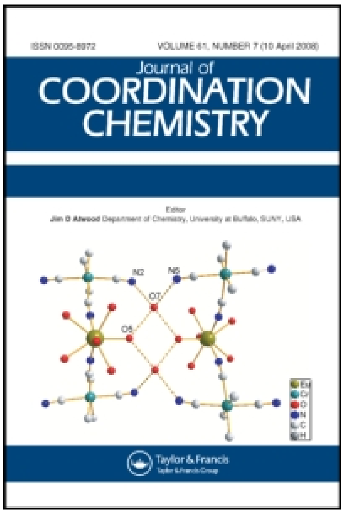

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 46. THE CRYSTAL AND MOLECULAR STRUCTURE OF $[Co(NH_3)_4Ox_2(S_4O_6)\cdot H_2O$ (I)

Ivan Bernal[a]; James Cetrullo[ab]; Fernando Somoza[b]
[a] Chemistry Department, University of Houston, Houston, Texas [b] R.A. Welch Foundation.,

To cite this Article Bernal, Ivan , Cetrullo, James and Somoza, Fernando(1996) 'THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 46. THE CRYSTAL AND MOLECULAR STRUCTURE OF $[Co(NH_3)_4Ox_2(S_4O_6)\cdot H_2O$ (I)', Journal of Coordination Chemistry, 40: 1, 57 — 69
To link to this Article: DOI: 10.1080/00958979608022846
URL: http://dx.doi.org/10.1080/00958979608022846

J. Coord. Chem., 1996, Vol. 40, pp. 57–69
Reprints available directly from the publisher
Photocopying permitted by license only

THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 46. THE CRYSTAL AND MOLECULAR STRUCTURE OF $[Co(NH_3)_4Ox_2(S_4O_6)\cdot H_2O$ (I)

IVAN BERNAL*, JAMES CETRULLO† and FERNANDO SOMOZA†

Chemistry Department University of Houston, Houston, Texas 77024-5641

(Received 21 November 1995; Revised 7 February 1996; In final form 26 February 1996)

Red specimens of $[Co[(NH)_4Ox]_2(S_4O_6)\cdot H_2O$ (I), $Co_2S_4O_{15}N_8C_4H_{26}$, crystallize in the monoclinic space group *P*2₁/*c*. The cell is defined by the following constants: a = 7.7601(7), b = 10.079(1), c = 29.865(3) Å, β = 90.914(8)°, V = 2335.59 Å^3, d (z = 4; M.W. = 672.42 gm – mole^{-1}) = 1.912 gm-cm^{-3}. A total of 3430 data was collected in the interval $4.0° \le 2\Theta \le 50.0°$ of which 1915 were unique and had intensities greater than $3\sigma(I)$. The data were corrected for absorption using empirical Psi scan curves (five reflections, $\mu = 18.395$ cm^{-1}); the relative transmission coefficients ranged from 0.9697 to 0.9988. The final values of the discrepancy parameters were R(F) = 0.0388 and $R_w(F) = 0.0484$.

The axial Col-N distances are 1.950(4) and 1.936(4) Å, while those associated with Co2 are 1.949(5) and 1.952(4) Å. Col-N distances in the equatorial plane are 1.942(3) and 1.918(4) Å, respectively. For the second cation, the equatorial Co-N distances are 1.910(4) and 1.938(4) Å. Thus, the feature of short and long Co-N distances is consistent for both cations. The Col-O distances are 1.906(3) and 1.896(3) Å, while those for Co2 are 1.914(3) and 1.899(4) Å, showing a distortion in these bonds which we have observed in earlier studies of bidentate oxalates and carbonates of Co(III) amines, and which seem to parallel the inequivalence of the Co-N bonds.

The stereochemistry of the tetrathionate anion is as follows: (a) the outer $S\text{-}S(O_3)$ bonds are 2.127(2) and 2.120(2) Å in length, while the central S-S distance is 2.014(2) Å (b) the S-O distances range from 1.430(4) to 1.461(4) Å with mean value of 1.445(4) Å. The S1-S2-S3-S4 torsional angle is 97.8°, which is a few degrees larger than the value found in its alkali salts - a result, no doubt, of the hydrogen bonding to the amines of the two cations.

