dation and the University of California, Davis, NMR Facility for support and the Johnson Matthey Corp. for a generous loan of rhodium salts.

Registry No. 5, 75361-61-4; 7, 76069-01-7; $Rh(Ph_2Ppy)_2(CO)Cl$, 75361-60-3; $[Rh(CO)_2(\mu\text{-}Cl)]_2$, 14523-22-9.

Supplementary Material Available: A listing of structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Department,
University of Houston, Houston, Texas 77004

Crystal Structure and Absolute Configuration of Tartrate Derivatives. 2. $[\Lambda(\delta\delta\delta)\text{-}Co(en)_3][(+)_{589}\text{-}(\boldsymbol{R},\boldsymbol{R})\text{-}tart^{2-}]Cl\cdot5H_2O$

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The structure and absolute configuration of the title compound were determined as part of a continuing project to structurally document the mechanism(s) of chiral resolution of simple resolving agents such as tartaric acid and its derivatives. The substance crystallizes in the triclinic space group $P1$ with cell constants $a = 8.136$ (5) Å, $b = 8.253$ (7) Å, $c = 8.517$ (6) Å, $\alpha = 102.32$ (6)°, $\beta = 101.32$ (6)°, $\gamma = 95.18$°, $V = 542.65$ Å^3, and d(calcd) ($Z = 1$) = 1.569 g cm^{-3}. When (R,R)-d-tartrate(2−) is used as the resolving agent, the absolute configuration of the $Co(en)_3{}^{3+}$ with which it is selectively crystallizes is $\Lambda(\delta\delta\delta)$. The main interactions observed between the cation, anions, and waters are as follows. (a) The cation has two "faces" perpendicular to the pseudo-threefold axis. One face consists of three axial N–H units bonded to the Cl^-, while the other has the opposite three axial N–H units hydrogen bonded to three oxygens of a given tartrate anion. (b) The tartrate dianion is involved in complicated hydrogen-bonding contacts with water and with two separate cationic units but never to another tartrate. (c) Every hydrogen of the five independent waters of crystallization is involved in an intermolecular bond with either tartrate or chloride anions or with another water. All five waters are mutually hydrogen bonded into a right-handed spiraling chain, linked through chloride ions. When one compares the nature of these interactions with those reported previously, it is clear that d-tartrate(2−) is not limited to a single mechanism of resolution for even simple tris(bidentate diamines). Instead, it is a flexible resolving agent capable of a variety of modes of interaction which can be quite different from one case to another.

Introduction

This study is our second contribution to a long-range project to structurally document the mechanism(s) of chiral resolution of simple resolving agents such as tartrate and its derivatives.[1] It is interesting to note that, while the structures and absolute configuration of four simple derivatives of $Co(en)_3{}^{3+}$ have been determined,[2] the structure and absolute configuration of $Co(en)_3{}^{3+}$ together with its resolving agent, tartrate, has not been studied in detail in its most commonly isolated form—the $[Co(en)_3](tart)Cl\cdot5H_2O$ derivative found in ref 3. Furthermore, the recent study of Yoneda et al.[4] does not give coordinates for the atoms and lacks vital information concerning the hydrogen atoms, details of the hydrogen bonding, and the role of water in the lattice. As shown below, when one examines the differential thermal calorimetric behavior of $[Co(en)_3](tart)Cl\cdot5H_2O$, one finds a very interesting phase transition associated with the loss of water, which is not readily interpretable based solely on Yoneda's work on the analogous bromide, in view of the absence of data on the structural behavior of the five waters.

Yoneda and associates[5,6] have made, however, interesting observations concerning stereoselectivity in ion pair formation for tartrate resolving agents, on the influence of tartaric acid and its derivatives on the mechanism of the Pfeiffer effect, and on discriminating action in these processes. We had already noted an interesting mode of interaction of dibenzoyltartrate with a bis(phosphine) dioxide being resolved into its diastereomers,[1] and we therefore decided to investigate the structure of the title compound as part of our series.

Table I. Summary of Data Collection and Processing Parameters

space group	$P1$, triclinic
cell consts	$a = 8.136$ (5) Å, $b = 8.253$ (7) Å, $c = 8.517$ (6) Å, $\alpha = 102.32$ (6)° $\beta = 101.32$ (6)° $\gamma = 95.18$ (6)° $V = 542.65$ Å^3, $Z = 1$
molecular formula	$C_{10}H_{38}O_{11}N_6CoCl$
mol wt	512.85
density	1.57 (calcd), 1.58 (measd) g cm^{-3}
abs coeff	$\mu = 9.10$ cm^{-1}
data collection range	$4° \leqslant 2\theta \leqslant 65°$
scan width	$\Delta\theta = (1.00 + 0.35 \tan\theta)°$
max scan time	300 s
scan speed range	0.31–3.5° min^{-1}
total data collected	3825
data with $I > 3\sigma(I)$	3545
total variables	393
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.026
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.022
weights	$w = \sigma(\lvert F\rvert)^{-2}$
approx orientation of data cryst	[110]

Experimental Section

1. X-ray Diffraction Measurements. The title compound was synthesized according to Angelici's method.[3] The resulting racemic mixture was resolved with use of barium d-tartrate, and orange crystals of optically active $[Co(en)_3](d\text{-}tart)Cl\cdot5H_2O$ were grown by slow evaporation of the aqueous solution. A crystal of dimensions 0.62 × 0.47 × 0.47 mm was coated with Krylon and mounted on a goniometer head.

