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Solubility Diagrams of Cobalt(III) Complexes Containing Amino Acid. I. Spontaneous Resolution of Tetraammine(valinato or leucinato)cobalt(III) Salts

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The binary and ternary solubility phase diagrams of the racemic and optically active complexes, [Co(val)(NH$_3$)$_4$]X$_2$ and [Co(leu)(NH$_3$)$_4$]X$_2$ (X=(1/2)SO$_4^{2-}$, Cl$^-$, Br$^-$, and I$^-$), were determined in water. Spontaneous resolution was found for [Co(DL-val)(NH$_3$)$_4$]X$_2$ (X=Cl$^-$ and Br$^-$) at 5—55 °C and for [Co(DL-leu)(NH$_3$)$_4$]SO$_4$ at 30—55 °C, the latter of which has been shown to crystallize as both a racemic compound (below 30 °C) and a conglomerate (above 30 °C).

A variety of metal complexes containing racemic amino acid have been prepared, but in most of the cases it remains unknown whether the complex is a racemic mixture (conglomerate) or a racemic compound (double salt between enantiomers), because no solubility isotherm has been reported for the system of such amino acid complexes.

The present paper deals with the binary and ternary solubility diagrams of cobalt(III) complexes, [Co(L- or DL-val)(NH$_3$)$_4$]X$_2$ and [Co(L- or DL-leu)(NH$_3$)$_4$]X$_2$, where val and leu denote a valinate and a leucinate ligand, respectively, and X stands for a univalent anion of Cl$^-$, Br$^-$, I$^-$, or (1/2)SO$_4^{2-}$. The tetraammine type complexes have the only chirality based on that of amino acid.[1] In the case of spontaneous resolution of such a complex, optical resolution of amino acid is realized in each of crystals. Therefore, if an effective recovery route from the metal complex is established, this procedure will be applicable to optical resolution of amino acid. Few reports have been published for the utilization of metal chelate compounds for the optical resolution of racemic amino acids.[2]

Experimental

Materials. *[Co(L-val)(NH$_3$)$_4$]SO$_4$·H$_2$O*: The complex was prepared from [Co(H$_2$O)(NH$_3$)$_5$](ClO$_4$)$_3$ and L-valine according to the method of Yasui *et al.*[3] and separated on a column of SP-Sephadex C-25 (Na$^+$ form) by elution of 0.15 mol dm^{-3} Na$_2$SO$_4$. The orange red eluate was evaporated to give the desired crystals, which were recrystallized from water at 50 °C. Found: C, 16.82; H, 6.76; N, 19.75%. Calcd for [Co(L-val)(NH$_3$)$_4$]SO$_4$·H$_2$O=C$_5$H$_{24}$N$_5$O$_7$SCo: C, 16.81; H, 6.77; N, 19.60%.

[Co(DL-val)(NH$_3$)$_4$]SO$_4$·2H$_2$O: This cymplex was prepared by the same procedure as described above except for the use of DL-valine instead of L-valine. Found: C, 16.17; H, 6.83; N, 18.76%. Calcd for [Co(DL-val)(NH$_3$)$_4$]SO$_4$·2H$_2$O=C$_5$H$_{26}$N$_5$O$_8$SCo: C, 16.00; H, 6.98; N, 18.66%.

[Co(L-val)(NH$_3$)$_4$]X$_2$(X=Cl, Br, and I): The above sulfate salt of L-valinato complex was converted into the desired salts by ion exchangers (Dowex 50W-X2 for Cl$^-$ or Br$^-$ form; QAE-Sephadex A-25 for I$^-$ form). Found for chloride salt: C, 19.18; H, 7.05; N, 22.27%. Calcd for [Co(L-val)(NH$_3$)$_4$]Cl$_2$=C$_5$H$_{22}$N$_5$O$_2$Cl$_2$Co: C, 19.12; H, 7.06; N, 22.29%. Found for bromide salt: C, 15.02; H, 5.52; N, 17.35%. Calcd for [Co(L-val)(NH$_3$)$_4$]Br$_2$=C$_5$H$_{22}$N$_5$O$_2$Br$_2$Co: C, 14.90; H, 5.50; N, 17.37%. Found for iodide salt: C, 12.18; H, 4.48; N, 13.94%. Calcd for [Co(L-val)(NH$_3$)$_4$]I$_2$=C$_5$H$_{22}$N$_5$O$_2$I$_2$Co: C, 12.08; H, 4.46; N, 14.09%.

