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Crystal and Molecular Structure of Λ-[1,1,1-Tris(((2-aminoethyl)amino)methyl)ethane]cobalt(III) Chloride *d*-Tartrate Hexahydrate and the Mode of Chiral Discrimination of Trigonal $[Co(N)_6]^{3+}$ Complexes by the *d*-Tartrate Ion in Solids and in Solution

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The crystal and molecular structure of the more soluble diastereomer Λ-[1,1,1-tris(((2-aminoethyl)amino)methyl)ethane]cobalt(III) chloride *d*-tartrate hexahydrate, Λ-$[Co(C_{11}H_{30}N_6)]Cl(C_4H_4O_6)\cdot 6H_2O$, has been determined by single-crystal X-ray diffraction techniques ($R = 0.033$, orthorhombic crystals, space group $P2_12_12_1$ with $a = 17.707$ (4) Å, $b = 13.596$ (3) Å, $c = 10.812$ (4) Å, and $Z = 4$). The two hydroxyl oxygens and one carboxyl oxygen of the *d*-tartrate anion form three hydrogen bonds with three axial NH hydrogens of the complex cation in lel_3 conformation, along the C_3 axis. The remaining carboxyl group hydrogen bonds to the neighboring complex cation along the C_2 axis, forming an infinite zigzag chain along the *c* axis. The mode of chiral discrimination of trigonal $[Co(N)_6]^{3+}$ complexes by the *d*-tartrate ion in solids and in solution is discussed.

Introduction

Recently, we have studied the chiral interaction between trigonal $[Co(N)_6]^{3+}$ complexes and *d*- and *l*-tartrate ions in solution.[1] From the circular dichroism (CD) changes caused by tartrates, the association constants with *d*- and *l*-tartrates, K_d and K_l, have been determined for Δ-$[Co(en)_3]^{3+}$, Δ-$[Co(sen)]^{3+}$, Δ-$[Co(sep)]^{3+}$, Δ-*fac*- and Δ-*mer*-$[Co(l\text{-}pn)_3]^{3+}$, and Δ-$[Co(l\text{-}chxn)_3]^{3+}$, where en = ethylenediamine, sen = 1,1,1-tris(((2-aminoethyl)amino)methyl)ethane, sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane, l-pn = (−)-1,2-propanediamine, and l-chxn = (−)-*trans*-1,2-cyclohexanediamine. Among these complexes, the Δ-$[Co(sen)]^{3+}$ ion showed the highest degree of chiral discrimination, where the degree of chiral discrimination is defined by $(K_l - K_d)/(K_l + K_d)$. The origin of this high degree of discrimination, as well as the suggested mode of chiral interaction in solution, has prompted us to determine the structure of the diastereomer, Λ-$[Co(sen)]Cl(d\text{-}C_4H_4O_6)\cdot 6H_2O$.

On the other hand, the structure and the absolute configuration of Δ- or Λ-$[Co(sen)]^{3+}$ attracted our interest in its own right. It is well-known that many of the trigonal $[Co(N)_6]^{3+}$ complexes can be resolved optically either by diastereoisomer formation in halide *d*-tartrate form or by ion-exchange chromatography with the *d*-tartrate ion as the eluent. From the CD spectrum and its change due to phosphate ions, Sarneski and Urbach[2] assigned the Δ absolute configuration to the enantiomer of $[Co(sen)]^{3+}$ that forms the less soluble diastereomer with *d*-tartrate in the chloride *d*-tartrate form. They noted that this assignment contradicts the observation that tris(diamine) complexes with Λ or $M(C_3)$ absolute configuration form the less soluble halide *d*-tartrate salts, though such a correlation of absolute configuration can only be applied to isomorphous complexes. Thus, the absolute configuration of this cation seemed to await unambiguous assignment through single-crystal X-ray analysis.

