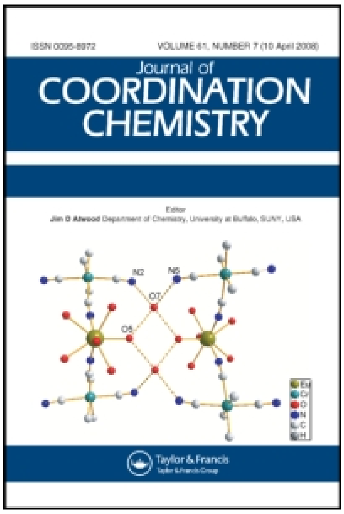

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KRYPTORACEMIC CRYSTALLIZATION. PART 4. SYNTHESIS AND X-RAY STRUCTURE OF THE CONGLOMERATE $[Co(en)_2Ox]F\ 11.5H_2O(I)$, ANOTHER EXAMPLE OF A COORDINATION COMPOUND CRYSTALLIZING AS A KRYPTORACEMATE

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KRYPTORACEMIC CRYSTALLIZATION. PART 4. SYNTHESIS AND X-RAY STRUCTURE OF THE CONGLOMERATE $[Co(en)_2Ox]F \cdot 11.5H_2O$(I), ANOTHER EXAMPLE OF A COORDINATION COMPOUND CRYSTALLIZING AS A KRYPTORACEMATE

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A racemic solution of $[Co(en)_2Ox]F \cdot 11.5H_2O$(**I**), $CoFO_{15.5}N_4C_6H_{39}$, crystallizes as a kryptoracemate in the enantiomorphic space group C2 (No. 5) with lattice constants: $a = 21.150(19)$ Å, $b = 11.866(8)$, $c = 13.197(2)$ Å and $\beta = 101.62(8)°$; $V = 3243.97$ Å^3 and d(calc; M.W. = 493.92 gm-mol^{-1}, $z = 8) = 2.020$ g-cm^{-3}. A total of 2335 data were collected over the range of $4° \leq 2\theta \leq 45°$; of these, 1735 (independent and with $\mathbf{I} \geq 2.5\sigma(\mathbf{I})$) were used in the structural analysis. Data were corrected for absorption ($\mu = 10.75$ cm^{-1}) and the relative transmission coefficients ranged from 0.5557 to 0.7852. Refinement converged to final residuals of 0.063 and 0.072 for R(F) and R_W(F), respectively. There are two formula weights in the asymmetric unit of (**I**) and the absolute configuration was determined by the Flack test.

For (**I**), the absolute configuration at Co1 is $\Lambda(\delta\lambda)$ and for Co2 is $\Delta(\lambda\delta)$, which by comparison with the known absolute configurations of the chloride and bromide derivatives,[4] allows us to assign the full chiro-optical symbol for these cations. Thus, the cations present in the crystal selected for the structural study of (**I**) are characterized fully by the symbols (+)589-$\Lambda(\delta\lambda)$-$[Co1(en)_2Ox]F \cdot 11.5H_2O$ and (−)589-$\Delta(\lambda\delta)$-$[Co_2(en)_2Ox]F \cdot 11.5H_2O$. The two cations are located near a non-crystallographic, *pseudo*-inversion center located approximately at 1/4, 0, 1/4, as determined from the positions of the two independent Co atoms; however, this *pseudo*-inversion center is only approximately shared by the four nitrogens and two oxygens in the coordination sphere, and is seriously violated by the other atoms of the metal ligands.

This is, to our knowledge, the first coordination compound of Co(III) which crystallizes, from a racemic solution, in an enantiomorphic lattice with a fluoride as its anion. Moreover, this is also the first fluoride to crystallize as a kryptoracemate.

Keywords: kryptoracemates; coordination compounds of Co(III); cobalt bisethylenediamine oxalato cation; fluorides of cobalt

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INTRODUCTION

Note: As defined in our previous three papers on the subject,[1–3] kryptoracemic crystallization is the phenomenon whereby a racemic solution produces enantiomorphic crystals whose asymmetric unit consists of racemic pairs. Thus, the true nature of the asymmetric unit (a racemic pair) is hidden (thus, the prefix krypto) in an enantiomorphic lattice. Also Ox is the oxalato, $C_2O_4^{2-}$, ligand.

