April, 1991] *Bull. Chem. Soc. Jpn., 64, 1183—1191 (1991)*

# Structural Study of Optical Resolution. XV. Chiral Discrimination of the Facial Isomer of the Tris((*R*,*S*)-1,2-cyclohexanediamine)cobalt(III) Cation with (*R*,*R*)-Tartrate Anion

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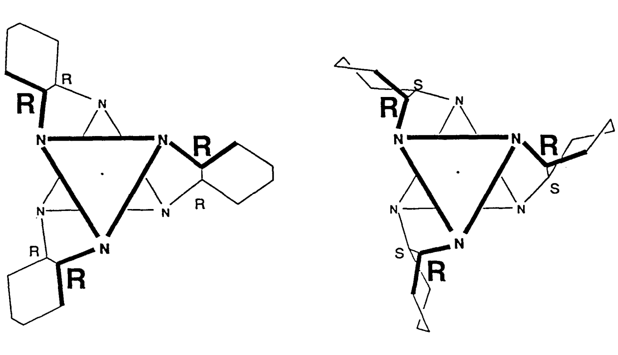
(Received October 18, 1990)

Crystal structures of the two diastereomeric salts of the title *Δ* complex cation with (*R*,*R*)-tartrate anion, *Δ*-*fac*-[Co(*R*,*S*-chxn)$_3$](ClO$_4$)(d-tart)·*m*H$_2$O (**1**) and *Δ*-*fac*-[Co(*R*,*S*-chxn)$_3$]Cl(d-tart)·*n*H$_2$O (**2**) (*R*,*S*-chxn=(*R*,*S*)-1,2-cyclohexanediamine and d-tart=dextro-rotatory (*R*,*R*)-tartrate dianion), have been determined by single crystal X-ray diffraction techniques. The former crystal **1** is orthorhombic with the space group $P22_12_1$, $a$=12.358(3), $b$=22.094(5), $c$=32.770(7) Å, and $Z$=12, while the latter **2** is trigonal with the space group $P3_121$, $a$=15.367(7), $c$=26.208(4) Å, and $Z$=6. In **1** are found two similar face-to-face contact modes in both of which the d-tart$^{2-}$ ion directs its four almost coplanar O atoms to the complex along the C$_3$ axis, and three of them, two alcoholic and one carboxylic, are triply hydrogen-bonded to the three N–H protons on one of the triangular faces of the *Δ* complex denoted as the *Δ*-*cis* RRR face, where R stands for the chirality of the carbon atom adjacent to the N–H group hydrogen-bonded to the d-tart$^{2-}$ ion. The other triangular face of the complex denoted as the *Δ*-*cis* SSS face is so crowded that only two O atoms of the d-tart$^{2-}$ ion are hydrogen-bonded to the face. In **2** is found one face-to-face contact mode in which the d-tart$^{2-}$ ion approaches the *Δ* complex similarly, but the three O atoms are each placed midway between two of the three N–H protons on the triangular *Δ*-*cis RRR* face to form three bifurcated hydrogen bonds to them, and the d-tart$^{2-}$ ion tactfully avoids the steric repulsion marginally by inclining its molecular plane a little relative to the triangular face at the least expense of the multiple hydrogen bonds to the face. Based on the assumption that the face-to-face contact mode found in **2** is the most probable interaction mode conceivable in solution, the elution order and separation factor obtained by ion-exchange chromatography for some related [Co(chxn)$_3$]$^{3+}$ complexes are rationally interpreted.

It is well-known that naturally occurring dextrorotatory (*R*,*R*)-tartrate anion (abbreviated as d-tart$^{2-}$ hereafter) serves as an effective resolving agent for many chiral metal-amine complex cations, and several studies have been reported on the mechanisms by which the d-tart$^{2-}$ anion discriminates the chirality of these complexes in solution and in the solid state.[1,2] In the preceding paper of this series,[3] a crystal structure analysis has been carried out on a pair of diastereomeric salts of the *lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ complex (chxn=1,2-cyclohexanediamine) with d-tart$^{2-}$ and Cl$^-$ ions. It has been found there that the d-tart$^{2-}$ anion makes a favorable face-to-face contact with the *Λ*-*lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ complex through multiple hydrogen bonds to the three N–H protons on one of the two triangular faces along the C$_3$ axis. In the *Δ*-*lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ complex salt, on the other hand, the d-tart$^{2-}$ ion is forced to rotate its distal carboxylate group when it makes a similar face-to-face contact, because one of the bulky chxn ligands of the *Δ* complex would otherwise impose a severe steric repulsion on the carboxylate group. These observations indicate that the *Λ* complex has two favorable triangular faces which allow a smooth access of the d-tart$^{2-}$ ion along the C$_3$ axis. These faces are denoted here as the *Λ*-*trans* SSS face (Fig. 1), where S stands for the chirality of the carbon atom adjacent to the N–H group hydrogen-bonded to the d-tart$^{2-}$ ion. In contrast, the two *Δ*-*trans* RRR faces (Fig. 1) possessed by the *Δ* complex serve only as a "less-favorable" interaction site, as mentioned above. In this way, highly efficient chiral discrimination attained in these systems has been reasonably interpreted in terms of the steric repulsion expected stereoselectively between the distal carboxylate group and one of the chxn ligands on the *Δ* complex.

Ab initio MO calculations performed on d-tart$^{2-}$ ion[3] have revealed that the rotation of the carboxylate group leads to a substantial destabilization of isolated d-tart$^{2-}$ ion, which is fully compensated in the *Δ*-*lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ complex salt, by the multiple hydrogen bonds not only to the triangular face of the



( a )      ( b )

Fig. 1. A schematic presentation of the *Δ*-*trans* RRR face (a) and the *Δ*-*cis* RRR face (b). The *Λ*-*trans* SSS and *Λ*-*cis* SSS faces are enantiomeric to (a) and (b), respectively, and the *Δ*-*cis SSS* face is on the opposite side of the *Δ*-*cis* RRR face in (b) and is enantiomeric to the *Λ*-*cis* RRR face.

complex but also to another neighboring $\Delta$ complex. However, d-tart$^{2-}$ ion does not readily assume such an unstable conformation, particularly in solution where another neighboring complex is absent to support the conformational change. Therefore, d-tart$^{2-}$ ion has to adopt a contact mode different from that found in the $\Delta$ complex salt, when it makes a face-to-face contact in solution with the "less-favorable" $\Delta$-*trans* RRR face of the $\Delta$ complex. In the present study, X-ray crystal analyses have been made on the two salts with d-tart$^{2-}$ ion of the $\Delta$-*fac*-$[Co(\textit{cis}\text{-chxn})_3]^{3+}$ complex which has one triangular $\Delta$-*cis* RRR face (Fig. 1) similar to the "less-favorable" $\Delta$-*trans* RRR face of the $\Delta$-*lel*$_3$-$[Co(\textit{trans}\text{-chxn})_3]^{3+}$ complex, in addition to one $\Delta$-*cis* SSS face (Fig. 1), in a hope to search for another interaction mode by which d-tart$^{2-}$ ion makes a face-to-face contact with the "less-favorable" face of these $\Delta$ complexes having bulky chxn ligands.

