A Study on Spontaneous Resolution of Cobalt(III) Complex Salts

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Solubility of the racemic and optically active isomers of $[Co(ox)en_2]X$, $[CoCO_3en_2]X$, *cis*-$[Co(NO_2)_2en_2]X$ and $M[Co(edta)]$ in water was determined at 5—60 °C (X=Cl, Br, and I; M=NH_4 and K). The correlation between solubility of the spontaneously resolved racemic complex and of the corresponding optically active isomer is discussed. Spontaneous resolutions were observed for $[Co(ox)en_2]X$ (X=Cl, $Cl\cdot H_2O$, and $Br\cdot H_2O$), *cis*-$[Co(NO_2)_2en_2]X$ (X=Cl and Br) and $M[Co(edta)]\cdot 2H_2O$ (M=NH_4 and K).

It is believed that so-called spontaneous resolution can be observed in limited cases. Only some dozen metal complexes have been reported to be spontaneously resolved.[1–8] It is evident that solubility plays an extremely important role in spontaneous resolution and related phenomena such as optical resolution by the formation of diastereomer or so-called configurational activity.[9–11] Systematic investigation of solubility of metal complexes is necessary for an explanation of these phenomena; nevertheless, only a few reports have been published so far. The present paper deals with the solubility and spontaneous resolution of (1 : 1) electrolyte salts containing configurationally chiral cobalt(III) complexes.

Experimental

Preparation and Resolution. *(1) Bis(ethylenediamine)-oxalatocobalt(III) Complex, $[Co(ox)en_2]X$, (X=Cl^-, Br^-, and I^-)*: The chloride salt was prepared and resolved by the method of Dwyer *et al.*[12] The racemic and optically active bromides or iodides were obtained by adding a calculated amount of NH_4Br or NH_4I to an aqueous solution of the corresponding chloride. The spontaneous resolution of monohydrated bromide salt was observed for the rhombic crystals prepared as follows: about 0.7 g of the racemic bromide monohydrate was dissolved in 50 ml of water at 50 °C and the solution was kept standing in refrigerator (at about 5 °C) for several days for crystallization.

(2) cis-*Bis(ethylenediamine)dinitrocobalt(III) Complex,* cis-*$[Co(NO_2)_2en_2]X$, (X=Cl^-, Br^-, and I^-)*: The nitrite salt *cis*-$[Co(NO_2)_2en_2]NO_2$ was prepared by the reaction of *trans*-$[CoCl_2en_2]Cl$ (20 g) and KNO_2 (20 g) in 100 ml of water at 50 °C and optically resolved by the method of Dwyer and Garvan.[13] The chloride and iodide salts were derived from the bromide by treating with AgCl and AgI, respectively. Crystallization was carried out as follows: 1.5 g of the racemic chloride (0.5 and 0.2 g of the bromide and iodide, respectively) was dissolved in 20 ml of water at 40 °C and the solution was kept standing in a refrigerator (at about 5 °C) for several days.

(3) Carbonatobis(ethylenediamine)cobalt(III) Complex, $[CoCO_3en_2]X$, (X=Cl^-, Br^-, and I^-): Racemic chloride salt was prepared by Werner's method[14] and racemic bromide or iodide salt was obtained by adding an appropriate amount of NH_4Br or KI to an aqueous solution of the chloride. Optically active chloride and bromide salts were derived from the active iodide, which was resolved by the method of Dwyer *et al.*,[15] by treating with the corresponding silver halides.

(4) Ethylenediaminetetraacetatocobaltate(III) Complex, $M[Co(edta)]$, (M=K^+ and NH_4^+): The potassium salt dihydrate was prepared and resolved by the method of Dwyer and Garvan.[16] The ammonium salt was similarly obtained by using ammonium acetate instead of potassium acetate. The desired crystals of potassium and ammonium salts were gradually crystallized from the solution containing 6 g of potassium salt (5 g for ammonium salt) in 10 ml of warm water (50 °C) by being kept standing at room temperature.