In an earlier report[4] derived from our studies on the mechanism of conglomerate crystallization of coordination compounds, we reported the structures of crystals of $[Co(en)_2Ox]X{\cdot}nH_2O$ (X = Cl, n = 4 (**II**); X = Br, n = 1(**III**); X = I, n = 0 (**IV**)). Since that time, we have noted that there are no examples of $[Co(en)_2L_2]$ cations shown to crystallize as conglomerates with fluoride as their counter anions (L = any pair of monodentate ligands, such as $(NO_2)_2$, or bidentate ligands, such as oxalate). As discussed in our previous papers,[1–3] there were only four other known cases of kryptoracemism among coordination compounds (see below); this is the fifth such example.

Compound	*Space Group*	*z*	*Ref*
1. $[Co(en)_3]_2[Pb_2Cl_9]Cl \cdot 3H_2O$	$P2_1$	4	5
2. $[Co(tren)(NO_2)_2]_2Br(ClO_4) \cdot 3H_2O$	$P2_12_12_1$	4	1
3. $\{[Co(en)_3][(Ox)I]\}_2 \cdot 3H_2O$	$P2_12_12_1$	4	2
4. $[Co(Me_2\text{-}trien)(NO_2)_2]Cl \cdot H_2O$	C2	8	3

Among organic compounds,[1–3] the Cambridge Structural Database (CSD)[6] shows the existence of about two dozen examples of kryptoracemates. For a list of those examples present in the CSD, see refs. 1–3.

EXPERIMENTAL

Synthesis

Compound (**I**) was prepared as the chloride(**II**) by the published procedure[4] and converted to the fluoride by the addition of finely crushed, solid AgF to a warm, stirred, saturated, solution of (**II**) in water. The solution was stirred for two h allowed to cool, filtered, and set aside to crystallize in total darkness. After several months, crystals suitable for single-crystal, x-ray diffraction studies were collected. The precaution of avoiding light was caused by the observation that Co and Cr amine oxalates are sometimes light sensitive. For details the reader is referred to our previous studies (see refs. 2 and 4).

Elemental Analysis

The elemental analysis of the chloride(**II**) was already published. The quantitative addition of AgF and subsequent determination of the weight of the AgCl precipitate is sufficient to pin down the composition of (**I**).

Crystallography

Data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[7] of the SDP-Plus software package.[8] The procedure used for crystal alignment, cell constant determination, space group determination, and data collection were the same as in previous studies.[1–4] They were centered with data in the $20° \leq 2\Theta \leq 30°$ range and examination of the cell constants, absences, and Niggli matrix[9] clearly showed (**I**) crystallizes in a C-centered, monoclinic lattice. Examination of the systematic absences clearly show the absence of any glide planes; thus, its space group is either C2, Cm or C2/m.

Attempts to solve the structure in either Cm or C2/m failed to produce an acceptable structure of the cation, which was severely distorted in both. For example, in C2/m, we found that (a) the two biggest atoms(presumably Co) found by direct methods are only about 2 Å apart and (b) ligands (L) around the unique Co produced, upon refinement, short Co-L distances (*ca.* 1.5 Å) and/or L-Co-L angles as small as 37°. In Cm, the results are equally unacceptable.

Solution of the structure in space group C2 produced two independent Co(III) cations which are equidistant from a point having approximate coordinates 1/4, 0, 1/4; therefore, we shifted the origin to that point, placed a single cobalt atom to phase a difference Fourier map and, again, tried to refine the structure in space group C2/m. The resulting structure displays two Co(III) cations linked by a bridging ligand atom, presumably an oxygen or a nitrogen. After all these failures in higher symmetry space groups, we assumed the correct space group is, indeed, C2. In what follows, the description of the structure is that derived from the enantiomorphic choice. Finally, the crystals lose waters of crystallization at different rates depending on their location in the lattice, which resulted in values of their thermal parameters differing by a factor of approximately 2. We tried assigning different values of the occupancies to account for the loss of water but, eventually, this proved to be a guessing game and the atoms affected were assigned isotropic thermal parameters, resulting in a much more reasonable refinement.

