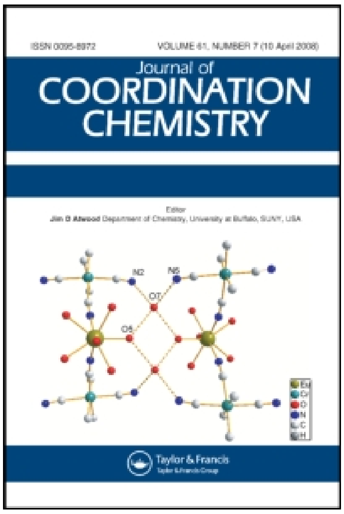

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION, PART 41. THE CRYSTALLIZATION BEHAVIOR OF (H_5O_2)[*cis*-α-Co(edda)ox](I), K[*cis*-β-Co(edda)ox]·H_2O (II) AND K[*cis*-α-Co(edda)malonate]·$3H_2O$ (III)

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION, PART 41. THE CRYSTALLIZATION BEHAVIOR OF (H_5O_2)[*cis*-α-Co(edda)ox](I), K[*cis*-β-Co(edda)ox]·H_2O (II) AND K[*cis*-α-Co(edda)malonate]·$3H_2O$ (III)

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(H_5O_2)[*cis*-α-Co(edda)ox]·H_2O (I), $CoO_{10}N_2C_8H_{15}$, crystallizes, at 22°C, from a dilute HCl solution of K[*cis*-α-Co(edda)ox] in space group $P2_1/n$ (a variant of No. 14), with lattice constants: a = 9.370(2), b = 9.872(3), c = 14.433(2) Å, β = 106.43(1)°; V = 1280.50 Å^3 and d(calc; MW = 358.15, Z = 4) = 1.858 g-cm^{-3}. A total of 3687 data were collected over the range of $4° \leqslant 2\theta \leqslant 50°$; of these, 2572 (independent and with $I \geqslant 3\sigma(I)$) were used in the structural analysis. Data were corrected for absorption (μ = 13.902 cm^{-1}) and the transmission coefficients ranged from 0.7678 to 0.9993. The final $R(F)$ and $R_w(F)$ residuals were, respectively 0.0378 and 0.0348. The anions exist in the lattice as enantiomeric pairs with chiropital descriptors Λ(δλδ)[*cis*-α-Co(edda)ox] and Δ(λδλ)[*cis*-α-Co(edda)ox].

K[*cis*-β-Co(edda)ox]·H_2O (II), $CoKO_9N_2C_8H_{12}$, crystallizes from water at 22°C in space group $P2_1/c$ (No. 14), with lattice constants: a = 8.993(2), b = 10.302(3), c = 14.900(2) Å, β = 106.24(2)°; V = 1297.66 Å^3 and d(calc; MW = 378.23, Z = 4) = 1.936 g-cm^{-3}. A total of 3252 data were collected over the range of $4° \geqslant 2\tau \geqslant 55°$; of these, 1695 (independent and with $I \geqslant 3\sigma(I)$) were used in the structural analysis. Data were corrected for absorption (μ = 16.861 cm^{-1}) and the transmission coefficients ranged from 0.8507 to 0.9978. The final $R(F)$ and $R_w(F)$ residuals were, respectively 0.0293 and 0.0302. The anions exist in the lattice as enantiomeric pairs with chiroptical descriptors Δ(λδδ) and Λ(δλλ).

K[*cis*-α-Co(edda)malonate]·$3H_2O$ (III), $CoKO_{11}N_2C_9H_{18}$, crystallizes from water at 22°C in space group $P2_1/n$ (variant of No. 14), with lattice constants: a = 9.302(2), b = 10.962(4), c = 15.419(5) Å, β = 91.96(2)°; V = 1571.39 Å^3 and d(calc; MW = 428.28, Z = 4) = 1.811 g-cm^{-3}. A total of 4568 data were collected over the range of $4° \leqslant 2\theta \leqslant 60°$; of these, 3820 (independent and with $I \geqslant 3\sigma(I)$) were used in the structural analysis. Data were corrected for absorption (μ = 14.10 cm^{-1}) and the transmission coefficients ranged from 0.8943 to 0.9982. The final $R(F)$ and $R_w(F)$ residuals were, respectively 0.041 and 0.063. The anions exist in the lattice as enantiometric pairs with chiroptical descriptors Δ(λδλ)[*cis*-α-Co(edda)malonate] and Λ(δλδ)[*cis*-α-Co(edda)malonate]. The six-membered Co(malonato) ring is in the chair conformation.

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KEYWORDS: conglomerate crystallization, racemates, mechanisms of crystallization, metal diaminediacetates, metal oxalates, pentahydrodioxo cations, hydronium ion traps, amine polycarboxylates.

INTRODUCTION

Structural studies of [*cis*-α-Co(trien)$(NO_2)_2$]X·H_2O (trien = 1,8-diamino-3,6-diazaoctane; X = Cl, I)(**IV, V**)[1] demonstrated both these substances crystallize as conglomerates. Subsequent investigations revealed that the basic reason for the selection of this crystallization mode was general and equally applicable to K[*cis*-α-Co(edda)$(NO_2)_2$](**VI**) (edda = ethylenediamine-N,N'-diacetate).[2] In all three cases, it was found that the Co complex anions form infinite helices in which the components are hydrogen bonded (-NO_2 oxygens to basal plane NH hydrogens) to one another by three-point attachments to adjacent Co anions. Rows of counterions (and, where relevant, waters of crystallization) then stitch the spirals into homochiral, two-dimensional layers. Adjacent layers are shifted from one another in such a way that the helical spirals of those above and below a given layer are above and below the rows of counterions (and, where relevant, waters of crystallization) of the one in between them. Thus, a homochiral, three-dimensional array of enantiomorphic crystals is created.