All measurements were done on a computer controlled Enraf-Nonius CAD-4 automatic diffractometer equipped with a graphite monochromator aligned to select Mo Kα radiation. The lattice parameters used in data collection were obtained from a least-squares fit of 25 automatically centered reflections. The final lattice constants and other pertinent crystal data are given in Table I. The space group was determined from the systematic absences to be either $P1$ or $P\bar{1}$,

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(1) For part 1, see H. Brunner, J. D. Korp, and I. Bernal, *Chem. Ber.*, in press.
(2) Review by Y. Saito, *Top. Stereochem.*, **10**, 95–174 (1978).
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(5) T. Taura, H. Tamada, and H. Yoneda, *Inorg. Chem.*, **17**, 3127 (1978).
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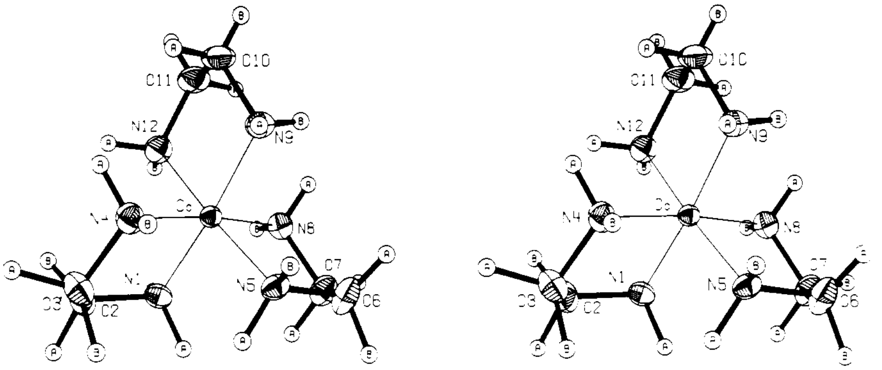

Figure 1. Stereoscopic view of the $\Lambda(\delta\delta\delta)$-Co(en)$_3^{3+}$ complex cation projected down the pseudo-threefold axis. The thermal ellipsoids are 50% equiprobability envelopes, with hydrogens of arbitrary size. The (lel)$_3$ configuration is readily apparent.

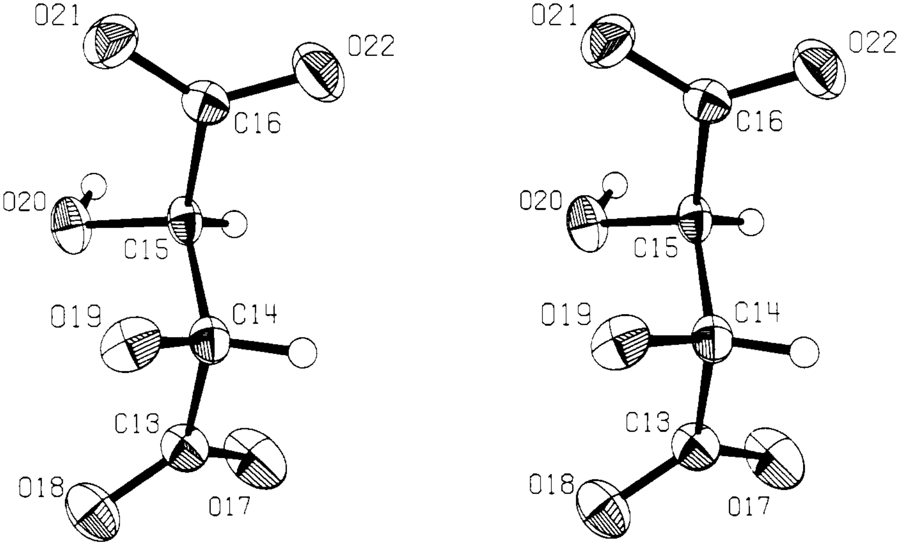

Figure 2. Stereoscopic view of the (*R*,*R*)-tartrate dianion, with 50% equiprobability envelopes and hydrogens of arbitrary size. The hydrogen on O19 could not be located and is omitted from the drawing.

and the measured density gave 1 formula weight per unit cell. Intensity data were collected by using the ω–2θ scan technique in bisecting position, over the range $4° \leq 2\theta \leq 65°$. Two standard reflections were monitored after every 2 h of exposure time to check electronic reliability and crystal stability. A total of 3825 independent reflections were collected of which 3545 having $I > 3\sigma(I)$ were used for structural analysis. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Since there is only 1 formula unit per cell and the cation and anion are both optically active, the noncentrosymmetric space group *P*1 was chosen. A Patterson function yielded the Co–Cl vector, and since the Co atom can be at any arbitrarily fixed coordinates in this space group, the Cl position was then known also. The remaining atoms were all found in subsequent different Fourier syntheses, except for the hydrogen on O19, which could not be located. All atoms were refined by full-matrix least squares, with nonhydrogen atoms anisotropic and hydrogen atoms isotropic. In the final cycle of full-matrix least squares, 393 variables were refined, including an overall scale factor. The final agreement factors were $R = 0.026$ and $R_w = 0.022$, where the weighting scheme used was $w = \sigma(|F|)^{-2}$. Final positional and thermal parameters are presented in Table II, according to the atom labels of Figures 1 and 2. The atomic scattering factors for the nonhydrogen atoms were computed from numerical Hartree–Fock wave functions;[7] for hydrogen those of Stewart, Davidson, and Simpson were used.[8] The anomalous dispersion coefficients of Cromer and Liberman[9] were used for cobalt and chlorine. Intramolecular bond lengths and angles are given in Table III and IV, respectively, with standard deviations calculated from the inverse matrix of the last cycle of refinement. Table V gives hydrogen bonding parameters.

