The Crystal Structure of *fac*(*N*)-*Δ*-Tris(L-asparaginato)-cobalt(III) Trihydrate

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The crystal structure of tris(L-asparaginato)cobalt(III) trihydrate, $[Co(L\text{-}H_2NCOCH_2CHNH_2COO)_3]\cdot 3H_2O$, has been determined by the X-ray diffraction method, and refined by a block-diagonal least-squares method to give $R=0.055$ for 1302 non-zero reflections. The crystals are orthorhombic with a space group $P2_12_12_1$, $a=39.082(4)$, $b=7.523(2)$, $c=6.643(2)$ Å, and $Z=4$. The complex molecule has a slightly distorted octahedral coordination with *fac*(*N*)-*Δ* geometry. The three bidentate ligand ions form five-membered planar chelate rings with coordination through amino nitrogen and carboxyl oxygen atoms. The amide groups of the two side-chains approach the central atom, and the oxygen atoms are connected through intramolecular hydrogen bonds. Another amide group is, however, far from the central atom. The complex molecules are hydrogen-bonded to one another to form layers parallel to the (100) plane. These layers are piled up through hydrogen bonds to complete a three-dimensional network.

Transition metal complexes of L-asparaginate ion (L-2-aminosuccinamate ion, $L\text{-}H_2NCOCH_2CHNH_2COO^-$) have been widely investigated,[1-5] and it has been concluded that the ligand ion is terdentate or bidentate. The terdentate ligand occupies the *facial* positions of the octahedron and the amide group is of *N*-[3] or *O*-coordination.[4] The coordination modes of the bidentate ligand are various.[2,5] According to the spectroscopic investigation by Takenaka and Shibata[2] on the stereochemistry of trivalent cobalt complexes, the bidentate ligand may coordinate through amino nitrogen and carboxyl oxygen atoms forming a five-membered chelate ring, and the amide group may remain free. If this assumption is correct, the bulky side-chain including the amide group is expected to have considerable effects on the neighboring molecules in the crystal. To ascertain these effects and to confirm the assumed structure, a single-crystal structure analysis of tris(L-asparaginato)cobalt(III) trihydrate has been carried out.

Experimental

The crystals which were prepared by Professor Muraji Shibata of Kanazawa University were dark pink needles. A crystal was shaped into a ball with the diameter of *ca.* 0.05 mm, and the intensities were measured on a Philips PW1100 four-circle diffractometer with Cu $K\alpha$ radiation ($\lambda=1.5418$ Å) monochromated by a graphite plate. The θ-2θ scan technique was used at a scan rate of 0.0666°/s in θ with a scan width of $(1.20+0.20\tan\theta)°$. The intensities of the three reference reflections were monitored every 2 h and remained constant within experimental error during data collection. Of 1392 independent reflections measured up to $\theta=65°$, 1302 with $|F|>3\sigma$ were used for the structure analysis. No corrections were made for absorption and extinction effects ($\mu r=0.2$). Cell dimensions were obtained by a least-squares method based on 17 2θ values measured by diffractometry.

Crystal data:
$Co(H_2NCOCH_2CHNH_2COO)_3\cdot 3H_2O$. *F.W.*=506.31. $a=39.082$ (4), $b=7.523$ (2), and $c=6.643$ (2) Å. $U=1953$ (2) Å^3. $Z=4$. $D_x=1.722$ g cm^{-3}. Orthorhombic. Space group $P2_12_12_1$. $\mu=78$ cm^{-1} (Cu $K\alpha$ radiation, $\lambda=1.5418$ Å).