We also found that [Co(en)$_2$ox]X·nH_2O [X = Cl, n = 4(**VII**); X = Br, n = 1 (**VIII**); X = 1, n = 0(**IX**)][3] crystallize as conglomerates and exhibit the same infinite spiral string interactions; here, the hydrogen bonds are between terminal oxalate oxygens and basal plane amino hydrogens of adjacent cations. The spiral strings are then joined to one another by hydrogen-bonded interactions with the anions (and, where relevant, the waters of crystallization). For details, readers are referred to the original references.[1-3]

Recently, however, we found that {[*cis*-α-Co(trien)ox]Cl}$_2$·9H_2O and related linear tetraamine oxalates crystallize as racemates[4] probably due to the inability of their terminal oxalato oxygens to form suitable hydrogen-bonded helical strings as a result of steric hindrance caused by the presence of the ethylene fragment of the central ring and by the stereochemistry of the -HN-$(CH_2)_2$-NH- hydrogens of the linear amines. We found[1] that the -NO_2 ligand oxygens of (**IV**) and (**V**) can get around that barrier since they can rotate about the Co-N vector and, having two oxygens on each ligand, meaningful hydrogen bonds can still be formed and helical strings created. However, evading this barrier is impossible for bidentate oxalato ligands given the orientation of the non-bonded pairs on their terminal oxygens and that the twisting maneuver is impossible for them. Finally, we observed that the isostructural double salts with composition, (Cation)[M(en)$_2$ox]X·2H_2O (Cation = NH_4^+, M = Cr;[5] Cation = OH_3^+, M = Co[6]) crystallize as racemates, unlike the simple parent compounds, (**VII→IX**). In those latest reports, we suggested[5,6] that the cause for the change in crystallization pathway is the disruption of the spiral strings by the ammonium (or hydronium) cation which are much more effective in forming hydrogen bonds with the terminal oxalato oxygens, thereby impeding the formation of the cationic helical strings.

Given the above background information, it seemed reasonable to test the generality of the proposals expounded earlier;[1-6] thus, we prepared the three title compounds and, below, we give the results of our investigations into their preference for crystallization pathway at room temperature (*ca.* 22°C).

EXPERIMENTAL DETAILS

Synthesis of (I)

A compound of composition K[*cis*-α-Co(edda)$(NO_2)_2$] (**X**) was synthesized according to the procedure of Douglas and Jordan.[8] An attempt to convert (**X**) to the oxalato derivative of composition K[*cis*-α-Co(edda)ox] by the addition of $H_2C_2O_4 \cdot H_2O$ (1:1) plus a few drops of HCl produced, first, a mechanical mixture of crystals of (**X**) and of K[*cis*-α-Co(edda)$(NO_2)_2$]$\cdot H_2O$(**XI**). The second batch of crystals contained thin orange plates, eventually found to be (**I**). This has been described in detail elsewhere.[2] We have never been able to obtain X-ray quality single crystals of K[*cis*-α-Co(edda)ox] either from Houston syntheses or from material prepared by Jordan.

Synthesis of (II)

It was prepared according to the procedure of van Saun and Douglas except with the omission of activated charcoal.[9] The crystalline material was dissolved in deionized water and the solution was filtered and allowed to crystallize at 22°C. Crystals of the potassium salt, suitable for X-ray analysis, were obtained after some days. Note that the presence of activated charcoal is necessary to obtain compound (**I**); in its absence, its geometrical isomer, (**II**), is obtained. In both cases the elemental analysis is correct if crystalline samples taken from the reaction product are examined.[8–9]

Synthesis of (III)

[*cis*-α-Co(edda)malonate] was obtained as the calcium salt following separation from the *cis*-β isomer on an anion exchange column by eluting with $CaCl_2$ according to the method of Coleman, Legg and Steele.[10] A one gram sample was dissolved in water and poured onto a column of Dowex 50WX8 cation exchange resin (20–50 mesh) in the K^+ form. It was eluted with water and evaporated to near dryness. The crystalline product was filtered and recrystallized from a minimum of hot water by allowing it to cool overnight. The large crystals thus obtained were washed with a little water and, finally absolute ethanol.

Elemental Analyses

(**II**) and (**III**) were analyzed previously.[8,9] Analyses for (**I**) were carried out by Galbraith Laboratories, Inc.[11]

Compound (**I**): Theory for $CoO_{10}N_2C_8H_{15}$: C: 26.83%; H: 4.22%; N: 7.82%. Experimental: C: 26.75%; H: 4.30%; N: 7.68%.

^{1}H NMR Spectra

(I) 2.604(d, J = 9Hz, H1). 3.097(m, H2), 3.180(d, J = 18Hz, H3), 4.077(m, H4). H2 and H4 were split by interaction with -NH, while H1 and H3 were not (for labels, see Fig. 1); therefore, H2 and H4 must be *cis* to -NH. (II) 2.608 (d, J = 9Hz, H1), 3.105(d, J = 9Hz, H2), 3.184(d, J = 18Hz, H3), 4.803(d, J = 18Hz, H4). Pmr data for (III) have already been reported by van Saun and Douglas.[9]

X-ray Diffraction

Data were collected for all three compounds with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[12] of the SDP-Plus software package.[13] The crystals were centered with data in the 24° $\leq 2\Theta$ 36° range and examination of the cell constants and Niggli matrix[14] and systematic absences clearly showed (I) and (III) to crystallize in a primitive, monoclinic lattice whose systematic absences belong to those of the space group $P2_1/n$(a variant of No. 14) while (II) crystallizes in space group $P2_1/c$ (No. 14). The $F(hkl)_{obs}$ sets were corrected for absorption using empirical curves derived from Psi scans[12,13] of suitable reflections. The scattering curves were taken from

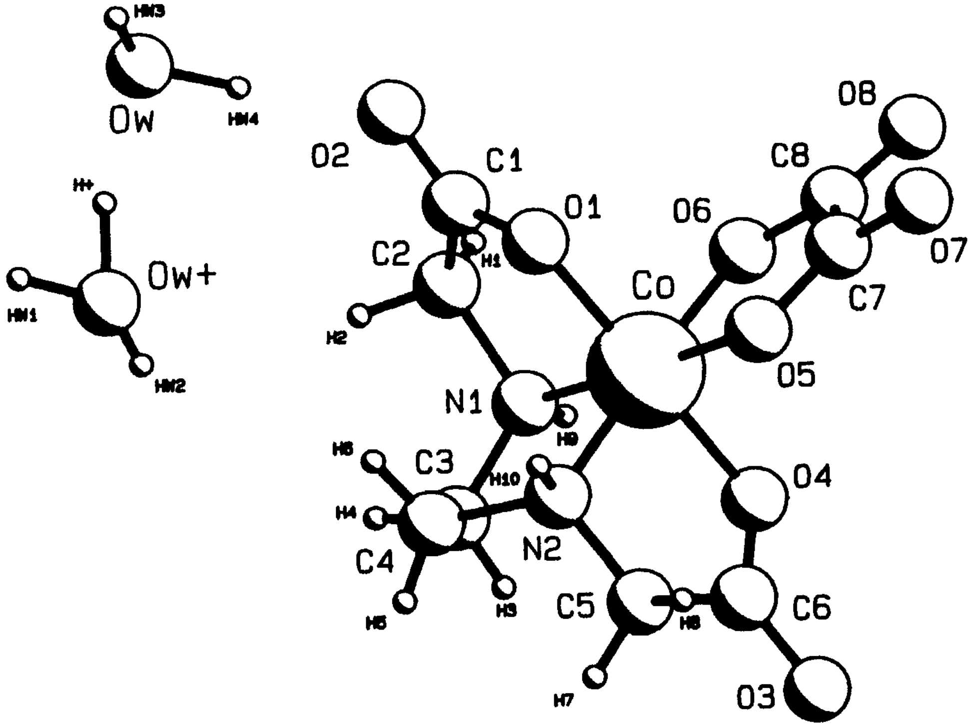

Figure 1 The contents of the asymmetric unit of compound (I) and the labelling system used in numbering the atoms present therein. The K cation and water of crystallization were placed at the crystallographic positions nearest to the anion insofar as hydrogen bonded interactions are concerned.