Further, the $[Co(sep)]^{3+}$ ion, which has two covalent caps ($N(CH_2)_3$ groups) along the D_3 polar region of $[Co(en)_3]^{3+}$, was found to exchange electrons some 10^5-fold faster than the parent $[Co(en)_3]^{3+}$ ion, despite an apparent similarity in the electronic states of these ions.[3] This rather astonishing rate difference does not seem to be properly explained; Sargeson reported that the only plausible explanation can be found in the overall size of the ions.[4] Quite recently, Geselowitz[5] proposed a ligand strain as the major factor for the difference. Thus, it seemed to us that examination of ligand strain and redox properties of $[Co(sen)]^{3+}$ might contribute to the elucidation of the anomalous properties of capped ions, though $[Co(sen)]^{3+}$ has only one covalent cap along the C_3 axis of $[Co(en)_3]^{3+}$.

Experimental Section

Collection of the X-ray Diffraction Data. The yellow rhombic crystal used for the data collection was the more soluble diastereomer, Λ-$[Co(C_{11}H_{30}N_6)]Cl(C_4H_4O_6)\cdot 6H_2O$, prepared according to Sarneski and Urbach[2] and had the dimensions of 0.38 × 0.37 × 0.42 mm. The determination of cell constants and the intensity data was carried out on a Rigaku AFC-5 automated four-circle diffractometer with Mo Kα radiation ($\lambda = 0.71069$ Å) monochromated by a graphite plate. The cell constants, determined by a least-squares method using 25 independent reflections ($2\theta > 26°$), were $a = 17.707$ (4) Å, $b = 13.596$ (3) Å, $c = 10.812$ (4) Å, and $V = 2603.0$ (13) Å^3. The space group was determined to be $P2_12_12_1$ (D_2^4, No. 19) from the systematic absences for $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), and $00l$ ($l = 2n + 1$). The measured density of 1.51 g/cm^3 obtained by a flotation technique using a $CHCl_3$–$CHBr_3$ mixed solution agrees well with the calculated value of 1.52 g/cm^3 for $Z = 4$. The intensity data were collected by the ω–2θ scan technique to a maximum 2θ value of 55° at a scan rate of 8°/min (50 kV, 170 mA). The ω scan range was $(1.2 + 0.5 \tan \theta)°$. As a check on experimental stability, intensities of 3 standard reflections were monitored at 200-reflection intervals. Out of 5521 independent reflections measured, 3046 reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure determination. No absorption correction was made since the linear absorption coefficient of $\mu = 8.6$ cm^{-1} was low.

Structure Determination and Refinement. The structure was solved by standard heavy-atom techniques. The position of the Co atom was determined from the three-dimensional Patterson map. The remaining atoms except hydrogen atoms were all revealed in subsequent difference Fourier maps and refined isotropically by block-diagonal least squares to an R_1 value, $\sum(|F_o| - |F_c|)/\sum|F_o|$, of 0.054 and an R_2 value, $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, of 0.073. The subsequent difference Fourier maps revealed the positions of hydrogen atoms. All atoms including hydrogen atoms were refined three cycles, non-hydrogen atoms anisotropically and hydrogen atoms isotropically (with $U = 44 \times 10^{-3}$ Å^2), to $R_1 = 0.037$ and $R_2 = 0.046$. A further two cycles of least-squares refinement, including non-hydrogen atoms with variable anisotropic temperature factors and hydrogen atoms with variable isotropic temperature parameters, converged to $R_1 = 0.033$ and $R_2 = 0.039$. A final difference Fourier map revealed no peaks

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Table I. Atomic Coordinates for Non-Hydrogen Atoms of Λ-[Co(sen)]Cl(d-$C_4H_4O_6$)·$6H_2O$

