alternate least-squares cycles. No hydrogen atoms were included. Refinement of the non-hydrogen atoms with anisotropic temperature factors was carried out except for the disordered atoms.

[Nd(EO4)$_2$]$_4$[NdCl$_6$]Cl$_9$. The space group was determined to be either the centric *I4/mmm* or acentric *I4m2*, *I42m*, *I4mm*, or *I422* from the systematic absences. The subsequent solution and successful refinement of the structure were carried out in the acentric space group *I422*. The alcoholic hydrogen atoms were not included in the final refinement. Two partially occupied sites were observed for the Cl(4) atom. This atom was refined at 50% occupancy. The two possible positions are symmetry related and are surrounded by the [Nd(EO4)$_2$]$^{3+}$ cations, as discussed under Results.

[NdCl$_2$(OH$_2$)(EO5)]Cl·H$_2$O. The alcoholic and water hydrogen atoms were not included in the final refinement.

[Nd(OH$_2$)$_2$(EO7)]Cl$_3$·H$_2$O. The alcoholic and water hydrogen atoms were not included in the final refinement.

[Nd(OH$_2$)$_7$(OHMe)$_2$]Cl$_3$. The methyl hydrogen atoms were included as rigid groups with rotational freedom at the bonded carbon atom (C–H

= 0.95 Å, *B* = 5.5 Å^2). The remaining hydrogen atoms were not included in the final refinement.

Supplementary Material Available: Tables SI–SXXVIII, listing crystal data and data collection and refinement parameters, bond distances and angles, hydrogen atom coordinates, thermal parameters, hydrogen-bonding contact geometries, and torsion angles, and Figures SI–SIV, showing the unit cells for the 18-crown-6, EO6, and EO7 complexes and the Nd^{3+} ion coordination environment in [Nd(OH$_2$)$_7$(OHMe)$_2$]Cl$_3$ (44 pages); tables of observed and calculated structure factors or amplitudes (59 pages). Ordering information is given on any current masthead page.

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Chiral Discriminations and Crystal Packing. Two Diastereomeric Compounds Involving Complex Ions of D_3 Symmetry, Tris(ethylenediamine)cobalt(III) and Tris(oxalato)rhodate(III)

Reiko Kuroda

Factors governing the chiral recognition of three-bladed-propeller type metal complexes were analyzed. Crystal structures of two diastereomeric compounds of [Co(en)$_3$]$^{3+}$ (en = 1,2-diaminoethane) and [Rh(ox)$_3$]$^{3-}$ (ox = oxalate dianion) have been determined by single-crystal X-ray structure analysis. Crystal I, Λ-[Co(en)$_3$]-Λ-[Rh(ox)$_3$] is rhombohedral, with *a* = 13.069 (2) Å, *c* = 9.877 (3) Å, space group *R*3, and *Z* = 3, and the structure was refined to *R* = 0.025. It is made up of columns of alternating cations and anions along the *c* axis with the molecular *C$_3$* axes colinear. Crystal II contains optically impure [Co(en)$_3$]$^{3+}$ (60% Λ and 40% Δ) and Δ-[Rh(ox)$_3$]$^{3-}$. It is monoclinic, with *a* = 8.172 (2) Å, *b* = 15.343 (3) Å, *c* = 8.325 (2) Å, *β* = 102.99 (1)°, space group *P2$_1$*, and *Z* = 2, and the final *R* value was 0.054. The structure containing Δ-[Rh(ox)$_3$]$^{3-}$ accommodates either Δ- or Λ-[Co(en)$_3$]$^{3+}$ equally well without any unusually close contacts between the complex ions. All the hydrogen atoms in I and II are involved in hydrogen bonding. The crystal-packing mode is compared with that of reported *D$_3$*-type structures and discussed in the context of chiral recognitions and optical resolution. For those complexes where dispersion forces are dominant, nearly parallel or nearly tetrahedrally tilted arrangements of molecular *C$_3$* axes are often adopted, in agreement with our previous theoretical calculations. When hydrogen bonding is available, this will become a dominant factor. In these cases, the frequently observed *C$_3$* colinear cation–anion mutual orientations afford full use of hydrogen bonding regardless of the chirality of the complex ions or the stacking conformation. Hydrogen bonds perpendicular to the *C$_3$* axes appear to contribute toward successful chiral discriminations.

Introduction

Chirality and optical resolution of chiral compounds are becoming increasingly important in fields related to biology and medicine. However, at present, the molecular basis of optical resolution is poorly understood. To investigate the mechanism of chiral recognitions and discriminations in the crystalline state, we have studied the crystal structures of several different classes of chiral compound including organic molecules with helical morphology,[1,2] sodium ammonium tartrate[3] originally described by Pasteur, and metal complexes.[4,5] We have been particularly interested in conformationally rigid chiral compounds of high symmetry. Tris-bidentate metal complexes with octahedral coordination exhibit the highest chiral symmetry, D_3, which facilitates spectroscopic and theoretical analysis of chiral discriminations. These compounds adopt a propeller type structure and exist as optical isomers of Δ (right-handed propeller) and Λ (left-handed propeller) forms, even when the ligand is achiral. Previously, we calculated the chiral discrimination dispersion energy of a model neutral D_3 metal complex, for both an active pair, Δ–Δ or Λ–Λ configuration, and a racemic pair, Δ–Λ configuration, on the basis of an extended monopole model.[6] The

theoretical analysis showed that there are preferred mutual orientations of the molecules both in the active and racemic system.

