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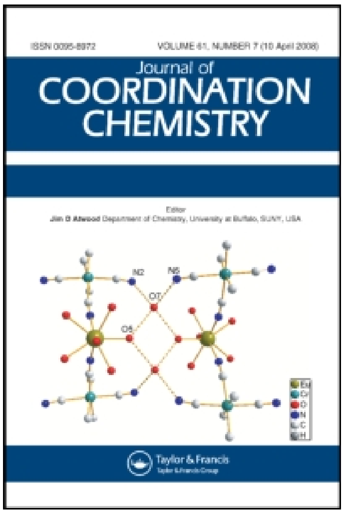

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 49. THE CRYSTALLIZATION BEHAVIOR OF K[cis-β-(EDDA)(ox)l · H_2O(I), AND OF [*mer*-Co(dien)(NH_3(ox)]BR (II)

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To cite this Article Bernal, Ivan , Cai, Jiwen and Somoza, Fernando(1997) 'THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 49. THE CRYSTALLIZATION BEHAVIOR OF K[cis-β-(EDDA)(ox)l · H_2O(I), AND OF [*mer*-Co(dien)(NH_3(ox)]BR (II)', Journal of Coordination Chemistry, 42: 1, 33 — 44

To link to this Article: DOI: 10.1080/00958979708045278

URL: http://dx.doi.org/10.1080/00958979708045278

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J. Coord. Chem., 1997, Vol. 42, pp. 33–44
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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 49.

THE CRYSTALLIZATION BEHAVIOR OF K[*cis*-β-(EDDA)(ox)] • H_2O(I), AND OF [*mer*-Co(dien)(NH_3(ox)]BR (II)

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(Received 28 June 1996; Revised 28 August 1996; In final form 18 October 1996)

Racemic solutions of K[*cis*-β-(edda)(ox)]·H_2O (I) $CoKO_9N_2C_8H_{12}$, crystallize as racemic crystals, space group $P2_1/c$ (No. 14) with cell constants of $a = 8.993(4)$, $10.302(4)$, $c = 14.590(9)$, $\beta = 106.24(4)°$, $V = 1297.44$ Å^3, $d = 1.936$ gm-cm^3. (MW = 378.22 gm-mole^{-1}; $z = 4$). A total of 3081 data were collected over the range of $4° \leq 2\theta \leq 50°$; of these, 1695 (independent and with $1 \geq 2.5\sigma(I)$) were used in the structural analysis. Data were corrected for absorption ($\mu = 16.861$ cm^{-1}) and the transmission coefficients ranged from 0.9163 to 0.9965. The final R(F) and R_W(F) residuals were, respectively 0.0299 and 0.0322. The anions exist in the lattice as enantiomeric pairs and the conformation of the central, five-membered ring for the molecule described here is δ(N1-C1-C2-N2 = +47.3°); that of the five-membered acetato ligands are, respectively, δ(+162.0°) and λ(−156.8°). The secondary nitrogens are both R. The potassium cation is bonded to the six oxygens.

Racemic solutions of [*mer*-Co(dien)(NH_3)(ox)]Br (II), $BrCoO_4N_4C_6H_{16}$, crystallize as racemic crystals, space group $P2_1/c$ (No. 14) with cell constants of $a = 7.733(3)$, $10.191(4)$, $c = 14.608(4)$ Å, $\beta = 98.86(3)°$, $V = 1137.54$ Å^3, $d = 2.026$ gm-cm^3 (MW = 347.05 gm-mole^{-1}; $z = 4$). A total of 3544 data were collected over the range of $4° \leq 2\theta \leq 60°$; of these, 2120 (independent and with $1 \geq 2.5\sigma(I)$) were used in the structural analysis. Data were corrected for absorption ($\mu = 49.90$ cm^{-1}) and the transmission coefficients ranged from 0.678 to 0.961. The final R(F) and R_W(F) residuals were, respectively 0.051 and 0.056. The cations exist in the lattice as racemic pairs and the conformations of the two, five-membered dien rings for the molecule described here are λ(N1-C1-C2-N2 = −54.6°) and δ(N2-C3-C4-N3 = +51.6°).