Determination and Refinement of the Structure

The coordinates of the cobalt atom were determined from a Patterson map; successive Fourier syntheses gave the approximate skeletal structure. The block-diagonal least-squares refinement was carried out based on 1302 reflections with a unit weight. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[6]

After several cycles of refinement with isotropic temperature factors the *R*-value became 0.077. At this stage the oxygen and nitrogen atoms of each amide group could be distinguished by interatomic distances. Anisotropic temperature factors were, then, introduced for all the non-hydrogen atoms with the anomalous scattering factor of the cobalt atom for Cu $K\alpha$ radiation ($f'=-2.464$, $f''=3.608$).[6] The *R*-value was reduced to 0.064. Of all 27 hydrogen atoms, 23 appeared in a difference Fourier map. Their positional parameters were refined with isotropic temperature factors of 4.0 Å^2. Four hydrogen atoms attached to C(3) and O(1w) could not be found. The final *R*-value was 0.055. The final atomic parameters are listed in Table 1, and a list of the observed and calculated structure amplitudes has been deposited with the Chemical Society of Japan (Document No. 7903).

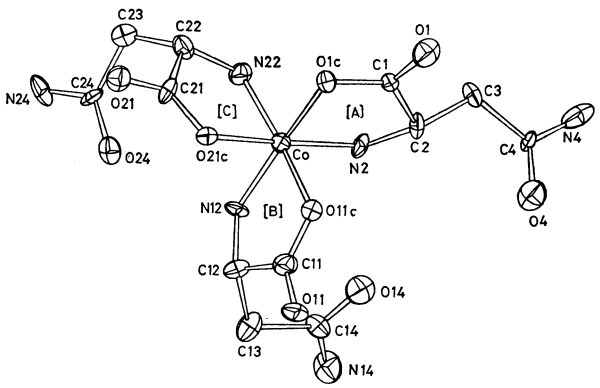

Fig. 1. The molecular structure and the absolute configuration with the anisotropic thermal ellipsoids of the atoms at 50% probability level.

The absolute configuration of the complex was determined by a comparison of the absolute configuration of the coordinated ligand ion with that of the free ligand molecule, and by a comparison of the *R*-values between the correct structure (0.055) and the mirror image (0.116). To confirm the result, another set of reflections ($\bar{h}\bar{k}l$) was measured by diffractometry with Cu $K\alpha$ radiation. All 363 Friedel pairs satisfying $|F(hkl)|/|F(\bar{h}\bar{k}\bar{l})| < 0.9$ or > 1.1 gave coincident intensity relations with those calculated, except for 14 weak pairs.

The refinement of the structure and the drawing of thermal ellipsoids were carried out with HBLS-IV[7] and ORTEP[8] programs, respectively. Other calculations were carried out with programs written by the author. A FACOM 230-35 computer at the Data Processing Center of Kanazawa University and a

TABLE 1a. FINAL ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES
Thermal parameters are in the form: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$.
Values are multiplied by 10^4.