The orientations of complexes in the crystalline state were studied and compared in [Cr(pd)$_3$] (III)[4] (pd = 1,2-diaminopropane), and [Cr{(−)-bdtp}$_3$] (IV)[5] (bdtp = dimethylethylene dithionato anion). Both compounds were chosen for analysis because they are neutral and devoid of solvent molecules of crystallization: the presence of counterions and solvent molecules contributes to the crystal-packing mode, complicating the analysis of chiral recognition. The theoretical predictions and the observed crystal packings were in reasonable agreement.[4,5] We have now extended the work to a diastereomeric system, [Co(en)$_3$]$^{3+}$[Rh-(ox)$_3$]$^{3-}$, where both the cation and the anion possess the simplifying feature of D_3 symmetry. In this system, the complex ions carry electrostatic charges, while the ox and en ligands function as potential hydrogen-bond acceptors and donors, respectively. Thus, not only the shape of the molecules but also electrostatic interactions including hydrogen bonding are expected to play an important role in the chiral discriminations. Two diastereomeric crystals (I and II) were made, and their crystal structures were determined. The crystal packing mode of the structures as well as those of other known diastereomeric D_3 tris(bidentate)metal complexes, K-Λ-[Ni(phen)$_3$]-Λ-[Co(ox)$_3$]·2H$_2$O (V)[7] (phen =

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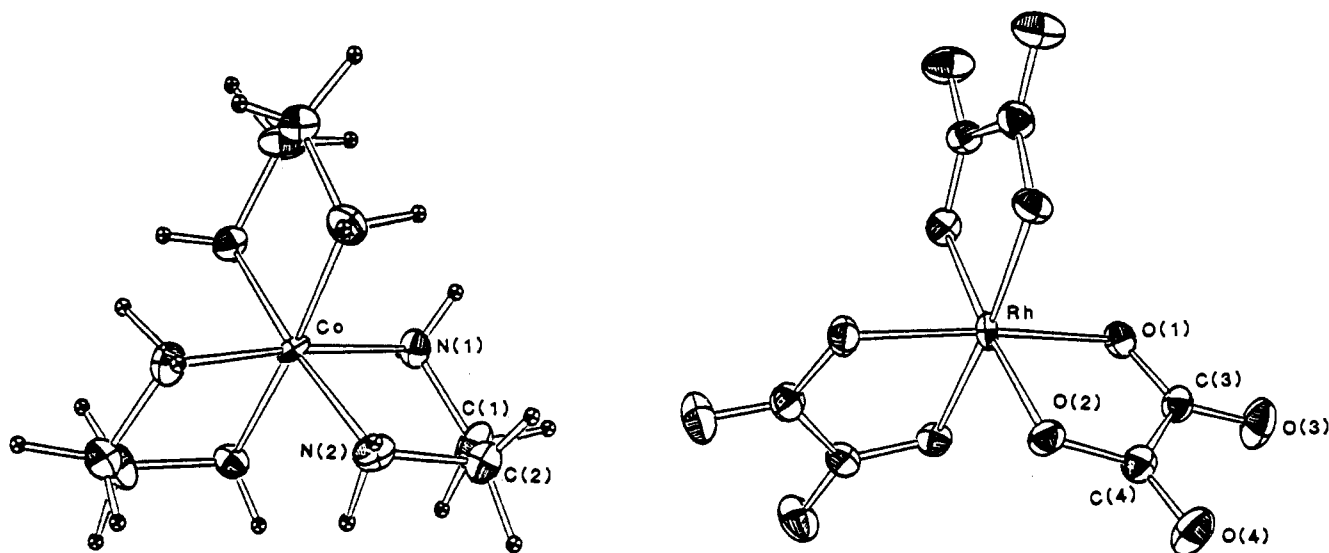(7) Butler, K. R.; Snow, M. R. *J. Chem. Soc. A* **1971**, 565.

Figure 1. Molecular structure of Λ-[Co(en)₃] and Λ-[Rh(ox)₃] in crystal I.

1,10-phenanthroline) and Δ-[Co{(−)-pn}₃]-Λ-[Cr(mal)₃]·3H₂O (VI)[8] (pn = 1,2-diaminopropane, mal = malonate dianion), are analyzed and discussed in the context of chiral discrimination.

Experimental Section

Preparation of Compounds and Crystals. Both [Co(en)₃]³⁺ and [Rh(ox)₃]³⁻ ions were synthesized and optically resolved according to literature methods.[9,10] Crystals of the diastereomers were grown at room temperature by the diffusion method: two sample bottles each containing a 0.03 M aqueous solution of the complex cation and anion, respectively, were placed in an empty beaker, and then distilled water was gently added until the two bottles were submerged. For the homochiral crystal, I, optically pure Λ-K₃[Rh(ox)₃]·2H₂O and Λ-[Co(en)₃]Cl₃·2H₂O were employed. After two days, small orange needlelike crystals started to appear on the wall of the Rh-containing sample bottle. These crystals were carefully removed, washed with H₂O, and used for structure determination.

Preparation of crystals of the other diastereomer, Λ-[Co(en)₃]-Δ-[Rh(ox)₃], was very difficult, and only fluffy non-crystalline material was obtained under various conditions. However, crystallization was successful using optically pure Δ-K₃[Rh(ox)₃]·2H₂O and only partially resolved [Co(en)₃]Cl₃·2H₂O (optical purity of the Co complex: 76.1% Δ and 23.9% Λ based on the *g* factor). Two types of crystals were obtained. The first type appeared after 1 week, had a needlelike shape similar to I, and was later confirmed by X-ray photography to be Δ-[Co(en)₃]-Δ-[Rh(ox)₃], the enantiomer of I. Very small disk-shaped crystals appeared after 2 weeks as a minor component. X-ray photography confirmed that the crystal II had completely different cell parameters from I.

Spectroscopy. The optical purity of the component metal complex ions was checked by absorption and circular dichroism spectroscopy, measured on Cary 17 and Jasco J40CS instruments, respectively.