The details of data collection are summarized in Table I. The intensity data set was corrected for absorption using empirical curves derived from Psi scans[7–8] of suitable reflections. The data were processed with the PC version of NRCVAX.[10]

TABLE I Summary of data collection and processing parameters for $[Co(en)_2Ox]F \cdot 11.5H_2O(I)$

Space Group	C2(No. 5)
Cell Constants	$a = 21.150(19)$ Å
	$b = 11.866(8)$
	$c = 13.197(2)$
	$\beta = 101.62$ (8) °
Cell Volume	$V = 3243.97$ Å^3
Molecular Formula	$CoO_{15.5}N_4C_6H_{39}$
Molecular Weight	493.92 g-mole^1
Density (calc; z = 4 mol/cell)	2.020 g-cm^{-3}
Radiation Employed	MoKα ($\lambda = 0.71073$ Å)
Absorption Coefficient	$\mu = 10.75$ cm^{-1}
Relative Transmission Coefficients	0.5557 to 0.7852
Data Collection Range	$4° \leq 2\Theta \leq 45°$
Scan Width	$\Delta\Theta = 0.90 + 0.35\tan\Theta$
Total Data Collected	2335
Data Used In Refinement[a]	1735
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.063
$R_w = [\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.072
Weights Used	$w = [\sigma(F_0)]^{-2}$

[a] The difference between this number and the total is due to substraction of 600 data that were systematically absent reflections, redundant data collected to obtain reflections suitable for the absorption correction, symmetry related, standards or did not meet the criterion that $I \geq 2.5s(I)$.

After refinement of the scale factor and the positional parameters of the two independent cobalt atoms, a difference Fourier map produced most of the non-hydrogen atoms of the cations. The remaining atoms were found in subsequent difference maps. Heavy atoms were refined isotropically until convergence, at which point the hydrogen atoms of the cations were added at idealized positions (N-H, C-H = 0.95 Å). The final R(F) and $R_w(F)$ factors are listed in Table I. Idealized positions of the hydrogen atoms of the cations were calculated after every cycle of refinement.

It was impossible to distinguish between the waters of crystallization and the fluoride anions since we found the water hydrogens at reasonable positions in only a few cases, and never both hydrogens. Thus, we ignored the hydrogens. However, it is possible to limit the choices drastically because (a) the fluorides cannot be lost from the lattice as is the case with waters; thus, the ones with the large thermal parameters (indicative of loss) must be waters (b) the fluorides cannot be the three atoms at special lattice positions; otherwise, charge compensation is violated. Nonetheless, since O^{2-} and F^- have the same scattering power, we labeled all the atoms Ow/FX (X = 1 to 15), as they appear in the table of coordinates (Table II) and in Figure 1.

TABLE II Atomic Parameters x, y, z and Biso. E.S.D.s. refer to the last digit printed

	x	*y*	*z*	*Biso*
Co	0.7247(3)	0.00000	0.9331(3)	2.73(22)
Co2	0.75510(24)	0.16564(23)	0.5679(3)	2.33(21)

TABLE II (*Continued*)