The two independent cations are linked to one another by hydrogen-bonded interactions with the O_3S - fragments of the tetrathionates in such a way that there are approximate (non-crystallographic) mirror planes perpendicular to all three axes. We suggest this is the reason why this substance crystallizes via the racemic pathway.

Keywords: conglomerate crystallization; tetrathionate; cobalt (III); structures; hydrogen bonding

---

* Author for correspondence; Bitnet: IBernal@UH.EDU.
† Fellow of the R.A. Welch Foundation.

INTRODUCTION

Notes

(1) The meaning of the term 'conglomerate crystallization' has been given in refs.[9–17] (2) The cation of (I) can be chiral only in the solid state where the orientation of the -NH_3 ligands, with intermolecular hydrogen bonds, are locked at orientations such that the cation acquires a C_1 point group symmetry. This is evident in the left-most cation in Figure 1, and the point has been discussed in detail for related species (for example in references[9–11]). The tetrathionate anion is always chiral having only C_2 symmetry (for details, see reference[20]). With these caveats, we can proceed to the reasons why this study was undertaken.

Sometime ago, we[1] demonstrated that while $[Co(NH_3)_4Ox]I{\cdot}H_2O$ crystallizes as a racemate, the nitrate salt of composition $[Co(NH_3)_4Ox]NO_3{\cdot}H_2O$ crystallizes as a conglomerate, space group $P2_12_12_1$. In that report, we suggested[1] that the reason for different crystallization pathways was the fact that the nitrate anion formed very strong hydrogen bonds with the -NH_3 hydrogens on the cations and locked it into a dissymmetric configuration.

This proposal was made plausible by the observation that both *cis*- and *trans*- $[Co(NH_3)_4(NO_2)_2]NO_3$ salts also crystallize in enantiomorphic crystals, space group $P2_12_12_1$. In these latter species, rich hydrogen bonding occurs between cations and anions. Moreover, it is known that closely related compounds, which lack the outside lock on amine conformation, caused by ion pair formation, crystallize as racemates. Among these are $[Co(NH_3)_3(NO_2)_2Br$ [2] (here the two -NO_2 ligands are *cis* to each other) and $[Co(NH_3)_3(NO_2)_2Cl]$[3] in which the -NO_2 ligands are *trans*.

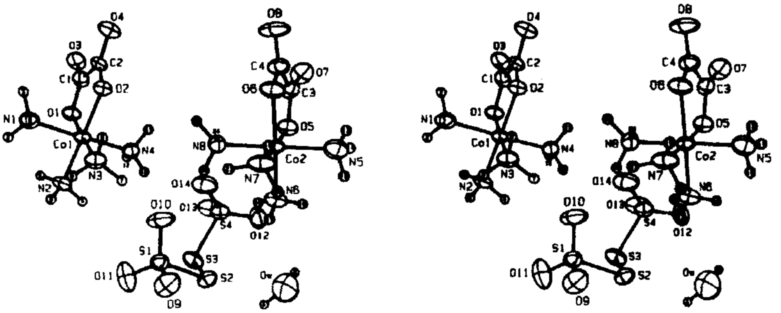

FIGURE 1 The ions and the water of crystallization defining the asymmetric unit of (I). Note there is nearly an inversion center between the two cations halfway between N4 and N8 and located at the intersection of the three non-crystallographic mirror plane (at 0.359, 0.405, –0.280). Also, note the hydrogen bonds formed by the oxygens on O1 and O4 with the amine hydrogens of N4 and N8. Finally, the water was placed at the symmetry position giving shortest hydrogen bond.