[Co(DL-val)(NH$_3$)$_4$]X$_2$·nH$_2$O (X=Cl, Br, and I): These complexes were prepared by the same method as that for the corresponding L-valinato complexes. Found for chloride salt: C, 19.13; H, 7.01; N, 22.18%. Calcd for [Co(DL-val)(NH$_3$)$_4$]Cl$_2$=C$_5$H$_{22}$N$_5$O$_2$Cl$_2$Co: C, 19.12; H, 7.06; N, 22.29%. Found for bromide salt: C, 14.82; H, 5.50; N, 17.27%. Calcd for [Co(DL-val)(NH$_3$)$_4$]Br$_2$=C$_5$H$_{22}$N$_5$O$_2$Br$_2$Co: C, 14.90; H, 5.50; N, 17.37%. Found for iodide salt: C, 11.89; H, 4.65; N, 13.52%. Calcd for [Co(DL-val)(NH$_3$)$_4$]I$_2$·0.5H$_2$O=C$_5$H$_{23}$N$_5$O$_{2.5}$I$_2$Co: C, 11.87; H, 4.58; N, 13.84%.

[Co(L-leu)(NH$_3$)$_4$]SO$_4$ and [Co(DL-leu)(NH$_3$)$_4$]SO$_4$·2H$_2$O: These complexes were prepared by the same method as that for [Co(L-val)(NH$_3$)$_4$]SO$_4$ with the use of L-leucine or DL-leucine instead of L-valine. Found for L-leucinato complex: C, 20.16; H, 6.82; N, 19.61%. Calcd for [Co(L-leu)(NH$_3$)$_4$]SO$_4$=C$_6$H$_{24}$N$_5$O$_6$SCo: C, 20.40; H, 6.85; N, 19.82%. Found for DL-leucinato complex: C, 17.96; H, 7.20; N, 17.41%. Calcd for [Co(DL-leu)(NH$_3$)$_4$]SO$_4$·2H$_2$O=C$_6$H$_{28}$N$_5$O$_8$SCo: C, 18.06; H, 7.34; N, 17.58%.

[Co(L-leu)(NH$_3$)$_4$]X$_2$·H$_2$O and [Co(DL-leu)(NH$_3$)$_4$]X$_2$·H$_2$O (X=Cl, Br, and I): These complexes were prepared from the corresponding sulfate salt by the ion exchangers described above. Found for chloride of L-leucinato complex: C, 20.65; H, 7.44; N, 20.01%. Calcd for [Co(L-leu)(NH$_3$)$_4$]Cl$_2$·H$_2$O=C$_6$H$_{26}$N$_5$O$_3$Cl$_2$Co: C, 20.82; H, 7.57; N, 20.23%. Found for bromide of L-leucinato one: C, 16.55; H, 5.98; N, 16.02%. Calcd for [Co(L-leu)(NH$_3$)$_4$]Br$_2$·H$_2$O=C$_6$H$_{26}$N$_5$O$_3$Br$_2$Co: C, 16.56; H, 6.02; N, 16.10%. Found for iodide of L-leucinato one: C, 13.63; H, 4.96; N, 13.35%. Calcd for [Co(L-leu)(NH$_3$)$_4$]I$_2$·H$_2$O=C$_6$H$_{26}$N$_5$O$_3$I$_2$Co: C, 13.62; H, 4.95; N, 13.24%. Found for chloride of DL-leucinato one: C, 20.89; H, 7.43; N, 19.90%. Calcd for [Co(DL-leu)(NH$_3$)$_4$]Cl$_2$·H$_2$O=C$_6$H$_{26}$N$_5$O$_3$Cl$_2$Co: C, 20.82; H, 7.57; N, 20.23%. Found for bromide of DL-leucinato one: C, 16.47; H, 5.95; N, 15.97%. Calcd for [Co(DL-leu)(NH$_3$)$_4$]Br$_2$·H$_2$O=C$_6$H$_{26}$N$_5$O$_3$Br$_2$Co: C, 16.56; H, 6.02; N, 16.10%. Found for iodide of DL-leucinato one: C, 13.66; H, 4.96; N, 13.37%. Calcd for [Co(DL-leu)(NH$_3$)$_4$]I$_2$·H$_2$O=C$_6$H$_{26}$N$_5$O$_3$I$_2$Co: C, 13.62; H, 4.95; N, 13.24%.