Measurements. Solubility measurements were carried out spectrophotometrically with a Beckman DU spectrophotometer at 5—60 °C. Saturation equilibrium of solutions was attained in an Erlenmeyer flask, which was maintained in a thermostat regulated within ±0.1°C. An aqueous solution containing an excess of solid complex salt in the flask was stirred mechanically at the desired temperature and the resulting saturated solution was sampled by sucking up with a pipet through a filter. The sample solution was weighed exactly, diluted to an appropriate volume and its optical density was measured at the maximum wavelength of the first absorption band of the complex. To detect the occurrence of spontaneous resolution, the crystal of racemic complex was arbitrarily chosen and dissolved in a small amount of water, and the optical rotatory dispersion (RD) curve was measured with a Yanagimoto recording spectropolarimeter model-187.

General Consideration

The correlation between solubility of the racemic compound and of the corresponding optically active isomers has not been discussed by means of an explicit formula except for some qualitative treatment using phase

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diagrams.[17,18] Racemic complexes are classified into two groups on the basis of the mode of crystallization. In the first group, a racemic complex forms racemic crystals, the unit cell of which contains an equal number of the Δ and Λ enantiomeric complexes. In the second group, a racemic complex forms a racemic mixture, which is a mixture of the pure Δ and Λ crystals. The latter case has been named the spontaneous resolution.

The solubility product (K_{SP}) for an optically active (Δ, for example) complex salt of the $[\mathrm{M}]^+\mathrm{X}^-$ type[19] at t °C is given by

$$\begin{aligned} K_{\mathrm{SP}}^{\Delta} &= \{[\mathrm{M}]^+\}_{\Delta}\cdot\{\mathrm{X}^-\} \\ &= S_{\Delta}f_{[\mathrm{M}]}^{\Delta}\cdot S_{\Delta}f_{\mathrm{X}}^{\Delta} = (S_{\Delta})^2\cdot f_{[\mathrm{M}]}^{\Delta}f_{\mathrm{X}}^{\Delta} \end{aligned} \tag{1}$$

where $\{[\mathrm{M}]^+\}$ and $\{\mathrm{X}^-\}$ denote the activities of the complex cation and the counter simple anion, respectively, S_{Δ} the molar solubility of the optically active Δ salt, and $f_{[\mathrm{M}]}^{\Delta}$ and f_{X}^{Δ} the activity coefficients of the complex cation and the counter anion, respectively. If the spontaneous resolution occurs for the corresponding racemic complex salt, the solubility product for the Δ isomer in the racemic mixture, $K_{\mathrm{SP}}^{\Delta(\Delta\Lambda)}$, is represented as follows, since the Δ isomer in the racemic mixture behaves independently of the Λ isomer.

$$\begin{aligned} K_{\mathrm{SP}}^{\Delta(\Delta\Lambda)} &= K_{\mathrm{SP}}^{\Lambda(\Delta\Lambda)} = \{[\mathrm{M}]^+\}_{\Delta\text{ or }\Lambda}\cdot\{\mathrm{X}^-\} \\ &= \frac{1}{2}S_{\Delta\Lambda}f_{[\mathrm{M}]}^{\Delta\Lambda}\cdot S_{\Delta\Lambda}f_{\mathrm{X}}^{\Delta\Lambda} = \frac{1}{2}(S_{\Delta\Lambda})^2\cdot f_{[\mathrm{M}]}^{\Delta\Lambda}f_{\mathrm{X}}^{\Delta\Lambda} \end{aligned} \tag{2}$$

where $f_{[\mathrm{M}]}^{\Delta\Lambda}$ and $f_{\mathrm{X}}^{\Delta\Lambda}$ denote the activity coefficients of the complex cation and the counter anion in the racemic solution, respectively. Since the relation $K_{\mathrm{SP}}^{\Delta}=K_{\mathrm{SP}}^{\Delta(\Delta\Lambda)}$ should hold, we have

$$S_{\Delta\Lambda} = \sqrt{2}\, S_{\Delta}(f_{[\mathrm{M}]}^{\Delta}\cdot f_{\mathrm{X}}^{\Delta})^{1/2}/(f_{[\mathrm{M}]}^{\Delta\Lambda}\cdot f_{\mathrm{X}}^{\Delta\Lambda})^{1/2} \tag{3}$$

