March, 1982] © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 769—774 (1982)

Solubility Diagrams of Cobalt(III) Complexes Containing Amino Acid. II.[1) Spontaneous Resolution of Bis(ethylenediamine)glycinatocobalt(III) Salts

Satoshi Kaki,* Kazuaki Yamanari, and Yoichi Shimura

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

(Received June 30, 1981)

The binary and ternary solubility phase diagrams of the racemic and optically active complexes $[Co(gly)(en)_2]X_2$ were determined in water ($X_2=SO_4$, S_2O_3, $(NO_3)_2$, $(SCN)_2$, $(CH_3CO_2)_2$, $(ClO_4)_2$, $(CH_3CO_2)ClO_4$, and $[Sb_2(d\text{-tart})_2]$). Spontaneous resolution was found for the double salt of $[Co(gly)(en)_2](CH_3CO_2)ClO_4$ at 5—50 °C and for $[Co(gly)(en)_2]SO_4$ at 39—50 °C; the latter of these has been shown to crystallize as both a racemic compound (below 39 °C) and a conglomerate (above 39 °C).

The solubility diagrams of tetraammine(leucinato)cobalt(III) sulfate have revealed that the sulfate has a large solubility ratio of DL-complex/L-complex and crystallizes as both a racemic compound (below 30 °C) and a conglomerate (above 30 °C).1) It is of interest to clarify whether this is characteristic of the counter ion SO_4^{2-} or not. The present paper deals with the binary and ternary solubility diagrams of a variety of salts of the glycinato complex $[Co(gly)(en)_2]X_2$, where X_2 stands for SO_4, S_2O_3, $(CH_3CO_2)_2$, $(ClO_4)_2$, $(CH_3CO_2)ClO_4$, $(NO_3)_2$, $(SCN)_2$, and $[Sb_2(d\text{-tart})_2]$ (tart=tartrate(4−) ion, $C_4H_2O_6^{4-}$).

Experimental

Materials. rac-$[Co(gly)(en)_2]X_2$: Iodide salt obtained by the method of Meisenheimer2) was converted into acetate salt through an anion exchanger column of Dowex 1-X8 ($CH_3CO_2^-$ form). Found: C, 28.95; H, 7.45; N, 16.79%. Calcd for $[Co(gly)(en)_2](CH_3CO_2)_2\cdot 2.5H_2O = C_{10}H_{31}N_5O_{8.5}Co$: C, 28.85; H, 7.51; N, 16.82%. Sulfate and thiosulfate salts were prepared from an aqueous solution of the acetate salt by adding a calculated amount of $(NH_4)_2SO_4$ or $Na_2S_2O_3$. Found for sulfate salt: C, 17.46; H, 6.44; N, 16.99%. Calcd for $[Co(gly)(en)_2]SO_4\cdot 3.5H_2O = C_6H_{27}N_5O_{9.5}SCo$: C, 17.48; H, 6.60; N, 16.99%. Found for thiosulfate salt: C, 19.52; H, 5.61; N, 18.87%. Calcd for $[Co(gly)(en)_2]S_2O_3\cdot 0.5H_2O = C_6H_{21}N_5O_{5.5}S_2Co$: C, 19.25; H, 5.61; N, 18.71%. For the preparation of perchlorate, nitrate, and thiocyanate salts, a slight excess of $Ba(ClO_4)_2$, $Sr(NO_3)_2$, or $Ba(SCN)_2$ was added to the solution of sulfate salt. The desired crystals were obtained by evaporating the filtrate. Found for perchlorate salt: C, 14.79; H, 4.97; N, 14.31%. Calcd for $[Co(gly)(en)_2](ClO_4)_2\cdot 2H_2O = C_6H_{24}N_5O_{12}Cl_2Co$: C, 14.76; H, 4.96; N, 14.35%. Found for nitrate salt: C, 18.16; H, 5.57; N, 24.98%. Calcd for $[Co(gly)(en)_2](NO_3)_2\cdot H_2O = C_6H_{22}N_7O_9Co$: C, 18.23; H, 5.61; N, 24.81%. Found for thiocyanate salt: C, 25.99; H, 5.46; N, 26.58%. Calcd for $[Co(gly)(en)_2](SCN)_2 = C_8H_{20}N_7O_2S_2Co$: C, 26.02; H, 5.46; N, 26.55%. Acetate perchlorate double salt was obtained by mixing equimolar amounts of the perchlorate salt and the acetate salt. Found: C, 23.47; H, 5.67; N, 16.95%. Calcd for $[Co(gly)(en)_2](CH_3CO_2)ClO_4 = C_8H_{23}N_5O_8ClCo$: C, 23.34; H, 5.63; N, 17.01%.

