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Circular Dichroism and Stereochemistry of Tetranuclear Cobalt(III) Complexes of Hexol Type. I. Dodecaammine-hexa-μ-hydroxo-tetracobalt(III) Ion, $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$

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From the circular dichroism spectra of optically active dodecaammine-hexa-μ-hydroxo-tetracobalt(III) ion, $(+)_{589}$-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$, measured in the visible and ultraviolet region in several solvents such as 0.01M-HCl and 0.17M-Na_2SeO_3, the d-d transitions of the complex are assigned in consideration of the ion-pairing effect. The absolute configuration of $(+)_{589}$ isomer is assigned as Δ based upon a negative sign of the E_a component for the CoO_6 chromophore. The circular dichroism change by the ion-pairing is attributed to the vicinal effect of chiral oxygen centers stereospecifically produced by the ion-pair formation, and the importance of the oxygen chirality is discussed on the basis of the time-course of circular dichroism change in the solutions.

Dodecaammine-hexa-μ-hydroxo-tetracobalt(III) complex salt was firstly prepared by Jörgensen,[1] and was resolved into optical isomers as the first purely inorganic complex by Werner,[2] who named the complex "hexol" after the bridging ligands. The structure of the polynuclear cation has been established by an X-ray crystal structure analysis of the racemic chloride salt,[3] and there have been done several investigations concerning the optical activity of the resolved isomers and related hexa-μ-hydroxo-tetracobalt(III) type complex ions.[2,4–7] Heretofore there have been two different assignments for the absolute configuration of this type of complexes.[5,7] To solve the problem, a detailed CD investigation of the dodecaammine-hexa-μ-hydroxo-tetracobalt(III) ion, $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$, which is the most basic of this type of complexes, will be reported in the present paper; the absolute configuration will be determined mainly on the basis of the effect of ion-pairing on the CD spectra.

Experimental

Preparation and Optical Resolution. *(1)* $[Co\{(OH)_2Co(NH_3)_4\}_3]Cl_6\cdot 6H_2O$: The sulfate salt $[Co\{(OH)_2Co(NH_3)_4\}_3](SO_4)_3\cdot 4H_2O$ which was prepared by an established method[8] was converted into the chloride salt by treating with $BaCl_2$. Found: H, 6.13; N, 19.29; Cl, 25.05 %. Calcd for $H_{42}O_6N_{12}Cl_6Co_4\cdot 6H_2O$: H, 6.31; N, 19.48; Cl, 24.65%.

(2) $(+)_{589}$-$[Co\{(OH)_2Co(NH_3)_4\}_3](ClO_4)_6\cdot 2.5H_2O\cdot 0.5NaClO_4$: The optical resolution was achieved by a modification of the procedure of Goodwin *et al.*,[4] which was for the corresponding ethylenediamine complex $[Co\{(OH)_2Co(en)_2\}_3]^{6+}$. The racemic chloride hexahydrate (2.00 g, 2.32×10^{-3} mol) was dissolved in 200 cm^3 of cold water, and to this dark brown solution the first quarter of cold solution of $Na_2[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 2.5H_2O$ (2.18 g, 3.48×10^{-3} mol) in 160 cm^3 of water was added dropwise with stirring. During the reaction the vessel was cooled in an icebath. A voluminous pale-brown precipitate of the less soluble diastereoisomer deposited, which was filtered, washed with cold water, and air-dried. The filtrate was again cooled in an icebath, whereupon the second quarter of $[Sb_2(d\text{-}C_4H_2O_6)_2]^{2-}$ solution was added to it, and the second fraction of the diastereoisomer was obtained. The procedure was repeated 4 times in total. The time for the separation of each fraction did not exceed 20 min.

Each fraction was converted into the perchlorate as follows. A mixture of the less soluble diastereoisomer and solid $NaClO_4$ (*ca.* 2 g) was ground up finely in a mortar, and then to this mixture was added 7 cm^3 of ice-cold water which was in advance acidified to pH 5 with $HClO_4$. This mixture was rubbed with a pestle, the vessel being cooled in an ice bath. The resulting mixture was filtered, washed with an ethanol-water (2: 1) mixture, ethanol and then ether. The brown violet powdery crystals were dried in a vacuum desiccator over $CaCl_2$. The $\Delta\varepsilon_{614}$ values of the fractions were -13.5, -12.9, -6.23, and -1.35 in the order of precipitation. In other experiments the racemic compound was treated to yield 8 fractions or 16 fractions. But the $\Delta\varepsilon_{614}$ value of each the first fraction was same as that described above ($\Delta\varepsilon_{614}=-13.5$). Found: H, 3.78, N, 13.56 %. Calcd for $H_{42}O_{30}N_{12}Cl_6Co_4\cdot 2.5H_2O\cdot 0.5NaClO_4$: H, 3.80; N, 13.50 %.