Keywords: Conglomerate crystallization; racemates; mechanisms of crystallization; amine oxalato cobalt compounds; cobalt halides

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INTRODUCTION

We have previously investigated the crystallization behavior of metal(III) amine oxalato(ox) derivatives with the hope that we can shed some light, at the molecular level, as to why some of these compounds crystallize as conglomerates, whereas closely related species crystallize as racemates either in centrosymmetric space groups or in polar space groups. A summary of those results is given in Table I.

The above results suggest three important conclusions: (a) the counterion of the chiral species plays a crucial role in determining the crystallization pathway, as illustrated, for example, by the crystallization mode for the cations of the [*cis*-Co(en)$_2$(ox)] + series. This has been reported in previous publications.[1-10] (b) all enantiomorphic ions that crystallize as conglomerates form infinite helical chains of hydrogen-bonded chiral ions, and if the formation of these helical chains is impeded by the counterion, the compounds invariably crystallize as racemates.

This has been discussed at some length[1-10] (c) the number of compounds of the amino oxalate series that crystallize as conglomerates is small; evidently the

TABLE I Space groups of metal (III) amine oxalato complexes

Compound	*Sp. Group*	*Ref*
$\mathrm{NH_4[(NH_3)_2Co(NO_2)_2(ox)]}$	C2/c	1
$[\textit{cis}\text{-}\beta\text{-}\mathrm{Co(trien)(NO_2)_2}][\textit{trans}\text{-}\mathrm{(NH_3)_2Co(NO_2)_2(ox)}]$	P2$_1$/c	1
$[\textit{trans}\text{-}\mathrm{Co(en)_2(NO_2)_2}][\textit{trans}\text{-}\mathrm{(NH_3)_2Co(NO_2)_2(ox)}]$	P$\bar{1}$	1
$\mathrm{[Co(NH_3)_4(ox)]NO_3{\cdot}H_2O}$	P2$_1$2$_1$2$_1$	2
$\mathrm{[Co(NH_3)_4(ox)]I{\cdot}H_2O}$	P2$_1$/n	2
$\mathrm{NH_4[Cr(en)_2(ox)]Cl_2H_2O}$	P2$_1$/c	3
$\mathrm{[Co(NH_3)_4(ox)]_2}[\textit{trans}\mathrm{(NH_3)(OH)Co(ox)_2]{\cdot}4H_2O}$	Pnma	4
$\mathrm{[Co(en)_2(ox)]Cl{\cdot}4H_2O}$	P2$_1$2$_1$2$_1$	5
$\mathrm{[Co(en)_2(ox)]Br{\cdot}H_2O}$	P2$_1$2$_1$2$_1$	5
$\mathrm{[Co(en)_2(ox)]PF_6}$	P2$_1$/c	5
$\mathrm{[Co(en)_2(ox)]I}$	C2+C2/c*	5
$\mathrm{[Co(tn)_2(ox)]Br{\cdot}H_2O}$	P2$_1$/c	6
$\mathrm{[Co(tn)_2(ox)]I{\cdot}H_2O}$	P2$_1$/c	6
$\mathrm{[Co(tn)_2(ox)]ClO_4}$	P$\bar{1}$	6
$\mathrm{(H_3O^+)[Co(en)_2(ox)]Cl_2{\cdot}H_2O}$	P2$_1$/c	7
$\{[\textit{cis}\text{-}\alpha\text{-}\mathrm{Co(trien)(ox)]Cl}\}_2\mathrm{{\cdot}9H_2O}$	P$\bar{1}$	8
$[\textit{cis}\text{-}\mathrm{Co(3,2,3\text{-}tet)(ox)]Cl{\cdot}4H_2O}$	P2$_1$/c	8
$\{\textit{cis}\text{-}\mathrm{Co(trien}\{\mathrm{(ox)](NO_3}\}_2\mathrm{{\cdot}H_2O}$	P2$_1$/c	8
$[\textit{mer}\text{-}\mathrm{Co(dien)(ox)\ (NO_2)}\}$	Cm	8
$\Lambda(\delta\lambda)\text{-}[\mathrm{Co}\{\textit{trans}\text{-}\mathrm{(R,S)(N\text{-}meen)_2(ox)}\}]\mathrm{Pb_2Cl_5{\cdot}2H_2O}$	P2$_1$/n	9
$\Lambda(\lambda\lambda)\text{-}\{[\mathrm{Co}\{\textit{trans}\text{-}\mathrm{(R,R)(N\text{-}meen)_2(ox)}\})\mathrm{Br}\}_2\mathrm{{\cdot}3H_2O}$	Pn	9
$\Delta(\delta\lambda)\text{-}[\mathrm{Co}\{\textit{cis}\text{-}\mathrm{(R,S)(N\text{-}meen)_2(ox)}\}]\mathrm{I}$	P2$_1$/n	9
$\mathrm{(H_5O_2{}^+)}[\textit{cis}\text{-}\alpha\text{-}\mathrm{Co(edda)(ox)}]$	P2$_1$/n	10
$\mathrm{K}[\textit{cis}\text{-}\beta\text{-}\mathrm{Co(edda)(ox)]{\cdot}H_2O}$	P2$_1$/c	10
$\mathrm{[Co(dien)(NH_3)(ox)]NO_3}$	P2$_1$2$_1$2$_1$	11
$\mathrm{[Co(dien)(NH_3)(ox)]PF6}$	Cc	11**