Optical Resolution of $[Co(gly)(en)_2]^{2+}$: The resolving agent $Na_2[Sb_2(d\text{-tart})_2]\cdot 5H_2O$ (9.7×10^{-2} mol) was added to the dilute solution of the acetate salt (16.2×10^{-2} mol) in 800 cm³ of water. The less soluble Δ-diastereomer which deposited was removed by filtration and recrystallized from warm water. Further addition of $Na_2[Sb_2(d\text{-tart})_2]\cdot 5H_2O$ (9.7×10^{-2} mol) to the filtrate gave Λ-diastereomer. Each diastereomer was purified by the fractional crystallization until the CD values became constant. Found for Δ-diastereomer: C, 19.46; H, 3.77; N, 8.11%. Calcd for Δ-$[Co(gly)(en)_2][Sb_2(d\text{-tart})_2]\cdot 4H_2O = C_{14}H_{32}N_5O_{18}Sb_2Co$: C, 19.53; H, 3.75; N, 8.14%. Found for Λ-diastereomer: C, 19.57; H, 3.76; N, 8.20%. Calcd for Λ-$[Co(gly)(en)_2][Sb_2(d\text{-tart})_2]\cdot 4H_2O = C_{14}H_{32}N_5O_{18}Sb_2Co$: C, 19.53; H, 3.75, N, 8.14%. The Δ-diastereomer was added to an aqueous solution containing ion exchange resin Dowex 1-X8($CH_3CO_2^-$ form) and stirred for 2 h at 50 °C. The resin was removed by filtration and the filtrate was evaporated to give the acetate salt. Found: C, 27.84; H, 7.41; N, 16.59%. Calcd for Δ-$[Co(gly)(en)_2](CH_3CO_2)_2\cdot 3H_2O = C_{10}H_{32}N_5O_9Co$: C, 28.24; H, 7.58; N, 16.47%. The other Δ- or Λ-salts were prepared by the same method as was used the corresponding racemic salts. Found for sulfate salt: C, 19.61; H, 6.03; N, 19.11%. Calcd for Δ-$[Co(gly)(en)_2]SO_4\cdot H_2O = C_6H_{22}N_5O_7SCo$: C, 19.62; H, 6.04; N, 19.07%. Found for thiosulfate salt: C, 19.59; H, 5.49; N, 19.19%. Calcd for Δ-$[Co(gly)(en)_2]S_2O_3 = C_6H_{20}N_5O_5S_2Co$: C, 19.73; H, 5.52; N, 19.17%. Found for perchlorate salt: C, 15.47; H, 4.84; N, 14.99%. Calcd for Δ-$[Co(gly)(en)_2](ClO_4)_2\cdot H_2O = C_6H_{22}N_5O_{11}Cl_2Co$: C, 15.33; H, 4.72; N, 14.90%. Found for nitrate salt: C, 18.77; H, 5.37; N, 25.75%. Calcd for Λ-$[Co(gly)(en)_2](NO_3)_2\cdot 0.5H_2O = C_6H_{21}N_7O_{8.5}Co$: C, 18.66; H, 5.48; N, 25.39%. Found for thiocyanate salt: C, 26.14; H, 5.45; N, 26.72%. Calcd for Λ-$[Co(gly)(en)_2](SCN)_2 = C_8H_{20}N_7O_2S_2Co$: C, 26.02; H, 5.46; N, 26.55%. Found for acetate perchlorate double salt: C, 23.10; H, 5.68; N, 16.92%. Calcd for Δ-$[Co(gly)(en)_2](CH_3CO_2)ClO_4 = C_8H_{23}N_5O_8ClCo$: C, 23.34; H, 5.63; N, 17.01%.