Measurement. The visible and ultraviolet absorption measurements were made by a Shimadzu UV-200 spectrophotometer. The CD spectra were recorded on a JASCO MOE-1 spectropolarimeter. The time-course of CD change was followed at 614 and 505 nm in H_2O, 0.01M-HCl, 0.17M-Na_2SeO_3, 0.17M-Na_2tart, 0.17M-H_2tart, and NaOH aqueous solutions (pH 8.1 and 10.4) at 22 °C (tart stands for $(+)_{589}$-tartrate(2−) ion). The time-course of absorption change was followed at 625 and 505 nm in each case. The CD measurements in 0.17M-Na_2SeO_3 were made with the solutions prepared freshly every about 10 minutes, and the CD curve was obtained by extrapolating the spectra back to zero time.

Results and Discussion

The absorption and CD spectra are shown in Fig. 1 and the numerical data in Table 1. Since mutarotation of this complex was very fast in water, the CD spectra were measured in 0.01M-HCl solution, in which the complex is considerably stable for the mutarotation. The CD spectra in 0.17M-Na_2SeO_3 were obtained by extrapolating the observed $\Delta\varepsilon$ values back to zero time. The dodecaammine-hexa-μ-hydroxo-tetracobalt(III) ion, $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$, is regarded as composed of a $Co(OH)_6$ and three $Co(OH)_2(NH_3)_4$ chromophores. In the following discussion the former chromophore will be abbreviated to CoO_6 one, and the latter to CoN_4O_2 one. The CoO_6 chromophore has a configurational chirality, Δ or Λ, due to the tris-chelate type structure of the whole complex, while each the CoN_4O_2 chromo-

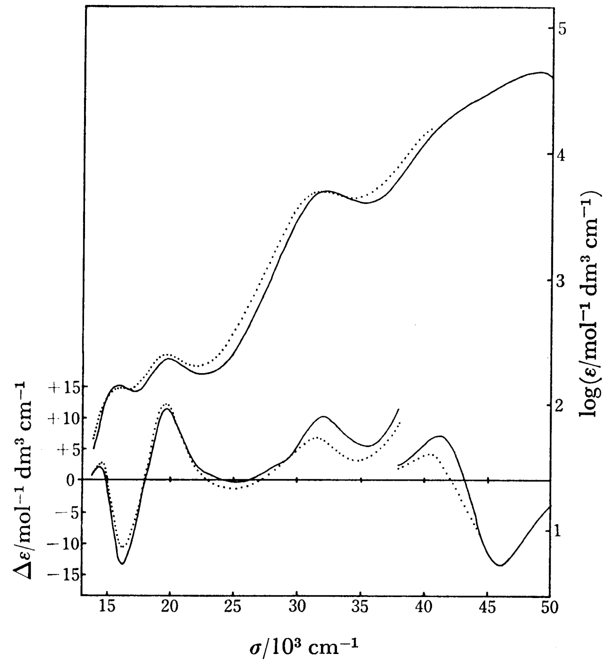

Fig. 1. Absorption and CD curves of $(+)_{589}$-$[Co\{(OH)_2Co(NH_3)_3\}_3]^{6+}$ in 0.01 M-HCl (——) and 0.17 M-Na_2SeO_3 (······).

