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Formation of Racemic Solid Solutions and the Solubility Isotherms of [Co(DL-leucinato)$(NH_3)_4$]X_2 (X = Br and I)

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The ternary solubility phase diagrams, [Co(L-leu)$(NH_3)_4$]X_2 – [Co(D-leu)$(NH_3)_4$]X_2 – H_2O (leu = leucinate(1-); X = Br and I) were determined at 25 °C. Only one isotherm is obtained in each system and the D:L ratios of the solid phases are variable over entire region from D:L = 100:0 to 0:100. This means that the solid solutions of the enantiomers form in both systems. These phase diagrams are the first examples of solid solutions of metal complexes containing natural amino acids.

Crystalline racemates belong to one of the three different classes, racemic compound, conglomerate, and solid solution. The examples of the latter two types are very limited in metal complexes, though we reported about 20 conglomerates.[1-3] Especially, solid solution is extremely rare[4] and (DL-ethylvalinate-N,N-diacetato)diaquacopper(II) is the only such example in metal complexes.[5] Finding other solid solutions is important for deeper understanding of chiral discrimination mechanism.

The ternary system, [Co(L-leu)$(NH_3)_4$]Br_2 – [Co(D-leu)$(NH_3)_4$]Br_2 – H_2O was already measured[2] but the isotherm for the racemic compound [Co(DL-leu)$(NH_3)_4$]$Br_2.H_2O$ is very flat and different from a normal type. Now we redetermine this system carefully and determine a new iodide system.

The syntheses of the bromides and the iodides were described elsewhere.[2] [Co(L-leu)$(NH_3)_4$]$Br_2.H_2O$: ε(493 nm) = 81.9; $\Delta\varepsilon$(459 nm) = -0.318. [Co(DL-leu)$(NH_3)_4$]$Br_2.H_2O$: ε(493 nm) = 81.9. [Co(L-leu)$(NH_3)_4$]$I_2.H_2O$: ε(492 nm) = 81.0; $\Delta\varepsilon$(459 nm) = -0.314. [Co(DL-leu)$(NH_3)_4$]$I_2.H_2O$: ε(492 nm) = 81.0. The absorption spectra were measured with a Hitachi 330 spectrophotometer and the circular dichroism(CD) spectra with a JASCO J-500 spectropolarimeter. The solid phases were identified by elemental analyses, IR spectra, and X-ray powder diffractions.[6]

Table 1 shows the equilibrium of the two systems. Measurements for the bromide were made as follows: to a point 1 (L 100%) a small amount of the DL salt was added. After stirring ca. 24 h at 25 °C, the equilibrated solution and solid compositions of the next point 2 were determined on the basis of the absorption and CD spectral measurements, and finally point 5 was measured. The points from the racemic side, 10, 9, 8, 7, 6, and 4, were also measured by adding the L salt to point 11 (D 50% and L 50%). The measurements for the iodide were carried out in the same way.

Figure 1(a) shows the bromide system. The solubility curves starting from the racemic side and the enantiomeric side completely overlap to give only one isotherm. It should be noted that no invariant point appears. The part of the phase diagram lying below the solubility curve constitutes a single region in which the tie lines diverse widely and do not converge to any apex of the racemate or the pure enantiomer. The solid phases at points 1, 4, 9, and 11 give the same infrared spectra and all solid phases at points 1, 2, 9, and 11 are monohydrate by elemental analyses. Furthermore, X-ray powder patterns of points 1, 9, and 11 are the same. These results mean that the bromide forms a solid solution over the entire range of concentrations. The situation is all the same for the iodide system(Fig. 1(b)), therefore, single solid solution over the entire range of concentrations is also found for the iodide. Both isotherms are very flat and resemble a isotherm of ideal solid solution. However, the

Table 1. Equilibrium of the system, $[Co(L\text{-}leu)(NH_3)_4]X_2$ – $[Co(D\text{-}leu)(NH_3)_4]X_2$ – H_2O (X = Br and I), at 25 °C

