Inorganica Chimica Acta, *132* (1987) 11–20

Structural Study of Optical Resolution. XIII. The Crystal Structures of the Racemic (Δ,Λ-d,l) and the Optically-active (Δ-d) Tartrate Salts of the Tris(ethylenediamine)nickel(II) Complex

TSUTOMU MIZUTA, HAYAMI YONEDA*

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730, Japan

and YOSHIHIKO KUSHI

The Institute of Chemistry, College of General Education, Osaka University, Machikaneyama-machi, Toyonaka, Osaka 560, Japan

(Received November 27, 1986)

Abstract

The crystal structures of Δ,Λ-[Ni(en)$_3$]d,l-tart·H$_2$O and Δ-[Ni(en)$_3$]d-tart·$\frac{4}{3}$H$_2$O have been determined by single crystal X-ray techniques. The crystals of the former were orthorhombic, with the space group *Pbca*, $a = 14.153(3)$, $b = 17.706(3)$, $c = 14.672(3)$ Å, and $Z = 8$. Crystals of the latter were also orthorhombic, with the space group $C222_1$, $a = 8.860(3)$, $b = 16.142(4)$, $c = 37.286(7)$ Å, and $Z = 8$. The cations and anions in each crystal have the normal geometries usually found. A unique face-to-face ion-pair structure was found for the Δ-l and the Λ-d combinations in the two crystal structures, but not for Δ-d and Λ-l.

Introduction

It has long been known that the d-tartrate ion (d-$C_4H_4O_6^{2-}$, hereafter abbreviated as d-tart^{2-} ion) is an effective chiral selector in optical resolution of the [M(en)$_3$]$^{3+}$ complex ion [1–4]. We have previously performed the crystal structure analyses of three kinds of less-soluble diastereomeric salts containing Λ-[M(en)$_3$]$^{3+}$ and d-tart^{2-} ions and found that a unique face-to-face ion-pair structure is formed between Λ-[M(en)$_3$]$^{3+}$ and d-tart^{2-}. In the face-to-face ion-pair four oxygen atoms of the d-tartrate ion face the triangular facet composed of three NH$_2$ groups of the complex [5]. It is remarkable to find this unique face-to-face ion-pair structure in three different crystals which differ in composition, cell dimensions, and space group symmetry. We therefore assumed that such face-to-face ion-pair formation also plays a key role in chiral discrimination of the [M(en)$_3$]$^{3+}$ type complexes in solution. On the basis of this ion-pair structure, it would be expected that optical resolution should be achieved by the d-tart^{2-} for any complexes having three NH$_2$ groups in a triangular facet of the octahedron. Several examples of successful optical resolution by chromatography have been reported using the d-tart^{2-} ion as a chiral selector based on this assumption [4, 6].

Furthermore the analysis of the CD spectra of Δ- and Λ-[Co(N)$_6$]$^{3+}$ type complex ions in the presence of the d-tart^{2-} ion reveals that the d-tart^{2-} ion approaches the complex along the C$_3$ axis and chiral discrimination is thereby effected [7]. Thus, the chromatography studies and the CD spectra seem to support face-to-face ion-pair formation in solution. However, the question still remains whether the face-to-face Λ-d ion-pair structure is really energetically more favorable than the Δ-d combination in crystals. If face-to-face close contact were found only for the Λ-d but not for the Δ-d in a crystal which is composed of both the Δ and Λ complex ions and the d-tart^{2-} ions, it could be safely concluded that the Λ-d combination is energetically more favorable than the Δ-d combination. However, since the reported crystals are composed only of the Λ-d combination, it cannot be concluded that the face-to-face Λ-d ion-pair structure is more favorable than the face-to-face Δ-d ion-pair structure. If determination of the crystal structure of the salt composed of the Δ- and Λ-[M(en)$_3$]$^{n+}$ complex ions and d- and l-tart^{2-} ions, revealed the face-to-face ion-pair structure in the Λ-d and Δ-l combinations, but not in the Δ-d and Λ-l combinations we could conclude that the face-to-face Λ-d ion-pair is more favorable than the Δ-d ion-pair. With this expectation in mind, the structure determination was attempted for Δ,Λ-[Ni(en)$_3$]d,l-tart. In addition, we determined the crystal structure of the diastereomeric salt composed of either Δ- or Λ-[Ni(en)$_3$]$^{2+}$ and d-tart^{2-} ions with the expectation that a face-to-face ion-pair structure would also be found.

---

*Author to whom correspondence should be addressed.

0020-1693/87/$3.50

Experimental

Preparation of [Ni(en)$_3$]d,l-tart·H$_2$O (I) and [Ni(en)$_3$]$_{1.5}$d-tart$_{1.5}$·2H$_2$O (II)

I was prepared as follows. Three grams of $NiCl_2\cdot 6H_2O$ were dissolved in 4 ml of water. To this solution was added 10 ml of an aqueous solution containing 3 g of Na$_2$d,l-tart. Light-green Ni d,l-tart was rapidly deposited. This was filtered off and washed with cold water. Two grams of the precipitate were suspended in a mixture of 3 ml of water and 2.2 ml of free ethylenediamine. The violet solution thus obtained was left standing at room temperature for several days. Violet crystals were deposited, and a crystal of suitable size was selected for the structure analysis. *Anal.* Found: C, 29.66; H, 7.58; N, 20.46. Calc. for [Ni(en)$_3$]d,l-tart·H$_2$O (**I**): C, 29.65; H, 7.46; N, 20.75%.

II was prepared in a similar way using Na$_2$d-tart instead of Na$_2$d,l-tart. *Anal.* Found: C, 29.76; H, 7.57; N, 20.77. Calc. for [Ni(en)$_3$]$_{1.5}$d-tart$_{1.5}$·2H$_2$O (**II**): C, 29.21; H, 7.52; N, 20.45%.

