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# Structural Study of Optical Resolution. XVI. The Crystal Structures of a Pair of Diastereomeric Salts of the *lel*$_3$-Tris(*trans*-1,2-cyclohexanediamine)nickel(II) Complex with *d*-Tartrate Dianion

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The crystal structures of the diastereomeric salt pair, *Λ-lel*$_3$-[Ni(*S,S*-chxn)$_3$](*d*-tart)·3H$_2$O (**1**) and *Δ-lel*$_3$-[Ni(*R,R*-chxn)$_3$](*d*-tart)·5H$_2$O (**2**) (chxn=*trans*-1,2-cyclohexanediamine and *d*-tart=(+)-(*R,R*)-tartrate dianion), have been determined by single-crystal X-ray diffraction techniques. Crystal **1** is orthorhombic with the space group $P2_12_12_1$, $a$=10.093(2), $b$=13.589(4), $c$=22.011(4) Å, and $Z$=4. Crystal **2** is also orthorhombic with the same space group, $a$=11.197(2), $b$=13.102(2), $c$=22.402(2) Å, and $Z$=4. In **1**, the *d*-tart ion makes a familiar face-to-face contact with the *Λ* complex, in which the two alcoholic and one carboxylic O atoms of the *d*-tart ion are involved in the multiple hydrogen bonds to the three H–N groups on the triangular face of the complex. This contact mode resembles the one found earlier in the chloride *d*-tart salt of the corresponding *Λ* Co(III) complex, *Λ-lel*$_3$-[Co(*S,S*-chxn)$_3$]Cl(*d*-tart)·2H$_2$O (**3**). On the other hand, no such face-to-face contact is present in **2**, though it has been found in the corresponding *Δ* Co(III) complex salt, *Δ-lel*$_3$-[Co(*R,R*-chxn)$_3$]Cl(*d*-tart)·2H$_2$O (**4**) in which the *d*-tart ion is obliged to rotate the distal carboxylato group so as to avoid the steric repulsion otherwise imposed on it by one of the bulky chxn ligands. Detailed comparison of the above four crystal structures revealed that the packing modes of the respective complex cations and counterions are surprisingly similar to one another, indicating that the absence of such a face-to-face contact in **2** is attributed to the weaker affinity of the *d*-tart ion for the divalent *Δ* Ni(II) complex, rather than to the steric demands of the crystal packing in **2**. In **2** are found two deformed contact modes similar to each other, in which the *d*-tart ion directs its three O atoms to the triangular face, but only one of them is hydrogen-bonded to one or two of the three H–N groups on the triangular face. The *d*-tart ion thereby avoids the steric repulsion that would be imposed on it if it should make a usual face-to-face contact with the *Δ* complex.

(+)-(*R,R*)-Tartrate dianion (abbreviated as *d*-tart ion hereafter) is known as an effective resolving agent not only for chiral amines but also for metal–amine complexes.[1,2] To elucidate how this simple chiral anion recognizes the chirality of these complexes, we and other groups have analyzed several crystal structures of *d*-tart salts with some tris(diamine)cobalt(III) complex cations.[3–10] They found a common face-to-face contact mode in which the two alcoholic and one carboxylic O atoms of the *d*-tart ion are hydrogen-bonded to the three H–N groups on the triangular face of the complex along the $C_3$ axis. When the complex has a *Λ* configuration, the above-mentioned multiple hydrogen bonds are favorably formed without any steric repulsion. On the other hand, the *Δ* complex imposes a steric repulsion on the distal carboxylato group of the *d*-tart ion if it should make a similar face-to-face contact with the triangular face. As a result, either the *d*-tart ion rotates its distal carboxylato group to maintain the face-to-face contact,[9] or the multiple hydrogen bonds to the triangular face are more or less damaged in number and/or in strength.[10] In this way, chiral discrimination with *d*-tart ion is effectively attained, particularly for those metal–amine complexes which have bulky substituents on their chelate rings, such as *lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ or *fac*- and *mer*-[Co(*cis*-chxn)$_3$]$^{3+}$ (chxn=1,2-cyclohexanediamine), because the bulkier the substituents, the more severe the steric repulsion that *Δ* enantiomers of these complexes impose on the distal carboxylato group.[9,10] However, most of the diastereomeric salts investigated are those of trivalent Co(III) complex cations, and only two divalent Ni(II) complex salts, i.e., *Λ,Λ*-[Ni(en)$_3$](*dl*-tart)·H$_2$O[11] and *Δ*-[Ni(en)$_3$]$_3$(*d*-tart)$_3$·4H$_2$O[11] (en=1,2-ethanediamine) having no substituent on each chelate, have been so far examined. In the present study, the crystal structures have been determined for a pair of diastereomeric salts of the divalent *lel*$_3$-[Ni(*trans*-chxn)$_3$]$^{2+}$ complex with *d*-tart ion, with the aim of elucidating how the valency of the complex cation affects the contact modes with the *d*-tart ion when the complex carries bulky substituents on the diamine chelates.