## Experimental

**X-Ray Structure Analysis.** $\Delta$-*fac*-$[Co(\textit{cis}\text{-chxn})_3](ClO_4)(\text{d-tart})\cdot m H_2O$ (**1**) formed on mixing $\Delta$-*fac*-$[Co(\textit{cis}\text{-chxn})_3](ClO_4)_3$[4] with sodium d-tartrate in water, was dissolved in water, and orange crystals were grown by slow evaporation. Orange crystals of $\Delta$-*fac*-$[Co(\textit{cis}\text{-chxn})_3]Cl(\text{d-tart})\cdot n H_2O$ (**2**) were obtained in a similar manner starting with the corresponding chloride salt.[4] X-Ray data collection was carried out on a Syntex R3 and a Rigaku AFC5 diffractometer for **1** and **2**, respectively with graphite-monochromated Mo$K\alpha$ radiation. The crystal data are summarized in Table 1. The structures were solved by the same procedures as applied previously.[3] The number $m$ and the positions of water molecules present in **1** were not precisely determined because some of them were disordered. The crystal **2** was not big enough to collect ample reflections with $|F_o|>3\sigma(F_o)$, so that the $R$ value was converged only to 9.5%, and since some water molecules were also disordered, they were not unambiguously allocated and counted. However, the molecular structures thus derived were proved to be reasonable both in **1** and **2**, and the accompanying uncertainties had no practical influence on the validity of our discussions described below. With the coordinates of the non-hydrogen atoms thus determined, all hydrogen atoms, except those of water molecules and hydroxyl groups, were assigned idealized positions on the basis of a bond length of 1.09 Å and 1.00 Å for each C–H and N–H bonds, respectively, and a tetrahedral angle around each carbon and nitrogen atoms.

All the computations were done on a HITAC M-680H computer using the programs UNICS-III[5] and ORTEP.[6]

**Chromatographic Separation.** A racemic mixture of *fac*-$[Co(\textit{cis}\text{-chxn})_3]^{3+}$ and its related complexes[4,7] were absorbed on an SP-Sephadex ion-exchange column and were eluted with aqueous 0.2 mol dm$^{-3}$ sodium d-tartrate. Experimental conditions used were the same as described previously.[3] Elution orders and conventional separation factors were determined as before by monitoring the absorption and circular dichroism spectra of the effluents.[4,7]

## Results and Discussion

**X-Ray Crystallography.** All the allocated atomic coordinates in $\Delta$-*fac*-$[Co(\textit{cis}\text{-chxn})_3](ClO_4)(\text{d-tart})\cdot m H_2O$ (**1**) and $\Delta$-*fac*-$[Co(\textit{cis}\text{-chxn})_3]Cl(\text{d-tart})\cdot n H_2O$ (**2**) except for hydrogen atoms are given in Tables 2 and 3, respectively.[8] The bond distances and angles of the composite ions in both crystals are found to be fairly reasonable and they are deposited as Document No. 9108 at the Office of the Editor of Bull. Chem. Soc. Jpn.[8] The numbering schemes adopted for the respective atoms are those given in several figures that follow.

In the former crystal **1**, the asymmetric unit is composed of three sets each of which is represented as $\Delta$-*fac*-$[Co(\textit{cis}\text{-chxn})_3](ClO_4)(\text{d-tart})\cdot m H_2O$, each complex cation directs its $C_3$ axis almost parallel to the c-axis of the unit cell, and each d-tart$^{2-}$ ion is sandwiched between the two complex cations. In the

Table 1. Crystallographic Data

| Crystal | **1** | **2** |
|---|---|---|
| Formula | $C_{18}H_{42}N_6Co$,<br>$C_4H_4O_6\cdot ClO_4\cdot H_2O$$^{a)}$ | $C_{18}H_{42}N_6Co$,<br>$C_4H_4O_6\cdot Cl\cdot 2.75H_2O$$^{a)}$ |
| $a$/Å | 12.358(3) | 15.367(7) |
| $b$/Å | 22.094(5) | |
| $c$/Å | 32.770(7) | 26.208(4) |
| $V$/Å$^3$ | 8948(4) | 5357(4) |
| $Z$ | 12 | 6 |
| Space group | $P2\,2_12_1$ | $P3_12\,1$ |
| $T$/°C | 20 | 20 |
| $\lambda$/Å | 0.71069 | 0.71069 |
| $\rho$ calcd/g cm$^{-3}$ $^{b)}$ | 1.486 | 1.183 |
| $\rho$ obsd/g cm$^{-3}$ | 1.469 | 1.330 |
| $\mu$ (Mo $K\alpha$)/cm$^{-1}$ $^{b)}$ | 7.255 | 5.988 |
| $R$$^{c)}$ | 0.088 | 0.095 |
| $R_w$$^{d)}$ | 0.077 | 0.109 |

a) Numbers of water molecules that could be located on a difference map and could be refined.
b) Values based on the above tentative formulae. c) $R=\sum(||F_o|-|F_c||)/\sum|F_o|$.
d) $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Table 2. Atomic Coordinates (×10$^4$) and Equivalent Temperature Factors for Non-Hydrogen Atoms in $\Delta$-*fac*-[Co(*cis*-chxn)$_3$](ClO$_4$)(d-tart)·$m$H$_2$O (**1**)