X-ray Measurements

The systematic absences of reflections suggested the following space groups: *Pbca* for Δ,Λ-[Ni(en)$_3$]d,l-tart·H$_2$O (**I**); *C*222$_1$ for Δ-[Ni(en)$_3$]$_{1.5}$d-tart$_{1.5}$·2H$_2$O (**II**). Determination of cell constants and collection of intensity data were carried out on a SYNTEX diffractometer for **I** and on a Rigaku AFC-5 diffractometer for **II** with graphite-monochromated Mo Kα radiation ($\lambda = 0.76107$ Å). Unit cell constants were determined by least-squares refinement of data for 25 reflections for each compound. Intensity data were collected by an ω scan mode up to $2\theta = 55°$ and by an ω–2θ scan mode up to $2\theta = 50°$ for **I** and **II**, respectively. No corrections were made for absorption effect (μ(Mo Kα) = 11.3 and 11.4 cm^{-1} for **I** and **II**). The numbers of reflections included ($F_o > 3\sigma F_o$) were 3289 and 1741 for **I** and **II**, respectively (see Table I).

Determination and Refinement of the Structures

The structure of each compound was solved by the heavy-atom method. The parameters for all the non-hydrogen atoms were refined anisotropically. Several cycles of the block-diagonal least-squares refinement reduced the R value ($R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$) to 0.062 and 0.078 for **I** and **II**, respectively. At this stage, all the hydrogen atom positions included were calculated ones (1.0 Å for N–H and C–H bond distances and tetrahedral angle). The final refinement including these H atoms with isotropic temperature factors caused the R value to converge to 0.043 and 0.067 for **I** and **II**, respectively. In the refinement, the quantity minimized was $\omega(|F_o| - k|F_c|)^2$. The weighting scheme used was $\omega = (\sigma cs^2 + a|F_o| + b|F_o|^2)^{-1}$, where σcs is the standard deviation obtained from the counting statistics for each reflection; the a and b values chosen were 0.2 and 0.0009, respectively. The final atomic coordinates for non-hydrogen and hydrogen atoms, and the final thermal parameters are given in Tables II and III. All the computations were carried out on a HITAC computer at the Hiroshima University Information Processing Center. The computer programs used were UNICS-III [8] and ORTEP [9].

TABLE I. Crystallographic Data^a

	I	II
Space group	*Pbca*	*C*222$_1$
Z	8	8
Cell dimensions		
a (Å)	14.153(3)	8.860(3)
b (Å)	17.706(3)	16.142(4)
c (Å)	14.672(3)	37.286(7)
V (Å^3)	3676(1)	5332.6(27)
Density (obs.) (g/cm^3)	1.43	1.52
Density (calc.) (g/cm^3)	1.46	1.53
No. unique reflections	4707	2193
No. reflections with $F_o > 3\sigma$	3289	1741
Final R (%)	4.3	6.7

^{a}**I**: Δ,Λ-[Ni(en)$_3$]d,l-tart·H$_2$O; **II**: Δ-[Ni(en)$_3$]$_{1.5}$(d-tart)$_{1.5}$·2H$_2$O.

Results and Discussion

Description of the Crystal Structure of I

Cation and anion geometries

The crystal structure consists of discrete Δ- and Λ-[Ni(en)$_3$]$^{2+}$ cations, d- and l-tart^{2-} anions, and water molecules. Figures 1 and 2 show the projections of the crystal structure along the a- and c-axis respectively. The bond distances and angles within the complex cation and the tartrate anion are listed in Table IV.

The three en ligands in the complex cation are oriented around the Ni atom in a (lel)$_3$ conformation. Thus, the complex ion exists either in Δ(λλλ) or in Λ(δδδ) form. The average atom distance between the two N atoms of the en ligand is 2.79 Å, and the average bond angle, N–Ni–N, is 82.1°. The twist angle between the two triangular faces, (N1 N3 N5) and (N2 N4 N6) of the octahedron is 50.6° on average. These values are all in good accordance with those reported previously [10, 11].

The bond distances and angles of the tart^{2-} anion are also in good agreement with those found in the previous studies [12]. Four carbon atoms lie almost in a plane, and the atomic groups (CT1, CT2, O1, O2, O3) and (CT3, CT4, O4, O5, O6) are also planar (see Table VIII). Thus, the tart^{2-} anions adopt the conformation usually found in simple tartrate salts.

TABLE II. Positional and Thermal Parameters for Δ,Λ-[Ni(en)$_3$]d,l-tart·H$_2$O

Atom	*x*	*y*	*z*	B_{eq} (Å^2)[a]
Ni	0.2162(0)	0.1302(0)	0.1941(0)	1.9
N1	0.2965(2)	0.1411(2)	0.3145(2)	2.6
N2	0.1058(2)	0.1075(2)	0.2880(2)	2.5
N3	0.1864(2)	0.2487(2)	0.1958(2)	2.7
N4	0.1238(2)	0.1342(2)	0.0803(2)	2.7
N5	0.3391(2)	0.1402(2)	0.1097(2)	2.9
N6	0.2428(2)	0.0133(2)	0.1756(2)	2.6
C1	0.2304(3)	0.1489(2)	0.3912(3)	3.2
C2	0.1490(3)	0.0939(2)	0.3777(3)	3.3
C3	0.1443(3)	0.2683(2)	0.1074(3)	3.6
C4	0.0751(3)	0.2077(2)	0.0803(3)	3.6
C5	0.3835(3)	0.0650(3)	0.1062(3)	4.0
C6	0.3080(3)	0.0050(2)	0.0987(3)	3.5
CT1	−0.0495(2)	0.3050(2)	0.2710(2)	2.3
CT2	−0.0018(2)	0.3825(2)	0.2752(2)	2.2
CT3	0.0097(2)	0.4089(2)	0.3727(2)	2.1
CT4	0.0738(3)	0.4788(2)	0.3767(2)	2.5
O1	−0.0092(2)	0.2517(1)	0.3094(2)	3.2
O2	−0.1257(2)	0.3013(2)	0.2276(2)	3.7
O3	−0.0514(2)	0.4370(1)	0.2221(2)	3.3
O4	−0.0811(2)	0.4205(2)	0.4114(2)	3.2
O5	0.0429(2)	0.5398(1)	0.4044(2)	3.9
O6	0.1573(2)	0.4680(2)	0.3511(2)	3.8
OW	0.2651(3)	0.3535(2)	0.4145(2)	6.4
H(N1)1	0.339	0.187	0.311	3.9
H(N1)2	0.338	0.096	0.324	3.9
H(N2)1	0.069	0.062	0.268	3.9
H(N2)2	0.061	0.152	0.291	3.9
H(N3)1	0.246	0.278	0.206	3.9
H(N3)2	0.141	0.261	0.246	3.9
H(N4)1	0.076	0.092	0.085	3.9
H(N4)2	0.160	0.128	0.022	3.9
H(N5)1	0.384	0.179	0.135	3.9
H(N5)2	0.321	0.157	0.046	3.9
H(N6)1	0.182	−0.015	0.164	3.9
H(N6)2	0.272	−0.009	0.233	3.9
H(C1)1	0.204	0.207	0.394	3.9
H(C1)2	0.267	0.137	0.455	3.9
H(C2)1	0.176	0.036	0.381	3.9
H(C2)2	0.096	0.102	0.431	3.9
H(C3)1	0.201	0.272	0.056	3.9
H(C3)2	0.109	0.323	0.112	3.9
H(C4)1	0.017	0.206	0.130	3.9
H(C4)2	0.046	0.219	0.013	3.9
H(C5)1	0.425	0.056	0.169	3.9
H(C5)2	0.432	0.062	0.048	3.9
H(C6)1	0.268	0.012	0.035	3.9
H(C6)2	0.339	−0.051	0.099	3.9
H(CT2)1	0.068	0.380	0.242	3.9
H(CT3)1	0.040	0.365	0.417	3.9
H(O4)1	−0.074	0.435	0.477	3.9
H(OW)1	0.305	0.334	0.362	3.9
H(OW)2	0.225	0.396	0.391	3.9