X-ray Structure Determination. X-ray photographs were taken to determine the crystal class. The intensities were measured using monochromated Mo Kα radiation by 2θ–ω scan mode on an Enraf-Nonius CAD-4 diffractometer. Crystal decomposition and orientation were checked in the usual fashion, and no correction was applied. Absorption,[11] extinction, and anomalous dispersion corrections[12] were applied. The structure of I was solved by standard heavy-atom methods and refined by full-matrix least-squares techniques based on *F*. All the hydrogen atoms were clearly revealed in a difference Fourier map and refined with isotropic thermal factors. The final *R* value was 0.025.

Because of the small size of crystal II, the intensity data were of poor quality. The structure solved by heavy-atom methods showed disorder of the cation. There are two CoN₆ clusters and a unique set of en carbon atoms. Both CoN₆ clusters form reasonable chelate rings with the unique set of carbon atoms. Various difference Fourier syntheses confirmed that

Table I. Crystallographic Data for I and II

	I	II
formula	(C₆H₂₄N₆Co)(C₆O₁₂Rh)	(C₆H₂₄N₆Co)(C₆O₁₂Rh)
fw	606.20	606.20
cryst syst	rhombohedral	monoclinic
a, Å	13.069 (2)	8.172 (2)
b, Å		15.343 (3)
c, Å	9.877 (3)	8.325 (2)
β, deg		102.99 (1)
V, Å³	1461 (1)	1017.2 (8)
Z	3	2
ρ_{calcd}, g cm⁻³	2.067	1.979
ρ_{obsd}, g cm⁻³	2.07	1.98
space group	*R*3 (No. 146)	*P*2₁ (No. 3)
T, °C	20	20
λ, Å	0.710 69	0.710 69
μ(Mo Kα), cm⁻¹	17.93	17.17
R	0.025	0.054
$R_w{}^a$	0.026	0.061

$^a R_w = [\sum w(|F_o| - |F_c|)/\sum w|F_o|)]$, where $w = 1/\sigma(F_o)$.

Table II. Atomic Coordinates and Equivalent Temperature Factors (Å²) for I

atom	*x*	*y*	*z*	B_{eq}
Co	0.0	0.0	0.5034 (2)	1.128 (7)
N(1)	0.0140 (3)	0.1290 (3)	0.3906 (4)	1.86 (7)
N(2)	0.1241 (3)	0.1258 (3)	0.6152 (3)	1.59 (7)
C(1)	0.1137 (4)	0.2446 (4)	0.4369 (5)	2.14 (8)
C(2)	0.1244 (4)	0.2381 (4)	0.5876 (5)	2.29 (9)
Rh	0.0	0.0	0.0000 (2)	1.253 (4)
O(1)	−0.0039 (3)	0.1279 (2)	−0.1110 (3)	1.84 (6)
O(2)	0.1167 (2)	0.1358 (3)	0.1123 (3)	1.70 (6)
O(3)	0.0728 (3)	0.3219 (3)	−0.1059 (4)	2.70 (7)
O(4)	0.1958 (3)	0.3300 (3)	0.1247 (4)	2.82 (8)
C(3)	0.0621 (3)	0.2321 (3)	−0.0594 (5)	1.86 (8)
C(4)	0.1316 (3)	0.2355 (3)	0.0700 (4)	1.61 (7)

the observation of two sets of en atoms was not due to an artifact. The best refinement results were obtained when a fixed ratio of 6/4 was assigned for the two clusters. No attempt was made to refine further the site occupancy factor due to the weak intensity data set. Disordered nitrogen atoms were refined isotropically and the rest of the atoms anisotropically. Hydrogen atoms were generated at their ideal geometry, and the positional and isotropic thermal parameters were fixed during the refinement. The final *R* value was 0.054.

Atomic scattering factors were taken from ref 12. All the computations were carried out on a PDP11/34A computer using the SDP crystallographic program system.[12] Crystal data, conditions for data collection and structure refinements are summarized in Table I for each of the compounds. Final atomic parameters are listed in Tables II and III. Anisotropic thermal parameters, hydrogen atom parameters, bond lengths and angles, and observed and calculated structure factors are

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Table III. Atomic Coordinates and Equivalent or Isotropic Temperature Factors (Å^2) for II