Measurements. Solubility in water was determined according to the previously reported method.[4] The absorption and CD maximum values which were used for the calculations of concentrations of complexes in solutions are summarized in Table 1. The solid phases were identified from elemental analyses, absorption, CD, and infrared spectra. Optical densities were measured with a JASCO UVIDEC-1 spectrophotometer, CD with a JASCO MOE-1 spectropolarimeter, and infrared spectra with a JASCO DS-402G spectrophotometer.

Table 1. Absorption and CD maximum values used for calculation of solubility[a)]

Complex salt	$\varepsilon(\lambda_{max})$	$\Delta\varepsilon(\lambda_{max})$
[Co(L-val)(NH$_3$)$_4$]SO$_4$	83.48(495)	−0.426(462)
[Co(DL-val)(NH$_3$)$_4$]SO$_4$	83.48(495)	
[Co(L-val)(NH$_3$)$_4$]Cl$_2$	81.98(495)	−0.418(462)
[Co(DL-val)(NH$_3$)$_4$]Cl$_2$	81.98(495)	
[Co(L-val)(NH$_3$)$_4$]Br$_2$	82.88(495)	−0.405(462)
[Co(DL-val)(NH$_3$)$_4$]Br$_2$	82.88(495)	
[Co(L-val)(NH$_3$)$_4$]I$_2$	72.91(495)	−0.366(462)
[Co(DL-val)(NH$_3$)$_4$]I$_2$	72.90(495)	
[Co(L-leu)(NH$_3$)$_4$]SO$_4$	82.30(492)	−0.326(459)
[Co(DL-leu)(NH$_3$)$_4$]SO$_4$	82.28(492)	
[Co(L-leu)(NH$_3$)$_4$]Cl$_2$	81.33(492)	−0.329(459)
[Co(DL-leu)(NH$_3$)$_4$]Cl$_2$	81.33(492)	
[Co(L-leu)(NH$_3$)$_4$]Br$_2$	81.95(492)	−0.319(459)
[Co(DL-leu)(NH$_3$)$_4$]Br$_2$	81.95(492)	
[Co(L-leu)(NH$_3$)$_4$]I$_2$	82.36(492)	−0.327(459)
[Co(DL-leu)(NH$_3$)$_4$]I$_2$	82.37(492)	

a) The ε and λ (in parentheses) values are given in the unit of mol^{-1} dm^3 cm^{-1} and nm, respectively.

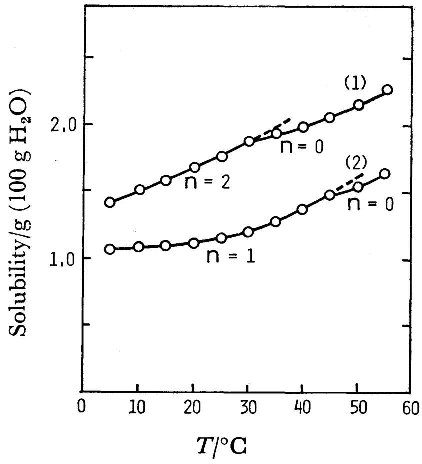

Fig. 1. Solubility curves of [Co(L-val)(NH$_3$)$_4$]SO$_4$·nH$_2$O (1) and [Co(DL-val)(NH$_3$)$_4$]SO$_4$·nH$_2$O (2).

Results and Discussion

The binary solubility data are given in Table 2 and Figs. 1, 3, and 5, and the ternary data in Tables 3 and 4 as well as in Figs. 2, 4, and 6—8. In the triangular isotherms the top part (H$_2$O corner) is enlarged for the sake of convenience and the tie lines are omitted.

