CHEMISTRY LETTERS, pp. 1551 - 1554, 1991.

Conglomeratic Solid Solutions in trans(N,t-N)-[Co(leucinato)-(tren)]I_2 and trans(N,t-N)-[Co(norleucinato)(tren)]$(ClO_4)_2$ (tren = tris(2-aminoethyl)amine)

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Ternary solubility isotherms of trans(N,t-N)-[Co(leu)(tren)]I_2 and trans(N,t-N)-[Co(n-leu)(tren)]$(ClO_4)_2$ (leu = leucinate(1-), n-leu = norleucinate(1-), and tren = tris(2-aminoethyl)amine) at 25 °C consist of two branches of solubility curve and one eutectic point, but the tie lines do not converge to any apex of the pure enantiomers and diverge widely. These facts mean that both racemates form a conglomerate and simultaneously a solid solution. The X-ray crystal analysis of the former iodide (D : L = 63 : 37; space group $P3_2$) confirms the existence of this conglomeratic solid solution.

Recently we have communicated the racemic solid solutions of $[Co(leu)(NH_3)_4]Br_2.H_2O$ and $[Co(leu)(NH_3)_4]I_2.H_2O$ at 25 °C over the entire region of concentrations.[1)] These phase diagrams consist of single isotherm and do not have any eutectic point in both systems. The first finding of the solid solutions containing natural amino acidate has prompted us to study the phase diagrams of other amino acidato complexes. In this paper we describe new kind of solid solutions in trans(N,t-N)-[Co(leu)(tren)]I_2 and trans(N,t-N)-[Co(n-leu)(tren)]$(ClO_4)_2$.

The complexes were prepared according to the literature:[2)] [Co(L- or DL-leu)(tren)]I_2 and [Co(L- or DL-n-leu)(tren)]$(ClO_4)_2$ were obtained from an aqueous solution of the corresponding chloride by adding a calculated amount of KI and $NaClO_4$, respectively. In both systems only orange isomer was obtained, though two geometrical isomers are possible. The orange isomer was assigned to trans(N,t-N)[2,3)] where the NH_2 group of amino acidate is positioned trans to the tertiary amine of tren. Found for the DL-leu complex: C, 24.51; H, 5.12; N, 11.84%. Found for the L-leu complex: C, 24.34; H, 5.10; N, 11.81%. Calcd for trans(N,t-N)-

[Co(leu)(tren)]I$_2$ = $C_{12}H_{30}N_5O_2CoI_2$: C, 24.46; H, 5.13; N, 11.89%. ε_{DL}(471 nm) = 122.7, ε_L(471 nm) = 122.7, and $\Delta\varepsilon_L$(455 nm) = -0.760. Found for the DL-n-leu complex: C, 27.21; H, 5.75; N, 13.10%. Found for the L-n-leu complex: C, 26.87; H, 5.73; N, 13.04%. Calcd for trans(N,t-N)-[Co(n-leu)(tren)](ClO$_4$)$_2$ = $C_{12}H_{30}N_5O_{10}CoCl_2$: C, 26.98; H, 5.66; N, 13.11%. ε_{DL}(471 nm) = 124.7, ε_L(471 nm) = 123.4, $\Delta\varepsilon_L$(455 nm) = -0.827. The absorption spectra were measured with a Hitachi 330 spectrophotometer and the circular dichroism (CD) spectra with a JASCO J-500 spectropolarimeter. Solubility in water was determined according to the previously reported method.[4)] The solid phases were characterized by elemental analyses, and absorption, CD, and infrared spectra.

Table 1 shows the binary solubilities of trans(N,t-N)-[Co(leu)(tren)]I$_2$ at 5 – 55 °C. The racemate is more soluble than the enantiomer over the entire measured region. The solubility ratio DL / L is 1.24 at 5 °C, 1.25 at 25 °C, and 1.25 at 50 °C. The values are very close to $2^{1/3}$ = 1.26, which is expected for a spontaneously resolvable MX$_2$ electrolyte.[5)] The racemate and the enantiomer are both anhydrate and show the same infrared spectra. These facts mean that the racemic iodide forms a conglomerate or/and a solid solution at 5 – 55 °C.

