  Bull. Chem. Soc. Jpn., 54, 2317—2322 (1981)

Solubility Isotherms of Systems Containing Optically Active Tris(ethylenediamine)cobalt(III) Ion. II.[1] Reciprocal Salt-pairs, (Λ-$[Co(en)_3]^{3+}$, Δ-$[Co(en)_3]^{3+}$)-(I^-, (R,R)-$C_4H_4O_6^{2-}$), at 25 °C

Akira Fuyuhiro,* Kazuaki Yamanari, and Yoichi Shimura

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

(Received February 3, 1981)

A four-component solubility isotherm consisting of (Λ-$[Co(en)_3]^{3+}$, Δ-$[Co(en)_3]^{3+}$)-(I^-, (R,R)-$C_4H_4O_6^{2-}$)-H_2O was determined at 25 °C. It was found that four double salts *rac*-$[Co(en)_3]I_3\cdot H_2O$, Λ-$[Co(en)_3]I(d\text{-}C_4H_4O_6)\cdot 2H_2O$, Λ-$[Co(en)_3]_{0.48}\cdot\Delta$-$[Co(en)_3]_{0.52}(d\text{-}C_4H_4O_6)_{1.5}\cdot 5H_2O$, and Δ-$[Co(en)_3]I(d\text{-}C_4H_4O_6)\cdot nH_2O$ exist, six invariant points appearing. Application of this phase diagram to practical optical resolution is discussed in comparison with a system containing Br^-. Some models of phase diagram for effective optical resolution in reciprocal salt-pairs are proposed.

In a previous paper,[1] we reported on the determination of the solubility isotherm of reciprocal salt-pairs of the system (Λ-$[Co(en)_3]^{3+}$, Δ-$[Co(en)_3]^{3+}$)-(Br^-, d-H_2tart^{2-}) at 25 °C (d-H_2tart^{2-}=(R,R)-$C_4H_4O_6^{2-}$), which revealed the region of the well-known diastereomer Λ-$[Co(en)_3]Br(d\text{-}H_2tart)\cdot 5H_2O$, establishing excellent optical resolution of $[Co(en)_3]^{3+}$. On the other hand, the system containing I^- instead of Br^- has not been hitherto used for optical resolution. Thus, it is desirable to confirm the existence of a diastereomer Λ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot nH_2O$, the extent of region it occupies, whether optical resolution of $[Co(en)_3]^{3+}$ is possible, and what kind of solid exists in the region corresponding to that of gelatinous precipitate in the system of Br^-.

In order to clarify these questions, the solubility isotherm of reciprocal salt-pairs (Λ-$[Co(en)_3]^{3+}$, Δ-$[Co(en)_3]^{3+}$)-(I^-, d-H_2tart^{2-}) was determined at 25 °C and the solubility of Λ- and *rac*-$[Co(en)_3]I_3$, and Λ- and Δ-$[Co(en)_3]I(d\text{-}H_2tart)$ was measured in the range 5—60 °C. The isotherm is discussed as regards fundamental models of optical resolution in reciprocal salt-pairs.

Experimental

Materials. $[Co(en)_3]I_3\cdot H_2O$: The Λ-, Δ-, and *rac*-$[Co(en)_3]I_3\cdot H_2O$ were obtained by the method of Broomhead *et al.*[2] Found: C, 11.29; H, 4.06; N, 13.16%. Calcd for Λ-$[Co(en)_3]I_3\cdot H_2O$: C, 11.30; H, 4.11; N, 13.17%. Found: C, 11.36; H, 4.06; N, 13.12%. Calcd for Δ-$[Co(en)_3]I_3\cdot H_2O$: C, 11.30; H, 4.11; N, 13.17%. Found: C, 11.31; H, 4.12; N, 13.13%. Calcd for *rac*-$[Co(en)_3]I_3\cdot H_2O$: C, 11.30; H, 4.11; N, 13.17%.

$[Co(en)_3](d\text{-}H_2tart)_{1.5}\cdot nH_2O$: The Λ- and Δ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}\cdot nH_2O$ and the Λ-$[Co(en)_3]_{0.48}\cdot\Delta$-$[Co(en)_3]_{0.52}(d\text{-}H_2tart)_{1.5}\cdot 5H_2O$ diastereomers were the same as reported.[1]

$[Co(en)_3]I(d\text{-}H_2tart)\cdot nH_2O$: The Λ- and Δ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot nH_2O$ diastereomers were prepared by mixing solutions of Λ-$[Co(en)_3]I_3$ and Λ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}$, and Δ-$[Co(en)_3]I_3$ and Δ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}$, respectively, in a 1 : 2 mole ratio. Found: C, 21.85; H, 5.85; N, 15.34%. Calcd for Λ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot 2H_2O$: C, 21.83; H, 5.86; N, 15.27%. Found: C, 21.40; H, 5.88; N, 14.78%. Calcd for Δ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot 2.5H_2O$: C, 21.48; H, 5.95; N, 15.03%.

Measurements. The solubility in water was determined in molality.[1] Since the CD intensity of $[Co(en)_3]^{3+}$ is affected by coexisting d-H_2tart^{2-}, the CD spectra of $[Co(en)_3]^{3+}$ were measured under calibrated conditions in HBr solution. The concentration of I^- was determined by titration with a $AgNO_3$ solution. The solid phases were identified by elemental analysis, absorption and CD spectra. Optical densities were measured with a JASCO UVIDEC-1 spectrophotometer and CD with a JASCO MOE-1 spectropolarimeter.