Cromer and Waber's compilation.[15] The structures were solved by the Patterson method using Co as the heavy atom. Refinement, followed by difference maps, produced the heavy atoms which were refined to convergence with anisotropic thermal parameters. The hydrogens of the anions were placed at idealized positions (C-H = N-H = 0.95 Å; B = 5.00 Å^2) and added as a fixed contribution to the calculated structure factors. In all three cases, a difference Fourier map computed prior to the final cycles of refinement produced the hydrogens of the waters and of the $H_2O_5{}^+$ cation. For ideal as well as experimentally located hydrogens, positional parameters were fixed and thermal parameters of 5.0 Å^2 were assigned. Details of data collection and processing are listed in Tables 1, 2 and 3. Their asymmetric units are shown in Figs. 1, 2 and 3. In those figures, the counterions and waters were placed at the positions displaying the shortest hydrogen bond. The packing of the cations and anions in the unit cells is shown in Figs. 4, 5 and 6. Tables 4, 5 and 6 contain the positional parameter for the complexes. Bond lengths, angles, torsional angles and hydrogen bonded interactions are listed in Tables 7, 8 and 9.

RESULTS AND DISCUSSION

Figure 1 shows the asymmetric unit present in crystals of (**I**). Note that the $H_5O_2{}^+$ cation is asymmetric (see Table 9) and has Ow$^+$-H$^+$ = 1.073 Å while Ow-H$^+$ = 1.548 Å. Fig. 3 shows the asymmetric unit of (**III**) where it is evident that one of the hydrogens of Ow$^+$ points directly at the oxygen of Ow. The average value of the O-H distances (Ow$^+$ to Hw1, Hw2, H$^+$ and Ow to Hw3 and Hw4) is 0.965 Å, whereas the Ow$^+$-H$^+$ distance is 1.548 Å. Å suggesting an asymmetric hydrogen bond between the two fragments. This result is in agreement with the findings of Mootz and Oellers[16] who studied the stereochemistry of the $H_5O_2{}^+$ cation in $H_2SiF_6 \cdot 4H_2O$, $H_2SiF_6 \cdot 6H_2O$ and $H_2SiF_6 \cdot 9.5H_2O$ where asymmetric bonds were

Table 1 Summary of data collection and processing parameters for (H_5O_2)[*cis*-α-Co(edda)ox] (**I**)

Space group	$P2_1/n$ (No. 14)
Cell constants	a = 9.370(2)Å
	a = 9.872(3)
	c = 14.433(2)
	β = 106.43 (1)°
Cell volume	V = 1280.44 Å^3
Molecular formula	$CoO_{10}N_2C_8H_{15}$
Molecular weight	358.15 gm-mole^{-1}
Density (*calc*; z = 4 mol/cell)	1.858 gm-cm^{-3}
Radiation employed	MoK$_\alpha$ (λ = 0.71073Å)
Absorption coefficient	μ = 13.902 cm^{-1}
Relative transmission coefficients	0.7678 to 0.9993
Data collection range	$4° \leq 2\Theta \leq 50°$
Scan width	$\Delta\Theta = 1.00 + 0.35\tan\Theta$
Total unique data collected	3687
Data used in refinement*	2572
$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$	0.0394
$Rw = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma\lvert F_o\rvert^2]^{1/2}$	0.0350
Weights used	$w = [\sigma(F_o)]^{-2}$

* The difference between this number and the total is due to substraction of 1115 that were standards, symmetry related or did not meet the criterion that $I \geq 3\sigma(I)$.

Table 2 Summary of data collection and processing parameters for K[*cis*-β-Co(edda)ox]·H_2O **(II)**

Space group	$P2_1/c$ (No. 14)
Cell constants	a = 8.993(2) Å
	b = 10.302(3)
	c = 14.900(2)
	β = 106.24(2)°
Cell volume	V = 1297.66 $Å^3$
Molecular formula	$CoO_9N_2C_8H_{12}$
Molecular weight	378.23 $gm\text{-}mole^{-1}$
Density (*calc; z* = 4 mol/cell)	1.936 $gm\text{-}cm^{-3}$
Radiation employed	$MoK_\alpha(\lambda = 0.71073Å)$
Absorption coefficient	μ = 16.861 cm^{-1}
Relative transmission coefficients	0.8705 to 0.9978
Data collection range	$4° \le 2\Theta \le 55°$
Scan width	$\Delta\Theta$ = 1.00 + 0.35tanΘ
Total unique data collected	3252
Data used in refinement*	1695
$R = \Sigma\Vert F_o\vert-\vert F_c\Vert/\Sigma\vert F_o\vert$	0.0293
$Rw = [\Sigma w(\vert F_o\vert-\vert F_c\vert)^2/\Sigma\vert F_o\vert^2]^{1/2}$	0.0302
Weights used	$w = [\sigma(F_o)]^{-2}$

* The difference between this number and the total is due to subtraction of 1115 that were standards, symmetry related or did not meet the criterion that $I \ge 3\sigma(I)$.

also found. The average values for their O-H distances are 0.995 and 1.524 Å close to the values we found which is remarkable given the widely different nature of the compounds and the temperatures at which they were studied.

The $H_5O_2^+$ cation is hydrogen bonded to the anion, as shown, and as documented in Table 3(D). The relevant bonds are O2-Hw4 = 1.63 Å, O3-Hw1 = 2.51 Å, O3, Hw2 = 2.35 Å, O7-Hw1 = 2.47 Å, O7-Hw2 = 2.35 Å and O8-Hw3 = 2.17 Å. The other hydrogen bonds are longer than 2.55 Å and were disregarded as being too weak to take into account. O1 and O6 form intramolecular hydrogen bonds (O1-H10 = 1.97 Å, O6-H9 = 1.96 Å) which are fairly substantial since the O-H-N angles are *ca.* 168°. But, there is no evidence of intermolecular N-H....O hydrogen bonds between anions such as we found in the case of the *cis*-dinitro and oxalato compounds, **(II)** to **(VI)** mentioned above, no doubt due to the fact that the oxalato oxygens also form hydrogen bonds with the $H_5O_2^+$ cation.