Thus, if we assume an ideal solution, the solubility of a spontaneously resolved racemic complex salt of the $[\mathrm{M}]^+\mathrm{X}^-$ type must be $\sqrt{2}$ times larger than that of the corresponding optically active complex salt. Activity coefficients decrease in most cases with increasing ionic strength in the concentration range 10^{-3}—10^{-1} mol/l. Since the spontaneously resolved racemic complex salt is more soluble than the active isomers, we have $f_{[\mathrm{M}]}^{\Delta\Lambda}<f_{[\mathrm{M}]}^{\Delta}$ and $f_{\mathrm{X}}^{\Delta\Lambda}<f_{\mathrm{X}}^{\Delta}$. Therefore, Eq. (3) shows that *the solublity of the spontaneously resolved racemic salt of the* $[M]^+X^-$ *type is* $\sqrt{2}$ *or more times larger than that of the corresponding optically active salt.*

The treatment can be extended to other types of complex electrolytes and to the complex molecule also. For the $[\mathrm{M}]^{n+}(\mathrm{X}^-)_n$ type we obtain

$$S_{\Delta\Lambda} = \sqrt[n+1]{2}\, S_{\Delta}(f_{[\mathrm{M}]}^{\Delta}\cdot f_{\mathrm{X}}^{\Delta})^{1/(n+1)}/(f_{[\mathrm{M}]}^{\Delta\Lambda}\cdot f_{\mathrm{X}}^{\Delta\Lambda})^{1/(n+1)} \tag{4}$$

and for the complex molecule

$$S_{\Delta\Lambda} = 2S_{\Delta}(f_{[\mathrm{M}]}^{\Delta}/f_{[\mathrm{M}]}^{\Delta\Lambda}) \tag{5}$$

In the case of true racemic crystal, $[\mathrm{M}]^+{}_{\Delta}[\mathrm{M}]^+{}_{\Lambda}(\mathrm{X}^-)_2$, which contains an equal number of the Δ and Λ complexes in its unit cell, the solubility product is given by

$$\begin{aligned} K_{\mathrm{SP}}^{\Delta\Lambda} &= \{[\mathrm{M}]^+\}_{\Delta}\cdot\{[\mathrm{M}]^+\}_{\Lambda}\cdot\{\mathrm{X}^-\}^2 \\ &= \frac{1}{2}S_{\Delta\Lambda}f_{[\mathrm{M}]}^{\Delta\Lambda}\cdot\frac{1}{2}S_{\Delta\Lambda}f_{[\mathrm{M}]}^{\Delta\Lambda}\cdot(S_{\Delta\Lambda}f_{\mathrm{X}}^{\Delta\Lambda})^2 \\ &= \frac{1}{4}(S_{\Delta\Lambda})^4\cdot(f_{[\mathrm{M}]}^{\Delta\Lambda}f_{\mathrm{X}}^{\Delta\Lambda})^2 \end{aligned} \tag{6}$$

In this case the solubility $S_{\Delta\Lambda}$ is independent of that of the corresponding pure Δ or Λ enantiomer, not exceeding $\sqrt{2}S_{\Delta}$ or $\sqrt{2}S_{\Lambda}$ in an ideal solution. The general conclusion is summarized in Table 1.

Results and Discussion

The solubility data are summarized in Table 2.

(1) Bis(ethylenediamine)oxalatocobalt(III) Complexes: Solubility curves of the complex halides are shown in Fig. 1—3. Of these halides the chloride salt has been reported to show the so-called spontaneous re-

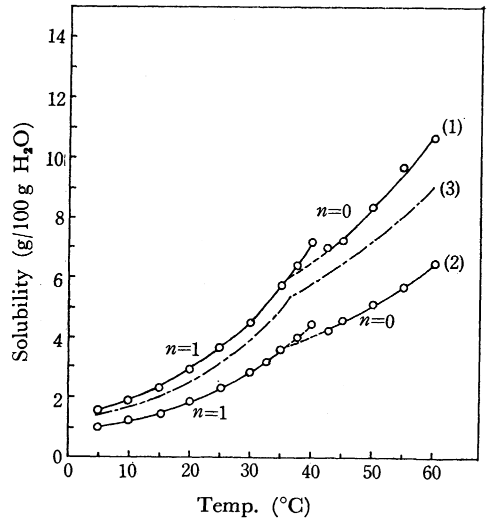

Fig. 1. Solubility curves of $[\mathrm{Co(ox)en_2}]\mathrm{Cl}\cdot n\mathrm{H_2O}$: (1) racemic form, (2) Λ form and (3) calculated curve: (2)×$\sqrt{2}$.

