January, 1980] © *1980 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***53***, *125—132 (1980)* 125

Structural Study of Optical Resolution. VII. The Crystal Structure of $(-)_{589}$-Oxalatobis(ethylenediamine)cobalt(III) Hydrogen-*d*-tartrate Dihydrate and Comparison between the Crystal Structures of the More- and Less-soluble Diastereoisomers

Masahiro Kuramoto, Yoshihiko Kushi, and Hayami Yoneda*

Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-senda-machi, Hiroshima 730

(Received August 14, 1978)

The single crystals of the more-soluble diastereoisomeric salt including the hydrogen-*d*-tartrate anion as a resolving agent, $(-)_{589}$-[Co(ox)en$_2$]H-*d*-tart·2H$_2$O, have been newly obtained, and the crystal structure has been determined by three-dimensional X-ray analysis. The crystals are orthorhombic, space group $P2_12_12$, $Z=4$, $a=16.583(5)$, $b=14.186(5)$, and $c=7.403(2)$ Å. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method to a conventional R-value of 0.044 for the 1907 independent reflections. One of the two ethylenediamine rings is of the *ob* form. The other ring has a conformational disorder, the proportion of the *ob* to the *lel* form being 50:50. The absolute configuration of the complex cation is denoted as $\Delta[(50\%\text{-}\delta, 50\%\text{-}\lambda)\delta]$. The framework of the crystal structure is built up of a stack of complex cations and H-*d*-tart anions along the c-axis in a "head-to-tail" arrangement. The shortest interatomic distance between the H-*d*-tart anions is 2.473 Å(O–H···O), while that between the complex cations is 2.995 Å (N–H···O). A comparison of the crystal structure of the more-soluble diastereoisomer with that of the less-soluble one revealed that the {H-*d*-tart}$_\infty$ chain is structurally different from that in the latter; the chain is spiral in the latter, but not in the former. The structural feature in the {H-*d*-tart}$_\infty$ chain is considered to play an important role in the discrimination of the chirality of the [Co(ox)en$_2$]$^+$ cation. The conformational disorder is discussed in connection with the dehydration of crystals.

Recently, we reported the crystal structure of the less-soluble diastereoisomeric salt, $(+)_{589}$-[Co(ox)en$_2$] H-*d*-tart·H$_2$O,[1] which is obtained as an intermediate in the course of the optical resolution of the [Co(ox)en$_2$]$^+$ cation using the hydrogen-*d*-tartrate anion (*d*-$C_4H_5O_6^-$, abbr. H-*d*-tart) as a resolving agent.[2] The optically active complex cation, Δ-$\delta\lambda$-$(+)_{589}$-[Co(ox)en$_2$]$^+$, was found to be locked in the right-handed spiral chains of {H-*d*-tart}$_\infty$.[1]

It has been thought that the comparison of a pair of crystal structures of less- and more-soluble diastereoisomeric salts would give valuable information on the mechanism of optical resolution. Therefore, we have attempted to determine the crystal structure of the more-soluble diastereoisomer, $(-)_{589}$-[Co(ox)en$_2$] H-*d*-tart·2H$_2$O, and to compare it with the structure of the less-soluble diastereoisomer, $(+)_{589}$-[Co(ox)en$_2$] H-*d*-tart·H$_2$O.

Experimental

The preparation of the more-soluble diastereoisomer, $(-)_{589}$-[Co(ox)en$_2$]H-*d*-tart·2H$_2$O, was reported in our earlier paper.[1] A red crystal with dimensions of 0.15×0.15×0.30 mm^3 was used for the X-ray analysis. The unit-cell dimensions were determined by the least-squares refinement of the angular settings of 25 reflections measured on a diffractometer. The crystal data are as follows: $C_{10}H_{25}O_{12}N_4Co$, orthorhombic, $P2_12_12$, $a=16.583(5)$, $b=14.186(5)$, $c=7.403(2)$ Å, $D_m=1.72$(by flotation in CHCl$_3$–CHBr$_3$), and $D_x=1.73(1)$ g cm^{-3} for $Z=4(\mu(\text{Mo } K\alpha)=11.0\text{ cm}^{-1})$.

The intensity data were measured on an automatic Rigaku AFC-5 four-circle diffractometer, equipped with a rotating anode(50 kV, 170 mA), using graphite-monochromated Mo-$K\alpha$ radiation ($\lambda=0.71069$ Å) and a monitor-counting technique. The ω-2θ scan mode with a scan rate of 16° min^{-1} employed. The θ scan range was $(1.0+0.45\tan\theta)°$. The intensity data of 2034 independent reflections were collected with $(\sin\theta)/\lambda\leq0.65$ Å^{-1}; of these, 1907 were measured with $|F_o|\geq3\sigma|F_o|$ and used in the present X-ray analysis. No absorption correction was applied.

Determination and Refinement of Crystal Structure

The position of the Co atom was determined from the Patterson map. Successive Fourier refinements with phases based initially on the Co atom revealed the locations of the remaining 27 nonhydrogen atoms. Block-diagonal least-squares refinement with anisotropic thermal parameters for these atoms converged to $R=0.101$ $(R=\sum||F_o|-|F_c||/\sum|F_o|)$. The different synthesis showed the "50%-*ob*, 50%-*lel*" type conformational disorder in one of the etylenediamine chelate rings.[3] The subsequent refinement for all the nonhydrogen atoms gave $R=0.063$. All the hydrogen-atom coordinates were found from the difference map; these 35 hydrogen atoms with fixed positional and isotropic thermal ($B=3.5$ Å^2) parameters were included in the final refinement. The convergence was attained at $R=0.044$. The final difference map showed no peaks higehr than 0.4 electron/Å^3. The quantity minimized was $\sum w(|F_o|-k|F_c|)^2$, where $w=1/(a+|F_o|+b|F_o|^2)$ with $a=16.0$ and $b=0.012$.[4] The atomic scattering factors from the International Tables for X-Ray Crystallography[5] were used. The effect of the anomalous dispersion of the Co atom was included in the calculation.[6] All the computations were carried out by a HITAC-8700 computer at the Hiroshima University Computer Center. The computer programs used were FOUR-MMM (Fourier synthesis)[7] and HBLS-IV (Least-square calculation), with a slight modification.[8] The final atomic parameters, the temperature factors (with their estimated standard deviations), and the occupation numbers are listed in Tables 1a, 1b, and 2 respectively. Complete lists of the $10|F_o|$ and $10|F_c|$ values have been