atom	x	y	z
Co	0.71273 (2)	0.22416 (3)	0.49162 (4)
Cl	0.73139 (6)	0.23344 (8)	0.09235 (8)
N1	0.7083 (2)	0.3245 (2)	0.6231 (2)
N2	0.7122 (2)	0.1264 (2)	0.6263 (3)
N3	0.8239 (1)	0.2306 (2)	0.4878 (3)
N4	0.7224 (2)	0.1191 (2)	0.3681 (3)
N5	0.7049 (2)	0.3265 (2)	0.3633 (2)
N6	0.6013 (2)	0.2152 (2)	0.4815 (3)
C1	0.7236 (2)	0.2768 (3)	0.7443 (3)
C2	0.6881 (2)	0.1759 (3)	0.7415 (3)
C3	0.8511 (2)	0.1737 (3)	0.3780 (4)
C4	0.8020 (2)	0.0834 (3)	0.3669 (4)
C5	0.6240 (2)	0.3571 (3)	0.3542 (4)
C6	0.5768 (2)	0.2657 (3)	0.3669 (4)
C7	0.7552 (2)	0.4153 (3)	0.6060 (3)
C8	0.8602 (2)	0.3300 (2)	0.4921 (4)
C9	0.7571 (2)	0.4137 (3)	0.3729 (4)
C10	0.8043 (2)	0.4153 (2)	0.4899 (3)
C11	0.8508 (2)	0.5108 (3)	0.4893 (4)
OT1	0.5000 (2)	−0.1225 (2)	0.6243 (3)
OT2	0.5759 (2)	0.0063 (2)	0.6477 (3)
OT3	0.6020 (2)	−0.1967 (2)	0.2283 (3)
OT4	0.6369 (2)	−0.0439 (2)	0.1836 (3)
OH1	0.6737 (1)	−0.0658 (2)	0.4765 (2)
OH2	0.5491 (2)	0.0321 (2)	0.3670 (2)
CT1	0.5552 (2)	−0.0697 (3)	0.5941 (3)
CT2	0.5982 (2)	−0.1041 (2)	0.4796 (3)
CT3	0.5585 (2)	−0.0716 (3)	0.3620 (3)
CT4	0.6028 (2)	−0.1062 (3)	0.2485 (3)
OW1	0.4392 (2)	0.7176 (2)	0.5169 (4)
OW2	0.6347 (2)	0.6043 (3)	0.5363 (4)
OW3	0.5634 (2)	0.6081 (3)	0.2868 (3)
OW4	0.5271 (2)	0.6341 (3)	0.7374 (4)
OW5	0.5520 (2)	0.3808 (2)	0.6436 (3)
OW6	0.4685 (2)	0.5133 (3)	0.4956 (3)

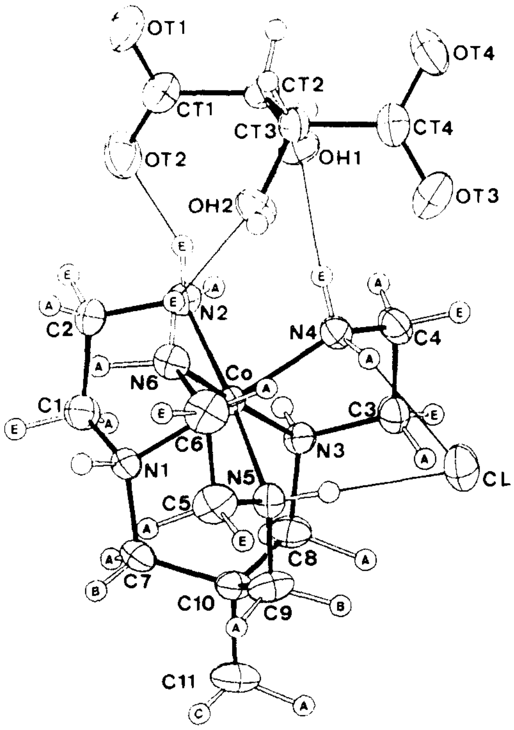

Figure 1. Local contact of Λ-[Co(sen)]$^{3+}$ with d-tartrate and chloride ions, showing also the atom-numbering scheme. The d-tartrate anion hydrogen bonds, along the C_3 axis, to three axial NH hydrogens and the chloride ion hydrogen bonds to two equatorial NH hydrogens, along the C_2 axis.