* Crystals of both are deposited in the same crystallization batch. Both types of crystals are of poor quality; for details the reader is referred to the original (ref. 5).

** The space group reported is incorrect. The correct space group is Ama2, as corrected in reference 12.

rigid oxalato ligand finds it difficult, except with the simplest amine co-ligands, to form the necessary, hydrogen-bonded, helical strings observed in all cases of conglomerate crystallization. Note that $[Co(en)_2(ox)]Cl{\cdot}4H_2O$ and $[Co(en)_2(ox)]Br{\cdot}H_2O$ crystallize as conglomerates; however, $\{[$*cis*-α-$Co(trien)(ox)]Cl\}_2{\cdot}9H_2O$ and related species crystallize as racemates. This has been attributed[8] to the inability of the rigid oxalato ligand to properly form hydrogen bonds with the pair of secondary amino hydrogen atoms that, in any case, are sterically hindered by the presence of the methylidine fragments of the central ring. For the *cis*-dinitro series and the oxalato series, the hydrogen bonds in question are formed by the terminal oxygens of the ligands and the amino hydrogens of an adjacent ion. If the stereochemistry of the amine ligands around the central ion impedes the formation of helical chains, the compounds crystallize as racemates. This is shown by comparing the crystallization behavior of the series $[Co(en)_2(ox)]^+$ and $[Co(tn)_2(ox)]^+$.[5,6]

This study further documents which amine oxalato compounds crystallize as conglomerates and which crystallize as racemates. We suspect that the geometrical requirements for the successful formation of helical strings are fairly stringent in the oxalato series. For example we note that, of those we have studied, [*cis*-α-Co(trien)(ox)]X, [*cis*-β-Co(trien)(ox)]X and [*cis*-Co(3,2,3-tet)(ox)]X crystallize as racemates; however, within the series $[Co(dien)(NH_3)(ox)]X$, the nitrate is reported to be a conglomerate while the hexafluorophosphate is said to be a racemate.[11] This report adds further information on the crystallization behavior of that series. We also address the issue of whether a *cis*-β isomer, or *cis*-β-like, is likely to crystallize as a conglomerate. Thus far, all structural studies available report racemates in polar or centrosymmetric space groups.

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EXPERIMENTAL

Syntheses

Compound (**I**): K[*cis*-β-(edda)(ox)]$\cdot H_2O$ (**I**), $CoKO_9N_2C_8H_{12}$, was obtained according to the procedure published earlier[13] to prepare the *cis*-α derivative. Without the use of activated charcoal in the reaction vessel produces (**I**). It was recrystallized from a deionized water solution (*ca.* 22 C) that produced crystals suitable for x-ray diffraction.

Compound (**II**): $[Co(dien)(NH_3)(ox)]Br$ was prepared according to the procedure of Couldwell, *et al.*,[11] using $CoBr_2{\cdot}6H_2O$ as the starting material. It was recrystallized from deionized water (*ca.* 22 C) and suitable crystals were found among the first crystallization batch.

Elemental Analyses: Compounds (**I**) and (**II**) were analyzed by Galbraith Laboratories.[14] Compound (**I**), theory for $CoKO_9N_2C_8H_{12}$: C = 25.41, H = 3.2, N = 7.41. Found: C = 25.36, H = 3.18, N = 7.40. Compound (**II**), theory for $BrCoO_4N_4C_6H_{16}$: C = 20.77, H = 4.65, N = 16.14. Found: C = 20.76, H = 4.67, N = 16.16.