	x	*y*	*z*	*Biso*
N1	0.6434(13)	−0.037(3)	0.9482(21)	3.9(6)
N2	0.6928(12)	0.1496(24)	0.9259(19)	3.3(5)
N3	0.7688(9)	0.0017(20)	1.0812(14)	2.4(4)
N4	0.8076(15)	0.045(3)	0.9279(25)	3.9(7)
N5	0.6348(12)	−0.2882(24)	0.4452(11)	2.8(6)
N6	0.8055(10)	0.0079(22)	0.5724(17)	2.0(5)
N7	0.7501(8)	−0.3358(19)	0.5784(12)	1.9(4)
N8	0.6868(10)	0.1171(19)	0.5821(16)	1.7(4)
O1	0.7570(7)	−0.1563(15)	0.9296(11)	1.9(3)
O2	0.6930(8)	−0.0118(18)	0.7825(14)	2.7(4)
O3	0.7426(7)	−0.2931(15)	0.8056(12)	2.6(3)
O4	0.7091(7)	−0.1281(15)	0.6597(12)	1.7(3)
O5	0.7960(7)	0.1737(17)	0.7135(11)	1.9(3)
O6	0.7407(7)	−0.1793(15)	0.4253(12)	2.0(3)
O7	0.6962(9)	−0.2052(20)	1.1514(17)	4.1(5)
O8	0.7625(8)	−0.0481(16)	1.3132(12)	2.8(3)
C1	0.6022(20)	0.047(4)	0.917(3)	5.6(11)
C2	0.6330(16)	0.164(4)	0.961(3)	3.1(8)
C3	0.8342(16)	0.000(4)	1.097(3)	4.7(8)
C4	0.8528(18)	0.078(3)	1.025(3)	3.6(8)
C5	0.7395(8)	−0.1935(17)	0.8320(14)	0.1(3)
C6	0.7162(11)	−0.1079(23)	0.7536(19)	0.7(5)
C7	0.9070(14)	0.107(3)	0.5817(22)	2.8(6)
C8	0.8705(16)	0.012(4)	0.548(3)	4.0(8)
C9	0.8241(15)	−0.332(3)	0.5980(23)	2.9(6)
C10	0.6521(20)	0.092(4)	0.476(3)	6.0(10)
C11	0.7967(14)	0.270(3)	0.752(3)	4.3(7)
C12	0.7588(23)	0.360(5)	0.671(4)	8.5(12)
Ow/F1	0.6311(11)	0.258(3)	0.7210(17)	5.0(12)
Ow/F2	0.8668(12)	−0.0997(21)	0.7790(22)	3.7(12)
Ow/F3	0.9474(14)	−0.041(3)	1.3319(24)	5.3(15)
Ow/F4	1.0100(12)	−0.002(3)	1.1665(23)	5.6(14)
Ow/F5	0.5580(16)	0.211(3)	1.1759(24)	7.7(19)
Ow/F6	0.5206(18)	0.174(3)	0.666(3)	9.7(21)
Ow/F7	0.609(3)	−0.002(4)	1.166(3)	9.9(31)
Ow/F8	0.5861(18)	−0.190(3)	0.780(3)	9.6(23)
Ow/F9	0.6090(19)	−0.344(3)	0.6557(24)	12.6(17)
Ow/F10	0.9144(16)	0.367(3)	0.7049(22)	7.0(17)
Ow/F11	1.00000	−0.172(5)	1.50000	8.6(27)
Ow/F12	0.50000	0.356(6)	1.00000	10.1(36)
Ow/F13	0.482(3)	−0.286(4)	0.875(4)	16.9(32)
Ow/F14	0.5124(21)	−0.062(3)	0.647(4)	9.9(24)
Ow/F15	0.50000	−0.185(3)	0.50000	10.6(25)
H1	0.644	−0.053	1.019	4.7
H2	0.630	−0.103	0.908	4.7
H3	0.593	0.050	0.843	6.3
H4	0.563	0.035	0.940	6.3
H5	0.639	0.168	1.034	3.8
H6	0.609	0.227	0.931	3.8
H7	0.686	0.174	0.856	4.0
H8	0.725	0.196	0.967	4.0
H9	0.755	−0.062	1.114	3.2
H10	0.756	0.068	1.112	3.2
H11	0.852	0.021	1.166	5.5

TABLE II (*Continued*)

	x	*y*	*z*	*Biso*
H12	0.849	0.074	1.084	5.5
H13	0.846	0.154	1.044	4.4
H14	0.897	0.068	1.020	4.4
H15	0.804	0.109	0.883	4.7
H16	0.827	−0.015	0.899	4.7
H17	0.880	0.271	0.601	3.6
H18	0.635	−0.265	0.514	3.6
H19	0.922	0.103	0.654	3.6
H20	0.943	0.111	0.549	3.6
H21	0.866	0.008	1.475	4.8
H22	0.894	−0.052	0.579	4.8
H23	0.777	−0.036	0.523	2.8
H24	0.807	−0.023	0.639	2.8
H25	0.736	−0.403	0.606	2.7
H26	0.733	−0.272	0.608	2.7
H27	0.841	−0.355	0.667	3.7
H28	0.838	−0.257	0.588	3.7
H29	0.660	0.016	0.459	6.7
H30	0.607	0.103	0.471	6.7
H31	0.666	0.176	0.611	2.5
H32	0.689	0.052	0.624	2.5