Table IV. Intramolecular Bond Distances (Å) with Least-Squares Estimated Standard Deviations in Parentheses[a]

Co-N1	1.972 (3)	N3-C8	1.496 (5)
Co-N2	1.971 (3)	N5-C9	1.507 (5)
Co-N3	1.970 (3)	C7-C10	1.526 (5)
Co-N4	1.963 (3)	C8-C10	1.525 (5)
Co-N5	1.970 (3)	C9-C10	1.516 (5)
Co-N6	1.981 (3)	C10-C11	1.538 (6)
N1-C1	1.487 (5)	OT1-CT1	1.256 (5)
N2-C2	1.479 (5)	OT2-CT1	1.241 (5)
N3-C3	1.497 (5)	OT3-CT4	1.250 (5)
N4-C4	1.491 (5)	OT4-CT4	1.256 (5)
N5-C5	1.495 (5)	OH1-CT2	1.435 (4)
N6-C6	1.482 (5)	OH2-CT3	1.422 (4)
C1-C2	1.509 (5)	CT1-CT2	1.526 (5)
C3-C4	1.508 (5)	CT2-CT3	1.519 (5)
C5-C6	1.504 (6)	CT3-CT4	1.531 (5)
N1-C7	1.500 (5)		

Table V. Intramolecular Bond Angles (deg) with Least-Squares Estimated Standard Deviations in Parentheses

N1-Co-N2	86.2 (1)	C10-C7-N1	114.6 (3)
N3-Co-N4	86.0 (1)	C10-C8-N3	114.0 (3)
N5-Co-N6	86.3 (1)	C10-C9-N5	113.9 (3)
Co-N1-C1	109.0 (2)	C7-C10-C8	110.9 (3)
Co-N3-C3	108.4 (2)	C7-C10-C9	111.9 (3)
Co-N5-C5	108.1 (2)	C8-C10-C9	111.1 (3)
Co-N2-C2	108.4 (2)	C7-C10-C11	108.0 (3)
Co-N4-C4	109.0 (2)	C8-C10-C11	107.2 (3)
Co-N6-C6	108.0 (2)	C9-C10-C11	107.6 (3)
N1-C1-C2	107.6 (3)	CT2-CT1-OT1	115.1 (3)
N2-C2-C1	108.1 (3)	CT2-CT1-OT2	119.2 (3)
N3-C3-C4	107.4 (3)	CT3-CT4-OT3	115.9 (3)
N4-C4-C3	106.2 (3)	CT3-CT4-OT4	119.2 (3)
N5-C5-C6	107.3 (3)	OT1-CT1-OT2	125.7 (4)
N6-C6-C5	107.3 (3)	OT3-CT4-OT4	124.9 (4)
C7-N1-Co	117.3 (2)	CT1-CT2-CT3	111.0 (3)
C7-N1-C1	111.5 (3)	CT2-CT3-CT4	110.1 (3)
C8-N3-Co	117.9 (2)	OH1-CT2-CT1	111.9 (3)
C8-N3-C3	110.7 (3)	OH1-CT2-CT3	107.8 (3)
C9-N5-Co	117.7 (2)	OH2-CT3-CT2	108.1 (3)
C9-N5-C5	111.9 (3)	OH2-CT3-CT4	113.3 (3)

higher than 0.4 e/Å^3. The quantity minimized was $\sum w(|F_o| - k|F_c|)^2$. The weighting scheme used was $w = (\sigma_{cs} + a|F_o|^2 + b|F_o|)^{-1}$, where σ_{cs} is the standard deviation obtained from the counting statistics for each reflection and the values of a and b used in the final refinement were 0.0009 and 0.2, respectively. All the atomic scattering factors were taken from Cromer and Waber.[6] The final atomic coordinates for non-hydrogen and hydrogen atoms and final anisotropic thermal parameters are given in Tables I, II, and III, respectively, according to the atom labels of Figure 1 (Tables II and III are supplementary material). The anomalous dispersion coefficients of Cromer and Liberman[7] were used for Co and Cl atoms. All the computations were carried out by a HITAC M-200 computer at the Hiroshima University Information Processing Center. The computer programs used were FOUR-MMM (Fourier syntheses) and HBLS-IV (least-squares calculation) with a slight modification.[8] ORTEP drawing[9] was carried out by the computer system XTL on a Syntex R3 automated four-circle diffractometer. A table of observed and calculated structure factor amplitudes is available as supplementary material.