Point No.	X = Br Liquid phase[a) (wt %) L	 D	 Solid phase[b) (%) L : D	X = I Liquid phase[a) (wt %) L	 D	 Solid phase[b) (%) L : D
1	10.4	0	100:0	3.33	0	100:0
2	9.81	0.40	90:10	3.07	0.23	93:7
3	8.93	1.23	86:14	2.97	0.33	88:12
4	8.49	1.49	81:19	2.69	0.59	80:20
5	8.34	1.57	78:22	2.66	0.59	79:21
6	8.12	1.87	69:31	2.56	0.69	76:24
7	7.57	2.29	64:36	2.34	0.91	71:29
8	7.05	2.87	60:40	2.17	1.06	66:34
9	6.08	3.62	58:42	1.99	1.24	60:40
10	5.50	4.17	51:49	1.79	1.43	55:45
11	4.94	4.94	50:50	1.61	1.61	50:50

a) Solubility of anhydrous salt.
b) L:D ratio of $[Co(L_pD_{1-p}\text{-}leu)(NH_3)_4]X_2\cdot H_2O$.

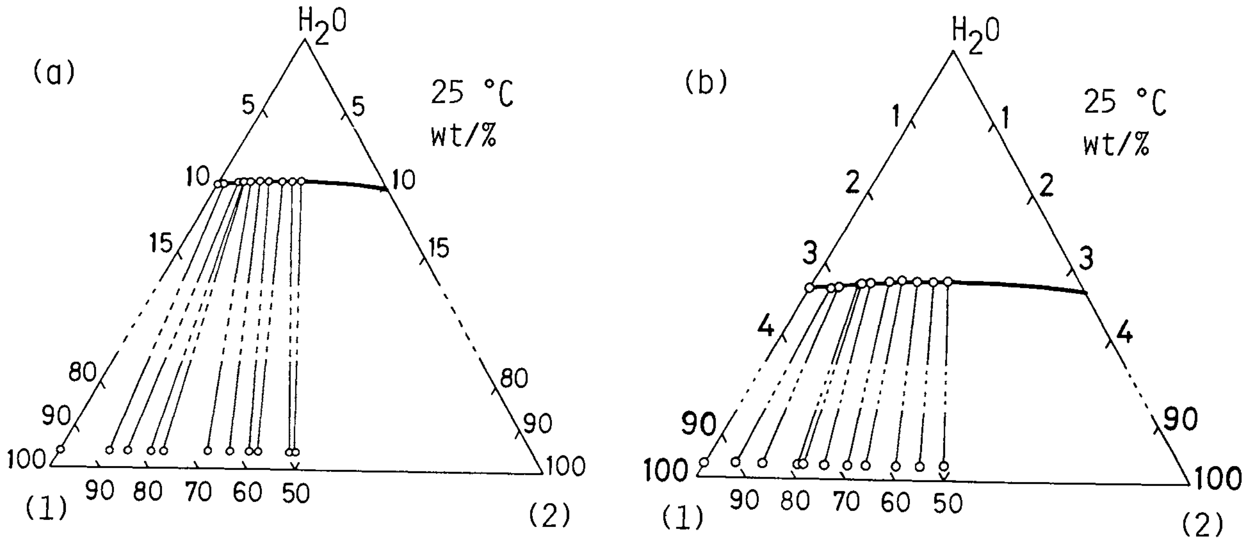

Fig. 1. Ternary solubility isotherms of [Co(L-leu)$(NH_3)_4$]X_2(1) – [Co(D-leu)$(NH_3)_4$]X_2(2) – H_2O (X = Br(a) and X = I(b)) at 25 °C.