TABLE 1a. OCCUPATION NUMBERS(o), FINAL ATOMIC PARAMETERS, AND TEMPERATURE FACTORS (WITH THEIR e.s.d.'s)

Atom	o	x	y	z	B/Å^2
Co	1.0	0.25184(5)	0.55094(4)	0.91996(10)	a)
O(X1)	1.0	0.2749(4)	0.8093(3)	0.7571(9)	a)
O(X2)	1.0	0.2602(3)	0.6875(3)	0.4656(6)	a)
O(X3)	1.0	0.2596(3)	0.6851(3)	0.9386(6)	a)
O(X4)	1.0	0.2538(3)	0.5706(3)	0.6639(5)	a)
O(T1)	1.0	0.4269(3)	0.8715(3)	0.0416(6)	a)
O(T2)	1.0	0.4722(3)	0.7250(3)	0.0118(6)	a)
O(T3)	1.0	0.3823(3)	0.8389(3)	0.3872(6)	a)
O(T4)	1.0	0.5585(3)	0.8078(3)	0.3735(6)	a)
O(T5)	1.0	0.5163(3)	0.7588(4)	0.6993(6)	a)
O(T6)	1.0	0.4369(3)	0.6411(3)	0.6113(6)	a)
N(1)	1.0	0.3695(3)	0.5406(4)	0.9255(8)	a)
N(2)	1.0	0.1343(3)	0.5588(3)	0.9205(7)	a)
N(3)	1.0	0.2434(3)	0.5384(4)	1.1817(7)	a)
N(4)	1.0	0.2520(4)	0.4153(3)	0.8829(8)	a)
C(E1A)(*ob*)	0.5	0.3949(7)	0.4467(8)	0.8684(16)	2.1(2)
C(E1B)(*lel*)	0.5	0.3928(10)	0.4399(11)	0.9167(23)	4.1(3)
C(E2)	1.0	0.1084(3)	0.5822(4)	1.1080(9)	a)
C(E3)	1.0	0.1584(4)	0.5233(5)	1.2355(9)	a)
C(E4A)(*ob*)	0.5	0.3367(9)	0.3788(11)	0.9383(22)	3.7(3)
C(E4B)(*lel*)	0.5	0.3280(10)	0.3874(12)	0.7948(24)	4.1(3)
C(X1)	1.0	0.2652(4)	0.7247(4)	0.7835(9)	a)
C(X2)	1.0	0.2591(4)	0.6570(4)	0.6193(8)	a)
C(T1)	1.0	0.4401(3)	0.7936(4)	0.1016(7)	a)
C(T2)	1.0	0.4210(3)	0.7645(4)	0.2929(8)	a)
C(T3)	1.0	0.5003(4)	0.7344(4)	0.3840(7)	a)
C(T4)	1.0	0.4832(3)	0.7094(4)	0.5839(7)	a)
O(W1)	0.5	0.0000(0)	0.5000(0)	0.5276(21)	a)
O(W2)	1.0	0.4138(3)	0.5130(4)	0.3322(8)	a)
O(W3)	0.5	0.3302(9)	0.3692(10)	0.5055(20)	5.7(3)

a) See Table 2.

TABLE 1b. OCCUPATION NUMBERS(o) AND POSITIONAL PARAMETERS OF HYDROGEN ATOMS

Atom	o	x	y	z	Atom	o	x	y	z
H(OT2)	1.0	0.483	0.740	−0.125	H(N41)a)	0.5	0.240	0.399	0.752
H(OT3)	1.0	0.343	0.800	0.450	H(N42)a)	0.5	0.210	0.383	0.959
H(OT4)	1.0	0.612	0.784	0.435	H(N43)b)	0.5	0.204	0.396	0.808
H(W11)	0.5	0.037	0.540	0.545	H(N44)b)	0.5	0.249	0.381	1.000
H(W12)	0.5	0.028	0.450	0.515	H(C11)a)	0.5	0.453	0.431	0.906
H(W21)	1.0	0.462	0.512	0.325	H(C12)a)	0.5	0.393	0.445	0.720
H(W22)	1.0	0.407	0.532	0.430	H(C13)b)	0.5	0.391	0.408	1.051
H(W31)	0.5	0.305	0.432	0.460	H(C14)b)	0.5	0.453	0.429	0.871
H(W32)	0.5	0.340	0.338	0.615	H(C21)	1.0	0.047	0.568	1.125
H(N11)a)	0.5	0.391	0.551	1.052	H(C22)	1.0	0.119	0.654	1.136
H(N12)a)	0.5	0.395	0.591	0.846	H(C31)	1.0	0.146	0.544	1.369
H(N13)b)	0.5	0.392	0.572	1.039	H(C32)	1.0	0.141	0.452	1.220
H(N14)b)	0.5	0.394	0.575	0.820	H(C41)a)	0.5	0.349	0.313	0.879
H(N21)	1.0	0.110	0.498	0.881	H(C42)a)	0.5	0.344	0.376	1.075
H(N22)	1.0	0.115	0.610	0.836	H(C43)b)	0.5	0.329	0.417	0.654
H(N31)	1.0	0.265	0.598	1.241	H(C44)b)	0.5	0.335	0.315	0.776
H(N32)	1.0	0.278	0.485	1.225	H(CT2)	1.0	0.382	0.708	0.280
					H(CT3)	1.0	0.524	0.675	0.312

a) These hydrogens belong to the *ob* ring. b) These hydrogens belong to the *lel* ring.