| Atom | *x* | *y* | *z* | $B_{eq}$$^{a)}$/Å$^2$ |
|---|---|---|---|---|
| CoA | 5966(1) | 3193(1) | 4349(0) | 2.7 |
| N1A | 4705(8) | 2939(4) | 4685(3) | 2.8 |
| N2A | 4891(7) | 3674(4) | 4026(3) | 2.4 |
| N3A | 6318(9) | 3875(5) | 4737(3) | 3.7 |
| N4A | 7134(8) | 3536(4) | 4005(3) | 2.9 |
| N5A | 6963(8) | 2658(5) | 4655(3) | 3.2 |
| N6A | 5751(8) | 2486(5) | 3975(3) | 3.8 |
| C1A | 3700(10) | 3268(6) | 4547(3) | 3.0 |
| C2A | 3471(10) | 3860(6) | 4790(4) | 3.1 |
| C3A | 2465(11) | 4181(6) | 4641(4) | 3.7 |
| C4A | 2626(11) | 4331(6) | 4176(4) | 4.5 |
| C5A | 2872(12) | 3789(6) | 3929(4) | 4.1 |
| C6A | 3816(10) | 3399(6) | 4099(3) | 3.2 |
| C7A | 7230(11) | 4259(6) | 4573(4) | 3.4 |
| C8A | 8295(10) | 4096(7) | 4762(4) | 4.3 |
| C9A | 9250(11) | 4449(7) | 4580(4) | 4.7 |
| C10A | 9268(12) | 4376(7) | 4117(4) | 5.2 |
| C11A | 8173(12) | 4505(6) | 3910(4) | 4.4 |
| C12A | 7240(11) | 4188(5) | 4098(4) | 3.5 |
| C13A | 7067(12) | 2031(5) | 4443(4) | 3.8 |
| C14A | 6354(13) | 1578(6) | 4663(4) | 4.3 |
| C15A | 6436(16) | 966(6) | 4435(5) | 6.7 |
| C16A | 6041(15) | 1052(6) | 3986(4) | 5.7 |
| C17A | 6743(16) | 1514(7) | 3760(5) | 7.0 |
| C18A | 6801(11) | 2139(6) | 4004(4) | 3.9 |
| C19A | 6418(10) | 4497(6) | 2732(4) | 3.3 |
| C20A | 5522(10) | 4019(5) | 2849(3) | 2.2 |
| C21A | 6012(10) | 3391(5) | 2847(3) | 2.7 |
| C22A | 5040(10) | 2935(5) | 2898(3) | 2.0 |
| O1A | 6791(8) | 4459(4) | 2384(3) | 5.1 |
| O2A | 6618(7) | 4904(4) | 2988(3) | 4.1 |
| O3A | 5144(7) | 4173(3) | 3241(2) | 3.6 |
| O4A | 6797(7) | 3335(4) | 3160(2) | 3.5 |
| O5A | 4838(7) | 2710(4) | 3226(2) | 3.6 |
| O6A | 4515(7) | 2861(4) | 2572(3) | 3.7 |
| ClA | 8236(3) | 2253(2) | 2535(1) | 5.2 |
| O7A | 7319(11) | 2082(6) | 2738(5) | 11.0 |
| O8A | 8554(9) | 2837(4) | 2693(4) | 7.6 |
| O9A | 9059(9) | 1842(5) | 2564(5) | 12.6 |
| O10A | 7835(16) | 2330(6) | 2122(4) | 14.1 |
| CoB | 7629(1) | 3501(1) | 7511(0) | 2.1 |
| N1B | 8604(8) | 3079(4) | 7903(3) | 2.4 |
| N2B | 7512(8) | 2705(4) | 7238(2) | 2.1 |
| N3B | 6366(7) | 3354(4) | 7877(3) | 2.4 |
| N4B | 6554(8) | 3824(4) | 7113(3) | 2.5 |
| N5B | 7851(8) | 4310(4) | 7787(3) | 2.9 |
| N6B | 8836(8) | 3730(4) | 7143(3) | 2.8 |
| C1B | 8765(10) | 2402(5) | 7796(3) | 2.9 |
| C2B | 7934(12) | 2003(5) | 8034(3) | 3.6 |
| C3B | 8039(13) | 1331(6) | 7868(4) | 4.6 |
| C4B | 7761(12) | 1337(5) | 7402(4) | 3.8 |
| C5B | 8517(12) | 1718(5) | 7161(4) | 3.6 |
| C6B | 8555(10) | 2366(5) | 7317(3) | 2.3 |
| C7B | 5352(9) | 3565(5) | 7689(4) | 2.6 |
| C8B | 4996(11) | 4216(5) | 7827(4) | 4.0 |
| C9B | 3968(11) | 4419(6) | 7615(5) | 4.4 |
| C10B | 4178(11) | 4440(6) | 7145(5) | 5.2 |
| C11B | 4509(12) | 3793(7) | 6981(5) | 5.2 |
| C12B | 5491(10) | 3556(6) | 7214(3) | 3.1 |
| C13B | 8821(9) | 4614(5) | 7596(3) | 2.4 |
| C14B | 9835(10) | 4507(6) | 7827(4) | 3.3 |
| C15B | 10784(11) | 4814(7) | 7643(5) | 4.9 |
| C16B | 10955(11) | 4599(6) | 7196(5) | 4.6 |
| C17B | 9923(12) | 4662(5) | 6945(4) | 4.0 |
| C18B | 8879(12) | 4424(5) | 7142(4) | 3.7 |
| C19B | 5792(11) | 2647(5) | 5776(4) | 3.3 |
| C20B | 6858(10) | 2554(6) | 6022(3) | 3.4 |
| C21B | 7641(10) | 3081(5) | 6003(4) | 3.2 |
| C22B | 8753(12) | 2844(6) | 6147(3) | 3.5 |
| O1B | 5924(7) | 2825(4) | 5411(2) | 4.2 |
| O2B | 4945(7) | 2502(4) | 5945(3) | 4.6 |
| O3B | 6560(9) | 2455(5) | 6440(3) | 5.8 |
| O4B | 7345(8) | 3579(4) | 6261(2) | 4.3 |
| O5B | 9087(8) | 2946(4) | 6493(2) | 4.0 |
| O6B | 9287(7) | 2564(4) | 5882(3) | 4.7 |
| ClB | 5248(3) | 4506(2) | 5771(1) | 4.5 |
| O7B | 4458(10) | 4047(5) | 5770(4) | 8.5 |
| O8B | 6302(10) | 4252(5) | 5662(3) | 8.5 |
| O9B | 5007(9) | 4977(6) | 5479(4) | 9.8 |
| O10B | 5356(12) | 4760(6) | 6152(4) | 10.9 |
| CoC | 7898(1) | 3384(1) | 10900(1) | 3.0 |
| N1C | 7213(8) | 4030(4) | 10579(3) | 3.3 |
| N2C | 6680(9) | 3490(5) | 11281(3) | 3.8 |
| N3C | 7084(8) | 2763(4) | 10580(3) | 2.8 |
| N4G | 8462(9) | 2666(5) | 11229(3) | 3.6 |
| N5C | 9145(8) | 3369(5) | 10521(3) | 3.4 |
| N6C | 8783(8) | 3974(4) | 11214(3) | 3.0 |
| C1C | 6201(11) | 4271(6) | 10766(4) | 4.2 |
| C2C | 5154(12) | 3991(6) | 10589(4) | 4.3 |
| C3C | 4169(12) | 4201(6) | 10811(5) | 5.5 |
| C4C | 4227(12) | 4051(7) | 11274(5) | 5.8 |
| C5C | 5282(11) | 4283(6) | 11480(4) | 4.0 |
| C6C | 6309(12) | 4163(6) | 11237(4) | 3.8 |
| C7C | 7376(11) | 2122(5) | 10701(4) | 3.8 |
| C8C | 8321(11) | 1872(6) | 10452(4) | 3.8 |
| C9C | 8539(13) | 1229(6) | 10586(4) | 4.2 |
| C10C | 8888(13) | 1211(6) | 11054(5) | 5.2 |
| C11C | 8029(13) | 1543(6) | 11320(4) | 5.1 |
| C12C | 7617(11) | 2148(5) | 11159(4) | 3.3 |
| C13C | 10069(11) | 3765(6) | 10658(4) | 3.5 |
| C14C | 10069(11) | 4353(6) | 10428(4) | 4.0 |
| C15C | 10994(12) | 4729(6) | 10595(4) | 5.2 |
| C16C | 10755(14) | 4885(6) | 11066(5) | 6.1 |
| C17C | 10762(12) | 4274(6) | 11292(4) | 4.1 |
| C18C | 9935(11) | 3838(6) | 11128(4) | 3.4 |
| C19C | 7945(13) | 4464(8) | 8955(5) | 6.4 |
| C20C | 8195(13) | 3767(6) | 8967(4) | 4.2 |
| C21C | 8016(11) | 3467(6) | 9389(4) | 3.6 |
| C22C | 6843(11) | 3309(6) | 9483(4) | 3.7 |
| O1C | 7804(12) | 4685(5) | 8638(3) | 9.5 |
| O2C | 7969(10) | 4742(5) | 9293(3) | 8.1 |
| O3C | 7594(8) | 3470(4) | 8661(2) | 5.1 |
| O4C | 8519(9) | 3803(5) | 9690(3) | 6.2 |
| O5C | 6524(9) | 3326(4) | 9846(3) | 5.8 |
| O6C | 6260(8) | 3116(4) | 9196(3) | 5.4 |
| ClC | 212(5) | 2398(3) | 8935(2) | 10.8 |
| O7C | 776(12) | 2216(6) | 9278(4) | 12.3 |
| O8C | −843(10) | 2268(8) | 8974(7) | 19.0 |
| O9C | 399(16) | 3030(6) | 8867(7) | 19.8 |
| O10C | 753(19) | 1985(9) | 8598(6) | 21.4 |
| OW1 | 8198(10) | 3730(5) | 2026(3) | 7.7 |
| OW2 | 5610(10) | 2783(6) | 1866(3) | 8.4 |
| OW3 | 974(14) | 2535(9) | 53(4) | 15.3 |