Crystallography

Data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[15] of the SDP-Plus software package.[16] The procedures used for crystal alignment, cell constant determination, space group determination, and data collection were uniform for both crystals. Processing of the data was carried out with the PC version of the NRCVAX package.[17] Crystals were centered with data in the $20° \leq 2\Theta \leq 40°$ range and examination of the cell constants, absences, and Niggli matrix[18] clearly showed that (**I**) and (**II**) crystallize in primitive, monoclinic lattices whose systematic absences belong, unambiguously, to those of the space group $P2_1/c$.

The details of data collection for compounds (**I**) and (**II**) are summarized in Table II and Table III respectively. The intensity data sets were corrected for absorption using empirical curves derived from Psi scans[14–15] of suitable reflections. The scattering curves were taken from Cromer and Waber's compilation.[19]

The structures of (**I**) and (**II**) were solved from their Patterson maps using their heaviest atom as the initial phasing species for a difference Fourier map. After refinement of the scale factor and the positional parameters of the heaviest atom, a difference Fourier map produced, in both cases, most of the non-hydrogen atoms. The remaining ones 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) with fixed thermal parameters. Conversion of the heavy atoms to anisotropic motion resulted in refinement of the overall structure to final R(F) and R_W(F) factorrs listed in Table II and Table III.

TABLE II Summary of data collection and processing parameters for K{*cis*-β-(edda)(ox)]·H_2O (I)

Space Group	$P2_1/c$ (No.14)
Cell Constants	a = 8.993(4)Å
	b = 10.302(4)
	c = 14.590(9)
	β = 106.24(4)°
Cell Volume	V = 1297.44 Å^3
Molecular Formula	$CoKO_9N_2C_8H_{12}$

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TABLE II (*Continued*)

Molecular Weight	378.22 gm-mole^{-1}
Density (calc; z = 4 mol/cell)	1.936 gm-cm^{-3}
Radiation Employed	MoK$_{\alpha}$ (λ = 0.71073 Å)
Absorption Coefficient	μ = 16.861 cm^{-1}
Relative Transmission Coefficients	0.9163 to 0.9965
Data Collection Range	$4° \leq 2\Theta \leq 50°$
Scan Width	$\Delta\Theta = 0.95 + 0.35\tan\Theta$
Total Unique Data Collected	3081
Data Used in Refinement*	1695
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.0299
$R_w = [\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma\|F_o{}^2]^{1/2}$	0.0322
Weights Used	$w = [\sigma(F_o)]^{-2}$

* The difference between this number and the total is due to subtraction of 1386 that were standards, symmetry related or did not meet the criterion that $I \geq 2.5\sigma(I)$.

TABLE III Summary of data collection and processing parameters for [mer-Co(dien)(NH$_3$)(ox)] Br (**II**)

Space Group	P2$_1$/c(No. 14)
Cell Constants	a = 7.733(3)Å
	b = 10.191(4)
	c = 14.608(4)
	β = 98.86(3)°
Cell Volume	V = 1137.54 Å^3
Molecular Formula	$BrCoO_4N_4C_6H_{16}$
Molecular Weight	347.05 gm-mole^{-1}
Density (calc; z = 4 mol/cell)	2.026 gm-cm^{-3}
Radiation Employed	MoK$_{\alpha}$ (λ = 0.71073 Å)
Absorption Coefficient	μ = 49.90 cm^{-1}
Relative Transmission Coefficients	0.678 to 0.961
Data Collection Range	$4° \leq 2\Theta \leq 60°$
Scan width	$\Delta\Theta = 0.95 + 0.35\tan\Theta$
Total Unique Data Collected	3544
Data Used In Refinement*	2120
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.051
$R_w = [\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma\|F_o{}^2]^{1/2}$	0.056
Weights Used	$w=[\sigma(F_o)]^{-2}$

* The difference between this number and the total is due to subtraction of 1424 that were standards, symmetry related or did not meet the criterion that $I \geq 2.5\sigma(I)$.

RESULTS AND DISCUSSION

Figures 1 and 2 give labeled views of the asymmetric units found for molecules (**I**) and (**II**). Figures 3 and 4 depict the packing of the molecules in their respective unit cells. Final positional and equivalent-isotropic thermal parameters are given in Tables IV and V. Bond lengths, angles are listed in Tables VI and VII. The few torsional angles of interest are given in the text.