## Experimental

**Preparation of *Λ*-[Ni(*S,S*-chxn)$_3$](*d*-tart)·3H$_2$O (1).** To an aqueous solution of (1*S*,2*S*)-cyclohexanediamine[9] (2.9 g) in 20 ml of water, was added 1.5 g of nickel *d*-tartrate prepared by mixing sodium *d*-tartrate with an equivalent amount of NiCl$_2$·6H$_2$O in water. 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, 44.07; H, 8.98; N, 13.80%. Calcd for *Λ*-[Ni(*S,S*-chxn)$_3$](*d*-tart)·3H$_2$O (**1**): C, 43.79; H, 8.69; N, 13.93%.

**Preparation of *Δ*-[Ni(*R,R*-chxn)$_3$](*d*-tart)·5H$_2$O (2).** **2** was prepared in a similar manner using (1*R*,2*R*)-cyclohexanediamine.[9] Anal. Found: C, 41.27; H, 8.72; N, 13.01%. Calcd for *Δ*-[Ni(*R,R*-chxn)$_3$](*d*-tart)·5H$_2$O (**2**): C, 41.33; H,

Table 1. Crystallographic Data

| Crystal | 1 | 2 |
|---|---|---|
| Formula | $C_{18}H_{42}N_6Ni$, $C_4H_4O_6$, $3H_2O$ | $C_{18}H_{42}N_6Ni$, $C_4H_4O_6$, $5H_2O$ |
| $a$/Å | 10.093(2) | 11.197(2) |
| $b$/Å | 13.589(4) | 13.102(2) |
| $c$/Å | 22.011(4) | 22.402(2) |
| $V$/Å$^3$ | 3018.8(11) | 3286.4(10) |
| $Z$ | 4 | 4 |
| Fw | 603.4 | 639.4 |
| Space group | $P2_12_12_1$ | $P2_12_12_1$ |
| $T$/°C | 20 | 20 |
| $\lambda$/Å | 0.71069 | 0.71069 |
| $\rho_{calcd}$/g cm$^{-3}$ | 1.328 | 1.292 |
| $\rho_{obsd}$/g cm$^{-3}$ | 1.34 | 1.30 |
| $\mu$ (Mo $K\alpha$)/cm$^{-1}$ | 6.96 | 6.47 |
| $R$[a] | 0.044 | 0.047 |
| $R_w$[b] | 0.047 | 0.056 |

a) $R=\sum(||F_o|-|F_c||)/\sum|F_o|$. b) $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w(F_o)^2]^{1/2}$ and $w=1/(\sigma(F_o))^2$.

8.83; N, 13.14%.

**X-Ray Structure Analysis.** Cell dimensions were determined and refined on a Syntex R3 single-crystal diffractometer. The results are given in Table 1. The intensity data were collected by the $\omega$-scan technique with graphite-monochromated Mo $K\alpha$ radiation ($\lambda$=0.71069 Å). Three check reflections monitored after every 197 reflections showed no decrease in intensity during the data collection. Corrections for Lorentz and polarization effects were applied to the intensities, but no absorption and extinction corrections were made.

Each structure was solved by the well-established heavy-atom methods described in the previous work.[9,12,13] The anomalous dispersion coefficient was used for the Ni atom only,[14] and the absolute configuration of the complex cation was confirmed to be $\Lambda$ for **1** and $\Lambda$ for **2**.[15] The final $R$ and $R_w$ values are given in Table 1 together with the crystallographic data on **1** and **2**. Final positional parameters for non-hydrogen atoms are given in Tables 2 and 3 for **1** and **2**,

Table 2. Atomic Coordinates and Equivalent Temperature Factors for Non-Hydrogen Atoms in $\Lambda$-[Ni($S,S$-chxn)$_3$]($d$-tart)·$3H_2O$ (**1**)