2. Differential Thermal Calorimetry. Calorimetric measurements were performed for us by Dr. W. W. Wendlandt (University of Houston), who found that at approximately 60 °C there is a rapid loss of mass of the sample which amounts to 17.8% of the total. The theoretical fraction of the total molecular weight which is constituted by water is 17.6%. Consequently, it appears that all five waters are lost at once from this compound, suggesting that they are associated with one another as a block. This point is, of course, a natural question for single-crystal structural studies and constituted one of the reasons for our current study.

Results and Discussion

Cation. The Co(en)$_3^{3+}$ cation is shown in Figure 1 projected down the pseudo-threefold axis, from which orientation the ligands are readily seen to be in the (lel)$_3$ configuration.[10] Averages of chemically equivalent bonds and angles are as follows: Co–N, 1.96 Å; N–C, 1.49 Å; C–C, 1.50 Å; internal N–Co–N, 85.6°; external N–Co–N, 91.5°; Co–N–C, 109.5°. These values are in good agreement with the majority of previously published results.[11-15] Unfortunately, a published

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Table II. Atomic Coordinates and Thermal Parameters (× 1000, Co and Cl × 10 000)

atom	*x/a*	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0.4500 (0)	0.6300 (0)	0.5800 (0)	155 (1)	178 (1)	172 (1)	28 (1)	44 (1)	42 (1)
Cl	0.1419 (1)	0.8616 (1)	0.2942 (1)	428 (4)	354 (4)	464 (5)	64 (3)	−98 (3)	104 (3)
N1	0.4093 (3)	0.5856 (3)	0.3391 (3)	25 (1)	27 (1)	21 (1)	8 (1)	6 (1)	7 (1)
C2	0.3507 (4)	0.4038 (4)	0.2683 (4)	37 (2)	31 (1)	25 (1)	0 (1)	2 (1)	0 (1)
C3	0.4537 (4)	0.3092 (3)	0.3740 (3)	40 (2)	27 (1)	29 (1)	8 (1)	7 (1)	1 (1)
N4	0.4574 (4)	0.3876 (3)	0.5500 (3)	31 (1)	22 (1)	27 (1)	3 (1)	7 (1)	6 (1)
N5	0.6956 (3)	0.6694 (3)	0.6071 (3)	17 (1)	29 (1)	27 (1)	3 (1)	6 (1)	9 (1)
C6	0.7560 (4)	0.8523 (4)	0.6498 (4)	23 (1)	33 (2)	52 (2)	−4 (1)	4 (1)	9 (1)
C7	0.6229 (4)	0.9340 (4)	0.5584 (4)	33 (2)	26 (1)	42 (2)	0 (1)	9 (1)	10 (1)
N8	0.4584 (3)	0.8706 (3)	0.5931 (3)	26 (1)	24 (1)	26 (1)	6 (1)	4 (1)	5 (1)
N9	0.4708 (3)	0.6634 (4)	0.8192 (3)	24 (1)	31 (1)	24 (1)	4 (1)	7 (1)	9 (1)
C10	0.3020 (4)	0.6188 (5)	0.8538 (4)	32 (2)	46 (2)	29 (1)	3 (1)	16 (1)	11 (1)
C11	0.1724 (4)	0.6722 (4)	0.7321 (4)	23 (1)	48 (2)	37 (2)	7 (1)	14 (1)	9 (1)
N12	0.2047 (3)	0.6050 (4)	0.5653 (3)	20 (1)	35 (2)	30 (1)	5 (1)	5 (1)	7 (1)
C13	−0.2229 (4)	0.5887 (3)	0.1982 (3)	32 (1)	30 (1)	25 (1)	6 (1)	12 (1)	10 (1)
C14	−0.1295 (3)	0.5361 (3)	0.0602 (3)	22 (1)	30 (1)	21 (1)	7 (1)	7 (1)	9 (1)
C15	−0.2105 (3)	0.3628 (3)	−0.0461 (3)	20 (1)	27 (1)	24 (1)	7 (1)	6 (1)	13 (1)
C16	−0.1179 (3)	0.3175 (3)	−0.1870 (3)	28 (1)	22 (1)	26 (1)	4 (1)	9 (1)	6 (1)
O17	−0.1982 (3)	0.5147 (3)	0.3128 (3)	75 (2)	54 (1)	38 (1)	32 (1)	34 (1)	28 (1)
O18	−0.3197 (3)	0.6955 (3)	0.1890 (3)	36 (1)	37 (1)	45 (1)	13 (1)	22 (1)	15 (1)
O19	−0.1323 (3)	0.6505 (2)	−0.0438 (2)	36 (1)	28 (1)	23 (1)	−3 (1)	10 (1)	9 (1)
O10	−0.3858 (2)	0.3644 (3)	−0.1059 (2)	18 (1)	32 (1)	42 (1)	2 (1)	6 (1)	16 (1)
O21	−0.1860 (3)	0.3326 (3)	−0.3272 (2)	40 (1)	41 (1)	23 (1)	6 (1)	7 (1)	9 (1)
O22	0.0232 (3)	0.2720 (3)	−0.1478 (3)	39 (1)	57 (1)	40 (1)	26 (1)	18 (1)	17 (1)
O23	0.1713 (4)	0.0375 (4)	0.0011 (4)	61 (2)	60 (2)	53 (2)	23 (1)	21 (1)	23 (1)
O24	0.4887 (3)	0.0607 (3)	−0.0566 (3)	37 (1)	40 (1)	34 (1)	−1 (1)	3 (1)	8 (1)
O25	0.7580 (4)	0.0136 (4)	0.1521 (5)	67 (2)	48 (2)	88 (2)	2 (1)	−23 (2)	36 (2)
O26	0.9645 (3)	0.2772 (3)	0.4052 (3)	51 (1)	52 (1)	50 (1)	23 (1)	21 (1)	19 (1)
O27	0.2242 (3)	0.1506 (4)	0.6425 (3)	35 (1)	60 (2)	42 (1)	10 (1)	15 (1)	4 (1)