Compound (**I**) is a genuine *cis*-β geometrical isomer while (**II**) is a *cis*-β-like compound in that the triamine is *mer*. Since the NH_3 is in an axial position with respect to the basal plane defined by the *mer*-dien, these two ligands produce in

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TABLE IV Positional parameters and their esd's for (**I**)

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)	1.75(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*
H1	−0.6435	0.3614	0.3120	5*
H2	−0.5729	0.2920	0.4088	5*
H3	−0.6274	0.1362	0.2986	5*
H4	−0.6234	0.2187	0.3882	5*
H5	0.0627	0.3179	0.3251	5*
H6	0.0993	0.3102	0.4354	5*
H7	−0.0209	0.1669	0.4964	5*
H8	0.0957	0.2534	0.4635	5*
H9	−0.0359	0.4218	0.3227	5*
H10	−0.4048	0.5773	0.3640	5*

* Hydrogen atoms were added at idealized positions with fixed thermal parameters of 5.0 $Å^2$. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3)* $[a^2{*}\beta_{11} + b^2{*}\beta_{22} + C^2{*}\beta_{11} + ab(\cos\gamma){*}\beta_{12} + ac(\cos\beta){*}\beta_{13} + bc(\cos\alpha){*}\beta_{23}]$

TABLE V Atomic parameters *x*, *y*, *z* and biso. for (**II**) E.S.Ds. refer to the last digit printed

	x	*y*	*z*	*Biso*
Br	0.31507(10)	0.84760(8)	0.03331(6)	3.01(3)
Co	0.62110(9)	0.90344(9)	0.34648(6)	1.31(3)
O1	0.4575(5)	0.7689(4)	0.3023(3)	1.75(17)
O2	0.4229(5)	0.9930(5)	0.3820(3)	2.13(18)
O3	0.1694(5)	0.7367(5)	0.2746(4)	2.53(19)
O4	0.1379(6)	0.9669(5)	0.3779(4)	2.87(21)
N1	0.5872(6)	0.9752(5)	0.2208(4)	1.92(20)
N2	0.8114(6)	0.8038(5)	0.3097(3)	1.47(18)
N3	0.6712(7)	0.8097(6)	0.4648(4)	2.24(23)
N4	0.7712(7)	1.0508(6)	0.3910(4)	2.35(22)
C1	0.7314(9)	0.9294(7)	0.1731(5)	2.4(3)
C2	0.7755(8)	0.7924(7)	0.2068(5)	2.16(24)
C3	0.8291(8)	0.6826(7)	0.3639(5)	2.3(3)

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TABLE V (*Continued*)

	x	*y*	*z*	*Biso*
C4	0.8289(8)	0.7240(8)	0.4629(5)	2.7(3)
C5	0.2957(7)	0.8012(7)	0.3072(5)	1.88(22)
C6	0.2773(8)	0.9296(7)	0.3596(5)	2.1(3)
H1	0.587	1.069	0.223	2.7
H2	0.478	0.946	0.188	2.7
H3	0.696	0.930	0.108	3.3
H4	0.831	0.985	0.188	3.3
H5	0.875	0.760	0.183	3.0
H6	0.679	0.735	0.188	3.0
H7	0.913	0.857	0.327	2.3
H8	0.733	0.625	0.344	3.1
H9	0.935	0.638	0.358	3.1
H10	0.824	0.649	0.501	3.6
H11	0.934	0.771	0.485	3.6
H12	0.573	0.757	0.474	3.0
H13	0.695	0.871	0.515	3.0
H14	0.889	1.023	0.405	3.2
H15	0.762	1.118	0.344	3.2
H16	0.736	1.087	0.445	3.2