To confirm the above expectation, we measured the ternary solubility isotherm of trans(N,t-N)-[Co(leu)(tren)]I$_2$ at 25 °C. In Fig. 1(a), points A and C represent the equal solubilities of the pure enantiomers. The two branches of solubility curve AB and BC separate the domain of unsaturated solutions. Point B denotes the eutectic where two solids P and R coexist, and there is no liquid line equilibrated with the solid phases between PR. No isotherm denoting a racemic compound appears in the middle region. The aspects seem to be typical for a conglomerate. However, it should be noted that the present system is definitively different from a normal conglomerate system concerning about their tie lines: in a normal conglomerate all tie lines converge to the pure enantiomers, whereas in this system the tie lines diverge widely between two ranges of concentrations except for PR. For example, the saturated racemic solution is in equilibrium with two kinds of crystals of (D : L = 37 : 63) and (D : L = 63 : 37). Similarly, each point on the AB and BC is in equilibrium

Table I. Solubility of trans(N,t-N)-[Co(DL- or L-leu)-(tren)]I$_2$ (Grams of anhydrous salt in 100 g of water)

T/°C	DL	L	DL/L
5.0	1.54	1.24	1.24
10.0	1.75	1.42	1.23
15.0	2.00	1.60	1.25
20.0	2.28	1.83	1.25
25.0	2.59	2.07	1.25
30.0	2.97	2.37	1.25
35.0	3.35	2.71	1.24
40.1	3.85	3.06	1.26
45.0	4.35	3.47	1.25
50.0	4.88	3.91	1.25
55.0	5.57	4.45	1.25

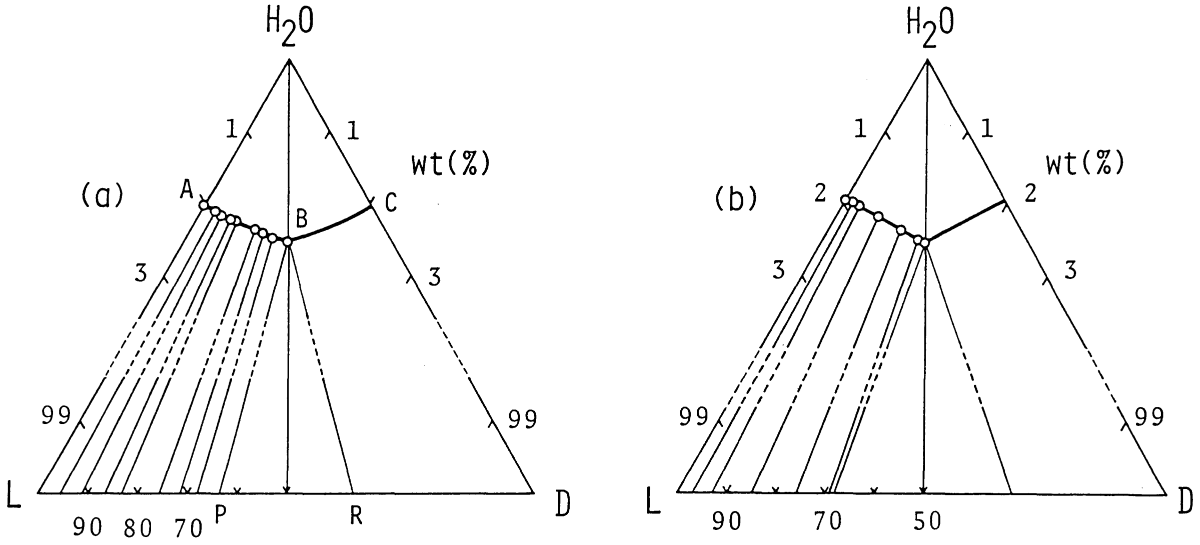

Fig. 1. Ternary solubility isotherms of trans(N,t-N)-[Co(leu)(tren)]I_2(a) and trans(N,t-N)-[Co(n-leu)(tren)]$(ClO_4)_2$(b) at 25 °C.

with the solid of 7 – 27% higher enantiomeric excess (ee). These facts lead to the conclusion that the present system forms a conglomerate and simultaneously a solid solution. This is the first example having both features of a conglomerate and a solid solution. We would like to call such a solid solution as a conglomeratic solid solution.

In a normal conglomerate, optical resolution of the racemate or purification of the optically impure enantiomer is relatively easy because all liquid lines are tied with the pure enantiomers. However, in trans(N,t-N)-[Co(leu)(tren)]I_2, the equilibrated solid phases have only 7 – 27% higher ee and therefore repeated recrystallization would be necessary for purifying the optically impure enantiomer.