Measurements. The solubility of complexes in water was determined in the same way as previously reported.3) The absorption and CD values which were used for the calculations of concentrations of complexes in solutions are summarized in Table 1. The solid phases were identified from the elemental analysis and the 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 binary solubility data are given in Table 2 and Figs. 1 and 3, and the ternary data in Table 3 as well as Figs. 2, 4, and 5. In the triangular isotherms the top part (H_2O corner) is enlarged for the sake of convenience and the tie lines are omitted.

The Sulfate and Thiosulfate Salts. The solubility curves of *rac*-$[Co(gly)(en)_2]SO_4$ and Δ-$[Co(gly)(en)_2]SO_4$ are shown in Fig. 1. The curve of racemate intersects the curve of the active one at *ca.* 21 °C, the solubility of racemic salt being less than that of the active one below this temperature. The solubiliity curve of racemate shows an inflection at *ca.* 39 °C where the solid phase changes from 3.5-hydrate (below 39 °C) to monohydrate (above 39 °C), whereas the curve of the optically active complex shows no inflection. The slope of the racemic curve above 39 °C is similar to that of the optically active salt. The solubility ratio of racemate/Δ-complex is 0.46 at 5 °C, 1.34 at 25 °C, and 2.68 at 40 °C.

Generally spontaneous resolution is expected in the case in which the solubility of racemic salt is more than $2^{1/2}(=1.41)$ times that of the corresponding optically active salt, for a 1:1 electrolyte.[4] Thus, the sulfate salt would be spontaneously resolvable above 39 °C, above which both racemate and Δ-complex crystallize as monohydrate salt. To confirm the expectation, the solubility isotherms of the ternary system, H_2O–Δ-$[Co(gly)(en)_2]SO_4$–Λ-$[Co(gly)(en)_2]SO_4$, were measured at three temperatures: 10, 30, and 45 °C (Fig. 2). The isotherm at 10 or 30 °C shows two invariant points, between which the formation of racemic compound Δ-$[Co(gly)(en)_2]$·Λ-$[Co(gly)(en)_2](SO_4)_2\cdot 7H_2O$=*rac*-$[Co(gly)(en)_2]SO_4\cdot 3.5H_2O$ is observed. However, this racemic compound disappears in the isotherm at 45 °C, and the two enan-

TABLE 1. ABSORPTION AND CD MAXIMUM VALUES USED FOR CALCULATION OF SOLUBILITY OF $[Co(gly)(en)_2]X_2$[a]

Absolute configuration	X_2	ε (486 nm) mol^{-1} dm^3 cm^{-1}	Δε (508 nm) mol^{-1} dm^3 cm^{-1}
Δ	SO_4	101.0	−2.61
rac	SO_4	100.7	—
Δ	S_2O_3	102.6	−2.53
rac	S_2O_3	102.7	—
Δ	$(ClO_4)_2$	99.76	−2.65
rac	$(ClO_4)_2$	100.0	—
Λ	$(NO_3)_2$	100.1	+2.55
rac	$(NO_3)_2$	98.83	—
Λ	$(SCN)_2$	100.1	+2.60
rac	$(SCN)_2$	98.83	—
Δ	$(CH_3CO_2)_2$	101.5	−2.57
rac	$(CH_3CO_2)_2$	100.5	—
Δ	$(CH_3CO_2)ClO_4$	98.96	−2.62
rac	$(CH_3CO_2)ClO_4$	98.81	—
Δ	$[Sb_2(d\text{-tart})_2]$	104.5	−2.33
Λ	$[Sb_2(d\text{-tart})_2]$	100.8	+2.30

a) The ε and Δε values are given in the units of mol^{-1} dm^3 cm^{-1}.