Table 2. Anisotropic temperature factors ($\times 10^3$ Å^2) expressed in the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	23.2(2)	18.5(3)	28.1(3)	1.1(3)	2.7(4)	−1.2(3)
O(X1)	104(5)	21(2)	72(4)	−15(3)	−27(4)	8(2)
O(X2)	45(3)	51(3)	34(2)	−4(2)	0(3)	11(2)
O(X3)	39(2)	23(2)	39(2)	−2(2)	−9(2)	−4(2)
O(X4)	41(2)	26(2)	29(2)	−4(2)	4(2)	−6(1)
O(T1)	46(2)	38(2)	34(2)	17(2)	13(2)	13(2)
O(T2)	63(3)	31(2)	19(2)	7(2)	8(2)	1(2)
O(T3)	39(2)	36(2)	36(2)	10(2)	13(2)	0(2)
O(T4)	34(2)	50(3)	28(2)	−18(2)	−3(2)	11(2)
O(T5)	60(3)	53(3)	21(2)	−15(3)	−1(2)	−9(2)
O(T6)	51(3)	33(2)	27(2)	−12(2)	5(2)	6(2)
N(1)	26(2)	32(2)	48(3)	−2(2)	−3(2)	13(3)
N(2)	24(2)	29(2)	33(2)	0(2)	−8(2)	−2(2)
N(3)	27(2)	43(3)	33(2)	10(2)	−6(2)	6(2)
N(4)	40(3)	19(2)	64(4)	−4(2)	26(4)	2(2)
C(E2)	26(3)	33(3)	36(3)	4(2)	3(3)	−6(3)
C(E3)	32(3)	39(3)	31(3)	3(2)	3(3)	−7(3)
C(X1)	37(4)	21(2)	42(2)	−6(2)	−17(3)	1(2)
C(X2)	34(3)	32(3)	30(3)	−2(3)	−2(3)	1(2)
C(T1)	22(2)	25(2)	23(3)	−5(2)	−4(2)	4(2)
C(T2)	28(3)	23(3)	24(2)	−3(2)	3(2)	1(2)
C(T3)	32(3)	32(3)	20(2)	−1(2)	1(2)	1(2)
C(T4)	28(3)	32(3)	18(2)	4(2)	1(2)	10(2)
O(W1)	120(10)	91(8)	127(11)	22(7)	0(0)	0(0)
O(W2)	45(3)	62(3)	55(3)	12(3)	−11(3)	−15(3)

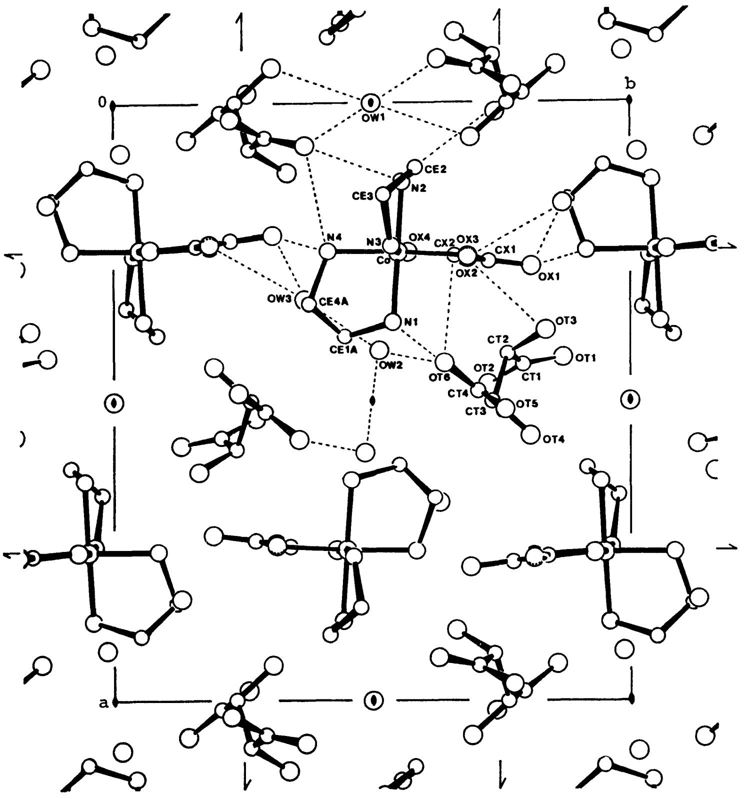


Fig. 1. A perspective drawing of the contents of the unit cell viewed down the c-axis. Possible hydrogen bonds and short contacts are indicated by broken lines. The carbon atoms of the *lel* ring, C(E1B)-C(E4B), are omitted for clarity.

preserved by the Chemical Society of Japan (Document No. 8004).

Results and Discussion

Figures 1 and 2 show the projections of the crystal structure along the c- and b- axes respectively. The structure consists of discrete $(-)_{589}$-$[Co(ox)en_2]^+$ cations, H-*d*-tart anions, and water molecules. The bond distances and angles in the complex cation and the H-*d*-tart anion are listed in Table 3.

Cation and Anion Geometries. The absolute configuration of the $(-)_{589}$-$[Co(ox)en_2]^+$ cation is identified as Δ based on that of the H-*d*-tart anion.[9] This is in accordance with the absolute configuration of $(-)_{589}$-$[Co(ox)en_2]^+$ reported by Aoki *et al.*[10] and Toriumi *et al.*[11] However, in the present complex cation, one ethylenediamine ring is in the "50%-*ob*(N(1)–C(E1A)–C(E4A)–N(4)), 50%-*lel*(N(1)–C(E1B)–C(E4B)–N(4))" form, as was described in the last section. The other ethylenediamine ring(N(2)–C(E2)–C(E3)–N(3)) is in the *ob* form. Thus, the absolute configuration should be denoted as $\Delta[50\%\text{-}\delta,50\%\text{-}\lambda)\delta]$. The structure is illustrated in Fig. 3.