Biso is the Mean of the Principal Axes of the Thermal Ellipsoid

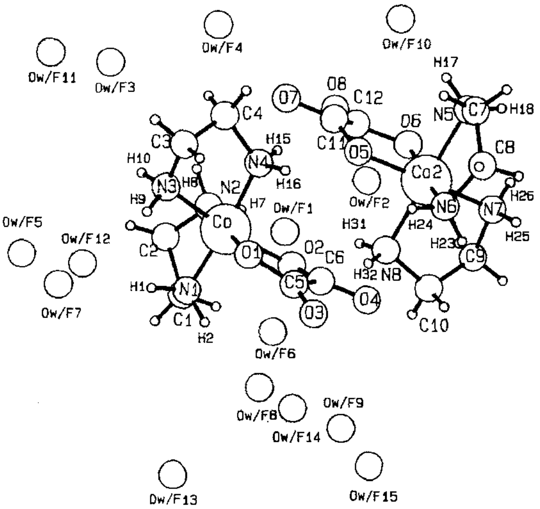

FIGURE 1 A view of the asymmetric unit of (I). The labels of the methylene hydrogens were left out in order to avoid clutter; however, their numbering system is evident from that of the terminal amino hydrogens. All waters and fluoride anions are labelled Ow/F since we cannot be sure which is which due to the quality of the data, which was affected by the loss of waters of crystallization (see Results). Note the hydrogen bonding of the pairs of cations: O2 and O4 form hydrogen bonds with the -NH_2 hydrogens on N8 (H31 and H32) while O5 and O7 form hydrogen bonds with the pair of hydrogens on N4(H15 and H16), making the cations of the asymmetric unit into a racemic dimer. Such dimeric, racemic pairs are readily observed in the packing diagram, Figure 2.

Figures 1 and 2 are, respectively, a labeled figure of the contents of the asymmetric unit and a packing diagram. Final positional and equivalent-isotropic thermal parameters are given in Table II. Bond lengths and angles are listed in Table III.

TABLE III Bond Distances (Å) and Bond Angles (°)

A. Bond Distances			
Co–N1	1.82(3)	N8–C10	1.48(5)
Co–N2	1.89(3)	O1–C5	1.341(24)
Co–N3	1.989(19)	O2–C6	1.33(3)
Co–N4	1.85(3)	O3–C5	1.24(3)
Co–O1	1.980(17)	O4–C6	1.24(3)
Co–O2	1.970(18)	O5–C11	1.25(4)
Co2–N5a	2.02(3)	O6–Co2b	1.876(18)
Co2–N6	1.98(3)	O6–C12b	1.35(5)
Co2–N7a	1.897(16)	O7–C11c	1.29(4)
Co2–N8	1.999(21)	O8–C12c	1.21(6)
Co2–O5	1.885(15)	C1–C2	1.59(6)
Co2–O6a	1.876(18)	C3–C4	1.43(5)
N1–C1	1.34(5)	C5–C6	1.46(3)
N2–C2	1.44(4)	C7–N5a	1.52(4)
N3–C3	1.36(4)	C7–C8	1.39(5)
N4–C4	1.49(5)	C9–C10b	1.49(5)
N5–Co2b	2.02(3)	C10–C9a	1.49(5)
N5–C7b	1.52(4)	C11–O7d	1.29(4)
N6–C8	1.47(4)	C11–C12	1.61(6)
N7–Co2b	1.897(16)	C12–O6a	1.35(5)
N7–C9	1.53(4)	C12–O8d	1.21(6)
B. Bond Angles			
N1–Co–N2	84.3(13)	Co–N2–C2	114.7(23)
N1–Co–N3	99.2(11)	Co–N3–C3	114.2(18)
N1–Co–N4	175.1(14)	Co–N4–C4	119.5(23)
N1–Co–O1	96.4(11)	Co2b–N5–C7b	105.8(18)
N1–Co–O2	87.5(10)	C02–N6–C8	106.0(22)
N2–Co–N3	97.6(10)	Co2b–N7–C9	103.8(14)
N2–Co–N4	93.2(13)	Co2–N8–C10	105.3(19)
N2–Co–O1	175.9(9)	Co–O1–C5	107.5(13)
N2–Co–O2	88.3(10)	Co–O2–C6	106.3(15)
N3–Co–N4	76.9(11)	Co2–O5–C11	116.3(19)
N3–Co–O1	86.3(8)	Co2b–O6–C12b	114.8(25)
N3–Co–O2	171.4(8)	N1–C1–C2	110(3)
N4–Co–O1	86.4(12)	N2–C2–C1	95(3)
N4–Co–O2	96.6(11)	N3–C3–C4	107(2)
O1–Co–O2	87.6(8)	N4–C4–C3	100(3)
N5a–Co2–N6	87.3(10)	O1–C5–O3	124.4(18)
N5a–Co2–N7a	89.5(9)	O1–C5–C6	116.0(19)
N5a–Co2–N8	178.9(10)	O3–C5–C6	119.5(18)
N5a–Co2–O5	92.4(9)	O2–C6–O4	118.4(22)
N5a–Co2–O6a	85.3(9)	O2–C6–C5	119.0(20)
N6–Co2–N7a	92.6(9)	O4–C6–C5	121.9(23)
N6–Co2–N8	91.7(9)	N5a–C7–C8	109(3)
N6–Co2–O5	90.6(9)	N6–C8–C7	116(3)
N6–Co2–O6a	171.1(8)	N7–C9–C10b	109(3)
N7a–Co2–N8	91.0(8)	N8–C10–C9a	109(3)