[a] $B_{eq} = \frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33})$. The anisotropic thermal parameters have been stored by the Editor-in-Chief.

Crystal packing

The crystal structure of **I** is depicted in Figs. 1 and 2, and the distances and angles of the hydrogen bonds are listed in Table VI.

TABLE III. Positional and Thermal Parameters for Δ-$[Ni(en)_3]_{1.5}(d\text{-}tart)_{1.5}\cdot 2H_2O$

Atom	*x*	*y*	*z*	B_{eq} (Å)[a]
Ni1	0.0500(0)	0.0547(0)	0.0250(0)	2.7
Ni2	0.3262(1)	0.2714(1)	0.0790(1)	2.5
N1	0.4785(18)	0.6379(8)	0.2095(4)	4.5
N2	0.2598(15)	0.5579(7)	0.2498(5)	4.2
N3	0.5151(15)	0.4471(7)	0.2134(3)	3.0
N4	0.1650(16)	0.2158(7)	0.0438(4)	4.1
N5	0.1664(17)	0.2330(8)	0.1183(4)	4.6
N6	0.4615(14)	0.1615(8)	0.0801(5)	4.6
N7	0.4862(17)	0.3107(8)	0.1184(4)	4.1
N8	0.4524(14)	0.3155(8)	0.0351(3)	3.5
N9	0.2316(15)	0.3924(7)	0.0756(4)	4.0
C1	0.3209(25)	0.6735(12)	0.2117(6)	6.6
C2	0.2122(20)	0.6132(12)	0.2196(7)	6.4
C3	0.5369(28)	0.3698(10)	0.2343(6)	6.4
C4	0.0551(21)	0.1717(12)	0.0655(6)	5.6
C5	0.0286(21)	0.2122(12)	0.0989(6)	5.7
C6	0.5965(25)	0.1781(15)	0.0986(8)	8.4
C7	0.5937(24)	0.2434(17)	0.1244(6)	8.1
C8	0.3821(25)	0.3943(12)	0.0234(6)	6.7
C9	0.3210(26)	0.4418(9)	0.0517(5)	5.2
CT1	−0.1149(19)	0.3901(9)	0.0225(4)	3.5
CT2	−0.1069(18)	0.4858(9)	0.0187(4)	3.7
CT3	0.1140(19)	0.3868(10)	0.1819(5)	4.4
CT4	−0.0277(18)	0.4410(9)	0.1818(5)	3.8
CT5	−0.0725(19)	0.4624(10)	0.1437(5)	4.2
CT6	−0.2231(19)	0.5079(11)	0.1415(5)	4.4
O1	−0.0192(15)	0.3500(7)	0.0059(4)	5.3
O2	−0.2183(15)	0.3624(7)	0.0415(4)	6.0
O3	−0.2263(25)	0.5225(6)	0.0385(3)	5.3
O4	0.2288(13)	0.4134(8)	0.1665(4)	5.1
O5	0.1026(15)	0.3221(7)	0.1987(4)	6.2
O6	−0.1426(15)	0.4029(8)	0.1991(4)	6.6
O7	−0.0718(15)	0.3930(9)	0.1217(4)	6.7
O8	−0.3216(14)	0.4773(7)	0.1229(4)	5.8
O9	−0.2375(16)	0.5733(7)	0.1599(4)	5.7
OW1	0.3819(15)	0.5407(9)	0.1349(4)	7.2
OW2	0.3555(20)	0.2079(9)	0.1981(5)	8.5
H(N1)1	0.495	0.614	0.185	3.9
H(N1)2	0.553	0.684	0.213	3.9
H(N2)1	0.222	0.582	0.273	3.9
H(N2)2	0.211	0.502	0.247	3.9
H(N3)1	0.597	0.459	0.196	3.9
H(N3)2	0.416	0.443	0.200	3.9
H(N4)1	0.216	0.176	0.027	3.9
H(N4)2	0.111	0.258	0.029	3.9
H(N5)1	0.148	0.278	0.137	3.9
H(N5)2	0.207	0.183	0.132	3.9
H(N6)1	0.488	0.144	0.055	3.9
H(N6)2	0.405	0.155	0.092	3.9
H(N7)1	0.431	0.324	0.142	3.9
H(N7)2	0.538	0.363	0.111	3.9
H(N8)1	0.453	0.274	0.015	3.9
H(N8)2	0.561	0.325	0.043	3.9
H(N9)1	0.229	0.420	0.101	3.9
H(N9)2	0.124	0.391	0.067	3.9
H(C1)1	0.300	0.700	0.187	3.9
H(C1)2	0.322	0.718	0.230	3.9
H(C2)1	0.177	0.640	0.225	3.9

(continued)