atom	x	y	z	$B_{eq}/B_{iso}{}^a$
Co	0.3117 (3)	0.7488 (2)	0.3845 (3)	1.81 (4)
N(1)	0.364 (3)	0.795 (2)	0.188 (3)	1.9 (5)
N(2)	0.402 (3)	0.645 (2)	0.317 (3)	2.5 (5)
N(3)	0.077 (3)	0.727 (1)	0.272 (3)	1.2 (4)
N(4)	0.261 (3)	0.695 (2)	0.572 (3)	2.3 (5)
N(5)	0.241 (3)	0.868 (1)	0.441 (3)	1.0 (4)
N(6)	0.539 (3)	0.786 (2)	0.515 (3)	2.7 (5)
N(1′)	0.509 (4)	0.705 (2)	0.335 (4)	1.4 (6)
N(2′)	0.208 (5)	0.753 (3)	0.149 (5)	2.6 (8)
N(3′)	0.230 (5)	0.637 (3)	0.428 (5)	1.9 (7)
N(4′)	0.090 (5)	0.793 (3)	0.433 (5)	2.7 (8)
N(5′)	0.424 (6)	0.760 (4)	0.614 (6)	4 (1)
N(6′)	0.382 (4)	0.872 (2)	0.344 (4)	1.7 (6)
C(7)	0.355 (4)	0.727 (2)	0.057 (2)	6.2 (7)
C(8)	0.468 (3)	0.663 (2)	0.169 (3)	4.6 (6)
C(9)	−0.001 (3)	0.700 (3)	0.410 (3)	8.4 (9)
C(10)	0.095 (3)	0.640 (2)	0.506 (3)	6.6 (7)
C(11)	0.425 (4)	0.914 (1)	0.526 (2)	4.2 (6)
C(12)	0.529 (3)	0.852 (2)	0.630 (3)	4.3 (5)
Rh	−0.0099 (2)	0.0000 (1)	0.0500 (2)	1.96 (2)
O(1)	0.165 (1)	−0.068 (1)	−0.025 (1)	2.5 (3)
O(2)	−0.135 (1)	−0.0134 (9)	−0.184 (1)	2.5 (3)
O(3)	−0.100 (2)	−0.1061 (9)	0.124 (1)	2.4 (3)
O(4)	−0.202 (2)	0.057 (1)	0.127 (2)	3.3 (3)
O(5)	0.130 (1)	0.0226 (7)	0.275 (1)	2.0 (3)
O(6)	0.086 (2)	0.120 (1)	−0.004 (2)	4.0 (4)
O(7)	0.192 (2)	−0.150 (1)	−0.231 (2)	5.4 (4)
O(8)	−0.099 (2)	−0.074 (1)	−0.411 (2)	4.6 (4)
O(9)	−0.305 (2)	−0.151 (1)	0.240 (2)	4.9 (4)
O(10)	−0.404 (2)	0.022 (2)	0.249 (2)	7.0 (6)
O(11)	0.329 (2)	0.119 (1)	0.411 (2)	5.0 (4)
O(12)	0.287 (2)	0.208 (1)	0.113 (2)	6.4 (5)
C(1)	0.123 (3)	−0.094 (1)	−0.166 (3)	3.1 (5)
C(2)	−0.051 (2)	−0.060 (1)	−0.264 (2)	2.3 (4)
C(3)	−0.233 (2)	−0.094 (1)	0.188 (2)	2.8 (4)
C(4)	−0.282 (2)	0.004 (2)	0.192 (2)	3.0 (4)
C(5)	0.219 (2)	0.091 (1)	0.282 (3)	2.6 (4)
C(6)	0.206 (3)	0.143 (2)	0.124 (3)	3.8 (5)

^{a} Nitrogen atoms were refined isotropically. Site occupancy factors for unprimed and primed nitrogen atoms are 0.6 and 0.4, respectively.
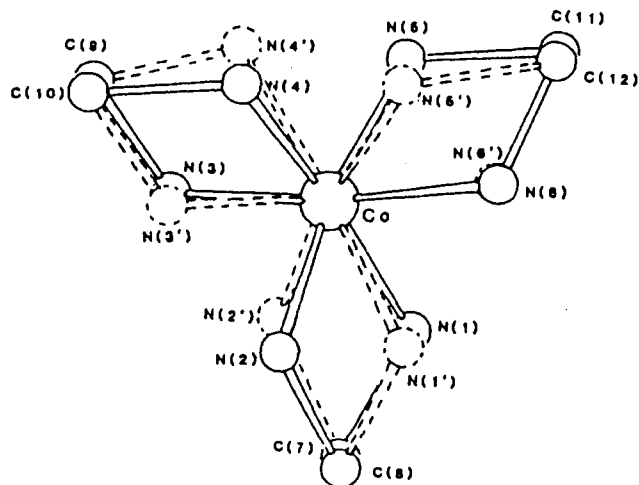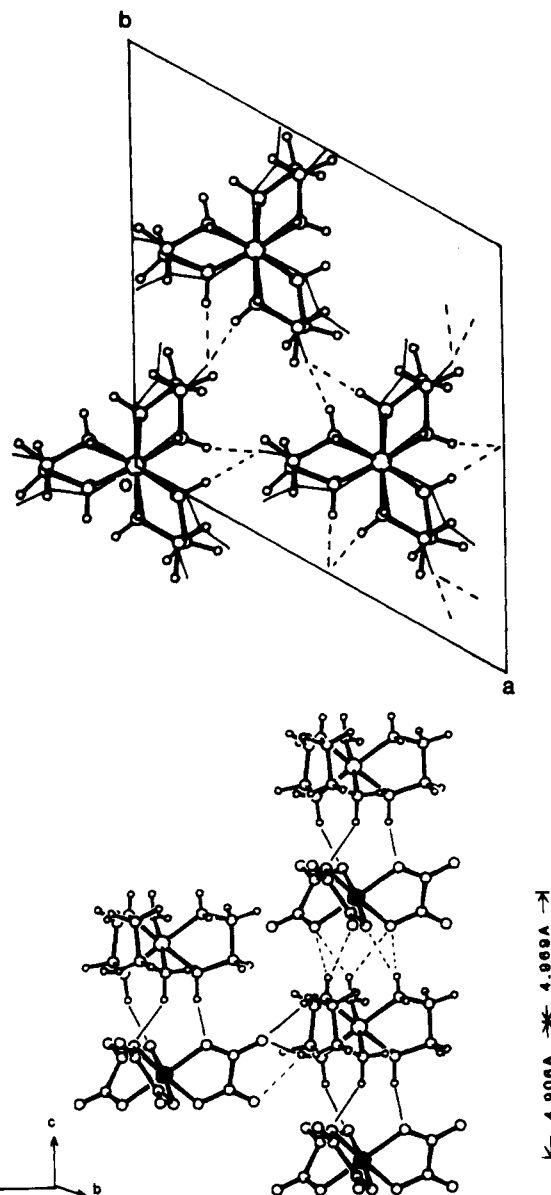

Figure 3. Hydrogen bonding network of I as viewed along the crystal c axis (a) and perpendicular to the C_3-colinear column (b). In part b, Rh atoms are indicated as solid circles.

