August, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 61, 2817—2823 (1988)* 2817

The Crystal Structures of Δ-, Λ-, and Pseudoracemic Forms of Bis(ethylenediamine)oxalatocobalt(III) Aspartates

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(Received March 7, 1988)

The crystal structures of Δ-[Co(ox)(en)$_2$](L-Hasp)·3H$_2$O, Λ-[Co(ox)(en)$_2$](L-Hasp)·3H$_2$O and *rac*-[Co(ox)(en)$_2$](L-Hasp) have been determined by means of X-ray diffraction. The absolute configurations of (−)-and (+)-cations were assigned as $\Delta(\delta\lambda)$ and $\Lambda(\delta\lambda)$, respectively, on the basis of that of L-Hasp$^-$ ion. The counter ion is extended with C-C-C-C near 180° in all cases, but the other torsion angles are somewhat affected by surroundings. Both α and β carboxyl groups of the anion are ionized, therefore its NH$_2$ group is protonated. In the three compounds, the cations and the anions are alternately arranged, forming a layer through N-H···O hydrogen bonds in a very similar way to each other. The lattice of the more soluble Δ-isomer consists of such single cation-anion layers, between which water molecules are inserted. In the less soluble Λ-diastereoisomer the cation-anion layers are doubled by N-H···O bonds between cations from neighboring layers. The less soluble racemic salt is anhydride where the similar cation-anion layers are connected by hydrogen bonds between cations and between anions alternately. In connection to optical resolution, the difference in solubility was discussed in terms of the density, unoccupied fraction and electrostatic energy.

An useful method to isolate one of the enantiomers for a racemic mixture is to add a suitable chiral reagent. When a cationic racemate is precipitated with an optically active anion, two different diastereoisomeric salts may result and sometimes their solubility difference allows both of them to be isolated. In view of this, Kuramoto et al. have developed structural studies of optical resolution on various pairs of diastereoisomeric salts.[1,2] Gajhede and Larsen have recently related the crystal structure to solubility for the diastereoisomeric salts which are obtained from bis(ethylenediamine)glycinatocobalt(III) and bis-μ-[(R,R)-tartrato(4−)]-diantimonate(III).[3] On the other hand, an application of L-amino acid anion as a resolving agent for some metal complexes was examined on the systems of $(-)_{589}$- and $(+)_{589}$-[Co(ox)(en)$_2$]X with X=L-hydrogenglutamate (L-Hglu$^-$) and L-hydrogenaspartate (L-Hasp$^-$) by Yamanari et al.[4] They determined these solubility phase diagrams and confirmed that the former anion L-Hglu$^-$ is an excellent resolving agent, while the latter anion L-Hasp$^-$ forms the pseudoracemate, *rac*-[Co(ox)(en)$_2$](L-Hasp). We have succeeded in preparing $(-)_{589}$-, $(+)_{589}$-, and *rac*-[Co(ox)(en)$_2$](L-Hasp) and also $(-)_{589}$- and $(+)_{589}$-[Co(ox)(en)$_2$](L-Hglu) salts as suitable single crystals for X-ray analysis. In the hydrogenaspartate system, [Co(ox)(en)$_2$](L-Hasp)·nH$_2$O, the $(-)_{589}$ diastereoisomer (n=3) **1** is more soluble than the $(+)_{589}$ isomer (n=3) **2** and the rac-complex (n=0) **3**; for example the values of solubility as expressed by grams of anhydrous salt in 100 g water are 71.0, 12.4, and 11.9 at 20 °C and 127, 44.8, and 18.8 at 60 °C for **1**, **2**, and **3**, respectively. On the other hand, in the hydrogenglutamate system [Co(ox)(en)$_2$](L-Hglu)·nH$_2$O the $(-)_{589}$ diastereoisomer (n=2) **4** is more soluble than the $(+)_{589}$ isomer (n=5) **5**. In order to understand such an appreciable difference in solubility the crystal structures of these five complexes have been determined by X-ray diffraction methods. The absolute configuration of the common cation [Co(ox)(en)$_2$]$^+$ was determined by reference to that of the L-amino acid anion. The present paper is concerned with the results of the hydrogenaspartates and the next with the hydrogenglutamate ones.

Experimental

Preparation. The three aspartates were prepared by the methods described in the previous paper and recrystallized from water.[4] The density was measured by pycnometry with kerosine or floatation with kerosine-bromoform mixture. The number of water of crystallization was estimated by thermogravimetry and precisely determined from X-ray structure analysis. The prepared samples were identified by elemental analysis, thermal analysis, absorption and circular dichroism spectra.[4]

X-Ray Structure Determination. The lattice parameters and the space groups were determined preliminary with Weissenberg and precession cameras and confirmed by single crystal diffractometers. Intensity data were collected on Rigaku AFC-4 (Mo$K\alpha$, 30 kV, 200 mA) for **1** and **3** and on Rigaku AFC-5 (Mo$K\alpha$, 50 kV, 150 mA) for **2**. Graphite monochromated Mo$K\alpha$ radiation (λ=0.71069 Å) and the ω-2θ scan technique (at 4° min^{-1} in ω) were used throughout the experiment. Intensities were corrected for Lorentz-polarization and absorption effects; empirical absorption correction factors on F were 0.993—1.013 about [c] axis for **1**, 1.009—1.034 about [b] for **2** and 1.020—1.131 about [c] for **3**.[5] Other experimental conditions and refinement details are listed in Table 1.