TABLE III. *(continued)*

Atom	x	y	z	B_{eq} (Å)^{a}
H(C2)2	0.199	0.576	0.197	3.9
H(C3)1	0.653	0.367	0.240	3.9
H(C3)2	0.516	0.321	0.219	3.9
H(C4)1	0.093	0.112	0.069	3.9
H(C4)2	−0.042	0.167	0.051	3.9
H(C5)1	−0.033	0.263	0.096	3.9
H(C5)2	−0.035	0.173	0.115	3.9
H(C6)1	0.680	0.190	0.082	3.9
H(C6)2	0.626	0.125	0.113	3.9
H(C7)1	0.577	0.215	0.148	3.9
H(C7)2	0.702	0.265	0.124	3.9
H(C8)1	0.299	0.383	0.006	3.9
H(C8)2	0.461	0.430	0.010	3.9
H(C9)1	0.408	0.469	0.065	3.9
H(C9)2	0.260	0.490	0.041	3.9
H(CT2)1	−0.008	0.504	0.029	3.9
H(CT4)1	−0.009	0.494	0.198	3.9
H(CT5)1	0.009	0.502	0.133	3.9
H(O3)1	−0.287	0.475	0.050	3.9
H(O6)1	−0.113	0.348	0.207	3.9
H(O7)1	−0.176	0.388	0.110	3.9
H(OW1)1	0.490	0.518	0.131	3.9
H(OW1)2	0.325	0.494	0.147	3.9
H(OW2)1	0.320	0.158	0.184	3.9
H(OW2)2	0.266	0.248	0.199	3.9

$^{a}B_{eq} = \frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33})$. The anisotropic thermal parameters have been stored by the Editor-in-Chief.

TABLE IV. Bond Distances and Angles for Δ,Λ-$[Ni(en)_3]$d,l-tart·H_2O (e.s.d.s in parentheses)

(a) Bond distances l (Å)

Ni–N1	2.109(3)	N1–C1	1.470(5)	C1–C2	1.521(6)	CT1–O1	1.238(4)
Ni–N2	2.121(3)	N2–C2	1.470(5)	C3–C4	1.506(6)	CT1–O2	1.254(4)
Ni–N3	2.142(3)	N3–C3	1.468(5)	C5–C6	1.511(6)	CT4–O5	1.235(4)
Ni–N4	2.123(3)	N4–C4	1.472(5)	CT1–CT2	1.531(4)	CT4–O6	1.254(4)
Ni–N5	2.143(3)	N5–C5	1.473(5)	CT2–CT3	1.514(5)	CT2–O3	1.425(4)
Ni–N6	2.120(3)	N6–C6	1.465(5)	CT3–CT4	1.536(5)	CT3–O4	1.420(4)

(b) Bond angles ϕ (°)

N1–Ni–N2	82.6(1)	N1–C1–C2	108.8(3)	CT1–CT2–CT3	111.2(3)
N3–Ni–N4	81.6(1)	N2–C2–C1	109.1(3)	CT1–CT2–O3	111.5(3)
N5–Ni–N6	82.1(1)	N3–C3–C4	109.2(3)	CT3–CT2–O3	111.2(3)
Ni–N1–C1	107.9(2)	N4–C4–C3	109.0(3)	CT2–CT3–CT4	110.4(3)
Ni–N2–C2	107.8(2)	N5–C5–C6	109.6(3)	CT2–CT3–O4	108.9(3)
Ni–N3–C3	107.6(2)	N6–C6–C5	108.6(3)	CT4–CT3–O4	113.8(3)
Ni–N4–C4	108.5(2)	O1–CT1–O2	126.0(3)	CT3–CT4–O5	120.6(3)
Ni–N5–C5	107.0(2)	O1–CT1–CT2	117.5(3)	CT3–CT4–O6	115.0(3)
Ni–N6–C6	108.0(2)	O2–CT1–CT2	116.5(3)	O5–CT4–O6	124.4(3)

The inspection of Figs. 1 and 2 reveals that the complex and the tart^{2-} ions are linked together to form layers. Figure 1 shows the projection of two such layers along the *a*-axis. It is clearly seen that a unit cell is divided into two zones at a plane $c = \frac{1}{2}$. The two layers in the two zones, $c = 0 \sim \frac{1}{2}$ and $c = \frac{1}{2} \sim 1$, are related to each other by inversion. Figure 2 shows a perspective drawing of one such layer ($c = 0 \sim \frac{1}{2}$) in which all the hydrogen bonds are indicated as dotted lines. Here, it is notable that 'favorable' face-

TABLE V. Bond Distances and Angles for Δ-$[Ni(en)_3]_{1.5}(d\text{-}tart)_{1.5}\cdot 2H_2O$ (e.s.d.s. in parentheses)

(a) Bond distances l (Å)

Ni1–N1	2.109(16)	N1–C1	1.513(29)	C1–C2	1.400(36)	CT1–O1	1.232(22)
Ni1–N2	2.135(20)	N2–C2	1.497(33)	C3–C3	1.342(30)	CT1–O2	1.242(23)
Ni1–N3	2.122(14)	N3–C3	1.482(28)	C4–C5	1.426(32)	CT2–O3	1.421(21)
Ni2–N4	2.136(15)	N4–C4	1.454(26)	C6–C7	1.428(40)	CT3–O4	1.244(23)
Ni2–N5	2.131(15)	N5–C5	1.458(27)	C8–C9	1.412(33)	CT3–O5	1.221(25)
Ni2–N6	2.141(17)	N6–C6	1.405(34)	CT1–CT2	1.553(24)	CT4–O6	1.387(24)
Ni2–N7	2.137(15)	N7–C7	1.463(31)	CT2–CT2	1.466(23)	CT5–O7	1.388(24)
Ni2–N8	2.107(13)	N8–C8	1.482(27)	CT3–CT4	1.530(26)	CT6–O8	1.220(23)
Ni2–N9	2.130(15)	N9–C9	1.434(27)	CT4–CT5	1.516(26)	CT6–O9	1.265(23)
				CT5–CT6	1.526(26)		

(b) Bond angles ϕ (°)