Fig. 2 was drawn in an orientation selected to avoid as much overlap as possible while showing the orientation of the -NH– hydrogens on N1 and N2. These clearly point in opposite directions, making access to them by the terminal oxygens of rigid oxalato ligand essentially impossible. The fact is that neither H9, nor H10, make hydrogen bonds with oxalato oxygens of any significance (if any, they are larger than 2.55 Å). The figure also shows the anti-clockwise nature of the torsional angle of the HN-CH_2-CH_2-NH fragment (it is λ, <N1-C3-C4-N4 = −48.5°). The glycinato fragments, as usual, are nearly planar (their torsional angles are 5.5 and 9.9°). The oxalato ligand is essentially planar, as demonstrated by the O5-C7-C8-O8 torsional angle, which is −176.1°.

Fig. 3 show the asymmetric unit of **(III)**. Here the hydrogens of the waters were also found experimentally to make excellent sense from the standpoint of their configuration with respect to adjacent species. Note that Ow2 is hydrogen bonded to Ow1 through Hw4, while Hw3 forms a hydrogen bond with Ow3. The potassium

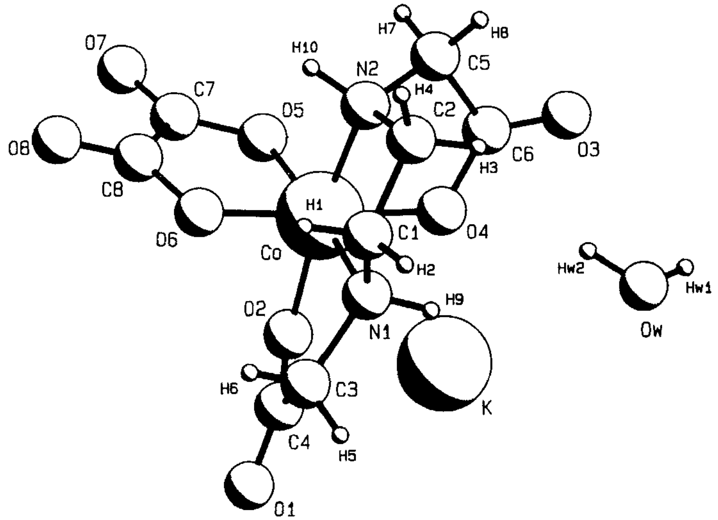

Figure 2 The contents of the asymmetric unit of compound (II) and the labelling system used in numbering the atoms present therein. The H_2O was placed at the crystallographic positions nearest to the anion insofar as hydrogen bonded interactions are concerned.

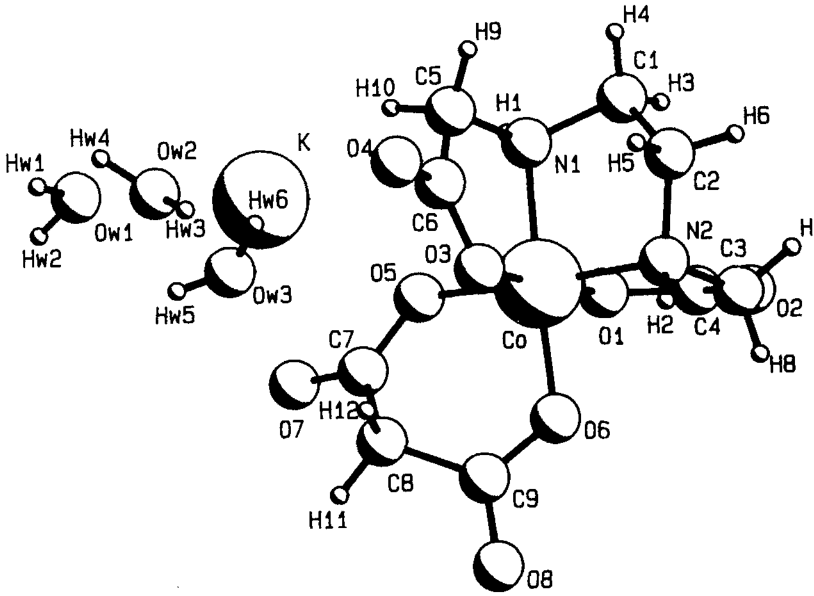

Figure 3 The contents of the unit cell of compound (III) and the labelling system used in numbering the atoms present therein. The cation and the waters of crystallization were placed at the positions at which they have the shortest distance to one of its neighbors.

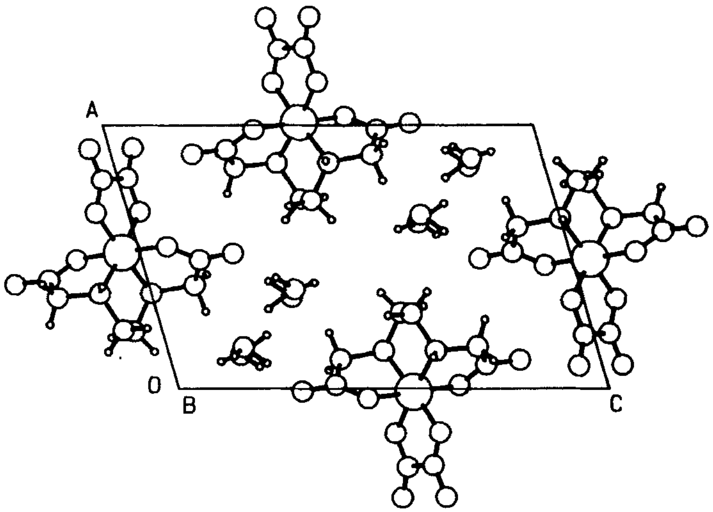

Figure 4 The packing of the ions in the unit cells of (**I**). Note that the *b*-projection shown illustrates clearly the enantiomorphic relationship between the upper-left and lower-right portions of the unit cell, which are related by the inversion center located at (1/2, 1/2, 1/2). Also, note that the terminal oxygens of the oxalato ligands do not point to the amine hydrogens of adjacent anions but to the water hydrogens (see Table 7(c)); and, rows of hydrogen bonded $H_5O_2^+$ cations are interspered between rows of anions and stitch them together, as illustrated in the lower-left and upper-right sections of the unit cell.