Every structure was solved by a direct method based on MULTAN78[6] and refined by block-diagonal least-squares on F. Most of O, N and C atoms were located by Fourier syntheses and their remaining atoms and most H atoms were found in difference Fourier maps. Anisotropic thermal parameters were applied to all non-hydrogen atoms in **1** and **2**, while they were only to Co atoms in **3** because of its poor intensity data. In the final refinements all H atoms were included at fixed positions (calculated from C-H=1.10,

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Table 1. Experimental Conditions and Refinement Details

	1	**2**	**3**
Crystal size (mm)	0.06X0.12X0.18	0.10X0.12X0.20	0.06X0.13X0.18
Number of reflections and 2θ range(°) used for measuring lattice parameters	30 $17<2\theta<28$	25 $18<2\theta<24$	40 $15<2\theta<28$
$2\theta_{\max}$ (°)	55	50	55
Ranges of h	−12 to 12	−16 to 16	−13 to 13
k	−14 to 14	−7 to 0	−16 to 16
l	−8 to 0	−12 to 12	0 to 7
Systematic absences	None	$0kl$: k odd	None
Standard reflections and their intensity variations	$00\bar{2},400,03\bar{3}$ 0.970—1.023	$\bar{5}00,220,003$ 0.943—1.009	$003,\bar{1}01,0\bar{4}1$ 0.981—1.053
$R_{\mathrm{int}}=(\sum\|\|F\|-<\|F\|>\|)/\sum\|F\|$		0.052	
Number of reflections measured	4280	3643	3531
Number of unique reflections with $\|F_o\|>3\sigma(F_o)$	3732	1668	1780
$R=\sum(\|\|F_o\|-\|F_c\|\|)/\sum\|F_o\|$	0.050	0.034	0.078
$R_w=[\sum W(\|F_o\|-\|F_c\|)^2/\sum W\|F_o\|^2]^{1/2}$	0.051	0.043	0.050
Weight $W=[\sigma^2(F_o)+a\|F_o\|+b\|F_o\|^2]^{-1}$	$a=-0.0065$ $b=0.0009$	$a=0.0070$ $b=0.0008$	$a=0.0000$ $b=0.0000$
$S=[\sum W(\|F_o\|-\|F_c\|)^2/(m-n)]^{1/2}$	1.036	0.977	1.336
Number of observed reflections used for refinements, m	3732	1668	1169($2\theta<43$°)
Number of refined parameters, n	245	245	184
$(\Delta\rho)_{\max}$, $(\Delta\rho)_{\min}$ (e Å^{-3})	0.67, −0.59	0.34, −0.31	0.76, −0.68
$(\Delta/\sigma)_{\mathrm{av}}$, $(\Delta/\sigma)_{\max}$	0.08, 0.59	0.03, 0.21	0.08, 0.28

N-H=1.02 and O-H=0.96 Å) with isotropic temperature factors. Neutral atomic scattering factors and anomalous dispersion terms were taken from International Tables for X-ray Crystallography.[7] The programs MULTAN78, ORTEPII and UNICS-OSAKA were used for calculations at the Information Processing Center of Kobe University.[6,8,9] The final atomic parameters are listed in Tables 2—4.[10]

Crystal Data. Crystal data are as follows:

(**1**) $[Co(C_2O_4)(C_2H_8N_2)_2]^+$ $(C_4H_6NO_4)^-\cdot 3H_2O$, $M_r=453.3$, triclinic, $P1$, $a=8.968(3)$, $b=9.953(4)$, $c=6.084(2)$ Å, $\alpha=103.49(3)$, $\beta=79.17(3)$, $\gamma=117.43(3)$°, $V=466.7(3)$ Å^3, $Z=1$, $D_m=1.58(2)$, $D_x=1.61$ g cm^{-3}, $F(000)=238$, $T=298$ K, $\mu(\mathrm{Mo}\,K\alpha)=10.05$ cm^{-1}.

(**2**) $[Co(C_2O_4)(C_2H_8N_2)_2]^+(C_4H_6NO_4)^-\cdot 3H_2O$, $M_r=453.3$, monoclinic, $P2_1$, $a=14.319(4)$, $b=6.1043(7)$, $c=10.771(2)$ Å, $\beta=96.96(3)$°, $V=934.5(3)$ Å^3, $Z=2$, $D_m=1.61(2)$, $D_x=1.61$ g cm^{-3}, $F(000)=476$, $T=298$ K, $\mu(\mathrm{Mo}\,K\alpha)=10.24$ cm^{-1}.

(**3**) $[Co(C_2O_4)(C_2H_8N_2)_2]^+$ $(C_4H_6NO_4)^-$, $M_r=399.2$, triclinic, $P1$, $a=10.363(3)$, $b=12.964(4)$, $c=6.091(1)$ Å, $\alpha=102.78(2)$, $\beta=86.47(3)$, $\gamma=104.59(3)$°, $V=772.4(3)$ Å^3, $Z=2$, $D_m=1.73(2)$, $D_x=1.72$ g cm^{-3}, $F(000)=416$, $T=298$ K, $\mu(\mathrm{Mo}\,K\alpha)=12.22$ cm^{-1}.

Results and Discussion

Cation and Anion Geometries. The perspective drawings of the $(-)_{589}$- complex cation and the counter anion are given in Fig. 1 with the atomic numbering scheme. The absolute configurations of the $(-)_{589}$-$[Co(ox)(en)_2]^+$ and the $(+)_{589}$-$[Co(ox)(en)_2]^+$ cations were identified to be $\Delta(\delta\lambda)$ and $\Lambda(\delta\lambda)$, respectively, on the basis of L-aspartate ion as an internal reference. These configurations are consistent with the assignments made by analyses of the circular dichroism spec-

Table 2. Fractional Atomic Coordinates and Thermal Parameters (Å^2) of Non-Hydrogen Atoms (with e.s.d.'s) for Structure **1**