Results and Discussion

The solubility data are given in Tables 1 and 2, and Figs. 1—5. A saturated solution is expressed as a point defined by summing up the position vectors of the solubility of the component salt(s) contained.[3]

Binary Systems between 5 and 60 °C. As regards the binary solubility of the complexes (Table 1), the solubility ratio of *rac*-$[Co(en)_3]I_3$/Λ-$[Co(en)_3]I_3$ is 0.362 (5 °C) and 0.312 (60 °C), not being so small as in the corresponding bromide (0.173 (5 °C) and 0.294 (60 °C)). The ratio indicates[4] that the iodide as well as bromide are not spontaneously resolvable. This is also evident from the ternary system (Fig. 1). The Λ-$[Co(en)_3]I(d\text{-}H_2tart)$ diastereomer is more soluble below 28 °C than Λ-$[Co(en)_3]Br(d\text{-}H_2tart)$, which is unusual since a metal complex bromide is generally more soluble than the corresponding iodide. On the other hand, the

Table 1. Solubility of $[Co(en)_3]^{3+}$ salts in water (molality m/mol kg^{-1} of anhydrous salt)

T/°C	No. of salt[a]			
	(1)	(2)	(3)	(4)
5	0.0321	0.0886	0.0633	0.0886
10	0.0394	0.110	0.0795	0.114
15	0.0488	0.136	0.103	0.148
20	0.0589	0.167	0.123	0.192
25	0.0720	0.208	0.148	0.248
30	0.0865	0.249	0.179	0.319
35	0.103	0.302	0.215	0.422
40	0.123	0.367	0.258	0.542
45	0.145	0.439	0.307	0.696
50	0.173	0.538	0.376	0.905
55	0.203	0.646	0.445	1.10
60	0.242	0.775	0.532	1.35

a) (1): *rac*-$[Co(en)_3]I_3\cdot H_2O$, (2): Λ-$[Co(en)_3]I_3\cdot H_2O$, (3): Λ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot 2H_2O$, (4): Δ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot nH_2O$, n=4—5.

Table 2. Equilibrium of (Λ-$[Co(en)_3]^{3+}$, Δ-$[Co(en)_3]^{3+}$)-(I^-,d-H_2tart^{2-})-H_2O system at 25 °C

In liquid phases, solubility is presented in molality m of the component ions. Abbreviations are as follows: Λ-$[Co(en)_3]^{3+}=\Lambda^{3+}$, Δ-$[Co(en)_3]^{3+}=\Delta^{3+}$, Λ-$[Co(en)_3]I_3\cdot H_2O=\Lambda I_3$, Δ-$[Co(en)_3]I_3\cdot H_2O=\Delta I_3$, *rac*-$[Co(en)_3]I_3\cdot H_2O=\Lambda\Delta I_6$, Λ-$[Co(en)_3]I(d$-$H_2tart)\cdot 2H_2O=\Lambda I$ (tart), Λ-$[Co(en)_3]I(d$-$H_2tart)\cdot H_2O=[\Lambda I$ (tart)], Δ-$[Co(en)_3]I(d$-$H_2tart)\cdot nH_2O$(n=4—5)$=\Delta I$(tart), Λ-$[Co(en)_3](d$-$H_2tart)_{1.5}\cdot nH_2O$($n\gtrsim 7$)$=\Lambda(tart)_{1.5}$, Δ-$[Co(en)_3]$-$(d$-$H_2tart)_{1.5}\cdot nH_2O$($n\simeq 8$)$=\Delta(tart)_{1.5}$, Λ-$[Co(en)_3]_{0.48}\cdot\Delta$-$[Co(en)_3]_{0.52}(d$-$H_2tart)_{1.5}\cdot 5H_2O=(\Lambda, \Delta)(tart)_{1.5}$.
*; metastable state. Paste=a paste-like substance (composition unknown).

