Solubility Isotherms of Systems Containing Optically Active Tris(ethylenediamine)cobalt(III) Ion. III.[1] Quaternary System, (Λ-$[Co(en)_3]^{3+}$, Δ-$[Co(en)_3]^{3+}$, H^+)-(*R*,*R*)-$C_4H_4O_6^{2-}$-H_2O, at 25 °C

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A part of quaternary solubility isotherm, (Λ-$[Co(en)_3]^{3+}$, Δ-$[Co(en)_3]^{3+}$, H^+)-(*R*,*R*)-$C_4H_4O_6^{2-}$-H_2O, $C_{H^+} \leqq C_{(R,R)\text{-}C_4H_4O_6^{2-}}$, was determined at 25 °C. It was found that three double salts Λ- and Δ-$[Co(en)_3](d\text{-}C_4H_5O_6)\cdot(d\text{-}C_4H_4O_6)\cdot nH_2O$ and Λ-$[Co(en)_3]_{0.48}\cdot\Delta$-$[Co(en)_3]_{0.52}(d\text{-}C_4H_4O_6)_{1.5}\cdot 5H_2O$ exist, three invariant points appearing. The yield for optical resolution of $[Co(en)_3]^{3+}$ found to be constant regardless of $[H^+]$. The existence of complete ternary system containing double salts, Λ-$[Co(en)_3](d\text{-}C_4H_5O_6)(d\text{-}C_4H_4O_6)$-$\Delta$-$[Co(en)_3](d\text{-}C_4H_5O_6)$-$(d\text{-}C_4H_4O_6)$-$H_2O$, was found and the solubilities of Λ- and Δ-$[Co(en)_3](d\text{-}C_4H_5O_6)(d\text{-}C_4H_4O_6)$ were measured at 5—65 °C.

The diastereomer of double salt Λ-$[Co(en)_3]X(d\text{-}H_2tart)$ (X^-=Br^- and I^-; $d\text{-}H_2tart^{2-}$=(*R*,*R*)-$C_4H_4O_6^{2-}$) can be used for the optical resolution of $[Co(en)_3]^{3+}$ ion. The particular role of the optically inactive component X^- has been revealed by the solubility phase diagrams of reciprocal salt-pairs, (Λ-$[Co(en)_3]^{3+}$, Δ-$[Co(en)_3]^{3+}$)-(X^-, $d\text{-}H_2tart^{2-}$)-H_2O.[1,2] A similar compound Λ-$H[Co(en)_3](d\text{-}H_2tart)_2\cdot 3H_2O$ was recently reported by Tada *et al.*[3] This diastereomer can be considered to be Λ-$[Co(en)_3](d\text{-}H_3tart)(d\text{-}H_2tart)\cdot 3H_2O$ corresponding to the case of X^-=$d\text{-}H_3tart^-$ in the above formula and have, so to speak, two optically active resolving agents. The system containing this diastereomer will be completely described by a quaternary system (Λ-$[Co(en)_3]^{3+}$, Δ-$[Co(en)_3]^{3+}$, H^+)-$d\text{-}H_2tart^{2-}$-H_2O. When the concentration of H^+ is lower than that of $d\text{-}H_2tart^{2-}$, a part of the system, however, can be formally regarded as the following reciprocal salt-pairs (Λ-$[Co(en)_3]^{3+}$, Δ-$[Co(en)_3]^{3+}$)-($d\text{-}H_3tart^-$, $d\text{-}H_2tart^{2-}$)-H_2O.

In this paper, we report the solubility isotherm of quaternary system (Λ-$[Co(en)_3]^{3+}$, Δ-$[Co(en)_3]^{3+}$, H^+)-$d\text{-}H_2tart^{2-}$-H_2O. This system was covered incompletely by the present experiment because the body of the solubility phase diagram does not form a closed space owing to the lack of solid phases Λ- and Δ-$[Co(en)_3](d\text{-}H_3tart)_3\cdot nH_2O$, and Λ-$[Co(en)_3]_p\cdot\Delta$-$[Co(en)_3]_q(d\text{-}H_3tart)_{3(p+q)}\cdot n'H_2O$. As regards optical resolution, the isotherms of X^-=$d\text{-}H_3tart^-$, however, can be effectively compared with those of X^-=Br^- and I^-.

