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Synthesis and Properties of T-Cage-Type Se-Bridged Polynuclear Co(III) and Rh(III) Complexes with 2-Aminoethaneselenolate (aese). Crystal Structure of $[\{Co(aese)_3\}_4Zn_4O](ClO_4)_6$

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The novel T-cage-type Se-bridged polynuclear complexes with 2-aminoethaneselenolate (aese), $[\{Co(aese)_3\}_4Zn_3Cl]^{5+}$, $[\{Co(aese)_3\}_4Zn_4O]^{6+}$, and $[\{Rh(aese)_3\}_4Zn_4O]^{6+}$, have been synthesized. Of these complexes, the spontaneous resolution was recognized for $[\{Co(aese)_3\}_4Zn_4O]Cl_6$ and $[\{Rh(aese)_3\}_4Zn_4O](NO_3)_6$ with a "complete" $[Zn_4O]^{6+}$ core. The crystal structure of $(-)^{\mathrm{CD}}_{600}$-$[\{Co(aese)_3\}_4Zn_4O](ClO_4)_6 \cdot 4H_2O$ was determined by the X-ray diffraction method. The crystal is cubic, space group $P2_13$, a=19.646(2) Å, U=7582.2(7) Å^3, Z=4, and R=0.0725. The four octahedral fac(Se)-$[Co(aese)_3]$ subunits are bound to the tetrahedral $[Zn_4O]^{6+}$ core in a tetrahedral arrangement, giving an approximate T symmetrical (T-cage-type) structure. The three Se atoms in each fac(Se)-$[Co(aese)_3]$ subunit are bound to the three different Zn atoms. For the $(-)^{\mathrm{CD}}_{600}$ isomer, the chiral configurations are regulated to Δ for all four fac(Se)-$[Co(aese)_3]$ subunits, and S for all 12 bridging Se atoms. The electronic absorption and CD spectral behavior of the complexes are discussed in comparison with those of the related mononuclear and linear-type trinuclear complexes, and the corresponding T-cage-type S-bridged polynuclear complexes.

Recently, the S-bridged linear-type trinuclear and T-cage-type polynuclear complexes with 2-aminoethanethiolate (aet) have been extensively investigated, because of their unique stereochemical and spectrochemical properties.[1-6)] Especially, the most fascinating is the formation of the T-cage-type S-bridged octanuclear complexes, $[\{M(aet)_3\}_4Zn_mO]^{n+}$ (M=Co(III) and Rh(III); m,n=3,4 and/or 4,6), in which the four mononuclear complexes of the same chirality aggregate so as to be spontaneously resolved.[4-7)] Hence, in order to elucidate the formation reactions and some properties of the T-cage-type polynuclear complexes, we have undertaken the preparation of the T-cage-type polynuclear complexes with 2-aminoethaneselenolate (aese). This paper deals with the preparation and the spectrochemical and stereochemical properties of the T-cage-type Se-bridged polynuclear complexes with the aese ligands (Fig. 1), and with the X-ray crystal structure analysis of $[\{Co(aese)_3\}_4Zn_4O]$ $(ClO_4)_6$. The aese complexes obtained are characterized on the basis of the absorption, CD, and ^{13}C NMR spectra in comparison with those of the related mononuclear and polynuclear complexes.

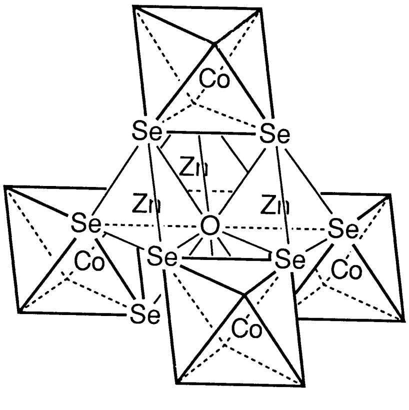

Fig. 1. Polyhedral presentation of the T-cage-type Se-bridged octanuclear complex, $[\{Co(aese)_3\}_4Zn_4O]^{6+}$.

Experimental

Materials. All reagents were purchased from the Wako Pure Chemical Ind. Co., Ltd. and were used without further purification. $(NH_2CH_2CH_2Se-)_2 \cdot 2HCl$[8)] and fac(Se)-$[Co(aese)_3]$[9)] were prepared by the procedure described in the literature.

Preparation of Complexes. 1) $[\{Co(aese)_3\}_4Zn_3Cl]Cl_5$ (1). To a suspension containing 2.0 g (2.4 mmol) of fac(Se)-$[Co(aese)_3]$ in 80 cm^3 of water was added a solution containing 6.0 g (44 mmol) of $ZnCl_2$ in 20 cm^3 of water. The mixture was stirred at room temperature for 30 min, and then the dark green precipitate was collected by filtration. This precipitate was dissolved into a small amount of water (ca. 20 cm^3) and the insoluble fac(Se)-$[Co(aese)_3]$ was removed by filtration. To the green filtrate was added a few drops of saturated NaCl aqueous solution, followed by cooling in a refrigerator for 2 h. The resulting dark green precipitate was collected by filtration, washed with ethanol and ether, and then dried in a vacuum desiccator. Yield: 0.98 g (66%). Found: C, 11.66; H, 3.51; N, 6.74; Co, 9.21; Zn, 7.59%. Calcd for $[\{Co(aese)_3\}_4Zn_3Cl]Cl_5 \cdot 7H_2O \cdot 4NaCl = C_{24}H_{72}N_{12}Se_{12}Cl_6Co_4Zn_3 \cdot 7H_2O \cdot 4NaCl$: C, 11.61; H, 3.49; N, 6.77; Co, 9.50; Zn, 7.91%.