Atom	*x*	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	1143(1)	7107(3)	9043(3)	2(1)	56(3)	87(4)	0(2)	−0(2)	0(8)
O(1c)	1206(2)	6236(11)	6376(11)	3(1)	88(15)	92(20)	−2(5)	−10(5)	34(31)
O(1)	1610(2)	5560(13)	4173(13)	4(1)	179(20)	95(20)	−16(6)	−7(7)	23(41)
C(1)	1522(3)	5883(15)	5896(19)	2(1)	83(20)	129(28)	0(7)	−2(8)	101(53)
C(2)	1786(3)	5990(16)	7615(18)	1(1)	90(22)	126(29)	6(7)	−8(8)	−34(49)
N(2)	1595(3)	6105(14)	9571(14)	2(1)	117(20)	65(23)	−11(6)	−8(6)	−16(37)
C(3)	2049(3)	4504(16)	7542(21)	3(1)	88(23)	196(36)	8(7)	−15(9)	88(54)
C(4)	2411(3)	5188(18)	7863(19)	1(1)	128(25)	135(32)	−12(7)	−8(8)	115(51)
O(4)	2491(3)	6769(12)	7983(15)	4(1)	94(17)	246(27)	6(6)	7(7)	−80(40)
N(4)	2649(3)	3845(16)	7966(18)	5(1)	136(23)	168(30)	−30(8)	4(9)	−18(50)
O(11c)	1349(2)	9295(11)	8326(12)	3(1)	78(15)	128(21)	−2(5)	−4(6)	40(33)
O(11)	1408(2)	12103(11)	9303(14)	4(1)	54(13)	198(24)	−0(6)	1(7)	72(38)
C(11)	1325(3)	10520(16)	9666(18)	4(1)	86(23)	117(32)	−9(8)	−9(9)	18(46)
C(12)	1156(3)	10060(15)	11624(17)	3(1)	75(20)	91(25)	−8(8)	9(9)	3(40)
N(12)	1097(3)	8132(11)	11720(14)	4(1)	26(15)	93(21)	−0(6)	−3(7)	27(33)
C(13)	1365(3)	10695(18)	13462(19)	3(1)	130(26)	117(32)	−11(8)	−5(8)	−97(50)
C(14)	1731(3)	9973(16)	13476(17)	4(1)	80(21)	66(26)	7(8)	−1(8)	−9(41)
O(14)	1852(3)	9264(12)	11946(13)	5(1)	138(20)	126(22)	−6(6)	−2(7)	−13(39)
N(14)	1901(3)	10198(16)	15170(17)	4(1)	165(25)	164(30)	19(8)	16(8)	−11(50)
O(21c)	710(2)	8081(11)	8297(12)	3(1)	63(14)	151(22)	−3(5)	−2(6)	61(33)
O(21)	161(2)	7429(11)	7882(13)	3(1)	84(17)	152(22)	0(5)	−2(6)	−32(34)
C(21)	460(3)	7012(16)	8397(16)	2(1)	96(21)	58(24)	−9(7)	−2(7)	−85(46)
C(22)	528(3)	5119(15)	9092(20)	3(1)	65(20)	133(29)	5(7)	−13(9)	−10(52)
N(22)	890(3)	4979(14)	9782(15)	3(1)	99(19)	90(24)	−14(7)	−12(7)	28(39)
C(23)	271(3)	4475(15)	10665(18)	3(1)	67(21)	88(28)	−1(7)	8(8)	−45(44)
C(24)	241(3)	5707(15)	12455(18)	2(1)	56(20)	132(29)	−10(6)	10(8)	5(43)
O(24)	396(2)	7161(11)	12512(12)	3(1)	77(14)	126(19)	11(5)	−4(6)	−71(36)
N(24)	31(3)	5202(14)	13931(17)	5(1)	122(21)	109(24)	15(7)	−25(8)	21(47)
O(1w)[a]	2356(3)	224(12)	9105(16)	6(1)	111(18)	213(26)	3(6)	−12(9)	39(46)
O(2w)[a]	833(3)	3849(12)	13945(15)	5(1)	136(18)	157(23)	−5(6)	6(8)	−89(43)
O(3w)[a]	536(3)	1360(13)	6448(21)	7(1)	104(19)	518(50)	6(7)	−29(11)	75(55)

a) Oxygen atoms of the water molecules.

TABLE 1b. POSITIONAL PARAMETERS OF HYDROGEN ATOMS ($\times 10^3$)
The e.s.d.'s are 15—17 ($\times 10^3$).

	x	*y*	*z*		*x*	*y*	*z*
H(C2)	194	702	740	H(C22)	49	445	775
H(N2-a)	178	716	1061	H(N22-a)	85	464	1133
H(N2-b)	158	484	996	H(N22-b)	99	393	899
H(N4-a)	267	428	884	H(C23-a)	34	317	1117
H(N4-b)	258	173	812	H(C23-b)	0	421	991
H(C12)	88	1080	1181	H(N24-a)	17	413	1359
H(N12-a)	125	753	1232	H(N24-b)	3	588	1528
H(N12-b)	79	785	1200	H(2w-a)	89	485	1493
H(C13-a)	120	1038	1463	H(2w-b)	108	436	1402
H(C13-b)	139	1215	1346	H(3w-a)	57	−10	679
H(N14-a)	219	1024	1512	H(3w-b)	75	288	583
H(N14-b)	176	981	1664				

FACOM 230-75 computer at the Computation Center of Nagoya University were used.