The Valinato Complexes. The solubility curves of sulfate salt are shown in Fig. 1. The L-complex shows an inflection at 30 °C, at which the solid phase changes from dihydrate to anhydrate. A similar inflection appears at 45 °C for the DL-complex, corresponding to the transition from monohydrate to anhydrate. Since the solubility of L-complex is larger than that of DL-complex at 5—55 °C, the sulfate salt is not spontaneously resolvable.[5)] The ternary isotherm at 25 °C shows the formation of racemic compound [Co(L-val)(NH$_3$)$_4$][Co(D-val)(NH$_3$)$_4$](SO$_4$)$_2$·4H$_2$O= [Co(DL-val)(NH$_3$)$_4$]SO$_4$·2H$_2$O (Fig. 2).[4)]

The solubility curves of bromide salt are shown in Fig. 3. The solubility ratio of DL-complex/L-complex is 1.46 at 5 °C and 1.40 at 55 °C. For a spontaneously resolvable 1 : 2 electrolyte, the ratio must be larger than $2^{1/3}=1.26$.[5)] Therefore, the bromide salt is spontaneously resolvable. The ternary solubility isotherm at 25 °C (Fig. 4) shows the only one invariant point. This fact confirms that the two enantiomers form a racemic mixture in the solid state. The racemate of free valine does not form a racemic mixture. This is the first example, in which the complexation of amino acid enabled the spontaneous resolution. The chloride salt shows a similar solubility relationship to the bromide salt, the ratio of DL-complex/L-complex being 1.30 at 5 °C and 1.28 at 55 °C. A crystal, which precipitated out of the racemic solution, showed the same CD

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	11	12	13	14	15	16	17	18	19
5	1.42		1.07		12.6	16.4	7.00	10.2	3.62	1.19	1.47	4.37		147	66.1	6.90	6.32	1.76	1.68
10	1.50		1.08		13.8	18.0	7.75	11.2	4.59	2.12	1.49	4.59		153	73.5	7.90	7.21	2.07	1.95
15	1.58		1.10		15.0	19.5	8.60	12.5	5.71	3.05	1.53	4.87		162	81.2	9.07	8.34	2.46	2.36
20	1.68		1.12		16.4	21.3	9.71	14.1	6.83	4.28	1.59	5.19		172	90.5	10.4	9.64	2.86	2.77
25	1.77		1.15		17.7	23.0	11.2	16.3	8.17	5.56	1.63	5.56		184	99.8	11.9	11.0	3.40	3.26
30		1.88	1.20		19.2	25.0	12.5	18.2	9.79	6.99	1.68	5.93		195	112	13.5	12.4	3.95	3.82
35		1.93	1.27		20.5	26.7	14.0	20.4	11.6	8.38	1.74		6.27			15.4	14.1	4.61	4.46
40		1.99	1.37		22.7	29.2	15.7	22.8	13.4	9.98	1.78		6.75			17.6	16.0	5.37	5.20
45		2.05		1.47	24.0	31.2	17.5	25.5	15.4	11.6	1.85		7.10			20.0	18.3	6.25	6.07
50		2.14		1.53	25.6	33.4	19.6	28.0	17.7	13.6	1.92		7.68			22.7	20.7	7.21	7.01
55		2.26		1.63	27.6	35.4	21.9	30.6	20.3	16.0	2.00		8.29			25.7	23.3	8.25	8.02

a) **1**: [Co(L-val)(NH$_3$)$_4$]SO$_4$·H$_2$O, **2**: [Co(L-val)(NH$_3$)$_4$]SO$_4$, **3**: [Co(DL-val)(NH$_3$)$_4$]SO$_4$·2H$_2$O, **4**: [Co(DL-val)(NH$_3$)$_4$]SO$_4$, **5**: [Co(L-val)(NH$_3$)$_4$]Cl$_2$, **6**: [Co(DL-val)(NH$_3$)$_4$]Cl$_2$, **7**: [Co(L-val)(NH$_3$)$_4$]Br$_2$, **8**: [Co(DL-val)(NH$_3$)$_4$]Br$_2$, **9**: [Co(L-val)(NH$_3$)$_4$]I$_2$, **10**: [Co(DL-val)(NH$_3$)$_4$]I$_2$·0.5H$_2$O, **11**: [Co(L-leu)(NH$_3$)$_4$]SO$_4$, **12**: [Co(DL-leu)(NH$_3$)$_4$]SO$_4$·2.5H$_2$O, **13**: [Co(DL-leu)(NH$_3$)$_4$]SO$_4$, **14**: [Co(L-leu)(NH$_3$)$_4$]Cl$_2$·H$_2$O, **15**: [Co(DL-leu)(NH$_3$)$_4$]Cl$_2$·H$_2$O, **16**: [Co(L-leu)(NH$_3$)$_4$]Br$_2$·H$_2$O, **17**: [Co(DL-leu)(NH$_3$)$_4$]Br$_2$·H$_2$O, **18**: [Co(L-leu)(NH$_3$)$_4$]I$_2$·H$_2$O, and **19**: [Co(DL-leu)(NH$_3$)$_4$]I$_2$·H$_2$O.