a)	b)	Liquid phase[c] $m/10^{-1}$ mol kg^{-1} Λ^{3+}	Δ^{3+}	I^-	Solid phase
A	2	2.08 (±0.05)		6.24 (±0.15)	ΛI_3
E_3	2	0.360 (±0.003)	0.360 (±0.003)	2.16 (±0.02)	$\Lambda\Delta I_6$
E_3 ↕ E_1	3	0.484 0.609 0.775 0.962 1.39 1.71	0.272 0.177 0.101 0.056 0.01 0.01	2.27 2.35 2.63 3.05 4.20 5.16	$\Lambda\Delta I_6$
E_1	3	2.08 (±0.03)	0.00	6.24 (±0.08)	ΛI_3 +$\Lambda\Delta I_6$
E_3 ↕ E_2	3	0.251 0.147 0.074 0.02 0.01	0.512 0.663 0.873 1.16 1.72	2.29 2.43 2.84 3.55 5.19	$\Lambda\Delta I_6$
E_2	3	0.00	2.08 (±0.03)	6.24 (±0.08)	ΔI_3 +$\Lambda\Delta I_6$
B	2		2.08 (±0.05)	6.24 (±0.15)	ΔI_3
D ↕ H_1	3	1.64 1.68 1.86 1.89 1.99 2.06 2.20		0.31 0.37 0.61 0.64 0.75 0.84 1.03	$\Lambda(tart)_{1.5}$
H_1	3	2.29 (±0.02)		1.16 (±0.05)	$\Lambda(tart)_{1.5}$ +ΛI(tart)
H_1 ↕ H_3	3	2.19 2.03 1.96 1.83 1.69 1.63 1.54		1.15 1.18 1.22 1.26 1.34 1.37 1.44	ΛI(tart)
H_3	2	1.48 (±0.02)		1.48 (±0.02)	ΛI(tart)
H_3 ↕ H_2	3	1.41 1.37 1.35 1.38 1.52 1.62 1.84 2.25 2.40 2.61		1.63 1.79 2.00 2.37 2.95 3.40 4.06 5.30 5.78 6.38	ΛI(tart)
H_2	3	2.83 (±0.05)		7.05 (±0.06)	ΛI(tart) +ΛI_3
A ↕ H_2	3	2.22 2.42 2.55 2.65		6.39 6.65 6.74 6.88	ΛI_3
H_1 ↕ H_4*	3	2.40* 2.58* 2.61* 2.84*		1.30* 1.53* 1.56* 1.86*	$\Lambda(tart)_{1.5}$*
H_4*	3	3.10* (±0.03)		2.17* (±0.03)	$\Lambda(tart)_{1.5}$* +Paste*
H_5*	3	3.08* (±0.04)		2.98* (±0.01)	[ΛI(tart)]* +Paste*
H_5* ↕ H_6*	3	3.02* 2.97* 2.90* 2.83* 2.78* 2.79* 2.99* 3.18* 3.29* 3.40* 3.56* 3.59* 3.75* 3.83*		3.01* 3.08* 3.27* 3.44* 3.72* 4.14* 5.23* 6.00* 6.40* 6.56* 7.30* 7.24* 7.82* 7.95*	[ΛI(tart)]*
H_6*	3	3.94* (±0.02)		8.33* (±0.07)	[ΛI(tart)]* +ΛI_3*
H_2 ↕ H_6*	3	3.12* 3.26* 3.43* 3.84*		7.36* 7.52* 7.79* 8.15*	ΛI_3*
E_1 ↕ P_1	4	2.46 2.59 2.67	0.00 0.00 0.00	6.67 6.78 6.86	ΛI_3 +$\Lambda\Delta I_6$
P_1	4	2.87 (±0.09)	0.00	7.11 (±0.07)	ΛI_3 +$\Lambda\Delta I_6$ +ΛI(tart)
P_1 ↕ P_4	4	2.61 2.46 2.22 1.77 1.54 1.42 1.37 1.36 1.34 1.33 1.36 1.35 1.36 1.36 1.37 1.37 1.40 1.42	0.00 0.00 0.02 0.06 0.15 0.27 0.38 0.44 0.54 0.76 0.85 0.89 1.00 1.02 1.22 1.24 1.39 1.60	6.52 6.01 5.28 3.98 3.33 3.07 2.99 2.98 2.97 3.04 3.08 3.09 3.13 3.17 3.27 3.29 3.36 3.50	$\Lambda\Delta I_6$ +ΛI(tart)
P_4	4	1.43 (±0.01)	1.70 (±0.02)	3.55 (±0.04)	$\Lambda\Delta I_6$ +ΛI(tart) +(Λ, Δ)-$(tart)_{1.5}$

TABLE 2. (Continued)