| Atom | $x$ | $y$ | $z$ | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|
| Ni | 0.28897(6) | 0.85323(4) | 0.14173(3) | 2.3 |
| N1 | 0.1567(4) | 0.9765(3) | 0.1391(2) | 3.0 |
| N2 | 0.4037(4) | 0.9478(3) | 0.0849(2) | 2.6 |
| N3 | 0.1885(4) | 0.7826(3) | 0.0681(2) | 2.7 |
| N4 | 0.4174(4) | 0.7306(3) | 0.1317(2) | 2.8 |
| N5 | 0.1652(4) | 0.7823(3) | 0.2061(2) | 2.8 |
| N6 | 0.3840(4) | 0.9029(3) | 0.2221(2) | 3.0 |
| C1 | 0.2036(5) | 1.0492(3) | 0.0932(2) | 2.7 |
| C2 | 0.1467(6) | 1.1514(4) | 0.1043(2) | 4.1 |
| C3 | 0.2047(8) | 1.2281(4) | 0.0603(3) | 5.2 |
| C4 | 0.3564(7) | 1.2277(4) | 0.0633(3) | 5.3 |
| C5 | 0.4115(6) | 1.1254(4) | 0.0503(2) | 4.1 |
| C6 | 0.3556(5) | 1.0497(4) | 0.0949(2) | 2.7 |
| C7 | 0.2356(5) | 0.6793(3) | 0.0653(2) | 2.7 |
| C8 | 0.1978(6) | 0.6266(4) | 0.0065(2) | 4.2 |
| C9 | 0.2539(7) | 0.5209(4) | 0.0043(3) | 5.0 |
| C10 | 0.4034(7) | 0.5241(4) | 0.0103(3) | 4.5 |
| C11 | 0.4426(6) | 0.5759(4) | 0.0696(3) | 4.0 |
| C12 | 0.3876(5) | 0.6801(3) | 0.0730(2) | 2.6 |
| C13 | 0.1861(5) | 0.8288(3) | 0.2659(2) | 2.9 |
| C14 | 0.1271(6) | 0.7705(4) | 0.3193(2) | 4.2 |
| C15 | 0.1545(7) | 0.8216(5) | 0.3802(3) | 5.7 |
| C16 | 0.3038(7) | 0.8372(5) | 0.3882(2) | 5.9 |
| C17 | 0.3650(6) | 0.8947(5) | 0.3351(2) | 4.4 |
| C18 | 0.3346(5) | 0.8441(4) | 0.2743(2) | 3.0 |
| C19 | 0.7368(7) | 1.0437(4) | 0.2549(3) | 4.8 |
| C20 | 0.7639(5) | 0.9794(4) | 0.1983(2) | 3.3 |
| C21 | 0.7811(5) | 0.8711(4) | 0.2162(2) | 3.2 |
| C22 | 0.8154(5) | 0.8071(4) | 0.1598(2) | 3.4 |
| O1 | 0.8254(5) | 1.0480(3) | 0.2948(2) | 7.2 |
| O2 | 0.6298(5) | 1.0888(3) | 0.2549(2) | 6.7 |
| O3 | 0.6575(4) | 0.9915(3) | 0.1572(2) | 4.4 |
| O4 | 0.6656(4) | 0.8400(3) | 0.2472(2) | 4.5 |
| O5 | 0.7394(4) | 0.7362(3) | 0.1480(2) | 6.0 |
| O6 | 0.9180(3) | 0.8286(3) | 0.1322(2) | 4.4 |
| OW1 | 0.8267(5) | 0.6148(3) | 0.0534(2) | 6.8 |
| OW2 | 0.6308(5) | 0.6321(4) | 0.2483(2) | 7.3 |
| OW3 | 0.9117(7) | 0.5780(5) | 0.2225(4) | 14.8 |

Table 3. Atomic Coordinates and Equivalent Temperature Factors for Non-Hydrogen Atoms in $\Lambda$-[Ni($R,R$-chxn)$_3$]($d$-tart)·$5H_2O$ (**2**)

| Atom | $x$ | $y$ | $z$ | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|
| Ni | 0.32019(6) | 0.80530(6) | 0.35908(3) | 2.6 |
| N1 | 0.2361(4) | 0.7502(4) | 0.4382(2) | 2.9 |
| N2 | 0.4326(4) | 0.6771(4) | 0.3754(2) | 3.3 |
| N3 | 0.1967(4) | 0.7218(3) | 0.3044(2) | 3.4 |
| N4 | 0.3985(4) | 0.8327(3) | 0.2738(2) | 3.1 |
| N5 | 0.2117(4) | 0.9398(4) | 0.3527(2) | 3.5 |
| N6 | 0.4337(4) | 0.9084(4) | 0.4061(2) | 3.3 |
| C1 | 0.2712(5) | 0.6411(4) | 0.4457(2) | 2.9 |
| C2 | 0.2366(6) | 0.5977(5) | 0.5065(3) | 4.1 |
| C3 | 0.2821(7) | 0.4865(5) | 0.5142(3) | 5.3 |
| C4 | 0.4141(7) | 0.4821(5) | 0.5047(3) | 4.7 |
| C5 | 0.4483(6) | 0.5229(5) | 0.4427(3) | 4.2 |
| C6 | 0.4066(5) | 0.6325(4) | 0.4352(2) | 3.1 |
| C7 | 0.2044(5) | 0.7649(4) | 0.2426(2) | 3.1 |
| C8 | 0.1360(6) | 0.7022(6) | 0.1969(3) | 5.0 |
| C9 | 0.1548(7) | 0.7441(6) | 0.1349(3) | 6.5 |
| C10 | 0.2854(8) | 0.7491(7) | 0.1192(3) | 6.7 |
| C11 | 0.3545(6) | 0.8143(6) | 0.1646(2) | 4.5 |
| C12 | 0.3366(6) | 0.7721(4) | 0.2268(2) | 3.2 |
| C13 | 0.2482(6) | 1.0094(5) | 0.4017(2) | 3.3 |
| C14 | 0.1943(7) | 1.1160(5) | 0.3953(3) | 4.9 |
| C15 | 0.2370(9) | 1.1863(6) | 0.4457(3) | 7.5 |
| C16 | 0.3721(9) | 1.1902(6) | 0.4481(3) | 7.5 |
| C17 | 0.4293(7) | 1.0855(6) | 0.4523(3) | 5.3 |
| C18 | 0.3839(6) | 1.0144(4) | 0.4023(2) | 3.6 |
| C19 | 0.9136(6) | 0.6921(5) | 0.4132(2) | 4.1 |
| C20 | 0.7971(5) | 0.6837(5) | 0.3771(2) | 3.5 |
| C21 | 0.8195(6) | 0.6469(4) | 0.3133(2) | 3.4 |
| C22 | 0.7013(5) | 0.6458(4) | 0.2784(2) | 3.4 |
| O1 | 0.9894(4) | 0.7544(4) | 0.3929(2) | 4.9 |
| O2 | 0.9177(5) | 0.6420(4) | 0.4597(2) | 6.3 |
| O3 | 0.7178(5) | 0.6168(4) | 0.4066(2) | 7.0 |
| O4 | 0.8721(4) | 0.5484(4) | 0.3130(2) | 5.8 |
| O5 | 0.6652(4) | 0.5604(3) | 0.2600(2) | 5.0 |
| O6 | 0.6477(4) | 0.7290(3) | 0.2730(2) | 4.7 |
| OW1 | 0.5832(5) | 1.0293(3) | 0.2323(2) | 5.2 |
| OW2 | 0.3308(4) | 1.4220(4) | 0.1691(2) | 5.0 |
| OW3 | 0.3017(6) | 1.3675(4) | 0.3229(2) | 7.3 |
| OW4 | −0.0756(5) | 0.9262(4) | 0.3347(2) | 7.6 |
| OW5 | 0.0864(7) | 1.4520(6) | 0.2888(3) | 12.4 |