atom	*x/a*	*y/b*	*z/c*	*U*, Å²	atom	*x/a*	*y/b*	*z/c*	*U*, Å²
H1A	0.529 (4)	0.617 (4)	0.302 (4)	34 (9)	H10B	0.284 (4)	0.659 (4)	0.949 (4)	30 (0)
H1B	0.322 (5)	0.640 (5)	0.285 (4)	42 (10)	H11A	0.182 (4)	0.811 (5)	0.746 (4)	52 (10)
H2A	0.365 (4)	0.355 (4)	0.139 (4)	45 (10)	H11B	0.080 (5)	0.636 (5)	0.759 (5)	50 (0)
H2B	0.229 (6)	0.357 (6)	0.265 (5)	78 (13)	H12A	0.146 (4)	0.490 (4)	0.520 (4)	31 (8)
H3A	0.385 (4)	0.169 (4)	0.350 (4)	41 (9)	H12B	0.147 (5)	0.656 (4)	0.486 (4)	36 (10)
H3B	0.584 (4)	0.311 (4)	0.334 (4)	37 (8)	H14	−0.017 (3)	0.529 (3)	0.130 (3)	14 (6)
H4A	0.360 (5)	0.336 (4)	0.592 (4)	40 (9)	H15	−0.199 (3)	0.291 (3)	0.024 (3)	20 (0)
H4B	0.559 (4)	0.359 (4)	0.611 (4)	25 (8)	H20	−0.407 (5)	0.261 (5)	−0.110 (5)	50 (10)
H5A	0.728 (5)	0.594 (6)	0.498 (5)	70 (13)	H23A	0.187 (6)	0.015 (6)	0.097 (6)	70 (0)
H5B	0.749 (5)	0.628 (5)	0.697 (5)	41 (10)	H23B	0.129 (7)	0.101 (6)	−0.013 (6)	70 (0)
H6A	0.778 (3)	0.906 (3)	0.776 (3)	15 (6)	H24A	0.561 (5)	0.052 (5)	0.038 (5)	50 (10)
H6B	0.876 (5)	0.865 (4)	0.607 (4)	50 (0)	H24B	0.375 (7)	0.087 (6)	−0.008 (6)	93 (15)
H7A	0.614 (4)	0.890 (4)	0.428 (4)	44 (9)	H25A	0.843 (5)	0.082 (5)	0.248 (5)	51 (0)
H7B	0.625 (4)	1.055 (4)	0.592 (4)	36 (8)	H25B	0.790 (6)	−0.055 (7)	0.164 (6)	70 (0)
H8A	0.440 (5)	0.934 (5)	0.699 (5)	50 (0)	H26A	−0.076 (6)	0.295 (6)	0.501 (6)	70 (0)
H8B	0.354 (5)	0.897 (5)	0.508 (5)	60 (0)	H26B	0.001 (6)	0.211 (6)	0.476 (6)	70 (0)
H9A	0.539 (4)	0.596 (4)	0.851 (4)	31 (9)	H27A	0.150 (5)	0.184 (5)	0.697 (5)	62 (12)
H9B	0.481 (5)	0.779 (6)	0.858 (5)	60 (0)	H27B	0.195 (6)	0.080 (6)	0.569 (6)	70 (0)
H10A	0.284 (4)	0.494 (4)	0.834 (4)	29 (7)					

Table III. Intramolecular Bond Lengths[a] (Å)