Atom	x	y	z	B_{eq}
Co	0.7082(1)	0.7212(1)	0.7189(2)	1.93(1)
O(1)	0.7321(4)	0.5324(3)	0.6169(5)	2.6(1)
O(2)	0.8097(4)	0.7394(3)	0.9805(5)	2.5(1)
O(3)	0.8315(5)	0.3951(4)	0.7307(6)	3.9(1)
O(4)	0.9143(4)	0.6170(4)	1.1216(5)	3.0(1)
O(5)	0.2809(4)	0.2015(4)	0.1491(7)	4.1(1)
O(6)	0.5209(5)	0.4117(4)	0.1121(6)	3.5(1)
O(7)	0.5017(4)	−0.0090(4)	0.6456(6)	3.6(1)
O(8)	0.6545(5)	0.0076(4)	0.3132(5)	3.7(1)
O(9)	0.1995(5)	0.9155(5)	0.8594(7)	4.5(1)
O(10)	0.0442(6)	0.3288(6)	0.2731(10)	7.2(1)
O(11)	0.2667(5)	0.7509(6)	0.1298(9)	6.1(1)
N(1)	0.9294(4)	0.8317(3)	0.5622(6)	2.4(1)
N(2)	0.7125(5)	0.9212(4)	0.8333(6)	2.5(1)
N(3)	0.4830(5)	0.6087(5)	0.8676(6)	2.8(1)
N(4)	0.5903(5)	0.6871(4)	0.4584(6)	2.6(1)
N(5)	0.7174(5)	0.3005(4)	0.1936(6)	2.6(1)
C(1)	0.8034(6)	0.5067(5)	0.7541(7)	2.5(1)
C(2)	0.8476(5)	0.6312(5)	0.9724(7)	2.3(1)
C(3)	0.9553(7)	0.9891(6)	0.5539(9)	3.4(1)
C(4)	0.8831(7)	1.0423(6)	0.7857(9)	3.8(1)
C(5)	0.3639(6)	0.5162(6)	0.6896(8)	3.3(1)
C(6)	0.4060(6)	0.6234(6)	0.5204(8)	3.2(1)
C(7)	0.4353(6)	0.2759(6)	0.1454(7)	2.8(1)
C(8)	0.5362(6)	0.1928(5)	0.1872(7)	2.4(1)
C(9)	0.4692(6)	0.1295(6)	0.4096(8)	2.9(1)
C(10)	0.5485(6)	0.0346(5)	0.4545(8)	2.6(1)

$B_{\mathrm{eq}}=(4/3)\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.
$T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Table 3. Fractional Atomic Coordinates and Thermal Parameters (Å^2) of Non-Hydrogen Atoms (with e.s.d.'s) for Structure **2**

Atom	x	y	z	B_{eq}
Co	0.68676(4)	0.23158(18)	0.71632(5)	1.94(1)
O(1)	0.6830(2)	0.2562(6)	0.5377(3)	2.4(1)
O(2)	0.6228(2)	−0.0438(6)	0.6808(3)	2.5(1)
O(3)	0.6355(2)	0.0642(7)	0.3654(3)	3.1(1)
O(4)	0.5654(2)	−0.2474(7)	0.5183(3)	2.8(1)
O(5)	0.0897(3)	0.3557(9)	0.5742(3)	4.8(1)
O(6)	0.2079(2)	0.2628(7)	0.4695(3)	3.1(1)
O(7)	0.2527(3)	0.2494(9)	1.0204(3)	4.1(1)
O(8)	0.3178(4)	0.0093(9)	0.9052(4)	6.0(1)
O(9)	0.9583(3)	0.2738(9)	0.3659(4)	5.9(1)
O(10)	0.9273(4)	0.3455(12)	0.1147(5)	7.3(1)
O(11)	0.0886(4)	0.4770(10)	0.0285(4)	6.3(1)
N(1)	0.5660(3)	0.3855(7)	0.7088(3)	2.4(1)
N(2)	0.6751(3)	0.1855(6)	0.8932(3)	2.6(1)
N(3)	0.8114(3)	0.0938(7)	0.7222(4)	2.8(1)
N(4)	0.7556(3)	0.5057(7)	0.7446(3)	2.4(1)
N(5)	0.3098(3)	0.0739(8)	0.6599(4)	3.1(1)
C(1)	0.6431(3)	0.0919(8)	0.4782(4)	2.3(1)
C(2)	0.6063(3)	−0.0846(8)	0.5641(4)	2.3(1)
C(3)	0.5377(4)	0.4033(10)	0.8373(5)	3.2(1)
C(4)	0.5735(3)	0.2034(12)	0.9075(4)	3.2(1)
C(5)	0.8808(3)	0.2662(10)	0.7010(5)	3.3(1)
C(6)	0.8577(4)	0.4608(10)	0.7769(5)	3.2(1)
C(7)	0.1669(3)	0.2654(9)	0.5646(4)	2.9(1)
C(8)	0.2139(3)	0.1458(9)	0.6810(4)	2.7(1)
C(9)	0.2189(4)	0.2857(9)	0.8000(4)	3.4(1)
C(10)	0.2652(4)	0.1703(9)	0.9178(4)	3.3(1)

$B_{eq}=(4/3)\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

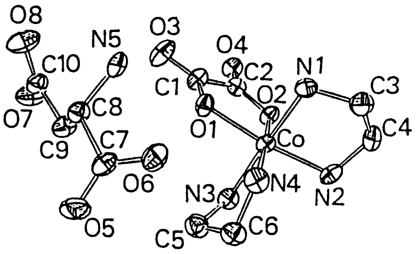

Fig. 1. Absolute configurations of $(-)_{589}$-$[Co(ox)(en)_2]^+$ cation and L-$Hasp^-$ anion.