Table 1. The absorption and CD data of $(+)_{589}$-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ (Wave numbers are given in 10^3cm^{-1} unit and logε or $\Delta\varepsilon$ values (in parentheses) mol^{-1} dm^3 cm^{-1}).

solvent	σ_{max}	(log ε)	σ_{ext}	($\Delta\varepsilon$)
0.01M-HCl			14.47	(+ 2.07)
	15.97	(2.15)	16.28	(−13.5)
	19.86	(2.36)	19.78	(+11.3)
			25.44	(− 0.29)
	32.21	(3.70)	32.00	(+10.0)
			41.20	(+34.4)
	48.90	(4.64)	46.00	(−67.1)
$0.17M\text{-}Na_2SeO_3$			14.61	(+ 2.63)
	16.27	(2.13)	16.30	(−10.8)
	19.76	(2.39)	19.60	(+11.9)
			25.09	(− 1.34)
	31.85	(3.70)	31.55	(+ 6.65)
			40.40	(+19.9)

phore itself has no chirality.

The first and second d-d transition bands of $[Co(H_2O)_6]^{3+}$ are located at 16500 and 24700 cm^{-1}, respectively,[9] and those of *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ at 19900 and 28100 cm^{-1}. Therefore, the absorption bands of $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ at 15970 and 19860 cm^{-1} in 0.01M-HCl are assigned to the first d-d transition bands of CoO_6 and CoN_4O_2 chromophores, respectively. The second d-d transition bands of both chromophores seem to be masked by an intense band at 32210 cm^{-1}, which is due to the charge transfer transition from the OH bridge group to the central metal, $p\pi(O) \rightarrow e_g(Co)$. These assignments of the absorption bands are consistent with earlier assignments for those of similar hexa-μ-hydroxo-tetracobalt(III) type ions.[5–7]

Upon going from in 0.01M-HCl to in 0.17M-Na_2SeO_3, the peak of the first d-d absorption band of CoO_6 chromophore shifted to higher energy side, while the peak of CoN_4O_2 chromophores to lower energy side. The charge transfer band shifted to lower energy side. For the CD spectra, the intensity of the longer wavelength extremum of CoO_6 chromophore increased with shifting to higher energy side, but the intensity of the shorter wavelength one of CoO_6 chromophore drastically decreased without shifting. The CD band of CoN_4O_2 chromophore shifted to lower energy side and the intensity increased slightly. Both CD bands at about 32000 and 41000 cm^{-1} shifted to lower energy side and their intensities decreased.

It has been well known that the CD spectra of Λ-$[Co(en)_3]^{3+}$ with D_3 symmetry show strong ion-pairing effect in the region of the first d-d absorption band when a kind of oxoanion species such as PO_4^{3-} or SeO_3^{2-} is added; the CD intensity of E_a component of the first d-d transition decreases, and those of A_2 component of the first d-d transition and E_b component of the second d-d transition increase.[10–12] Mason and Norman proposed that hydrogen bonds played an important role in the ion-pair formation between PO_4^{3-} and $[Co(en)_3]^{3+}$,[11] and this view has been supported by an X-ray crystal structure analysis of $[Co(en)_3]_2(HPO_4)_3\cdot 9H_2O$[13] and another CD study of [Co{1,1,1-tris(2-aminoethylaminomethyl)ethane}]$^{3+}$.[14] In a similar way, hydrogen bonds may occur between SeO_3^{2-} and the OH bridge groups of $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$, because a set of three OH groups is available each on the upper face and below the downward face of the ion of D_3 symmetry. The CD intensities increased at the bands of 14500, 19800, and 25400 cm^{-1}, while decreased at the band of 16300 cm^{-1} (Fig. 1 and Table 1). Therefore, the bands at 14500 and 16300 cm^{-1} can be assigned to A_2 and E_a component of the CoO_6 chromophore respectively.

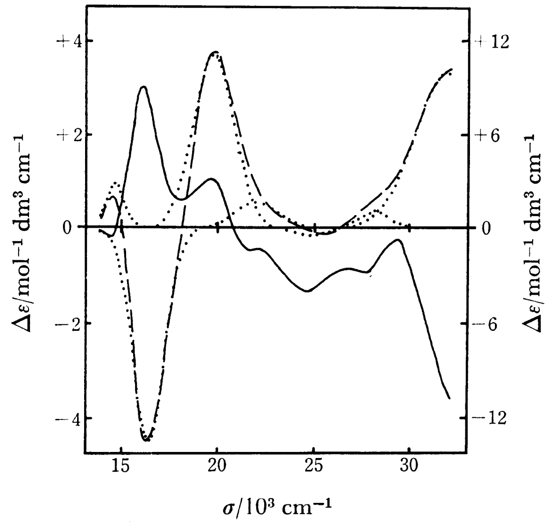

Fig. 2. The ion-pairing effect curve, $\{\Delta\varepsilon_{(in\ 0.17M-Na_2SeO_3)} - \Delta\varepsilon_{(in\ 0.01M-HCl)}\}$, (——) (the left ordinate), and CD curve of $(+)_{589}$-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ in 0.01 M-HCl (-----) and its component curves separated by curve analysis (······) (the right ordinate).