N1–Co	1.960 (3)	C11–N12	1.494 (5)
N4–Co	1.970 (3)	C13–C14	1.530 (4)
N5–Co	1.955 (3)	C13–O17	1.251 (4)
N8–Co	1.959 (3)	C13–O18	1.239 (4)
N9–Co	1.967 (3)	C14–C15	1.530 (4)
N12–Co	1.965 (3)	C14–O19	1.425 (4)
C2–N1	1.488 (4)	C14–H14	1.004 (3)
C2–C3	1.498 (5)	C15–C16	1.537 (4)
C3–N4	1.493 (4)	C15–O20	1.420 (3)
C6–N5	1.488 (4)	C15–H15	0.925 (3)
C7–C6	1.503 (5)	O20–H20	0.845 (4)
C7–N8	1.499 (4)	C16–O21	1.251 (3)
C10–N9	1.491 (5)	C16–O22	1.245 (4)
C11–C10	1.493 (5)		

[a] The N-H distances are given in Table V, along with other hydrogen bonding parameters. The C–H distances range from 0.88 (3) to 1.21 (4) Å.

Table IV. Intramolecular Bond Angles (Deg)

N-Co–N[a]	85.6	O19–C14–C13	112.4 (2)
N-Co–N[b]	91.5	O19–C14–C15	108.4 (2)
N-Co–N[c]	174.9	C16–C15–C14	108.4 (2)
C-N-Co[d]	109.5	O20–C15–C14	109.5 (2)
C-C-N[d]	107.4	O20–C15–C16	111.9 (2)
O17–C13–O18	124.3 (3)	H20–O20–C15	91.3 (25)
O17–C13–C14	116.1 (3)	O21–C16–C15	118.7 (2)
O18–C13–C14	119.6 (3)	O22–C16–C15	115.4 (2)
C15–C14–C13	109.9 (2)	O22–C16–O21	125.9 (3)

[a] Average of the three angles internal to the (en) rings. [b] Average of the nine angles external to the (en) rings. [c] Average of the three axial angles. [d] Average of the six angles in the (en) rings.

investigation of the bromine analogue of the title compound listed neither bond distances nor atomic coordinates, and so these comparisons cannot be made.[4] The CoN_6 core differs significantly from octahedral geometry due to the strain of compression of the ethylenediamine bite. The absolute configuration of the cation was not forced by the casual method of knowing the tartrate handedness in advance but was instead determined independently from the measurement of ten Bijvoet pairs,[16] each having an observed difference of between 10%

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(16) J. M. Bijvoet, A. F. Peerdeman, and A. J. VanBommel, *Nature (London)*, **168**, 271 (1951).

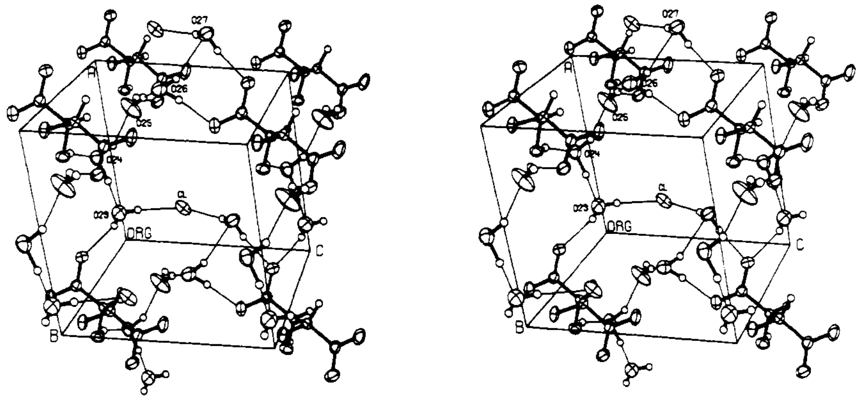

Figure 3. Stereoscopic view of the arrangement of anions and waters of crystallizaton in the unit cell. The complex cation occupies the cavity in the center of the cell. Note the right-handed spiral chain of water molecules and chloride ions and the intricate hydrogen bonding.

Table V. Hydrogen-Bonding Parameters

A1, H, A2	H–A1, Å	H···A2, Å	A1···A2, Å	A1–H···A2, deg
N1, H1A, O18	1.10 (4)	1.86 (4)	2.926 (4)	161 (3)
N1, H1B, Cl	0.97 (4)	2.44 (4)	3.318 (4)	149 (3)
N4, H4A, O27	1.02 (4)	1.98 (4)	2.936 (5)	154 (3)
N4, H4B, O20	0.96 (3)	2.35 (3)	3.011 (4)	125 (3)
N4, H4B, O21	0.96 (3)	2.08 (3)	2.995 (4)	158 (3)
N5, H5A, O17	1.09 (4)	1.81 (5)	2.889 (4)	167 (4)
N5, H5B, O19	0.95 (4)	2.19 (4)	3.070 (4)	154 (3)
N8, H8A, O24	0.98 (4)	2.07 (4)	3.011 (4)	161 (3)
N8, H8B, Cl	1.07 (4)	2.20 (4)	3.229 (4)	161 (3)
N9, H9A, O20	0.86 (4)	2.14 (4)	2.959 (5)	157 (3)
N9, H9B, O24	0.93 (5)	2.27 (5)	3.204 (5)	176 (3)
N12, H12A, O26	0.98 (3)	2.11 (3)	3.069 (5)	165 (3)
N12, H12B, Cl	0.94 (4)	2.59 (4)	3.449 (4)	152 (3)
O19, ...,[a] Cl			3.307 (4)	
O20, H20, O24	0.84 (4)	1.97 (4)	2.768 (4)	157 (4)
O23, H23A, Cl	0.87 (5)	2.37 (6)	3.181 (4)	156 (4)
O23, H23B, O22	0.67 (5)	2.14 (6)	2.770 (5)	157 (6)
O24, H24A, O25	0.92 (4)	1.79 (4)	2.651 (5)	153 (4)
O24, H24B, O23	1.10 (6)	1.69 (6)	2.720 (4)	152 (4)
O25, H25A, O26	0.99 (3)	1.90 (4)	2.849 (5)	159 (4)
O25, H25B, O18	0.66 (6)	2.23 (6)	2.743 (5)	135 (5)
O26, H26A, O21	0.93 (5)	1.84 (5)	2.767 (4)	172 (4)
O26, H26B, O27	0.93 (5)	2.24 (5)	3.043 (4)	145 (4)
O27, H27A, O22	0.86 (3)	1.90 (5)	3.533 (4)	169 (4)
O27, H27B, Cl	0.74 (4)	2.57 (5)	3.293 (4)	169 (5)