TABLE 2. SOLUBILITY OF THE COMPLEX SALTS (GRAMS OF ANHYDROUS SALT IN 100 g OF WATER)

t/°C	No. of complex salt[a]									
	1	2	3	4	5	6	7	8	9	10
5	3.05		6.61				78.2	157	6.32	14.2
10	3.99		6.76						8.15	19.1
15	5.30		6.96	0.157[b]	0.193[b]				10.5	24.2
20	6.90		7.14	0.193	0.228				14.4	32.6
25	9.70		7.26	0.214	0.264				20.5	46.0
30	12.3		7.38	0.236	0.290				29.8	63.7
35	16.1		7.45	0.261		0.326			39.7	
40		20.2	7.55	0.286		0.351			63.2	
45		20.4	7.66	0.314		0.375			83.1	
50		20.5	7.68	0.342		0.417				
55		20.5	7.65	0.370		0.457				

t/°C	No. of complex salt[a]								
	11	12	13	14	15	16	17	18	19
5	13.7	8.79	5.40	8.39[c]	7.14	2.90	3.35	0.0819	0.216
10	14.4	10.0	6.56	10.3[c]	8.51	3.66	4.25	0.0991	0.258
15	16.1	11.0	8.40	13.3[c]	10.7	4.50	5.10	0.121	0.308
20	17.8	12.2	10.6	17.1[c]	13.4	5.65	6.42	0.147	0.360
25	19.6	13.6	13.6	21.6[c]	16.5	7.14	7.93	0.187	0.433
30	21.6	14.9	17.1	28.3[c]	20.9	8.86	10.1	0.209	0.517
35	24.1	16.6	21.6	37.5[c]	25.5	11.0	12.6	0.255	0.607
40	26.4	18.3	27.4	45.5[c]	31.4	14.0	15.8	0.294	0.705
45	28.9	20.0	33.6	57.7[c]	38.6	17.9	20.1	0.354	0.846
50	32.0	22.2	44.3	71.4[c]	50.3[c]	22.3	25.3	0.427	0.991
55								0.512	1.15

a) 1: *rac*-[ ]$SO_4\cdot 3.5H_2O$, 2: *rac*-[ ]$SO_4\cdot H_2O$, 3: Δ-[ ]$SO_4\cdot H_2O$, 4: Δ-[ ]S_2O_3, 5: *rac*-[ ]$S_2O_3\cdot 0.5H_2O$, 6: *rac*-[ ]S_2O_3, 7: *rac*-[ ]$(CH_3CO_2)_2\cdot 2.5H_2O$, 8: Δ-[ ]$(CH_3CO_2)_2\cdot 3H_2O$, 9: *rac*-[ ]$(ClO_4)_2\cdot 2H_2O$, 10: Δ-[ ]$(ClO_4)_2\cdot H_2O$, 11: *rac*-[ ]$(CH_3CO_2)ClO_4$, 12: Δ-[ ]$(CH_3CO_2)ClO_4$, 13: *rac*-[ ]$(NO_3)_2\cdot H_2O$, 14: *rac*-[ ]$(NO_3)_2\cdot H_2O$, 15: Λ-[ ]$(NO_3)_2\cdot 0.5H_2O$, 16: *rac*-[ ]$(SCN)_2$, 17: Λ-[ ]$(SCN)_2$, 18: Δ-[ ]$[Sb_2(d\text{-tart})_2]\cdot 4H_2O$, 19: Λ-[ ]$[Sb_2(d\text{-tart})_2]\cdot 4H_2O$. b) Measured at 13 °C. c) Metastable solid phase.

TABLE 3. SOLUBILITY IN THE TERNARY SYSTEM, H_2O-Δ-$[Co(gly)(en)_2]X$-Λ-$[Co(gly)(en)_2]X_2$
Solubility is given in mole fraction x of anhydrous salt. Abbreviation for solid phase: Δ-$[Co(gly)(en)_2]X_2\cdot nH_2O=\Delta$-$X_2\cdot nH_2O$, Λ-$[Co(gly)(en)_2]X_2\cdot nH_2O=\Lambda$-$X_2\cdot nH_2O$, *rac*-$[Co(gly)(en)_2]X_2\cdot nH_2O=$ *rac*-$X_2\cdot nH_2O$.