Results and Discussion

Description of the Structure. Intramolecular bond distances and bond angles, with least-squares estimated standard deviations, are listed in Tables IV and V. Intermolecular hydrogen bonds are listed in Table VI. A perspective view of the local contact of the [Co(sen)]$^{3+}$ cation, the d-tartrate anion, and chloride anion is shown in Figure 1. The contents of one unit cell are shown by stereopairs in Figure 2 (supplementary

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Table VI. Intermolecular Hydrogen Bonding with Least-Squares *Estimated Standard Deviations in Parentheses*[a]

D	H	A	D···A, Å	D–H, Å	H···A, Å
N1	HN1	OW5	2.879 (4)	1.03 (4)	1.85 (4)
N2	HN2A	OT4^{i}	2.963 (4)	0.93 (4)	2.04 (4)
N2	HN2E	OT2	2.924 (4)	0.93 (4)	2.07 (4)
N2	HN2E	OH1	3.149 (4)	0.93 (4)	2.42 (4)
N3	HN3	OT3^{i}	2.949 (4)	0.89 (4)	2.11 (4)
N4	HN4A	Cl	3.366 (3)	0.91 (4)	2.50 (4)
N4	HN4E	OH1	2.905 (4)	0.95 (5)	2.04 (5)
N5	HN5	Cl	3.225 (3)	0.96 (4)	2.27 (4)
N6	HN6A	OW5	2.984 (4)	1.04 (5)	2.11 (5)
N6	HN6E	OH2	2.929 (4)	0.89 (4)	2.21 (5)
OH1	HOH1	Cl^{i}	3.096 (3)	0.86 (5)	2.24 (5)
OH2	HOH2	OW3^{ii}	2.793 (5)	0.79 (4)	2.01 (4)
OW1	HOW1A	OT1^{iii}	2.689 (5)	0.87 (5)	1.84 (5)
OW1	HOW1B	Cl^{iv}	3.251 (5)	0.81 (5)	2.46 (5)
OW2	HOW2A	OW4	2.919 (6)	1.25 (6)	1.68 (6)
OW2	HOW2B	Cl^{v}	3.295 (5)	0.83 (6)	2.48 (6)
OW3	HOW3A	OW2	2.979 (6)	1.03 (5)	2.77 (5)
OW3	HOW3B	OT3^{iii}	2.812 (5)	1.03 (6)	1.96 (6)
OW4	HOW4A	OW1	3.065 (6)	0.96 (6)	2.13 (6)
OW4	HOW4B	OT2^{vi}	2.808 (5)	1.15 (6)	1.72 (6)
OW5	HOW5A	OT1^{vi}	2.673 (4)	0.83 (5)	1.84 (5)
OW5	HOW5B	OW6	2.827 (5)	0.76 (4)	2.07 (4)
OW6	HOW6A	OW1	2.836 (6)	1.02 (5)	1.91 (5)
OW6	HOW6B	OT4^{iv}	2.800 (5)	0.93 (5)	1.88 (5)

[a] Atoms are related to those given in Table I as follows: (i) $1.5 - x, -y, 0.5 + z$; (ii) $1.0 - x, -0.5 + y, 0.5 - z$; (iii) $x, 1.0 + y, z$; (iv) $1.0 - x, 0.5 + y, 0.5 - z$; (v) $1.5 - x, 1.0 - y, 0.5 + z$; (vi) $1.0 - x, 0.5 + y, 1.5 - z$.

material). In both figures, the thermal ellipsoids have been drawn to include 50% of the probability distribution. In Figure 2, *all* hydrogen atoms are omitted for clarity. The absolute configuration of the complex cation was determined to be Λ from comparison with the known absolute configuration of the *d*-tartrate anion.[10] The absolute configuration determined here agrees with the assignment based on the CD spectrum.[2]