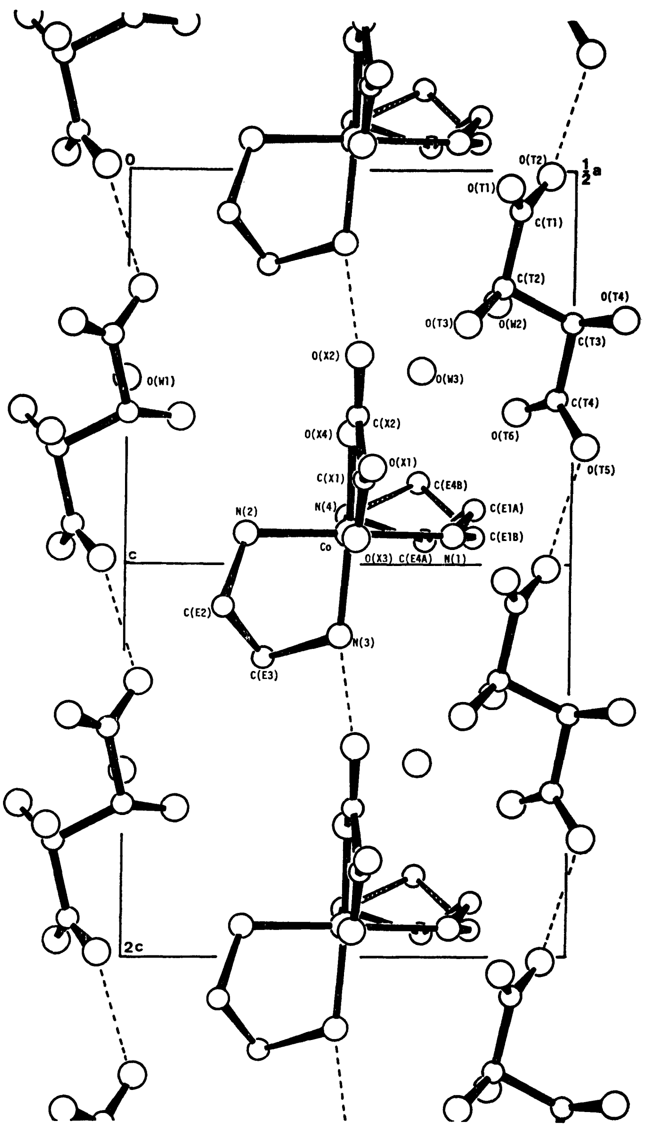


Fig. 2. A boundary projection of the crystal structure viewed along the b-axis.

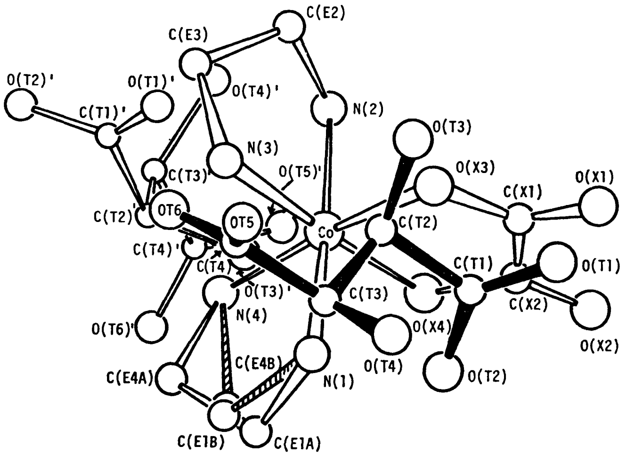


Fig. 3. The arrangement of the complex cation and H-*d*-tart anions projected down the quasi-threefold axis of the complex cation.

The structure of the H-*d*-tart anion is in agreement with those obtained in the previous studies.[1,12–14] The two planar halves of the anion, O(T1)O(T2)-O(T3)C(T1)C(T2) and C(T3)C(T4)O(T4)O(T5)-O(T6), make an interplanar angle of 61.3°. The angle is larger than the corresponding angle (55.8°) of the H-*d*-tart anion in $(+)_{589}$-$[Co(ox)en_2]$H-*d*-tart·H_2O.[1]

Crystal Packing. The intermolecular bond distances and angles are summarized in Table 4. The H-*d*-tart anions are arranged to make a "head-to-tail" chain structure in which two adjacent anions related by the translation along the c-axis (Fig. 2). The hydrogen-bond distance of O(T2)$^{\rm II}$···O(T5) is 2.473 Å. This value is close to the corresponding one in $(+)_{589}$-$[Co(ox)en_2]$H-*d*-tart·H_2O(2.44 Å).[1] Along the c-axis, there is also a chain of complex cations which are joined by the N(3)···O(X2)$^{\rm II}$ hydrogen bond (2.995 Å). The chain of H-*d*-tart anions and that of the complex cations have the following short contacts: N(1)···O(T6), N(2)···O(T1)$^{\rm I}$, N(4)···O(T1)$^{\rm I}$, O(X2)···O(T3), C(X2)···O(T6), and C(E2)···O(T5)$^{\rm IV}$. Moreover, adjacent H-*d*-tart anions are connected through water molecules(O(W1) and O(W2)): O(T3)$^{\rm V}$···O(W1), O(T4)$^{\rm V}$···O(W1), and O(T6)···O(W2). There is no short contact between the complex cation and the water molecule lying on the twofold axis(O(W1)).