X_2	t/°C	Liquid phase		Solid phase
		10^4x_Δ	10^4x_Λ	
$[Sb_2(d\text{-tart})_2]$	25	0.426	0	Δ-$[Sb_2(d\text{-tart})_2]\cdot 4H_2O$
		0.300	0.468	Δ-$[Sb_2(d\text{-tart})_2]\cdot 4H_2O$
		0.263	0.783	Δ-$[Sb_2(d\text{-tart})_2]\cdot 4H_2O$
		0.249	0.945	Δ-$[Sb_2(d\text{-tart})_2]\cdot 4H_2O+$ Λ-$[Sb_2(d\text{-tart})_2]\cdot 4H_2O$
		0.233	0.958	Λ-$[Sb_2(d\text{-tart})_2]\cdot 4H_2O$
		0	1.01	Λ-$[Sb_2(d\text{-tart})_2]\cdot 4H_2O$
SO_4	10	35.9	0	Δ-$SO_4\cdot H_2O$
		36.1	1.82	Δ-$SO_4\cdot H_2O$
		36.8	3.33	Δ-$SO_4\cdot H_2O$
		37.0	4.21	Δ-$SO_4\cdot H_2O+$ *rac*-$SO_4\cdot 3.5H_2O$
		36.5	4.13	*rac*-$SO_4\cdot 3.5H_2O$
		31.4	4.49	*rac*-$SO_4\cdot 3.5H_2O$
		27.9	4.90	*rac*-$SO_4\cdot 3.5H_2O$
		20.8	5.66	*rac*-$SO_4\cdot 3.5H_2O$
		15.5	7.00	*rac*-$SO_4\cdot 3.5H_2O$
		13.3	8.09	*rac*-$SO_4\cdot 3.5H_2O$
		11.2	9.41	*rac*-$SO_4\cdot 3.5H_2O$
		10.6	10.0	*rac*-$SO_4\cdot 3.5H_2O$
		10.1	10.1	*rac*-$SO_4\cdot 3.5H_2O$
SO_4	30	38.1	0	Δ-$SO_4\cdot H_2O$
		38.6	0.465	Δ-$SO_4\cdot H_2O$
		39.6	3.38	Δ-$SO_4\cdot H_2O$
		40.3	5.36	Δ-$SO_4\cdot H_2O$
		40.4	6.10	Δ-$SO_4\cdot H_2O$
		41.6	9.60	Δ-$SO_4\cdot H_2O$
		42.8	13.7	Δ-$SO_4\cdot H_2O$
		43.6	15.9	Δ-$SO_4\cdot H_2O$
		44.2	18.7	Δ-$SO_4\cdot H_2O$
		45.3	23.3	Δ-$SO_4\cdot H_2O+$ *rac*-$SO_4\cdot 3.5H_2O$
		42.8	24.3	*rac*-$SO_4\cdot 3.5H_2O$
		41.1	25.3	*rac*-$SO_4\cdot 3.5H_2O$
		38.7	26.3	*rac*-$SO_4\cdot 3.5H_2O$
		35.6	28.5	*rac*-$SO_4\cdot 3.5H_2O$
		34.0	29.1	*rac*-$SO_4\cdot 3.5H_2O$
		33.2	29.9	*rac*-$SO_4\cdot 3.5H_2O$
		31.3	31.3	*rac*-$SO_4\cdot 3.5H_2O$
SO_4	45	39.1	0	Δ-$SO_4\cdot H_2O$
		39.4	0.578	Δ-$SO_4\cdot H_2O$
		39.9	2.51	Δ-$SO_4\cdot H_2O$
		41.1	5.56	Δ-$SO_4\cdot H_2O$
		41.7	7.61	Δ-$SO_4\cdot H_2O$
		42.5	11.6	Δ-$SO_4\cdot H_2O$
		44.2	16.2	Δ-$SO_4\cdot H_2O$
		47.2	26.7	Δ-$SO_4\cdot H_2O$
		50.8	43.1	Δ-$SO_4\cdot H_2O$
		53.2	53.2	Δ-$SO_4\cdot H_2O+\Lambda$-$SO_4\cdot H_2O$
$(CH_3CO_2)ClO_4$	20	53.1	0	Δ-$(CH_3CO_2)ClO_4$
		52.0	1.94	Δ-$(CH_3CO_2)ClO_4$
		49.5	5.41	Δ-$(CH_3CO_2)ClO_4$
		49.1	9.75	Δ-$(CH_3CO_2)ClO_4$
		43.6	22.8	Δ-$(CH_3CO_2)ClO_4$