TABLE III (*Continued*)

N7a–Co2–O5	176.4(9)	O5–C11–O7d	126(3)
N7a–Co2–O6a	92.3(8)	O5–C11–C12	111(3)
N8–Co2–O5	87.2(8)	O7d–C11–C12	116(3)
N8–Co2–O6a	95.7(8)	O6a–C12–O8d	123(4)
O5–Co2–O6a	84.8(8)	O6a–C12–C11	107(4)
Co–N1–C1	110(3)	O8d–C12–C11	129(4)

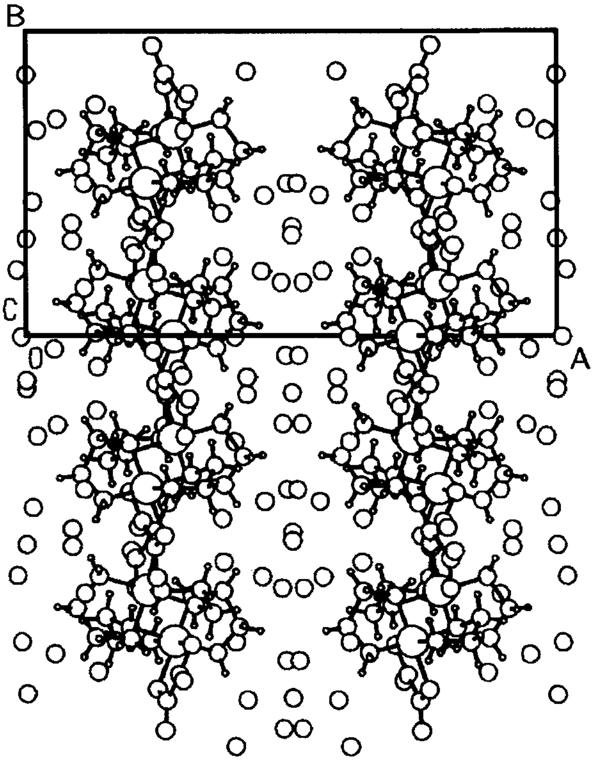

FIGURE 2 A view down the *c*-direction displaying the packing of the ions and waters in the unit cell of (**I**). A *pseudo*-inversion center can readily be seen at the central water of the nine-water cluster at $a = 1/2$, $b = -0.17$ the four pairs of waters surrounding the central one are not properly inverted into one another, either. For that matter, the ten-atom clusters, above and below the one mentioned above, are also not properly inverted into one another.