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

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Temperature Factors for Non-Hydrogen Atoms in *Δ*-*fac*-[(Co(*cis*-chxn)$_3$]Cl(d-tart)·$n$H$_2$O (**2**)

| Atom | *x* | *y* | *z* | $B_{eq}/Å^2$ |
|---|---|---|---|---|
| Co | 3593(2) | 5155(2) | 2145(1) | 2.7 |
| N1 | 3800(13) | 4626(13) | 1502(5) | 3.0 |
| N2 | 5050(13) | 6030(12) | 2125(6) | 3.0 |
| N3 | 3350(16) | 6151(17) | 1771(6) | 4.5 |
| N4 | 3531(13) | 5834(13) | 2762(6) | 3.1 |
| N5 | 2141(13) | 4184(14) | 2182(6) | 3.3 |
| N6 | 3700(13) | 4146(14) | 2539(5) | 2.6 |
| C1 | 4820(18) | 5110(18) | 1319(7) | 3.2 |
| C2 | 5081(19) | 5960(20) | 931(8) | 4.5 |
| C3 | 6186(19) | 6466(19) | 773(8) | 5.1 |
| C4 | 6861(17) | 6979(17) | 1230(9) | 4.3 |
| C5 | 6560(15) | 6111(18) | 1674(9) | 4.1 |
| C6 | 5460(17) | 5466(18) | 1790(8) | 3.6 |
| C7 | 3256(19) | 6867(20) | 2128(9) | 4.4 |
| C8 | 2179(21) | 6503(21) | 2180(8) | 5.1 |
| C9 | 2005(20) | 7169(21) | 2619(10) | 6.0 |
| C10 | 2541(20) | 7187(19) | 3132(8) | 5.2 |
| C11 | 3629(20) | 7487(19) | 3051(8) | 4.8 |
| C12 | 3814(17) | 6931(18) | 2621(8) | 3.8 |
| C13 | 1923(19) | 3249(18) | 2453(7) | 4.0 |
| C14 | 1745(22) | 2411(20) | 2088(10) | 6.7 |
| C15 | 1703(30) | 1539(21) | 2393(11) | 10.6 |
| C16 | 2608(25) | 1751(22) | 2732(10) | 7.7 |
| C17 | 2676(22) | 2567(25) | 3043(10) | 6.7 |
| C18 | 2761(20) | 3507(18) | 2792(8) | 4.7 |
| C19 | 5564(21) | 7294(22) | 4098(9) | 5.8 |
| C20 | 5955(20) | 6839(20) | 3698(9) | 5.2 |
| C21 | 5429(19) | 5694(18) | 3718(8) | 4.1 |
| C22 | 6063(19) | 5395(17) | 3361(7) | 4.0 |
| O1 | 5405(17) | 6879(17) | 4538(6) | 8.2 |
| O2 | 5402(24) | 7932(22) | 3975(7) | 12.4 |
| O3 | 5897(15) | 7161(15) | 3199(6) | 6.7 |
| O4 | 4406(12) | 5264(14) | 3571(5) | 5.1 |
| O5 | 5713(12) | 5044(12) | 2944(4) | 4.1 |
| O6 | 6841(12) | 5499(13) | 3565(5) | 4.7 |
| Cl | 5592(6) | 8389(6) | 1638(3) | 7.3 |
| OW1 | 3386(27) | 7656(18) | 905(7) | 15.2 |
| OW2 | 1353(21) | 6973(18) | 893(8) | 13.2 |
| OW3[a)] | 3283(36) | 2358(38) | 637(14) | 10.2 |
| OW4[a,b)] | 0(0) | 3188(58) | 1667(0) | 13.3 |

a) The probability was treated as half. b) Lies on a C$_2$ symmetry element.

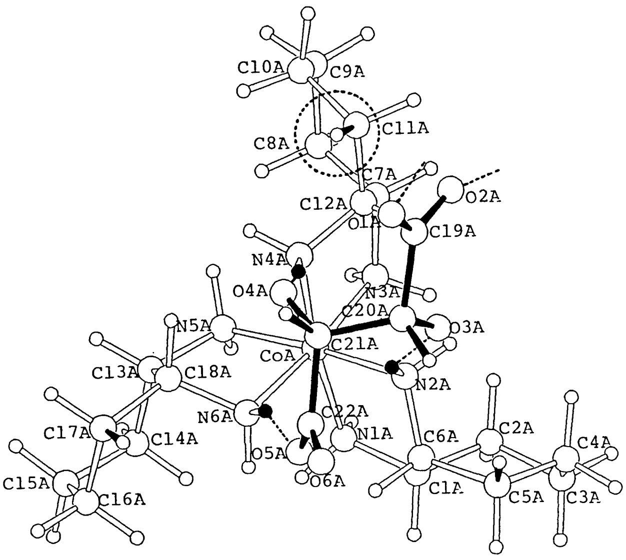


Fig. 2. One face-to-face contact mode of d-tart$^{2-}$ ion with the triangular *Δ*-*cis* RRR face found in **1** as viewed down the C$_3$ axis.

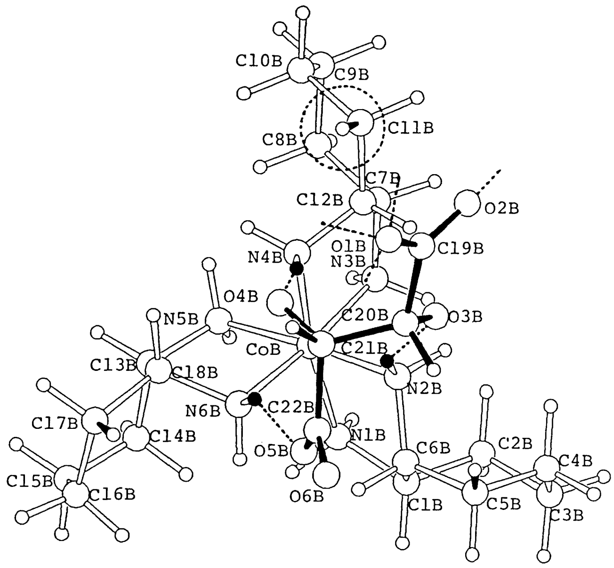


Fig. 3. The other face-to-face contact mode of d-tart$^{2-}$ ion with the triangular *Δ*-*cis* RRR face found in **1** as viewed down the C$_3$ axis.

latter crystal **2**, on the other hand, the asymmetric unit is represented simply as *Δ*-*fac*-[Co(*cis*-chxn)$_3$]Cl(d-tart)·$n$H$_2$O, in which the complex cation is arranged such that its C$_3$ axis makes an angle of ca. 52° to the 3$_1$ screw axis (c-axis), and each d-tart$^{2-}$ ion connects the two complex cations in a different fashion from those found in **1**. That is, the two crystals **1** and **2** are completely different not only in the space group and lattice constants (Table 1) but also in the packing mode. Consequently, it is almost impossible to compare the two crystals even qualitatively with respect to the counter ion effect on the interaction mode of the complex cation with the d-tart$^{2-}$ ion. However, since similar contact modes between the complex and the d-tart$^{2-}$ ions are found in common in **1** and **2**, which we have so far asserted to play a key role in the chiral discrimination, we focus our attention exclusively on these contact modes in the following.