Figure 2 shows the difference CD curve between in 0.01M-HCl and in 0.17M-Na_2SeO_3; this presents the ion-pairing effect of SeO_3^{2-} ion on the CD of $(+)_{589}$-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$. The curve have six extrema at 14200, 16000, 19600, 21600, 24600, and 27800 cm^{-1} in the d-d transition region. The first and next extrema, at 14200 and 16000 cm^{-1}, correspond to the increment of the positive A_2 component and the decrement of the negative E_a component, respectively, of the first d-d transition of CoO_6 chromophore. The extrema at 19600 and 21600 cm^{-1} correspond to the first d-d transition components of CoN_4O_2 chromophores, and it seems that the last two extrema, at 24600 and 27800 cm^{-1}, correspond to the second d-d transition components of CoO_6 or CoN_4O_2 chromophores. Since the second d-d transition CD bands have been observed at 24300 and 26500 cm^{-1} for Λ-$[Co(ox)_3]^{3-}$[15] and at 26500 and 29400 cm^{-1} for Λ-$[Co(en)_2(H_2O)_2]^{3+}$,[16] it seems that the extremum at 24600 cm^{-1} shows the increment due to the ion-pairing effect on the longer wavelength negative CD component of the second band of CoO_6 chromophore. The extremum at 27800 cm^{-1} corresponds to the longer wavelength CD component of the second band of CoN_4O_2 chromophore or the shorter wavelength CD component of the CoO_6 one. Gaussian curve analysis of the CD spectra measured in 0.01M-HCl showed six CD components at 14680 cm^{-1} ($\Delta\varepsilon = +3.00$), 16340 ($-13.54$), 19690 ($+11.10$), 21980 ($+1.65$), 24460 ($-0.28$), and 28120 ($+1.07$) (Fig. 2). These extremum positions are well close to the extrema on the ion-pairing effect curve.

As for the chirality of the hexol type ions, two different assignments of absolute configuration have been offered.[5,7] Both assignments based on the CD sign of E_a component of CoO_6 chromophore, the assignments of the E_a component being reversed. Mason and Wood[5] have assigned the E_a component from the intensity, because the E_a component is invariably stronger than the A_2 component in many trigonal cobalt(III) complexes. The major CD band of CoO_6 chromophore of the hexol type complexes situated at higher energy side than the minor band, and they assigned Λ-configuration to the complex which has a positive sign in the higher energy CD component. On the other hand, Masuda and Douglas[7] have assigned the E_a component on the basis of the CD extremum position, because the E_a component appears usually at lower energy side of the A_2 component for many trigonal cobalt(III) complexes. Thus they assigned the complex which has a positive sign in the lower energy CD band as having the absolute configuration Λ.

From the present study of the ion-pairing effect, it is shown that the intensity of the lower energy CD band of CoO_6 chromophore increases upon ion-pairing, while that of the higher energy CD band decreases. In consequence the higher energy band can be assigned to the E_a component; this suports the assignment of Mason and Wood. As a conclusion the $(+)_{589}$-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ which shows a negative sign in the 16280 cm^{-1} CD band is assigned as having Δ-configuration.

Table 2 summarizes the rates of mutarotation, k, of the $(+)_{589}$ isomer determined from the time-course of CD change at 614 and 505 nm for the early reaction stage. The values of $\Delta\varepsilon_{614}$ and $\Delta\varepsilon_{505}$ are also presented, which were obtained by extrapolating the CD values back to zero time by using the rate constants k_{614} and k_{505}. In a NaOH solution of pH 8.1, $(+)_{589}$ isomer lost the optical activity completely within 3 min. In a NaOH solution of pH 10.4 the complex decomposed immediately. During the mutarotation, the absorption intensities at 625 and 505 nm did not change for more than 30 min in H_2O, for more than 120 min in 0.17M-H_2tart, 0.17M-Na_2tart, and 0.17M-Na_2SeO_3, for more than 2 days in 0.01M-HCl, and for more than 5 min in a NaOH solution of pH 8.1; in these periods the absorption spectra did not change in the d-d transition region.