TABLE 3. (Continued)

X_2	t/°C	Liquid phase 10^4x_Δ	 10^4x_Λ	Solid phase
$(CH_3CO_2)ClO_4$	20	40.6	32.0	Δ-$(CH_3CO_2)ClO_4$
		39.3	39.3	Δ-$(CH_3CO_2)ClO_4$+ Λ-$(CH_3CO_2)ClO_4$
S_2O_3	45	1.51	0.193	Δ-S_2O_3
		1.51	0.340	Δ-S_2O_3
		1.51	0.381	Δ-S_2O_3
		1.57	0.451	Δ-S_2O_3
		1.59	0.465	Δ-S_2O_3+*rac*-S_2O_3
		1.47	0.539	*rac*-S_2O_3
		1.07	0.746	*rac*-S_2O_3
		0.992	0.810	*rac*-S_2O_3
		0.933	0.841	*rac*-S_2O_3
		0.871	0.871	*rac*-S_2O_3
$(NO_3)_2$	45	77.7	77.7	*rac*-$(NO_3)_2\cdot H_2O$
		48.9	126	*rac*-$(NO_3)_2\cdot H_2O$
		38.6	151	*rac*-$(NO_3)_2\cdot H_2O$
		33.7	178	*rac*-$(NO_3)_2\cdot H_2O$
		0	181	*rac*-$(NO_3)_2\cdot H_2O$+ Λ-$(NO_3)_2\cdot 0.5H_2O$
		4.37[a)]	182[a)]	Λ-$(NO_3)_2\cdot 0.5H_2O$[a)]
		8.35[a)]	181[a)]	Λ-$(NO_3)_2\cdot 0.5H_2O$[a)]
		34.2[a)]	177[a)]	Λ-$(NO_3)_2\cdot 0.5H_2O$[a)]
		132[a)]	132[a)]	*rac*-$(NO_3)_2\cdot H_2O$[a)]
		127[a)]	137[a)]	*rac*-$(NO_3)_2\cdot H_2O$[a)]
		123[a)]	145[a)]	*rac*-$(NO_3)_2\cdot H_2O$[a)]

a) Metastable phase.

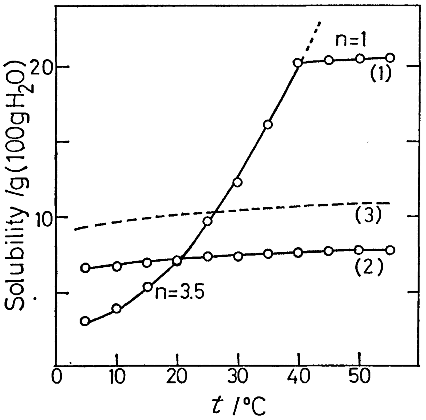

Fig. 1. Solubility curves of *rac*-$[Co(gly)(en)_2]SO_4\cdot nH_2O$(1), Δ-$[Co(gly)(en)_2]SO_4\cdot H_2O$(2), and calculated curve(3): (2)$\times 2^{1/2}$.

tiomers form a conglomerate.[3)] The intersection of the solubility curves at about 21 °C in Fig. 1 has no special meaning with respect to spontaneous resolution. The racemic sulfate $[Co(gly)(en)_2]SO_4$ crystallizes as both a racemic compound (below 39 °C) and a conglomerate (above 39 °C). A similar case has been found for $[Co(leu)(NH_3)_4]SO_4$[1)] but the examples such as $K_3[Co(ox)_3]\cdot H_2O$ and [Rh(*rac*-cptn)$_3$]-$(ClO_4)_3\cdot 12H_2O$ reported by Jaeger[5)] do not seem to be exact enough in some details (cptn=*trans*-1,2-cyclopentanediamine).

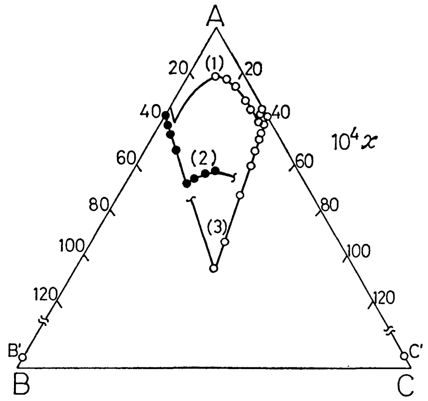

Fig. 2. Solubility isotherms of H_2O(A)-Λ-$[Co(gly)(en)_2]SO_4$(B)-Δ-$[Co(gly)(en)_2]SO_4$(C) at 10 °C(1), 30 °C(2), and 45 °C(3).