The sen ligand of the complex cation is in the lel_3 conformation (the C–C bonds are approximately parallel to the C_3 axis), presumably because the trimethyleneethane group links three nitrogen atoms (N1, N3, and N5) of the parent $[Co(en)_3]^{3+}$ skeleton. Averages of chemically equivalent bonds and angles of the "ethylenediamine" rings are as follows: Co–N, 1.971 (6) Å; N–C, 1.489 (7) Å; C–C, 1.507 (3) Å; internal N–Co–N, 86.1 (2)°; Co–N–C, 108.5 (5)°. These values are in agreement with the values of the previously reported Λ-$[Co(en)_3]Cl(d\text{-}C_4H_4O_6)\cdot 5H_2O$.[11] Thus, the trimethyleneethane capping does not affect the structure of the central $[Co(en)_3]$ moiety. The strain can be observed for the angles around the four carbon atoms C7, C8, C9, and C10 and the three nitrogen atoms N1, N3, and N5. These angles deviate slightly from the tetrahedral value (see Table V). The three hydrogen atoms bound to C11 (HC11A, HC11B, and HC11C) are located trans to C7, C9, and C8 atoms, respectively.

In the *d*-tartrate anion, the averages of the chemically equivalent bond distances are as follows: C–C(carboxylate), 1.529 (4) Å; C–O(carboxylate), 1.251 (6) Å; C–O(hydroxyl), 1.429 (9) Å. These features are in excellent agreement with those reported previously.[11,12,15–17] The dihedral angle between the two nearly planar moieties, each containing OC–COO, is 34.3°. The four carbon atoms are exactly coplanar (the CT1–CT2–CT3–CT4 torsion angle is 0.4°), and this C–C–C–C plane is exactly perpendicular to the threefold axis of the complex cation (the dihedral angle between the CT1–CT2–CT3–CT4 plane and the N2–N4–N6 plane is 0.3°). These features can also be seen in Λ-$[Co(en)_3]Cl(d\text{-}C_4H_4O_6)\cdot 5H_2O$[11] and Λ-$[Co(en)_3]Br(d\text{-}C_4H_4O_6)\cdot 5H_2O$,[13] in which the dihedral angle between the planes containing the $OC\text{–}COO^-$ group is 36° and the C–C–C–C torsion angle is 2°. For comparison, the dihedral angle between the OC–COO planes is 62° in $(NH_4)_2(d\text{-}C_4H_4O_6)$,[14] 33° in $(H_3NCH_2CH_2NH_3)(l\text{-}C_4H_4O_6)$,[15] 50.8° in Λ-$[Co(Hbg)_3]Cl(d\text{-}C_4H_4O_6)\cdot 5H_2O$ (Hbg = biguanide, $C_2H_7N_5$),[16] and 62.1° in Δ-$[Co(Hbg)_3]Cl(d\text{-}C_4H_4O_6)\cdot 3H_2O$[17] and the dihedral angle between the C–C–C–C plane and the N–N–N plane is 22.1° in Λ-$H[Co(en)_3](d\text{-}C_4H_4O_6)_2\cdot 3H_2O$.[19]

The chloride anion has a total of five close contacts, two to NH hydrogens, two to water oxygens, and one to the hydroxyl oxygen of *d*-tartrate. All are at reasonable distances.[11,12a,19] Six water molecules are all tetrahedrally surrounded and bound quite tightly in the crystal lattice.

Crystal Packing. The most interesting feature is the face-to-face contact consisting of the $[Co(sen)]^{3+}$ cation and the *d*-tartrate anion. Three axial NH hydrogens (HN2E, HN4E, and HN6E) of the cation bind to three oxygens of the anion (two hydroxyl and one carboxyl: OH1, OH2, and OT2) (see Figure 1). The average of the three O···N distances is 2.919 (13) Å. This face-to-face contact mode exists commonly in many $[M(en)_3]$···anion systems, where the anion includes not only the *d*-tartrate ion but also other anions containing three suitably disposed oxygen atoms, like PO_4^{3-}, SO_4^{2-}, or NO_3^-.[20] The remaining carboxyl group (CT4, CT3, OT4), which does not take part in the face-to-face hydrogen bonding, bonds to the neighboring complex cation along the twofold axis of the cation, with an average O···N distance of 2.956 (10) Å. As a result, an infinite zigzag chain composed of the $[Co(sen)]^{3+}$ cation and the *d*-tartrate anion is formed along the crystallographic *c* axis (see Figure 2). Though previous workers did not mention this point at all, this zigzag chain can be found also in Λ-$[Co(en)_3]Cl(d\text{-}C_4H_4O_6)\cdot 5H_2O$[11] and Λ-$[Co(en)_3]Br(d\text{-}C_4H_4O_6)\cdot 5H_2O$.[13] The remaining two twofold axes of the cation are occupied by one chloride anion and one water molecule (OW5), instead of two water molecules in the case of the $[Co(en)_3]^{3+}$ systems.