RESULTS AND DISCUSSION

To determine the chirality and enantiomorphism of the space group, it is unfortunate that we cannot test a water solution, derived from one large, single crystal, for the presence of optically active molecules. A kryptoracemate, as a true racemate, contains an equal number of ions with the opposite chiro-optical symbol; that is, in both cases the crystals are heterochiral. However, the Flack test[9] gives clear evidence of enantiomorphism in the case of (**I**) since it refines to 0.57 indicative of the fact that the correct structure, for the crystal used, is the enantiomer of the initial trial structure.

The CoN_4O_2 portions of the two cations are related to one another by a non-crystallographic (*pseudo*) inversion center located half-way between the Co atoms (at *ca.* 1/4, 0, 1/4); however, (a) the relationship is only approximate (b) it is only approximately obeyed by the four nitrogens and two oxygens of the coordination sphere, and is violated to different degrees by the other atoms of the cations. Thus, there is no crystallographic symmetry relationship between cations which would suggest that the lattice is of higher symmetry. A search for hidden symmetry, using the routine MYSSYM of the NRCVAX program[10] failed to reveal additional elements of symmetry unless disorder was permitted, and we find no evidence of such disorder in space group C2. If the cations are truly disordered, one should see the disorder in either space group. For further details of the only-approximate nature of the inversion centers present in the lattice, see the figure captions of Figures 1 and 2, where more commentary and graphic details have been added.

Compound (**I**) crystallizes as a kryptoracemate in the enantiomorphic space group C2 (No. 5) with two molecules in the asymmetric unit, shown in Figures 1 and 2 to be hydrogen-bonded, dimeric cations in which the hydrogen bonds are from the terminal oxalato oxygens of one cation to the $-NH_2$ hydrogens of the en ligands on an adjacent one. This feature is evident in both the molecular diagram of the asymmetric unit (Figure 1) and in the packing diagram, Figure 2.

For (**I**), the absolute configuration at Co1 is $\Lambda(\delta\lambda)$ with torsional angles of 51.9° and –47.3° and for Co2 is $\Delta(\lambda\delta)$ with torsional angles of –45.9° and 51.1°. Comparison of the conformation and configuration of the two cations with the results obtained in the case of the chloride and bromide analogues,[4] for which absolute configurations were derived, tell us that the correct chiro-optical symbol for Co(1) is $(+)589\text{-}\Lambda(\delta\lambda)\text{-}[Co1(en)_2Ox]F\cdot 11.5H_2O$ while that for Co2 is $(-)589\text{-}\Delta(\lambda\delta)\text{-}[Co_2(en)_2Ox]F\cdot 11.5H_2O$, demonstrating the presence of a racemic pair in the asymmetric unit, thus making this compound a kryptoracemate—the first one of its class.

Aside from the fact that this molecule crystallizes as a kryptoracemate, there are no additional features of either the geometry, conformation or configuration of the cations which are in any way unique or notable. In fact, their geometrical properties resemble those already discussed in the cases of the other three halides described in detail earlier.[4] The chloride and bromide crystals were of much better quality; for physical data of the cations of the $[Co(en)_2Ox]X$ series consult reference 4.

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SUPPLEMENTARY MATERIAL

The original CAD4.DAT;1 file, anisotropic thermal parameters and structure factor tables for both compounds are available in hard copy or PC diskette format from I. Bernal.

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[7] TEXRAY-230 is a modification of the SDP-Plus[8] set of X-ray crystallographic programs distributed by Molecular Structure Corporation, 3200 Research Forest Dr., The Woodlands, TX 77386 for use with their automation of the CAD-4 diffractometer.

[8] SDP-Plus is the Enraf-Nonius Corporation X-ray diffraction data processing programs distributed by B.A. Frenz, & Associates, 1140 East Harvey Road, College Station, TX, 77840.

[9] R.B. Roof, 'A Theoretical Extension of the Reduced Cell Concept in Crystallography', Report LA-4038, Los Alamos Scientific Laboratory, 1969.

[10] The NRCVAX Crystal Structure System, A.C. Larson, F.L. Lee, Y. Le Page, M. Webster, J.P. Charland & E.J. Gabe, as adapted for PC use by Peter S. White, University of North Carolina, Chapel Hill, NC, 27599-3290. For details of the Flack test, see H. Flack, *Acta Cryst.*, **A39**, 876 (1983).