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Preparation of Polynuclear (Diamine)telluratocobalt(III) Complexes

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Penta- and hexa-nuclear condensates of mono(diamine)cobalt(III) complexes and tellurates have been prepared and some of the optically active isomers separated. They are $[\{Co(TeO_6H_4)(diamine)\}(Te_2O_{10})\{Co(TeO_6H_4)(diamine)\}]^{6-}$ (brown complexes) and $[\{Co(TeO_6H_4)(diamine)\}(TeO_6)\{Co(TeO_6H_4)(diamine)\}]^{4-}$ (blue complexes), where diamine=ethylenediamine, (*R*)-(−)-propylenediamine, and (*R*,*R*)-(−)-1,2-cyclohexanediamine. The structures have been determined from the visible and ultraviolet absorption and circular dichroism spectra; the electrostatic repulsion between cobalt(III) and tellurium(VI) atoms is considered in detail.

Continued efforts have been made to synthesize polynuclear complexes of a hybrid type between a metal chelate and a heteropoly condensed complex. Several cobalt(III) compounds such as $[Co_2(Te_2O_{10}H_4)(en)_4]Cl_2$,[1] $H_3[Co_4I_3O_{18}(en)_3]$,[2] and $Na_5[Co(Nb_6O_{19})(dien)]$[3] were reported in previous papers. The former tetranuclear complex $[Co_2(Te_2O_{10}H_4)(diamine)_4]^{2+}$ prepared by dehydration condensation of a binuclear complex $[Co(TeO_6H_4)(diamine)_2]^+$ has a chain structure consisting of two bis(diamine)cobalt(III) and two tellurate(VI) octahedra. The present report is concerned with the preparation of similar polynuclear condensates of mono(diamine)cobalt(III) complexes and tellurates. Some pentanuclear $[Co_2Te_3O_{18}H_8(diamine)_2]^{4-}$ and hexanuclear $[Co_2Te_4O_{22}H_8(diamine)_2]^{6-}$ complexes have been obtained which also have chain structures consisting of five or six octahedra sharing edges. Ordinary compact structures, which have been found in iso- and hetero-poly oxoanions such as $Nb_6O_{19}^{8-}$ and $[CoMo_6O_{24}H_6]^{3-}$, are unfavorable for the present complexes. Reasonable chain structures have been inferred by considering the need to avoid electrostatic repulsion between cobalt(III) and tellurium(VI) atoms. The bidentate diamine ligands used are ethylenediamine (en), (*R*)-(−)-propylenediamine (*l*-pn), and (*R*,*R*)-(−)-1,2-cyclohexanediamine (*l*-chxn).

Experimental

Preparation, Separation, and Optical Resolution of Complexes. *(1)* $Li_4[\{Co(TeO_6H_4)(en)\}(TeO_6)\{Co(TeO_6H_4)(en)\}]\cdot 6H_2O$ *(Blue en Complex)*: A solution of 2.3 g (10 mmol) of $Te(OH)_6$ in 20 cm³ of water was added to a solution of 1.3 g (5 mmol) of *trans*(NH_3)-$[CoCl_2(NH_3)_2(en)]Cl\cdot H_2O$[4] in 15 cm³ of water. To the mixture was added a solution of 0.8 g (20 mmol) of sodium hydroxide in 10 cm³ of water. The resulting solution was stirred mechanically at about 65 °C until the evolution of ammonia ceased. After being cooled in an ice-bath, the solution was poured into a column (3 cm × 70 cm) of anion exchanger (QAE Sephadex A-25, Cl^- form). The adsorbed band was eluted with 0.2 mol dm^{-3} lithium chloride solution (pH 10 by 1 mol dm^{-3} lithium hydroxide); during that time the column was cooled by flushing it with ice-water. Several red and blue bands eluted rapidly. To the combined eluates was added a large amount of acetone. The precipitate was then separated by a centrifuge, washed a few times with acetone, and dried in a stream of air. This solid was dissolved in a small amount of water and the solution was poured into a column of the type mentioned above, and the adsorbed band was eluted with the same eluting reagent. Three colored bands, purple, blue, and brown, were eluted in this order. The first purple eluate was discarded in this work. The last brown eluate was preserved for the treatment in (2) to obtain another complex. The blue middle eluate was concentrated at 15 °C in a rotary evaporator, and a large amount of methanol–acetone (1:10) mixture was added to the concentrated solution. After the mixture had been kept in a refrigerator overnight, the blue precipitate was collected by a centrifuge, recrystallized at 0 °C from lithium hydroxide solution (pH 10) by adding methanol–acetone mixture, and washed repeatedly with methanol and acetone. Found: C, 4.56; H, 3.45; N, 5.32; Co, 11.2; Te, 36.4%. Calcd for $Li_4[\{Co(TeO_6H_4)(en)\}(TeO_6)\{Co(TeO_6H_4)(en)\}]\cdot 6H_2O$: C, 4.78; H, 3.39; N, 5.23; Co, 10.5; Te, 36.3%. Cobalt was weighed as Co_3O_4 and tellurium as the metal.