**Contact Modes in 1.** The two similar face-to-face contact modes found in **1** are shown in Figs. 2 and 3 in both of which the *Δ*-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ complex cation assumes a *lel*$_3$ conformation[4)] and the d-tart$^{2-}$ anion, a normal one usually found.[3)] Consequently, the three N–H protons on each of the two triangular faces[9)] of the complex are disposed almost parallel to the C$_3$ axis like those of the *lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ complex.[3)] It appears that conformationally labile metal complexes with three five-membered diamine chelates assume preferentially a *lel*$_3$ conformation when they form salts with d-tart$^{2-}$ ion or other hydrogen-bonding anions.10,11)

The two contact modes found in **1** are surprisingly similar to each other; the d-tart$^{2-}$ ion directs its four O atoms (O2, O3, O4, and O5) to the $\Delta$ complex along the $C_3$ axis, with three of them (O3, O4, and O5) each hydrogen-bonded to each of the three N–H protons on the "less-favorable" triangular $\Delta$-*cis* RRR face of the complex. However, these contact modes are apparently different from those found in the $\Delta$-*lel*$_3$-[Co(en)$_3$]$^{3+}$ (en=1,2-ethanediamine) and $\Delta$-*lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ salts.3,12) In the former salt, the d-tart$^{2-}$ ion comes close to the complex along the $C_3$ axis and the three O atoms each lie midway between two of the three N–H protons on the triangular face to form three bifurcated hydrogen bonds to them; the d-tart$^{2-}$ ion enjoys up to six hydrogen bonds to the complex without feeling any appreciable steric repulsion from the small en chelates (Table 4). Thus, this contact mode is considered close to an ideal one for the d-tart$^{2-}$ ion coming to the triangular face, and it is adopted with the $\Lambda$-*lel*$_3$-[Co(en)$_3$]$^{3+}$ as well.13) In the $\Delta$-*lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ salt, the three O atoms of the d-tart$^{2-}$ ion are similarly hydrogen-bonded to one of the "less-favorable" $\Delta$-*trans* RRR faces of the complex, but the distal carboxylate group is greatly rotated to avoid the steric repulsion from the C–H proton on one of the bulky chxn ligands; the multiple hydrogen bonds to the complex are almost fully retained at the expense of the conformational energy (Table 4).3)

In the present crystal, on the other hand, the d-tart$^{2-}$ ion avoids a similar steric repulsion from the "less-favorable" $\Delta$-*cis* RRR face at the expense of the multiple hydrogen bonds to the complex. That is, the d-tart$^{2-}$ ion approaches the complex along the $C_3$ axis as usual but it rotates itself clockwise as a whole relative to the complex to avoid the repulsion from the C–H proton marked with a broken circle on the chxn ligand (Figs. 2 and 3), and the number of the hydrogen bonds formed is accordingly reduced from six virtually to three. However, the remaining three hydrogen bonds (O3··H–N2, O4··H–N4, and O5··H–N6) are fairly improved with respect to length and angle (Table 4), and the distal carboxylate group is placed such that its two O atoms (O1 and O2) form intimate hydrogen bonds to the N–H group(s) of other neighboring complexes in the $\Delta$-*fac*-[Co(*cis*-chxn)$_3$](ClO$_4$)(d-tart)$\cdot m$H$_2$O (**1**), as shown by dotted lines in Figs. 2 and 3. In this respect, the hydrogen-bonding scheme found in the present crystal is similar to that found in the $\Lambda$-*ob*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ salt where all of the three N–H groups are oblique to the $C_3$ axis, so that practically only three but linear hydrogen bonds are formed to them.11) The hydrogen bonds associated with these face-to-face contact modes are all compared numerically in Table 4.

The other triangular face of the $\Delta$-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ denoted as the $\Delta$-*cis* SSS face, is depicted in Fig. 4a. It is seen there that the three C–H protons marked with broken circles on the chxn ligands are

Table 4. Comparison of Hydrogen-Bond Distances and Angles in Some Face-to-Face Contacts

| Acceptor<br>Donor | O3<br>H1N2 | O3<br>H1N4 | O4<br>H1N4 | O4<br>H1N6 | O5<br>H1N6 | O5<br>H1N2 |
|---|---|---|---|---|---|---|
| Distances of O···H/Å | | | | | | |
| (**1**)-Aa) | 1.97 | 3.11 | 1.84 | 2.75 | 1.81 | 2.68 |
| (**1**)-Bb) | 2.06 | 3.13 | 2.01 | 2.58 | 1.90 | 2.58 |
| (**2**)c) | 2.33 | 2.61 | 1.94 | 2.30 | 2.01 | 2.38 |
| $\Delta$-*lel*$_3$d) | 2.94 | 1.98 | 2.32 | 2.07 | 2.10 | 2.02 |
| $\Delta$-en$_3$e) | 2.33 | 2.26 | 2.22 | 2.14 | 2.21 | 2.14 |
| $\Lambda$-*ob*$_3$f) | 2.03 | 3.00 | 2.11 | 2.47 | 1.92 | 2.52 |
| Distances of O···N/Å | | | | | | |
| (**1**)-A | 2.82 | 3.78 | 2.83 | 3.51 | 2.75 | 3.38 |
| (**1**)-B | 2.92 | 3.74 | 3.01 | 3.45 | 2.76 | 3.17 |
| (**2**) | 3.22 | 3.36 | 2.87 | 3.10 | 2.89 | 3.08 |
| $\Delta$-*lel*$_3$ | 3.72 | 2.93 | 3.12 | 2.97 | 3.04 | 3.01 |
| $\Delta$-en$_3$ | 3.08 | 3.10 | 3.07 | 2.99 | 2.99 | 2.96 |
| $\Lambda$-*ob*$_3$ | 3.02 | 3.29 | 3.05 | 3.10 | 2.88 | 2.84 |
| Angles of O···H–N/° | | | | | | |
| (**1**)-A | 141 | 126 | 172 | 133 | 155 | 127 |
| (**1**)-B | 144 | 127 | 172 | 144 | 143 | 118 |
| (**2**) | 149 | 131 | 154 | 135 | 145 | 126 |
| $\Delta$-*lel*$_3$ | 128 | 144 | 130 | 137 | 142 | 150 |
| $\Delta$-en$_3$ | 138 | 141 | 141 | 133 | 133 | 138 |
| $\Lambda$-*ob*$_3$ | 168 | 98 | 157 | 120 | 162 | 93 |

a) The mode in Fig. 2. b) The mode in Fig. 3. c) The mode in Fig. 6. d) $\Delta$-*lel*$_3$-[Co(*trans*-chxn)$_3$]Cl(d-tart)$\cdot$2H$_2$O in Ref. 3. e) $\Delta$-*lel*$_3$-[Co(en)$_3$]$_2$(d-tart)$_3\cdot$11.5H$_2$O in Ref. 12. f) $\Lambda$-*ob*$_3$-[Co(*trans*-chxn)$_3$]Cl(d-tart)$\cdot$3.5H$_2$O in Ref. 11.