[a] H19 could not be located but is probably directed toward Cl.

and 24%, with no counter-indications. The reflections used were 021, $\bar{3}20$, 221, $\bar{1}52$, $5\bar{3}2$, $0\bar{3}2$, $\bar{2}\bar{3}2$, $\bar{3}\bar{3}2$, $\bar{2}22$, and $\bar{2}32$. The correct configuration is that in Figure 1, designated $\Lambda(\delta\delta\delta)$ according to IUPAC convention,[17] and one of the two low-energy conformations.[10] This seems to be the preferred configuration when *d*-tartrate is used as the resolving agent.[4,18,19]

Tartrate Dianion. The $(+)_{589}$-tartrate dianion is shown in Figure 2, with the O19 hydrogen omitted. The dianion is in the *R*,*R* configuration, consistent with the known *d*-tartrate structure.[16] The averages of the chemically equivalent bond distances listed in Table III are C–C(carboxylate) = 1.53, C–O(carboxylate) = 1.25, and C–O(hydroxyl) = 1.42 Å. Each of these values is in excellent agreement with other results in the literature,[20,21] as well as with the values reported for a neutron diffraction study of the enantiomer, *l*-tartrate.[22] As is usually found, the tartrate dianion in the present structure consists of two nearly planar halves, each containing OC–COO^{2-}. The dihedral angle between them is 36°, and they are aligned such that the four carbon atoms are almost exactly coplanar (the C–C–C–C torsion angle is 178°). For comparison, the dihedral angle in tartaric acid is 55°,[23] in ammonium tartrate 62°,[21] and in ethylenediamine *l*-tartrate 33°.[22] In the present structure, the angle between the two planes consisting solely of the carboxylate groups is 29°. It is undoubtedly affected by the extensive intermolecular hydrogen bonding in the system which will be described in detail below. The intermolecular hydrogen bonding involving three oxygens of this tartrate dianion has forced this angle to decrease and tends to make these three O···O contacts more equidistant, as follows. On one side of the carbon backbone of the tartrate dianion there are four oxygens (two hydroxyl and two carboxylate), three of which bind to a given cation (see lower right quadrant of Figure 4). The other carboxylate oxygen is involved in more complicated contacts involving water and a different cationic unit. In the three oxygens which bind to a common face, the carboxylate group shows a more pronounced torsional angle with respect to the hydroxyl oxygen (O21–C16–C15–O20 = 19.3° vs. O18–C13–C14–O19 = 15.6°) than is noted for the other carboxylate group. The effect of this increased rotation makes the three O···O contacts more nearly equal, i.e., O19···O20 = 2.876 (4), O19···O21 = 3.095 (4), and O20···O21 = 2.708 (4) Å vs. O18···O19 = 2.715 (4), O19···O20 = 2.876 (4), and O18···O20 = 3.216 (4) Å.

Waters and Chloride. There are five water molecules of crystallization associated with the ionic species contained in the structural unit. Each of them is bound in the crystal lattice at approximately the same strength, as indicated by their simultaneous loss during thermal gravimetric measurements. As can be seen in Figure 3, clusters of five waters are mutually hydrogen bonded into a spiralling chain linked by chloride ions at the ends. The sense of rotation of the helical, infinite chains is seen to be right-handed, with the repeating unit being the five waters and one chloride of the full unit cell. The principal axis of the helix parallels the crystallographic *a* axis exactly. This intriguing arrangment of waters was never mentioned in the structural report of the bromine analogue,[4] and so it must be assumed that the authors overlooked it entirely. Spiral chains of H–*d*-tartrate have been noted in similar structures[15,24] and have been theorized to play an important role in the discrimination between Δ and Λ enantiomeric cations,[15] so it could be that the right-handed helix found in the present case