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

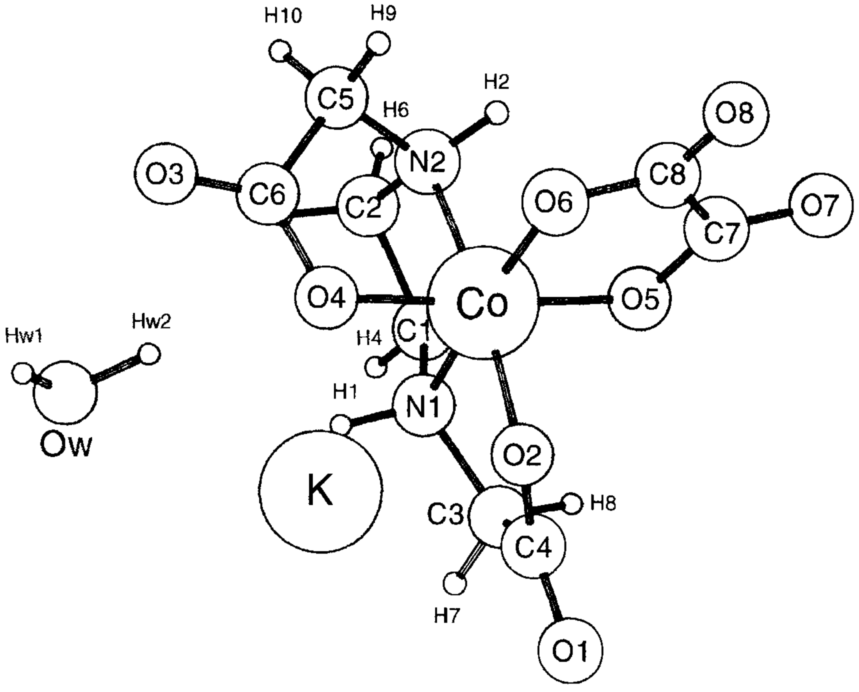

FIGURE 1 The ions in the asymmetric unit of (**I**). The potassium and the water of crystallization were placed at that symmetry position in which they form shortest bonds to adjacent species. Note hydrogen bonds between Hw2 and O3 and O4 and between K and O2 and O4.

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TABLE VI Bond distances (Å) and angles (°) for (**I**)

A) Distances

Atom1	*Atom2*	*Distance*	*Atom1*	*Atom2*	*Distance*	*Atom1*	*Atom2*	*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)			

B) Angles

Atom1	*Atom2*	*Atom3*	*Angle*	*Atom1*	*Atom2*	*Atom3*	*Angle*	*Atom1*	*Atom2*	*Atom3*	*Angle*
O2	Co	O4	91.73(8)	N1	Co	N2	88.7(1)	O1	C4	O2	125.1(3)
O2	Co	O5	90.94(8)	Co	O2	C4	113.9(2)	O1	C4	C3	120.4(3)
O2	Co	O6	94.58(9)	Co	O4	C6	114.4(2)	O2	C4	C3	114.4(3)
O2	Co	N1	84.42(9)	Co	O5	C7	113.3(2)	N2	C5	C6	107.5(2)
O2	Co	N2	172.25(9)	Co	O6	C8	112.7(2)	O3	C6	O4	123.3(3)
O4	Co	O5	176.81(9)	Co	N1	C1	107.0(2)	O3	C6	C5	121.5(3)
O4	Co	O6	92.24(8)	Co	N1	C3	106.8(2)	04	C6	C5	115.2(2)
O4	Co	N1	91.79(9)	C1	N1	C3	116.9(2)	O5	C7	O7	124.7(3)
O4	Co	N2	84.98(9)	Co	N2	C2	108.2(2)	O5	C7	C8	114.3(2)
O5	Co	O6	85.81(8)	Co	N2	C5	106.5(2)	O7	C7	C8	121.0(3)
O5	Co	N1	90.21(9)	C2	N2	C5	111.8(2)	O6	C8	O8	126.0(3)
O5	Co	N2	92.59(9)	N1	C1	C2	105.8(2)	O6	C8	C7	113.5(2)
O6	Co	N1	175.87(9)	N2	C2	C1	109.4(2)	O8	C8	C7	120.5(3)
O6	Co	N2	92.56(9)	N1	C3	C4	107.9(3)				

Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE VII Bond Distances (Å) and Bond Angles (°) for (**II**)