Experimental

Materials. *[Co(en)$_3$](d-H$_2$tart)$_{1.5}$·nH$_2$O*: 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.[2]

d-*H$_4$tart*: A guaranteed reagent of Nakarai Chemicals Ltd. was employed.

[Co(en)$_3$](d-H$_3$tart)(d-H$_2$tart)·nH$_2$O: The Λ- (or Δ-)$[Co(en)_3](d\text{-}H_3tart)(d\text{-}H_2tart)\cdot nH_2O$ diastereomer was prepared by mixing solutions of Λ- (or Δ-)$[Co(en)_3](d\text{-}H_2tart)_{1.5}\cdot nH_2O$ and $d\text{-}H_4tart$ in a 2:1 mole ratio. Found: C, 28.55; H, 6.62; N, 14.30%. Calcd for Λ-$[Co(en)_3](d\text{-}H_3tart)(d\text{-}H_2tart)\cdot 3H_2O$: C, 28.48; H, 6.66; N, 14.23%. Found: C, 24.84; H, 7.08; N, 12.49%. Calcd for Δ-$[Co(en)_3](d\text{-}H_3tart)(d\text{-}H_2tart)\cdot 7.5H_2O$: C, 25.04; H, 7.20; N, 12.52%.

Measurements. The solubility in water was determined in molality and the calibration of CD was also carried out according to the previous method.[2] The concentration of H^+ was determined by titration with a 0.01 mol dm^{-3} NaOH solution. The solid phases were identified by elemental analysis, absorption and CD spectra. Optical densities were measured with a Hitachi 330 spectrophotometer and CD with a JASCO MOE-1 spectropolarimeter. The absorption maximum value, ε(466 nm)=88.4, was used in this study.

Results and Discussion

Ternary System Λ-*[Co(en)$_3$](d-H$_2$tart)$_{1.5}$*-Λ-*[Co(en)$_3$](d-H$_3$tart)$_3$*-*H$_2$O*. The ternary system, Λ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}$-$d\text{-}H_4tart$-$H_2O$, was partially determined at 25 °C (Fig. 1 and Table 1). The axis (1) expresses the molality of Λ-$[Co(en)_3](d\text{-}H_3tart)_3$, though the salt does not exist as solid. When the concentration of H^+ is lower than that of $d\text{-}H_2tart^{2-}$, the present system can be represented formally as the ternary one, Λ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}$(4)-$\Lambda$-$[Co(en)_3](d\text{-}H_3tart)_3$(1)-$H_2O$, and then can be compared with

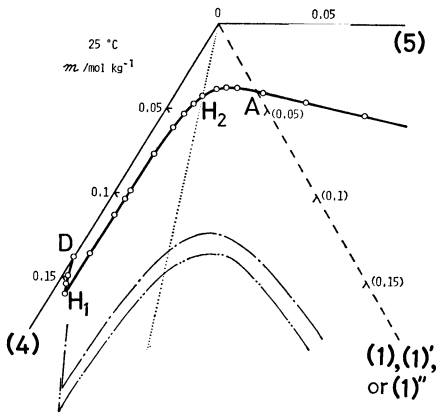

Fig. 1. Solubility isotherm (partial) of the ternary system, Λ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}$(4)-$(d\text{-}H_4tart)_{1.5}$(5)-$H_2O$, at 25 °C.
Solubility is presented in molality *m* of anhydrous salt.
—·—: The ternary system, Λ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}$(4)-$\Lambda$-$[Co(en)_3]Br_3$(1)′-$H_2O$, —··—: the ternary system, Λ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}$(4)-$\Lambda$-$[Co(en)_3]I_3$(1)″-$H_2O$.