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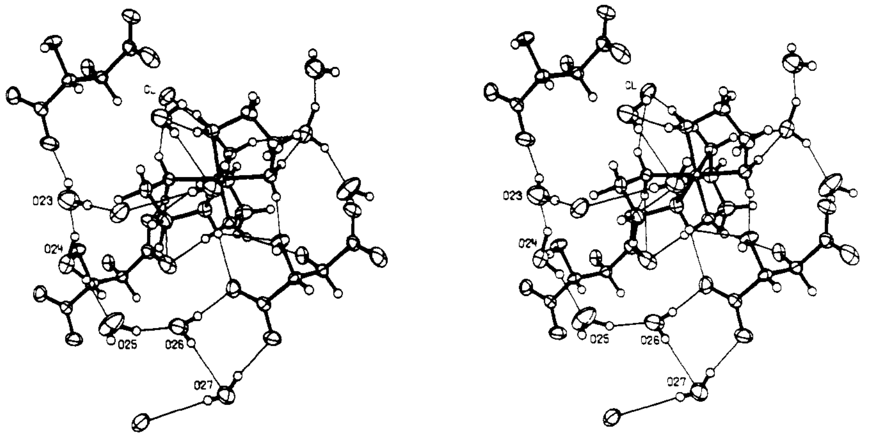

Figure 4. Stereoscopic view of the hydrogen bonding to the complex cation. Note that *every* amino hydrogen participates. The "local block" formed by the cation, and the chlorine and tartrate ions across from the two amino "faces", is clearly shown. The relationship to the helical chains of waters is also apparent.

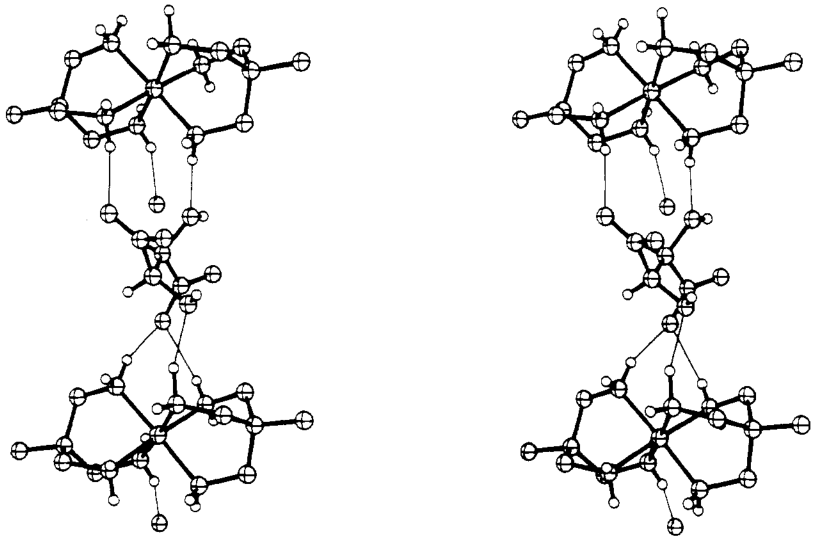

Figure 5. Stereoscopic view of a portion of the structure of Co(tame)$_2$Cl(tart)·5.4H$_2$O (reproduced with permission[20]). Note that the cation has six amino "faces" as opposed to just two in Figure 1. Hence, the "local block" is of a different nature.

is specific for the $\Lambda(\delta\delta\delta)$ configuration of the complex cation.

As can be seen in Figure 3, the water molecules are bound quite tightly into the crystal lattice, with *every* hydrogen participating in an intermolecular bond to either a tartrate or chloride ion or another water. All of the water hydrogens were located in difference maps and seem to be resonably refined with regard to overall chemical sense of the model. All of the water intermolecular contacts are shown in the bottom half of Table V. The average O···O distance between waters is 2.816 Å, and the average water O···Cl distance is 3.237 Å. These values are well within the reported ranges for similar bonding interactions.[11,15,20,25,26]

Intermolecular Hydrogen Bonding. In addition to the water–water bonds just discussed, there are also bonds from waters to tartrate oxygens and ethylenediamine nitrogens, having average O···O and O···N distances of 2.762 (excluding O27···O22) and 3.054 Å, respectively. The tartrate O to the ethylenediamine N distances average 2.975 Å. Each of these conforms well with literature results;[12,18,20,27] the individual values are shown in Table V. It is interesting to note that the N···O(T) distances are shorter than those noted in two similar structures, including the bromine analogue,[4,19] and that in our compound there are *no* tartrate–tartrate contacts. The chloride ions have a total of six close contacts: two to water oxygens (vide supra), three to nitrogens, and one to a tartrate oxygen. All are at reasonable distances,[12,14,20,28] and the seemingly large number of contacts is not unprecedented with halogen receptors.[29]

Figure 4 shows a single cation and its associated hydrogen bonds. The most important feature is the bonding to the two "faces" of the cation perpendicular to the pseudo-threefold axis, each of which has three axial N–H units pointing outward. One face is occupied by a chloride ion, while the other bonds to three oxygens of the tartrate (two hydroxyl and one carboxyl). This local [M(en)$_3$]Cl(*d*-tart) unit has been observed in earlier structural reports,[4] as has the "sandwich" type of complex [M(en)$_3$](*d*-tart)$_2$.[18,19] These "face-to-face" interactions are extremely common in several M(en)$_3$ series such as Ni(en)$_3$(NO$_3$)$_2$[30] and [Co(en)$_3$]$_2$(HPO$_4$)$_3$,[11] in which three oxygen atoms mutually bridge the three axial NH hydrogens. The theory that the "local block" formed by the cation and *d*-tartrate is of key importance in the process of optical res-