respectively. Tables of the full listing of the crystallographic data, hydrogen atom coordinates, anisotropic thermal parameters for non-hydrogen atoms, bond distances and angles, hydrogen bond distances and angles, and a list of observed and calculated structure factors are deposited as Document No. 9119 at the Office of the Editor of Bull. Chem. Soc. Jpn.

## Results and Discussion

**Contact Modes in 1 and 2.** There has been found a familiar face-to-face contact in the *Λ*-[Ni(*S,S*-chxn)$_3$](*d*-tart)·3H$_2$O (**1**), which is depicted in Fig. 1 with the numbering schemes adopted for the respective atoms. The geometries of the complex cation in **1** are in complete agreement with those reported previously.[16] The *d*-tart ion takes a normal conformation and directs its four O atoms (O2, O3, O4, and O5) to the triangular face of the complex along the $C_3$ axis. Of the four, two alcoholic and one carboxylic O atoms (O3, O4, and O5) are triply hydrogen-bonded to the three H–N groups (H2–N2, H2–N6, and H2–N4) on the triangular face without any steric repulsion. The two O atoms (O1 and O2) of the distal carboxylato group are far from any of the bulky chxn ligands, but they are hydrogen-bonded to the H1–N5 and H1–N4 groups of another neighboring complex, which are directed along the $C_2$ axis. Thus, the above contact mode resembles those so far found in some diastereomeric salts of trivalent *Λ* Co(III) complexes such as *Λ*-*lel*$_3$-[Co(en)$_3$]X(*d*-tart)·5H$_2$O[3,5,6] (X=Cl or Br), *Λ*-[Co(sen)]Cl(*d*-tart)·6H$_2$O[4,6] (sen=*N,N'*-bis(2-aminoethyl)-2-[[(2-aminoethyl)-amino]methyl]-2-methyl-1,3-propanediamine), and *Λ*-*lel*$_3$-[Co(*S,S*-chxn)$_3$]Cl(*d*-tart)·2H$_2$O (**3**).[9] It is then confirmed that a familiar face-to-face contact is maintained even in the divalent Ni(II) complex salt with bulky diamine chelates, provided that the complex has a *Λ* configuration. Actually, a similar face-to-face contact mode has been found in the *Λ,Λ*-[Ni(en)$_3$](*dl*-tart)·H$_2$O[11] as well, where the *d*-tart ion makes such a contact with the *Λ* enantiomer only and the *l*-tart ion does with the *Δ* enantiomer only, as expected. The hydrogen bonds pertinent to these face-to-face contact modes are numerically compared in Table 4.

In contrast, no such face-to-face contact mode is present in the *Λ*-[Ni(*R,R*-chxn)$_3$](*d*-tart)·5H$_2$O (**2**). Instead, each *d*-tart ion is sandwiched between the two triangular faces and connects them through the two "deformed" contact modes in **2**, as seen in Fig. 2. One of them is depicted down to the $C_3$ axis in Fig. 3 together with the atom numbering schemes, where the *d*-tart ion with a usual conformation directs the three O atoms (O1, O2, and O4) to the triangular face, but only the O1 atom is disposed close enough to form a bifurcated hydrogen bond to the H1–N1 and H1–N3 groups on the triangular face. The O2 atom is hydrogen-bonded to the two H–N groups (H2–N1 and H2–N6) directed along the $C_2$ axis of another neighboring complex and the O4 atom is to a water molecule.