2) $(-)^{\mathrm{CD}}_{600}$-$[\{Co(aese)_3\}_4Zn_4O]$ $(ClO_4)_6$ (2). To a solution containing 0.5 g (0.2 mmol) of **1** in 200 cm^3 of water was added a solution containing 0.3 g (0.9 mmol) of potassium antimonyl *d*-tartrate in 60 cm^3 of water. After cooling the solution in a refrigerator for 4 d, the resulting antimonyl *d*-tartrate salt of the $(-)^{\mathrm{CD}}_{600}$ isomer was collected by filtration. The antimonyl *d*-tartrate salt was converted to the perchlorate salt by adding 0.5 g of sodium perchlorate to its aqueous solution. The $(-)^{\mathrm{CD}}_{600}$ isomer was recrystallized from water by cooling in a refrigerator. Yield: 0.16 g (30%). Found: C, 10.75; H, 3.07; N, 6.15; Co, 7.74; Zn, 9.64%. Calcd for $(-)^{\mathrm{CD}}_{600}$-$[\{Co(aese)_3\}_4Zn_4O](ClO_4)_6 \cdot 5H_2O = C_{24}H_{72}N_{12}O_{25}Se_{12}Cl_6Co_4Zn_4 \cdot 5H_2O$: C, 10.77; H, 3.09; N, 6.28; Co, 8.80; Zn, 9.77%.

The green crystals suitable for the X-ray diffraction measurements were obtained by the slow recrystallization from water at room temperature.

3) $[\{\mathrm{Co(aese)_3}\}_4\mathrm{Zn_4O}]\mathrm{Cl_6}$ (3). This complex (3) was obtained by the slow evaporation at room temperature of the aqueous solution containing the dark green precipitate of **1**. The resulting complex showed the identical absorpbion spectrum with $(-)^{\mathrm{CD}}_{600}$-$[\{\mathrm{Co(aese)_3}\}_4\mathrm{Zn_4O}](\mathrm{ClO_4})_6$ (**2**). Further, each crystal, which was spontaneously resolved and picked up from the bulk, showed the same CD spectral pattern as that of **2** or its enantiomeric pattern.

4) $[\{\mathrm{Rh(aese)_3}\}_4\mathrm{Zn_4O}](\mathrm{NO_3})_6$ (4). To a suspension containing 0.2 g (0.42 mmol) of fac(Se)-$[\mathrm{Rh(aese)_3}]$[10] in 20 cm^3 of water was added a solution containing 0.16 g (0.54 mmol) of $\mathrm{Zn(NO_3)_2}$ in 2.0 cm^3 of water. The mixture was stirred at room temperature for 20 min, whereupon the suspension became a clear red solution. To this was added ca. 1 g of $\mathrm{NaNO_3}$ in 68 cm^3 of water, followed by cooling in a refrigerator for a few days. The resulting precipitate was collected by filtration (Yield: 22%). When this precipitate was recrystallized from water, the red-orange crystals, which were spontaneously resolved, were collected by filtration, and washed with ethanol and ether. The CD spectra of the crystals, which were picked up from the bulk, were measured and their concentrations were evaluated by the absorption spectral data. Found: C, 10.85; H, 3.17; N, 8.99; Zn, 9.03; Rh, 14.34%. Calcd for $[\{\mathrm{Rh(aese)_3}\}_4\mathrm{Zn_4O}](\mathrm{NO_3})_6\cdot7\mathrm{H_2O}=\mathrm{C_{24}H_{72}N_{18}O_{19}Se_{12}Zn_4Rh_4\cdot7H_2O}$: C, 10.82; H, 3.25; N, 9.46; Zn, 9.82; Rh, 15.45%.

Measurements. The electronic absorption spectra were recorded on a JASCO UVIDEC or Ubest-55 spectrophotometer, and the CD spectra on a J-600 spectropolarimeter. All the measurements were carried out in aqueous solutions at room temperature. The ^{13}C NMR spectra were recorded on a Bruker AM-500 NMR spectrometer in a deuterium oxide at the probe temperature. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as an internal reference. The concentrations of the cobalt and zinc atoms in the complexes were determined by the plasma spectral analyses with a Jarrel-Ash ICPA 575 ICP spectrophotometer. The cyclic voltammograms were recorded with a CV-1B apparatus (Bioanalytical Systems, Inc. (BAS)) using a glassy-carbon working electrode (BAS, GCE). An aqueous Ag/AgCl/NaCl (3 mol dm^{-3}) electrode (BAS, RE-1) and platinum wire were used as reference and auxiliary electrodes, respectively. Electrochemical experiments were conducted at 22 °C in a 0.1 mol dm^{-3} $\mathrm{NaNO_3}$ aqueous solution as the supporting electrolyte and complex concentrations of 1.0 mmol dm^{-3}.