Figure 2. Disordered $[Co(en)_3]^{3+}$ in crystal II as viewed along the pseudo-C_3 axis. Two sets sharing the cobalt and the carbon atoms are related by a pseudo mirror plane perpendicular to the C_3 axis.

available as supplementary material.

Results and Discussion

Molecular Structure. Crystal I. Both of the complex ions adopt an exact 3-fold symmetry as indicated by the $R3$ space group and Z value. All the bond lengths and angles are normal. The Co complex adopts the lel_3 form, $\Lambda(\lambda\lambda\lambda)$ (Figure 1).

Crystal II. In crystal II, the two disordered sets of CoN_6 clusters and the unique carbon atoms of en form enantiomeric $[Co(en)_3]^{3+}$

ions. The optical isomers are related to each other by a pseudo mirror plane, which is perpendicular to the molecular C_3 axis and runs through the Co atom (Figure 2). Thus, the crystal can be described as containing $[Co(en)_3]^{3+}$ in the ratio of 60% Λ form and 40% Δ form as well as 100% Δ-$[Rh(ox)_3]^{3-}$. It is not clear whether the Δ/Λ ratio is common to all crystals of II. Two other crystals obtained had the same cell parameters; however, they were too small for structural analysis. The Co complex is in the lel_3 form. Estimated standard deviations of bond lengths and angles are 2–3 times larger than those of crystal I, and part of the cation's geometry is less satisfactory, probably due to the disorder and the weak intensity data.

Crystal Packing and Hydrogen Bonding. Crystal I. The crystal is made up of columns of alternating cations and anions along the crystal c axis in which the C_3 axes of cations and anions are exactly colinear as required from the space group symmetry. The complex ions stack almost on top of each other, as seen in Figure 3a, with a dihedral angle of $5.2°$ between the C_2 axes of the cation and the anion. The two average ring planes make a dihedral angle of $8.5°$ to each other. According to the dispersion energy calculations,[6] both the racemic and the active pair can pack adequately well along the C_3 axis. For the active complex, packing is most favored with the ring planes almost parallel and one
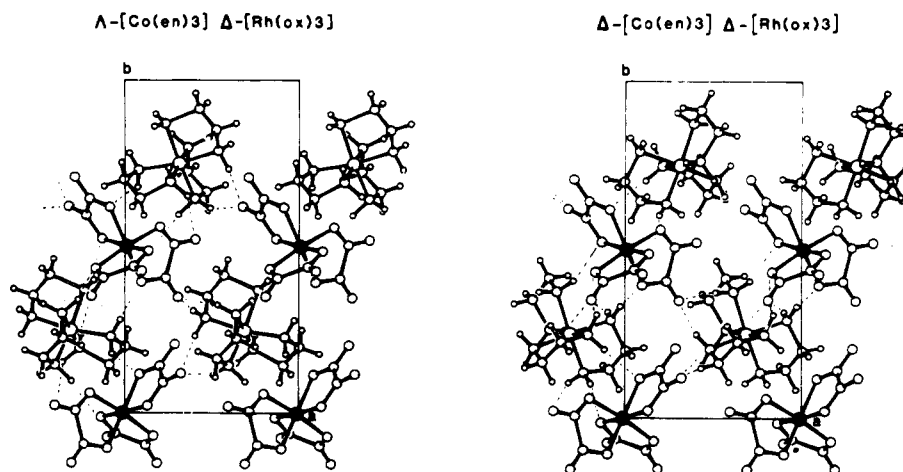
Crystal II

Λ-[Co(en)3] Δ-[Rh(ox)3]   Δ-[Co(en)3] Δ-[Rh(ox)3]

Figure 4. Crystal packing and possible hydrogen-bonding network of II analyzed as Δ-[Co(en)₃]-Δ-[Rh(ox)₃] and Λ-[Co(en)₃]-Δ-[Rh(ox)₃]. Hydrogen atoms are in calculated positions. Rh and Co atoms are shown as solid and open circles, respectively.

molecule is rotated by a small angle with respect to the other about the common C_3 axis. This is exactly what was observed in crystal I.

This mutual orientation of the cations and anions is equally favorable for the formation of hydrogen bonds. The equatorial amino hydrogen of the en ligands and the coordinating oxygen atoms of the ox ligands form hydrogen bonds (Table IV and Figure 3b). Along the c axis, the cations and the anions are distributed at slightly different distances, and single hydrogen bonds (designated as type a) are found where the Rh–Co distance is shorter. Somewhat weaker bifurcated hydrogen bonding involving two ligating oxygen atoms of an anion (type a′) is observed on the side where the Rh–Co distance is slightly longer (Figure 3b). In this way, the cations and anions form a continuous hydrogen-bonded network along the column.

All three columns in the unit cell and hence all the molecular C_3 axes in the crystal are parallel as required from the space group symmetry. The dispersion energy calculation predicts[6] that D_3 type complexes with planar chelate rings pack economically in the plane perpendicular to the parallel molecular C_3 axes only when adjacent molecules adopt opposite absolute configurations, because the packing allows the contiguous chelate rings of racemic neighbors in the plane to assume a parallel mutual orientation. The contiguous chelate rings of two adjacent molecules with the same absolute configuration are tilted in opposite directions, resulting in poor crystal packing. Parallel orientation of the contiguous plane is achieved only when the two molecular C_3 axes become mutually orientated at the tetrahedral angle or its supplement. Nearly tetrahedral dihedral angles have been observed in III[4] and IV.[5] In crystal I, efficient parallel orientation of homochiral molecules (Λ-Co and Λ-Rh ions) is achieved by 3_1 symmetry operations along the c axis (120° rotation and shift by 3.292 Å with respect to each other), rather than adopting the tetrahedral arrangement.