Description of the Structure and Discussion

The molecular structure is shown in Fig. 1, together with the thermal ellipsoids of the non-hydrogen atoms. The bond distances and angles are listed in Table 2. The projections of the crystal structure on the (010) and (100) planes are shown in Figs. 2 and 3, respectively. The hydrogen bonds are shown in these figures and in Table 3.

The three ligand ions act bidentately through amino nitrogen and carboxyl oxygen atoms forming three five-membered chelate rings in the *Δ* configuration. The cobalt atom is, thus, surrounded by three nitrogen atoms and three oxygen atoms in *fac*(*N*) geometry. This structural feature agrees with the assumption based on the spectroscopic investigation by Takenaka and

Table 2. Interatomic distances and angles within the complex molecule

Co–O(1c)	1.90(1)Å	Co–O(11c)	1.89(1)Å	Co–O(21c)	1.91(1)Å
Co–N(2)	1.95(1)	Co–N(12)	1.95(1)	Co–N(22)	1.94(1)
C(1)–O(1c)	1.30(2)	C(11)–O(11c)	1.28(2)	C(21)–O(21c)	1.27(2)
C(1)–O(1)	1.22(2)	C(11)–O(11)	1.26(2)	C(21)–O(21)	1.26(2)
C(1)–C(2)	1.54(2)	C(11)–C(12)	1.50(2)	C(21)–C(22)	1.52(2)
C(2)–N(2)	1.50(2)	C(12)–N(12)	1.47(2)	C(22)–N(22)	1.49(2)
C(2)–C(3)	1.52(2)	C(12)–C(13)	1.54(2)	C(22)–C(23)	1.53(2)
C(3)–C(4)	1.52(2)	C(13)–C(14)	1.53(2)	C(23)–C(24)	1.51(2)
C(4)–O(4)	1.23(2)	C(14)–O(14)	1.24(2)	C(24)–O(24)	1.25(2)
C(4)–N(4)	1.38(2)	C(14)–N(14)	1.32(2)	C(24)–N(24)	1.33(2)
O(1c)–C(1)–O(1)	122(2)°	O(11c)–C(11)–O(11)	122(2)°	O(21c)–C(21)–O(21)	123(2)°
O(1c)–C(1)–C(2)	116(2)	O(11c)–C(11)–C(12)	118(2)	O(21c)–C(21)–C(22)	118(2)
O(1)–C(1)–C(2)	121(2)	O(11)–C(11)–C(12)	120(2)	O(21)–C(21)–C(22)	119(2)
C(1)–C(2)–C(3)	113(2)	C(11)–C(12)–C(13)	112(1)	C(21)–C(22)–C(23)	113(2)
C(1)–C(2)–N(2)	108(1)	C(11)–C(12)–N(12)	110(1)	C(21)–C(22)–N(22)	109(1)
C(3)–C(2)–N(2)	114(1)	C(13)–C(12)–N(12)	111(1)	C(23)–C(22)–N(22)	113(2)
C(2)–C(3)–C(4)	112(2)	C(12)–C(13)–C(14)	113(1)	C(22)–C(23)–C(24)	113(1)
C(3)–C(4)–O(4)	125(2)	C(13)–C(14)–O(14)	120(2)	C(23)–C(24)–O(24)	121(2)
C(3)–C(4)–N(4)	113(2)	C(13)–C(14)–N(14)	116(2)	C(23)–C(24)–N(24)	117(2)
O(4)–C(4)–N(4)	122(2)	O(14)–C(14)–N(14)	124(2)	O(24)–C(24)–N(24)	122(2)
Co–O(1c)–C(1)	115(1)	Co–O(11c)–C(11)	115(1)	Co–O(21c)–C(21)	115(1)
Co–N(2)–C(2)	109(1)	Co–N(12)–C(12)	110(1)	Co–N(22)–C(22)	110(1)
O(1c)–Co–N(2)	85(1)	O(11c)–Co–N(12)	86(1)	O(21c)–Co–N(22)	86(1)
O(1c)–Co–O(11c)	91(1)	O(11c)–Co–O(21c)	89(1)	O(21c)–Co–O(1c)	90(1)
N(2)–Co–N(12)	94(1)	N(12)–Co–N(22)	93(1)	N(22)–Co–N(2)	96(1)