Crystallography. X-Ray Data Collection. Unit cell parameters and intensity data for the single green crystal (ca. $0.25\times0.33\times0.33$ mm^3) of **2** were measured on an Enraf Nonius CAD4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.71073$ Å). Unit-cell parameters were determined by least-squares refinement from 25 reflections with $23°<2\theta<25°$. Crystal data: $\mathrm{C_{24}H_{80}N_{12}O_{29}Se_{12}Cl_6Co_4Zn_4}$, $M=2658.5$, cubic, space group $P2_13$, $a=19.646(2)$ Å, $U=7582.2(7)$ Å^3, $Z=4$, $D_c=2.33$ g cm^{-3}, $F(000)=4663$, $\mu=79.1$ cm^{-1}, and room temperature.

The intensity data were collected by the ω–2θ scan mode up to $2\theta=52°$ ($h, k, l\leqq24$) with scan width $(0.7+0.350\tan\theta)°$ and scan rate was varied from 1 to 5° min^{-1} (on ω). The intensities were corrected for Lorenatz and polarization, and not for absorption. A total of 878 independent reflections with $|F_o|>5\sigma(|F_o|)$ of the measured 3072 reflections were considered as "observed" and used for structure determination.

Determination of Crystal Structure. The cobalt, selenium, and zinc atoms were located by the direct methods of the crystallographic program package SDP.[11] The remaining non-hydrogen atoms were found by conventional difference Fourier techniques to give a trial structure. All the oxygen atoms of the perchlorate ions were fixed by geometrical constrains (Cl–O=1.45 Å)[12] and isotropic thermal parameters ($U=0.20$ Å^2). The structure was refined by the full-matrix least-squares on F (SHELX76[13]) using anisotropic thermal parameters for the cobalt, selenium, zinc, chlorine, nitrogen, and central oxygen atoms, and isotropic thermal parameters for the carbon and oxygen (water molecules) atoms. The hydrogen atoms were not included in the calculation. The occupancy factors for the atoms on the special positions and disordered perchlorate ions were listed in Table 1. The scattering factors with corrections for anomalous dispersion

Table 1. Final Atomic Coordinates, Equivalent Isotropic ($B_{\mathrm{eq}}/\text{Å}^2$) or Isotropic ($B/\text{Å}^2$) Thermal Parameters, and Occupancy Factors (ocf) for Non-H Atoms
$B_{\mathrm{eq}}=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$

Atom	x	y	z	B_{eq}	ocf
Co(1)	0.6157(4)	0.6969(4)	0.8966(3)	6.9(4)	
Co(2)	0.5692(3)			4.9(2)	1/3
Zn(1)	0.6929(3)	0.6014(3)	0.7303(3)	4.9(3)	
Zn(2)	0.7514(3)			6.2(3)	1/3
O	0.6928(14)			4.2(10)	1/3
Se(1)	0.6151(3)	0.5968(3)	0.8290(3)	6.0(3)	
Se(2)	0.5739(3)	0.7681(3)	0.8105(3)	6.1(3)	
Se(3)	0.7311(3)	0.7185(3)	0.8702(3)	7.6(3)	
Se(4)	0.6582(3)	0.5252(2)	0.6388(2)	5.6(3)	
N(1)	0.648(3)	0.637(3)	0.974(2)	12(4)	
N(2)	0.512(2)	0.679(4)	0.914(2)	11(3)	
N(3)	0.617(2)	0.772(3)	0.953(4)	13(4)	
N(4)	0.513(3)	0.493(2)	0.603(2)	7(2)	
Cl(1)	0.9431(7)			7.4(6)	1/3
Cl(2)	0.1664(9)			9.2(8)	1/3
Cl(3)	0.4361(10)			12(1)	1/3
Cl(4)	0.181(2)	0.173(2)	0.444(2)	15(3)	1/2
Cl(5)	0.118(2)	0.174(2)	0.488(2)	12(3)	1/2
				B	
C(11)	0.671(3)	0.541(2)	0.898(3)	6(1)	
C(12)	0.646(3)	0.559(3)	0.970(3)	9(2)	
C(21)	0.477(3)	0.739(3)	0.814(3)	7(1)	
C(22)	0.460(3)	0.677(4)	0.843(4)	10(2)	
C(31)	0.737(4)	0.810(3)	0.925(3)	9(2)	
C(32)	0.663(5)	0.799(5)	0.961(5)	15(3)	
C(41)	0.609(4)	0.447(3)	0.683(3)	9(2)	
C(42)	0.539(5)	0.464(5)	0.659(5)	13(3)	
O(11)	0.932(3)	0.926(3)	1.0140(8)	15.79	
O(12)	0.9005(7)			15.79	1/3
O(21)	0.218(2)	0.125(1)	0.199(3)	15.79	
O(22)	0.1238(9)			15.79	1/3
O(31)	0.488(2)	0.468(3)	0.395(1)	15.79	
O(32)	0.3935(10)			15.79	1/3
O(451)	0.154(2)	0.236(1)	0.471(2)	15.79	
O(452)	0.166(2)	0.118(1)	0.490(2)	15.79	
O(43)	0.152(4)	0.160(3)	0.378(2)	15.79	1/2
O(44)	0.255(2)	0.180(3)	0.437(4)	15.79	1/2
O(53)	0.067(3)	0.160(3)	0.436(3)	15.79	1/2
O(54)	0.085(3)	0.181(3)	0.553(3)	15.79	1/2
O(W1)	0.398(3)	0.417(3)	0.197(3)	14(2)	
O(W2)	0.348(7)	0.224(7)	0.309(8)	11(4)	1/3