Table 4. Fractional Atomic Coordinates and Thermal Parameters (Å^2) of Non-Hydrogen Atoms (with e.s.d.'s) for Structure **3**

Atom	x	y	z	B_{eq}[a)]/B_{iso}
Co(A)	0.9633(3)	0.9456(3)	0.6160(6)	1.6(1)[a)]
Co(B)	0.4409(3)	0.3530(3)	0.3215(6)	2.1(1)[a)]
O(1A)	1.144(1)	0.936(1)	0.582(2)	1.9(3)
O(2A)	1.004(1)	1.008(1)	0.940(3)	2.8(3)
O(3A)	1.334(1)	0.993(1)	0.760(2)	2.6(3)
O(4A)	1.189(1)	1.054(1)	1.147(2)	2.3(3)
O(5A)	0.231(2)	0.710(1)	−0.267(3)	4.3(4)
O(6A)	0.114(1)	0.785(1)	0.016(2)	1.3(3)
O(7A)	0.695(1)	0.844(1)	0.028(3)	2.9(3)
O(8A)	0.577(1)	0.875(1)	0.349(3)	4.1(4)
O(1B)	0.256(1)	0.350(1)	0.381(2)	1.8(3)
O(2B)	0.390(1)	0.282(1)	0.032(2)	1.9(3)
O(3B)	0.060(1)	0.285(1)	0.188(2)	2.4(3)
O(4B)	0.218(1)	0.224(1)	−0.201(3)	2.9(3)
O(5B)	1.159(1)	0.567(1)	1.222(2)	1.5(3)
O(6B)	1.276(1)	0.489(1)	0.947(2)	2.2(3)
O(7B)	0.703(1)	0.404(1)	0.865(3)	3.3(4)
O(8B)	0.831(1)	0.449(1)	0.581(2)	1.2(3)
N(1A)	0.999(2)	1.077(1)	0.527(3)	2.5(4)
N(2A)	0.779(1)	0.961(1)	0.675(3)	1.3(3)
N(3A)	0.920(1)	0.791(1)	0.704(3)	3.0(4)
N(4A)	0.924(2)	0.859(1)	0.304(3)	1.5(3)
N(5A)[b)]	0.296	0.798	0.312	3.0
N(1B)	0.396(2)	0.203(1)	0.410(3)	2.1(4)
N(2B)	0.617(2)	0.323(1)	0.254(3)	2.3(4)
N(3B)	0.479(1)	0.488(1)	0.248(3)	1.0(3)
N(4B)	0.488(2)	0.428(1)	0.626(3)	2.2(4)
N(5B)	1.089(1)	0.488(1)	0.630(3)	1.4(3)
C(1A)[b)]	1.209	0.976	0.736	2.0
C(2A)[b)]	1.128	1.011	0.955	2.0
C(3A)	0.866(2)	1.115(2)	0.506(4)	2.3(5)
C(4A)	0.774(2)	1.074(2)	0.714(4)	3.8(6)
C(5A)	0.922(2)	0.713(1)	0.493(3)	0.7(4)
C(6A)	0.849(2)	0.744(1)	0.321(3)	1.5(4)
C(7A)	0.224(2)	0.765(1)	−0.071(3)	1.5(4)
C(8A)	0.348(2)	0.839(2)	0.076(4)	2.4(5)
C(9A)	0.470(2)	0.793(1)	−0.005(3)	1.5(4)
C(10A)	0.590(2)	0.835(2)	0.134(4)	3.5(6)
C(1B)[b)]	0.180	0.298	0.180	2.0
C(2B)[b)]	0.271	0.263	−0.026	2.0
C(3B)	0.514(2)	0.172(2)	0.417(4)	3.5(6)
C(4B)	0.602(2)	0.209(2)	0.246(4)	1.7(4)
C(5B)	0.494(2)	0.575(2)	0.450(5)	4.6(6)
C(6B)	0.543(2)	0.544(2)	0.638(4)	3.8(6)
C(7B)	1.181(2)	0.519(2)	1.027(4)	3.9(6)
C(8B)	1.059(2)	0.520(2)	0.868(4)	1.5(4)
C(9B)	0.939(2)	0.440(2)	0.924(4)	2.0(5)
C(10B)	0.816(2)	0.431(2)	0.779(4)	2.4(5)

a) $B_{eq}=(4/3)\sum_i\sum_j\beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$. b) Atom was not refined.

tra of the complexes.[4] The assignments also agree with those in the compounds with various counter ions such as Br^-,[11] $(+)_{589}$-$[Co(CN)_2(mal)(NH_3)_2]^-$,[12] and H-*d*-$tart^-$.[1,2] It was therefore confirmed that the *lel-ob* conformation is the most stable form among the possible three, *lel-lel, lel-ob, ob-ob,* for the two ethylenediamine ligands. Selected bond lengths and angles within the ions are listed in Table 5. The corresponding values for the four complex cations are in fair agreement with each other, as well as with those found in the literature.[2,11]

The bond lengths and angles in the L-aspartate ion are consistent with the values reported for the free acid and its metal complexes.[13–15] In the present cases, the L-$Hasp^-$ ion is not coordinated to the Co(III) atom, but acts as a counter anion to the complex cation $[Co(ox)(en)_2]^+$. The anion is therefore extended with the carbon atom skeleton, C(7)-C(8)-C(9)-C(10), in almost planar, zigzag conformation. The molecule in the crystalline state of free L-aspartic acid (LASP) is in the zwitterionic form and the ionized α-carboxyl group and the un-ionized β-carboxyl group are clearly distinguished; the C-O distances in the ionized COO^- group are 1.242 and 1.252 Å, whereas in the un-ionized COOH group they are 1.202 and 1.306 Å.[14] A comparison with these values indicates that both α and β car-

Table 5. Bond Lengths (l/Å) and Angles (ϕ/°)