The mutual orientation related by 3_1 facilitates hydrogen bonding between the columns. An exocyclic oxygen atom of ox forms a pair of acceptor hydrogen bonds with two axial amino hydrogen atoms each belonging to different en chelate rings of a cation. The hydrogen bonds are shown by dotted lines in Figure 3a and designated as type b. The intercolumn Rh–Co distances are 7.716 and 7.730 Å, which are much longer than the corresponding intracolumn distances. In the crystal, all the possible donor atoms engage in hydrogen bonding (Table IVa).

Crystal II. Because of the type of disorder, the direction of the molecular C_3 axes of the Co complex ions is independent of the chirality of the molecules. Some short Rh–Co distances are 5.121, 5.454, 6.931, 7.562, 7.681, and 7.765 Å. The C_3 axes of cations and anions are either nearly parallel or nearly perpendicular to each other. The crystal structure is conveniently analyzed by

comparing the interactions of the Rh ion with surrounding Λ- or alternatively Δ-Co cations (Figure 4).

The positions of the hydrogen atoms were generated assuming an ideal geometry. The possible hydrogen-bonding network in the homochiral Δ-[Co(en)₃]-Δ-[Rh(ox)₃] pair is quite different from that seen for the homochiral crystal I, but it shares some features in common. Although there is no homochiral column in the structure, there is a cation–anion pair with their C_3 axes almost colinear, and the Rh–Co distance is as short as 5.121 Å, comparable to 4.908 or 4.969 Å in I. This part of the orientation is presented schematically in Figure 5 together with a similar arrangement found in I for comparison. The ring planes are almost parallel to each other and hydrogen bonding of type a is indicated (Table IV).

A similar C_3 colinear arrangement is also found in the heterochiral structure, Λ-Co and Δ-Rh. The dispersion force and contact discrimination calculation for flat-ring model D_3 compounds predicts[6] that a C_3-colinear mutual orientation for the heterochiral pair is efficient when the molecules are rotated about the C_3 axis by 60° with respect to each other. Unexpectedly, the rotation angle is as small as 14.3°, and hydrogen bonds of type a are suggested between the complex ions (Figure 5 and Table IV). The partially stacked chelate rings are tilted by 63–70° to each other.

Hydrogen bonds of type b could also be formed in crystal II, for both the homochiral and heterochiral structures. In addition to the types a and b, other types of hydrogen bonds are formed between different donor–acceptor combinations, which are also shown in Table IVa and Figure 4. Thus, in crystal II, as in I, all the hydrogen atoms are most likely involved in the hydrogen-bonding network, regardless of the chirality of the cation.

No unusually close contacts between the cations and anions are observed in crystal II, whether the cation adopts the Δ or Λ configuration. This means that the crystal structure made up of one enantiomer of [Rh(ox)₃]³⁻ can accommodate either Δ or Λ [Co(en)₃]³⁺ almost equally well. This fact explains why optically impure crystals can be formed.

Principles of Chiral Discriminations: Comparison with Other Diastereomeric Crystals. To date several diastereomeric crystals have been reported where both the anion and cation are of the D_3 three-bladed-propeller shape. A homochiral crystal K-Λ-(+)-[Ni(phen)₃]-Λ-(−)-[Co(ox)₃]·2H₂O (V) crystallizes in the cubic system with space group $P2_13$.[7] The complex forms columns of alternating cations and anions with the molecular C_3 axes colinear with the column as required by the space group symmetry. The arrangement is similar to what is observed in I. Both of the planar chelate rings of the anions and the cations stack almost on top of each other with a small dihedral angle of 3.3° between the respective C_2 axes (Figure 5). The space group also dictates
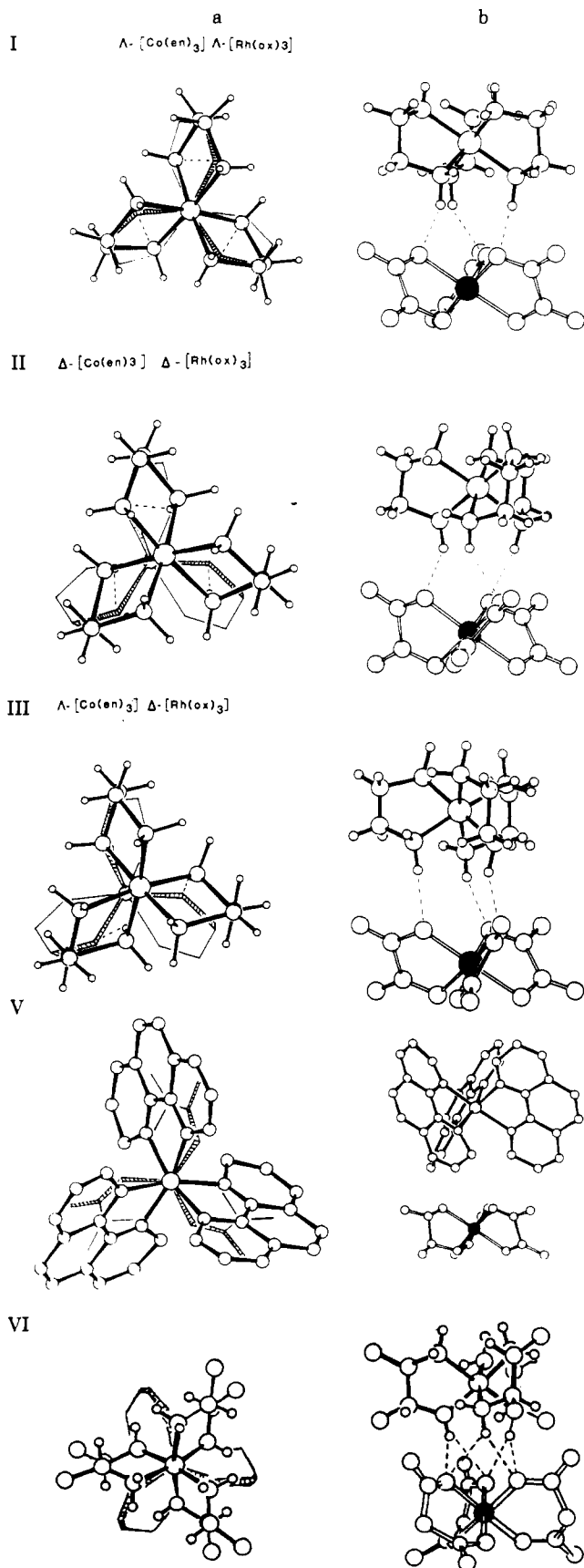
a   b