were taken from literature.14) The final refinement in the $(-)^{\rm CD}_{600}$ isomer gave R=0.0725 and R_w=0.0728 with the weighting scheme $w=0.5278/\{\sigma^2(F_o)+0.014259F_o^2\}$; S=0.52 and $\Delta_{\rm max}=0.17\sigma$. The refinements in the enantiomeric atomic parameters resulted in the residual values of R=0.0750 and R_w=0.0760 ($w=0.7422/\{\sigma^2(F_o)+0.008639F_o^2\}$). This suggests that the enantiomeric structure could be rejected at the 0.005 significance level by Hamilton test ($R_{1,681,\,0.005}\simeq 1.006$);15) that is, the complex cation takes the ΔΔΔΔ configuration. The final difference Fourier synthesis indicated no significant peaks larger than 0.74 eÅ^{-3}. All the calculations were performed on the FACOM M-1800/20 computer at the Computer Center of the University of Tsukuba. Atomic positional parameters are given in Table 1.16)

Results and Discussion

Structure of $(-)^{\rm CD}_{600}$-[{Co(aese)$_3$}$_4$Zn$_4$O] (ClO$_4$)$_6$. The crystal of **2**, which showed a negative CD value at 600 nm, consists of the discrete complex cation, perchlorate anions, and water molecules. There are four crystallographically independent perchlorate anions, one of which exhibited positional disorder [Cl(4) and Cl(5)]. The total occupancy factor of the perchlorate anions indicates that the entire complex cation is hexavalent (Table 1). A perspective drawing of the entire complex cation is given in Fig. 2. The selected bond distances and angles in the complex cation are listed in Table 2.

The entire complex cation has crystallographically imposed C_3 symmetry, and the Co(2), O, and Zn(2) atoms lie on the 3-fold axis. The complex cation consists of four approximately octahedral fac(Se)-[Co(aese)$_3$] subunits, four Zn atoms, and one central μ_4-O atom, forming the T-cage-type Se-bridged octanuclear structure as in the case of [{M(aet)$_3$}$_4$Zn$_4$O]$^{6+}$ (M=Co(III) and Rh(III)).4,6) The four Zn atoms are tetrahedrally bound to the central O atom to form the [Zn$_4$O]$^{6+}$ core (Fig. 2 and Table 2). The Zn–Zn distances of 3.190(8)—3.191(8) Å in the aese complex are similar to those (3.177(2)—3.186(2) Å) of the corresponding aet complex, [{Co(aet)$_3$}$_4$Zn$_4$O]$^{6+}$.6) To each of four triangle faces of the [Zn$_4$O]$^{6+}$ core [Zn(k)–Zn(l)–Zn(m) (k, l, m=1 and/or 2) angles are 60.0(2)°], each of the four fac(Se)-[Co(aese)$_3$] subunits bridges with the facial three Se atoms. The Zn–Co distances (4.038(8)—4.066(9) Å) in the aese compex are significantly larger than those (3.895(2)—3.921(2) Å) of the aet complex (Table 2).6) This is attributed to the difference in the size between the bridging Se and S atoms. The Co–Se (2.343(9)—2.373(8) Å; av 2.360 Å) and Zn–Se (2.437(7)—2.487(8) Å; av 2.463 Å) distances in the aese complex are larger than those of the aet one (av 2.266 Å for Co–S and av 2.364 Å for Zn–S). This also reflects the difference in the size between the bridging Se and S atoms. Other bond distances (except the Se–C distances (av 2.04 Å)) and angles in the aese complex are similar to those of the aet one.6)

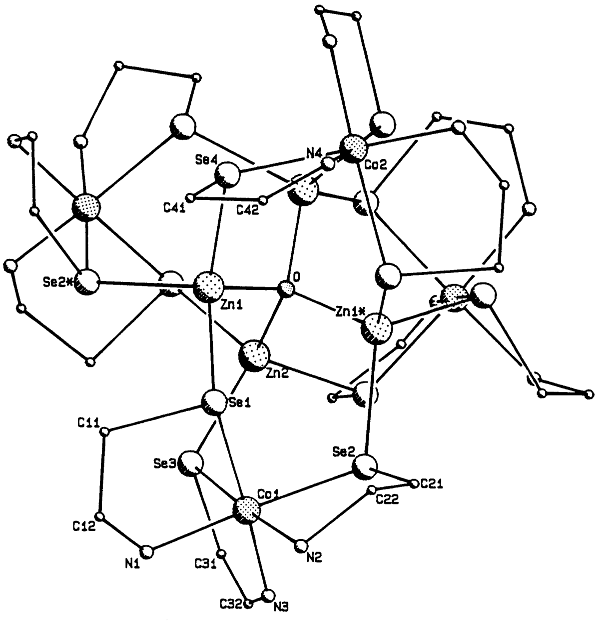

Fig. 2. Perspective view of the complex cation of **2** with the atomic labeling scheme.