The other "deformed" contact mode is the one in which the remaining three O atoms (O3, O5, and O6) of the *d*-tart ion are directed to the triangular face of another complex cation in the above layer and similar hydrogen bonds are formed without any steric repulsion; O6 to H1–N4 on the triangular face and to H–OW3 (water molecule), O5 to H2–N4 and H2–N5 directed along the $C_2$ axis of the neighboring complex in the same layer, and O5 to H–OW1 (water molecule). Consequently, it is evident that the overall hydrogen-bonding interaction of the *d*-tart ion with the triangular face of the complex is by far weaker in **2** than in **1** or **3**,

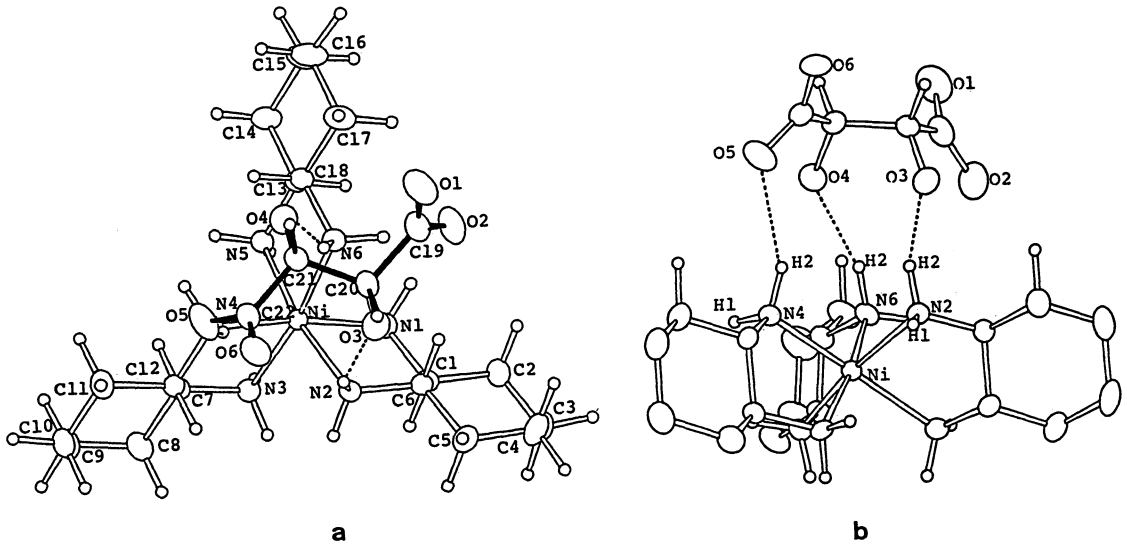


Fig. 1. Drawing of the face-to-face contact mode found in *Λ*-[Ni(*S,S*-chxn)$_3$](*d*-tart)·3H$_2$O (**1**), as viewed down (a) and normal to (b) the $C_3$ axis of the complex. Possible hydrogen bonds are shown by broken lines and most of the CH protons are omitted for clarity in (b).

Table 4. Comparison of Hydrogen-Bond Distances and Angles in the Face-to-Face Contacts of *d*-Tart Ion with Some Relevant *Λ* Complex Cations

| *d*-tart<br>Complex ion | O3<br>H(N2) | O3<br>H(N6) | O4<br>H(N6) | O4<br>H(N4) | O5<br>H(N4) | O5<br>H(N2) |
|---|---|---|---|---|---|---|
| | | | Distances of O··H/Å | | | |
| *Λ*-$[Co(en)_3]^{3+}$ | 2.17 | 2.50 | 2.05 | 2.34 | 2.06 | 2.47 |
| *Λ*-$[Co(sen)]^{3+}$ | 2.06 | 2.50 | 2.01 | 2.34 | 2.04 | 2.62 |
| *Λ*-$[Co(chxn)_3]^{3+}$ | | 2.44 | 2.06 | | 1.95 | 2.14 |
| *Λ*-$[Ni(en)_3]^{2+}$ | 2.23 | | 2.14 | | 1.94 | |
| *Λ*-$[Ni(chxn)_3]^{2+}$ | 2.19 | | 2.10 | | 2.34 | |
| | | | Distances of O··N/Å | | | |
| *Λ*-$[Co(en)_3]^{3+}$ | 3.072(7) | 3.212(8) | 2.976(8) | 3.050(8) | 3.005(8) | 3.173(8) |
| *Λ*-$[Co(sen)]^{3+}$ | 2.930(4) | 3.289(5) | 2.905(4) | 3.150(4) | 2.927(5) | 3.391(4) |
| *Λ*-$[Co(chxn)_3]^{3+}$ | | 3.096(9) | 2.938(9) | | 2.870(8) | 3.036(9) |
| *Λ*-$[Ni(en)_3]^{2+}$ | 3.120(4) | | 3.093(4) | | 2.899(4) | |
| *Λ*-$[Ni(chxn)_3]^{2+}$ | 3.074(5) | | 3.019(5) | | 3.270(6) | |
| | | | Angles of O··H–N/° | | | |
| *Λ*-$[Co(en)_3]^{3+}$ | 149 | 128 | 153 | 127 | 157 | 127 |
| *Λ*-$[Co(sen)]^{3+}$ | 144 | 135 | 148 | 138 | 146 | 134 |
| *Λ*-$[Co(chxn)_3]^{3+}$ | | 122 | 145 | | 155 | 149 |
| *Λ*-$[Ni(en)_3]^{2+}$ | 147 | | 158 | | 161 | |
| *Λ*-$[Ni(chxn)_3]^{2+}$ | 146 | | 153 | | 154 | |