TABLE 1. SOLUBILITY RELATIONSHIP BETWEEN THE RACEMIC AND THE OPTICALLY ACTIVE (Δ) ISOMERS OF THE $[\mathrm{M}]^{n+}(\mathrm{X}^-)_n$ AND $([\mathrm{M}]^+)_n\mathrm{X}^{n-}$ TYPE COMPLEX SALTS IN AN IDEAL SOLUTION

$S_{\Delta\Lambda}$; Solubility of the racemic compound.

S_{Δ}; Solubility of the Δ form.

Solid phase	$[\mathrm{M}]^{n+}(\mathrm{X}^-)_n$	$([\mathrm{M}]^+)_n\mathrm{X}^{n-}$
True racemic crystal	$S_{\Delta\Lambda} < \sqrt[n+1]{2}\, S_{\Delta}$	$S_{\Delta\Lambda} < \sqrt[n/(n+1)]{2}\, S_{\Delta}$
Spontaneously resolved racemic mixture	$S_{\Delta\Lambda} = \sqrt[n+1]{2}\, S_{\Delta}$	$S_{\Delta\Lambda} = \sqrt[n/(n+1)]{2}\, S_{\Delta}$

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19) $[\mathrm{M}^+]$ denotes a unipositive complex cation and X^- a uninegative anion.

TABLE 2. SOLUBILITY OF THE COBALT(III) COMPLEX SALTS OF $[M]^+X^-$ TYPE (grams of anhydrous salt in 100 grams of water) 1)

Temp. (°C)	No. of complex salt 2)												
	1	2	3	4	5	6	7	8	9	10 3)	11	12	13 3)
5.0	1.55		1.00		0.743[a]	0.475	0.0862	0.251	8.63	12.5	2.43		2.54
10.0	1.88		1.24[b]		0.795	0.537	0.104	0.291	9.77	13.8	2.96		2.86
15.0	2.34[a]		1.49		0.989[a]	0.636	0.122	0.344	10.9	14.7	3.61	3.58[a]	3.20
20.0	2.93		1.84		1.17	0.763	0.153	0.381	11.9	16.0	4.31	4.06	3.55
25.0	3.65[a]		2.33		1.34[a]	0.853	0.164	0.443	13.1[b]	17.1	5.19	4.58	3.98
27.5	—		—		—	—	—	—	13.8	—	—	4.87	—
30.0	4.52		2.83		1.55	1.01[k]	0.206	0.515	14.4	18.4	6.23	5.09[i]	4.43
32.5	—		3.21		—	—	—	—	15.3[a]	—		5.41	—
35.0	5.77		3.59		1.86[e]	1.15[a]	0.241	0.585	16.0	19.9		5.77	4.96
37.5	6.42		4.02		—	—	—	—	16.7	—		—	—
40.0	7.19		4.46[a]		2.08[a]	1.31	0.287	0.660	17.2	(21.4)		6.43	(5.71)
42.5		7.02[a]		4.29[c]	—	—	—	—	18.1[a]	—		—	—
45.0		7.23[b]		4.61	2.37	1.48	0.332	0.768	19.1	(23.2)[b]		7.06	(6.53)
50.0		8.36		5.17	2.84	1.68[d]	0.376	0.839	20.7	(25.6)[b]		7.82	(7.41)
55.0		9.74[d]		5.71[c]	3.16[e]	1.96[b]	0.451[i]	0.940	22.8[a]	(29.2)[d]		8.71	(8.68)[h]
60.0		10.7		6.49[c]	3.58[a]	2.20	0.497[b]	1.11[l]	24.7	(33.0)[j]		9.50	(11.0)