Table 2. Selected Bond Distances (Å) and Angles (°)

Co(1)–Se(1)	2.373(8)	Co(2)–N(4)	1.98(4)
Co(1)–Se(2)	2.343(9)	Zn(1)–O	1.94(2)
Co(1)–Se(3)	2.364(11)	Zn(1)–Se(1)	2.471(7)
Co(1)–N(1)	2.03(4)	Zn(1)–Se(2)	2.487(8)
Co(1)–N(2)	2.09(4)	Zn(1)–Se(4)	2.437(7)
Co(1)–N(3)	1.84(5)	Zn(2)–O	1.99(5)
Co(2)–Se(4)	2.380(8)	Zn(2)–Se(3)	2.455(7)
Se(1)–Co(1)–Se(2)	95.1(3)	O–Zn(1)–Se(4)	107(1)
Se(1)–Co(1)–Se(3)	91.8(3)	Se(1)–Zn(1)–Se(2)	109.4(3)
Se(2)–Co(1)–Se(3)	94.0(3)	Se(1)–Zn(1)–Se(4)	112.6(3)
Se(4)–Co(2)–Se(4)	93.1(4)	Se(2)–Zn(1)–Se(4)	110.3(3)
Se(1)–Co(1)–N(1)	86(2)	O–Zn(2)–Se(3)	107.6(3)
Se(1)–Co(1)–N(3)	177(2)	Se(3)–Zn(2)–Se(3)	111.2(2)
Se(2)–Co(1)–N(1)	177(1)	Zn(1)–O–Zn(1)	111(1)
Se(2)–Co(1)–N(2)	83(1)	Zn(1)–O–Zn(2)	108(1)
Se(3)–Co(1)–N(2)	176(1)	Co(1)–Se(1)–Zn(1)	113.9(3)
Se(3)–Co(1)–N(3)	89(2)	Co(1)–Se(2)–Zn(1)	114.6(3)
Se(4)–Co(2)–N(4)	87(1)	Co(1)–Se(3)–Zn(2)	114.3(4)
O–Zn(1)–Se(1)	109.4(4)	Co(2)–Se(4)–Zn(1)	113.9(3)
O–Zn(1)–Se(2)	108.3(9)		

$(-)^{\rm CD}_{600}$-[{Co(aese)$_3$}$_4$Zn$_4$O]$^{6+}$ has two kinds of chiral centers, Δ or Λ for the fac(Se)-[Co(aese)$_3$] subunits and R or S for the bridging Se atoms. The absolute configurations of these chiral centers were determined by the anomalous scattering technique. All four fac(Se)-[Co(aese)$_3$] subunits take the Δ configuration and the bridging tweleve Se atoms take the S configuration. The five-membered chelate rings of the aese ligands take a mixture of the gauche (Se(1)–N(1) ring) and asymmetric envelope (the other rings) conformations. This differs from the situation in corresponding aet complex, which takes uniformly the gauche conformation.6)

Characterization. The ^{13}C NMR spectrum of **2** in D$_2$O is identical with that of **3**, and they exhibit three resonance lines due to two kinds of methylene carbon atoms of the twelve aese ligands. One resonance line (δ=27.72) for $-\underline{C}H_2Se$ appears at higher magnetic field (by ca. 6.5 ppm) than that (δ=34.21) for $-\underline{C}H_2S$ of $[\{Co(aet)_3\}_4Zn_4O]^{6+}$, and two resonance lines at δ=50.07 and 50.17 (ratio of the peak heights=ca. 3 : 1) for $-\underline{C}H_2NH_2$ correspond to that (δ=50.41) of the aet one.6) Taking account of the corresponding aet complex which takes the gauche conformation only, these facts suggest that the T-cage-type Se-bridged structure of **2** found in the crystalline state is retained in the solution, having the two kinds of conformations for the five-membered aese chelate rings.

In the orange crystals **4**, the ^{13}C NMR chemical shift for $-\underline{C}H_2Se$ was also observed at δ=26.61, but the methylene signal for $\underline{C}H_2NH_2$ showed one resonance line at δ=50.97, as in the case of the aet complex.6) This suggests that all of the aese ligands in the $[Rh(aese)_3]$ subunits are equivalent. Further, the crystal system of **4** is estimated to be cubic (a=19.186(4) Å) by the single crystal X-ray analysis, although the sufficient intensity data could not be collected because of the very small crystal size. This crystal system is consistent with those of $(-)^{CD}_{600}$-$[\{Co(aese)_3\}_4Zn_4O]^{6+}$ (cubic; a=19.646(2) Å) and the spontaneously resolved $[\{Co(aet)_3\}_4Zn_4O]^{6+}$ (cubic; a=18.981(1) Å),6) whose space groups are determined to be $P2_13$ and the complex cations have to be optically active. Two optical isomers of **4**, which were spontaneously resolved and picked up from the bulk, exhibit the CD spectra enantiomeric to each other. The CD spectrum of the $(-)^{CD}_{400}$ isomer of **4** is quite similar in pattern to that of $(-)^{CD}_{350}$-$\Delta\Delta\Delta\Delta$-$[\{Rh(aet)_3\}_4Zn_4O]^{6+}$,4,7) as shown in Fig. 3. Accordingly, these facts indicate that the $(-)^{CD}_{400}$ isomer of **4** is $\Delta\Delta\Delta\Delta$-$[\{Rh(aese)_3\}_4Zn_4O]^{6+}$.