a)	b)	Liquid phase[c] $m/10^{-1}$ mol kg^{-1} A^{3+}	Δ^{3+}	I^-	Solid phase
G_1 ↕ P_2	4	1.62	0.21	0.20	$(A,\Delta)(tart)_{1.5}$ $+A(tart)_{1.5}$
		1.75	0.22	0.36	
		1.75	0.22	0.39	
		1.84	0.23	0.51	
		1.86	0.23	0.55	
H_1 ↕ P_2	4	2.29	0.05	1.16	$A(tart)_{1.5}$ $+\Delta I(tart)$
		2.32	0.07	1.17	
		2.34	0.15	1.20	
		2.42	0.27	1.26	
P_2	4	2.41 (±0.02)	0.30 (±0.01)	1.27 (±0.01)	$(A,\Delta)(tart)_{1.5}$ $+A(tart)_{1.5}$ $+\Delta I(tart)$
P_2 ↕ P_4	4	2.32	0.32	1.30	$(A,\Delta)(tart)_{1.5}$ $+\Delta I(tart)$
		2.16	0.35	1.35	
		2.08	0.36	1.40	
		2.00	0.39	1.44	
		1.84	0.45	1.55	
		1.67	0.59	1.79	
		1.53	0.82	2.15	
		1.47	1.08	2.60	
		1.45	1.25	2.87	
C ↕ F_1	3		3.21	0.19	$\Delta(tart)_{1.5}$
			3.44	0.40	
			3.73	0.72	
			4.04	1.04	
			4.38	1.39	
F_1	3		4.87 (±0.02)	1.92 (±0.02)	$\Delta(tart)_{1.5}$ $+\Delta I(tart)$
F_1 ↕ F_3	3		4.83	1.90	$\Delta I(tart)$
			4.49	1.93	
			4.44	1.93	
			4.09	1.96	
			3.76	1.99	
			3.41	2.08	
			3.08	2.14	
			2.72	2.31	
F_3	2		2.48 (±0.01)	2.48 (±0.01)	$\Delta I(tart)$
F_3 ↕ F_2	3		2.41	2.66	$\Delta I(tart)$
			2.33	2.84	
			2.32	3.01	
			2.29	3.38	
			2.34	3.78	
			2.43	4.18	
			2.57	4.81	
			2.74	5.32	
			2.84	5.67	
			2.90	5.89	
			3.10	6.49	
			3.25	6.99	
			3.42	7.44	
F_2	3		3.58 (±0.05)	7.91 (±0.11)	$\Delta I(tart)$ $+\Delta I_3$
B ↕ F_2	3		2.23	6.46	ΔI_3
			2.52	6.76	
			2.81	7.09	
			3.12	7.39	
			3.50	7.81	
E_2 ↕ P_3	4	0.00	2.37	6.54	ΔI_3 $+A\Delta I_6$
		0.00	2.70	6.88	
		0.00	3.01	7.28	
P_3	4	0.00	3.63 (±0.02)	7.95 (±0.06)	ΔI_3 $+A\Delta I_6$ $+\Delta I(tart)$
P_3 ↕ P_5	4	0.00	3.53	7.78	$A\Delta I_6$ $+\Delta I(tart)$
		0.00	3.34	7.11	
		0.00	3.09	6.45	
		0.00	3.05	6.38	
		0.03	2.74	5.35	
		0.03	2.69	5.24	
		0.04	2.63	5.06	
		0.06	2.56	4.83	
		0.08	2.50	4.56	
		0.10	2.42	4.32	
		0.16	2.38	4.13	
		0.21	2.37	4.01	
		0.27	2.35	3.89	
		0.36	2.33	3.83	
		0.49	2.34	3.78	
		0.65	2.38	3.76	
		0.85	2.45	3.83	
P_5	4	1.01 (±0.01)	2.50 (±0.02)	3.89 (±0.02)	$(A,\Delta)(tart)_{1.5}$ $+A\Delta I_6$ $+\Delta I(tart)$
G_2 ↕ P_6	4	0.10	3.34	0.33	$(A,\Delta)(tart)_{1.5}$ $+\Delta(tart)_{1.5}$
		0.11	3.76	0.71	
		0.11	4.01	0.98	
		0.11	4.30	1.27	
P_6	4	0.13 (±0.02)	4.97 (±0.06)	1.98 (±0.05)	$(A,\Delta)(tart)_{1.5}$ $+\Delta(tart)_{1.5}$ $+\Delta I(tart)$
P_6 ↕ P_5	4	0.17	4.37	2.02	$(A,\Delta)(tart)_{1.5}$ $+\Delta I(tart)$
		0.19	4.23	2.05	
		0.19	4.10	2.09	
		0.19	4.07	2.08	
		0.22	3.97	2.11	
		0.24	3.82	2.14	
		0.23	3.77	2.15	
		0.26	3.45	2.22	
		0.30	3.33	2.29	
		0.38	3.11	2.46	
		0.43	2.85	2.60	
		0.48	2.76	2.71	
		0.53	2.73	2.82	
		0.60	2.67	2.96	
		0.69	2.57	3.20	
		0.78	2.54	3.25	
		0.94	2.51	3.76	
P_4 ↕ P_5	4	1.27	1.69	3.24	$(A,\Delta)(tart)_{1.5}$ $+A\Delta I_6$
		1.23	1.77	3.27	
		1.19	1.82	3.29	
		1.16	1.90	3.31	
		1.11	1.95	3.31	
		1.06	2.05	3.37	
		1.02	2.13	3.42	

a) Positions of points shown in Figs. 1—5. b) Number of components. c) Reported data for C, D, G_1, G_2, $D \leftrightarrow G_1$, and $G_1 \leftrightarrow G_2$[1] are not shown. Values in parentheses are estimated errors and calculated from twice the standard deviations of measurements repeated 3—11 times.

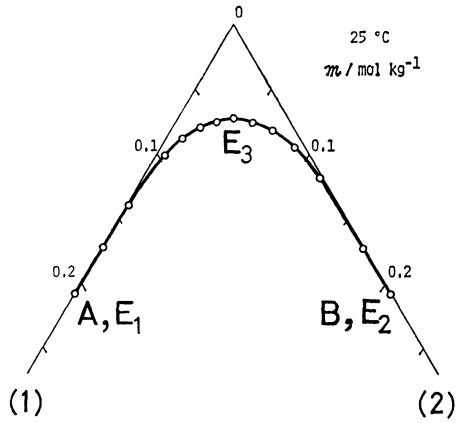

Fig. 1. Solubility isotherm of the ternary system, *Λ*-[Co(en)$_3$]I$_3$(1)–*Λ*-[Co(en)$_3$]I$_3$(2)–H$_2$O, at 25 °C. Solubility is presented in molality *m* of anhydrous salt.