The points at 30 °C(●) are plotted at a left side for convenience. The solid phase B′ or C′ is monohydrate of B or C, respectively.

The solubility of racemic thiosulfate salt is larger than that of the corresponding active salt in the range 12—55 °C. The curve has an inflection at *ca.* 35 °C where the solid phase changes from 0.5-hydrate (below 35 °C) to anhydrate (above 35 °C), whereas the solid phase of the optically active salt is anhydrate at 12—55 °C. The curve of racemic salt is lower than $2^{1/2}$ times that of the active salt. The ternary isotherm at 45 °C confirms the existence of the racemic compound Δ-[Co(gly)(en)$_2$]·Λ-[Co(gly)(en)$_2$](S$_2$O$_3$)$_2$=*rac*-[Co(gly)(en)$_2$]S$_2$O$_3$ (Table 3). It is interesting that the solubility of thiosulfate salt is much lower than that of sulfate salt, whether it is in racemate or active form.

The Acetate Perchlorate Double Salt. The solubility of the optically active perchlorate salt is larger than that of the racemic salt; two enantiomers form a racemic compound. The solubility of the acetate salt is determined at only 5 °C because of its extremely high solubility (Table 2). This salt also crystallizes as a racemic compound.

As described in the Experimental section, the double salt [Co(gly)(en)$_2$](CH$_3$CO$_2$)ClO$_4$ can be prepared from the constituent salt. Figure 3 shows the solubility curves of *rac*- and Δ-[Co(gly)(en)$_2$](CH$_3$CO$_2$)ClO$_4$. The double salt is not decomposed into the constituent salts in water at 5—50 °C. The solubility of the racemic salt is larger than $2^{1/3}$ times that of the optically active one and both the solid phases are anhydrous at 5—50 °C.$^{4)}$ Therefore, spontaneous resolution is expected for this double salt at 5—50 °C, though each constituent salt forms a racemic compound. The ternary isotherm at 20 °C is the only invariant point and confirms the formation of a conglomerate (Fig. 4). This case is the first one of spontaneous resolution found for a complex double salt.

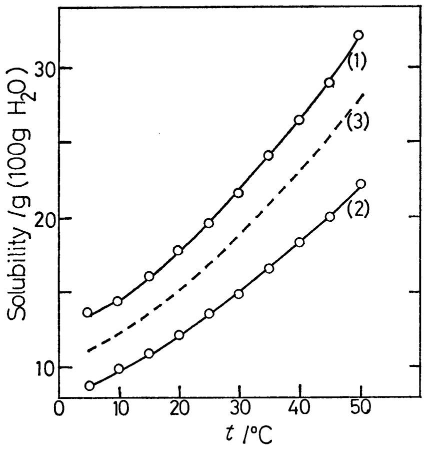

Fig. 3. Solubility curves of *rac*-[Co(gly)(en)$_2$](CH$_3$CO$_2$)ClO$_4$(1), Δ-[Co(gly)(en)$_2$](CH$_3$CO$_2$)ClO$_4$ (2), and calculated curve(3): (2)$\times 2^{1/3}$.

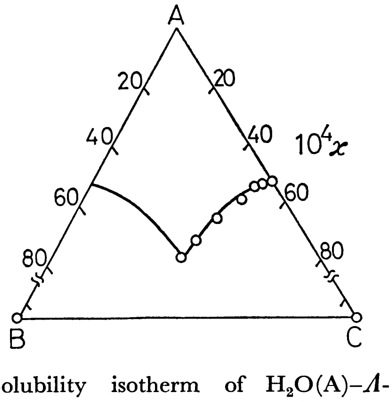

Fig. 4. Solubility isotherm of H$_2$O(A)-Λ-[Co(gly)(en)$_2$](CH$_3$CO$_2$)ClO$_4$(B)-Δ-[Co(gly)(en)$_2$](CH$_3$CO$_2$)ClO$_4$(C) at 20 °C.