(2) $Li_6[\{Co(TeO_6H_4)(en)\}(Te_2O_{10})\{Co(TeO_6H_4)(en)\}]\cdot 7H_2O$ *(Brown en Complex)*: The brown eluate from the chromatography in (1) was concentrated at about 20 °C in a rotary evaporator, and a large volume of methanol–acetone mixture was added to the concentrated solution. The brown product was isolated by a similar method to that used in (1). Found: C, 3.74; H, 2.74; N, 4.19; Co, 8.8; Te, 38.3%. Calcd for $Li_6[\{Co(TeO_6H_4)(en)\}(Te_2O_{10})\{Co(TeO_6H_4)(en)\}]\cdot 7H_2O$: C, 3.76; H, 3.00; N, 4.39; Co, 9.2; Te, 40.0%.

(3) $K_4H_2[\{Co(TeO_6H_4)(en)\}(Te_2O_{10})\{Co(TeO_6H_4)(en)\}]\cdot 4H_2O$: The brown en complex obtained in *(2)* was dissolved in 0.001 mol dm^{-3} potassium hydroxide solution, and to this was added an appropriate amount of potassium chloride. After the resulting solution had been kept in a refrigerator overnight, the product was separated by filtration, washed a few times with cold water, methanol, and acetone, and dried in a desiccator over calcium chloride. Found: C, 3.59; H, 2.64; N, 4.20%. Calcd for $K_4H_2[\{Co(TeO_6H_4)(en)\}(Te_2O_{10})\{Co(TeO_6H_4)(en)\}]\cdot 4H_2O$: C, 3.39; H, 2.56; N, 4.19%.

(4) $Li_4[\{Co(TeO_6H_4)(l\text{-}pn)\}(TeO_6)\{Co(TeO_6H_4)(l\text{-}pn)\}]\cdot 5.5H_2O$ *(Blue* l*-pn Complex) and* $Li_6[\{Co(TeO_6H_4)(l\text{-}pn)\}(Te_2O_{10})\{Co(TeO_6H_4)(l\text{-}pn)\}]\cdot 9H_2O$ *(Brown* l*-pn Complex)*: These were obtained by almost the same procedure as for the corresponding en complexes. A solution of 2.3 g (10 mmol) of $Te(OH)_6$ in 15 cm³ of water was added to a solution of 1.37 g (5 mmol) of *trans*(NH_3)-$[CoCl_2(NH_3)_2(l\text{-}pn)]Cl\cdot 4H_2O$[4] in 25 cm³ of water, and to the mixture was added a solution of 0.8 g (20 mmol) of sodium hydroxide in 15 cm³ of water. The solution was concentrated to about 15 cm³ at 70 °C with mechanical stirring, and poured into a column similar to that used in *(1)*. The column chromatography showed two colored bands, blue and brown, in this order. The blue and brown complexes were isolated as described in (1). Found: C, 6.68; H, 3.67; N, 5.23%. Calcd for $Li_4[\{Co(TeO_6H_4)(l\text{-}pn)\}(TeO_6)\{Co(TeO_6H_4)(l\text{-}pn)\}]\cdot 5.5H_2O$: C, 6.72; H, 3.67; N, 5.23%. Found: C, 5.41; H, 3.23; N, 4.16%. Calcd for $Li_6[\{Co(TeO_6H_4)(l\text{-}pn)\}(Te_2O_{10})\{Co(TeO_6H_4)(l\text{-}pn)\}]\cdot 9H_2O$: C, 5.38; H,

3.47; N, 4.18%.

The latter complex was dissolved in a small amount of water, and the solution was treated by column chromatography as described above. The adsorbed band separated gradually into two brown bands, 1 and 2 in this order, when eluted with 0.15 mol dm^{-3} lithium chloride solution (pH 10.5 by 1 mol dm^{-3} lithium hydroxide). Both eluates showed a similar absorption spectrum to that of the unseparated brown *l*-pn complex. The brown *l*-pn 1 and 2 complexes have $\Delta\varepsilon=+0.44$ and $+1.72$, respectively, at the Na D line.

(5) $Li_6[\{Co(TeO_6H_4)(l\text{-}chxn)\}(Te_2O_{10})\{Co(TeO_6H_4)(l\text{-}chxn)\}]\cdot 12H_2O$ *(Brown* l-*chxn Complex):* A solution in 15 cm^3 of water was made of 1.57 g (5 mmol) of *trans*(Cl)-[$CoCl_2(NH_3)_2$(*l*-chxn)]Cl, which was obtained according to the method[4] for the corresponding en complex using *l*-chxn instead of en. To this solution was added first a solution of 2.3 g (10 mmol) of $Te(OH)_6$ in 20 cm^3 of water and then a solution of 0.8 g (20 mmol) of sodium hydroxide in 15 cm^3 of water. The resulting solution was stirred mechanically at 60 °C for 3 h, and was then poured into a column similar to that in (*1*). The column chromatography showed one brown band predominantly. Found: C, 9.53; H, 3.84; N, 3.73; Te, 33.4%. Calcd for $Li_6[\{Co(TeO_6H_4)(l\text{-}chxn)\}(Te_2O_{10})\{Co(TeO_6H_4)(l\text{-}chxn)\}]\cdot 12H_2O$: C, 9.79; H, 4.11; N, 3.73; Te, 34.6%.