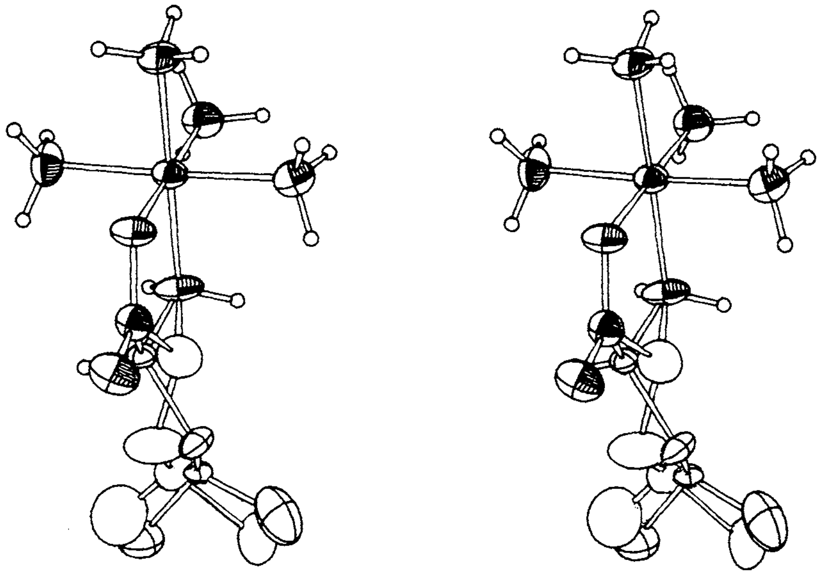

Fig. 2. Stereoview (50% probability) of a cation of [Co(DL-leu)$(NH_3)_4$]I_2.H_2O (D : L = 29 : 71).

enantiomeric excess of a saturated solution is a little larger than that of the solid in equilibrium because of slightly large solubility of the enantiomer. The salts [Co(DL-leu)$(NH_3)_4$]X_2.H_2O (X = Br and I) have the racemic composition of D : L = 50 : 50 but they are racemic solid solutions and not racemic compounds.

The IR spectra of the bromide and the iodide are very similar to each other. The X-ray crystal structure analyses confirm that the bromide and the iodide are isomorphous.[7)] Figure 2 shows a cation of [Co(DL-leu)$(NH_3)_4]I_2 \cdot H_2O$ (D : L = 29 : 71). This clearly demonstrates the coexistence of L-leucinate and D-leucinate at one site of the crystal lattice, that is, solid solution. The side chain of leucinate and the asymmetric carbon are disordered and the other atoms ordered. These are the first examples of solid solution of metal complexes containing natural amino acidate. Further investigation for metal complex systems containing other amino acidate is now in progress.

References

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6) Powder diffraction diagrams were recorded on Rigaku Model RAD-ROC at the X-ray Diffraction Service of the Department of Chemistry, using CuKα radiation.

7) The X-ray crystal analyses were carried out at the X-ray Diffraction Service of the Department of Chemistry, using MoKα radiation. Crystal data: $[Co(leu)(NH_3)_4]Br_2 \cdot H_2O$ (D:L = 22:78); $C_6H_{26}O_3N_5CoBr_2$, M = 435.04, triclinic, P1, a = 11.258(4) Å, b = 11.300(5) Å, c = 7.246(3) Å, α = 92.96(4)°, β = 101.97(3)°, γ = 114.87(3)°, V = 808.0(6) Å^3, Z = 2, D_{calcd} = 1.788 g cm^{-3}, R = 0.055 and R_w = 0.076 for 3744 independent reflections. $[Co(leu)(NH_3)_4]I_2 \cdot H_2O$ (D:L = 29:71); $C_6H_{26}O_3N_5CoI_2$, M = 529.05, triclinic, P1, a = 11.315(4) Å, b = 11.438(4) Å, c = 7.772(1) Å, α = 92.71(2)°, β = 102.00(2)°, γ = 115.30(2)°, V = 878.9(5) Å^3, Z = 2, D_{calcd} = 1.999 g cm^{-3}, R = 0.036 and R_w = 0.049 for 4042 independent reflections. $[Co(L\text{-}leu)(NH_3)_4]I_2 \cdot H_2O$ (L 100%); $C_6H_{26}O_3N_5CoI_2$, M = 529.05, triclinic, P1, a = 11.300(2) Å, b = 11.440(4) Å, c = 7.782(1) Å, α = 92.73(2)°, β = 101.99(1)°, γ = 115.20(2)°, V = 879.9(4) Å^3, Z = 2, D_{calcd} = 1.997 g cm^{-3}, R = 0.032 and R_w = 0.044 for 5135 independent reflections.

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