As Table 2 shows, the $\Delta\varepsilon_{614}$ values in 0.01M-HCl and H_2O were -13.5 and -13.7, respectively; they are approximately equal. In 0.17M-Na_2SeO_3, 0.17M-Na_2tart, and 0.17M-H_2tart, they were -10.5, -12.4, and -12.2, respectively. On the other hand, the $\Delta\varepsilon_{505}$ values were almost equal for different solvents. The ion-pair formation affects strongly the $\Delta\varepsilon_{614}$ values, but not the $\Delta\varepsilon_{505}$ values. Thus the ion-pairing affects in a large extent the CoO_6 chromophore and less the CoN_4O_2 chromophores. This means that the hydrogen bonding between oxygen atoms of the counter ion and the OH bridge groups of the complex is more important than that between the counter ion and the ammonia ligands.

It may be worthwhile to consider the chirality of the oxygen atoms of the bridging OH groups, because they bonded directly to the cobalt(III) atoms and it is expected to produce rather strong vicinal effect on the CD bands of the CoO_6 and CoN_4O_2 chromophores. Since each oxygen atom of the six OH bridge groups has probably a pseudo-tetrahedral configuration of the three different attached groups and a lone pair of electrons, it must be asymmetric. For the complexes of Δ-configuration, axial disposition of the OH bond (parallel to

TABLE 2. RATES OF MUTAROTATION FOR THE EARLY STAGE AND THE INITIAL $\Delta\varepsilon$ VALUES AT 614 nm (16280 cm^{-1}) AND 505 nm (19780 cm^{-1}) ($\Delta\varepsilon$ values are given in $mol^{-1}\,dm^3\,cm^{-1}$ unit).

Solvent	$\Delta\varepsilon_{614}$	$\Delta\varepsilon_{505}$	k_{614}/s^{-1}	k_{505}/s^{-1}	k_{mean}/s^{-1}
0.01M-HCl	-13.48	$+11.26$	1.63×10^{-6}	2.40×10^{-6}	2.01×10^{-6}
0.17M-H_2tart	-12.19	$+11.64$	2.67×10^{-5}	1.85×10^{-5}	2.26×10^{-5}
0.17M-Na_2tart	-12.36	$+11.34$	5.10×10^{-4}	4.17×10^{-4}	4.64×10^{-4}
0.17M-Na_2SeO_3	-10.53	$+11.87$	3.52×10^{-4}	3.18×10^{-4}	3.35×10^{-4}
H_2O	-13.67	$+11.11$	1.78×10^{-3}	2.98×10^{-3}	—
NaOH (pH 8.1)			*ca.* 4×10^{-2}	*ca.* 5×10^{-2}	—

the C_3 axis) constraint (*S*) chirality for the asymmetric oxygen atom. Recently, Dixon *et al.*[17] made an X-ray crystal structure analysis of *rac*-$[Co\{(OH)_2Co(en)_2\}_3](SCN)_4(NO_3)_2\cdot 2H_2O$, and the two allowed (tetrahedral) positions were calculated for the hydrogen atoms of the OH bridge groups and the correct choice was made on the basis of difference maps, which revealed that all five but one of the six oxygen atoms take the axial disposition, only one OH group taking equatorial disposition. A molecular model consideration also shows that the axial orientation of the OH bridge groups may be more stable than the equatorial orientation because of some steric repulsion found in the latter case. It can therefore, be pressumed that the six asymmetric oxygen atoms of the Δ-$(+)_{589}$-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ complex have predominantly (*S*) configurations in the perchlorate crystals.