(6) Optical Resolution of the Blue and Brown en Complexes: A solution of 0.012 g of Λ-$(+)_{589}$-[$Co(en)_3$]$Br_3\cdot H_2O$ in 10 cm^3 of water was added gradually to a solution of 0.15 g of the blue en complex in 20 cm^3 of lithium hydroxide solution of pH 11 at about 5 °C. After the resulting solution had been kept in a refrigerator overnight, the yellow green diastereomer was separated by filtration, and washed with cold water a few times. It was difficult to replace the $(+)_{589}$-[$Co(en)_3$]$^{3+}$ cation of the less soluble diastereomer by an ordinary cation such as K^+ or Na^+. Then, to the filtrate containing the more soluble diastereomer was added an appropriate amount of cation exchanger (SP Sephadex C-25, Na^+ or K^+ form) to remove $(+)_{589}$-[$Co(en)_3$]$^{3+}$. The cation exchanger was filtered and CD of the filtrate was measured. The blue en complex in this solution has $\Delta\varepsilon=-0.31$ at the Na D line.

The optical resolution of the brown en complex was made by the same procedure as that used for the blue en complex, using 0.13 g of the brown en complex and 0.024 g of Λ-$(+)_{589}$-[$Co(en)_3$]$Br_3\cdot H_2O$; the CD of the filtrate was measured after removing $(+)_{589}$-[$Co(en)_3$]$^{3+}$. The brown en complex has $\Delta\varepsilon=-0.52$ at the Na D line.

(7) $[\{Co(dien)(H_2O)\}(Te_2O_{10}H_4)\{Co(dien)(H_2O)\}]Cl_2\cdot 5H_2O$ *(Tetranuclear dien Complex):* A solution of 1.15 g (5 mmol) of $Te(OH)_6$ in 10 cm^3 of water was added, with mechanical stirring, to a solution of 1.35 g (5 mmol) of *mer*-[$CoCl_3$(dien)] in 20 cm^3 of water at 60—70 °C (dien=diethylenetriamine). A solution of 1.12 g (20 mmol) of potassium hydroxide in 10 cm^3 of water was added to the solution by portions. After being stirred mechanically at 65 °C for *ca.* 3 h, the mixture was kept in a refrigerator overnight. The light red precipitate was filtered, and to the filtrate was added an appropriate amount of acetone. After the solution had been kept in a refrigerator overnight again, the red oily precipitate was separated by decanting the supernatant liquid. The product was recrystallized from a small amount of cold water by adding acetone, and washed with a methanol–water (5:1) mixture, methanol, and ethanol. Found: C, 10.52; H, 4.38; N, 9.22; Te, 28.0%. Calcd for $[\{Co(dien)(H_2O)\}(Te_2O_{10}H_4)\{Co(dien)(H_2O)\}]Cl_2\cdot 5H_2O$: C, 10.62; H, 4.47; N, 9.29; Te, 27.8%.

Measurements. The visible and ultraviolet absorption spectra were taken on a Shimadzu UV-200 spectrophotometer. The CD spectra were recorded on a JASCO MOE-1 spectropolarimeter. The absorption and CD measurements of the present complexes (lithium salts) were made in aqueous lithium hydroxide solutions (pH 10) over the concentration range 10^{-3} to 10^{-5} mol dm^{-3} at *ca.* 10 °C. The ^{13}C nuclear magnetic resonance spectra were measured in deuterium oxide with a Varian XL-100-15 NMR spectrometer.

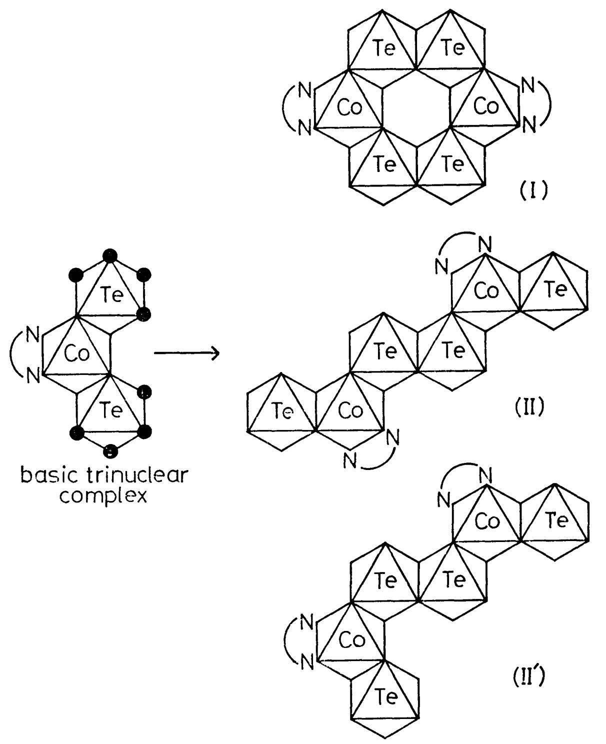

Fig. 1. Some condensation products of a basic trinuclear complex [$Co(TeO_6H_4)_2$(diamine)]$^-$. Hydroxo lignads of the basic complex are marked by circles.