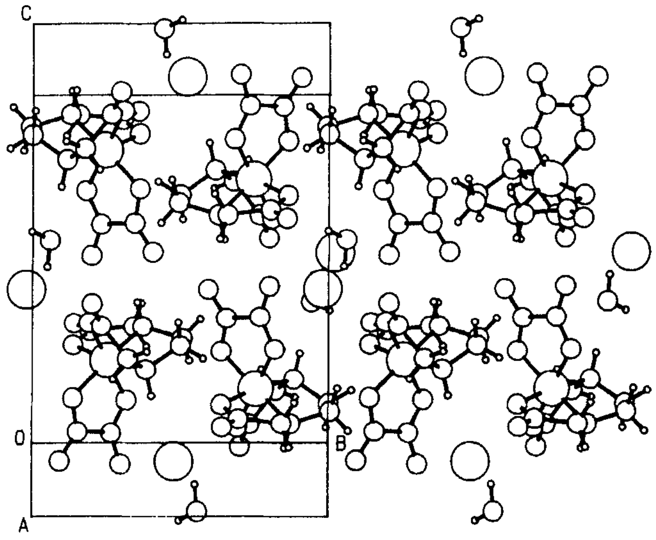

Figure 5 The packing of the ions in the unit cell of (**II**). This *a*-projection also illustrates the enantiomorphic relationship between the upper and lower portions of the unit cell, which are related by the inversion center. Also, note that, on a given row, the terminal oxygens of the oxalato ligands do not point to the amine hydrogens of adjacent cation; however, they do so in the columns along the *c*-axis, but there is only one hydrogen bond per terminal oxalato oxygen and both are to H9 on two different anions. Thus, spiral string formation of the type previously observed for conglomerates is impossible.

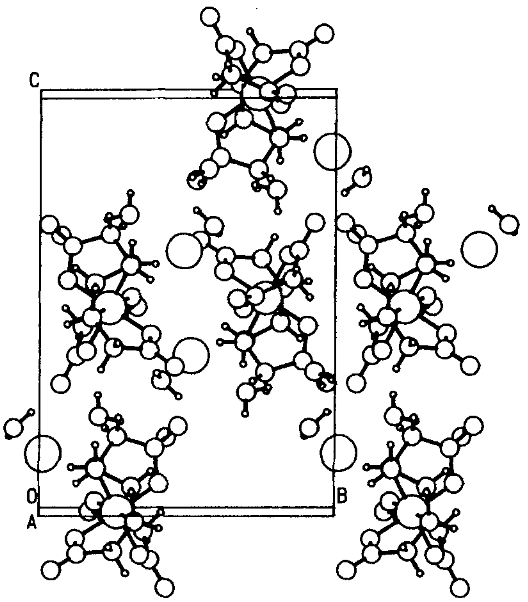

Figure 6 An *a*-projection of the unit cell of **(III)**. The center of the cell is at the inversion center relating ions and waters aligned along the *c*-axis. According to the data in Table 9(c), three of the oxygens of the malonate ligand form hydrogern bonds with the waters of crystallization while one (O5) forms one hydrogen bond with H1 of an adjacent anion.

ion is properly oriented to interact with non-bonded pairs of the waters as well as carboxylato oxygens of the Co anion. Table 9 details the values of the shorter of those bonds. The overall chirooptical symbol for the anion shown in Fig. 3 is $\Delta(\lambda\delta\lambda)$, the N1-C1-C2-N3 torsional angle is 51.2°, while those of the two glycinato fragments are N1-C5-C6-O3 = −16.4° and N2-C3-C4-O1 = −19.1°, respectively. The Co(malonato) fragment is puckered at C8 and is a chair, despite the flattening caused by the C=O pi bonds.

The packing diagram for **(I)** is shown in Fig. 4, which is a *b*-projection. There, one can clearly see that the hydrophobic (-CH_2-CH_2-) portion of the anions is turned inward and the hydrophilic, carboxylato, portion of the anions are directed out of the cell edges. Rows of $H_5O_2^+$ cations then join rows of anions in such a way that the upper-left anion row is enantiomorphic to the lower-right one inasmuch as the center of the cell is an inversion center of the space group. Note that there is no evidence of spiral string formation, a fact readily understood given that hydronium ions form hydrogen bonds with the glycinato oxygens, as is evident at the lower left and upper right of the diagram. In fact, the closest contacts between anions are depicted at the upper left and lower right portions of the diagram, and these contacts are between oxygens of glycinato and oxalato C=O moieties. Obviously, these must be repulsive interactions.

The packing diagram for **(II)** is shown in Fig. 5, which is an *a*-projection. Here, again, the anions have =CO groups directed at one another; however, near the center of the cell, one can also identify one CO....H(N) interaction exists between

Table 4 Positional parameters and their ESD's for compound (I)

Atom	*x*	*y*	*z*	*B*(Å^2)
Co	0.01244(7)	0.24944(9)	0.45806(4)	1.44(1)
Ow$^+$	0.3444(4)	0.4567(4)	0.3245(3)	4.2(1)
O1	0.0361(4)	0.1400(3)	0.5686(2)	1.88(8)
O2	0.0091(4)	0.1464(4)	0.7154(2)	3.06(9)
O3	-0.1090(4)	0.3579(4)	0.1888(2)	3.2(1)
O4	-0.0160(4)	0.3600(3)	0.3481(2)	1.98(8)
O5	0.1646(4)	0.1498(3)	0.4239(2)	1.91(8)
O6	0.1682(3)	0.3651(3)	0.5290(2)	1.69(7)
O7	0.4094(4)	0.1494(4)	0.4511(2)	2.79(9)
O8	0.4148(4)	0.3892(4)	0.5549(3)	2.96(9)
N1	-0.1400(4)	0.3444(4)	0.4994(3)	1.69(9)
N2	-0.1409(4)	0.1341(4)	0.3806(3)	1.48(9)
C1	-0.0190(6)	0.1896(5)	0.6335(3)	2.0(1)
C2	-0.1169(6)	0.3141(5)	0.6029(3)	2.4(1)
C3	-0.2861(5)	0.3026(5)	0.4354(4)	2.2(1)
C4	-0.2779(5)	0.1538(5)	0.4112(3)	2.1(1)
C5	-0.1575(6)	0.1673(5)	0.2777(3)	2.0(1)
C6	-0.0917(5)	0.3056(5)	0.2690(3)	1.9(1)
C7	0.2917(6)	0.1983(5)	0.4602(3)	2.0(1)
C8	0.2974(6)	0.3306(5)	0.5209(3)	1.9(1)
Ow1	0.1260(5)	0.4687(5)	0.1686(3)	5.1(1)
Hw1	0.0824	0.5392	0.2010	5
Hw2	0.1023	0.4313	0.1157	5
Hw3	0.3769	0.5371	0.3496	5
Hw4	0.4042	0.4101	0.2792	5
H$^+$	0.2993	-0.0490	0.2608	5