Figure 1(b) shows the ternary isotherm of trans(N,t-N)-[Co(n-leu)(tren)]$(ClO_4)_2$ at 25 °C. In this system, the isotherm has also two branches of solubility curve and one eutectic, and the tie lines diverge widely. The saturated racemic solution is in equilibrium with two kinds of crystals of (D : L = 32 : 68) and (D : L = 68 : 32). The racemate and the enantiomer are both anhydrate and exhibit the same infrared spectra. The situation is all the same as that in trans(N,t-N)-[Co(leu)-(tren)]I_2 and indicates the existence of a conglomeratic solid solution.

Figure 2 shows the X-ray crystal structure of trans(N,t-N)-[Co-(leu)(tren)]I_2 (D : L = 63 : 37).$^{6)}$ The space group $P3_2$ means that the complex is spontaneously resolved. The figure clearly demonstrates the coexistence of D-leucinate and L-leucinate at one site of the crystal lattice, that is, solid solution. The disorder is observed in the side

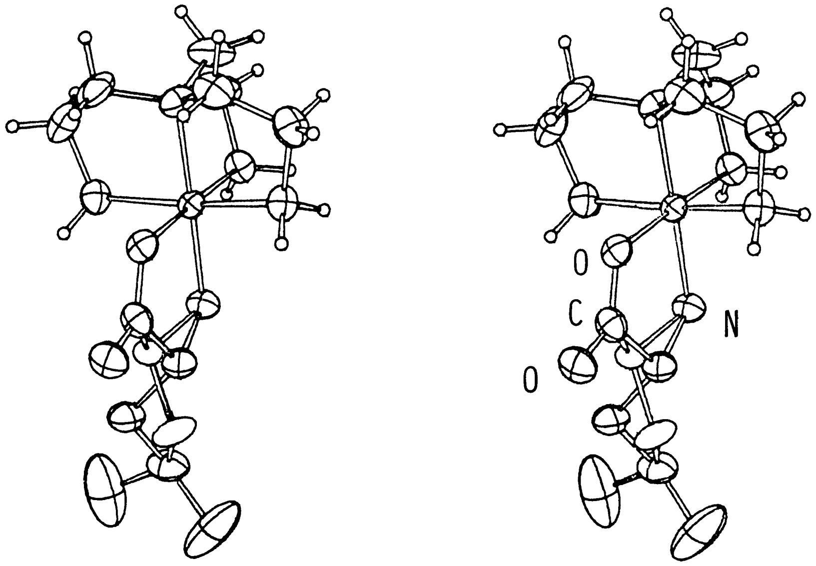

Fig. 2. Stereoview (50% probability) of the cation of trans(N,t-N)-[Co(leu)(tren)]I_2 (D : L = 63 : 37).

chain of leucinate and the asymmetric carbon as in [Co(leu)$(NH_3)_4$]$X_2 \cdot H_2O$ (X = Br and I)[1] though the terminal three carbons of the side chain of leucinate are solved as an accidental overlap for simplicity.

References

1) A. Fuyuhiro, K. Hibino, and K. Yamanari, Chem. Lett., 1991, 1041.
2) K. Akamatsu, T. Komorita, and Y. Shimura, Bull. Chem. Soc. Jpn., 54, 3000 (1981).
3) Y. Mitsui, J. Watanabe, Y. Harada, T. Sakamaki, Y. Iitaka, Y. Kushi, and E. Kimura, J. Chem. Soc., Dalton Trans., 1976, 2095.
4) Y. Shimura and K. Tsutsui, Bull. Chem. Soc. Jpn., 50, 145 (1977).
5) K. Yamanari, J. Hidaka, and Y. Shimura, Bull. Chem. Soc. Jpn., 46, 3724 (1973).
6) The X-ray crystal analysis was carried out at the X-ray Diffraction Service of the Department of Chemistry. The data were collected on a Rigaku AFC5R diffractometer using MoKα radiation and solved by TEXSAN. The absolute configuration was determined by using the anomalous dispersion terms. The occupancy of D : L was fixed according to the result of the phase diagram. Crystal data: trans(N,t-N)-[Co(leu)(tren)]I_2 (D : L = 63 : 37); $C_{12}H_{30}O_2N_5CoI_2$, M = 589.14, trigonal, $P3_2$, a = 9.193(2) Å, c = 20.798(3) Å, V = 1522.1(5) $Å^3$, Z = 3, D_{calcd} = 1.928 g cm^{-3}, R = 0.027 and R_w = 0.037 for 2981 independent reflections.

(Received June 10, 1991)