From absorption measurements during the time-course of CD change, other species expected for the original complex ion were not detected in the experimental time. Therefore the CD intensity decrease for the time-course can be ascribed to the racemization of Δ-$(+)_{589}$-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$. The origin of optical activity decrease of this complex is divided into the racemization of the chirality Δ for the CoO_6 chromophore and that of the chirality (*S*) for the asymmetric oxygen atoms. In an acid solution oxonium ions rapidly attack the lone-pair electrons enforcing the inversion of the oxygen chiral center, and the oxygen center may be regarded as being in an equilibrium $(R)\rightleftharpoons(S)$ (this kind of configurational equilibrium is denoted by *E* in the following); thus the racemization in this case corresponds to the reaction $\Delta(EEEEEE)\rightarrow\Lambda(EEEEEE)$. On the other hand, in the SeO_3^{2-} solution, the oxoanion enforces the OH groups to take the axial positions; then the racemization in this case corresponds predominantly to $\Delta(SSSEEE)\rightarrow\Lambda(RRREEE)$ or $\Delta(SSSSSS)\rightarrow\Lambda(RRRRRR)$, if 1 : 1 or 1 : 2 ion-pairing is assumed, respectively. Since the Na_2SeO_3 solution is alkaline (pH=10.4), the *k* value is much greater for the SeO_3^{2-} solution than for the HCl solution. Nevertheless the *k* value in SeO_3^{2-} solution is much less than that in NaOH solution of pH 10.4. Evidently the ion-pairing depressed the racemization. The *k* value in 0.17M-Na_2tart solution (pH=8.1) is about $10^{-1}\,min^{-1}$ and that in a NaOH solution of pH 8.1 about 2—3 min^{-1}. It has been well established that the tart^{2-} ion is also capable of forming ion-pairs with several cobalt(III) complexes.[18—20] Therefore, the difference in the *k* values at equal pH is due to the ion-pairing between the OH bridge groups and the doubly charged tartrate anion in the 0.17M-Na_2tart solution. It may be expected that the *k* value is smaller in 0.17M-Na_2tart (pH 8.1) than in 0.17M-Na_2SeO_3 (pH 10.4) in terms of the pH values. However the *k* value in 0.17M-Na_2tart (about $5\times10^{-4}\,s^{-1}$) is larger than that in 0.17M-Na_2SeO_3 (about $3\times10^{-4}\,s^{-1}$) (Table 2). This is because the ion-pairing effect of Na_2SeO_3 is larger than that of Na_2tart, as can be seen from the comparison of the $\Delta\varepsilon_{614}$ values.

Some plots of $\ln|\Delta\varepsilon|$ *vs.* time (min) for the mutarotation of $(+)_{589}$-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ were given in Figs. 3—5. The plots for the early stage gave a straight

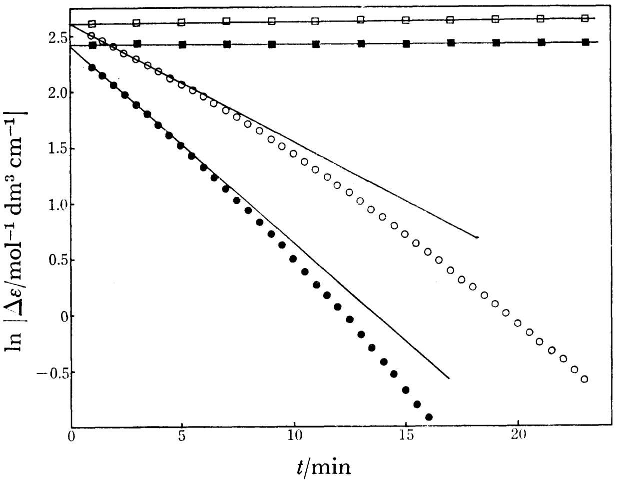

Fig. 3. Plots of $\ln|\Delta\varepsilon|$ *vs.* time for $(+)_{589}$-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ in 0.01 M-HCl ($\Delta\varepsilon_{614}$; □, $\Delta\varepsilon_{505}$; ■) and in water ($\Delta\varepsilon_{614}$; ○, $\Delta\varepsilon_{505}$; ●).

