by eluting with a 0.2 mol dm^{-3} aqueous solution of $\mathrm{K_2[Sb_2(}d\text{-}\mathrm{tart)_2] \cdot 3H_2O}$. After the separation into two bands, each adsorbed band was eluted with a 0.2 mol dm^{-3} aqueous solution of NaCl. It was found from the CD spectral measurements that the earlier moving band contained $(-)^{\mathrm{CD}}_{680}$-$[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$ and the later one contained $(+)^{\mathrm{CD}}_{680}$-$[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$. The $\Delta\varepsilon$ values of them were evaluated on the basis of the absorption spectrum of the racemic chloride salt.

4) Preparation and Resolution of $[\mathrm{Co\{Co(aet)_3\}_2}]\mathrm{(NO_3)_3}$: This complex was prepared from *fac*-$[\mathrm{Co(aet)_3}]$ and $\mathrm{CoCl_2 \cdot 6H_2O}$ by the method of Busch et al.[3] Three isomers, *ΔΔ*, *ΔΛ*, and *ΛΛ*, were chromatographically separated according to the procedures described in 2) and 3).

Measurements. The electronic absorption spectra were recorded with a JASCO UVIDEC-610A spectrophotometer, the diffuse reflection spectra with a JASCO UVIDEC-1 spectrophotometer, and the CD spectra with a JASCO J-20 spectropolarimeter. The ^{13}C NMR spectra were recorded with a JEOL JNM-FX-90Q NMR spectrometer at the probe temperature in a $\mathrm{D_2O}$ solvent. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as the internal reference. The cyclic voltammograms were recorded with a Hokuto Denko potentiogalvanostat, model HA-201, to which a linear potential scanner, model HB-103, was attached. A grassy carbon electrode, a Pt wire counter electrode with a sufficiently large surface area, and a 3.33 mol dm^{-3} KCl calomel reference electrode were used for the potentiostatic measurements in a 0.01 mol dm^{-3} sodium nitrate solution at room temperature (20±1 °C). The electrode potential data were corrected to those for the standard hydrogen electrode (SHE).

Results and Discussion

Two geometrical isomers, *fac* and *mer*, are possible for the tris(2-aminoethaneselenolato)cobalt(III) complex, $[\mathrm{Co(aese)_3}]$. The diffuse reflection spectrum of the selenolato complex which belongs to the $[\mathrm{Co(N)_3(Se)_3}]$ type is similar to that of the *fac* isomer of the corresponding thiolato complex, $[\mathrm{Co(aet)_3}]$ (Fig. 2). This suggests that the selenolato complex takes selectively the *fac* geometry as well as the corresponding thiolato complex.[3,14] The reflection spectrum of *fac*-$[\mathrm{Co(aese)_3}]$ shifts to lower energy than that of *fac*-$[\mathrm{Co(aet)_3}]$ in accordance with the fact that the ligand field strength is selenolate < thiolate.[15] Three isomers, *ΔΔ*, *ΔΛ*, and *ΛΛ*, are expected for $[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$, considering the absolute configurations of two terminal *fac*-$[\mathrm{Co(aese)_3}]$ (Fig. 1), as in the case of $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$.[4] The A-1 and A-2 isomers exhibit similar absorption spectra, showing two intense d-d bands at ca. 17 and 21×10^3 cm^{-1} and more intense charge transfer bands at ca. 26 and 33×10^3 cm^{-1} (Fig. 3). This absorption spectral behavior coincides well with that of the tricobalt(III) complex with 2-aminoethanethiolate, $[\mathrm{Co^{III}\{Co^{III}(aet)_3\}_2}]^{3+}$, whose molecular structure has been determined by single crystal X-ray analysis.[9] Therefore, both the A-1 and A-2 isomers can be assigned to the tricobalt(III) complex with 2-aminoethaneselenolate, $[\mathrm{Co^{III}\{Co^{III}(aese)_3\}_2}]^{3+}$. The absorption components of $[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$ commonly shift to lower energy than those of $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$ (Fig. 3) and this behavior is consistent with that of the cobalt(III) complexes with selenium- or sulfur-containing ligands.[15–20]

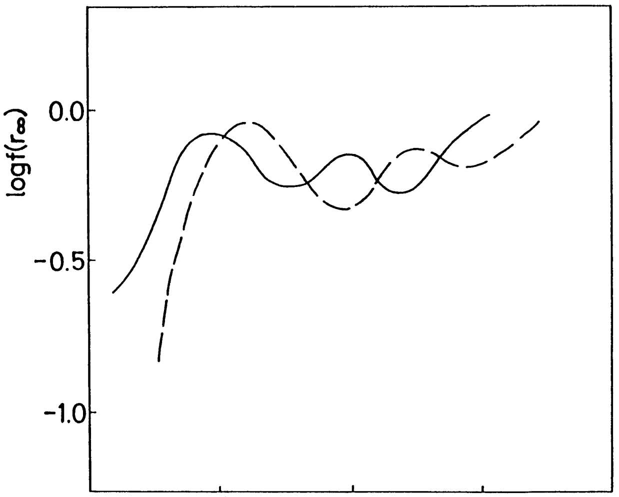

Fig. 2. Diffuse reflection spectra of *fac*-$[\mathrm{Co(aese)_3}]$ (——) and *fac*-$[\mathrm{Co(aet)_3}]$ (----).