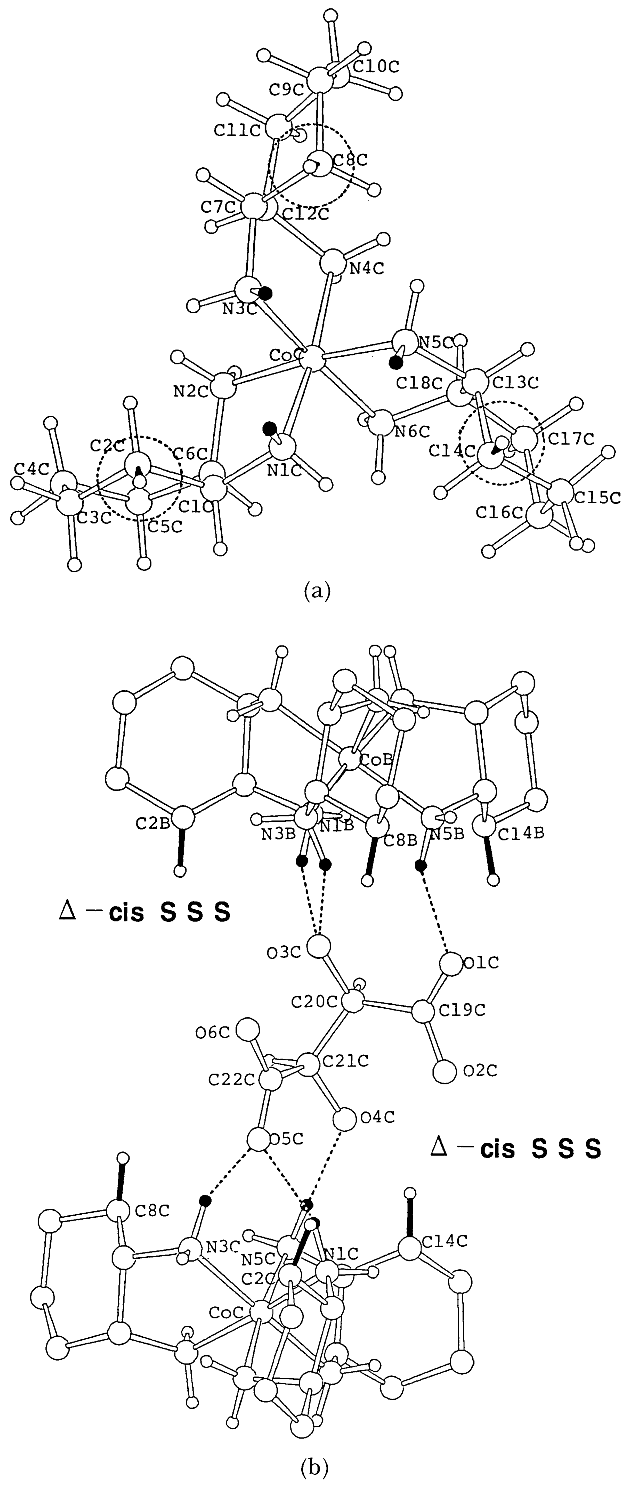


Fig. 4. The structure of the triangular $\Delta$-*cis* SSS face (a) and the contact mode of d-tart$^{2-}$ ion with the face (b). Most of the C-H protons are eliminated for clarity in (b).

disposed so closely to the N-H protons that any of them necessarily serves as an obstacle to the d-tart$^{2-}$ ion when it makes a face-to-face contact with the face. The contact mode of the $\Delta$-*cis* SSS face actually found in **1** is shown in Fig. 4b where the d-tart$^{2-}$ anion is sandwiched between the two $\Delta$-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ complex cations, and only two O atoms, one carboxylic and one alcoholic, of the d-tart$^{2-}$ ion are involved in the hydrogen bonding to the respective $\Delta$-*cis* SSS face. Thus, the $\Delta$-*cis* SSS face does not serve as an interaction site for the face-to-face contact, as supposed in Fig. 4a.

Since the $\Delta$-*cis* RRR face enantiomeric to the $\Delta$-*cis* SSS face depicted in Fig. 4a, is naturally crowded, it follows that the $\Delta$-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ complex has practically only one favorable triangular face available for the face-to-face contact, i.e., the $\Delta$-*cis* SSS face similar in structure to the favorable $\Delta$-*trans* SSS face of the $\Delta$-*lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ complex.

It is additionally noteworthy in Fig. 4b that the d-tart$^{2-}$ ion sandwiched between the two $\Delta$-*cis* SSS faces assumes a conformation appreciably different from a usual one; the torsion angle $\phi$ of the $^{-}$OOC-C-C-COO$^{-}$ group is 81.5°, whereas it is around 180°, i.e., the two COO$^{-}$ groups are trans to each other, in a usual conformer. To demonstrate how the observed angle of 81.5° is surprisingly unusual, the distribution of the torsion angle $\phi$ is shown in Fig. 5 for d-tart$^{2-}$ and d-tartH$^{-}$ ions in their simple salts[14] and diastereomeric salts with tris(diamine)-metal complexes.[3,15,16] The conformer found here is probably the first example in which the two COO$^{-}$ groups are in gauche positions.

**Contact Modes in 2.** In Fig. 6 is shown a face-to-face contact mode found in **2**, where the $\Delta$-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ takes a *lel*$_3$ conformation and the d-tart$^{2-}$ ion, a usual one as in **1**, and the triangular face used is naturally the $\Delta$-*cis* RRR face. It is evident that the contact mode bears a close resemblance to the ideal one found in the $\Delta$-*lel*$_3$-[Co(en)$_3$]$^{3+}$ salt;[3,12] the three O atoms of the d-tart$^{2-}$ ion are each placed almost midway between two of the three N-H protons on the triangular face and are involved in the three bifurcated hydrogen bonds to them. The hydrogen bonds pertinent to the present face-to-face contact mode found in **2** are summarized also in Table 4.