Another interesting observation is that the following oxalato metal amines crystallize in enantiomorphic space groups:

In 1975, Couldwell, *et al.*[8] reported the synthesis of mixed amine-dien oxalato complexes, [Co(dien)(NH_3)(oxalato)]X (X = PF_6^- and X = NO_3^-). A complete structure determination was carried out on the former (space group *Cc*; a polar, but non-enantiomorphic space group containing racemic pairs of cations) and the space group of the latter was reported as $P2_12_12_1$ - a conglomerate. The observation that [Co(dien)(NH_3)(oxalato)]PF_6 is a racemate while [Co(dien)(NH_3) (oxalato)] (NO_3) is a conglomerate is not surprising, given our previous discussion of the effect charge compensating counterions have on conglomerate crystallization.[9–17]

About a decade ago, Yoneda, *et al.*[18] determined the structure and absolute configuration of $(+)_{589}$-[*cis*-Co(en)$_2$(NH_3)Cl](d-3-bromcamphorsulfonate)$_2$·H_2O (II), the compound that Werner first succeeded in resolving.[19] In this report, Yoneda, *et al.*[18] described in detail the cation-anion interactions present in (**II**). These can be summarized thus, the sulfonate groups of the BCS anion bind the cation by short hydrogen-bonded contacts which are responsible for the known specificity of this resolution.

It occurred to us that if the hydrogen-bonded interactions described by Yoneda, *et al.*[18] were that important, an anion such as $S_4O_6^{2-}$ might similarly interact with Werner's cation, [*cis*-Co(en)$_2$(NH_3)Br]$^+$ and cause it to undergo conglomerate crystallization. That occurred and the resulting species, (+)-[*cis*-Co(en)$_2$ (NH_3)Br]$_2$(S_4O_6) crystallizes in space group $P2_1$.[20] Thus, we decided to determine the crystallization characteristics of the [Co(NH_3)$_4$Ox]$^+$ cation using the related tetrathionate anion, $S_4O_6^{2-}$. Thus, in order to explore the extent to which hydrogen bonding between cations and anions can exert an influence on the crystallization pathway of salts of [Co(NH_3)$_4$Ox]$^+$ and in order to further explore the influence which the tetrathionate anion may have on conglomerate crystallization of cobalt amine-oxalates, we prepared compound (**I**) and determined its crystal structure; the results are described in this manuscript.

EXPERIMENTAL

Synthesis

Co(NH_3)$_4$Ox](NO_3)·H_2O was prepared by the procedure of Bernal and Cetrullo[1] and [Co(NH_3)$_4$Ox$_2$(S_4O_6)·H_2O was prepared by the equimolar addition of solid $Na_2S_4O_6$ to a warm (60°C) solution of [Co(NH_3)$_4$Ox](NO_3)·H_2O, cooling and then filtering. Slow evaporation at room temperature produces the desired crystals.

X-Ray diffraction

Data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[21] of the SDP-Plus software package.[22] The crystal was centered with data in the $18° \leq 2\Theta \leq 25°$ range and examination of the cell constants and Niggli matrix[23] clearly showed it to crystallize in a primitive, monoclinic lattice whose systematic absences belong to those of the space group $P2_1/c$. The intensity data set was corrected for absorption using empirical curves derived from Psi scans[21–22] of five reflections. The scattering curves were taken from Cromer and Waber's compilation.[24] The structure was solved from the sections and lines of the Patterson function, which found the Co atoms. The missing atoms were found in subsequent difference maps. The oxygen of the water of hydration was also found.

Refinement proceeded smoothly. Heavy atoms were assigned anisotropic thermal parameters, hydrogens of the cations were added at computed positions (C-H = N-H = 0.95 Å). Hydrogens were assigned fixed, thermal parameters ($B = 4.0$ Å^2). The final R(F) and R_w (F) facors are 0.0388 and 0.0484, respectively. Details of data collection and processing are summarized in Table II.

TABLE I Structure of chelate complexes

Compound	*Space Group*	*Ref*
$[Co(en)_2Ox]Br{\cdot}H_2O$	$P2_1$	4, 5, 6
$[Co(en)_2Ox]Cl{\cdot}4H_2O$	$P2_12_12_1$	6
$[Co(en)_2(ox)]I$	C2	6
$[Cr(en)_2Ox]Br{\cdot}H_2O$	?*	4, 7
$[Rh(en)_2Ox]Br{\cdot}H_2O$	?*	7
$[Rh(en)_2Ox]Cl{\cdot}H_2O$	?*	7
$[Co(dien)(NH_3)Ox]NO_3$	$P2_12_12_1$	8

*These substance were identified as forming conglomerates either from solubility measurements, by seeding experiments or by measuring the CD spectra of resulting crystalline material. No structural data on them are yet available.