N1–Ni1–N2	81.5(07)	N1–C1–C2	112.5(20)	O4–CT3–O5	126.8(19)
N3–Ni1–N3	80.5(07)	N2–C2–C1	112.2(21)	O4–CT3–CT4	118.2(17)
N4–Ni2–N5	81.8(06)	N3–C3–C3	113.3(25)	O5–CT3–CT4	115.0(17)
N6–Ni2–N7	82.0(06)	N4–C4–C5	111.9(18)	CT3–CT4–CT5	110.3(15)
N8–Ni2–N9	81.5(05)	N5–C5–C4	113.7(19)	CT3–CT4–O6	112.0(15)
Ni1–N1–C1	107.9(12)	N6–C6–C7	117.1(24)	CT5–CT4–O6	109.7(15)
Ni1–N2–C2	109.3(14)	N7–C7–C6	117.2(22)	CT4–CT5–CT6	112.8(15)
Ni1–N3–C3	108.3(12)	N8–C8–C9	113.9(19)	CT4–CT5–O7	111.7(15)
Ni2–N4–C4	108.1(12)	N9–C9–C8	112.0(19)	CT6–CT5–O7	111.2(15)
Ni2–N5–C5	106.4(12)	O1–CT1–O2	127.2(17)	CT5–CT6–O8	117.4(16)
Ni2–N6–C6	109.2(15)	O1–CT1–CT2	116.4(15)	CT5–CT6–O9	117.5(16)
Ni2–N7–C7	108.5(13)	O2–CT1–CT2	116.4(15)	O8–CT6–O9	125.0(17)
Ni2–N8–C8	107.2(12)	CT1–CT2–CT2	113.5(15)		
Ni2–N9–C9	109.9(12)	CT1–CT2–O3	109.5(13)		
		CT2–CT2–O3	111.3(15)		

TABLE VI. Selected Intermolecular Distances and Angles for Δ,Λ-$[Ni(en)_3]d,l\text{-}tart\cdot H_2O$[a]

D––H. . . A[b]	D. . A l (Å)	H. . A l (Å)	D–H. . A ϕ (°)
N1––H(N1)1. . O2^{i}	3.015(4)	2.159	154
N1––H(N1)2. . O5^{ii}	3.181(4)	2.286	147
N1––H(N1)2. . O6^{ii}	3.178(4)	2.297	145
N2––H(N2)1. . O3^{iii}	3.120(4)	2.230	146
N2––H(N2)2. . O1	3.043(4)	2.050	169
N3––H(N3)1. . O2^{i}	3.034(4)	2.096	153
N3––H(N3)2. . O1	3.232(4)	2.327	149
N4––H(N4)1. . O5^{iii}	2.899(4)	1.927	160
N4––H(N4)2. . OW^{iv}	3.157(5)	2.191	161
N5––H(N5)1. . O1^{i}	3.149(9)	2.147	173
N5––H(N5)2. . OW^{iv}	3.052(4)	2.098	156
N6––H(N6)1. . O3^{iii}	3.380(4)	2.639	130
N6––H(N6)1. . O4^{iii}	3.094(4)	2.141	157
N6––H(N6)2. . O6^{ii}	3.045(4)	2.047	168
O4––H(O4)1. . O6^{v}	2.845(4)	1.844	172
OW––H(OW)1. . O2	2.754(5)	1.744	179
OW––H(OW)2. . O5^{i}	2.703(5)	1.694	179

[a] Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z: (i) $\frac{1}{2}+x, y, \frac{1}{2}-z$, (ii) $\frac{1}{2}-x, -\frac{1}{2}+y, z$, (iii) $-x, -\frac{1}{2}+y, \frac{1}{2}-z$, (iv) $x, -\frac{1}{2}-y, -\frac{1}{2}+z$, (v) $1-x, 1-y, 1-z$. [b] D, hydrogen donor; A, hydrogen acceptor.

to-face ion-pair structures are found for the Λ-d and the Δ-l combinations but not for Λ-l and the Δ-d, as expected. One such favorable ion-pair structure (Λ-d) is shown with black bonds. In this pair, a triangular face composed of N2, N4 and N6 of the Λ-complex is hydrogen-bonded to the face composed of O3,

TABLE VII. Selected Intermolecular Distances and Angles for Δ-$[Ni(en)_3]_{1.5}(d\text{-}tart)_{1.5}\cdot 2H_2O$[a]

D–H. . .A[b]	D. . A l (Å)	H. . A l (Å)	D–H. . A ϕ (°)
N1–H(N1)1. . .O9	3.293(20)	2.639	123
N1–H(N1)1. . .OW1	3.308(21)	2.436	146
N1–H(N1)2. . .O5^{i}	3.195(8)	2.329	143
N2–H(N2)1. . .O9^{ii}	3.383(24)	2.523	144
N2–H(N2)1. . .OW2^{ii}	3.269(22)	2.400	144
N2–H(N2)2. . .O6^{iii}	3.298(20)	2.632	123
N3–H(N3)1. . .O6^{iv}	3.188(19)	2.439	124
N3–H(N3)2. . .O4	3.128(17)	2.122	169
N4–H(N4)1. . .O3^{v}	3.271(16)	2.558	128
N4–H(N4)2. . .O1	3.058(18)	2.073	171
N5–H(N5)1. . .O5	3.369(21)	2.452	151
N5–H(N5)2. . .O9^{v}	3.125(18)	2.102	173
N6–H(N6)1. . .O1^{vi}	3.220(22)	2.265	156
N7–H(N7)1. . .O4	3.342(19)	2.478	141
N7–H(N7)2. . .O8^{iv}	3.186(18)	2.275	151
N8–H(N8)1. . .O1	3.089(17)	2.175	153
N8–H(N8)2. . .O2^{iv}	3.024(18)	2.047	160
N9–H(N9)1. . .O4	3.409(20)	2.462	152
O3–H(O3)1. . .O8^{iv}	3.338(19)	2.738	118
O7–H(O7)1. . .O2^{vii}	3.295(21)	2.611	124
OW1–H(OW1)1. . .O8^{iv}	2.854(19)	1.820	179
OW1–H(OW1)2. . .O4	2.731(19)	1.820	180
OW2–H(OW2)1. . .O9^{v}	2.726(20)	1.720	179
OW2–H(OW2)2. . .O5	2.900(21)	1.872	178

[a] Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z: (i) $\frac{1}{2}+x, \frac{1}{2}+y, z$, (ii) $-x, y, z$, (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$, (iv) $1+x, y, z$, (v) $\frac{1}{2}+x, -\frac{1}{2}+y, z$, (vi) $\frac{1}{2}+x, \frac{1}{2}-y, -z$, (vii) $x, 1+y, z$. [b] D, hydrogen donor; A, hydrogen acceptor.