A glance of Fig. 6a might lead us to suppose that the distal carboxylate group closely approaches one of the chxn ligands to suffer a severe steric repulsion from the C-H proton marked with a broken circle. However, if the contact mode is viewed normal to the $C_3$ axis (Fig. 6b), it is confirmed that the d-tart$^{2-}$ ion avoids the repulsion by inclining the plane consisting of the three O atoms a little relative to the "less-favorable" $\Delta$-*cis* RRR face of the complex. As a result, the nearest O2 atom of the distal carboxylate group is placed ca. 2.49 Å apart from the C-H proton to avoid the repulsion marginally, and some of the multiple hydrogen bonds are obliged to be somewhat longer[17] than the corresponding hydrogen bonds formed in the $\Delta$-*lel*$_3$-[Co(en)$_3$]$^{3+}$ salt (Table 4). For example, the O3··H-N4 bond distance is 2.61 Å in Fig. 6, while the corresponding distance is 2.26 Å in the $\Delta$-

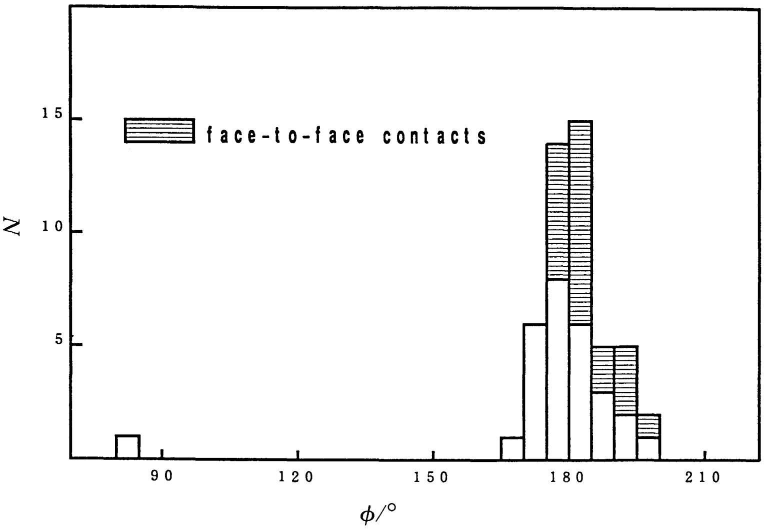


Fig. 5. The distribution of the $^{-}$OOC-C-C-COO$^{-}$ torsion angle (φ) in some salts of d-tart$^{2-}$ and d-tartH$^{-}$ ions.

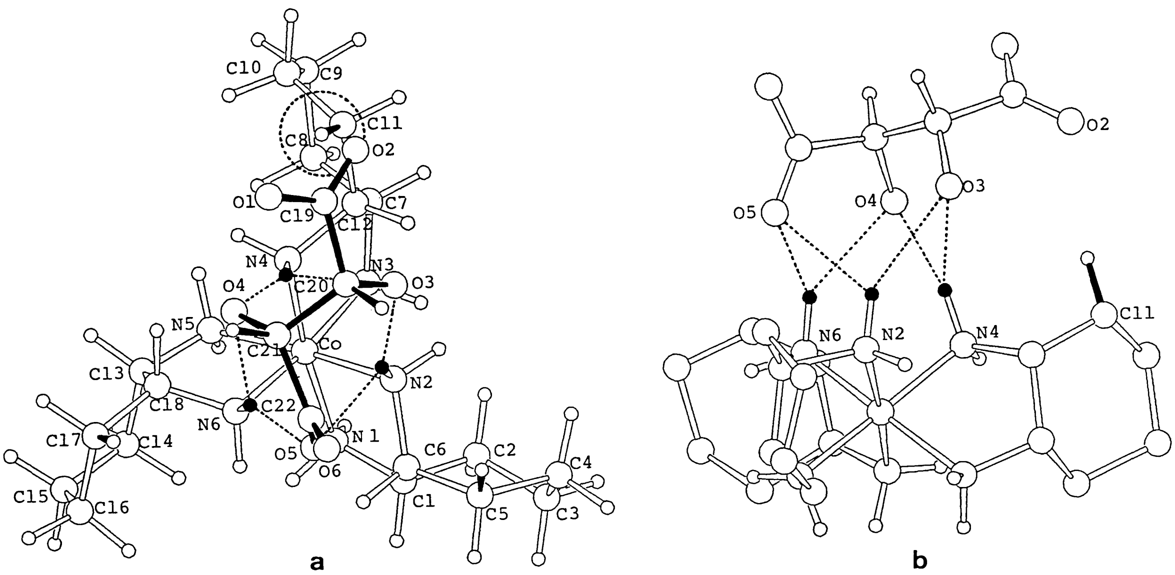


Fig. 6. The face-to-face contact mode of d-tart$^{2-}$ ion with the triangular *Δ-cis* RRR face found in **2** as viewed down (a) and normal to (b) the C$_3$ axis. Most of the C–H protons are eliminated for clarity in (b).

*lel*$_3$-[Co(en)$_3$]$^{3+}$ salt.[12] Instead, the distal carboxylate group is in a position to form multiple hydrogen bonds to the triangular *Δ-cis* SSS face of another neighboring complex cation in the *Δ-fac*-[Co(*cis*-chxn)$_3$]Cl(d-tart)·$n$H$_2$O (**2**) (vide infra).

The other triangular face of the *Δ* complex denoted as the *Δ-cis* SSS face is so crowded as mentioned in Fig. 4a, that it may accommodate only two O atoms of the d-tart$^{2-}$ ion coming to the face in **2**. The contact mode of the *Δ-cis* SSS face actually found in **2** is shown in Fig. 7, where the two O atoms (O1 and O2) of the distal carboxylate group are hydrogen-bonded to the face, as expected, and the remaining three O atoms (O3, O4, and O5) are involved in the face-to-face contact with the "less-favorable" *Δ-cis* RRR face of another neighboring *Δ* complex.[18] Thus, this *Δ-cis* SSS face is again proved to be of no use for the face-to-face contact, probably in solution as well.

We assume here that the face-to-face contact mode found in **2** and shown in Fig. 6 is the one in which the d-tart$^{2-}$ ion avoids the steric repulsion tactfully at the least expense of the multiple hydrogen bonds to the "less-favorable" *Δ-cis* RRR face without any disadvantageous conformational change, and that it is the most probable interaction mode conceivable in solution where another neighboring complex is absent to assist the conformational change. In addition, this contact mode will be adopted in solution by the *Δ-lel*$_3$-

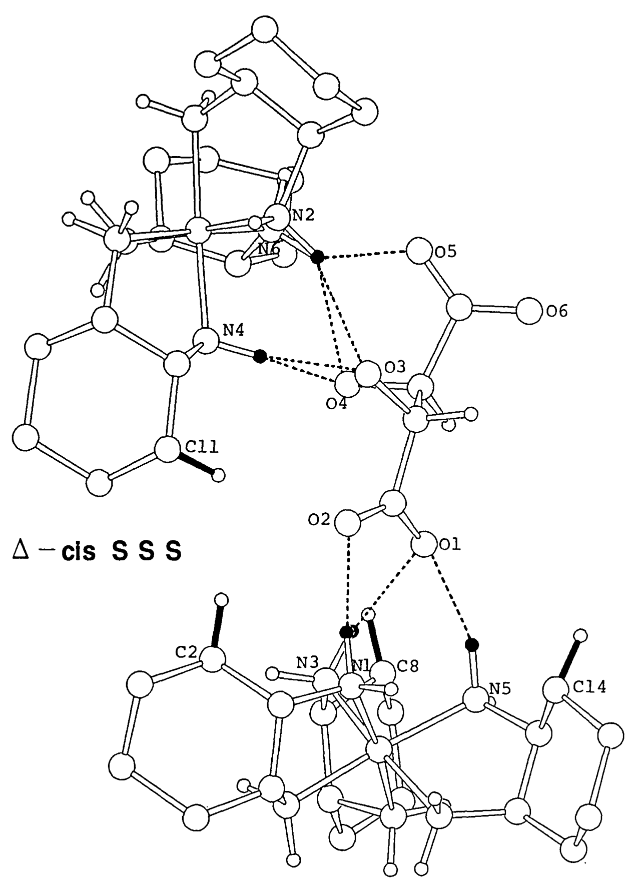


Fig. 7. The contact mode of d-tart$^{2-}$ ion with the triangular $\Delta$-*cis* SSS face found in **2**. Most of the C–H protons are eliminated for clarity.