	1	**2**	**3**	
			"A"	"B"
Co-O(1)	1.934(4)	1.924(3)	1.90(1)	1.92(1)
Co-O(2)	1.911(4)	1.930(3)	1.99(1)	1.84(1)
Co-N(1)	1.955(3)	1.961(4)	1.85(2)	2.06(2)
Co-N(2)	1.934(5)	1.953(4)	1.97(2)	1.96(2)
Co-N(3)	1.963(4)	1.967(4)	2.13(2)	1.85(2)
Co-N(4)	1.948(4)	1.947(4)	1.99(2)	1.92(2)
O(1)-C(1)	1.274(7)	1.286(6)	1.14	1.44
O(2)-C(2)	1.258(7)	1.274(5)	1.28	1.25
O(3)-C(1)	1.220(8)	1.218(5)	1.27	1.22
O(4)-C(2)	1.243(7)	1.226(6)	1.31	1.18
N(1)-C(3)	1.485(8)	1.492(6)	1.60(3)	1.39(3)
N(2)-C(4)	1.475(6)	1.485(6)	1.45(3)	1.43(3)
N(3)-C(5)	1.491(6)	1.484(7)	1.45(2)	1.46(3)
N(4)-C(6)	1.479(6)	1.487(6)	1.52(2)	1.45(3)
C(1)-C(2)	1.560(5)	1.554(7)	1.57	1.58
C(3)-C(4)	1.521(7)	1.493(9)	1.64(3)	1.43(3)
C(5)-C(6)	1.528(8)	1.502(8)	1.51(3)	1.45(4)
O(1)-Co-O(2)	85.0(2)	85.1(1)	86.6(6)	86.8(6)
N(1)-Co-N(2)	85.7(2)	86.0(2)	86.9(7)	83.3(7)
N(3)-Co-N(4)	85.5(2)	85.5(2)	84.5(7)	87.4(7)
Co-O(1)-C(1)	113.1(3)	113.2(3)	115.6	109.4
Co-O(2)-C(2)	113.4(3)	113.1(3)	103.7	120.0
Co-N(1)-C(3)	109.8(3)	109.5(3)	111.5(11)	108.2(13)
Co-N(2)-C(4)	109.9(4)	106.9(3)	111.4(12)	107.6(11)
Co-N(3)-C(5)	108.8(3)	108.3(3)	105.1(14)	110.8(15)
Co-N(4)-C(6)	110.5(3)	110.1(3)	107.4(13)	110.8(15)
O(1)-C(1)-O(3)	126.0(4)	125.9(5)	130.5	118.6
O(1)-C(1)-C(2)	113.3(5)	114.0(4)	113.3	112.2
O(3)-C(1)-C(2)	120.6(5)	120.1(4)	116.2	129.1
O(2)-C(2)-O(4)	125.5(4)	125.3(4)	119.7	132.0
O(2)-C(2)-C(1)	115.2(4)	114.6(4)	119.8	111.4
O(4)-C(2)-C(1)	119.3(5)	120.1(4)	120.1	116.6
N(1)-C(3)-C(4)	104.8(4)	107.2(4)	103.0(18)	109.0(22)
N(2)-C(4)-C(3)	108.0(4)	106.7(4)	101.6(17)	112.0(18)
N(3)-C(5)-C(6)	105.1(4)	106.3(4)	107.9(16)	111.8(21)
N(4)-C(6)-C(5)	107.2(5)	107.1(4)	106.1(14)	109.0(18)
O(5)-C(7)	1.233(6)	1.251(7)	1.26(2)	1.25(3)
O(6)-C(7)	1.253(6)	1.241(6)	1.29(2)	1.18(3)
O(7)-C(10)	1.265(6)	1.239(6)	1.23(3)	1.26(3)
O(8)-C(10)	1.240(6)	1.256(8)	1.31(3)	1.28(3)
N(5)-C(8)	1.480(5)	1.485(7)	1.65	1.45(3)
C(7)-C(8)	1.562(9)	1.534(7)	1.58(3)	1.65(3)
C(8)-C(9)	1.527(7)	1.534(7)	1.54(3)	1.48(3)
C(9)-C(10)	1.511(9)	1.531(7)	1.47(3)	1.56(3)
O(5)-C(7)-O(6)	127.0(6)	125.8(5)	122.8(17)	131.4(23)
O(5)-C(7)-C(8)	116.8(5)	116.5(4)	124.9(17)	106.8(19)
O(6)-C(7)-C(8)	116.2(4)	117.7(4)	111.1(15)	121.0(21)
N(5)-C(8)-C(7)	110.1(4)	109.7(4)	96.2(13)	111.7(16)
N(5)-C(8)-C(9)	109.5(4)	110.0(4)	106.5(17)	108.3(14)
C(7)-C(8)-C(9)	111.0(4)	112.9(4)	108.1(15)	107.1(18)
C(8)-C(9)-C(10)	114.8(4)	114.1(5)	117.5(17)	112.2(19)
O(7)-C(10)-O(8)	124.2(6)	123.7(5)	125.5(19)	122.0(20)
O(7)-C(10)-C(9)	115.0(5)	117.7(5)	114.9(21)	117.3(20)
O(8)-C(10)-C(9)	120.8(5)	118.4(5)	118.6(19)	120.8(17)

boxyl groups are ionized and consequently the amino groups are protonated in crystals of **1**, **2**, and **3**. The torsion angles of the L-Hasp$^-$ ions are compared in Table 6, where the corresponding values for LASP and DL-aspartic acid (DLASP) are also included.[14,15] The angles other than the carbon skeleton described above are more or less different from each other, possibly owing to the packing effect, especially to the hydrogen bonding scheme. The variation in torsion angle among the aspartates **1**, **2**, and **3** is considerably less than that between the two glutamates **4** and **5**, which are described in the next paper.

Crystal Structures. The crystal structures of the three aspartates are shown in Figs. 2—4. The distances and angles for intermolecular hydrogen bonds are given in Table 7.