Temp. (°C)	No. of complex salt 2)												
	14	15	16 3)	17	18	19	20	21	22	23	24	25	26
5.0	0.428		1.38	3.97	2.55	0.948	0.713	0.399	0.293	36.6	17.5		10.4
10.0	0.534		1.49	4.76	3.00	1.16	0.749	0.511	0.378	47.7	22.0	22.4	14.3
15.0	0.702		1.64[c]	5.56[b]	3.47	1.41	0.914	0.607	0.445[a]	55.9	26.9	28.6	17.1
20.0	0.830	0.793	1.90	6.46	3.98[a]	1.65	1.12	0.696	0.532	67.5	32.5	35.6	20.3
25.0	0.988	0.925	2.14	7.58	4.69	1.97	1.30	0.846	0.650	76.3	40.3	43.6	26.2
27.5	—	—	—	—	—	—	—	—	—	—	—	—	—
30.0	1.23	1.07	2.38	8.78[b]	5.29	2.34	1.59	1.02	0.754	89.1	52.2	52.9	30.9
32.5	—	—	—	—	—	—	—	—	—	—	—	—	—
35.0	1.49	1.23	2.80[i]	10.4[a]	6.14[c]	2.81	1.78	1.22	0.924	103	57.2	56.3	34.8
37.5	—	—	—	—	—	—	—	—	—	—	—	—	—
40.0	1.80	1.44	3.14	12.1[b]	7.01[b]	3.23[a]	2.12	1.47	1.12	110	65.4	69.6	41.6
42.5		—	—	—	—	—	—	—	—	—	—	—	—
45.0		1.63	(3.14)	13.9[d]	7.97[b]	3.87	2.48	1.74[b]	1.30	125	73.7	78.6	49.0
50.0		1.92	(2.49)	16.2[d]	9.11[d]	4.60	2.94	2.05[d]	1.53[b]	—	85.1	85.8	56.5
55.0		2.13	(2.64)	19.4[k]	10.3[g]	5.34		2.51[a]	1.77	155	91.1	99.8	64.2
60.0		2.48	(3.06)	22.1	11.9	6.26		2.96[c]	2.11	176	103	114	73.4

1) The deviation of temperature from the indicated value is shown by a small letter superscript; a: +0.1 °C, b: −0.1 °C, c: +0.2 °C, d: −0.2 °C, e: +0.3 °C, f: −0.3 °C, g: +0.4 °C, h: −0.4 °C, i: +0.5 °C, j: −0.5 °C, k: +0.8 °C, l: +1.0 °C.

2) 1: *rac*-$[Co(ox)en_2]Cl\cdot H_2O$, 2: *rac*-$[Co(ox)en_2]Cl$, 3: $\Lambda(+)$-$[Co(ox)en_2]Cl\cdot H_2O$, 4: $\Lambda(+)$-$[Co(ox)en_2]Cl$, 5: *rac*-$[Co(ox)en_2]Br\cdot H_2O$, 6: $\Lambda(+)$-$[Co(ox)en_2]Br\cdot H_2O$, 7: *rac*-$[Co(ox)en_2]I$, 8: $\Lambda(+)$-$[Co(ox)en_2]I$, 9: *rac*-$[CoCO_3en_2]Cl$, 10: $\Lambda(+)$-$[CoCO_3en_2]Cl$, 11: *rac*-$[CoCO_3en_2]Br\cdot 2H_2O$, 12: *rac*-$[CoCO_3en_2]Br$, 13: $\Delta(-)$-$[CoCO_3en_2]Br$, 14: *rac*-$[CoCO_3en_2]I\cdot 2H_2O$, 15: *rac*-$[CoCO_3en_2]I$, 16: $\Lambda(+)$-$[CoCO_3en_2]I$, 17: *rac-cis*-$[Co(NO_2)_2en_2]Cl$, 18: $\Delta(-)$-*cis*-$[Co(NO_2)_2en_2]Cl$, 19: *rac-cis*-$[Co(NO_2)_2en_2]Br$, 20: $\Delta(-)$-*cis*-$[Co(NO_2)_2en_2]Br$, 21: *rac-cis*-$[Co(NO_2)_2en_2]I$, 22: $\Delta(-)$-*cis*-$[Co(NO_2)_2en_2]I$, 23: *rac*-$K[Co(edta)]\cdot 2H_2O$, 24: $\Delta(+)_{546}$-$K[Co(edta)]\cdot 2H_2O$, 25: *rac*-$NH_4[Co(edta)]\cdot 2H_2O$, 26: $\Delta(+)_{546}$-$NH_4[Co(edta)]\cdot 2H_2O$.

3) Values in parentheses for the optically active carbonato complexes are invalid because of partial racemization.

solution.5,8) The solubility of racemic chloride salt is larger than $\sqrt{2}$ times that of its optically active isomer in the range 5—60 °C (Fig. 1). The solubility curves show an inflection at about 36 °C, where the solid phase changes from monohydrate (below 36 °C) to anhydrous (above 36 °C). The bromide salts show a quite similar relationship in solubility curves to those of the chlorides except that the former shows no inflection (Fig. 2). Therefore, spontaneous resolution is expected for the racemic salt. In fact, the crystal which was arbitrarily chosen showed the same RD curve as that of the resolved isomer. No hemihedral facets, however, were observed for the crystals. Contrary to the bromide salt, no optical activity was observed for the iodide crystals. This agrees with the solubility curve relation $S_{\Lambda}>S_{\Delta\Lambda}$ of the iodide salts (Fig. 3).