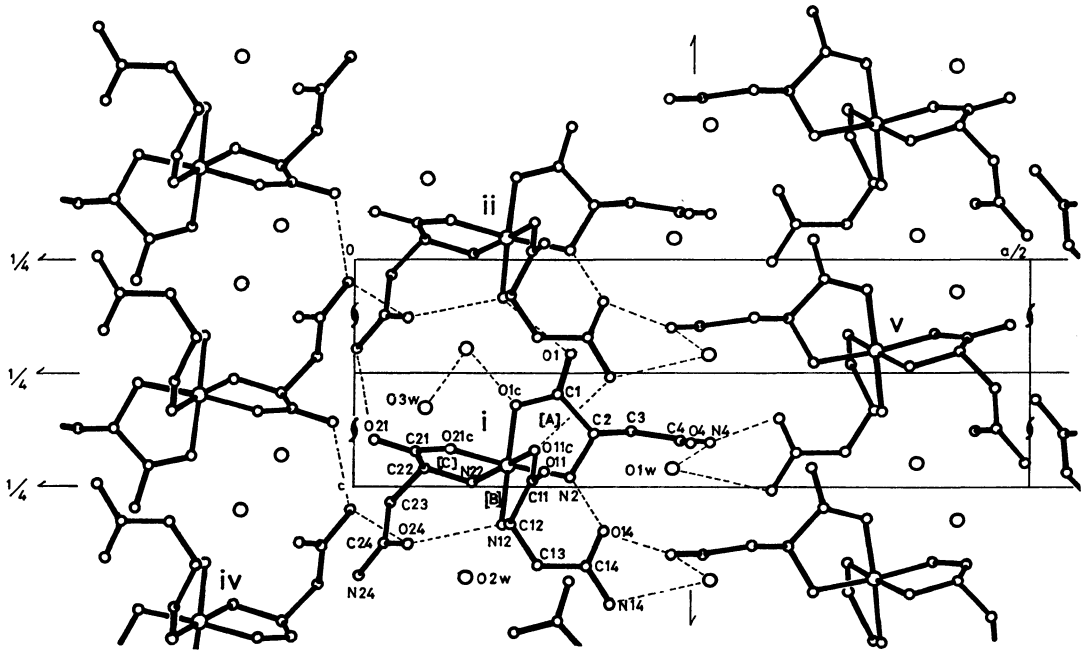

Fig. 2. Projection of the structure on the (010) plane. Dashed lines exhibit hydrogen bonds.