Table 1. Equilibrium of (Λ-$[Co(en)_3]^{3+}$, Δ-$[Co(en)_3]^{3+}$, H^+)-d-H_2tart^{2-}-H_2O system at 25 °C ($[H^+] \leqq [d\text{-}H_2tart^{2-}]$)

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-$[Co(en)_3](d\text{-}H_2tart)_{1.5}\cdot nH_2O (n \gtrsim 7) = \Lambda(tart)_{1.5}$, Δ-$[Co(en)_3](d\text{-}H_2tart)_{1.5}\cdot nH_2O (n \simeq 8) = \Delta(tart)_{1.5}$, Λ-$[Co(en)_3]_{0.48}\cdot\Delta$-$[Co(en)_3]_{0.52}(d\text{-}H_2tart)_{1.5}\cdot 5H_2O = (\Lambda,\Delta)(tart)_{1.5}$, Λ-$[Co(en)_3](d\text{-}H_3tart)(d\text{-}H_2tart)\cdot 3H_2O = \Lambda(Htart)(tart)$, Δ-$[Co(en)_3](d\text{-}H_3tart)(d\text{-}H_2tart)\cdot 8H_2O = \Delta(Htart)(tart)$.

Position of points (Figs. 1—4)	No. of components	Liquid phase[a], $m/10^{-1}$ mol kg^{-1}			Solid phase
		Λ^{3+}	Δ^{3+}	H^+	
D	3	1.49		0.07	$\Lambda(tart)_{1.5}$
↕		1.54		0.12	
H_1					
H_1	3	1.60 (±0.01)		0.202 (±0.002)	$\Lambda(tart)_{1.5}+\Lambda(Htart)(tart)$
H_1	3	1.36		0.204	$\Lambda(Htart)(tart)$
		1.13		0.212	
		1.04		0.217	
		0.985		0.222	
↕		0.769		0.244	
H_2		0.614		0.283	
		0.531		0.320	
		0.471		0.362	
		0.440		0.403	
H_2	2	0.426 (±0.001)		0.426 (±0.001)	$\Lambda(Htart)(tart)$
H_2	3	0.383		0.573	$\Lambda(Htart)(tart)$
↕		0.377		0.693	
A		0.376		0.868	
C	3		3.09	0.108	$\Lambda(tart)_{1.5}$
			3.27	0.223	
			3.40	0.349	
↕			3.42	0.399	
F_1			3.53	0.506	
			3.55	0.510	
			3.71	0.671	
			3.81	0.769	
			4.04	0.980	
F_1	3		4.35 (±0.03)	1.31 (±0.03)	$\Lambda(tart)_{1.5}+\Lambda(Htart)(tart)$
F_1	3		4.29	1.33	$\Lambda(Htart)(tart)$
			4.17	1.32	
			3.92	1.33	
			3.24	1.36	
↕			2.91	1.38	
F_2			2.67	1.44	
			2.32	1.52	
			2.15	1.59	
			2.06	1.68	
			1.96	1.75	
F_2	2		1.86 (±0.01)	1.86 (±0.01)	$\Lambda(Htart)(tart)$
F_2	3		1.75	2.18	$\Lambda(Htart)(tart)$
			1.67	2.58	
			1.67	2.87	
↕			1.70	3.44	
B			1.79	4.25	
			1.89	4.87	
			2.04	5.88	
H_1	4	1.58	0.05	0.205	$\Lambda(tart)_{1.5}+\Lambda(Htart)(tart)$
↕		1.60	0.09	0.217	
P_1		1.63	0.16	0.218	
P_1	4	1.66 (±0.01)	0.21 (±0.01)	0.226 (±0.004)	$\Lambda(tart)_{1.5}+\Lambda(Htart)(tart)$ $+(\Lambda,\Delta)(tart)_{1.5}$