TABLE VIII. Least-squares Planes and Dihedral Angles for Tartrate Ion in Δ,Λ-$[Ni(en)_3]$d,l-tart·H_2O

Atom	Plane 1	Atom	Plane 2	Atom	Plane 3
(a) Deviations (Å) of atoms from planes					
CT1	0.0756	CT1	−0.0099	CT3	0.0572
CT2	−0.0572	CT2	−0.0381	CT4	0.0120
CT3	−0.0738	O1	0.0276	O4	−0.0420
CT4	0.0605	O2	−0.0107	O5	0.0072
		O3	0.0317	O6	−0.0329
(b) Dihedral angles (°)					
plane 1–plane 2	59.98	plane 1–plane 3	64.87		
plane 2–plane 3	55.23				

O4 and O5 of the d-tart^{2-} ion (N2. . .O3 3.120 Å, N4. . .O5 2.899 Å and N6. . .O4 3.094 Å). These values are not very different from corresponding values found previously for $[M(en)_3]^{3+}$ and d-tart^{2-} ions [5]. Apart from this face-to-face hydrogen-bonding, the d-tart^{2-} ion is hydrogen-bonded to the three other complex ions. The two oxygen atoms O1 and O2 of a carboxylic group are linked by hydrogen-bonding to three axial N–H bonds of the second complex ion (Δ) along its C_3 axis. These three axial N–H bonds are located in a triangular face opposite to the triangular face which forms a 'favorable' face-to-face close contact to the l-tart^{2-} ion. This type of hydrogen-bonding (between the axial N–H bonds and two O atoms of a carboxyl group) is also found in the crystal structure of $[Ni(en)_3](CH_3COO)_2$ [11]. The two oxygen atoms, O5 and O6 of another carboxyl group are hydrogen-bonded to two equatorial N–H groups of the third complex ion (Δ) (O5. . .N1 3.181 Å, O6. . .N1 3.178 Å, O6. . .N6 3.045 Å). This

TABLE IX. Least-squares Planes and Dihedral Angles for Tartrate Ion in Δ-$[Ni(en)_3]_{1.5}(d\text{-}tart)_{1.5}\cdot 2H_2O$[a]

Atom	Plane 1	Atom	Plane 2	Atom	Plane 3
(a) Deviations (Å) of atoms from planes					
CT1	−0.0222	CT1	−0.0064	$CT1^{i}$	0.0066
CT2	0.0219	CT2	−0.0096	$CT2^{i}$	0.0105
$CT2^{i}$	0.0512	O1	0.0098	$O1^{i}$	−0.0089
$CT1^{i}$	−0.0464	O2	−0.0007	$O2^{i}$	−0.0001
		O3	0.0076	$O3^{i}$	−0.0075
(b) Dihedral angles (°)					
plane 1–plane 2	54.76		plane 1–plane 3	51.44	
plane 2–plane 3	73.82				

Atom	Plane 4	Atom	Plane 5	Atom	Plane 6
(a) Deviations (Å) of atoms from planes					
CT3	0.0433	CT3	0.0112	CT5	−0.0181
CT4	−0.0448	CT4	−0.0241	CT6	0.0066
CT5	−0.0375	O4	0.0078	O7	0.0176
CT6	0.0401	O5	−0.0119	O8	−0.0051
		O6	0.0171	O9	0.0009
(b) Dihedral angles (°)					
plane 4–plane 5	53.65		plane 4–plane 6	54.76	
plane 2–plane 3	71.59				

[a] Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z: (i) $(x, 1-y, -z)$.

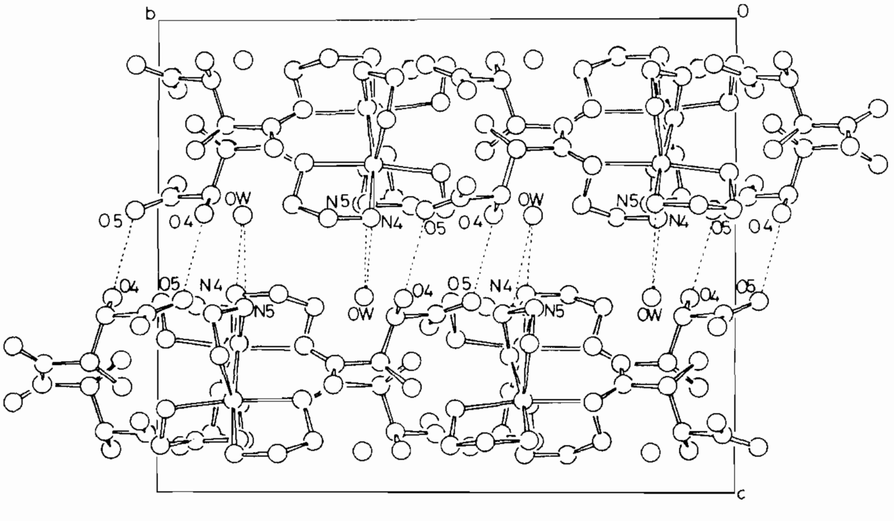

Fig. 1. A drawing of the crystal structure viewed down the a-axis for Δ,Λ-$[Ni(en)_3]$d,l-tart·H_2O. Hydrogen bonds which connect the layers are indicated by broken lines.

hydrogen-bonding mode was also found in the crystal structure determined previously [5]. Finally, the d-$tart^{2-}$ ion forms hydrogen-bonding to the fourth complex ion (Λ) on the side opposite to the face-to-face close contact to the first complex ion (Λ) (O1. . . N2 3.043 Å and O1. . . N3 3.234 Å). In addition, the d-$tart^{2-}$ ion is linked to two water molecules through hydrogen-bonding (O2. . . OW 2.754 Å and O6. . . OW 2.703 Å). All the hydrogen bonds mentioned above make a network throughout a whole layer ($c = 0 \sim \frac{1}{2}$).