TABLE II Summary of data collection and processing parameters for racemic $[Co(NH_3)_4Ox]_2(S_4O_6){\cdot}H_2O$

Space Group	$P2_1/c$
Cell Constants	$a = 7.7601(7)$ Å
	$b = 10.079(1)$
	$c = 29.865(3)$
	$\beta = 90.914(8)$
Cell Volume	$V = 2335.59$ Å^3
Molecular Formula	$Co_2S_4O_{15}N_8C_4H_{26}$
MolecularWeight	672.42 gm-mol^{-1}
Density(calc; z = 4 mol/cell)	1.912 gm-cm^{-3}
Radiation Employed	MoKα ($\lambda = 0.71073$ Å)
Absorption Coefficient	$\mu = 18.395$ cm^{-1}

TABLE II *(Continued)*

Transmission Coefficients	0.9697 to 0.9997
Data Collection Range	$4° \leq 2\theta \leq 50°$
Scan Width	$\Delta\theta = 0.90 + 0.35\tan\theta$
Total Data Collected	3430
Data Used In Refinement*	1915
$R = \Sigma\|\|F_o\| - \|F_o\|\|-\|F_o\|$	0.0388
$Rw = [\Sigma w^2(\|F_o\|- \|F_o\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.0484
Weights Used	$w =[\sigma (F_o)-2$

* The difference between this number and the total is due to subtraction of 1515 data which either were systematically absent (but collected for verification of space group) standards or did not meet the criterion that $I \leq 3\sigma(I)$.

Figure 1 gives a labelled stereoview of the asymmetric unit; Figure 2 depicts in stereo the packing of the ions in the unit cell. Final positional and equivalent-isotropic thermal parameters are given in Table III. Bond lengths, angles and torsional angles are given in Table IV.

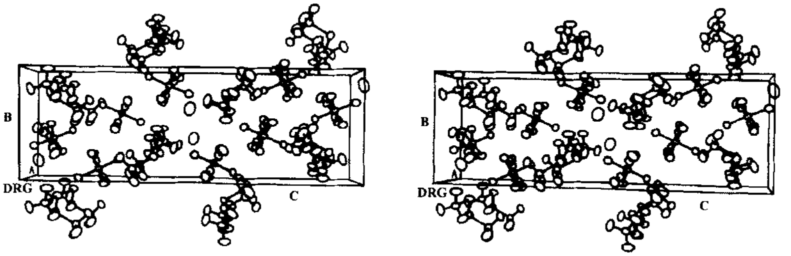

FIGURE 2 The packing of the constituents of compound (I) in the unit cell. Note the crystallographic inversion center at 1/2, 1/2, 1/2 located between a pair of waters of crystallization.

TABLE III Positional parameters and their estimated standard deviations

Atom	*x*	*y*	*z*	*B(A2)*
Co1	0.3588(1)	0.4055(1)	0.71980(4)	1.81(2)
Co2	0.3710(1)	0.6453(1)	0.93041(4)	1.90(2)
S1	–0.1340(3)	0.3833(2)	0.83568(8)	2.59(4)
S2	–0.1161(3)	0.2790(2)	0.89750(8)	2.92(5)
S3	0.0302(3)	0.1203(2)	0.88275(9)	3.39(5)
S4	0.2844(3)	0.1692(2)	0.90388(8)	2.68(4)
Ow	–0.013(2)	0.139(1)	1.0016(4)	9.6(3)
O1	0.5379(7)	0.2945(5)	0.6981(2)	2.3(1)
O2	0.5358(7)	0.5303(5)	0.7324(2)	2.2(1)
O3	0.8214(7)	0.2967(6)	0.6886(2)	3.3(1)
O4	0.8195(8)	0.5532(6)	0.7252(2)	3.4(1)
O5	0.5598(7)	0.5342(5)	0.9485(2)	2.6(1)
O6	0.5415(7)	0.7666(6)	0.9110(2)	2.8(1)
O7	0.8424(8)	0.5470(7)	0.9554(2)	4.0(2)
O8	0.8233(8)	0.7775(7)	0.9022(3)	4.6(2)