TABLE 1. (Continued)

Position of points (Figs. 1—4)	No. of components	Liquid phase[a], $m/10^{-1}$ mol kg^{-1} Λ^{3+}	Δ^{3+}	H^+	Solid phase
P_1 ↕ P_3	4	1.48	0.23	0.232	Λ(Htart)(tart) +(Λ,Δ)(tart)$_{1.5}$
		1.30	0.25	0.244	
		1.13	0.28	0.262	
		1.03	0.31	0.283	
		0.917	0.343	0.302	
		0.839	0.382	0.323	
		0.787	0.416	0.349	
		0.747	0.435	0.362	
		0.734	0.455	0.371	
		0.698	0.489	0.403	
		0.669	0.509	0.417	
		0.638	0.558	0.452	
		0.554	0.707	0.548	
		0.519	0.811	0.622	
		0.492	0.908	0.706	
		0.48	1.01	0.782	
		0.45	1.18	0.909	
		0.43	1.37	1.07	
		0.42	1.48	1.16	
		0.41	1.79	1.43	
		0.40	2.15	1.73	
P_3	4	0.40 (±0.01)	2.32 (±0.02)	1.90 (±0.02)	Λ(Htart)(tart) +Δ(Htart)(tart) +(Λ,Δ)(tart)$_{1.5}$
G_2 ↕ P_2	4	0.10	3.20	0.128	Δ(tart)$_{1.5}$+(Λ,Δ)(tart)$_{1.5}$
		0.11	3.44	0.368	
		0.11	4.05	0.920	
P_2	4	0.13 (±0.02)	4.48 (±0.02)	1.37 (±0.03)	Δ(tart)$_{1.5}$+Δ(Htart)(tart) +(Λ,Δ)(tart)$_{1.5}$
P_2 ↕ P_3	4	0.17	4.19	1.41	Λ(Htart)(tart) +(Λ,Δ)(tart)$_{1.5}$
		0.18	3.72	1.42	
		0.19	3.64	1.45	
		0.20	3.43	1.45	
		0.20	3.38	1.46	
		0.22	3.28	1.51	
		0.25	2.99	1.55	
		0.30	2.68	1.68	
		0.35	2.48	1.76	
P_3 ↕ I	4	0.39	2.24	1.93	Λ(Htart)(tart) +Δ(Htart)(tart)
		0.37	2.11	1.99	
		0.35	1.99	2.08	
		0.33	1.92	2.24	
I	3	0.33 (±0.01)	1.91 (±0.01)	2.24 (±0.01)	Λ(Htart)(tart) +Δ(Htart)(tart)
I ↕ E	4	0.31	1.85	2.44	Λ(Htart)(tart) +Δ(Htart)(tart)
		0.31	1.78	2.63	
		0.30	1.75	2.75	
		0.30	1.73	2.94	
		0.29	1.72	3.23	
		0.29	1.73	3.46	
		0.30	1.76	3.85	
		0.30	1.76	4.03	
		0.31	1.80	4.41	
		0.32	1.86	4.95	
		0.34	1.94	5.59	
		0.36	2.11	6.69	
		0.39	2.31	8.04	
H_2 ↕ I	3	0.400	0.101	0.501	Λ(Htart)(tart)
		0.390	0.168	0.558	
		0.376	0.248	0.624	
		0.353	0.431	0.784	
		0.335	0.678	1.01	
		0.325	0.941	1.27	
		0.32	1.24	1.57	
		0.32	1.58	1.91	

Table 1. (Continued)

Position of points (Figs. 1—4)	No. of components	Liquid phase,[a] $m/10^{-1}$ mol kg^{-1} Λ^{3+}	Λ^{3+}	H^+	Solid phase
F_2 ↕ I	3	0.16	1.88	2.04	Λ(Htart)(tart)

a) Reported data for C, D, G_1, G_2, D→G_1, and G_1→G_2[2] are not shown. Values in parentheses are estimated errors and calculated from twice the standard deviations of measurements repeated 5—8 times.