Each H atom is allocated an idealized position on the basis of each H–N bond length of 1.0 Å and a tetrahedral angle around each N atom. *Λ*-$[Co(en)_3]^{3+}$: *Λ*-$[Co(en)_3]Br(d\text{-tart})\cdot 5H_2O$ (Ref. 3), *Λ*-$[Co(sen)]^{3+}$: *Λ*-$[Co(sen)]Cl(d\text{-tart})\cdot 6H_2O$ (Ref. 4), *Λ*-$[Co(chxn)_3]^{3+}$: *Λ*-$[Co(S,S\text{-chxn})_3]Cl(d\text{-tart})\cdot 2H_2O$ (Ref. 9), *Λ*-$[Ni(en)_3]^{2+}$: *Λ*, *Λ*-$[Ni(en)_3](dl\text{-tart})\cdot H_2O$ (Ref. 11), and *Λ*-$[Ni(chxn)_3]^{2+}$: **1** (this work).

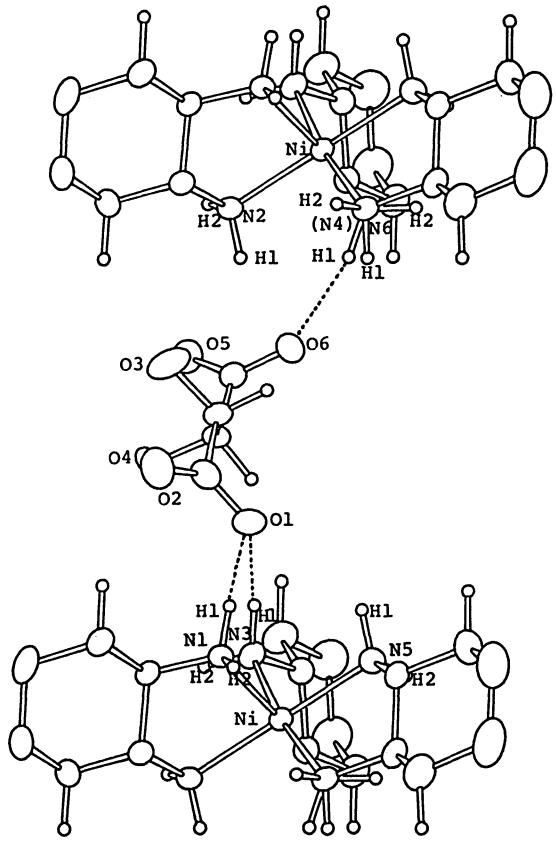


Fig. 2. Drawing of the two "deformed" contact modes found in **2**, as viewed normal to the $C_3$ axis of the complex. Possible hydrogen bonds are shown by broken lines and most of the CH protons are omitted for clarity.

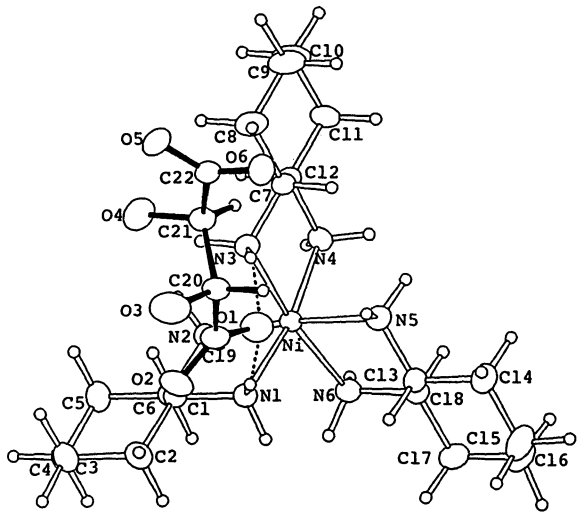


Fig. 3. Drawing of one of the "deformed" contact modes found in *Λ*-$[Ni(R,R\text{-chxn})_3](d\text{-tart})\cdot 5H_2O$ (**2**). Possible hydrogen bonds are shown by the broken lines.

but the *d*-tart ion experiences no steric repulsion from the bulky chxn ligands of the *Λ* complex in **2**.