Results and Discussion

The brown and blue complexes were separated by column chromatography from the reaction mixture of *trans*(NH_3)- or *trans*(Cl)-[$CoCl_2(NH_3)_2$(diamine)]$^+$, $Te(OH)_6$, and alkali in a proper molar ratio at 60—70 °C. Because all the complexes, particularly blue ones, were unstable in solution at room temperature, the solutions were carefully treated below 15 °C. The yields of blue complexes were much less than those of the brown ones.

The Brown Complexes. The composition M_6-[$Co_2Te_4O_{22}H_8$(diamine)$_2$] was confirmed by the preparative method and elemental analysis. A previous paper[1] reported that two binuclear complexes [$Co(TeO_6H_4)$(diamine)$_2$]$^+$ were prepared from the reaction mixture of *cis*-[$CoCl_2$(diamine)$_2$]Cl, $Te(OH)_6$, and alkali, the corresponding tetranuclear complexes [$Co_2(Te_2O_{10}H_4)$(diamine)$_2$]$^{2+}$ being obtained by dehydration condensation of the coordinated orthotellurate moieties of the binuclear complexes. Since the starting cobalt(III) complex used in the present study has only one diamine ligand, trinuclear complexes [$Co(TeO_6H_4)_2$(diamine)]$^-$ and hexanuclear condensates [$Co_2Te_4O_{22}H_8$(diamine)$_2$]$^{6-}$ may be formed in the

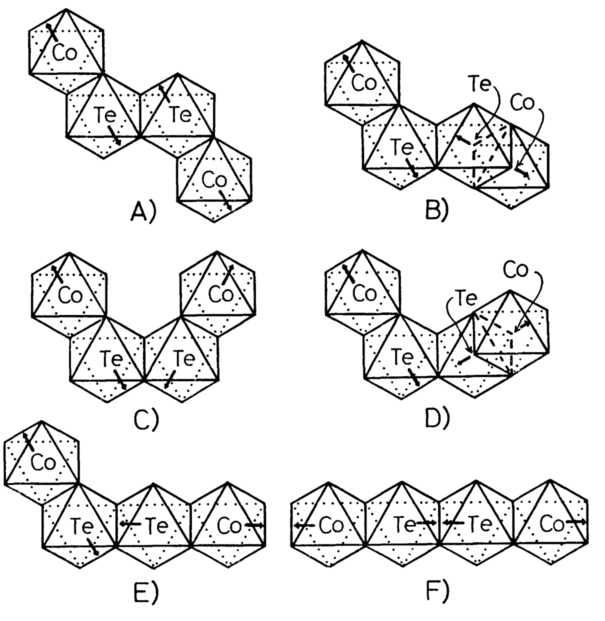

Fig. 2. Isomerism of the Co–Te–Te–Co tetra-octahedra.

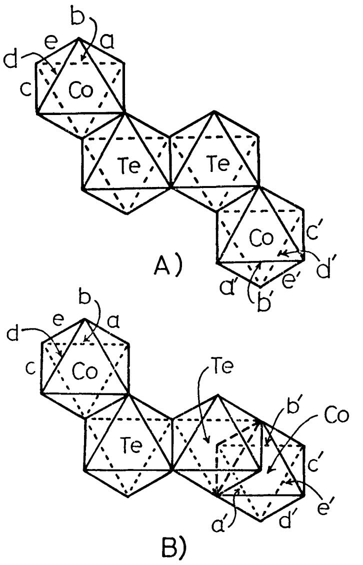

Fig. 3. Numbering for the edges of structures A) and B).

TABLE 1. POSSIBLE STRUCTURES OF HEXA-OCTAHEDRA DERIVED FROM A) OR B) STRUCTURE

They are denoted by the edges to which two more TeO_6 octahedra are added in Fig. 3.

	a'	b'	c'	d'	e'
a	aa'				
b	ba'	bb'			
c	ca'	cb'	cc'		
d	da'	db'	dc'	dd'	
e	ea'	eb'	ec'	ed'	ee'

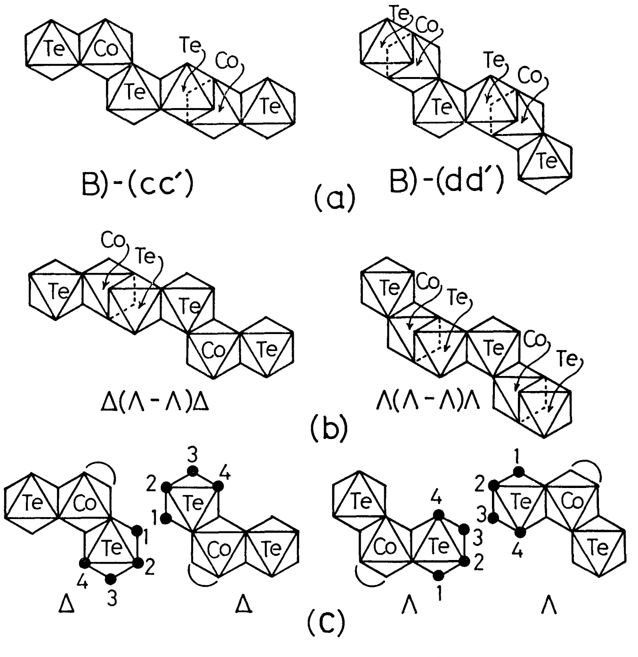

Fig. 4. Proposed structures of $[\{Co(TeO_6H_4)(diamine)\}(Te_2O_{10})\{Co(TeO_6H_4)(diamine)\}]^{6-}$.
(a) B)-(cc') and B)-(dd') structures. (b) Drawn along other direction. (c) Numbering of the apexes of *Δ*- and *Λ*-$[Co(TeO_6)_2(diamine)]$ groups.