The crystals of **3** were also spontaneously resolved and its CD spectral pattern was the same as that of $(-)^{CD}_{600}$-$[\{Co(aese)_3\}_4Zn_4O]^{6+}$ (Fig. 4). However, the present T-cage-type aese complexes, especially $[\{Co(aese)_3\}_4Zn_4O]^{6+}$, are less stable in the aqueous solution than the corresponding aet ones. Namely, the absorption and CD spectra of $[\{Co(aese)_3\}_4Zn_4O]^{6+}$ dissolved in water change gradually with time; the CD bands disappear after a few hours, and finally, the linear-type trinuclear complex $[Co\{Co(aese)_3\}_2]^{3+}$ 9) was isolated as a final product. In these solutions, the T-cage- and linear-type complexes are discriminated on the basis of their absorption spectral behavior (vide infra). On the other hand, the absorption and CD spectral changes in the aqueous solution were inconspicuous for the T-cage-type aet complexes. Therefore, the less stability for the aese complexes seems to make it difficult to follow the formation of the spontaneously resolved crystals for the Co(III) aese complexes.

The T-cage-type $[\{M(aese)_3\}_4Zn_4O]^{6+}$ (M=Co(III) and Rh(III)) complexes exhibit two d–d transition bands (ca. 16 and 21×10^3 cm^{-1} for M=Co(III) and ca. 26 and 30×10^3 cm^{-1} for Rh(III)), and two intense selenium-to-cobalt charge transfer (CT) bands (ca. 28 and 36×10^3 cm^{-1} for Co(III) and ca. 38 and 43×10^3 cm^{-1} for Rh(III)) (Figs. 3 and 4, and Table 3).9) These absorption spectra are quite similar to those of the corresponding aet

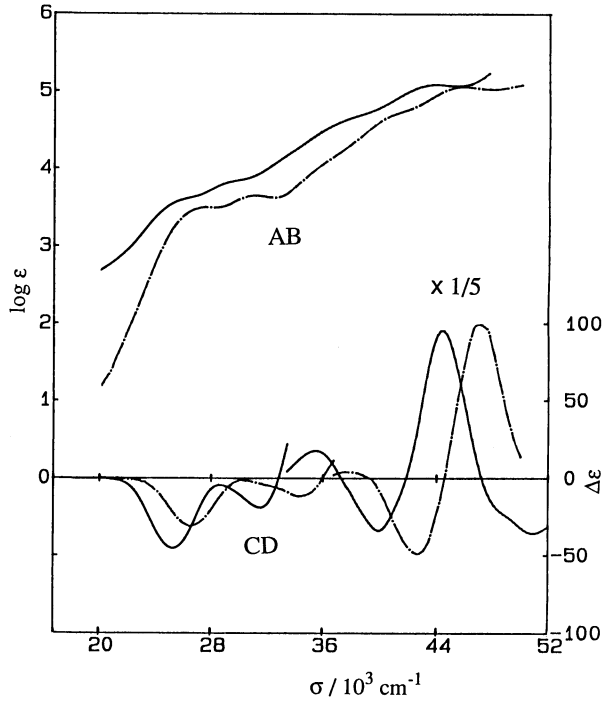

Fig. 3. Absorption and CD spectra of $\Delta\Delta\Delta\Delta$-$[\{Rh(L)_3\}_4Zn_4O]^{6+}$: L=aese (——) and aet (–•–•–).

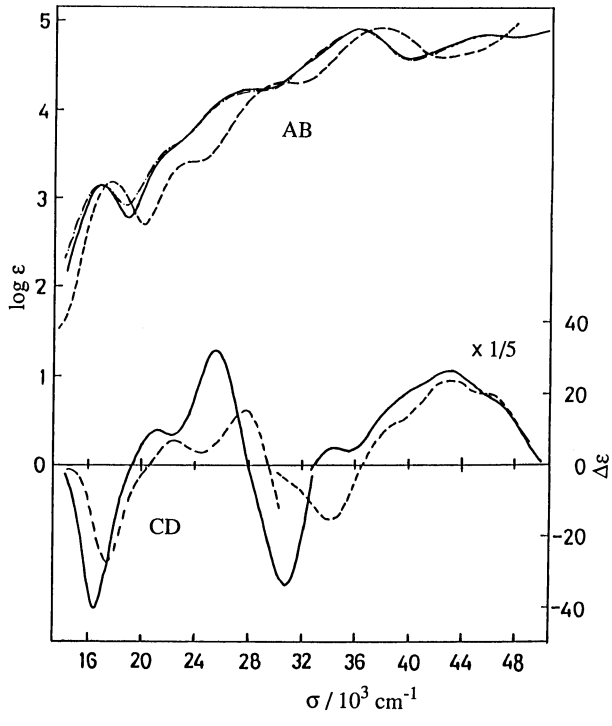

Fig. 4. Absorption and CD spectra of $[\{Co(aese)_3\}_4Zn_3Cl]^{5+}$ (–•–•–) and $\Delta\Delta\Delta\Delta$-$[\{Co(L)_3\}_4Zn_4O]^{6+}$: L=aese (——) and aet (------).