I   Λ- [Co(en)₃] Λ-[Rh(ox)3]

II   Δ-[Co(en)3]   Δ-[Rh(ox)₃]

III   Λ-[Co(en)₃] Δ-[Rh(ox)₃]

V

VI

Figure 5. Comparison of C_3-colinear arrangement of a cation and an anion observed in crystal structures I, II, V, and VI. Schematic views along the C_3 axis of the cation (a) and perpendicular to it (b) are given. Figures for V and VI were redrawn using the coordinates in refs 7 and 8, respectively. In VI, both ions are disordered on 32 symmetry sites. In part b, the metal atom of the anion is indicated as a solid circle.

that the four columns in the unit cell be tilted at the tetrahedral angle or its supplement to each other. Thus, the C_3 axes of the complex ions make a tetrahedral angle or its supplement resulting in a nearly parallel arrangement (dihedral angle of 5°) of the chelate ring planes. This is exactly what is predicted for a homochiral system by our dispersion energy calculations.[6] Unlike the present [Co(en)₃][Rh(ox)₃] system, there are no hydrogen-bond donor atoms in the cation [Ni(phen)₃]²⁺. Two water molecules of crystallization are disordered, and the involvement in hydrogen bonding to the ox ligands was not well established. A potassium ion interacts with six noncoordinating oxygen atoms of ox, two each from each surrounding anion. When the chelate rings are unsaturated and hence planar as in III–V, hydrogen bonding is not important and the compounds appear to pack in the crystal in accord with the dispersion energy calculations.

The homochiral pair is more stable than the heterochiral pair for the diastereomers of [Co(en)₃][Rh(ox)₃]. In contrast, the heterochiral pair is the stable diastereomer in the case of [Co{(-)-pn}₃][Cr(mal)₃]. The crystal structure of Δ-[Co{(-)-pn}₃]-Λ-[Cr(mal)₃]·3H₂O (VI) determined by Butler and Snow[8] is rhombohedral with space group R32. There are columns of alternating cations and anions whose C_3 axes are colinear, and three parallel columns in the unit cell are related by a 3₁ screw axis along the c axis. All the features are common to those of crystal I. The chelate rings of cations and anions in a column are staggered by 60° as predicted by our dispersion energy calculations (Figure 5). In the C_3 colinear heterochiral interactions of II, chelate rings of cations and anions stack almost on top of each other. The different mutual orientation along the C_3 axis can be explained by severe steric hindrance in the case of the pn–mal system: the bulky methyl groups of pn protrude toward the anion, and the noncoordinating oxygen atoms of mal protrude more toward the cation compared with ox. In the crystal, both complex ions are disordered on sites of symmetry 32. In the staggered mutual orientation of VI, a′ type intracolumn hydrogen bonding is observed. Analogy to structure I suggests b type hydrogen bonds between the columns of VI employing the exocyclic oxygen of mal and two axial amino hydrogen atoms of pn. However, water molecules adopt the role of the exocyclic oxygen atom of ox and serve as acceptors of two amino hydrogen atoms related by 2-fold symmetry. A water molecule at the same time acts as a donor to two exocyclic oxygen atoms belonging to different complexes.

Equally good a or a′ type hydrogen bonds were found for both homochiral (I and II) and heterochiral (II and VI) pairs, irrespective of whether the anion and the cation chelate rings are nearly eclipsed (I and II) or staggered by 60° (VI). Thus, it seems that intracolumn interactions in the frequently observed C_3-colinear columns of alternating anions and cations or C_3-colinear interactions between an anion and a cation cannot discriminate the handedness of these complex ions. Hydrogen bonding between the column, i.e. hydrogen bonding perpendicular to the C_3 axes, however, appears to be important in chiral discriminations. In I, inversion of the cation's chirality would break type b hydrogen bonding. Similarly in VI, waters of crystallization which form hydrogen bonds perpendicular to the C_3 axes seem to discriminate the chirality of the anion, as inversion of the chirality of mal will destroy the fully used tetrahedrally arranged hydrogen-bond network. Significantly, [Ni(phen)₃]²⁺, which has no potential hydrogen-bond donor, is not a successful resolving agent of racemic K₃[M(mal)₃]·xH₂O (M = Cr, Co).

There is no doubt that the homochiral crystal I is more stable than the mixed crystal II, as reflected in the 4% greater crystal density of I. However, the fact that crystal II can be obtained raises questions about the suitability of the much used tris(ethylenediamine)metal complexes as resolving agents for tris(oxalato) complexes. Indeed, there has been a report in the literature[13] questioning the discriminating ability of (+)-[Co(en)₃]Cl₃ for tris(ox) complexes of Co(III), Cr(III), or Rh(III),

(13) Sargeson, A. M. In *Chelating Agents and Metal Chelates*; Dwyer, F. P., Mellor, D. P., Eds.; Academic Press: New York, 1964; Chapter 5.