TABLE III *(Continued)*

Atom	*x*	*y*	*z*	*B(A2)*
O9	–0.2660(9)	0.4815(7)	0.8459(3)	4.4(2)
O10	0.0360(9)	0.4371(8)	0.8269(3)	5.1(2)
O11	–0.194(1)	0.2895(7)	0.8031(2)	5.3(2)
O12	0.2757(9)	0.2095(8)	0.9498(2)	4.6(2)
O13	0.3645(9)	0.0421(6)	0.8963(3)	4.5(2)
O14	0.3466(9)	0.2740(7)	0.8754(3)	4.7(2)
N1	0.3326(9)	0.4830(7)	0.6602(3)	2.7(2)
N2	0.1900(8)	0.2684(7)	0.7062(3)	2.7(2)
N3	0.1898(9)	0.5258(7)	0.7425(3)	2.7(2)
N4	0.3978(9)	0.3272(7)	0.7783(2)	2.5(1)
N5	0.375(1)	0.7187(8)	0.9908(3)	3.4(2)
N6	0.2106(9)	0.5125(7)	0.9483(3)	2.8(2)
N7	0.1958(9)	0.7707(7)	0.9111(3)	3.2(2)
N8	0.3744(9)	0.5660(7)	0.8708(2)	2.6(1)
C1	0.688(1)	0.3501(9)	0.7012(3)	2.3(2)
C2	0.685(1)	0.4890(7)	0.7213(3)	2.1(2)
C3	0.705(1)	0.5905(9)	0.9418(3)	2.6(2)
C4	0.696(1)	0.7222(9)	0.9162(3)	2.7(2)
Hw1	–0.0898	0.0703	0.9824	4.0*
Hw2	0.0917	0.1074	1.0136	4.0*
H1	0.2792	0.5625	0.6601	4.0*
H2	0.2648	0.4237	0.6397	4.0**
H3	0.4496	0.4992	0.6465	4.0**
H4	0.1660	0.1875	0.7324	4.0*
H5	0.2302	0.2195	0.6780	4.0**
H6	0.0773	0.3111	0.6987	4.0**
H7	0.1406	0.5000	0.7753	4.0*
H8	0.0901	0.5308	0.7211	4.0**
H9	0.2436	0.6168	0.7454	4.0**
H10	0.3046	0.3339	0.7988	4.0*
H11	0.5005	0.3696	0.7931	4.0**
H12	0.4217	0.2292	0.7747	4.0**
H13	0.4179	0.7929	0.9921	4.0*
H14	0.4403	0.6607	1.0118	4.0**
H15	0.2529	0.7293	1.0019	4.0**
H16	0.2226	0.4375	0.9335	4.0*
H17	0.0924	0.5454	0.9421	4.0**
H18	0.2292	0.4936	0.9804	4.0**
H19	0.2226	0.8554	0.9101	4.0*
H20	0.0955	0.7625	0.9320	4.0**
H21	0.1553	0.7448	0.8802	4.0**
H22	0.4179	0.6250	0.8417	4.0*
H23	0.2538	0.5378	0.8625	4.0**
H24	0.4508	0.4866	0.8717	4.0**

Starred atoms were not refined. Doubly starred atoms have calculated positions and were not refined. Anistropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) * [a2*B(1, 1) + b2*B(2, 2) + c2*B(3, 3) + ab (cos gamma) *B(1, 2) + ac(cos beta) *bc (cos alpha) *B(2, 3)].