Table 3. Absorption Spectral Data of T-Cage-Type Complexes

Complex ion	Absorption maxima $\sigma/10^3$ cm^{-1} (log ε/mol^{-1} dm^3 cm^{-1})	CD extrema $\sigma/10^3$ cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
$[\{Co(aese)_3\}_4Zn_3Cl]^{5+}$ (**1**)	16.81 (3.16)	
	22.99 (3.66 sh)[a]	
	27.78 (4.22 sh)	
	36.36 (4.90)	
	46.51 (4.83)	
$(-)^{\mathrm{CD}}_{600}$-$\Delta\Delta\Delta\Delta$-$[\{Co(aese)_3\}_4Zn_4O]^{6+}$ (**2**)	16.81 (3.14)	16.45 (−40.2)
	22.20 (3.56 sh)	21.10 (+9.49)
	27.63 (4.22 sh)	25.25 (+31.9)
	36.23 (4.89)	30.77 (−33.8)
	45.87 (4.82)	34.25 (+22.6)
		43.10 (+131.0)
$(-)^{\mathrm{CD}}_{400}$-$\Delta\Delta\Delta\Delta$-$[\{Rh(aese)_3\}_4Zn_4O]^{6+}$ (**4**)	25.91 (3.51 sh)	25.32 (−45.4)
	29.59 (3.78 sh)	28.65 (−4.51)
	37.88 (4.63 sh)	31.55 (−19.1)
	43.48 (5.08)	35.46 (+87.8)
		39.92 (−169.4)
		44.44 (+476.8)
		51.02 (−178.9)

a) sh denotes a shoulder.

Table 4. The $\varepsilon_{\mathrm{I}}/\varepsilon_{\mathrm{CT}}$ Value[a)] of the Mononuclear, Linear-Type Trinuclear and T-Cage-Type Complexes

Complex	Absorption maxima[b)]		$\varepsilon_{\mathrm{I}}/\varepsilon_{\mathrm{CT}}$	Ref.
	ε_{I}	$\varepsilon_{\mathrm{CT}}$		
fac(Se)-$[Co(aese)_3]$	295 (16.7)	10970 (34.7)	0.0269	(9, 10)
$[Co\{Co(aese)_3\}_2]^{3+}$	2041 (16.7)	23440 (33.5)	0.0871	(9, 10)
$[\{Co(aese)_3\}_4Zn_3Cl]^{5+}$	1445 (16.8)	77430 (36.4)	0.0187	**1**
$[\{Co(aese)_3\}_4Zn_4O]^{6+}$	1380 (16.8)	77630 (36.2)	0.0178	**2, 3**
fac(S)-$[Co(aet)_3]$	331 (17.3)	20890 (36.5)	0.0158	(6)
$[Co\{Co(aet)_3\}_2]^{3+}$	2188 (18.4)	25120 (36.2)	0.0871	(1b)
$[\{Co(aet)_3\}_4Zn_4O]^{6+}$	1445 (17.7)	63100 (38.0)	0.0229	(6)
fac(S)-$[Co(\text{L-cys})_3]^{3-}$	347 (17.2)	24550 (37.0)	0.0141	(18)
$[Co\{Co(\text{L-cys})_3\}_2]^{3-}$	2630 (17.8)	30200 (35.3)	0.0871	(19)
fac(S)-$[Rh(\text{L-cys})_3]^{3-}$	794 (25.4)	35480 (43.1)	0.0222	(2b)
$[\{Rh(aese)_3\}_4Zn_4O]^{6+}$	3236 (25.9)	120200 (43.5)	0.0269	**4**

a) The ε_{I} and $\varepsilon_{\mathrm{CT}}$ are the optical densities at the absorption maxima of the lower d–d transition and higher chalcogen-to-cobalt charge transfer bands, respectively. b) The ε value and wave number (in parentheses) are given in mol^{-1} dm^3 cm^{-1} and 10^3 cm^{-1} respectively.

complexes,[4,6,7)] except that the d–d and CT transition bands shift both to lower energies for the aese complexes, suggesting that the ligand field strength for Se is weaker than that for S.[17)] The CD spectral pattern of $\Delta\Delta\Delta\Delta$-$[\{Co(aese)_3\}_4Zn_4O]^{6+}$ also resembles that of $\Delta\Delta\Delta\Delta$-$[\{Co(aet)_3\}_4Zn_4O]^{6+}$ (Fig. 4 and Table 3).[6)]

The characteristic relationship in intensities was observed among the absorption spectra of the mononuclear, linear-type trinuclear, and T-cage-type octanuclear aet complexes.[6)] The absorption spectra of the linear-type complexes are markedly intensified in the region of 14—32×10^3 cm^{-1} compared with those of the mononuclear complexes, although the intensities of their CT bands at ca. 36×10^3 cm^{-1} coincide with each other. This indicates the incorporation of the CoS_6 chromophore in the linear-type trinuclear complexes in the region of 14—32×10^3 cm^{-1}. On the other hand, the absorption curves of the T-cage-type complex is close to four times that of the mononuclear complex over the whole region, which suggests that the electronic state of facially coordinated sulfur atoms of $[Co(aet)_3]$ is little affected by bridging with Zn(II). The present aese complexes also substantiate those characteristic absorption spectral relations. The absorption spectral deviations in the polynuclear complexes can be characterized by the $\varepsilon_{\mathrm{I}}/\varepsilon_{\mathrm{CT}}$ value as listed in Table 4, where ε_{I} and $\varepsilon_{\mathrm{CT}}$ denote the absorption maxima of the lower d–d transition and higher chalcogen-to-cobalt CT bands in the specified complex respectively. For example, the $\varepsilon_{\mathrm{I}}/\varepsilon_{\mathrm{CT}}$ value is ca. 0.087 for the linear-type trinuclear