Six water molecules concentrate in the gap between these zigzag chains and bind to each other through hydrogen bonding. This arrangement of water molecules is sufficiently different from that in $[Co(en)_3]^{3+}$ systems, in which all five waters form a right-handed spiral chain via the chloride (or bromide) anion along the crystallographic *a* axis.

Mode of Chiral Discrimination. Previously, we reported the structure of diastereomers containing $[M(en)_3]^{3+}$ and *d*-tartrate ions. These include Λ-$[Co(en)_3]Br(d\text{-}C_4H_4O_6)\cdot 5H_2O$,[13] Λ-$Li[Cr(en)_3](d\text{-}C_4H_4O_6)_2\cdot 3H_2O$,[21] and Λ-$H[Co(en)_3](d\text{-}C_4H_4O_6)_2\cdot 3H_2O$.[18] As for the present diastereomer, all these diastereomers are characterized by a specific face-to-face close

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contact between the complex cation and one *d*-tartrate anion.

The $[Co(sen)]^{3+}$ cation seems to bear a fairly hydrophobic character compared with $[Co(en)_3]^{3+}$ owing to the presence of the trimethyleneethane group. Thus, the packing modes of Λ-$[Co(sen)]Cl(d\text{-}C_4H_4O_6)\cdot 6H_2O$ and Λ-$[Co(en)_3]Cl(d\text{-}C_4H_4O_6)\cdot 5H_2O$ would be presumed to be considerably different. Actually, the less soluble diastereomer formed with *d*-tartrate contains the Δ isomer in the former system, while it contains the Λ isomer in the latter. Despite these differences, the common existence of the face-to-face contact mode in both systems as well as in other systems suggests strongly the following. If the complex cation has three axial NH hydrogens as in $[M(en)_3]^{3+}$, $[M(sen)]^{3+}$, $[M(pn)_3]^{3+}$, or $[M(chxn)_3]^{3+}$ and the anion has three oxygen atoms that can associate favorably with these NH hydrogens, a similar face-to-face close contact may be expected in solution as well as in the solid state.

That the mode of close contact in solution should be similar to that found in the solid state is supported by several experimental results.[1] These include the following.

(i) Δ-$[Co(en)_3]^{3+}$, Δ-$[Co(sen)]^{3+}$, Δ-*fac*- and Δ-*mer*-$[Co(1\text{-}pn)_3]^{3+}$, and Δ-$[Co(1\text{-}chxn)_3]^{3+}$, which have axial NH hydrogens suitable for triple hydrogen bonding along the C_3 (or pseudo-C_3) axis, discriminate more or less between the *d*- and *l*-tartrate ions in solution, as evidenced by chromatographic optical resolution and different ion association constants. In contrast, the $[Co(sep)]^{3+}$ ion, which lacks such NH hydrogens, does not discriminate at all. For example, $[Co(sen)]^{3+}$ was found to be resolved by ion-exchange chromatography with SP-Sephadex C-25 (cation exchanger); the complex was loaded on a column (1 × 30 cm) and eluted by a 0.1 M aqueous solution of sodium *d*-tartrate or sodium (*d*-tartrato)antimonate(III). For both eluents, the Λ enantiomer was eluted first, as for $[Co(en)_3]^{3+}$, $[Co(pn)_3]^{3+}$, and $[Co(chxn)_3]^{3+}$. Likewise, the association constants (at 25 °C and $\mu = 0.1$ with sodium perchlorate) for the *d*- and *l*-tartrates were $K_d = 50 \pm 1\ M^{-1}$ and $K_l = 72 \pm 1\ M^{-1}$ for Δ-$[Co(sen)]^{3+}$ and $K_d = K_l = 39 \pm 1\ M^{-1}$ for Δ-$[Co(sep)]^{3+}$.