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as (4/3) $*[a^2 * \beta_{11} + b^2 * \beta_{22} + c^2 * \beta_{33} + ab(\cos\gamma) * \beta_{12} + ac(\cos\beta) * \beta_{13} + \mathrm{bc}(\cos\alpha) *_{23}]$

Table 5 Positional parameters and their ESD's for compound (II)

Atom	*x*	y	z	B(Å^2)
Co	-0.28802(6)	0.25439(6)	0.32104(4)	1.353(8)
K	-0.2979(1)	-0.01997(9)	0.49182(7)	2.45(2)
O1	-0.6898(3)	0.1417(3)	0.3431(2)	2.73(7)
O2	-0.4471(3)	0.1384(3)	0.3314(2)	0.75(6)
O3	0.0932(3)	0.2023(3)	0.5246(2)	2.41(7)
O4	-0.1518(3)	0.1920(3)	0.4364(2)	1.73(6)
O5	-0.4138(3)	0.3179(3)	0.2038(2)	1.83(6)
O6	-0.2038(3)	0.1379(3)	0.2451(2)	1.79(6)
O7	-0.4424(3)	0.2003(3)	0.5475(2)	2.40(7)
O8	-0.2296(4)	0.0946(3)	0.0917(2)	2.76(7)
N1	-0.3830(4)	0.3717(3)	0.3879(2)	1.61(7)
N2	-0.1300(4)	0.3827(3)	0.3260(2)	1.66(7)
C1	-0.3375(5)	0.5055(4)	0.3667(3)	2.11(9)
C2	-0.1651(5)	0.4995(4)	0.3780(3)	2.16(9)
C3	-0.5501(5)	0.3414(4)	0.3594(3)	2.15(9)
C4	-0.5679(5)	0.1957(4)	0.3441(3)	1.82(8)
C5	0.0196(4)	0.3218(4)	0.3776(3)	1.96(9)
C6	-0.0107(4)	0.2332(4)	0.4534(3)	1.63(8)
C7	-0.3823(4)	0.2672(4)	0.1307(3)	1.57(8)
C8	-0.2613(4)	0.1561(4)	0.1551(3)	1.67(8)
Ow	-0.0284(4)	0.4407(3)	0.1544(2)	3.21(8)
Hw1	0.0390	0.5000	0.1816	5
Hw2	-0.0410	0.4667	0.0839	5

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as (4/3) $* [a^2 * \beta_{11} + b^2 * \beta_{22} + c^2 * \beta_{33} + ab(\cos\gamma) * \beta_{12} + ac(\cos\beta) * \beta_{13} + bc(\cos\alpha) * \beta_{23}]$

Table 6 Positional parameters and their ESD's for compound (III)

Atom	*x*	*y*	*z*	$B(\text{Å}^2)$
Co	0.91512(5)	0.23528(5)	0.49793(3)	1.038(16)
K	0.56622(11)	0.48710(9)	0.62855(6)	1.98(3)
Ow1	0.3067(4)	0.5873(4)	0.6841(3)	3.32(16)
O1	0.9656(3)	0.3763(3)	0.43389(19)	1.61(10)
Ow2	0.4693(5)	0.2996(4)	0.7153(3)	4.04(19)
O2	1.1435(4)	0.4568(3)	0.36081(22)	2.32(12)
O3	0.8774(3)	0.0936(3)	0.56415(18)	1.64(10)
Ow3	0.5539(5)	0.0706(4)	0.6674(3)	3.88(18)
O4	0.8611(4)	0.0299(4)	0.70006(22)	2.98(14)
O5	0.7338(3)	0.3106(3)	0.51896(19)	1.60(10)
O6	0.8509(3)	0.1575(3)	0.39244(18)	1.60(10)
O7	0.5015(3)	0.3301(3)	0.49078(21)	2.08(11)
O8	0.6835(4)	0.0708(3)	0.30926(21)	2.49(13)
N1	0.9898(4)	0.3081(3)	0.60488(22)	1.61(11)
N2	1.1082(3)	0.1754(3)	0.47833(22)	1.48(11)
C1	1.1487(5)	0.3058(4)	0.6041(3)	2.20(15)
C2	1.1922(5)	0.1863(4)	0.5628(3)	2.10(15)
C3	1.1683(4)	0.2497(4)	0.4075(3)	1.82(15)
C4	1.0899(4)	0.3711(4)	0.3995(3)	1.60(13)
C5	0.9276(5)	0.2377(4)	0.6771(3)	2.26(17)
C6	0.8864(5)	0.1098(4)	0.6478(3)	1.81(15)
C7	0.6135(4)	0.2705(4)	0.48674(24)	1.48(13)
C8	0.6100(4)	0.1448(4)	0.4455(3)	1.89(14)
C9	0.7206(4)	0.1234(4)	0.3777(3)	1.49(12)
Hw1	0.776	0.971	0.221	1.5
Hw2	0.727	0.897	0.164	1.5
Hw3	0.012	0.274	0.205	1.5
Hw4	0.577	0.697	0.234	1.5
Hw5	0.981	0.486	0.184	1.5
Hw6	0.128	0.455	0.203	1.5

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3) * [a^2 * \beta_{11} + b^2 * \beta_{22} + c^2 * \beta_{33} + ab)\cos\gamma) * \beta_{12} + ac(\mathrm{co}\beta) * \beta_{13} + bc(\cos\alpha) * \beta_{23}]$

adjacent anions along the *c*-direction. Finally, one such interaction exists between an NH hydrogen and a bonded oxalato oxygen. Such interactions occur along the *b* direction and the resulting strings are homochiral. However, adjacent strings along *b* are enantiomorphic to one another possibly as a result of the fact that the glue binding them together is a K·H_2O ion. Recall that in the introduction we mentioned that in the past, we have noted that K[*cis*-α-Co(edda)$(NO_2)_2$] (X) and K[*cis*-α-Co(edda)$(NO_2)_2$]·H_2O (XI) are, respectively, a conglomerate and a racemate and that the difference is caused by the change of K to K·H_2O as the glue linking the spiral strings. A phase diagram would be useful in this case and, if there is an anhydrous, conglomerate phase, it would be a very rare example since only one *cis*-β compound to our knowledge has produced a conglomerate phase.