TABLE IV

A) Bond Distances in Angstroms

Atom1	*Atom2*	*Distance*	*Atom1*	*Atom2*	*Distance*
		Co1 Cation			
Co1	O1	1.906(3)	Co1	O2	1.896(3)
Co1	N1	1.950(4)	Co1	N2	1.942(3)
Co1	N3	1.918(4)	Co1	N4	1.936(4)
O1	C1	1.291(5)	O2	C2	1.277(6)
O3	C1	1.234(7)	O4	C2	1.233(6)
C1	C2	1.524(6)	N1	H1	0.902(4)
N1	H2	0.999(3)	N1	H3	1.015(5)
N2	H4	1.148(4)	N2	H5	1.029(5)
N2	H6	0.997(3)	N3	H7	1.091(5)
N3	H8	0.995(3)	N3	H9	1.012(4)
N4	H10	0.958(5)	N4	H11	1.002(3)
N4	H12	1.010(4)			
		Co2 Cation			
Co2	O5	1.914(3)	Co2	O6	1.899(4)
Co2	N5	1.949(5)	Co2	N6	1.910(4)
Co2	N7	1.938(4)	Co2	N8	1.952(4)
O5	C3	1.277(6)	O6	C4	1.284(6)
O7	C3	1.219(5)	O8	C4	1.215(7)
C3	C4	1.534(7)	N5	H13	0.820(4)
N5	H14	0.991(4)	N5	H15	1.017(5)
N6	H16	0.880(4)	N6	H17	0.989(4)
N6	H18	0.987(4)	N7	H19	0.880(4)
N7	H20	1.009(5)	N7	H21	1.004(4)
N8	H22	1.107(4)	N8	H23	1.004(4)
N8	H24	0.997(4)			
		Anion and Water			
S1	S2	2.127(2)	S2	S3	2.014(2)
S3	S4	2.120(2)	S1	09	1.461(4)
S1	010	1.454(4)	S1	O11	1.430(4)
S4	012	1.435(5)	S4	O13	1.443(4)
S4	014	1.445(4)	Ow	Hw1	1.076(5)
Ow	Hw2	0.941(6)			

B) Bond Angles in Degrees

Atom1	*Atom2*	*Atom3*	*Angle*	*Atom1*	*Atom2*	*Atom3*	*Angle*
			Co1 Cation				
O1	Co1	O2	85.8(1)	O1	Co1	N1	89.5(2)
O1	Co1	N2	90.3(2)	O1	Co1	N3	176.2(1)
O1	Co1	N4	87.9(2)	O2	Co1	N1	88.8(2)
O2	Co1	N2	176.0(2)	O2	Co1	N3	90.4(2)
O2	Co1	N4	89.4(2)	N1	Co1	N2	92.0(2)
N1	Co1	N3	90.4(2)	N1	Co1	N4	176.9(2)
N2	Co1	N3	93.5(2)	N2	Co1	N4	89.7(2)
N3	Co1	N4	92.1(2)	O1	C1	O3	123.3(4)