Δ-(−)[Co(ox)(en)$_2$](L-Hasp)·3H$_2$O (1): In the most soluble aspartate, (−)[Co(ox)(en)$_2$]$^+$ cations and L-Hasp$^-$ anions are arranged alternately to form a layer parallel to (100) and water molecules are sandwiched between these layers (Fig. 2). Each complex cation donates its eight NH hydrogen atoms to eight oxygen atoms of one cation, four anions and two water molecules, forming eight N-H···O hydrogen bonds with distances ranging from 2.79 to 3.27 Å (av 2.96 Å). The ammonio group -NH$_3^+$ of the anion is hydrogen bonded to three oxygen atoms from two cations and one water molecule with a mean N-H···O distance of 2.99 Å, while three kinds of water molecules form six O-H···O hydrogen bonds (av 2.86 Å) with six oxygen atoms of two cation, three anions and one water molecule. Thus, the two types of hydrogen bonds, N-H···O and O-H···O, contribute to stabilize the crystal lattice, in addition to electrostatic interaction.

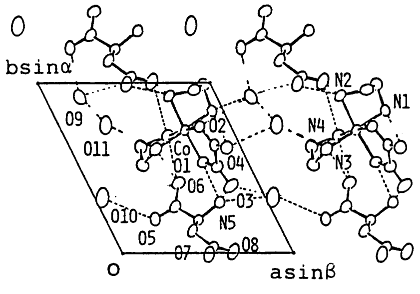

Fig. 2. Crystal structure of diastereoisomer **1** projected along [001]. Broken lines denote hydrogen bonds. Thermal ellipsoids are shown at 50% probability level.

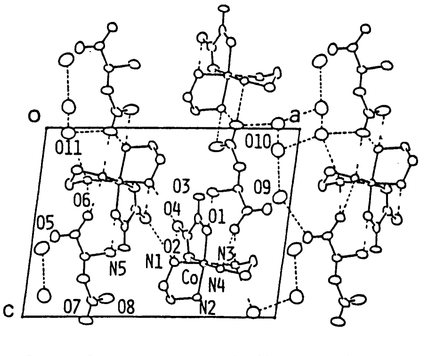

Fig. 3. Crystal structure of diastereoisomer **2** projected along [010]. Broken lines denote hydrogen bonds. Thermal ellipsoids are shown at 50% probability level.

Table 6. Torsion Angles (τ/°) of L-Aspartic Acid

Atom	1	2	3 "A"	3 "B"	LASP[14]	DLASP[15]
O(5)-C(7)-C(8)-N(5)	−176.0(4)	−172.5(4)	−135.5(17)	167.4(18)	144.8	172.3
O(6)-C(7)-C(8)-N(5)	3.9(6)	8.1(6)	57.6(17)	−3.9(30)	−37.8	−7.3
O(5)-C(7)-C(8)-C(9)	−54.6(6)	−49.4(6)	−26.0(26)	−73.8(23)	−94.2	−64.0
O(6)-C(7)-C(8)-C(9)	125.3(5)	131.2(5)	167.1(15)	114.9(24)	83.2	117.6
C(7)-C(8)-C(9)-C(10)	174.7(4)	179.8(4)	−168.5(16)	−178.6(18)	178.2	174.2
C(8)-C(9)-C(10)-O(7)	175.3(4)	−163.6(5)	−144.2(18)	−151.6(21)	131.4	3.1
C(8)-C(9)-C(10)-O(8)	−2.8(7)	20.5(7)	25.1(25)	29.4(31)	−51.3	−175.8
N(5)-C(8)-C(9)-C(10)	−63.5(6)	−57.2(5)	−66.4(20)	−57.7(24)	−61.9	−61.9