On the other hand, the familiar face-to-face contact mode has been found in the corresponding *Λ* Co(III) complex, *Λ*-*lel*$_3$-$[Co(R,R\text{-chxn})_3]Cl(d\text{-tart})\cdot 2H_2O$ (**4**),[9] in which the *d*-tart ion is obliged to rotate its distal carboxylato group greatly so as to avoid the steric repulsion that would be otherwise imposed on it by one of the chxn ligands. That is, the *d*-tart ion maintains

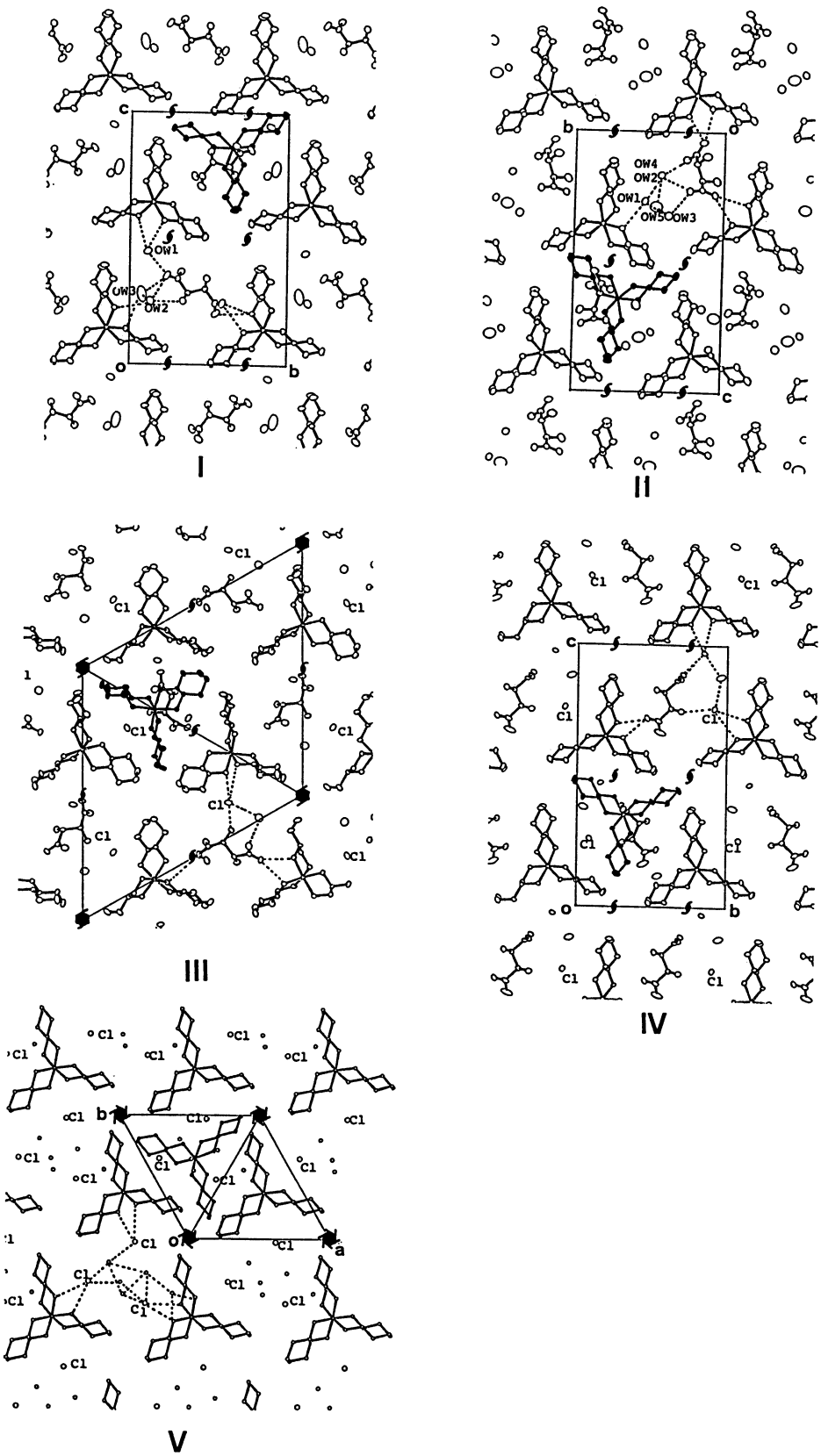


Fig. 4. Comparison of the packing modes in the relevant crystal structures. I: *Λ*-[Ni(*S,S*-chxn)$_3$](*d*-tart)·3H$_2$O (**1**), II: *Λ*-[Ni(*R,R*-chxn)$_3$](*d*-tart)·5H$_2$O (**2**), III: *Λ*-[Co(*S,S*-chxn)$_3$]Cl(*d*-tart)·2H$_2$O (**3**), IV: *Λ*-[Co(*R,R*-chxn)$_3$]Cl(*d*-tart)·2H$_2$O (**4**), and V: *Λ*-[Co(*S,S*-chxn)$_3$]Cl$_3$·5H$_2$O (**5**).

Table 5. Comparison of Space Groups and Cell Constants among Some Related Crystals

| Crystals | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Space group | $P2_12_12_1$ | $P2_12_12_1$ | $P6_3$ | $P2_12_12_1$ | $P6_1$ |
| $a$/Å | 10.093 | 11.197 | 22.068 | 9.666 | 12.34 |
| $b$/Å | 13.589 | 13.102 | 22.068 | 12.999 | 12.34 |
| $c$/Å | 22.011 | 22.402 | 10.492 | 22.950 | 33.52 |