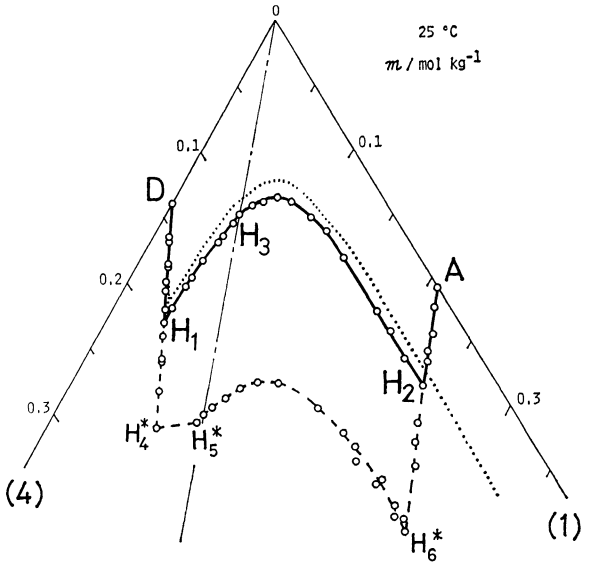

Fig. 2. Solubility isotherm of the ternary system, *Λ*-[Co(en)$_3$] (*d*-H$_2$tart)$_{1.5}$(4)–*Λ*-[Co(en)$_3$]I$_3$(1)–H$_2$O, at 25 °C. Solubility is presented in molality *m* of anhydrous salt. ---- and *: metastable state, ·····: the corresponding system of Br$^-$ at 25 °C (*Λ*-[Co(en)$_3$] (*d*-H$_2$tart)$_{1.5}$(4)–*Λ*-[Co(en)$_3$]Br$_3$(1)–H$_2$O).

solubility of *Δ*-[Co(en)$_3$]I(*d*-H$_2$tart) cannot be compared with that of *Δ*-[Co(en)$_3$]Br(*d*-H$_2$tart) because of the formation of gelatinous precipitate in the latter diastereomer. The solubility ratio of *Δ*-[Co(en)$_3$]I(*d*-H$_2$tart)/*Λ*-[Co(en)$_3$]I(*d*-H$_2$tart) is 1.40 (5 °C) and 2.54 60 °C).

Ternary System Λ-[*Co(en)*$_3$]*I*$_3$–Δ-[*Co(en)*$_3$]*I*$_3$–*H*$_2$*O*. This system at 25 °C (Fig. 1) is similar to the corresponding system of Br$^-$. The central solid phase is the racemic compound *Λ*-[Co(en)$_3$]·*Δ*-[Co(en)$_3$]I$_6$·2H$_2$O= *rac*-[Co(en)$_3$]I$_3$·H$_2$O, which occupies such a wide region ($E_1E_3E_2$) that the invariant points E_1 and E_2 exist nearly on the side axes. The solubility of racemic iodide at 25 °C (0.0720 mol kg^{-1} (E_3)) is lower than that of racemic bromide (0.178 mol kg^{-1}). The difference is considerably responsible for optical resolution in the four-component system described below.

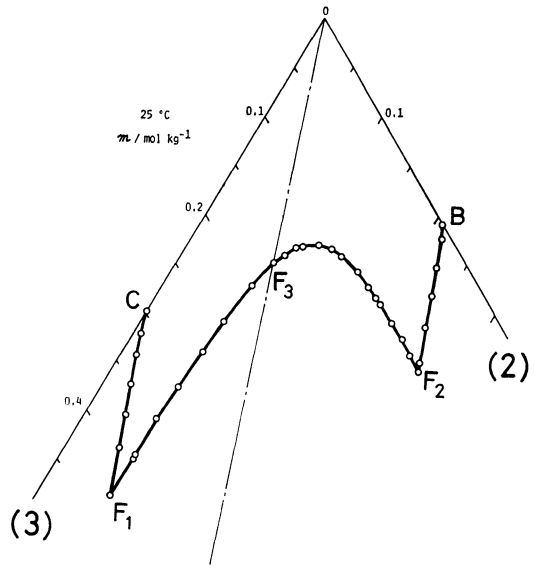

Fig. 3. Solubility isotherm of the ternary system, *Δ*-[Co(en)$_3$] (*d*-H$_2$tart)$_{1.5}$ (3)–*Δ*-[Co(en)$_3$] I$_3$(2) – H$_2$O, at 25 °C. Solubility is presented in molality *m* of anhydrous salt.

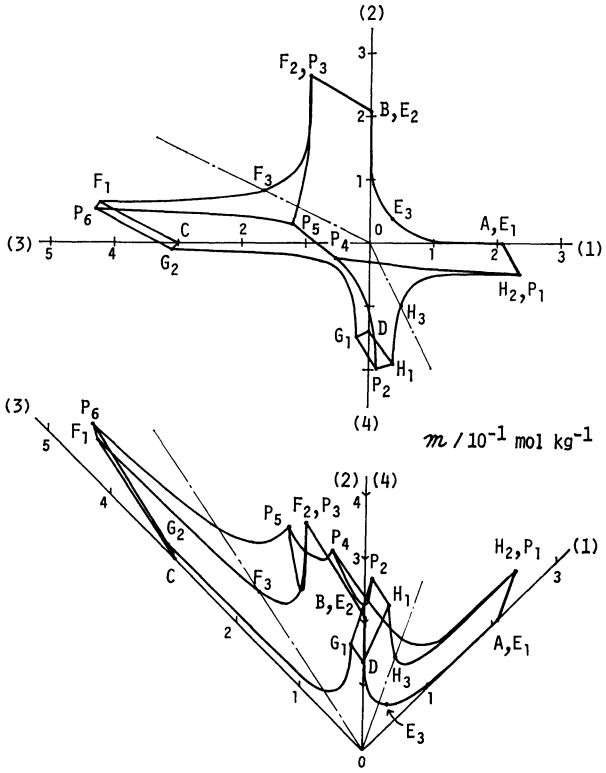

Fig. 4. The plane projection (upper) and the side elevation of solubility isotherm of the system, (*Λ*-[Co(en)$_3$]$^{3+}$, *Δ*-[Co(en)$_3$]$^{3+}$)–(I$^-$, *d*-H$_2$tart^{2-})–H$_2$O, at 25 °C. Solubility is presented in molality *m* of anhydrous salt. (1): *Λ*-[Co(en)$_3$]I$_3$, (2): *Δ*-[Co(en)$_3$]I$_3$, (3): *Δ*-[Co(en)$_3$](*d*-H$_2$tart)$_{1.5}$, (4): *Λ*-[Co(en)$_3$](*d*-H$_2$tart)$_{1.5}$.