Figure 3 shows the relative arrangement of the $(-)_{589}$-$[Co(ox)en_2]^+$ cation and the H-*d*-tart anions projected down the quasi-threefold axis of the complex cation. The close contacts are: N(1)···O(T2)$^{\rm II}$, N(4)···O(T1)$^{\rm I}$, N(4)···O(T3)$^{\rm I}$, and N(2)···O(T1)$^{\rm I}$. In this case, the "face-to-face"-type close contact found in the $[CoXY(en)_2]^{n+}$···*d*-bcs$^-$[15,16] and $[M(en)_3]^{3+}$···*d*-tart^{2-} systems[17–19] does not exist between any triangular face of the octahedral complex cation and the H-*d*-tart anion. This lack of any "face-to-face"-type close contact seems to be true of all salts containing the H-*d*-tart anion. In fact, the "face-to-face"-type close contact was not found in the structures of $(+)_{589}$-

TABLE 3. BOND DISTANCES AND ANGLES (e.s.d.'s IN PARENTHESES)

(a) Bond distances/Å

Co-N(1)	1.957(6)	N(4)-C(E4A)	1.552(18)	O(T1)-C(T1)	1.211(7)
Co-N(2)	1.952(5)	N(4)-C(E4B)	1.474(19)	O(T2)-C(T1)	1.294(8)
Co-N(3)	1.951(5)	O(X1)-C(X1)	1.226(10)	O(T3)-C(T2)	1.419(7)
Co-N(4)	1.944(6)	O(X2)-C(X2)	1.217(8)	O(T4)-C(T3)	1.422(8)
Co-O(X3)	1.913(4)	O(X3)-C(X1)	1.281(8)	O(T5)-C(T4)	1.234(8)
Co-O(X4)	1.917(5)	O(X4)-C(X2)	1.274(8)	O(T6)-C(T4)	1.253(7)
N(1)-C(E1A)	1.458(13)	C(E1A)-C(E4A)	1.459(20)	C(T1)-C(T2)	1.509(8)
N(1)-C(E1B)	1.481(18)	C(E1B)-C(E4B)	1.588(25)	C(T2)-C(T3)	1.537(8)
N(2)-C(E2)	1.490(8)	C(E2)-C(E3)	1.508(9)	C(T3)-C(T4)	1.548(8)
N(3)-C(E3)	1.481(8)	C(X1)-C(X2)	1.552(9)		

(b) Bond angles/°

N(1)-Co-N(4)	85.9(3)	N(1)-C(E1A)-C(E4A)	108.0(10)
N(2)-Co-N(3)	86.1(2)	N(1)-C(E1B)-C(E4B)	107.5(13)
O(X3)-Co-O(X4)	85.7(2)	N(2)-C(E2)-C(E3)	107.5(5)
Co-N(1)-C(E1A)	110.5(6)	N(3)-C(E3)-C(E2)	105.9(5)
Co-N(1)-C(E1B)	109.4(8)	N(4)-C(E4A)-C(E1A)	106.5(11)
Co-N(2)-C(E2)	107.6(4)	N(4)-C(E4B)-C(E1B)	101.6(13)
Co-N(3)-C(E3)	110.4(4)	O(X1)-C(X1)-C(X2)	119.2(6)
Co-N(4)-C(E4A)	107.1(7)	O(X2)-C(X2)-C(X1)	120.8(6)
Co-N(4)-C(E4B)	109.2(8)	O(X3)-C(X1)-C(X2)	115.2(6)
Co-O(X3)-C(X1)	112.1(4)	O(X4)-C(X2)-C(X1)	113.4(5)
Co-O(X4)-C(X2)	113.4(4)	O(X1)-C(X1)-O(X3)	125.5(7)
		O(X2)-C(X2)-O(X4)	125.8(6)
O(T1)-C(T1)-O(T2)	124.9(6)	O(T5)-C(T4)-O(T6)	126.8(6)
O(T1)-C(T1)-C(T2)	123.8(5)	O(T2)-C(T1)-C(T2)	111.3(5)
O(T3)-C(T2)-C(T1)	110.7(5)	O(T3)-C(T2)-C(T3)	112.1(5)
O(T4)-C(T3)-C(T2)	110.7(5)	O(T4)-C(T3)-C(T4)	110.1(5)
O(T5)-C(T4)-C(T3)	116.8(5)	O(T6)-C(T4)-C(T3)	116.4(5)
C(T1)-C(T2)-C(T3)	108.0(5)	C(T2)-C(T3)-C(T4)	109.1(5)

[Co(ox)en$_2$]H-*d*-tart·H_2O[1] and the less- and more-soluble *trans*(*O*)-[Co(gly)$_2$en]H-*d*-tart·nH_2O.[20] In the case of the H-*d*-tart anion, the chiral discrimination is effected in a different way from the "face-to-face"-type compact fit.[1]

*Comparison between the Crystal Structures of the More-soluble Salt, $(-)_{589}$-[Co(ox)en$_2$]H-*d*-tart·2H_2O, and the Less-soluble Salt, $(+)_{589}$-[Co(ox)en$_2$]H-*d*-tart·H_2O.*[1] The crystal structures of more- and less-soluble diastereoisomers are shown schematically in Figs. 4 and 5, where the ions are represented simply by cylinders. It is noticeable that, in a broad sense, there are some resemblances in the packing features of the two structures in Fig. 4: (1) The H-*d*-tart anions in both crystals are stacked along the axis of the cylinder and make the {H-*d*-tart}$_\infty$ chain of the "head-to-tail" type.[1,12] (2) The complex cations are also stacked along the cylinder axis and form a chain parallel to the chain of the H-*d*-tart anion. (3) The effective lengths of the unit cylinders of the H-*d*-tart anion are quite similar: 7.403 Å for the more-soluble salt and 7.294 Å for the less-soluble salt. There are, however, some different features between the crystal structures: (1) The H-*d*-tart chain denoted as A is formed by the stacking of H-*d*-tart anions related by the translation along the c-axis, but the A′ chain is formed by the stacking of H-*d*-tart anions related by the twofold screw axis. (2) The chain of the Δ-$(-)_{589}$-complex cation in Fig. 4(a) is formed by the repetition of translations of the complex cation, but that of the Λ-$(+)_{589}$-complex cation in Fig. 4(b) is formed by the linkages of the complex cation along the twofold screw axis.

The projected views along the c-axis of the $(-)_{589}$-salt and along the b-axis of the $(+)_{589}$-salt are illustrated in Fig. 5. The column of complex cations in each structure is surrounded by four columns of H-*d*-tart anions. The parallelogramic frames shown by the broken and solid lines are depicted by connecting the four H-*d*-tart chains. The size of the parallelogram of the $(-)_{589}$-salt (8.292×7.196×sin(100.6°)) is similar to that of the $(+)_{589}$-salt (8.256×7.009×sin(104.7°)),[21] though the space groups are different. The water molecules in the more-soluble $(-)_{589}$-salt serve to connect the B and C chains or the A and D chains, but not the A and B chains or the C and D chains. This situation is quite similar to that with the less-soluble $(+)_{589}$-salt, though the number of water molecules different from that in the more-soluble salt.