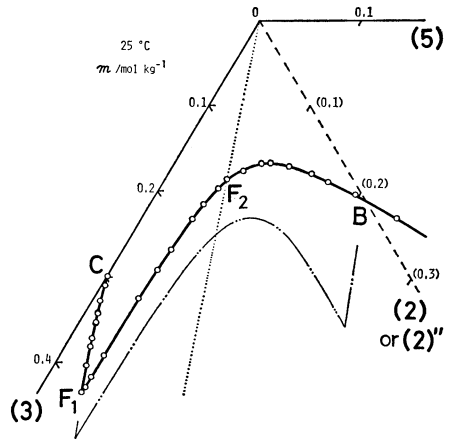

Fig. 2. Solubility isotherm (partial) of the ternary system, Λ-[Co(en)$_3$](d-H$_2$tart)$_{1.5}$(3)–(d-H$_4$tart)$_{1.5}$(5)–H$_2$O, at 25 °C.
Solubility is presented in molality m of anhydrous salt. —··—: the ternary system, Λ-[Co(en)$_3$](d-H$_2$tart)$_{1.5}$(3)–Λ-[Co(en)$_3$]I$_3$(2)"–H$_2$O.

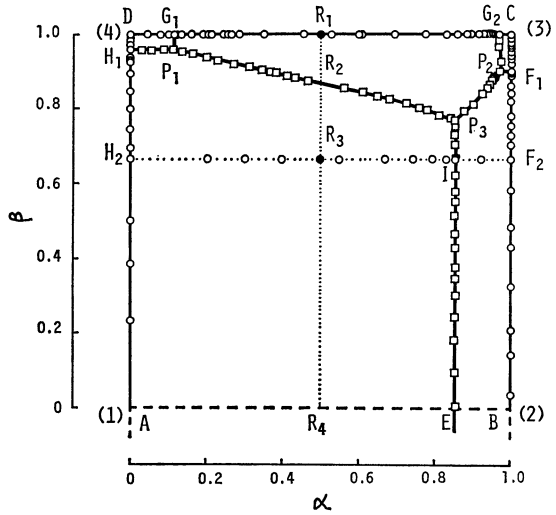

Fig. 3. The clinographic projection of solubility isotherm of the system, (Λ-[Co(en)$_3$]$^{3+}$, Δ-[Co(en)$_3$]$^{3+}$)–(d-H$_3$tart$^-$, d-H$_2$tart^{2-})–H$_2$O, at 25 °C.
α: Mole fraction of Λ-[Co(en)$_3$]$^{3+}$ to all the cations, β: mole fraction of (d-H$_2$tart)$_{1.5}^{3-}$ to {(d-H$_3$tart)$_3^{3-}$+(d-H$_2$tart)$_{1.5}^{3-}$}, (1): Λ-[Co(en)$_3$](d-H$_3$tart)$_3$, (2): Λ-[Co(en)$_3$](d-H$_3$tart)$_3$, (3): Λ-[Co(en)$_3$](d-H$_2$tart)$_{1.5}$, (4): Λ-[Co(en)$_3$](d-H$_2$tart)$_{1.5}$, □: solubility of four-components, ○: solubilities of two- or three-components. Each area has the following solids: DH$_1$P$_1$G$_1$: Λ-[Co(en)$_3$](d-H$_2$tart)$_{1.5}$·nH$_2$O, H$_1$H$_2$AR$_4$EIP$_3$R$_2$P$_1$: Λ-[Co(en)$_3$](d-H$_3$tart)(d-H$_2$trat)·3H$_2$O, F$_1$P$_2$P$_3$IEBF$_2$: Δ-[Co(en)$_3$](d-H$_3$tart)(d-H$_2$tart)·8H$_2$O, CG$_2$P$_2$F$_1$: Λ-[Co(en)$_3$](d-H$_2$tart)$_{1.5}$·nH$_2$O, G$_1$P$_1$R$_2$P$_3$-P$_2$G$_2$R$_1$: Λ-[Co(en)$_3$]$_{0.48}$·Δ-[Co(en)$_3$]$_{0.52}$(d-H$_2$tart)$_{1.5}$·5H$_2$O.