Ternary System Λ-[*Co(en)*$_3$](d-*H*$_2$*tart)*$_{1.5}$–Λ-[*Co(en)*$_3$]*I*$_3$–*H*$_2$*O*. This system consists of only *Λ*-salts (Fig. 2). The region $H_1H_3H_2$ shows a diastereomer of double salt *Λ*-[Co(en)$_3$]I(*d*-H$_2$tart)·2H$_2$O, its isotherm being

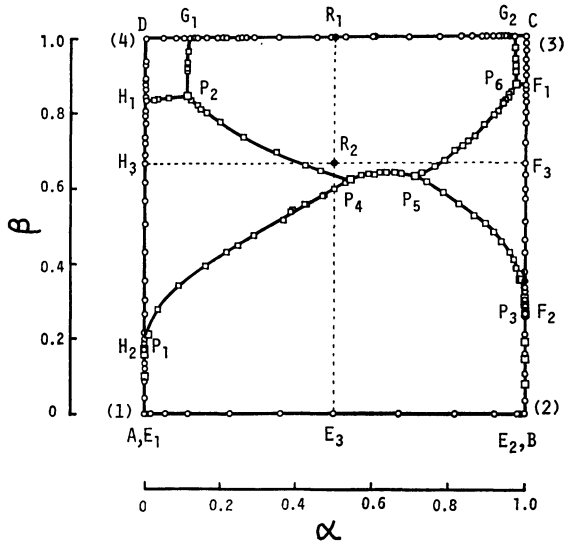

Fig. 5. The clinographic projection of solubility isotherm of the system, (Λ-$[Co(en)_3]^{3+}$, Λ-$[Co(en)_3]^{3+}$)-(I^-, d-H_2tart^{2-})-H_2O, at 25 °C.
α: mole fraction of Λ-$[Co(en)_3]^{3+}$ to all the cations, β: mole fraction of $(d\text{-}H_2tart)_{1.5}{}^{3-}$ to $\{(I_3)^{3-} + (d\text{-}H_2tart)_{1.5}{}^{3-}\}$, (1): Λ-$[Co(en)_3]I_3$, (2): Λ-$[Co(en)_3]I_3$, (3): Λ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}$, (4): Λ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}$, □: solubilities of four-components, ○: solubilities of two- or three-componts.

located a little lower than that of bromide double salt Λ-$[Co(en)_3]Br(d\text{-}H_2tart)\cdot 5H_2O$. The binary solubility of Λ-$[Co(en)_3]I(d\text{-}H_2tart)$ (H_3, m=0.148 mol kg^{-1} at 25 °C) is larger than that of Λ-$[Co(en)_3]Br(d\text{-}H_2tart)$ (m=0.135 mol kg^{-1}). The line AH_2 appears in a region different from that for the corresponding bromide double salt because of the solubility difference between Λ-$[Co(en)_3]Br_3$ and Λ-$[Co(en)_3]I_3$.

Some metastable states were measured in the system containing I^-; the supersaturated solutions coexist with the metastable solids, Λ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}\cdot nH_2O$ on H_1H_4* and Λ-$[Co(en)_3]I_3\cdot H_2O$ on H_2H_6*. The composition of a paste-like solid phase on H_4*H_5* is unknown. The line H_5*H_6* expresses the metastable isotherm for Λ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot H_2O$. However, this monohydrated diastereomer did not appear as a stable solid in the binary system at 5—60 °C (Table 1). On the other hand, the corresponding bromide double salt Λ-$[Co(en)_3]Br(d\text{-}H_2tart)$ exists as a monohydrated solid phase above 47 °C.

Ternary System Δ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}$-$\Delta$-$[Co(en)_3]I_3$-$H_2O$. In this system (Fig. 3), which differs entirely from the corresponding bromide system where the central part of the isotherms is blank owing to the appearance of a gelatinous substance, the isothermal line $F_1F_3F_2$, on which a saturated solution is in equilibrium with the solid Λ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot nH_2O$ can be measured. Point F_3 denotes the binary solubility of Λ-$[Co(en)_3]I(d\text{-}H_2tart)$.