Table IV. Analysis of Hydrogen Bonds

(a) Observed(I) and Possible(II) Hydrogen Bonds

A···H–B	A–H, Å	H–B, Å	A–B, Å	A–H–B, deg	sym code^a	type
Crystal I Parallel to C_3						
Intracolumn						
O(1)···H(N2e)^b–N(2)	2.47	0.86	3.19	142	2	a′
O(1)···H(N2e)–N(2)	2.45	0.86	3.17	141	3	a′
O(2)···H(N1e)–N(1)	2.17	0.97	3.04	149	1	a
Intercolumn						
O(4)···H(N1a)–N(1)	2.01	0.92	2.92	170	4	b
O(4)···H(N2a)–N(2)	2.07	0.92	2.90	149	5	b
Crystal II						
Δ-[Co(en)$_3$]-Δ-[Rh(ox)$_3$]						
Parallel to C_3						
O(1)···H(N2′e)–N(2′)	2.22	1.02	3.15	150	1	a
O(3)···H(N4′e)–N(4′)	2.11	0.98	3.08	168	1	a
O(5)···H(N6′e)–N(6′)	2.22	0.99	3.05	141	1	a
O(7)···H(N4′a)–N(4′)	1.95	0.96	2.89	166	2	b
O(7)···H(N5′a)–N(5′)	2.07	1.03	2.86	132	2	b
O(9)···H(N1′a)–N(1′)	1.95	0.92	2.80	153	3	b
O(9)···H(N6′a)–N(6′)	1.92	0.98	2.88	168	3	b
Perpendicular to C_3						
O(2)···H(N3′e)–N(3′)	2.13	0.96	3.04	157	4	
O(6)···H(N2′a)–N(2′)	2.17	1.01	3.16	165	4	
O(10)···HN(3′a)–N(3′)	2.33	0.99	3.25	153	5	
O(11)···H(N1′e)–N(1′)	1.65	1.08	2.68	157	6	
O(11)···H(N5′e)–N(5′)	2.09	1.08	3.04	145	6	
Λ-[Co(en)$_3$]-Δ-[Rh(ox)$_3$]						
Parallel to C_3						
O(1)···H(N1e)–N(1)	1.98	1.01	2.93	155	1	a
O(3)···H(N3e)–N(3)	2.07	0.97	3.04	171	1	a
O(5)···H(N5e)–N(5)	2.02	0.93	2.76	137	1	a
O(7)···H(N4a)–N(4)	2.08	1.01	3.03	157	2	b
O(7)···H(N5a)–N(5)	1.97	0.98	2.83	145	2	b
O(9)···H(N1a)–N(1)	1.84	0.97	2.78	165	3	b
O(9)···H(N6a)–N(6)	2.01	1.00	3.01	166	3	b
Perpendicular to C_3						
O(2)···H(N2a)–N(2)	2.22	1.06	3.26	167	4	
O(6)···H(N3a)–N(3)	2.04	1.02	2.91	142	4	
O(10)···H(N4e)–N(4)	2.24	1.05	3.13	142	5	
O(11)···H(N2e)–N(2)	1.90	1.02	2.85	153	6	
O(11)···H(N6e)–N(6)	1.85	1.04	2.83	157	6	

(b) Mutual Arrangement in Type a and a′ Hydrogen Bonding

	I	II		VI
		Δ-Co-Δ-Rh	Λ-Co-Δ-Rh	
angle between C_3 axes, deg	0	2.7	2.4	0
angle between C_2 axes, deg	5.4	5.8	14.3	60
angles between stacked chelate rings, deg	8.7	12, 15, 17	63, 64, 70	
distance between Co–Rh atoms, Å	4.908, 4.969	5.121	5.121	
distance between Co–Cr atoms, Å				5.03

^{a} Symmetry code for crystal I: (1) x, y, z; (2) $x, y, z - 1$; (3) $-y, x - y, z - 1$; (4) $-y + \frac{1}{3}, x - y + \frac{2}{3}, z - \frac{1}{3}$; (5) $y - x + \frac{1}{3}, -x + \frac{2}{3}, z - \frac{1}{3}$. Symmetry code for crystal II: (1) $x, y - 1, z$; (2) $x, y - 1, z - 1$; (3) $x - 1, y - 1, z$; (4) $-x, y - 0.5, -z$; (5) $-x, y - 0.5, -z + 1$; (6) $-x + 1, y - 0.5, -z$. ^{b} a and e designate axial and equatorial hydrogen atoms, respectively.

although successful resolution of oxalato complexes has also been reported not only with (+)-[Ni(phen)$_3$]$^{2+}$ [14] but also with [Co-(en)$_3$]$^{3+}$.[15]

Conclusion

This study has shown that there appear to be only a few favored types of packing mode in the crystal structure of D_3-type metal complexes with the three-bladed-propeller shape. For those complexes where dispersion forces are dominant such as III–V,

nearly parallel and nearly tetrahedrally tilted arrangements of molecular C_3 axes are quite often adopted. Where hydrogen bonding is available, as in I, II, and VI, this will become a dominant factor. Diastereomeric crystals frequently form columns of alternating cations and anions with their C_3 axes colinear and with full use of hydrogen bonding regardless of their chirality. Thus the intercolumn hydrogen bonds rather than intracolumn hydrogen bonds appear to contribute toward the successful optical resolution of this type of metal complex.

(14) Dwyer, F. P.; Sargeson, A. M. *J. Phys. Chem.* **1956**, *60*, 1331.
(15) Vaughn, J. W.; Magnuson, V. E.; Seiler, G. J. *Inorg. Chem.* **1969**, *8*, 1201.