TABLE 3. SOLUBILITY IN THE TERNARY SYSTEMS, H_2O–$[Co(L\text{-}val)(NH_3)_4]X_2$–$[Co(D\text{-}val)(NH_3)_4]X_2$
Solubility is given in weight % of anhydrous salt. Abbreviations: $[Co(L\text{-}val)(NH_3)_4]X_2\cdot nH_2O=[L]X_2\cdot nH_2O$, $[Co(D\text{-}val)(NH_3)_4]X_2\cdot nH_2O=[D]X_2\cdot nH_2O$, and $[Co(DL\text{-}val)(NH_3)_4]X_2\cdot nH_2O=[DL]X_2\cdot nH_2O$.

X	Liquid phase composition (wt%)		Solid phase
	$[L]X_2$	$[D]X_2$	
(1/2)SO_4	1.70	0	$[L]SO_4\cdot H_2O$
(25 °C)	1.69	0.05	$[L]SO_4\cdot H_2O$
	1.68	0.16	$[L]SO_4\cdot H_2O$
	1.68	0.22	$[L]SO_4\cdot H_2O$
	1.69	0.23	$[L]SO_4\cdot H_2O+[DL]SO_4\cdot 2H_2O$
	1.65	0.24	$[DL]SO_4\cdot 2H_2O$
	1.55	0.24	$[DL]SO_4\cdot 2H_2O$
	1.37	0.26	$[DL]SO_4\cdot 2H_2O$
	1.20	0.28	$[DL]SO_4\cdot 2H_2O$
	1.10	0.31	$[DL]SO_4\cdot 2H_2O$
	0.96	0.35	$[DL]SO_4\cdot 2H_2O$
	0.89	0.38	$[DL]SO_4\cdot 2H_2O$
	0.74	0.45	$[DL]SO_4\cdot 2H_2O$
	0.66	0.50	$[DL]SO_4\cdot 2H_2O$
	0.60	0.55	$[DL]SO_4\cdot 2H_2O$
	0.57	0.57	$[DL]SO_4\cdot 2H_2O$
Br	10.1	0	$[L]Br_2$
(25 °C)	10.0	0.15	$[L]Br_2$
	9.87	0.35	$[L]Br_2$
	9.66	0.72	$[L]Br_2$
	9.32	1.38	$[L]Br_2$
	9.01	2.01	$[L]Br_2$
	8.55	2.98	$[L]Br_2$
	8.32	3.72	$[L]Br_2$
	7.71	5.08	$[L]Br_2$
	7.46	5.85	$[L]Br_2$
	7.17	6.69	$[L]Br_2$
	7.09	6.95	$[L]Br_2$
	7.11	7.11	$[L]Br_2+[D]Br_2$
I	7.55	0	$[L]I_2$
(25 °C)	7.64	0.41	$[L]I_2+[DL]I_2\cdot 0.5H_2O$
	7.36	0.52	$[DL]I_2\cdot 0.5H_2O$
	6.86	0.53	$[DL]I_2\cdot 0.5H_2O$
	6.15	0.62	$[DL]I_2\cdot 0.5H_2O$
	5.53	0.89	$[DL]I_2\cdot 0.5H_2O$
	4.76	1.15	$[DL]I_2\cdot 0.5H_2O$
	4.25	1.42	$[DL]I_2\cdot 0.5H_2O$
	3.56	1.80	$[DL]I_2\cdot 0.5H_2O$
	3.43	2.09	$[DL]I_2\cdot 0.5H_2O$
	2.78	2.52	$[DL]I_2\cdot 0.5H_2O$
	2.64	2.64	$[DL]I_2\cdot 0.5H_2O$

TABLE 4. SOLUBILITY IN THE TERNARY SYSTEMS, H_2O–$[Co(L\text{-}leu)(NH_3)_4]X_2$–$[Co(D\text{-}leu)(NH_3)_4]X_2$
Solubility is given in weight % of anhydrous salt. Abbreviations: $[Co(L\text{-}leu)(NH_3)_4]X_2\cdot nH_2O=[L]X_2\cdot nH_2O$, $[Co(D\text{-}leu)(NH_3)_4]X_2\cdot nH_2O=[D]X_2\cdot nH_2O$, and $[Co(DL\text{-}leu)(NH_3)_4]X_2\cdot nH_2O=[DL]X_2\cdot nH_2O$.