The Solubility Isotherm of Reciprocal Salt-pairs, (Λ-$[Co(en)_3]^{3+}$, Δ-$[Co(en)_3]^{3+}$)-(I^-, d-H_2tart^{2-})-H_2O.
The ternary systems described above constitute a part of the system of reciprocal salt-pairs. This four-component body was projected on three planes,[3] the plane projection and the side elevation (Fig. 4), and the clinographic projection (Fig. 5). The upper side in Fig. 5 represents the ternary system, Λ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}$-$\Lambda$-$[Co(en)_3](d\text{-}H_2tart)_{1.5}$-$H_2O$, being common between two systems of X^-=Br^- and I^-, (Λ-$[Co(en)_3]^{3+}$, Λ-$[Co(en)_3]^{3+}$)-(X^-, d-H_2tart^{2-})-H_2O. Eight solid phases appear, the composition of each phase corresponding to the following solid: A=Λ-$[Co(en)_3]I_3\cdot H_2O$, B=Λ-$[Co(en)_3]I_3\cdot H_2O$, C=Λ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}\cdot nH_2O$, D=$\Lambda$-$[Co(en)_3](d\text{-}H_2tart)_{1.5}\cdot nH_2O$, E_3=*rac*-$[Co(en)_3]I_3\cdot H_2O$, F_3=Λ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot nH_2O$, (close of R_1)=Λ-$[Co(en)_3]_{0.48}\cdot\Lambda$-$[Co(en)_3]_{0.52}(d\text{-}H_2tart)_{1.5}\cdot 5H_2O$, and H_3=Λ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot 2H_2O$. The present system essentially resembles the corresponding bromide system except for two aspects: (a) appearance of the region of Λ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot nH_2O$, $P_3F_2F_3F_1P_6P_5P_3$, though in the bromide system the corresponding region could not be measured because of the formation of the gelatinous precipitate, and (b) a different combination of phase boundaries. If the gelatinous precipitate in the bromide system is assumed to be a solid phase, the regions of Λ-$[Co(en)_3]Br(d\text{-}H_2tart)\cdot 5H_2O$ and the gelatinous precipitate coexist on the boundary line. On the other hand, the corresponding regions of Λ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot 2H_2O$ ($H_1H_3H_2P_1P_4P_2H_1$) and Λ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot nH_2O$ do not coexist, and the regions of *rac*-$[Co(en)_3]I_3\cdot H_2O$ ($E_1E_3E_2P_3P_5P_4P_1E_1$) · and Λ-$[Co(en)_3]_{0.48}\cdot\Lambda$-$[Co(en)_3]_{0.52}(d\text{-}H_2tart)_{1.5}\cdot 5H_2O$ ($G_1P_2P_4P_5P_6G_2R_1G_1$) coexist on the boundary P_4P_5. Since Λ-$[Co(en)_3]Br(d\text{-}H_2tart)\cdot 5H_2O$ and Λ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot 2H_2O$ have almost the same solubility (H_3) and the upper side of the iodide system is the same as that of the bromide system, the positions of H_1 and P_2 or the lines H_1P_2 and G_1P_2 are almost the same as the corresponding points or lines in the bromide system. The line P_2P_4 is located at almost the same position as in the bromide system on the clinographic projection. However, the location of the line P_1P_4, on which *rac*-$[Co(en)_3]X_3\cdot nH_2O$ and Λ-$[Co(en)_3]X(d\text{-}H_2tart)\cdot nH_2O$ (X=Br and I) coexist, differs in the two systems. This results from the solubility difference between *rac*-$[Co(en)_3]Br_3$ and *rac*-$[Co(en)_3]I_3$ (E_3), irrespective of a similar solubility for Λ-$[Co(en)_3]Br(d\text{-}H_2tart)$ and Λ-$[Co(en)_3]I(d\text{-}H_2tart)$ (H_3).

Application to Optical Resolution. The line of α=0.5 (R_1E_3) in Fig. 5 is a "racemic line" where the concentrations of Λ-$[Co(en)_3]^{3+}$ and Λ-$[Co(en)_3]^{3+}$ are equal. If a region of a diastereomer containing only one enantiomer spreads across the "racemic line," such an isotherm can be used for perfect optical resolution. In the present system at 25 °C, the region of Λ-$[Co(en)_3]I(d\text{-}H_2tart)\cdot 2H_2O$ spreads across the "racemic line" and the system can be used for optical resolution. However, the useful region is too narrow to be used effectively.

Let us consider the following case of optical resolution of *rac*-$[Co(en)_3]X_3$ (X=Br or I) by the addition of x mol of $Ag_2(d\text{-}H_2tart)$ at 25 °C ($0\leqq x\leqq 1.5$).

$$rac\text{-}[Co(en)_3]X_3 + xAg_2(d\text{-}H_2tart) \longrightarrow$$
$$rac\text{-}[Co(en)_3]^{3+} + (3-2x)X^- + xd\text{-}H_2tart^{2-} + AgX\downarrow$$

In the case of $x=1$ (R_2 in Fig. 5) the first precipitate is Λ-$[Co(en)_3]_{0.48}$·Δ-$[Co(en)_3]_{0.52}$(d-$H_2tart)_{1.5}$·$5H_2O$, not Λ-$[Co(en)_3]X$(d-H_2tart)·nH_2O. Optical resolution is successful in the range $0.43<x<0.97$ in the bromide system.[1] Similarly in the case of iodide system optical resolution will be accomplished only in the range $0.89<x<0.95$. The maximum yield corresponding to P_4 will become only 15.7% for Λ-$[Co(en)_3]^{3+}$ (7.8% for *rac*-$[Co(en)_3]^{3+}$).

Thus, the solubility difference between Λ-$[Co(en)_3]I$-(d-H_2tart) and Δ-$[Co(en)_3]I$(d-H_2tart) is not directly related to whether optical resolution is successful or not.