reaction mixture. As is seen in Fig. 1, when the condensation occurs by edge-sharing in two tellurate ligands of each trinuclear complex simultaneously, only a ring structure (I) is possible. This structure has a C_{2h} symmetry unsuitable for the brown complexes optically resolved. When it occurs in one tellurate ligand of each trinuclear complex, many kinds of hexanuclear chain structures, such as (II) and (II'), are possible. The isomerism of this type of chain structure (Te–Co–Te–Te–Co–Te hexa-octahedra) can be formally treated as follows by starting from a tetranuclear Co–Te–Te–Co tetra-octahedra structure. For the tetra-octahedra, the six structures shown in Fig. 2 are possible. The adjacent tellurium(VI) and cobalt(III) atoms repulse each other electrostatically in the directions of the marked arrows, and hence the tellurium(VI)-tellurium(VI) repulsion increases in the order A)<B)<D)<C)<E)<F). Furthermore, because the two cobalt(III) octahedra are more separated for A) and B) than for C) and D), the former two have a smaller repulsion between the cobalt(III) octahedra than the latter two. Since this kind of electostatic repulsion should have the primary influence upon the structure of polynuclear complexes,[5] the structures A) and B) are probable for the tetra-octahedra of present complexes. Thus far only the structure A) has been found in $[Co(diamine)_2(Te_2O_{10}H_4)Co(diamine)_2]^{2+}$ (diamine=en and *l*-chxn)[1] and $[(en)_2Cr(OH)_2Cr(en)(OH)_2Cr(en)(OH)_2Cr(en)_2]^{6+}$.[6] As shown in Fig. 3, the edges of two cobalt(III) octahedra in the structure A) (C_i symmetry) and B) (C_2 symmetry) are named a,b,c,d,e,a',b',c',d', and e'. In the cases of both structures, A) and B), fifteen hexa-octahedra structures can be formed by adding two more TeO_6 octahedra, as shown in Table 1. Among the thirty structures, A)-(cc'), -(dd'), -(dc'), B)-(cc'), -(dd'), and -(dc') are expected to have less electrostatic

Table 2. Absorption data in the region of 14000—35000 cm^{-1}

Complex	Color	$\sigma_{\max}$[a] (log ε)[b]		
		1st band	2nd band	CT band
$[\{Co(TeO_6H_4)(en)\}(TeO_6)\{Co(TeO_6H_4)(en)\}]^{4-}$	Blue	17.7 (2.33)	25 sh (2.6)	30 sh (3.2)
$[\{Co(TeO_6H_4)(l\text{-pn})\}(TeO_6)\{Co(TeO_6H_4)(l\text{-pn})\}]^{4-}$	Blue	17.4 (2.38)	25 sh (2.6)	30 sh (3.4)
$[\{Co(TeO_6H_4)(en)\}(Te_2O_{10})\{Co(TeO_6H_4)(en)\}]^{6-}$	Brown	17.6 (2.43)	c)	28 sh (3.4)
$[\{Co(TeO_6H_4)(l\text{-pn})\}(Te_2O_{10})\{Co(TeO_6H_4)(l\text{-pn})\}]^{6-}$	Brown	17.7 (2.50)	c)	28 sh (3.4)
$[\{Co(TeO_6H_4)(l\text{-chxn})\}(Te_2O_{10})\{Co(TeO_6H_4)(l\text{-chxn})\}]^{6-}$	Brown	17.5 (2.50)	c)	28 sh (3.5)

a) In units of 10^3 cm^{-1}. b) The ε values are in units of mol^{-1} dm^3 cm^{-1}. c) The second absorption band is overlapped by the CT band at 28000 cm^{-1}.

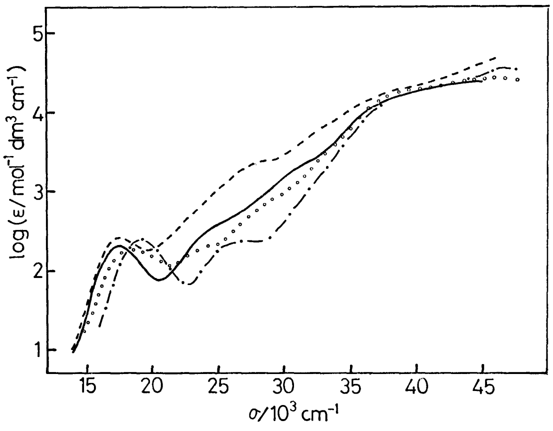

Fig. 5. Absorption spectrum of blue en complex $[\{Co(TeO_6H_4)(en)\}(TeO_6)\{Co(TeO_6H_4)(en)\}]^{4-}$ (——), brown en complex $[\{Co(TeO_6H_4)(en)\}(Te_2O_{10})\{Co(TeO_6H_4)(en)\}]^{6-}$ (----), $[\{Co(dien)(H_2O)\}(Te_2O_{10}H_4)\{Co(dien)(H_2O)\}]^{2+}$ (∘∘∘∘), and $[Co(en)_2(Te_2O_{10}H_4)Co(en)_2]^{2+}$ (—·—).