X	Liquid phase composition (wt%)		Solid phase
	$[L]X_2$	$[D]X_2$	
(1/2)SO_4	1.57	0	$[L]SO_4$
(25 °C)	1.58	0.07	$[L]SO_4$
	1.58	0.21	$[L]SO_4$
	1.60	0.46	$[L]SO_4$
	1.62	0.60	$[L]SO_4$
	1.67	0.93	$[L]SO_4$
	1.69	1.15	$[L]SO_4$
	1.73	1.24	$[L]SO_4$
	1.75	1.37	$[L]SO_4$
	1.83	1.54	$[L]SO_4$
	1.87	1.64	$[L]SO_4$
	1.94	1.80	$[L]SO_4$
	2.06	1.95	$[L]SO_4$
	2.14	2.06	$[L]SO_4$
	2.25	2.18	$[L]SO_4$
	2.33	2.29	$[L]SO_4$
	2.42	2.38	$[L]SO_4$
	2.51	2.43	$[L]SO_4+[DL]SO_4\cdot 2.5H_2O$
	2.47	2.47	$[DL]SO_4\cdot 2.5H_2O$
(1/2)SO_4	1.74	0	$[L]SO_4$
(35 °C)	1.72	0.08	$[L]SO_4$
	1.71	0.21	$[L]SO_4$
	1.74	0.27	$[L]SO_4$
	1.72	0.42	$[L]SO_4$
	1.74	0.51	$[L]SO_4$
	1.75	0.70	$[L]SO_4$
	1.78	0.86	$[L]SO_4$
	1.82	0.98	$[L]SO_4$
	1.87	1.14	$[L]SO_4$
	1.92	1.33	$[L]SO_4$
	1.99	1.55	$[L]SO_4$
	2.06	1.78	$[L]SO_4$
	2.10	1.89	$[L]SO_4$
	2.11	1.96	$[L]SO_4$
	2.19	2.06	$[L]SO_4$
	2.29	2.20	$[L]SO_4$
	2.38	2.32	$[L]SO_4$
	2.52	2.52	$[L]SO_4+[D]SO_4$
Br	10.6	0	$[L]Br_2\cdot H_2O$
(25 °C)	10.6	0.1	$[L]Br_2\cdot H_2O+[DL]Br_2\cdot H_2O$
	10.3	0.3	$[DL]Br_2\cdot H_2O$
	9.91	0.60	$[DL]Br_2\cdot H_2O$
	9.51	0.91	$[DL]Br_2\cdot H_2O$
	8.62	1.65	$[DL]Br_2\cdot H_2O$
	7.75	2.38	$[DL]Br_2\cdot H_2O$
	7.91	3.14	$[DL]Br_2\cdot H_2O$
	6.54	3.47	$[DL]Br_2\cdot H_2O$
	6.04	3.94	$[DL]Br_2\cdot H_2O$
	5.47	4.45	$[DL]Br_2\cdot H_2O$
	4.94	4.94	$[DL]Br_2\cdot H_2O$

spectra as that of the active complex.

With the iodide salt, the active complex (0.5-hydrate) is more soluble than the anhydrous racemate. No optical rotation was observed for the crystals out of the racemic solution. The result was confirmed by the ternary isotherm at 25 °C which indicates the existence of a racemic compound $[Co(L\text{-}val)(NH_3)_4][Co(D\text{-}val)(NH_3)_4]I_4=[Co(DL\text{-}val)(NH_3)_4]I_2$ (Tables 2 and 3).