The close contacts between the ions in both salts are summarized in Table 5. The $(+)_{589}$-salt has more short contacts than the $(-)_{589}$-salt. This suggests that the complex cation in the more-soluble $(-)_{589}$-salt is more loosely packed than that in the less-soluble $(+)_{589}$-salt. This situation is reflected in the difference between their densities (1.73(1) g cm^{-3} in the $(-)_{589}$-salt *vs.* 1.77(1) g cm^{-3} in the $(+)_{589}$-salt). The tight

TABLE 4. INTERMOLECULAR DISTANCES AND ANGLES

X-H···Y or X···Y	X···Y Å	H···Y Å	X-H···Y °	X-H···Y or X···Y	X···Y Å	H···Y Å	X-H···Y °
N(1)-H(N12)···O(T2)$^{\mathrm{II}}$	3.187(8)	2.60	117	C(E1B)-H(C13)···O(W2)$^{\mathrm{II}}$	3.264(18)	2.58	120
N(1)-H(N13)···O(T2)$^{\mathrm{II}}$	3.187(8)	2.56	119	N(3)-H(N31)···O(X2)$^{\mathrm{II}}$	2.995(7)$^{a)}$	2.09	146
N(1)-H(N12)···O(T6)	2.948(8)$^{a)}$	2.00	153	N(4)-H(N42)···O(X1)$^{\mathrm{III}}$	3.092(9)$^{a)}$	2.36	129
N(1)-H(N14)···O(T6)	2.948(8)$^{a)}$	1.94	177	N(4)-H(N44)···O(X1)$^{\mathrm{III}}$	3.092(9)$^{a)}$	2.10	172
N(2)-H(N21)···O(T1)$^{\mathrm{I}}$	2.858(7)$^{a)}$	1.98	145	C(E4A)-H(C42)···O(X1)$^{\mathrm{III}}$	3.079(18)	2.51	115
N(2)-H(N22)···O(T4)$^{\mathrm{V}}$	3.147(7)$^{a)}$	2.16	166	C(E3)-H(C32)···O(X1)$^{\mathrm{III}}$	3.233(10)	2.46	128
N(4)-H(N42)···O(T1)$^{\mathrm{I}}$	3.082(8)$^{a)}$	2.28	136	C(E1A)-H(C12)···O(W3)	3.095(19)	2.18	139
N(4)-H(N43)···O(T1)$^{\mathrm{I}}$	3.082(8)	2.46	119	C(E4A)-(C44)···O(W3)	3.209(22)	2.15	122
N(4)-H(N41)···O(T3)$^{\mathrm{I}}$	3.183(8)$^{a)}$	2.43	130	C(E2)···O(T1)$^{\mathrm{I}}$	3.241(8)	—	—
N(4)-H(N43)···O(NT3)$^{\mathrm{I}}$	3.183(8)$^{a)}$	2.18	168	C(E2)-H(C22)···O(T5)$^{\mathrm{IV}}$	3.075(9)	2.43	119
O(T3)-H(OT3)···O(X1)	3.294(8)	2.54	134	C(X2)···O(T6)	2.957(8)	—	—
O(T3)-H(OT3)···O(X2)	3.009(7)$^{a)}$	2.11	153	O(T3)$^{\mathrm{V}}$···O(W1)	3.070(16)	—	—
O(X2)···O(T6)	3.191(7)	—	—	O(W1)-H(W11)···O(T4)$^{\mathrm{V}}$	2.985(17)$^{a)}$	2.27	142
O(X4)···O(T6)	3.220(7)	—	—	O(T4)-H(OT4)···O(W3)$^{\mathrm{VII}}$	3.266(16)	2.43	135
C(T2)-H(CT2)···O(X2)	3.153(8)	2.46	124	O(W2)-H(W22)···O(T6)	2.778(8)$^{a)}$	2.11	144
N(1)-H(N11)···O(W2)$^{\mathrm{II}}$	3.124(9)$^{a)}$	2.18	155	O(T2)$^{\mathrm{II}}$-H(OT2)···O(T5)	2.473(8)$^{a)}$	1.44	166
N(1)-H(N13)···O(W2)$^{\mathrm{II}}$	3.124(9)$^{a)}$	2.35	132	O(T6)···O(T2)$^{\mathrm{II}}$	3.248(7)	—	—
N(3)-H(N32)···O(W2)$^{\mathrm{II}}$	3.059(8)	2.41	121	O(T5)···C(T1)$^{\mathrm{II}}$	3.272(8)	—	—
N(4)-H(N41)···O(W3)	3.150(16)$^{a)}$	2.40	130	O(T2)···C(T4)$^{\mathrm{VI}}$	3.181(8)	—	—
O(X1)···O(W3)$^{\mathrm{VIII}}$	2.746(17)	—	—	O(W2)$^{\mathrm{VII}}$-H(W21)···O(W2)	2.883(12)$^{a)}$	2.09	170
O(X2)···O(W3)$^{\mathrm{VIII}}$	2.989(16)	—	—	O(W3)-H(W31)···O(W2)	2.780(16)	2.34	104