repulsion between cobalt(III) and tellurium(VI) atoms in the local Te–Co–Te–Te tetra-octahedra units, since two such local tetra-octahedra units of these six structures have the structure A) or B). Because the brown en complex was optically resolved, the structures A)-(cc′) and -(dd′), which have a center of symmetry, are excluded from consideration. The ^{13}C-NMR spectrum of the brown en complex showed only a band at *ca.* 42 ppm with respect to TMS. Thus, the structures A)-(dc′) and B)-(dc′), which have no element of symmetry, are omitted. In this way it is concluded that the most probable structure is B)-(cc′) or -(dd′) of C_2 symmetry (Fig. 4-a). As is seen in Figs. 4-b and -c, a $\Delta(\Lambda\text{-}\Lambda)\Delta$-B)-(cc′) isomer is formed by condensing the apexes 1 and 1 as well as 2 and 2 of two Δ-$[Co(TeO_6)_2(diamine)]$ groups, and the enantiomer $\Lambda(\Delta\text{-}\Delta)\Lambda$-B)-(cc′) from two Λ-$[Co(TeO_6)_2(diamine)]$ groups. A $\Lambda(\Lambda\text{-}\Lambda)\Lambda$-B)-(dd′) isomer is formed by condensing the apexes 1 and 1 as well as 3 and 3 of two Λ-$[Co(TeO_6)_2(diamine)]$ groups, and the enantiomer $\Delta(\Delta\text{-}\Delta)\Delta$-B)-(dd′) from two Δ-$[Co(TeO_6)_2(diamine)]$ groups.

The absorption spectrum of brown en complex is characteristic of a *cis*-CoN_2O_4 type complex and similar to that of $[Co(CO_3)_2(en)]^-$ ($\sigma_{\max}$=17500 and 25600 cm^{-1})[7] in the d-d absorption band region (Fig. 5). The first absorption band (at 17600 cm^{-1}) is located at a lower energy than those of $[Co(en)_2(Te_2O_{10}H_4)Co(en)_2]^{2+}$ (at 19200 cm^{-1}) of the *cis*-CoN_4O_2 type and $[\{Co(dien)(H_2O)\}(Te_2O_{10}H_4)\{Co(dien)(H_2O)\}]^{2+}$ (at 18500 cm^{-1}) of the *mer*-CoN_3O_3 type. The second absorption band is obscured by overlapping with a strong absorption band at about 28000 cm^{-1} (long ε=3.4). The latter band is not observed for the ditellurate $[Te_2O_{10}H_{8-n}]^{n-}$ and orthotellurate $[TeO_6H_{6-n}]^{n-}$ ions, and also does not appear for $[Co(ox)_x(en)_{3-x}]^{n\pm}$ (x=1[8] and 2[9]) or $[Co(CO_3)_x(en)_{3-x}]^{n\pm}$ (x=1[8] and 2[7]). The strong band shifts to higher energy in the order of complex types: *cis*-CoN_2O_4 (at 28000 cm^{-1})→*mer*-CoN_3O_3 (at *ca.* 29000 cm^{-1})→*cis*-CoN_4O_2 (at *ca.* 33000 cm^{-1}). These bands are assigned to charge-transfer (CT) transitions from the coordinated orthotellurate or ditellurate oxygen ions to cobalt(III). Table 2 shows that the same absorption behavior is observed for all the complexes of the brown type.

The CD spectra of brown en and *l*-pn complexes are shown in Figs. 6 and 7. The CD curve of $(-)^{CD}_{589}$ brown en complex, which was obtained from the more soluble diastereomer with Λ-$(+)_{589}$-$[Co(en)_3]^{3+}$, consists of a main CD band with negative sign and a weak one with positive sign (at lower energy side) in the first absorption band region (Fig. 7 and Table 3). Since the Λ-$[Co(CO_3)_2(en)]^-$ and Λ-$[Co(ox)_2(en)]^-$ complexes show a main CD band with positive sign in this region,[7,10] the $(-)^{CD}_{589}$ brown en complex will have Δ-configuration in regard to skew pairs of the orthotellurate and ethylenediamine chelate rings about local cobalt(III) atoms (see Fig. 4), provided that the CD of this complex in the first absorption band region comes mainly from chiral configurations about local cobalt(III) atoms. Thus, the configuration of $(-)^{CD}_{589}$ brown en complex is tentatively assigned to be $\Delta(\Lambda\text{-}\Lambda)\Delta$-B)-(cc′) or $\Delta(\Delta\text{-}\Delta)\Delta$-B)-(dd′).