The Leucinato Complexes. The solubility curves of

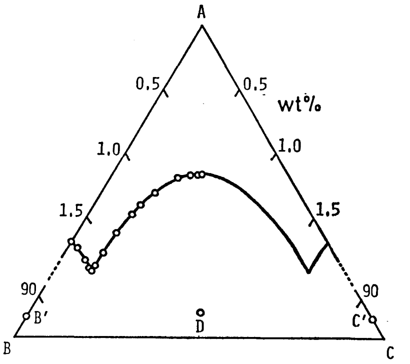

Fig. 2. Solubility isotherm of the system H_2O(A)–[Co(L-val)(NH$_3$)$_4$]SO$_4$(B)–[Co(D-val)(NH$_3$)$_4$]SO$_4$(C) at 25 °C. The solid phase B′ or C′ is monohydrate of B or C, respectively, and D [Co(DL-val)(NH$_3$)$_4$]SO$_4\cdot$2H$_2$O.

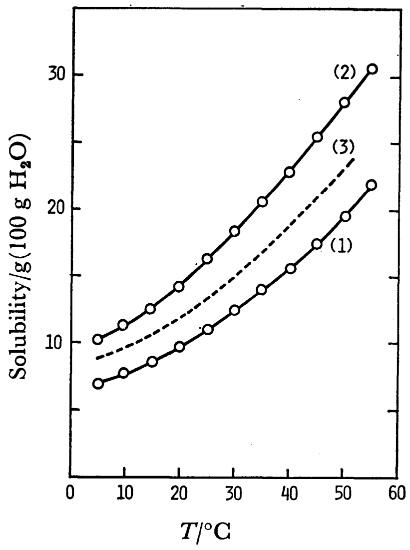

Fig. 3. Solubility curves of [Co(L-val)(NH$_3$)$_4$]Br$_2$(1), [Co(DL-val)(NH$_3$)$_4$]Br$_2$(2), and calculated curve (3) : $(1)\times\sqrt[3]{2}$.

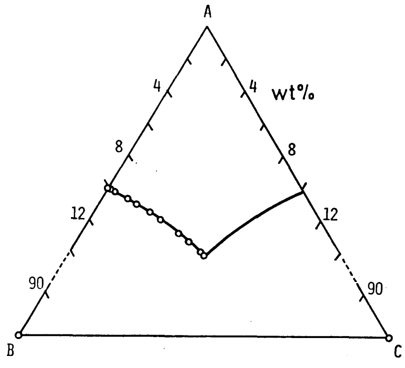

Fig. 4. Solubility isotherm of the system H_2O(A)–[Co(L-val)(NH$_3$)$_4$]Br$_2$(B)–[Co(D-val)(NH$_3$)$_4$]Br$_2$(C) at 25 °C.

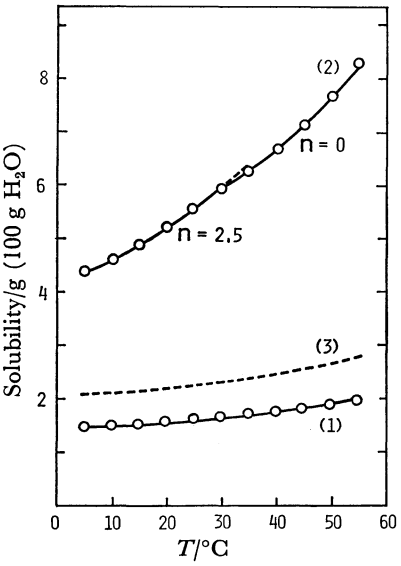

Fig. 5. Solubility curves of [Co(L-leu)(NH$_3$)$_4$]SO$_4$(1), [Co(DL-leu)(NH$_3$)$_4$]SO$_4\cdot n$H$_2$O(2), and calculated curve(3) : $(1)\times\sqrt{2}$.

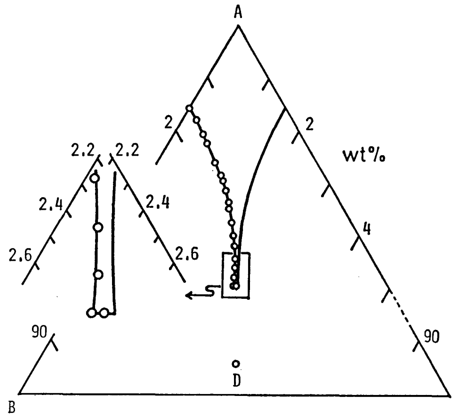

Fig. 6. Solubility isotherm of the system H_2O(A)–[Co(L-leu)(NH$_3$)$_4$]SO$_4$(B)–[Co(D-leu)(NH$_3$)$_4$]SO$_4$(C) at 20 °C.
The solid phase D is [Co(DL-leu)(NH$_3$)$_4$]SO$_4\cdot$2.5H$_2$O.