the previous systems,[1,2] Λ-[Co(en)$_3$](d-H$_2$tart)$_{1.5}$(4)–Λ-[Co(en$_3$)]X$_3$–H$_2$O, X$^-$=Br$^-$(1)′ and I$^-$(1)".

Point H$_2$ expresses the binary solubility of double salt Λ-[Co(en)$_3$](d-H$_3$tart)(d-H$_2$tart)·3H$_2$O. The region of the salt occupies a very wide region (H$_1$↔H$_2$↔A↔) and the salt exists in the area where the liquid phase contains little d-H$_2$tart^{2-} (the right area of A). The binary solubility for X$^-$=d-H$_3$tart$^-$ of Λ-[Co(en)$_3$]X(d-H$_2$tart) (m=0.0426 mol kg^{-1}) is much smaller than that for X$^-$=Br$^-$ and I$^-$ (m=0.135 and 0.148 mol kg^{-1}, respectively) at 25 °C. The isotherms of the latter two salts in the ternary systems locate in much lower region than that of the former salt. These facts relate to the appearance of a new ternary system, Λ-[Co(en)$_3$](d-H$_3$tart)(d-H$_2$tart)–Λ-[Co(en)$_3$]-(d-H$_3$tart)(d-H$_2$tart)–H$_2$O, which is useful for optical resolution.

Ternary System Δ-[*Co(en)*$_3$](d-*H*$_2$*tart*)$_{1.5}$–Δ-[*Co(en)*$_3$]-(d-*H*$_3$*tart*)$_3$–*H*$_2$*O*. The Λ-ternary system is shown in Fig. 2 and Table 1. Point F$_2$ shows the binary solubility of the new double salt Λ-[Co(en)$_3$](d-H$_3$tart)-(d-H$_2$tart), whose region spreads widely as in the case of Λ-system. The corresponding double salt for X$^-$=I$^-$ of Λ-[Co(en)$_3$]X(d-H$_2$tart) has a lower isotherm[1] than that for X$^-$=d-H$_3$tart$^-$, whereas this region for X$^-$=Br$^-$ cannot be measured because of a gelatinous precipitate.[2]

The Solubility Isotherm of Reciprocal Salt-pairs, (Λ-[*Co(en)*$_3$]$^{3+}$, Δ-[*Co(en)*$_3$]$^{3+}$)–(d-*H*$_3$*tart*$^-$, d-*H*$_2$*tart*$^{2-}$)–*H*$_2$*O*. Figure 3 shows the clinographic projection of the system of the reciprocal salt-pairs. The left and right sides correspond to Figs. 1 and 2, respectively, and the upper side is the same ternary system as in the previous systems. However, the lower side shows a imaginary ternary system because neither Λ- nor Δ-[Co(en)$_3$](d-H$_3$tart)$_3$ exists as a solid compound. The boundary curve P$_1$R$_2$P$_3$, where two solids Λ-[Co(en)$_3$](d-H$_3$tart)(d-H$_2$tart)·3H$_2$O and Λ-[Co(en)$_3$]$_{0.48}$·Δ-[Co(en)$_3$]$_{0.52}$(d-H$_2$tart)$_{1.5}$·5H$_2$O coexist, lies at the upper region than the corresponding curves of the Br$^-$ and I$^-$ systems. This fact is advantageous for the optical resolution because the less soluble diastereomer enlarges its region. The double salts Λ- and Δ-[Co(en)$_3$](d-H$_3$tart)(d-H$_2$tart) have a long boundary P$_3$↔I↔E↔. When we utilize the Λ-[Co(en)$_3$](d-H$_3$tart)(d-H$_2$tart) diastereomer for the optical resolution, the point corresponding to maximum yield lies on P$_3$IE. Since the curve is almost parallel to