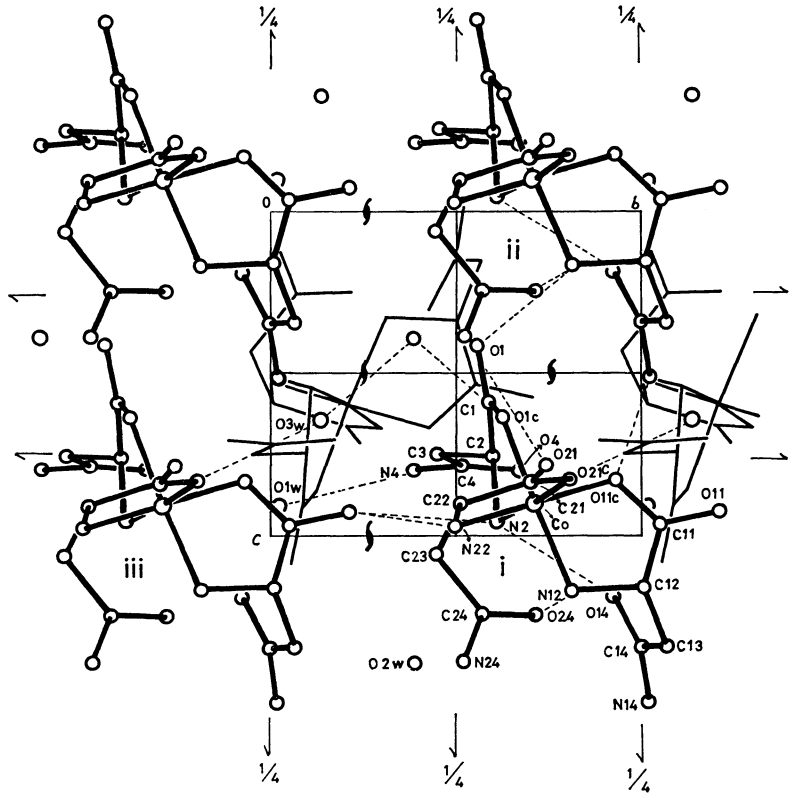

Fig. 3. Projection of the structure on the (100) plane.

Table 3. Short contacts due to hydrogen bonds

Key to symmetry operations			
i	x	y	z
ii	x	y	$-1+z$
iii	x	$-1+y$	z
iv	$-x$	$1/2+y$	$5/2-z$
v	$1/2-x$	$1-y$	$-1/2+z$

D	H	A[a]	D–A	D–H	A–H
N^{i}(2)	Ha	O^{i}(14)	3.02Å	1.28Å	1.83Å
N^{i}(12)	Hb	O^{i}(24)	2.88	1.23	1.66
N^{ii}(12)	Ha	O^{i}(1)	3.23	0.86	2.37
O^{i}(3w)	Hb	O^{ii}(2w)	2.76	1.47	1.49
O^{ii}(2w)	Ha	O^{i}(1c)	2.82	1.02	1.87
N^{ii}(14)	Hb	O^{i}(11c)	3.09	1.17	1.98
N^{ii}(24)	Hb	O^{i}(21)	3.15	1.03	2.14
N^{i}(2)	Hb	O^{iii}(11)	3.10	0.98	2.22
N^{i}(22)	Hb	O^{iii}(11)	2.98	1.02	2.16
O^{i}(3w)	Ha	O^{iii}(21c)	2.84	1.13	1.78
N^{iv}(24)	Ha	O^{i}(24)	2.99	0.99	2.75
N^{i}(4)	Hb	O^{v}(14)	3.12	1.62	2.46
N^{v}(14)	Ha	O^{i}(1w)	3.00	1.13	1.93

a) D, hydrogen donor; A, hydrogen acceptor.

Shibata.[2]

The Co–N bond lengths are 1.94—1.95 Å, which are longer than the Co–O bond lengths (1.89—1.91 Å). The coordination bond angles of the chelate rings are 85—86°. Thus the octahedron is slightly distorted. Each of the three five-membered chelate rings is nearly planar within 0.15 Å. Two side-chains of chelate rings **[B]** and **[C]** turn their amide groups toward the central atom, so that O(14) and O(24) are connected with N(2) and N(12), respectively, through intramolecular hydrogen bonds (Fig. 2 and Table 3). The side-chain of ring **[A]** is far from the central atom, and N(4) is hydrogen-bonded with O(14) of the neighboring molecule v.

The molecules i and ii are connected with one another through several hydrogen bonds to form columns parallel to the c axis. These columns are combined with each other by hydrogen bonds between molecules i and iii (Fig. 3), thus forming layers along the (100) plane. A three-dimensional network is completed by piling up of an infinite number of these layers through hydrogen bonds.

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