A. Bond Distances			
Co—O1	1.909(4)	O4—C6	1.211(8)
Co—O2	1.923(4)	N1—C1	1.479(8)
Co—N1	1.956(6)	N2—C2	1.489(8)
Co—N2	1.931(5)	N2—C3	1.463(9)
Co—N3	1.961(6)	N3—C4	1.504(9)
Co—N4	1.947(6)	C1—C2	1.503(10)
O1—C5	1.306(7)	C3—C4	1.506(11)
O2—C6	1.296(8)	C5—C6	1.534(10)
O3—C5	1.213(8)		
B. Bond Angles			
O1—Co—O2	85.29(18)	Co—O2—C6	113.1(4)
O1—Co—N1	87.99(21)	Co—N1—C1	108.8(4)
O1—Co—N2	91.25(19)	Co—N2—C2	106.9(4)
O1—Co—N3	88.79(22)	Co—N2—C3	107.8(4)
O1—Co—N4	175.14(21)	C2—N2—C3	117.9(5)
O2—Co—N1	94.52(21)	Co—N3—C4	108.4(4)
O2—Co—N2	176.45(20)	N1—C1—C2	106.8(5)
O2—Co—N3	92.89(22)	N2—C2—C1	104.8(5)
O2—Co—N4	90.15(21)	N2—C3—C4	105.6(6)
N1—Co—N2	86.17(22)	N3—C4—C3	107.6(5)
N1—Co—N3	171.66(24)	O1—C5—O3	124.2(6)
N1—Co—N4	90.69(25)	O1—C5—C6	114.0(5)
N2—Co—N3	86.21(22)	O3—C5—C6	121.8(5)
N2—Co—N4	93.33(22)	O2—C6—O4	123.8(6)
N3—Co—N4	93.1(3)	O2—C6—C5	114.0(5)
Co—O1—C5	113.0(4)	O4—C6—C5	122.2(6)

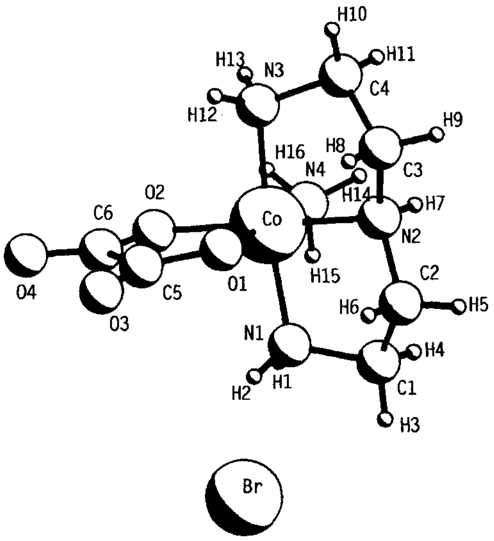

FIGURE 2 The ions in the asymmetric unit of (**II**). The bromide anions are hydrogen bonded to the cations *via* Br...H bonds, such as H2...Br shown at the bottom of the figure.

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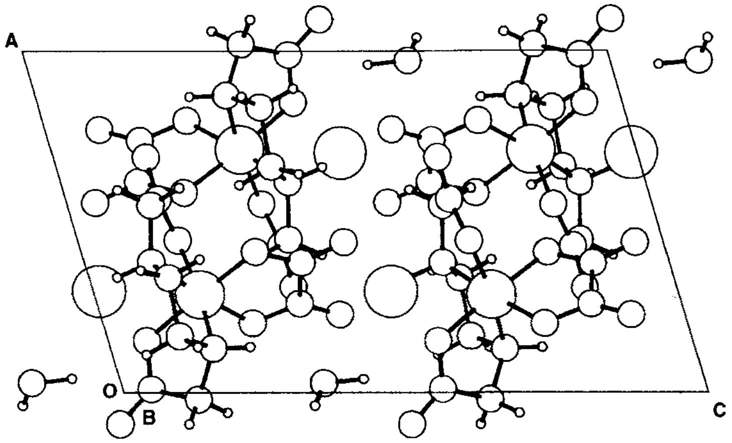

FIGURE 3 The packing of the ions in the unit cell of (**I**). The inversion center at 1/2, 1/2, 1/2 is obviously between a pair of potassium ions. The anions are linked together by the agency of hydrogen bonds to the water hydrogens, as depicted at the bottom and top of the figure, near c = 1/2. The anions are also linked to one another by the agency of K...O bonds, as shown in the middle of the figure.