TABLE IV *(Continued)*

Atom1	*Atom2*	*Atom3*	*Angle*	*Atom1*	*Atom2*	*Atom3*	*Angle*
			Co1 Cation				
O2	C2	O4	125.0(4)	O1	C1	C2	114.2(4)
O3	C1	C2	122.5(4)	O2	C2	C1	114.8(4)
O4	C2	C1	120.2(5)	Co1	O1	C1	112.4(3)
Co1	O2	C2	112.9(3)	Co1	N1	H1	113.6(4)
Co1	N1	H2	111.5(3)	Co1	N1	H3	110.6(2)
Co1	N2	H4	118.6(2)	Co1	N2	H5	107.4(3)
Co1	N2	H6	109.0(3)	Co1	N3	H7	114.7(3)
Co1	N3	H8	109.5(3)	Co1	N3	H9	108.7(3)
Co1	N4	H10	116.1(3)	Co1	N4	H11	109.7(3)
Co1	N4	H12	109.3(3)	H1	N1	H2	107.0(3)
H1	N1	H3	105.6(4)	H2	N1	H3	108.3(4)
H4	N2	H5	105.8(3)	H4	N2	H6	108.0(4)
H5	N2	H6	107.4(3)	H7	N3	H8	108.1(4)
H7	N3	H9	106.8(4)	H8	N3	H9	108.9(3)
H10	N4	H11	106.8(4)	H10	N4	H12	106.2(4)
H11	N4	H12	108.5(3)				
			Co2 Cation				
O5	Co2	O6	85.9(1)	O5	Co2	N5	87.7(2)
O5	Co2	N6	90.6(2)	O5	Co2	N7	174.6(2)
O5	Co2	N8	89.8(2)	O6	Co2	N5	92.1(2)
O6	Co2	N6	175.6(2)	O6	Co2	N7	88.8(2)
O6	Co2	N8	88.0(2)	N5	Co2	N6	90.5(2)
N5	Co2	N7	91.7(2)	N5	Co2	N8	177.5(2)
N6	Co2	N7	94.7(2)	N6	Co2	N8	89.2(2)
N7	Co2	N8	90.9(2)	O5	C3	O7	123.9(5)
O5	C3	C4	115.4(4)	O6	C4	O8	124.2(5)
O6	C4	C3	113.3(5)	O7	C3	C4	120.6(5)
O8	C4	C3	122.5(5)	Co2	O5	C3	111.6(3)
Co2	O6	C4	113.1(3)	Co2	N5	H13	113.3(5)
Co2	N5	H14	111.3(4)	Co2	N5	H15	109.9(3)
Co2	N6	H16	112.8(4)	Co2	N6	H17	108.6(3)
Co2	N6	H18	108.7(3)	Co2	N7	H19	118.5(3)
Co2	N7	H20	107.8 (3)	Co2	N7	1121	108.1(3)
Co2	N8	H22	120.1(3)	Co2	N8	H23	108.2(4)
Co2	N8	H24	108.5(3)	H13	N5	H14	107.8(4)
H13	N5	H15	105.4(5)	H14	N5	H15	108.9(5)
H16	N6	H17	107.6(3)	H16	N6	H18	107.8(4)
H17	N6	H18	111.5(5)	H19	N7	H20	106.5(5)
H19	N7	H21	107.0(4)	H20	N7	H21	108.4(3)
H22	N8	H23	104.9(3)	H22	N8	H24	105.4(4)
H23	N8	H24	109.4(3)				
			Anion and Water				
S1	S2	S3	103.40(9)	S2	S3	S4	106.00(7)
S2	S1	O9	100.9(2)	S2	S1	O10	107.1(2)
S2	S1	O11	106.2(2)	O9	S1	O10	115.2(3)
O9	S1	O11	106.2(2)	O10	S1	O11	114.4(3)
S3	S4	O12	107.0(2)	S3	S4	O13	98.5(2)
S3	S4	O14	108.2(2)	O12	S4	O13	115.4(3)
O12	S4	O14	112.2(3)	O13	S4	O14	114.1(3)
Hw1	Ow	Hw2	116.7(7)				

TABLE IV *(Continued)*

C) Hydrogen Bonds

Bond Dist. (Å)		*N-H...O Angle(°)*		
O1-H22	2.11	N8-22...O1	158.2	O1 at 1-x, 1/2+y, 3/2-z
O2-H12	2.04	N4-H 12...O2	178.7	O2 at 1-x, -1/2+y, 3/2-z
O3-H6	2.01	N2-H 6...O3	149.7	O3 at -1+x, y, z
O3-H21	2.13	N7-H 21...O3	142.4	O3 at 1-x, 1/2+y, 3/2-z
O4-H4	1.86	N2-H 4...O4	167.2	O4 at 1-x, -1/2+y, 3/2-z
O4-H8	2.12	N3-H 8...O4	136.8	O4 at -1+x, y, z
O7-H17	1.99	N6-H 17...O7	150.6	O7 at -1+x, y, z
O8-H2	2.05	N1-H 2...O8	166.9	O8 at 1-x, 1/-2+y, 3/2-z
O10-H7	1.86	N3-H 7...O10	171.3	
O10-H23	2.23	N8-H 23...O10	160.4	
O13-H3	1.99	N1-H 3...O13	163.0	O13 at 1-x, 1/2+y, 3/2-z
O13-H19	2.22	N7-H 19...O13	161.2	O13 at x, 1+y, z