Returning to Fig. 1, two kinds of hydrogen-bonding modes are found which connect the layers. One type is found between the water molecule in one layer and

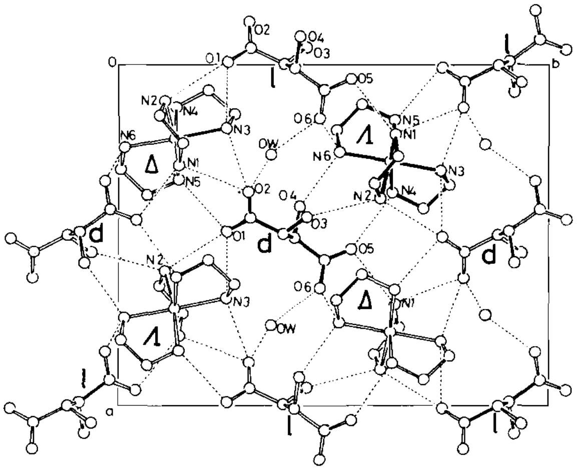

Fig. 2. A drawing of the part of the components $(c = 0 \sim \frac{1}{2})$ in the unit cell viewed down the c-axis for Δ,Λ-$[\mathrm{Ni(en)_3}]$d,l-tart$\cdot$$\mathrm{H_2O}$. Possible hydrogen bonds are indicated by broken lines.

a pair of equatorial N–H groups of the complex ion in another layer (OW. . N4 3.157 Å and OW. . .N5 3.052 Å), and another type is found between one hydroxyl group of the tart^{2-} ion in one layer and one carboxyl oxygen atom of the tart^{2-} ion in another layer. In this way, two tart^{2-} ions in two layers are doubly hydrogen-bonded to each other.

Description of the Crystal Structure of II

Cation and anion geometries

Our first expectation was that the less-soluble diastereomeric salt, Λ-$[\mathrm{Ni(en)_3}]$d-tart, should possess a favorable face-to-face Λ-d ion-pair structure. However, this expectation was not fulfilled. The crystals of **II** contain the Δ-complex cations but not the Λ-complex cations, which is understandable. Since the lattice energy, a main factor in controlling the solubility of a salt, is determined by the summation of all interactions among many cations and anions in the salt, it does not always parallel the energy of formation of a one-to-one cation-anion pair.

Bond distances and angles for **II** are listed in Table V, and least-squares planes and dihedral angles for the tartrate anion in **II** are in Table IX.

The unit cell contains two kinds of crystallographically independent complex ions, $\Delta(\lambda\lambda\lambda)$ and $\Delta(\lambda\delta\delta)$ (Fig. 3). While all the $\Delta(\lambda\lambda\lambda)$ complex ions are crystallographically independent, only one half of the $\Delta(\lambda\delta\delta)$ ions are related by the C_2 symmetry operation. The six coordinating N atoms of the en ligands form a distorted octahedron centered around the Ni atom [10, 11]. The C–C bond distance of each en ligand is 1.423 Å which is somewhat shorter than a normal C–C single bond distance (1.54) Å. This shortening of the C–C bond distance is believed to be only an apparent one, since the large temperature factor for the C atoms of the en ligand is assumed to make the average C–C distance appear shorter than the actual distance. The geometry of the d-tart^{2-} ion resembles closely that found in many normal tartrate salts [12].

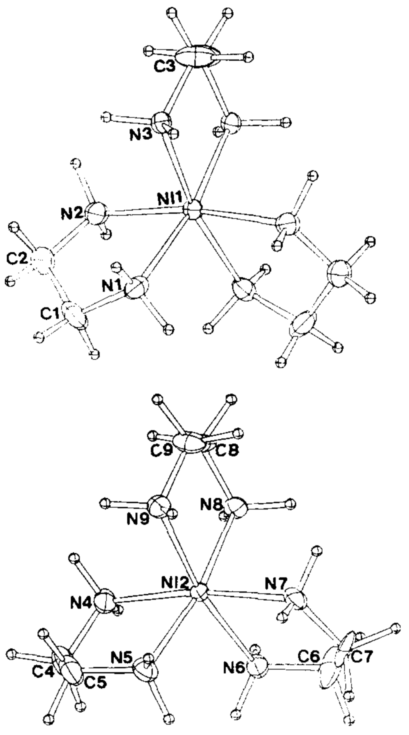

Fig. 3. Views (ORTEP) of two kinds of crystallographically independent complex ions in Δ-$[\mathrm{Ni(en)_3}]_{1.5}$d-tart$_{1.5}\cdot 2\mathrm{H_2O}$. The upper one is $\Delta(\lambda\lambda\lambda)$ conformation and the lower one is $\Delta(\lambda\delta\delta)$ conformation. Ellipsoids of 30% probability are used.

Crystal packing

The Δ-$[\mathrm{Ni(en)_3}]^{2+}$ and the d-tart^{2-} ions are linked together to form a complicated hydrogen-bonding network (Fig. 4 and Table VII). Since the main object of the present study was to see whether the crystal structure involves a face-to-face close contact between the complex ion and the d-tart^{2-} ion, the detailed description of the crystal structure has been omitted. Although the d-tart^{2-} ions are located near the C_3-axis and are hydrogen-bonded to the axial N–H groups of the complex, face-to-face close contact is not found (Fig. 5). In other words, a face-to-face hydrogen-bonded ion-pair structure is not found in the Δ and d combination.