Two diastereomeric isomers, 1 and 2, of $[\{Co(TeO_6H_4)(l\text{-pn})\}(Te_2O_{10})\{Co(TeO_6H_4)(l\text{-pn})\}]^{6-}$ were separated by column chromatography. The configurational and vicinal CD contributions are separable for many kinds of cobalt(III) complexes by utilizing an additivity rule for CD curves of a pair of diastereomeric isomers.[11] The calculated Δ-configurational CD curve agrees well with the observed CD curve of Δ-enantiomer of brown en complex (Fig. 7). The configurational CD ($\Delta\varepsilon_{ext}$=+0.64 at 17000 cm^{-1}) is weaker than the vicinal CD ($\Delta\varepsilon_{ext}$=+1.08 at 17000 cm^{-1}). From the sign patterns of isolated config-

Table 3. CD data in the region of 14000—35000 cm^{-1}

Complex	$\sigma_{ext}$$^{a)}$ ($\Delta\varepsilon$)$^{b)}$		
	1st band	2nd band	CT band
$(-)^{CD}_{589}$-$[\{Co(TeO_6H_4)(en)\}(TeO_6)\{Co(TeO_6H_4)(en)\}]^{4-}$	15.0 (+0.08) 17.2 (−0.32) 19.9 (+0.02)	23.5 (−0.03)	29.5 (+0.15)
$[\{Co(TeO_6H_4)(l\text{-pn})\}(TeO_6)\{Co(TeO_6H_4)(l\text{-pn})\}]^{4-}$ c)	15.5 (−0.15) 17.2 (+0.76) 20.0 (−0.02)	24.5 (+0.14)	30.0 (+0.17)
$(-)^{CD}_{589}$-$[\{Co(TeO_6H_4)(en)\}(Te_2O_{10})\{Co(TeO_6H_4)(en)\}]^{6-}$	15.0 (+0.13) 17.2 (−0.54)	23.5 (−0.14)	29.0 (+0.40) 30.5 (+0.49)
$[\{Co(TeO_6H_4)(l\text{-chxn})\}(Te_2O_{10})\{Co(TeO_6H_4)(l\text{-chxn})\}]^{6-}$ c)	15.5 (−0.17) 19.1 (+0.74)	23.5 (+0.13)	29.0 (+0.45)
$[\{Co(TeO_6H_4)(l\text{-pn})\}(Te_2O_{10})\{Co(TeO_6H_4)(l\text{-pn})\}]^{6-}$: BP1	15.6 (−0.31) 17.2 (+0.51) 19.2 (−0.15)	22.0 (+0.14) 23.5 (+0.17)	28.0 (+0.20)
: BP2	15.3 (−0.61) 17.2 (+1.81) 19.4 (−0.13)	23.8 (+0.51)	28 sh (−0.8)

a) In units of 10^3 cm^{-1}. b) The $\Delta\varepsilon$ values are given in units of mol^{-1} dm^3 cm^{-1}. c) Unresolved complex.

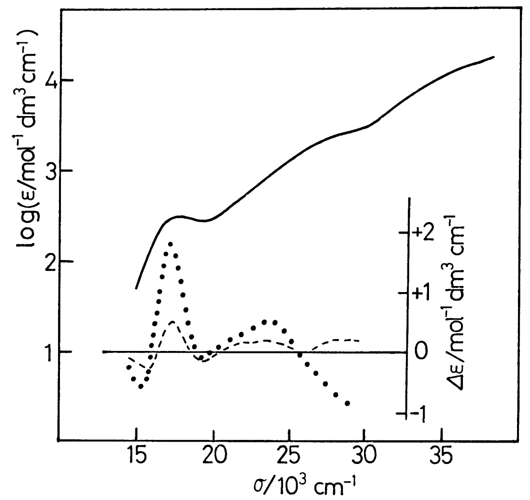

Fig. 6. Absorption spectrum of unresolved $[\{Co(TeO_6H_4)(l\text{-pn})\}(Te_2O_{10})\{Co(TeO_6H_4)(l\text{-pn})\}]^{6-}$ (——) and CD spectra of the resolved brown l-pn 1 (----) and and 2 (••••) diastereomeric isomers.

urational CD curves it is likely that the isomer 1 has $\Delta(\Lambda\text{-}\Lambda)\Delta$-B)-(cc′) or $\Delta(\Delta\text{-}\Delta)\Delta$-B)-(dd′) configuration and the isomer 2 $\Lambda(\Delta\text{-}\Delta)\Lambda$-B)-(cc′) or $\Lambda(\Lambda\text{-}\Lambda)\Lambda$-B)-(dd′).