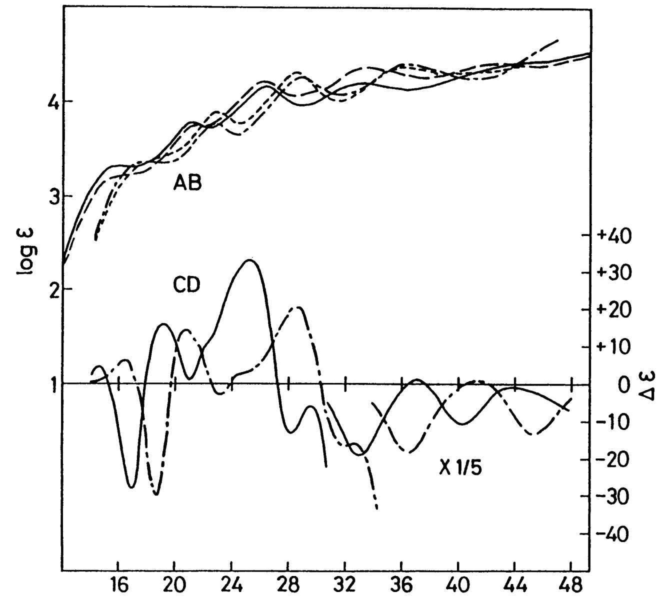

Fig. 3. Absorption and CD spectra of *ΛΛ*-$[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$ (——), *ΔΔ*-$[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$ (----), *ΛΛ*-$[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$ (-·-·-), and *ΔΔ*-$[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$ (------).

The A-2 isomer was optically resolved into the $(+)^{\mathrm{CD}}_{680}$ and $(-)^{\mathrm{CD}}_{680}$ ones, while the A-1 isomer could not. This result suggests that the A-1 and A-2 isomers take meso and racemic forms respectively, taking the similarity of their absorption spectra into consideration. This assignment is also supported by their ^{13}C NMR spectral behavior. Namely, both trinuclear isomers exhibit two ^{13}C NMR resonance lines due to two methylene carbons of the aese ligand; 27.09 and 49.68 ppm for the meso (A-1) isomer having S_6 symmetry, and 26.71 and 49.52 ppm for the racemic (A-2) isomer having D_3 symmetry. The $(+)^{\mathrm{CD}}_{680}$ isomer exhibits the CD spectrum enantiomeric to the $(-)^{\mathrm{CD}}_{680}$ one over the whole region. The CD spectral pattern of the $(+)^{\mathrm{CD}}_{680}$ isomer agrees well with that of *ΛΛ*-$[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$ (Fig. 3)[4] and furthermore, that of *Δ*LLL*Δ*LLL-[Co{Co(L-cys-*N,S*)$_3$}$_2$]$^{3-}$ whose absolute configuration has been determined by the single crystal X-ray analysis,[11] though the CD bands of the aese isomer shift significantly to lower energy than those of the aet isomer in parallel with their absorption spectral behavior. Accordingly, it is confidently assigned that the $(+)^{\mathrm{CD}}_{680}$ isomer is *ΛΛ*-$[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$ and the $(-)^{\mathrm{CD}}_{680}$ isomer is the *ΔΔ* one.

The trinuclear complexes, $[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$ and $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$, display a quasi-reversible cyclic response with $E_{1/2}=-0.47$ V for $[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$ and $E_{1/2}=-0.46$ V for $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$, and no other redox process is observed in the potential range of −0.7—+0.5 V. The anodic and cathodic peaks separation, $E_{\mathrm{pa}}-E_{\mathrm{pc}}$, is 95 mV for $[\mathrm{Co\{Co(aese)_3\}_2}]^{3+}$ and 65 mV for $[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$, and the anodic peak current and the cathodic peak current are nearly equal for the two complexes. A similar redox reaction ($E_{1/2}=-0.43$ V, $E_{\mathrm{pa}}-E_{\mathrm{pc}}=90$ mV) was observed for the tricobaltate(III) complex with L-cysteinate, $[Co\{Co(L\text{-cys-}N,S)_3\}_2]^{3-}$,[12] where the quasi-reversible redox reaction was assigned as the Co(III)/Co(II) redox process due to the central cobalt ion. Therefore, it is probable that the central cobalt ion is the active site of the redox reaction between Co(III) and Co(II) oxidation states for the present tricobalt(III) complexes with the aese and with the aet.

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