Conclusion

As we expected, we have found unique face-to-face close contact of the Λ-d and the Δ-l ion pairs in crystal **I**, whereas no such face-to-face close contact is found for the Λ-l and the Δ-d ion-pairs. We can thus conclude that the face-to-face ion-pair structure

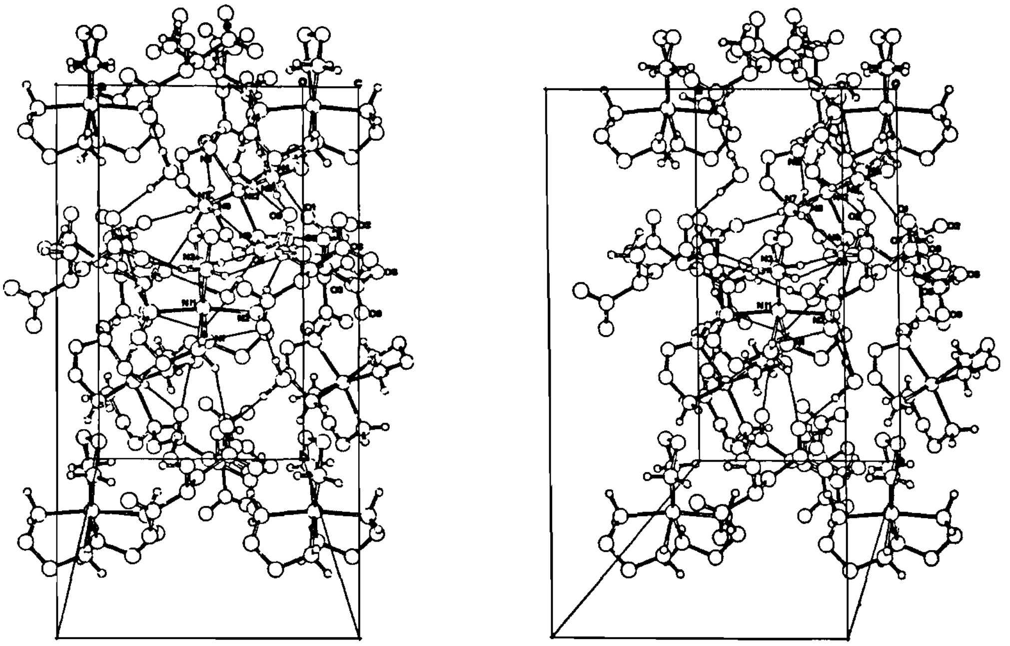

Fig. 4. A stereoview of the part of the components ($c = 0 \sim \frac{1}{3}$) in the unit cell of Δ-[Ni(en)$_3$]$_{1.5}$d-tart$_{1.5}$·2H$_2$O. Possible hydrogen bonds are indicated by solid lines.

of the Λ-d combination is more favorable than that of the Λ-l combination.

Such a face-to-face ion-pair structure was not found in crystal **II**. This observation does not conflict with our above results since the crystal contains only Δ-complex cations and the d-tart^{2-} anions.

Supplementary Material

Anisotropic thermal parameters are available from the Editor-in-Chief on request.

Acknowledgement

The present work was financially supported by a Grant-in-Aid for Scientific Research, No. 60470047 from the Ministry of Education, Science and Culture, Japan.

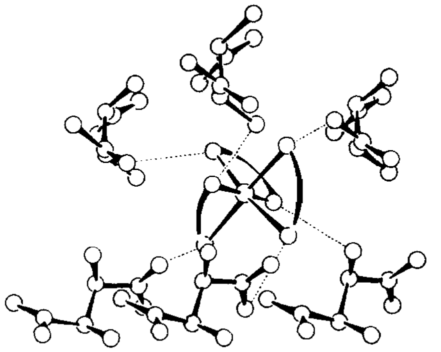

Fig. 5. A schematic drawing of the orientation of the tartrates around the complex in Δ-[Ni(en)$_3$]$_{1.5}$d-tart$_{1.5}$·2H$_2$O.

References

1 A. Werner, *Ber., 45,* 121 (1912).

2 Y. Yoshikawa and K. Yamasaki, *Inorg. Nucl. Chem. Lett., 6,* 523 (1970).

3 H. Yoneda and T. Miura, *Bull. Chem. Soc. Jpn., 43,* 574 (1970); H. Yoneda and T. Baba, *J. Chromatogr., 53,* 610 (1970); H. Yoneda, G. Takemoto and U. Sakaguchi, *Bull. Chem. Soc. Jpn., 47,* 513 (1974).

4 H. Yoneda, S. Suzuki and K. Miyoshi, *Bull. Chem. Soc. Jpn., 47,* 1661 (1974).

5 Y. Kushi, M. Kuramoto and H. Yoneda, *Chem. Lett.,* 135 (1976); 339 (1976); Y. Kushi, T. Tada and H. Yoneda, *Chem. Lett.,* 379 (1977); L. S. Magill, J. D. Corp and I. Bernal, *Inorg. Chem., 20,* 1187 (1981).

6 M. Fujita and H. Yamatera, *Bull. Chem. Soc. Jpn., 49,* 1301 (1976).

7 U. Sakaguchi, A. Tsuge and H. Yoneda, *Inorg. Chem., 22,* 1630 (1983).

8 T. Ashida, in T. Sakurai (Ed.), 'The Universal Crystallographic Comptation Program System', The Crystallographic Society of Japan, Tokyo, 1979.

9 C. K. Johnson, *Report ORTN-3794,* Oak Ridge National Laboratory, Oak Ridge, Tenn., 1976.

10 M. U. Haque, C. N. Caughlan and K. Emerson, *Inorg. Chem., 9,* 2421 (1970); R. E. Cramer and J. T. Hunke, *Inorg. Chem., 17,* 365 (1978); C. L. Raston, A. H. White and A. C. Willis, *Aust. J. Chem., 31,* 415 (1978); J. D. Korp, I. Bernal, R. A. Palmer and J. C. Robinson, *Acta Crystallogr., Sect. B, 36,* 560 (1980); J. G. H. D. Preez, H. E. Rohwer, B. J. van Brecht and M. R. Caira, *J. Chem. Soc., Dalton Trans.,* 975 (1984).

11 R. E. Cramer, W. van Doone and J. T. Hunke, *Inorg. Chem., 15,* 529 (1976).

12 J. M. Bijvoet, A. F. Peerdeman and A. J. van Bommel, *Nature (London), 168,* 271 (1951); R. Sadanaga, *Acta Crystallogr., 3,* 416 (1950); S. Preez, *Acta Crystallogr., Sect. B, 33,* 1083 (1977); D. H. Templeton, A. Zalkin, H. W. Ruben and L. K. Templeton, *Acta Crystallogr., Sect. B, 35,* 1608 (1979); L. S. Magill, J. D. Korp and I. Bernal, *Inorg. Chem., 20,* 1187 (1981).