The last packing diagram (Fig. 6) is that of (III), which is an *a*-projection also. Reference to this diagram and to Table 9(c) reveals that most of the hydrogen bonds present in this lattice are intramolecular and that only two are intermolecular (namely O3....H2 = 2.09 Å and O5....H1 = 2.56 Å). The latter is a very weak bond, being long and having <N1-H1...H5 = 87.2°, which renders it meaningless. Thus, there is no chance of forming meaningful spiral strings among the anions of this lattice, as we suspected from our earlier results.

Table 7 Bond distances, angles and selected H-bonds for compound (I)

(a) Bond distances in angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co	O1	1.887(2)	O3	C6	1.235(3)	N2	C4	1.483(3)
Co	O4	1.883(2)	O4	C6	1.280(3)	N2	C5	1.486(3)
Co	O5	1.908(2)	O5	C7	1.252(3)	C1	C2	1.522(4)
Co	O6	1.908(2)	O6	C8	1.295(3)	C3	C4	1.517(4)
Co	N1	1.938(2)	O7	C7	1.1245(3)	C5	C6	1.518(4)
Co	N2	1.924(2)	O8	C8	1.216(3)	C7	C8	1.565(4)
O1	C1	1.288(3)	N1	C2	1.478(3)	Ow	Hw3	0.890(4)
O2	C1	1.213(3)	N1	C3	1.477(3)	Ow	Hw4	1.077(4)
Ow	H+	1.548(4)	Ow+	Hw1	0.989(4)	Ow+	Hw2	0.820(4)
Ow+	H+	1.073(4)						

(b) Angles in degree

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	Co	O4	178.53(9)	Co	O1	C1	114.9(2)
O1	Co	O5	90.33(8)	C1	O2	Hw4	132.4(2)
O1	Co	O6	90.00(7)	Co	O4	C6	114.8(2)
O1	Co	N1	86.42(8)	Co	O5	C7	112.7(2)
O1	Co	N2	92.39(8)	Co	O6	C8	112.8(2)
O4	Co	O5	91.06(8)	C8	O8	Hw3	164.3(2)
O4	Co	O6	90.56(8)	Co	N1	C2	107.6(2)
O4	Co	N1	92.19(9)	Co	N1	C3	107.8(2)
O4	Co	N2	87.09(8)	C2	N1	C3	114.8(2)
O5	Co	O6	86.18(8)	Co	N2	C4	108.5(2)
O5	Co	N1	176.74(9)	Co	N2	C5	107.5(2)
O5	Co	N2	91.98(8)	C4	N2	C5	114.4(2)
O6	Co	N1	93.64(9)	O1	C1	O2	123.6(3)
O6	Co	N2	176.99(9)	O1	C1	C2	115.4(2)
N1	Co	N2	88.33(9)	O2	C1	C2	120.9(3)
N1	Co	N2	88.33(9)	O2	C1	C2	120.9(3)
N1	C2	C1	111.2(2)	N2	C5	C6	110.6(2)
N1	C3	C4	108.4(2)	O3	C6	O4	123.6(3)
N2	C4	C3	107.5(2)	O3	C6	C5	120.3(3)
Hw1	Ow+	Hw2	135.9(3)	O4	C6	C5	116.1(3)
Ow	H+	Ow+	159.3(3)	O5	C7	O7	125.0(3)
Hw1	Ow+	H+	85.0(3)	O5	C7	C8	115.6(3)
Hw3	Ow	Hw4	116.7(3)	O7	C7	C8	119.4(3)
Hw3	Ow	H+	118.5(3)	O6	C8	O8	126.9(3)
Hw4	Ow	H+	89.3(3)	O6	C8	C7	112.6(2)
Hw2	Ow+	H+	137.9(3)	O8	C8	C7	120.5(3)

(c) Selected hydrogen bonds

O1-H10	1.97	N2-H10....O1	167.5	N2 at −x, −y, 1 − z
O6-H9	1.96	N1-H9....O6	168.7	N1 at −x, −y, lmz
O2-Hw4	1.63	Ow-Hw4....O2	173.4	
O3-Hw1	2.51	Ow+-Hw1....O3	81.2	Ow+ at −x − 1/2, y + 1/2, 1/2 − z
O7-Hw1	2.47	Ow+-Hw1....O7	76.6	Ow+ at x + 1, y, z
O7-Hw2	2.35	Ow+-Hw2....O7	86.5	Ow+ at −x, −y, 1 − z
O8-Hw3	2.17	Ow-Hw3....O8	134.5	Ow at x − 1, y, z

Table 8 Bond distances, angles and selected H-bonds for compound(II)

(a) Bond distances in angstroms

Atom 1	Atom2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co	O2	1.902(2)	O3	C6	1.230(3)	N2	C2	1.502(4)
Co	O4	1.896(2)	O4	C6	1.294(3)	N2	C5	1.484(3)
Co	O5	1.885(2)	O5	C7	1.287(3)	C1	C2	1.513(4)
Co	O6	1.926(2)	O6	C8	1.283(3)	C3	C4	1.520(4)
Co	N1	1.900(2)	O7	C7	1.230(3)	C5	C6	1.517(4)
Co	N2	1.927(2)	O8	C8	1.218(3)	C7	C8	1.551(4)
O1	C4	1.226(3)	N1	C1	1.495(3)			
O2	C4	1.293(3)	N1	C3	1.476(4)			
O2	C4	1.293(3)	N1	C3	1.476(4)			

(b) Angles in degree

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O2	Co	O4	91.73(8)	N1	Co	N2	88.7(1)
O2	Co	O5	90.94(8)	Co	O2	C43	113.9(2)
O2	Co	O6	94.58(9)	Co	O4	C6	114.4(2)
O2	Co	N1	84.42(9)	Co	O5	C7	113.3(2)
O2	Co	N2	172.25(9)	Co	O6	C8	112.7(2)
O4	Co	O5	176.81(9)	Co	N1	C1	107.0(2)
O4	Co	O6	92.24(8)	Co	N1	C3	106.8(2)
O4	Co	N1	91.79(9)	C1	N1	C3	116.9(2)
O4	Co	N2	84.98(9)	Co	N2	C2	108.2(2)
O5	Co	O6	85.81(8)	Co	N2	C5	106.5(2)
O5	Co	N1	90.21(9)	C2	N2	C5	111.8(2)
O5	Co	N2	92.59(9)	N1	C1	C2	105.8(2)
O6	Co	N1	175.87(9)	N2	C2	C1	109.4(2)
O6	Co	N2	92.56(9)	N1	C3	C4	107.9(3)
O6	Co	N2	92.56(9)	N1	C3	C4	107.9(3)
O1	C4	O2	125.1(3)	O5	C7	O7	124.7(3)
O1	C4	C3	120.4(3)	O5	C7	C8	114.3(2)
O2	C4	C3	114.4(3)	O7	C7	C8	121.0(3)
N2	C5	C6	107.5(2)	O6	C8	O8	126.0(3)
O3	C6	O4	123.3(3)	O6	C8	C7	113.5(2)
O3	C6	C5	121.5(3)	O8	C8	C7	120.5(3)
O4	C6	C5	115.2(2)				