**1**: *Λ*-[Ni(*S,S*-chxn)$_3$](*d*-tart)·3H$_2$O, **2**: *Δ*-[Ni(*R,R*-chxn)$_3$](*d*-tart)·5H$_2$O, **3**: *Λ*-[Co(*S,S*-chxn)$_3$]-Cl(*d*-tart)·2H$_2$O, **4**: *Λ*-[Co(*R,R*-chxn)$_3$]Cl(*d*-tart)·2H$_2$O, and **5**: *Λ*-[Co(*S,S*-chxn)$_3$]Cl$_3$·5H$_2$O.

the face-to-face contact even with the *Δ* complex at the expense of the conformational energy. This is because the accompanying conformational destabilization is compensated for the most part in **4** by the intimate hydrogen bonds to the neighboring complex cations,[9] and also because the face-to-face contact with the trivalent Co(III) complex cation leads to a substantial stabilization. Then, the absence of the face-to-face contact in **2** implies that the neighboring complexes are not appropriately disposed in **2** to assist the conformational change, and/or that the attractive force of the divalent Ni(II) complex is not strong enough for the *d*-tart ion to make a face-to-face contact with its *Δ* enantiomer against the accompanying steric repulsion. So, the packing modes of the composite ions in **2** need to examine and compare with those of the relevant diastereomeric salts before we proceed to settle the above problem.

**Comparison of Packing Modes.** Now, the packing modes in the present crystals **1** and **2** are compared with those in the relevant diastereomeric salts of the Co(III) complex cations, *Λ-lel*$_3$-[Co(*R,R*-chxn)$_3$]Cl(*d*-tart)·2H$_2$O (**3**) and *Δ-lel*$_3$-[Co(*R,R*-chxn)$_3$]Cl(*d*-tart)·2H$_2$O (**4**).[9] The space groups and the cell dimensions of the four crystals are listed in Table 5 together with those of *Λ-lel*$_3$-[Co(*S,S*-chxn)$_3$]Cl$_3$·5H$_2$O (**5**).[17] The structures of these five crystals are depicted in Fig. 4, where each structure is projected along the *a*-axis for **1**, **2**, and **4**, and along the *c*-axis for **3** and **5**. The range projected is 0—1/2 for the former three, −1/4—1/4 for **3**, and −1/12—1/12 for **5**, and each range (layer) has a thickness of ca. 5 Å. To each of these structures, one complex is added in black to demonstrate that the complex is disposed at that position both above and below the layer.

It is evident in Fig. 4 that quite similar arrangements of the complex cations are found not only in **1**, **2**, and **4**, but also in **5**; each complex cation is arranged in a similar manner in the layer of ca. 5 Å thickness with its $C_3$ axis directed parallel to the projection axis and with the counterion(s) and water molecules packed in a cavity thus formed. In this respect, crystal **3** has also similar arrangements of the complex cations as well as the counterions and water molecules, though the $C_3$ axis of each complex is directed not exactly parallel to the projection axis in **3**. Furthermore, since each layer is related to the upper and lower layers by the two- and six-fold screw axes in **1**—**4** and in **5**, respectively, it follows that the counterion(s) is packed in a cavity surrounded by the five complex cations in all of the five crystal structures. Therefore, it can be said that the five crystals bear a close resemblance to one another with respect to the spatial arrangements of the complex cations as well as the counterions, and that their packing modes are governed primarily by the bulky complex cations.

The discussions presented above indicate that the face-to-face contact mode might be adopted in **2** on the spatial grounds mentioned above. However, no such mode is present in **2**, suggesting that the divalent Ni(II) complex is not attractive enough for the *d*-tart ion to make such a contact with its *Δ* enantiomer against the accompanying steric repulsion imposed on the distal carboxylato group. In fact, the acidity of the amino protons should be much lower in the Ni(II) complex, because the central metal ion is divalent and the donation of the lone-pair electrons on the amino groups is less pronounced in the Ni(II) complex than in the low-spin Co(III) complex. Consequently, it is concluded that the contact modes with the *d*-tart ion are readily subjected to the steric demands of the composite ions in the Ni(II) complex salts, while the face-to-face contact is maintained at all costs in the Co(III) complex salts[7—10] where it leads to a substantial stabilization.

Finally, it seems noteworthy that the two "deformed" contact modes found in **2** are quite similar to those found earlier in the *Δ*-[Ni(en)$_3$]$_3$(*d*-tart)$_3$·4H$_2$O (**6**),[11] where each *d*-tart ion is sandwiched between the two triangular faces of the two *Δ* complex cations and it directs to the respective faces the two O atoms of one carboxylato group and one alcoholic O atom on the asymmetric carbon atom to which the other carboxylato group is attached, like in **2**, forming intimate hydrogen bonds to the H–N groups on them. In addition, each *d*-tart ion adopting these "deformed" contact modes in **2** also serves to connect directly the two complex cations in the same layer as it is in, through the two bifurcated hydrogen bonds (N1–H2··O2··H2–N6 and N4–H2··O5··H2–N5), as seen in II shown in Fig. 4, and similar roles are played by each *d*-tart ion in **6**. Consequently, it is fairly reasonable that the "deformed" contact modes are adopted in the Ni(II) complex salts when the face-to-face contact is prohibited by the steric repulsion, i.e., when the complex carries bulky substituents on the chelate rings and has a *Δ* configuration.

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