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olution of the racemic cation has been proposed and defended.[18] Supporting evidence can be found in stereospecific solute–solvent studies, in which preferred solubilities and packings were reported,[31] as well as in circular dichroism studies wherein a model was proposed in which two hydroxyl and one carboxyl oxygen of *d*-tartrate gave the best "fit" to the face of $Co(en)_3$.[32] Of course, *l*-tartrate is also capable of forming a three-membered bite, and the reason why *d*-tartrate preferentially resolves $\Lambda(\delta\delta\delta)$-$Co(en)_3$ is unclear. In published studies of the structures of *both* the preferred and nonpreferred diastereomeric salts of $Co(en)_2(ox)$ and $Co(en)(gly)_2$, it was found that the preferred (less soluble) salt was more tightly packed and included spiral chains of anions.[15] The spiraled chain of waters and chlorides may thus play an equally important role, combined with the handedness of the tartrate, in preferentially selecting $\Lambda(\delta\delta\delta)$-$Co(en)_3$ in the present case. It seems obvious, however, that this explanation of optical resolution may not necessarily be the dominant factor, as there are too many uncertain parameters involved to allow a definite conclusion from the relatively few investigations into this phenomenon which have so far been reported. A good example of an alternative method of resolution by *d*-tartrate can be found in the structure of $Co(tame)_2Cl(tart)\cdot 5.4H_2O$, a portion of which is shown in Figure 5 (with permission of the authors).[20] In this case, the three axial hydrogens on each face of the cation, which allowed formation of the "local block" discussed earlier, are unavailable for bonding. The peripheral hydrogens are still available however, and the tartrates bind at these sites, but with only two-point attractions instead of three. The reason for this could be a more unfavorable angling of the equatorial hydrogens or a thermodynamically favorable arrangement by tartrate to take advantage of the greater number of equivalent "faces" presented by several neighboring cationic units. But whatever the rationale, it still demonstrates that resolution by *d*-tartrate is not limited to a single mechanism but instead is a complex and variable scheme which may have as many modes of interaction as there are resolved compounds containing tartrate, each being a unique energy minimum for the materials involved.

A final, interesting observation which has been made by many investigators who have resolved $Co(en)_3^{3+}$ with tartrate is that, after precipitation of large amounts of crystals of the preferred enantiomer, the solution thickens gradually until it forms what Sargeson refers to as the "nasty orange glue".[33] This presumably amorphous substance involving *d*-tartrate and $\Delta(\lambda\lambda\lambda)$-$Co(en)_3$ could conceivably be a polymeric chain involving pairs of two-point contacts as in $Co(tame)_2Cl(tart)\cdot 5.4H_2O$. But for some reason, the opposite handedness of the cation prevents the degree of close packing found in the preferred enantiomer complex.

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Registry No. $[Co(en)_3](d\text{-tart})Cl\cdot 5H_2O$, 71129-32-3.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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Metal–Metal Repulsion and Bonding in Confacial Bioctahedra. Crystal Structures of $Cs_3Y_2I_9$ and $Cs_3Zr_2I_9$ and Comparison with Related Phases

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The title compounds were synthesized by reaction of CsI_3 and Y or CsI, Zr, and ZrI_4 at 750–850 °C in welded Ta containers. Both were shown to have the $Cs_3Cr_2Cl_9$-type structure, space group $P6_3/mmc$. Positional and thermal parameters were established by full-matrix least-squares refinement of single-crystal diffractometer data. Data for the structures and the refinements of $Cs_3Y_2I_9$ and $Cs_3Zr_2I_9$ are respectively $a = 8.406$ (1) and 8.269 (1) Å, $c = 21.280$ (5) and 19.908 (3) Å, $R = 0.050$ and 0.082, and $R_w = 0.082$ and 0.077 for 328 and 610 independent reflections with $2\theta \leq 50$ and 60° collected with Mo Kα radiation. The transition from the yttrium to the zirconium compound is accompanied by a decrease of the metal–metal distance in the $M_2I_9^{3-}$ confacial bioctahedra from 4.052 (9) to 3.129 (4) Å owing to the formation of a Zr–Zr bond. Correspondingly large changes occur in the internal angles in the M–I–M bridges. Parameters of five M_2X_9 groups in the $Cs_3Cr_2Cl_9$-type structure and of $CsCdCl_3$, all of which lack M–M bonds, are considered in terms of a model which recognizes the existence of both longer M–X bridge bonds and comprise bridge angles. Nonbonding repulsion between M atoms is concluded to not be a significant factor in these structures. The effects of packing and metal–metal bonding are also considered.

Introduction

The collection of enneahalodimetalates(III), $A_3M_2X_9$, has been growing with the development of new techniques for their preparation.[3,4] However, very little is known about iodides of this stoichiometry, and little quantitative data, i.e., on their crystal structures, are available. Only $Cs_3Bi_2I_9$[5,6] and $Cs_3Sb_2I_9$,[6,7] both crystallizing from aqueous solution, have been investigated by means of single-crystal X-ray techniques.

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