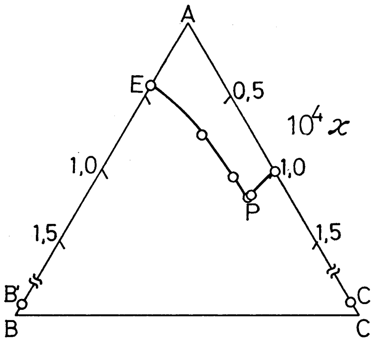

Fig. 5. Solubility isotherm of H$_2$O(A)-Δ-[Co(gly)(en)$_2$][Sb$_2$(*d*-tart)$_2$](B)-Λ-[Co(gly)(en)$_2$][Sb$_2$(*d*-tart)$_2$] (C).

The solid phase B′ or C′ is 4-hydrate of B or C, respectively.

The Nitrate and Thiocyanate Salts. In the system of nitrate salt, a metastable monohydrate phase is observed for the racemate. This phase is so stable that the solubility could be determined in the range 5—50 °C. The metastable solid phase in contact with the solution was stirred mechanically one day to undergo conversion into the stable solid phase. The solubility of the stable racemate is lower than that of the active one, whereas the solubility of the metastable racemate is larger than $2^{1/3}$ times that of the active complex. However, the ternary isotherm at 45 °C (Table 3) revealed the existence of the racemic compound Δ-[Co(gly)(en)$_2$]·Λ-[Co(gly)(en)$_2$](NO$_3$)$_4$·2H$_2$O=*rac*-[Co(gly)(en)$_2$](NO$_3$)$_2$·H$_2$O.

The solubility of optically active thiocyanate salt is larger than that of the racemate. This salt also forms a racemic compound Δ-[Co(gly)(en)$_2$]·Λ-[Co(gly)(en)$_2$](SCN)$_4$=*rac*-[Co(gly)(en)$_2$](SCN)$_2$.

The Optical Resolution of [*Co(gly)(en)*$_2$]$^{2+}$ *Complex.* This complex have been optically resolved by *d*-BCS$^{2,6)}$ and Ag$_2$[Sb$_2$(*d*-tart)$_2$]$^{7)}$ as a resolving agent (*d*-BCS=(+)$_{589}$-(1*R*,3*S*,4*S*,7*R*)-3-bromocamphor-9-sulfonate). However, we found that the combination of the acetate salt and the resolving agent Na$_2$[Sb$_2$(*d*-tart)$_2$]·5H$_2$O is more convenient. Figure 5 shows the ternary isotherm of H$_2$O-Δ-[Co(gly)(en)$_2$][Sb$_2$(*d*-tart)$_2$]-Λ-[Co(gly)(en)$_2$][Sb$_2$(*d*-tart)$_2$] at 25 °C; its only invariant point is P, at the right hand side. When an aqueous solution of an equimolar amount of the two diastereomers is concentrated at this temperature, the less soluble diastereomer Δ-[Co(gly)(en)$_2$][Sb$_2$(*d*-tart)$_2$]·4H$_2$O will crystallize out first and then the solution composition will change along the solubility curve EP. Finally, the solid phase will be composed of the two diastereomers at P. No pseudo racemic compound appears in this system.

References

1) K. Yamanari, S. Naito, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **54**, 3780 (1981).

2) J. Meisenheimer, L. Angermann, and H, Holsten, *Justus Liebigs Ann. Chem.*, **438**, 217 (1924).

3) Y. Shimura and K. Tsutsui, *Bull. Chem. Soc. Jpn.*, **50**, 145 (1977).

4) K. Yamanari, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **46**, 3724 (1973).

5) F. M. Jaeger, "Optical Activity and High Temperature Measurements," McGraw-Hill, New York (1930).

6) J.-P. Mathieu, *Bull. Soc. Chim. Fr.*, **6**, 873 (1939); I. Lifschitz, *Recl. Trav. Chim. Pays-Bas*, **58**, 785 (1939); *Proc. Acad. Amsterdam*, **42**, 173 (1939).

7) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).