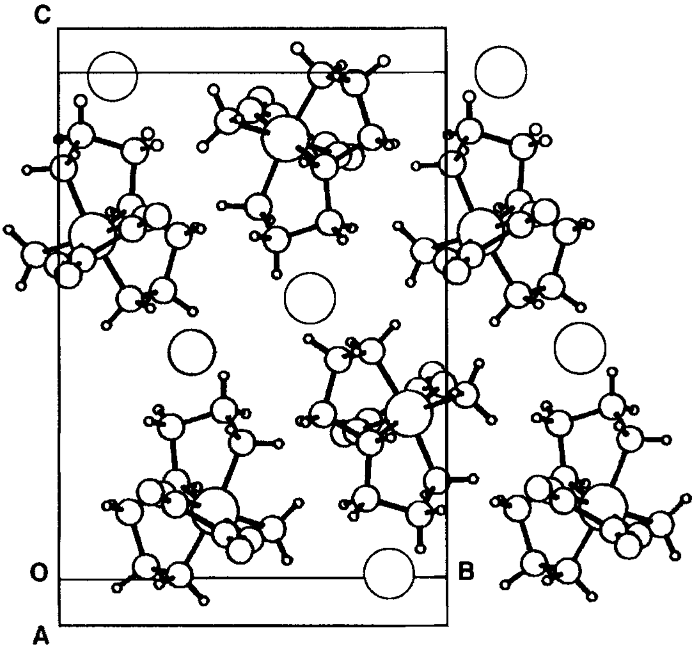

FIGURE 4 The packing of the contents of the unit cell of (**II**). This is an a-projection. Note that there is no direct link between cations and, therefore no formation of helical strings such as those found in the case of conglomerate crystallization. The anions stitch the cations together *via* H...Br bonds (with H2, H12 and H16), as shown near the center of the figure.

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(**II**) a geometry similar to that in the *cis*-β-trien derivative(**I**). This was the rationale behind our selection of these two compounds for their preferred crystallization pathway. We hoped that one or both would crystallize as a conglomerate and give some clues as to what is required by a *mer* and/or *cis*-β derivative to produce conglomerates. Unfortunately, this was not the case and the only indication that they do so comes from the report by Couldwell, *et al.*[11] that $[Co(dien)(NH_3)(ox)]NO_3$ crystallizes in space group $P2_12_12_1$; however, they also indicated the crystals were of extremely poor quality and could not determine its crystal and molecular structure. Additionally their structure of the $[Co(dien)(NH_3)(ox)]PF_6$ derivative was found to be incorrect due to an error in the determination of its space group.[12] In the absence of more convincing results, we must conclude that no *cis*-β or *cis*-β-like compound has been shown to produce conglomerate crystals. In a recent publication,[13] we explored an additional example of *cis*-β oxalates that crystallizes as a racemate.

Despite being unable to answer the original question, we can make a few useful comments concerning the packing patterns observed in these two species. Figure 3 is a *b*-projection of the monoclinic cell of (**I**). Note that there is no evidence of helical string formation of the type observed when cobalt amine oxalates crystallize as conglomerates.[5] In such compounds, as in the $[Co(en)_2(ox)]X$ (X = Cl, Br, I) series, the non-ligating oxygens of the oxalate ligand of every cation in the lattice form a series of hydrogen bonds with the amino hydrogens on the basal plane of an adjacent cation, thus forming an infinite helical string; the strings are then stitched together by the counterions (and, where relevant, the waters of crystallization) if the compounds are ionic. In the case of neutral species, hydrogen bonds between the elements of neutral, helical strings, stitch one another into an enantiomorphic lattice.[20–21]

Instead, in (**I**) the anions are stitched together by K-O bonds as well as water-O bonds, as can readily be seen in Figure 3 and documented by the distances listed in Table VI. Three K-O bonds (K to O2, O4 and O7) are formed by potassium and oxygens located at the positions listed in Table III. Three other K-O bonds are formed with anions located at symmetry-related positions. Hw2 forms a bond (2.413 Å) with O3 of the anion. Note however, that neither the K-O or the water-O bonds form a continuous string.

SUPPLEMENTARY MATERIAL

Compound (**I**): Anisotropic thermal parameters, structure factor table. Compound (**II**): Anisotropic thermal parameters, structure factor table can be obtained directly from I. Bernal.

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Acknowledgments

We thank the Robert A. Welch Foundation for support of this research (Grant E-592 to I. Bernal) and for fellowships granted to J. Cai and F. Somoza. We thank the National Science Foundation for the funds used in purchasing the diffractometer.

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[16] SDP-Plus is the Enraf-Nonius Corporation x-ray diffraction data processing programs distributed by B. A. Frenz & Associates, 209 University Dr. East, College Station, TX 77840. Version of 1985.
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