(c) Selected hydrogen bonds

O3-Hw2	2.29	Ow-Hw2....O3	119.6	Ow at 2-x,-y,1-z
O4-H9	2.44	N1-H9....O4	97.9	
O5-Hw1	1.99	Ow-Hw1....O5	175.9	Ow at 2-x,-y,1-z
O7-H9	2.04	N1-H9....O7	152.4	N1 at x, 1/2-y, z-1/2
O8-H9	2.43	N1-H9....O8	125.8	N1 at 1-x,y,1-z
Ow-H10	2.07	N2-H10....Ow	151.9	N2 at x, 1/2-y, z+1/2

Table 9 Bond distances, angles and selected H-bonds for compound (III)

(a) Bond distances in angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co	O1	1.902(4)	O3	C6	1.302(5)
Co	O3	1.898(5)	C3	C4	1.521(7)
Co	O5	1.915(3)	O4	C6	1.219(6)
Co	O6	1.914(3)	O5	C7	1.286(5)
Co	N1	1.939(4)	O6	C9	1.281(5)
Co	N2	1.946(3)	O7	C7	1.233(5)
N1	C1	1.479(6)	O8	C9	1.241(5)
N1	C5	1.487(6)	N2	C2	1.500(5)
C1	C2	1.517(7)	N2	C3	1.486(6)
C8	C9	1.510(6)	C5	C6	1.518(8)
O1	C4	1.290(5)	C7	C8	1.517(7)
O2	C4	1.227(6)	Ow1	Hw1	0.912(4)
Ow1	Hw2	0.815(4)	Ow2	Hw3	0.911(5)
Ow2	Hw4	0.902(4)	Ow3	Hw5	0.960(4)
Ow3	Hw6	0.908(4)			

(b) Angles in degree

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	Co	O3	176.29(13)	Co	N2	C2	107.1(3)
O1	Co	O5	88.42(17)	Co	N2	C3	107.6(3)
O1	Co	O6	89.79(17)	C2	N2	C3	113.3(3)
O1	Co	N1	91.11(18)	N1	C1	C2	107.4(3)
O1	Co	N2	86.98(17)	N2	C2	C1	107.2(3)
O3	Co	O5	94.67(17)	N2	C3	C4	110.4(3)
O3	Co	N1	86.94(18)	O1	C4	O2	123.4(4)
O3	Co	N2	89.80(17)	O1	C4	C3	116.0(4)
O5	Co	O6	94.90(15)	O2	C4	C3	120.5(4)
O5	Co	N1	88.29(16)	N1	C5	C6	110.9(3)
O5	Co	N2	174.04(14)	O3	C6	O4	123.3(4)
O6	Co	N1	176.71(14)	O3	C6	C5	115.3(4)
O6	Co	N2	88.87(16)	O4	C6	C5	121.4(4)
N1	Co	N2	88.02(17)	O5	C7	O7	121.6(4)
Co	O1	C4	114.8(3)	O5	C7	C8	118.6(3)
Co	O3	C6	114.5(3)	O6	C9	O8	121.3(4)
Co	N1	C1	108.4(3)	O6	C9	C8	119.7(3)
Co	N1	C5	106.6(3)	O8	C9	C8	119.0(4)
C1	N1	C5	114.3(3)	Hw5	Ow3	Hw6	99.3(4)
Hw	Ow1	Hw2	94.9(4)	Hw3	Ow2	Hw4	114.3(4)

(c) Selected Hydrogen Bonds

O1-Hw2	2.31	Ow1-Hw2....O1	161.5	
O2-H1	2.00	N1-H1....O2	161.7	
O2-Hw6	2.43	Ow3-Hw6....O2	128.8	
O3-H2	2.09	N2-H2....O3	166.8	N2 at x - 1/2, 3/2 - y, z - 1/2
Ow3-Hw3	1.85	Ow2-Hw3....Ow3	165.0	
O4-Hw6	2.18	Ow3-Hw6....O4	138.1	
O5-H1	2.56	N1-H1....O5	87.2	N1 at 1 - x, 1 - y, 1 - z
O6-Hw4	2.13	Ow2-Hw4....O6	166.8	
O8-Hw1	1.96	Ow1-Hw1....O8	168.3	
O8-Hw5	1.80	Ow3-Hw5....O8	163.2	

CONCLUSIONS

Given our experience with the crystallization of {[*cis*-α-Co(trien)ox]Cl}$_2 \cdot 9H_2O$[4] and that of (Cation)[M(en)$_2$ox]X·$2H_2O$ (Cation = $NH_4{}^+$, M = Cr;[5] Cation = $OH_3{}^+$, M = Co[6]) we expected that none of the three compounds under study would undergo conglomerate crystallization; however, our experience with these systems is still in its infancy and we could learn much from results opposite to our current beliefs. All the compounds have anions suffering from the same problem of access to the diamine hydrogens mentioned earlier and documented in the current Results. Thus, the formation of the spiral strings is precluded in all three cases herein reported. Moreover, the presence of a $H_5O_2{}^+$ cation was also expected to interfere with the formation of the spiral strings, as documented in the case of the onium oxalato double salts discussed above. In fact, the same hydrogen bonding patterns observed with (Cation)[Me(en)$_2$ox]X·$2H_2O$ (Cation = $NH_4{}^+$, Me = Cr;[5] Cation = $OH_3{}^+$, Me = Co[6]) are evident in the asymmetric unit and packing diagram of (**I**).

It is satisfying that the suggestions made earlier concerning the crystallization pathway selected by the compounds discussed in references 1–6 have been found to be equally valid here, giving additional evidence that such suggestions are not only reasonable, but may be more general than we suspected before.

SUPPLEMENTARY MATERIAL

Tables of structure factors for all three compounds are available from IB or WTJ.

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