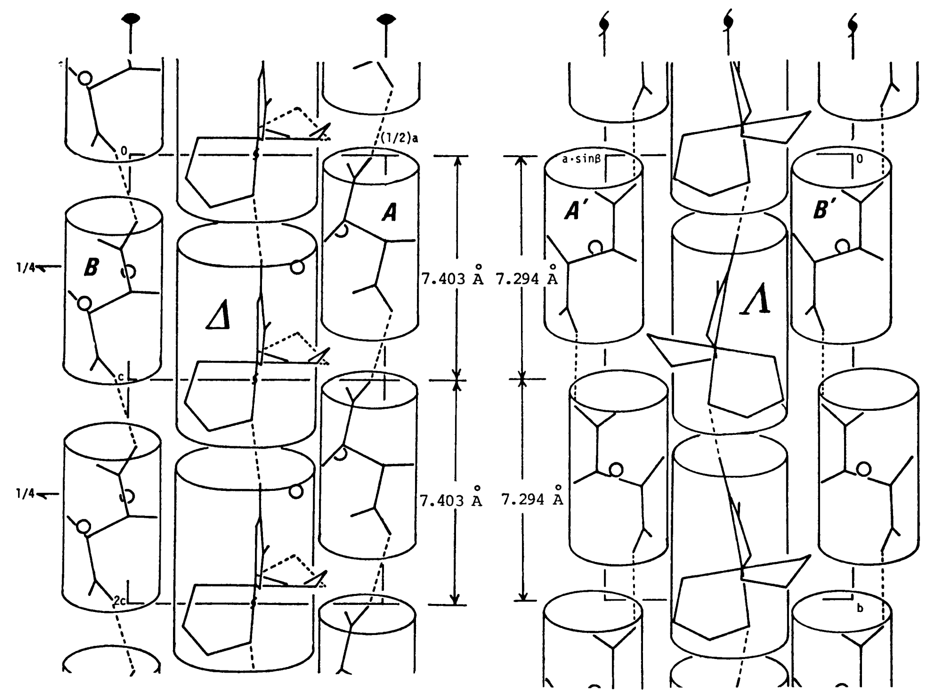
Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I	($1/2-x$, $-1/2+y$, $1-z$),	II (x, y, $1-z$)
III	($1/2-x$, $-1/2+y$, $2-z$),	IV ($-1/2+x$, $3/2-y$, $2-z$)
V	($-1/2+x$, $3/2-y$, $1-z$),	VI (x, y, $-1+z$)
VII	($1-x$, $1-y$, z),	VIII ($1/2-x$, $1/2+y$, $1-z$)

a) Possible hydrogen bonds.

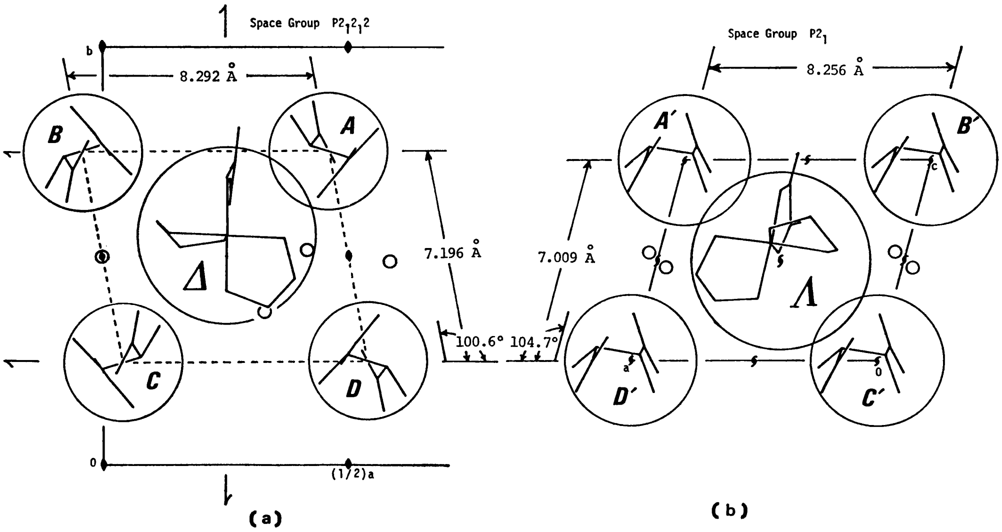
TABLE 5. SHORT CONTACTS BETWEEN COMPLEX CATION AND H-*d*-TART ANION FOR $(-)_{589}$-[Co(ox)en_2]H-*d*-tart·$2H_2O$ (The corresponding distances for $(+)_{589}$-[Co(ox)en_2]H-*d*-tart·H_2O[1] are shown in square brackets.)

Complex	H-*d*-tartrate					
	O(T1)	O(T2)	O(T3)	O(T4)	O(T5)	O(T6)
N(1)	— [2.91]	3.187(Å) [3.12]				2.948 [—]
N(2)	2.858 [—]			3.147 [2.97]		— [2.89]
N(4)	3.082 [—]		3.183 [3.24]			— [3.00]
O(X1)			3.294 [3.01]			
O(X2)	— [3.10]		3.009 [2.90]			3.191 [—]
O(X4)						3.220 [—]
C(E2)	3.241 [—]				3.075 [—]	
C(X1)				— [3.02]		
C(X2)	— [2.94]			— [3.06]		2.957 [—]



(a) (b)

Fig. 4. A schematic drawing of the crystal structures of the more- and the less-soluble diastereoisomeric salts. Broken lines denote hydrogen bonds and disorder of the ethylenediamine ring. Circles indicate water molecules:
(a) $(-)_{589}$-$[Co(ox)en_2]H$-*d*-tart$\cdot 2H_2O$, (b) $(+)_{589}$-$[Co(ox)en_2]H$-*d*-tart$\cdot H_2O$(all the *y* parameters in the less-soluble salt are shifted 3.10 Å along the b-axis from the reported values[1]) for the purpose of the comparison).