(2) Carbonatobis(ethylenediamine)cobalt(III) Complexes: The solubility curves of three optically active isomers deviate from the usual pattern at about 35 °C or above.

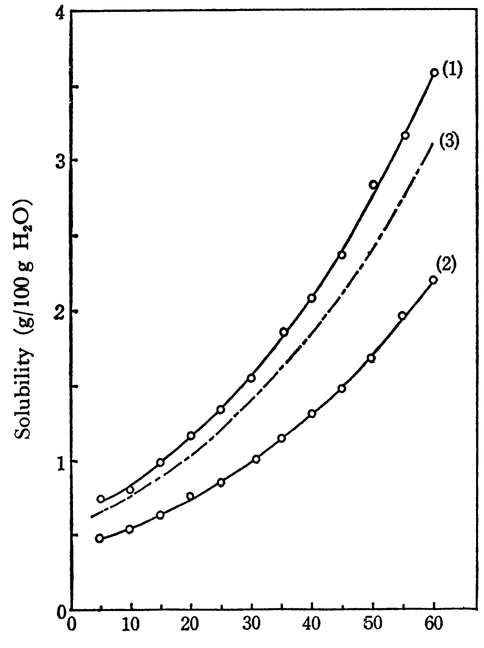

Fig. 2. Solubility curves of [Co(ox)en$_2$]Br·H$_2$O: (1) racemic form, (2) Λ form and (3) calculated curve: (2)×$\sqrt{2}$.

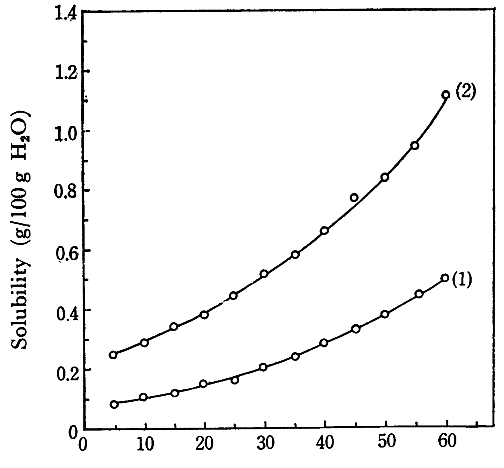

Fig. 3. Solubility curves of [Co(ox)en$_2$]I: (1) racemic form, (2) Λ form.

It was confirmed by the absorption and optical rotation measurements that these deviations arose from racemization. An inflection appears at 16 °C for the racemic bromide salt (Fig. 4) and at 17 °C for the racemic iodide one. These are the transition points from the dihydrates (below 16 °C or 17 °C) to the anhydrous (above 16 °C or 17 °C). The solubility curve of the racemic bromide (16—30 °C) shown by the dotted line is attributable to the metastable state of the dihydrate (Fig. 4). Both the chloride and iodide salts show $S_{\Delta}>S_{\Delta\Lambda}$ type. The bromide shows $S_{\Delta}<S_{\Delta\Lambda}$, but the curve of racemic salt is lower than the calculated $\sqrt{2}$ times curve of the active salt. Spontaneous resolution was not observed.

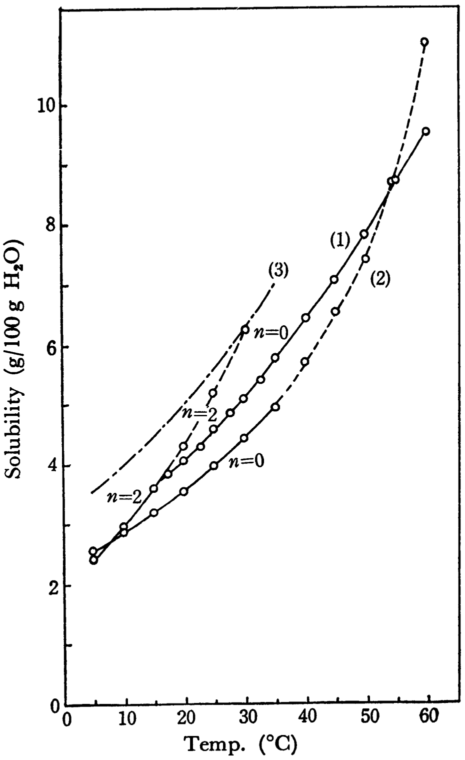

Fig. 4. Solubility curves of [CoCO$_3$en$_2$]Br·nH$_2$O: (1) racemic form, (2) Δ form and (3) calculated curve: (2)×$\sqrt{2}$.