Table 7. Distances D···A(l/Å) and Angles D-H···A(ϕ/°) of Hydrogen Bonds

	D···A	D-H···A		D···A	D-H···A
(1) Δ-form			(2) Λ-form		
N(1)-H(1)···O(4$^{\mathrm{iv}}$)	2.995(6)	168	N(1)-H(1)···O(4$^{\mathrm{iii}}$)	3.038(6)	150
N(1)-H(2)···O(9$^{\mathrm{ii}}$)	2.986(6)	162	N(1)-H(2)···O(4$^{\mathrm{xii}}$)	3.011(6)	152
N(2)-H(3)···O(7$^{\mathrm{iii}}$)	2.785(6)	170	N(2)-H(3)···O(7$^{\mathrm{xv}}$)	2.965(7)	177
N(2)-H(4)···O(8$^{\mathrm{viii}}$)	2.865(6)	165	N(2)-H(4)···O(8$^{\mathrm{xiii}}$)	2.929(7)	132
N(3)-H(5)···O(6$^{\mathrm{v}}$)	2.888(6)	172	N(3)-H(5)···O(6$^{\mathrm{xi}}$)	2.878(6)	172
N(3)-H(6)···O(11$^{\mathrm{v}}$)	2.936(7)	154	N(3)-H(6)···O(11$^{\mathrm{xi}}$)	2.972(8)	156
N(4)-H(7)···O(6)	2.927(6)	145	N(4)-H(7)···O(6$^{\mathrm{xii}}$)	2.889(6)	153
N(4)-H(8)···O(8$^{\mathrm{iii}}$)	3.273(6)	166	N(4)-H(8)···O(7$^{\mathrm{viii}}$)	2.950(7)	152
N(5)-H(9)···O(1)	3.008(6)	180	N(5)-H(9)···O(1$^{\mathrm{xi}}$)	2.891(6)	179
N(5)-H(10)···O(3$^{\mathrm{iv}}$)	3.022(6)	180	N(5)-H(10)···O(3$^{\mathrm{xii}}$)	3.114(6)	179
N(5)-H(11)···O(10$^{\mathrm{ii}}$)	2.935(8)	145			
O(9)-H(12)···O(5$^{\mathrm{viii}}$)	2.823(6)	179	O(9)-H(12)···O(5$^{\mathrm{ii}}$)	2.794(8)	179
O(9)-H(13)···O(7$^{\mathrm{iii}}$)	2.618(6)	179	O(9)-H(13)···O(5$^{\mathrm{xi}}$)	2.740(8)	179
O(10)-H(14)···O(3$^{\mathrm{i}}$)	3.183(8)	180	O(10)-H(14)···O(9)	2.723(9)	178
O(10)-H(15)···O(5)	2.848(8)	180	O(10)-H(15)···O(11$^{\mathrm{ii}}$)	2.713(10)	177
O(11)-H(16)···O(4$^{\mathrm{vi}}$)	2.813(7)	179	O(11)-H(16)···O(7$^{\mathrm{iv}}$)	2.740(8)	177
O(11)-H(17)···O(9$^{\mathrm{iv}}$)	2.880(7)	179	O(11)-H(17)···O(10$^{\mathrm{xiv}}$)	2.722(10)	179
(3) Rac-form "A"			(3) Rac-form "B"		
N(1A)-H(1A)···O(4A$^{\mathrm{iv}}$)	2.96(2)	164	N(1B)-H(1B)···O(4B$^{\mathrm{v}}$)	2.92(2)	162
N(1A)-H(2A)···O(4B$^{\mathrm{x}}$)	2.90(2)	154	N(1B)-H(2B)···O(4A$^{\mathrm{ix}}$)	2.81(2)	164
N(2A)-H(3A)···O(7A$^{\mathrm{v}}$)	2.87(2)	163	N(2B)-H(3B)···O(7B$^{\mathrm{iv}}$)	2.81(2)	108
N(2A)-H(4A)···O(8A)	2.82(2)	158	N(2B)-H(4B)···O(8B)	2.98(2)	143
N(3A)-H(5A)···O(6A$^{\mathrm{vii}}$)	2.88(2)	174	N(3B)-H(5B)···O(6B$^{\mathrm{vi}}$)	2.88(2)	173
N(3A)-H(6A)···O(7A$^{\mathrm{v}}$)	3.07(3)	145	N(3B)-H(6B)···O(7B$^{\mathrm{iv}}$)	3.39(2)	144
N(4A)-H(7A)···O(6A$^{\mathrm{ii}}$)	2.76(2)	153	N(4B)-H(7B)···O(6B$^{\mathrm{i}}$)	2.99(2)	144
N(4A)-H(8A)···O(7A)	2.93(2)	136	N(4B)-H(8B)···O(7B)	2.85(2)	153
N(5A)-H(9A)···O(1A$^{\mathrm{i}}$)	2.86(2)	179	N(5B)-H(9B)···O(1B$^{\mathrm{ii}}$)	2.92(2)	178
N(5A)-H(10A)···O(5B$^{\mathrm{vi}}$)	2.91(2)	179	N(5B)-H(10B)···O(5A$^{\mathrm{vii}}$)	2.83(2)	177

(i) $-1+x, y, z$; (ii) $1+x, y, z$; (iii) $x, 1+y, z$; (iv) $x, y, -1+z$; (v) $x, y, 1+z$; (vi) $-1+x, y, -1+z$; (vii) $1+x, y, 1+z$; (viii) $x, 1+y, 1+z$; (ix) $-1+x, -1+y, 1+z$; (x) $1+x, 1+y, 1+z$; (xi) $1-x, -1/2+y, 1-z$; (xii) $1-x, 1/2+y, 1-z$; (xiii) $1-x, 1/2+y, 2-z$; (xiv) $1-x, 1/2+y, -z$; (xv) $1-x, -1/2+y, 2-z$.

Recently, Miyoshi et al. have proposed an instructive mechanism of chiral recognition of octahedral metal complexes such as [Co(en)$_3$]$^{3+}$ and the related cations by bis-μ-(d-tartrato)-diantimonate(III) anion in solution.[16] It is pointed out in their association model that two amine protons of the octahedral cation are doubly hydrogen bonded to two oxygen atoms of the chiral [Sb$_2$(d-tart)$_2$]$^{3-}$ ion along the C$_3$ or C$_2$ axis of the octahedron. In the present case three pairs of double hydrogen bonding are recognized between a given cation and the three surrounding anions; these are a pair of N(2)-H(3)···O(7$^{\mathrm{iii}}$) and N(4)-H(8)···O(8$^{\mathrm{iii}}$), a pair of N(3)-H(5)···O(6$^{\mathrm{v}}$) and N(5$^{\mathrm{v}}$)-H(10$^{\mathrm{v}}$)···O(3) and a pair of N(4)-H(7)···O(6) and N(5)-H(9)···O(1), as can be seen in Table 7.

Λ-(+)[Co(ox)(en)$_2$](L-Hasp)·3H$_2$O (2): The less soluble aspartate has a crystal symmetry of $P2_1$ in contrast to $P1$ for compound **1**. Owing to the presence of twofold screw axes 2_1, the complex cations and the counter anions are packed into double layers parallel to (100), between which layers water molecules are inserted as shown in Fig. 3. Four NH$_2$ groups of each cation form eight N-H···O hydrogen bonds (av 2.95 Å) with eight oxygen atoms from two cations, four anions and one water molecule. The NH$_3$ group of an anion participates in only two N-H···O hydrogen bonds with two oxygen atoms of two cations (av 3.00 Å), and the remaining NH hydrogen atom is free. Three kinds of water molecules donate their six hydrdogen atoms to six oxygen atoms from three anions and three water molecules, forming O–H···O bonds with the average distance 2.74 Å.

In the complex **2**, three pairs of double N–H···O hydrogen bonds are also found between the cation and three surrounding anions in the same scheme as in **1**. Therefore, the formation of such double hydrogen bonds may not contribute to chiral discrimination. In both diastereoisomers, the chiral $[Co(ox)(en)_2]^+$ cations and L-Hasp⁻ anions are alternately arranged into layers through N–H···O hydrogen bonds. Additionally, in the complex **2**, two cations which are related by the twofold screw axis are hydrogen bonded, giving rise to the double layered structure against the single layer in **1**.