(ii) The effect of *d*- and *l*-tartrate ions upon the CD spectra of Δ-$[Co(sen)]^{3+}$, Δ-$[Co(en)_3]^{3+}$, Δ-*fac*- and Δ-*mer*-$[Co(1\text{-}pn)_3]^{3+}$, and Δ-$[Co(1\text{-}chxn)_3]^{3+}$ is such that they enhance the A_2 rotational strength, while the direction of CD change of Δ-$[Co(sep)]^{3+}$ is just the opposite. This observation is consistent with the idea that the tartrates approach the former group of cations along the C_3 axis, forming hydrogen bonds with three axial NH hydrogens. For Δ-$[Co(sep)]^{3+}$, which has only equatorial NH hydrogens directing approximately parallel to the C_2 axis, the tartrate ion will be forced to approach along the C_2 axis. This C_2 access will enhance the E_a rotational strength in the same way as the C_3 access enhances the A_2 rotational strength.

(iii) From the association constant and the difference CD spectrum due to tartrates, the CD spectrum of the ion pair Λ-$[Co(sen)]^{3+}\cdots d\text{-tartrate}^{2-}$ can be obtained. The CD spectrum of this ion pair tends to be similar in shape to that of Λ-$[Co(sep)]^{3+}$ itself, which has one more covalent cap than $[Co(sen)]^{3+}$ does. If we note that the CD of $[Co(sep)]^{3+}$ is dominated by the A_2 rotational strength, this observation will be seen to be in line with the idea that the addition of atoms or groups, whether covalent or hydrogen bonded, to the D_3 polar region of the $[Co(N)_6]^{3+}$ complexes enhances generally the A_2 rotational strength.[22]

All the above facts point to the relevance of the face-to-face contact mode in the crystal to the mode of stereoselective association in solution.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, final atomic coordinates for hydrogen atoms with isotropic thermal parameters (Table II), and final anisotropic thermal parameters for non-hydrogen atoms (Table III) and a stereoview of the unit cell (Figure 2) (9 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of Potassium Nonahydro(trimethylphosphine)tetraborate(1−)

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Potassium nonahydrotetraborate(1−) reacted with trimethylphosphine in tetrahydrofuran and gave the salt of a new complex anion $B_4H_9P(CH_3)_3^-$. The compound was stable below 0 °C but decomposed slowly at room temperature. A nonrigid, trigonal-pyramid structure having the phosphine attached at the apical boron was suggested for the anion on the basis of the NMR data (^{11}B, −26.4 (intensity 3), −35.8 ppm (1); ^1H, δ 1.23 (H_C, 1), 0.03 (H_B, 1); ^{31}P, 2.1 ppm). Diborane treatment of the adduct anion resulted in the formation of $B_4H_8\cdot P(CH_3)_3$. The reaction with HCl in tetrahydrofuran produced hydrogen gas and gave a mixture containing $B_4H_8\cdot P(CH_3)_3$, $(CH_3)_3P\cdot BH_3$, and $THF\cdot B_3H_7$ in a 1:2.4:1.8 molar ratio.

Introduction

Lewis base adducts of tetraborane(8), $B_4H_8\cdot L$, react with Lewis bases to give hypho class tetraborane adducts:

$$B_4H_8\cdot L + L' \rightarrow B_4H_8\cdot L\cdot L'$$

Thus, ammonia and methylamines add to $B_4H_8\cdot N(CH_3)_3$ in 1:1 molar ratios,[1,2] and $P(CH_3)_3$ adds to $B_4H_8\cdot P(CH_3)_3$ likewise.[3] Other examples are the additions of CH_3CN,[4] $(CH_3)_2O$,[4] and $N(CH_3)_3$[5] to $B_4H_8\cdot CO$. In these reactions the monobase adducts of tetraborane(8) are acting as Lewis acids toward the various bases.

The nonahydrotetraborate(1−) anion, $B_4H_9^-$, can formally be regarded as the hydride (H^-) adduct of B_4H_8. This for-

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