[Co(L-leu)(NH$_3$)$_4$]SO$_4$ and [Co(DL-leu)(NH$_3$)$_4$]SO$_4$ are shown in Fig. 5. The solubility ratio of DL-complex/L-complex is 2.97 at 5 °C and 4.15 at 55 °C which goes well beyond $2^{1/2}=1.41$ expected for 1 : 1 electrolyte.[5] The racemate shows an inflection at *ca.* 30 °C where the solid phase changes from 2.5-hydrate (below 30 °C) to anhydrate. On the other hand, the anhydrous active complex shows no solid phase change at 5—55 °C. If the racemate forms a racemic mixture, the racemate and the pure enantiomer must have the same composition and crystal structure. Therefore, spontaneous resolution seems to be possible at temperatures higher than 30 °C in this case. The ternary isotherm at 20 °C reveals the formation of racemic compound [Co(L-leu)(NH$_3$)$_4$][Co(D-leu)(NH$_3$)$_4$](SO$_4$)$_2\cdot$5H$_2$O= [Co(DL-leu)(NH$_3$)$_4$]SO$_4\cdot$2.5H$_2$O, though the region for this compound is significantly narrow as compared with those of the pure enantiomers (Fig. 6). The infrared spectra also indicate that the solid crystallized out of racemic solution at 20 °C is different from the optically active complex. As is shown in Fig. 7, the region of the racemic compound disappears at 35 °C and the only invariant point exists in the ternary isotherm. Thus, the racemic sulfate [Co(DL-leu)(NH$_3$)$_4$]SO$_4$ crystallizes as both the racemic compound (below 30 °C) and the conglomerate (above 30 °C).

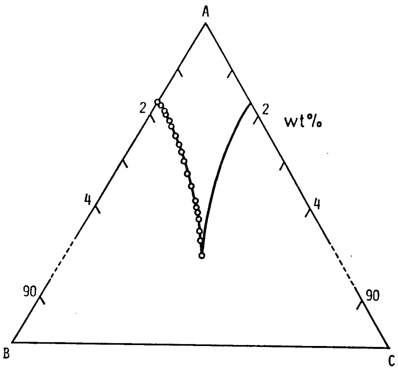

Fig. 7. Solubility isotherm of the system H_2O(A)–[Co(L-leu)$(NH_3)_4$]SO_4(B)–[Co(D-leu)$(NH_3)_4$]SO_4(C) at 35 °C.

The solubility ratio DL-complex/L-complex at temperatures of 5—30 °C goes well beyond $2^{1/2}=1.41$ (Fig. 5), but spontaneous resolution did not occur in this sulfate salt. This fact may be explained in relation to the characteristics of SO_4^{2-} ion, which has been reported to have a strong tendency to associate with various ammine or amine cobalt(III) complexes.[6] The ion-pair formation affects the activity coefficients of the complexes to a great extent and causes the apparent large solubility ratio.

All the halide salts of leucinato complexes are monohydrate regardless of whether it is racemate or active form. The solubility of racemate is lower than that of the corresponding active form, no spontaneous resolution being observed. Figure 8 shows the ternary isotherm of [Co(leu)$(NH_3)_4$]Br_2 at 25 °C. The extremely flat curve of the racemic compound is spread over a wide region and the region of pure enantiomers are much suppressed.

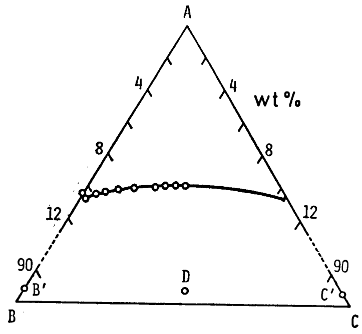

Fig. 8. Solubility isotherm of the system H_2O(A)–[Co(L-leu)$(NH_3)_4$]Br_2(B)–[Co(D-leu)$(NH_3)_4$]Br_2(C) at 20 °C. The solid phase B′ or C′ is monohydrate of B or C, respectively, and D [Co(DL-leu)$(NH_3)_4$]$Br_2 \cdot H_2O$.

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