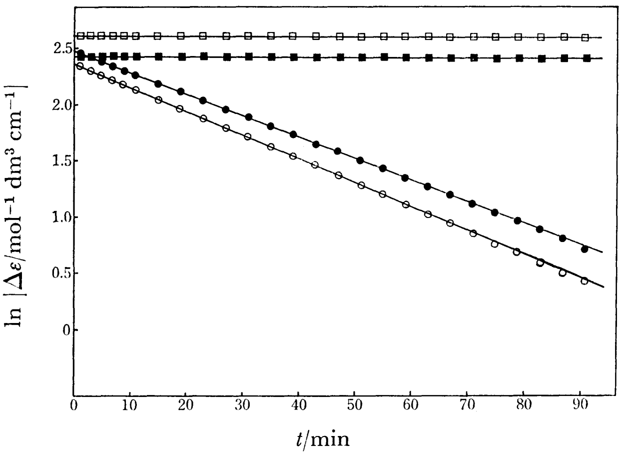

Fig. 4. Plots of ln $|\Delta\varepsilon|$ *vs.* time for $(+)_{589}$-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ in 0.01 M-HCl ($\Delta\varepsilon_{614}$; □, $\Delta\varepsilon_{505}$; ■) and in 0.17 M-Na_2SeO_3 ($\Delta\varepsilon_{614}$; ○, $\Delta\varepsilon_{505}$; ●).

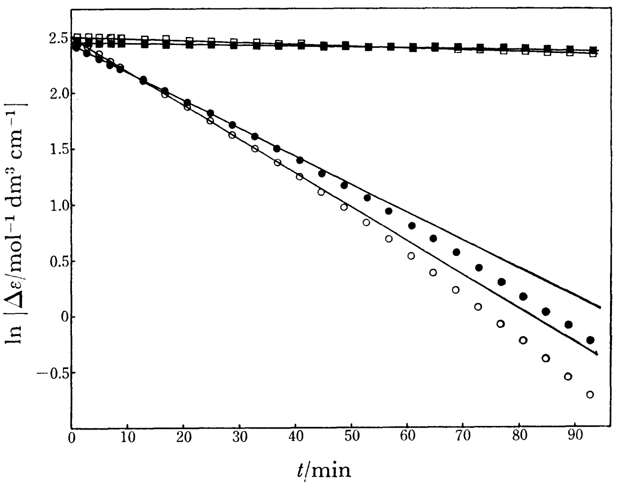

Fig. 5. Plots of $\ln|\Delta\varepsilon|$ *vs.* time for $(+)_{589}$-$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$ in 0.17 M-H_2tart ($\Delta\varepsilon_{614}$; □, $\Delta\varepsilon_{505}$; ■) and in 0.17 M-Na_2tart ($\Delta\varepsilon_{614}$; ○, $\Delta\varepsilon_{505}$; ●).

line; the lines in Figures were calculated by the least square method on the basis of the plots of initial stage. With elapse of time, a steep departure from the line was observed in H_2O (Fig. 3). In 0.17M-Na_2tart and 0.17M-Na_2SeO_3, with elapse of time, a slight departure from the line was observed (Figs. 4 and 5). While in 0.01M-HCl and 0.17M-H_2tart, only a slight departure from the line was observed (Figs. 4 and 5); the mutarotations in the latter two cases represent a true racemization $\Delta(EEEEEE)\rightarrow\Lambda(EEEEEE)$, $\Delta(SSSEEE)\rightarrow\Lambda(RRREEE)$, or $\Delta(SSSSSS)\rightarrow\Lambda(RRRRRR)$. It can be considered that the departure from a line, especially in the case in water, is due to a complicated configurational change due to the coexistence of different kinds of chiralities.

Sarneski and Ulbach[14] pointed out that the major source of CD change in the d-d transition region of Λ-$[Co(en)_3]^{3+}$–PO_4^{3-} ion-pair system may be the vicinal effect of chiral nitrogen centers stereospecifically produced at the primary amine donors by the ion-pair formation of Mason type. Similarly in the present polynuclear complex, the difference CD curve between in 0.01M-HCl and 0.17M-Na_2SeO_3 (Fig. 2) is regarded to have the origin in the vicinal effect of chiral oxygen centers stereospecifically produced by the ion-pair formation, because this curve corresponds to the difference $\Delta(SSSEEE)-\Delta(EEEEEE)$ or $\Delta(SSSSSS)-\Delta(EEEEEE)$. Thus the vicinal effect of the (*S*) oxygen atoms has a positive sign in the E_a component of the CoO_6 chromophore and this is in accord with the fact that the vicinal effect of (*R*) nitrogen center in the Λ-$[Co(en)_3]^{3+}$–PO_4^{3-} ion-pair system has a negative sign in the E_a component of the CoN_6 chromophore.

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