***rac*-[Co(ox)(en)$_2$](L-Hasp) (3):** The least soluble pseudoracemate **3** is anhydride, different from the optically active diastereomers **1** and **2**. The unit cell contains the Δ-complex cation centered at Co(A) and the Λ-cation centered at Co(B) in the molar ratio 1 : 1, as shown in Fig. 4. Each complex cation is surrounded by six counter anions and vice versa, suggesting dominant electrostatic interaction. The cation labeled 'A' (or 'B') forms eight N–H···O hydrogen bonds with seven oxygen atoms of two cations, A and B, and of four anions A (or B); the average distance is 2.90 Å for cation A (or 2.95 Å for B). Anion A (or B) also acts as hydrogen donor to two oxygen atoms of one cation A (or B) and one anion B (or A) with an average N–H···O distance of 2.89 (or 2.88) Å.

In the pseudoracemate **3**, two pairs of double hydrogen bonds are also formed between either cation and the neighboring L-Hasp⁻ ions; one pair is N(2A)–H(4A)···O(8A) and N(4A)–H(8A)···O(7A) and the other is N(4A)–H(7A)···O(6A^{ii}) and N(5A^{ii})–H(9A^{ii})···O(1A) for Δ-cation. As compared in Table 7, these schemes which are found in Λ-cation as well, are identical to two of three found in **1** and **2**. Two types of layers, one of which consists of Δ-cations and L-Hasp⁻ ions and the other of Λ-cations and L-Hasp⁻ ions, are stacked parallel to (010) plane. Thus formed layers are connected by hydrogen bonds between two different types of cations and between two anions alternately. Such anion-anion approach via N–H···O hydrogen bonds is recognized only in **3**. Besides these, no existence of water molecules provides the most dense packing for the least soluble **3**, as discussed later.

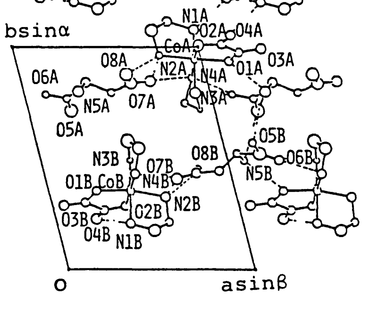

Fig. 4. Crystal structure of pseudoracemic salt **3** projected along [001]. Broken lines denote hydrogen bonds. Thermal ellipsoids are shown at 50% probability level.

Solubility and Crystal Structure. According to Yamanari et al. the Δ-salt is much more soluble in water than the other two aspartates.[4)] Such difference in solubility must be caused by the difference in packing scheme, because the three complexes are composed of the same cations and the same anions. Moreover, the numbers of water molecule of crystallization are equally three for the two diastereoisomers. The present X-ray study revealed that the three salts possess a common structural principle such that $[Co(ox)(en)_2]^+$ cations and L-Hasp⁻ anions form a layer by N–H···O hydrogen bonding in a very similar way to each other. The crystal lattice of Δ-isomer consists of such single cation-anion layers, while those of Λ and pseudoracemic salts contain doubled and multipled cation-anion layers, respectively. It was supposed that the difference in arrangement of ionic species and water molecules is responsible for the differences in density and solubility. However, the X-ray (or measured) densities are 1.61 (or 1.58), 1.61 (or 1.61), and 1.72 (or 1.73) for **1**, **2**, and **3**, respectively, indicating the increasing density is not necessarily correlated to the decreasing sulubility.

Another scale such as unoccupied (cavity) fraction CV/V where CV is the unoccupied space by atoms and V the unit cell volume was introduced to compare the extent of molecular packing. The calculation with van der Waals radii for peripheral atoms of ions or water molecules gave the values 31.3, 30.3, and 28.7% for **1**, **2**, and **3**, respectively.[17)] Although the order of magnitude of CV/V is compatible with that of solubility, this measure is still not sufficient to account for the solubility difference relatively. If the solubility is governed by molecular packing, the solubility difference between the pseudoracemic and Λ compounds would be greater than the observation.[4)]

In general, solubility is explicitly related to the change in the free energy upon solution. For the present diastereoisomers, fortunately, their entropy changes and hydration enthalpies would be equal and then the solubility difference would be attributed to the difference in enthalpy change. Such consideration lead us to estimate the electrostatic term of the lattice energy in accordance with the lattice sum method.[18)] The lattice sum was carried out over 125 (5×5×5 along ***a***, ***b***, ***c*** axes) unit cells around a given unit cell. The calculation was based on the electroneutrality principle and distributions of the charges of the cation, anion and water molecule on their peripheral atoms.[19)] The charge distributions for both ions were assigned from the electronegativity difference between bonding atoms as follows:[20] For the cation Co, −1.06; N, 0.23; H(N), 0.17; C(en), 0.05; H(C), 0.05; O(Co), 0.60; C(ox), 1.39; O(C), −1.20 and for the anion N, 0.35; H(N), 0.17; C(O), 1.39; O, −1.20; C(CH), 0.10; $C(CH_2)$, −0.09; H(C), 0.05. On the other hand, the "ST 2" model proposed by Stillinger and Rahman was adopted for the formal charges on a water molecule.[21] Such a typical set of charge distribution yielded electrostatic energies of −1214, −1476, and −1246 kJ mol^{-1} for **1**, **2**, and **3**, respectively. This order of magnitude was unchanged even for the electronic structure with the extreme ionic bonds. It was therefore ascertained that the less soluble isomer is characterized by the electrostatic energy higher than that of the more soluble Δ isomer.

In conclusion, the solubility difference between the Δ- and Λ-diastereoisomers could be explained in terms of density, unoccupied fraction and electrostatic interaction. However, there remained some uncertainty with respect to the solubility of the pseudoracemate, because this salt is anhydride, different from the other two. Other factors such as hydration enthalpy, hydrogen bonding interaction and entropy changes must be taken into account, but these terms are too complicated to be considered.

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