The Blue Complexes. These were obtained as a by-product in the preparation of the brown complexes. They have the chemical composition $M_4[Co_2Te_3O_{18}H_8(diamine)_2]$ as confirmed by the preparative procedure and elemental analysis. It is supposed that the complexes have a Te–Co–Te–Co–Te penta-octahedra structure. The isomerism of the penta-octahedra can be formally treated by edge-sharing of a TeO_6 octahedron with each outer cobalt(III) octahedron of a Co–Te–Co tri-octahedra structure. Then, from the same consideration as used for the brown en complex, the most probable structure is (I) or (II) of C_2 symmetry (Fig. 8). Because these structures have no axis of rotatory reflection, a pair of enantiomers are possible. In fact, the blue en complex was optically resolved. Two diastereomeric isomers are possible for the blue l-pn complex, but the chromatographic separation was unsuccessful. The absorption spectrum of blue en complex is similar to that of the brown en complex in the d-d absorption band region (Fig. 5 and Table 2.) The second absorption band appears as a shoulder because of overlapping with the CT absorption band at about 30000 cm^{-1} (log ε=3.2). The CT band is at higher energy than that for the brown complex. As is shown in Fig. 9 and Table 3, the CD pattern of $(-)^{CD}_{589}$ blue en complex is similar to that of $(-)^{CD}_{589}$ brown en complex (Fig. 7), though the former shows three CD

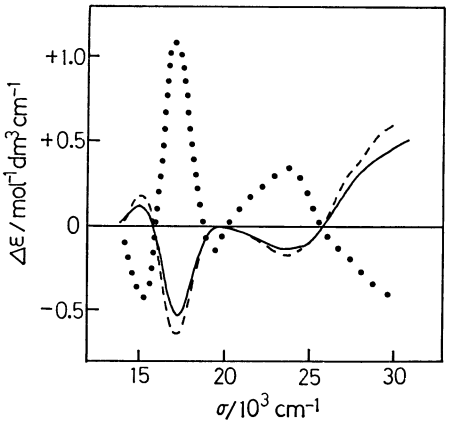

Fig. 7. Calculated configurational (----) and vicinal (••••) CD curves of $[\{Co(TeO_6H_4)(l\text{-pn})\}(Te_2O_{10})\{Co(TeO_6H_4)(l\text{-pn})\}]^{6-}$, and observed CD curve (——) of $(-)^{CD}_{589}$-$[\{Co(TeO_6H_4)(en)\}(Te_2O_{10})\{Co(TeO_6H_4)(en)\}]^{6-}$.

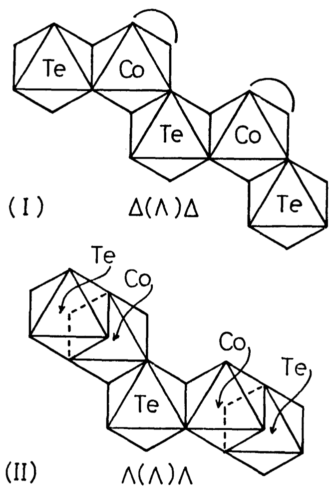

Fig. 8. Proposed structures of $[\{Co(TeO_6H_4)(diamine)\}(TeO_6)\{Co(TeO_6H_4)(diamine)\}]^{4-}$.

bands with positive, negative, and positive signs from the lower energy side in the first absorption band region. As the sign of the main CD band is negative, the configurations of local cobalt(III) octahedra will be Δ. Thus, $(-)^{\mathrm{CD}}_{589}$ blue en complex is tentatively assigned to be $\Delta(\Delta)\Delta$-(I) or $\Delta(\Delta)\Delta$-(II) (see Fig. 8).

Tetranuclear dien Complex. This complex was isolated from the reaction mixture of *mer*-$[CoCl_3(dien)]$, $Te(OH)_6$, and alkali in a proper molar ratio at 60—70 °C. In this case, only the tetranuclear complex was obtained, which corresponds to a condensate of the binuclear complex $[Co(TeO_6H_4)(dien)(H_2O)]^+$. The second d-d absorption band is obscured by overlapping with a strong CT absorption band at 29000 cm^{-1} ($\log \varepsilon = 2.9$). The CT band is located at lower energy than that for the blue diamine complexes (Fig. 5). This reflects the existence of Te_2O_{10} unit in the structure. As the first d-d absorption band is broad, the terdentate dien ligand may be coordinated meridionally.

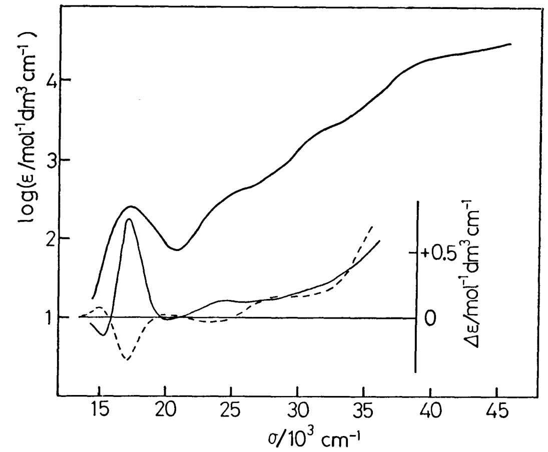

Fig. 9. Absorption and CD spectra (——) of unresolved $[\{Co(TeO_6H_4)(l\text{-}pn)\}(TeO_6)\{Co(TeO_6H_4)(l\text{-}pn)\}]^{4-}$ and CD spectrum (----) of $(-)^{\mathrm{CD}}_{589}$-$[\{Co(TeO_6H_4)(en)\}(TeO_6)\{Co(TeO_6H_4)(en)\}]^{4-}$.

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