(a) (b)

Fig. 5. A comparison of the arrangements of the H-*d*-tart anions and the complex cations.
(a) $(-)_{589}$-$[Co(ox)en_2]H$-*d*-tart$\cdot 2H_2O$, (b) $(+)_{589}$-$[Co(ox)en_2]H$-*d*-tart$\cdot H_2O$.

packing in the less-soluble salt is thought to be caused by the twofold spiral chain of $\{H\text{-}d\text{-tart}\}_\infty$. Indeed, the spiral chains of $\{H\text{-}d\text{-tart}\}_\infty$ were always found in several less-soluble diastereoisomeric salt, $(+)_{589}$-*trans*(*O*)-$[Co(gly)_2en]H$-*d*-tart$\cdot 3H_2O$,[20] (−)-adrenalinium H-*d*-tart,[12] (+)-[(−)-1-methy-3-benzoylpiperidinium H-*d*-tart]H_2O,[13] and (−)-[(−)-1-methyl-3-ethyl-3-benzoylpiperidinium H-*d*-tart].[14] Although the present more-soluble salt also has a $\{H\text{-}d\text{-tart}\}_\infty$ chain, the chain is in a non-spiral form. The discrimination of the optically active $[Co(ox)en_2]^+$ cation by the H-*d*-tart anion is attributable to such a structural difference in the $\{H\text{-}d\text{-tart}\}_\infty$ columns.

Dehydration of the Water of Crystallization and Conformational Disorder. The water molecule O(W3) with a one-half weight is located at an unusually short distance (2.16 Å) from the C(E4B) (*lel* form) in the disordered ethylenediamine ring. On the other hand, the distance from O(W3) to C(E4A) (*ob* form) is normal (3.12 Å). If this water molecule exists with weight one (this imaginary compound corresponds to 2.5 hydrate), the conformation of the ethylenediamine ring (N(1)–C(El)–C(E4)–N(4)) is thought to be restricted to the *ob* form in order to avoid such an abnormal short contact between the O(W3) and C(E4B) atoms. In other words, the change in conformation from *ob* to *lel* seems to be related to the partial loss of this water(O(W3)) of crystallization. Shimura and Tsutsui[22] reported that the more-soluble $(-)_{589}$-salt contains 2.5 mol of the water of crystallization. If the crystal of $(-)_{589}$-salt$\cdot 2.5H_2O$ is isomorphous to the $(-)_{589}$-salt$\cdot 2H_2O$, the complex cation in the former crystal is confirmed to have the *ob*-*ob* form exclusively.

Recntly, Brouty *et al.* reported the crystal structures of $(\pm)$-$[Cr(en)_3](SCN)_3\cdot 0.75H_2O$[23,24] and $[(+)$-$Co(en)_3(-)$-$Cr(en)_3](SCN)_3\cdot nH_2O$[25] at 293 K and 133 K respectively. They found that, in both cases, one ethylenediamine ring in the $[Cr(en)_3]^{3+}$ cation is in conformational disorder at 293 K. They mentioned that the partial loss of the water of crystallization plays some role in causing the change in conformation from *lel* to *ob*. However, in $(-)_{589}$-$[Co(ox)en_2]$-H-*d*-tart$\cdot 2H_2O$, such a loss causes the confromational change from *ob* to *lel*. The reason for such a difference still remains unsolved.

We wish to thank the Hiroshima University Computer Center for its generous allocation of computer time and acknowledge a Grant-in-Aid for Scientific Research from the Ministry of Education.

References

1) M. Kuramoto, Y. Kushi, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **51**, 3251 (1978).

2) W. T. Jordan, B. J. Brennan, L. R. Froebe, and B. E. Douglas, *Inorg. Chem.*, **12**, 1827 (1973).

3) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience, New York (1971), p. 129. The "*lel*, *ob*" notation was introduced by E. J. Corey and J. C. Bailar, Jr.(E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959)).

4) D. W. J. Cruickshank, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," ed by R. Pepinsky, J. M. Robertson, and J. C. Speakman, Pergamon Press, Oxford (1961), p. 45.

5) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1968), Vol. III, pp. 201—206.

6) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, p. 148.

7) Y. Kushi, unpublished work.

8) T. Ashida, "The Universal Crystallographic Computation Program System." ed by T. Sakurai, The Crystallographic Society of Janan (1967).

9) A. J. van Bommel and J. M. Bijvoet, *Acta Crystallogr.*, **11**, 61 (1958).

10) T. Aoki, K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **46**, 159 (1973).

11) K. Toriumi, S. Sato, and Y. Saito, *Acta Crystallogr., Sect. B*, **33**, 1378 (1977).

12) D. Carlstrøm, *Acta Crystallogr,. Sect. B*, **29**, 161 (1973).

13) G. Hite and J. R. Soares, *Acta Crystallogr., Sect. B*, **29**, 2935 (1973).

14) J. R. Ruble, G. Hite, and J. R. Soares, *Acta Crystallogr., Sect. B*, **32**, 136 (1976).

15) Y. Kushi, M. Kuramoto, and H. Yoneda, *Chem. Lett.*, **1976**, 663.

16) M. Kuramoto, Y. Kushi, and H. Yoneda, *Bull. Chem. Soc. Jpn.*, **51**, 3196 (1978).

17) Y. Kushi, M. Kuramoto, and H. Yoneda, *Chem. Lett.*, **1976**, 135.

18) Y. Kushi, M. Kuramoto, and H. Yoneda, *Chem. Lett.*, **1976**, 339.

19) T. Tada, Y. Kushi, and H. Yoneda, *Chem. Lett.*, **1977**, 379.

20) M. Kuramoto, *Bull. Chem. Soc. Jpn.*, in press.

21) The crystal data of $(+)_{589}$-$[Co(ox)en_2]$H-*d*-tart$\cdot H_2O$ were remeasured on a Syntex R3 computer-controlled four-circle diffractometer; $a=8.256(3)$, $b=14.588(4)$, $c=7.009(1)$ Å, $\beta=104.73(2)°$, $P2_1$, and $Z=2$.

22) Y. Shimura and K. Tsutsui, *Bull. Chem. Soc. Jpn.*, **50**, 145 (1977).

23) C. Brouty, P. Spinat, A. Whuler, and P. Herpin, *Acta Crystallogr., Sect. B*, **33**, 1913 (1977).

24) C. Brouty, P. Spinat, A. Whuler, and P. Herpin, *Acta Crystallogr., Sect. B*, **33**, 1920 (1977).

25) C. Brouty, A. Whuler, P. Spinat, and P. Herpin, *Acta Crystallogr., Sect. B*, **33**, 2563 (1977).