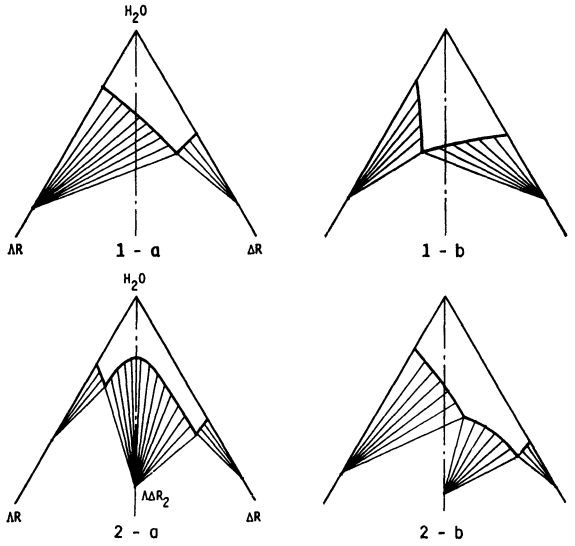

Fig. 6. Models of solubility isotherm of the ternary system ΛR–ΔR–H_2O for optical resolution.
Λ^+ and Δ^+:a pair of enantiomers, R^-: a resolving agent.

Models of Phase Diagram for Optical Resolution.
The simplest phase diagram applicable to optical resolution is the ternary system ΛR–ΔR–H_2O shown in Fig. 6, where ΛR is the less soluble diastereomer. Model **1-a** can be used for optical resolution and involves the practical examples Λ-$[Co(ox)(en)_2]$(d-H_3tart)·Δ-[Co(ox)$(en)_2$](d-H_3tart)–H_2O and Λ-$[Co(ox)(en)_2]$·Δ-[Co(edta)]–Δ-$[Co(ox)(en)_2]$·Δ-[Co(edta)]–H_2O.[5] Model **1-b** can also be available, and the diastereomer obtained is the more soluble ΔR and not the less soluble ΛR. Model **2-a** can not be used because of the formation of pseudoracemate $\Lambda\Delta R_2$ in the central part. In model **2-b** optical resolution is possible in spite of the formation of the pseudoracemate. Such a case is exemplified by the system Λ-$[Co(ox)(en)_2]$(d-bcs)–Δ-$[Co(ox)(en)_2]$(d-bcs)–H_2O at a temperature below 19 °C (d-bcs^-= (1*R*,3*S*,4*S*,7*R*)-$C_{10}H_{14}OBrSO_3^-$).[6] If we assume that **2-b** is a special case, the possibility of optical resolution of the ternary system depends upon whether the pseudoracemate $\Lambda\Delta R_2$ exists or not, and not on the solubility difference between the pair of diastereomers ΛR and ΔR.

Figure 7 shows several representative models of clinographic projections for the systems of reciprocal salt-pairs effective for optical resolution, (Λ^+, Δ^+)–(X^-, R^-)–H_2O. Effective optical resolution requires that the region of a diastereomer (ΛR, for example) spreads across the "racemic line." Model **3** without any double salt is effective for optical resolution. The upper side of **3** corresponds to the ternary system of **1-a**, introduction of a fourth ion X^- not being important. In **4** there exist two effective diastereomers ΛR and Λ_2XR which include the opposite enantiomer to each other. The upper side of **5** corresponds to **2-b** but the introduction of X^- makes the optical resolution possible: the ΛR diastereomer will be obtained in the coexistence of X^-. Similarly, in model **6** optical resolution is unsuccessful in the absence of X^-, and the effective diastereomer is a double salt Λ_2XR. The systems (Λ-$[Co(en)_3]^{3+}$, Δ-$[Co(en)_3]^{3+}$)–(X^-, d-H_2tart^{2-})–H_2O, X^-=Br^- and I^-, belong to a variety of **6**. Two kinds of diastereomers ΛR and Λ_2XR can be utilized in **7**.

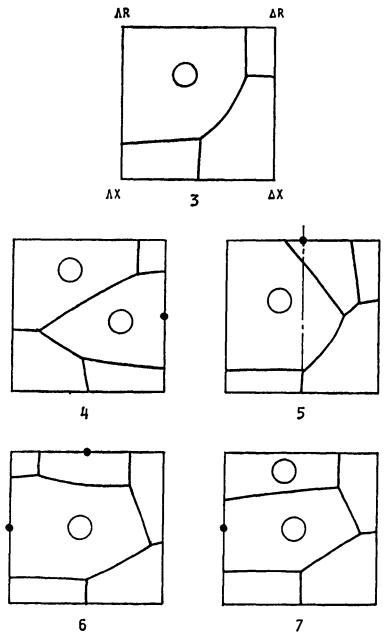

Fig. 7. Models of clinographic projection of solubility isotherm of the system (Λ^+, Δ^+)–(X^-, R^-)–H_2O for effective optical resolution.
Λ^+ and Δ^+: a pair of enantiomers, X^-: a optically inactive ion, R^-: a resolving agent, ○: the region of effective diasteromer for optical resolution, ●: double salt.

References

1) Part I of this series: A. Fuyuhiro, K. Yamanari, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **53**, 3577 (1980).
2) J. A. Broomhead, F. P. Dwyer, and J. W. Hogarth, *Inorg. Synth.*, **6**, 186 (1960).
3) A. Fuyuhiro, K. Yamanari, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **52**, 90 (1979).
4) K. Yamanari, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **46**, 3724 (1973).
5) Y. Shimura and K. Tsutsui, *Bull. Chem. Soc. Jpn.*, **50**, 145 (1977).
6) A. Fuyuhiro, K. Yamanari, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **52**, 1420 (1979).