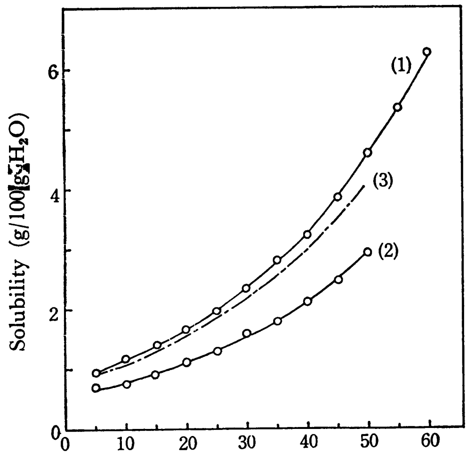

Fig. 5. Solubility curves of *cis*-[Co(NO$_2$)$_2$en$_2$]Br: (1) racemic form, (2) Δ form and (3) calculated curve: (2)×$\sqrt{2}$.

(3) cis-Bis(ethylenediamine)dinitrocobalt(III) Complexes: Spontaneous resolution is expected for the chloride and bromide salts, since both salts show a solubility $S_{\Delta\Lambda}$ larger than the calculated $\sqrt{2}$ times curve of the active salt (Table 2 and Fig. 5). The crystals from the racemic mixture show a similar RD curve to that of the resolved isomer. However, the crystals did not show any hemihedral facets. In contrast to the chloride and bromide salts, no optical rotation was observed for the crystals from the racemic iodide salt in spite of the $S_{\Delta\Lambda}>S_{\Delta}$ type (Fig. 6). This is acceptable in view of the relationship $S_{\Delta\Lambda}<\sqrt{2}S_{\Delta}$.

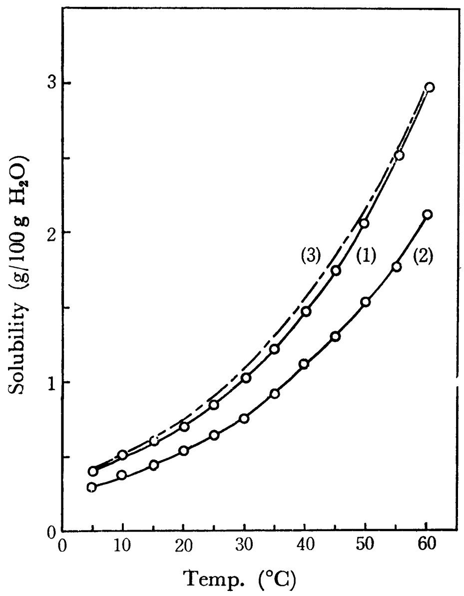

Fig. 6. Solubility curves of *cis*[$Co(NO_2)_2en_2$]I: (1) racemic form, (2) Δ form and (3) calculated curve: $(2)\times\sqrt{2}$.

(4) Ethylenediaminetetraacetatocobaltate(III) Complexes: Spontaneous resolution has been reported for NH_4-[Co(edta)]·$2H_2O$ and Rb[Co(edta)]·$2H_2O$, both of which belong to the space group $P2_12_12_1$. The solubility type of NH_4[Co(edta)]·$2H_2O$ is $S_{\Delta\Lambda}>\sqrt{2}S_{\Delta}$ in agreement with the above information. The curves of K[Co(edta)]·$2H_2O$ are quite similar to those of ammonium salts and suggest the possibility of spontaneous resolution. In fact, the crystal from the racemic mixture shows a quite similar RD curve to that of the resolved isomer. No distinguishable hemihedral facet could be observed.

The results confirm the view that spontaneous resolution is predictable from the relation between the solubility of racemic and optically active salts. The method we proposed is fairly useful for the investigation of spontaneous resolution, since distinguishable hemihedral facets are not always observable. The result suggests that the spontaneously resolvable salts are unexpectedly distributed in the cobalt(III) complexes of (1 : 1) electrolyte type.