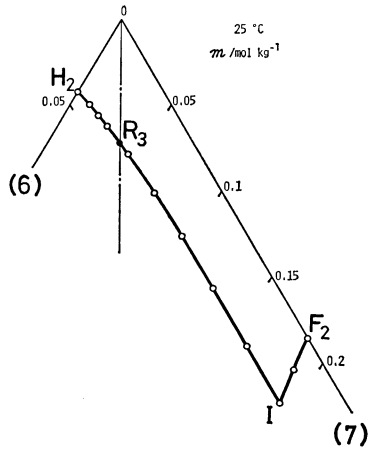

Fig. 4. Solubility isotherm of the ternary system, Λ-[Co(en)$_3$](d-H$_3$tart)(d-H$_2$tart)(6) – Δ-[Co(en)$_3$](d-H$_3$tart)(d-H$_2$tart)(7)–H$_2$O, at 25 °C.
Solubility is presented in molality m of anhydrous salt.

the ordinate, the yield is constant at 25 °C (83% for Λ-[Co(en)$_3$]$^{3+}$ and 42% for *rac*-[Co(en)$_3$]$^{3+}$) in spite of the large variation of [d-H$_3$tart$^-$]/[d-H$_2$tart^{2-}] in solution.

Ternary System Λ-[*Co(en)$_3$*](d-*H$_3$tart*)(d-*H$_2$tart*)–Δ-[*Co(en)$_3$*](d-*H$_3$tart*)(d-*H$_2$tart*)–*H$_2$O*. The ternary system, Λ-[Co(en)$_3$]X(d-H$_2$tart)–Δ-[Co(en)$_3$]X(d-H$_2$tart)–H$_2$O, is formed in the present case of X$^-$= d-H$_3$tart$^-$ (Fig. 4), though the participation of Λ-[Co(en)$_3$]$_{0.48}$·Δ-[Co(en)$_3$]$_{0.52}$(d-H$_2$tart)$_{1.5}$·5H$_2$O prevents from occurring such kind of ternary system for X$^-$=Br$^-$ or I$^-$. This system corresponds to β=2/3 in Fig. 3. Though the solubility of Λ-[Co(en)$_3$](d-H$_3$tart)(d-H$_2$tart) slightly decreased with the increase of Δ-[Co(en)$_3$](d-H$_3$tart)(d-H$_2$tart), it is interesting that the Δ-double salt shows the reverse relationship.

The solubilities of the double salts are listed in Table 2. The solubility ratio Δ/Λ becomes maximum (*ca.* 12.2) at the transition temperature (about 47 °C) from 8-hydrate to monohydrate of Δ-[Co(en)$_3$](d-H$_3$tart)(d-H$_2$tart). The ratio is 4.37 at 25 °C, and therefore the yield of optical resolution will be improved by experimenting at 47 °C.

Table 2. 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)-α	(2)-β
5	0.0201	0.0411	
10	0.0243	0.0583	
15	0.0295	0.0843	
20	0.0354	0.123	
25	0.0426	0.186	
30	0.0510	0.286	
35	0.0622	0.452	
40	0.0752	0.703	
45	0.0904	1.04	
50	0.110	1.48	1.22
55	0.134	1.95	1.30
60	0.166		1.39
65	0.203		1.50

a) (1): Λ-[Co(en)$_3$](d-H$_3$tart)(d-H$_2$tart)·3H$_2$O, (2): Δ-[Co(en)$_3$](d-H$_3$tart)(d-H$_2$tart)·nH$_2$O, n=8(α) and n=1(β).

References

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