Table 5. Redox Potentials[a)] of T-Cage-Type Complexes

Complex	Redox couple	E_{pc}	E_{pa}	$E^{\circ\prime}$ a)	ΔE_p c)
$[\{Co(aet)_3\}_4Zn_4O]^{6+}$ d)	I	−0.44	−0.36	−0.40	0.08
	II	−0.56	−0.48	−0.52	0.08
	III	−0.69	−0.61	−0.65	0.08
	IV	−0.87	−0.79	−0.83	0.08
$[\{Co(aese)_3\}_4Zn_4O]^{6+}$ (**2**, **3**)	I	−0.45	−0.38	−0.42	0.07
	II	−0.59	−0.52	−0.55	0.07
	III	−0.72	−0.65	−0.69	0.07
	IV	−0.90	−0.83	−0.87	0.07
$[\{Co(aese)_3\}_4Zn_3Cl]^{5+}$ (**1**)	I	−0.45	−0.35	−0.40	0.10
	II	−0.58	−0.49	−0.54	0.09
	III	−0.73	−0.65	−0.69	0.08
	IV	−0.91	−0.83	−0.87	0.08

a) In V vs. Ag/AgCl (3 mol dm^{-3} NaCl) from cyclic voltammetry; at 22° C in water (0.1 mol dm^{-3} $NaNO_3$) with scan rate 50 mV s^{-1}. b) $E^{\circ\prime}=(E_{pa}+E_{pc})/2$. c) $\Delta E=|E_{pc}-E_{pa}|$. d) Ref. 6.

Co(III) complexes with the aese, aet, and L-cysteinate ligands, while 0.02—0.03 for the mononuclear and T-cage-type octanuclear complexes (Table 4). A similar argument seems to be also applied to the Rh(III) complexes.

The empirical criterion mentioned above is applicable to the assignment of the aese dark green complex **1**. The $\varepsilon_1/\varepsilon_{CT}$ value of **1** is about 0.018, which agrees well with that (0.018) of **2** (Table 4). The plasma emission spectral analysis indicates that **1** contains Co and Zn in a ratio of 4 : 3, and **2** contains 4 : 4. Although the absorption spectrum of **1** resembles that of **2**, the absorption band at ca. 20×10^3 cm^{-1} of **1** is somewhat broader than the corresponding band of **2** (Fig. 4), and **1** exhibits larger spectral change with time than the latter complexes. Similar absorption spectral changes were observed for the T-cage-type heptanuclear complexes with "defective" $[Zn_3O]^{4+}$ and $[Zn_3Br]^{5+}$ cores.[5,6] Taking these facts and the formation reactions into consideration, it is probable that **1** is the precursory T-cage-type Se-bridged complex, $[\{Co(aese)_3\}_4Zn_3Cl]^{5+}$, with a "defective" core $[Zn_3Cl]^{5+}$. This assignment is supported by the electrochemical properties (vide infra).

Electrochemistry. The electrochemical experiments were performed in a 0.1 mol dm^{-3} $NaNO_3$ aqueous solution at a glassy carbon electrode. The cyclic voltammogram of $[\{Co(aese)_3\}_4Zn_4O]^{6+}$ initiated at 0.0 V with a negative potential scan yields four consecutive reduction waves and coupled four oxidation waves (Fig. 5 and Table 5). No other redox couple is observed in the potential region of +0.8—−1.2 V (vs. Ag/AgCl). The peak current is approximately proportional to the square root of the scan rate. At a scan rate of 50 mV s^{-1}, the ratio of cathodic to anodic peak current is approximately unity and the observed peak separation ($E_{pc}-E_{pa}$) is 70 mV for each redox couple. These results establish that the four redox processes (I to IV in Table 5) are electrochemically quasi-reversible. A similar trend was also observed for the corresponding aet complex.[6]

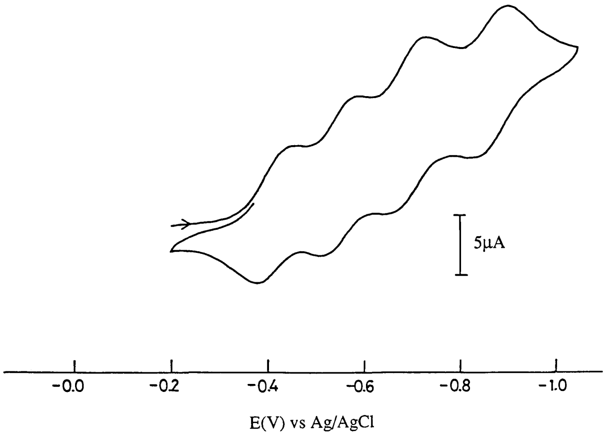

Fig. 5. Cyclic voltammogram of 1.0 mmol dm^{-3} $[\{Co(aese)_3\}_4Zn_4O]^{6+}$ in 0.1 mol dm^{-3} aqueous solution of $NaNO_3$. The scan rate is 50 mV s^{-1}.

Therefore, the four redox processes can be assigned as the step-wise reactions for four kinds of the Co^{III}/Co^{II} couples. It is noted that the $E^{\circ\prime}$ values of the aese complex are somewhat negative for those of the aet complex, but their redox systems are quite similar to each other.

The cyclic voltammograms of **1** gives also four consecutive redox couples (I to IV in Table 5), and their $E^{\circ\prime}$ values are almost the same as those of **2**. Each of four waves is also quasi-reversible but each peak becomes more broad than those of **2**. These suggest that **1** is more unstable than **2**, but they take a polynuclear structure containing four $[Co(aese)_3]$ subunits similar to **2**.

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