[Co(*trans*-chxn)$_3$]$^{3+}$ complex as well, since the complex has two "less-favorable" $\Delta$-*trans* RRR faces similar to the $\Delta$-*cis* RRR face. These assumptions are indirectly supported by the results of the chromatographic separation of some related complexes, which will be described in the next section. It goes without saying that the $\Delta$-*cis* SSS and $\Lambda$-*cis* RRR faces are neglected in counting the interaction sites available for the face-to-face contact with d-tart$^{2-}$ ion even in solution, because these faces are heavily crowded as seen in Fig. 4a.

**Elution Order in Chromatography.** The chromatographic separation was carried out for some [Co(chxn)$_3$]$^{3+}$ complexes on an SP-Sephadex ion-exchange column with aqueous sodium d-tartrate (0.2 mol dm$^{-3}$) as an eluent. The elution order obtained is $\Lambda$-*lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ $\gg$ $\Lambda$-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ $\gg$ $\Delta$-*lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ $>$ $\Delta$-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ $>$ $\Lambda$-*ob*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ $\gg$ $\Delta$-*ob*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$, and the conventional separation factor[3] for an enantiomeric pair is 1.57 for *lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$, 1.37 for *fac*-[Co(*cis*-chxn)$_3$]$^{3+}$, and 1.39 for *ob*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ (cf. 1.18 for [Co(en)$_3$]$^{3+}$ and 1.33 for *mer*-[Co(*cis*-chxn)$_3$]$^{3+}$). No practical separation of these complexes was attained with aqueous sodium chloride as an eluent, the [Co(*cis*-chxn)$_3$]$^{3+}$ complexes coming out slightly late.

It is notable that the $\Delta$-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ is eluted faster than the $\Lambda$-*ob*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$, though the latter complex has two triangular faces available for the three linear hydrogen bonds with d-tart$^{2-}$ ion.[11] If the $\Delta$-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ should adopt in solution the contact mode shown in Fig. 2 or 3 where only three linear hydrogen bonds are formed, the $\Lambda$-*ob*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ should be eluted faster. Therefore, the $\Delta$-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ as well as the $\Delta$-*lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ adopts in solution preferentially the contact mode shown in Fig. 6 where six hydrogen bonds, though some are somewhat long,[17] are formed.

Finally, the elution order and separation factors obtained are interpreted. First of all, the $\Lambda$-*lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ has two equivalent triangular faces ($\Lambda$-*trans* SSS) which allow a smooth access of d-tart$^{2-}$ ion along the C$_3$ axis, and thus it should be eluted the fastest. The $\Lambda$-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ has one such favorable face ($\Lambda$-*cis* SSS) and is eluted the second. Though no such favorable face is present in either the $\Delta$-*lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ or the $\Delta$-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$, the former has two "less-favorable" faces ($\Delta$-*trans* RRR) to which the d-tart$^{2-}$ ion forms six but somewhat long hydrogen bonds and the latter has one such face ($\Delta$-*cis* RRR). Consequently, they should be eluted the next in this order. The fact that the $\Delta$-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ is eluted faster than the $\Lambda$-*ob*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ which has two equivalent triangular faces available for the three linear hydrogen bonds with d-tart$^{2-}$ ion, suggests that d-tart$^{2-}$ ion interacts more strongly with these tris(diamine)cobalt(III) complexes when more hydrogen bonds are formed to them rather than when fewer but more linear hydrogen bonds are formed.[11,19,20] In this way, the elution order obtained is readily interpreted in terms of the number of available interaction sites counted above and the number of hydrogen bonds formed there, consistent with the proposals offered by Searle[21] and Sakakibara et al.[22] Consequently, it is concluded that the face-to-face contact mode found in **2** and shown in Fig. 6 but not in Fig. 2 or 3 is the one which is adopted in solution by both $\Delta$-[Co(*trans*-chxn)$_3$]$^{3+}$ and $\Delta$-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ complexes; the "less-favorable" $\Delta$-*trans* RRR or $\Delta$-*cis* RRR face is preferentially utilized for the association with the d-tart$^{2-}$ ion.

Since the magnitude of the separation factor has been already discussed for the *lel*$_3$ and *ob*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ complexes,[3] it needs to examine only for the *fac*-[Co(*cis*-chxn)$_3$]$^{3+}$. The conventional separation factor estimated for this complex is 1.37, which is considerably lower than 1.57 estimated for the *lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$. This is apparently because the $\Lambda$-*fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ has one favorable $\Lambda$-*cis* SSS face and one useless $\Lambda$-*cis* RRR faces but the enantiomer has one "less-favorable" *Δ-cis* RRR and one useless *Δ-cis* SSS faces, whereas the *Λ-lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ has as many as two favorable *Λ-trans* SSS faces but the enantiomer has two "less-favorable" *Δ-trans* RRR faces only. That is, the *Δ-lel*$_3$-[Co(*trans*-chxn)$_3$]$^{3+}$ is more handicapped with respect to the number of the available interaction sites than the *Δ-fac*-[Co(*cis*-chxn)$_3$]$^{3+}$ is, relative to the respective enantiomer.

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8) Tables of a full listing of crystallographic data, coordinates of hydrogen atoms, bond lengths and angles, hydrogen bond distances and angles, anisotropic thermal parameters of non-hydrogen atoms, and observed and calculated structure factors are kept as Document No. 9108 at the Office of the Editor of Bull. Chem. Soc. Jpn.

9) The three N–H protons on the *Δ-cis* RRR face are certainly disposed almost parallel to the $C_3$ axis (Fig. 2 or 3), whereas those on the opposite face (*Δ-cis* SSS) are faintly oblique to the $C_3$ axis (Fig. 4a), though the *Δ* complex itself assumes a *lel*$_3$ conformation.

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17) Some of the multiple hydrogen bonds in **2** are certainly longer but others are slightly shorter than the corresponding hydrogen bonds in the *Δ-lel*$_3$-[Co(en)$_3$]$^{3+}$ salt. However, the overall hydrogen-bonding interaction is definitely weaker in **2**, as judged from the bond lengths and angles (Table 4).

18) It is interesting to note that a contact mode similar to that shown in Fig. 7 has been found in the *rac*-[Ni(en)$_3$](*rac*-tart)·$H_2O$ salt,[15] where the three N–H protons on the triangular face of the *Δ*(*Λ*) complex are hydrogen-bonded to the distal carboxylate group of the d(l)-tart$^{2-}$ ion, the remaining three O atoms of which are making a usual face-to-face contact with the triangular face of the neighboring *Λ*(*Δ*) complex.

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