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

TABLE V Torsional Angles (°)

Atom 1	*Atom 2*	*Atom 3*	*Atom 4*	*Angle*
Co1	O1	C1	O3	−179.1
Co1	O1	C1	C2	0.2
Co1	O2	C2	O4	178.3
Co1	O2	C2	C1	−0.6
O1	Co1	O2	C2	0.6
O1	C1	C2	O2	0.3
O1	C1	C2	O4	−178.6
O2	Co1	O1	C1	−0.4
O3	C1	C2	O2	179.6
O3	C1	C2	O4	0.7
N1	Co1	O1	C1	88.5
N1	Co1	O2	C2	−89.0
N2	Co1	O1	C1	−179.6
N2	Co1	O2	C2	12.5
N3	Co1	O1	C1	0.2
N3	Co1	O2	C2	−179.4
N4	Co1	O1	C1	−89.9
N4	Co1	O2	C2	88.5
Co2	O5	C3	O7	170.9
Co2	O5	C3	C4	−7.4
Co2	O6	C4	O8	172.7
Co2	O6	C4	C3	−7.0
O5	Co2	O6	C4	2.7
O5	C3	C4	O6	10.0
O5	C3	C4	O8	−169.8
O6	Co2	O5	C3	3.0
O7	C3	C4	O6	−168.5
O7	C3	C4	O8	11.7
N5	Co2	O5	C3	−89.2
N5	Co2	O6	C4	90.3
N6	Co2	O5	C3	−179.7
N6	Co2	O6	C4	−35.5

TABLE V *(Continued)*

Atom 1	*Atom 2*	*Atom 3*	*Atom 4*	*Angle*
N7	Co2	O5	C3	–5.9
N7	Co2	O6	C4	–178.1
N8	Co2	O5	C3	91.1
N8	Co2	O6	C4	–87.2
O9	S1	S2	S3	169.7
O10	S1	S2	S3	–69.4
O11	S1	S2	S3	53.3
S1	S2	S3	S4	97.8
S2	S3	S4	O12	53.2
S2	S3	S4	O13	173.2
S2	S3	S4	O14	–67.9

DISCUSSION

The contents of the asymmetric unit are shown in Figure 1, where it is evident that the two $-SO_3^-$ termini of the tetrathionate anion are hydrogen bonded to the amine hydrogens of the two cations. The shortest contacts between $-SO_3^-$ oxygens and $-NH_3$ hydrogens are O10-H7 = 1.86 Å (<N8-H23....O10 = 171.2°) and O13-H3 = 1.99 Å (<N1-H3...O13 = 163.0°) both of which are not only fairly short but have N-H...O angles that are associated with strong hydrogen bonds. There are additional cation-anion hydrogen bonds, listed in Table III(C), but those are longer (*ca.* 2.22 Å).

The packing diagram (Figure 2) shows that the cations are so oriented to one another that there are hydrogen bonds between the terminal oxalato oxygens and the amine hydrogens on adjacent cations. Table IV(C) lists O4-H4 = 1.86 Å (<N2-H4....O4 = 167.2°), O7-H17 = 1.99 Å (<N6-H17...O7 = 150.6°), O3-H6 = 2.01 Å (<N2-6....O3 = 149.7°), O2-H12 = 2.04 Å (<N4-H12...O2 = 178.7°) and O8-H2 = 2.05 Å (<N1-H2....O8 = 166.9°), all of which are reasonably strong hydrogen bonds.

These observations indicate that hydrogen bonds of comparable magnitude with those present in $[Co(NH_3)_4Ox](NO_3)\cdot H_2O$[1] exist in this compound; therefore, the question is why does it not crystallize as a conglomerate, as was the case with the nitrate? It was suggested that locking the cation into a highly dissymmetric conformation and configuration by a combination of hydrogen bonds between cations and anions rendered the whole not only dissymmetric but rigid.[1] Since the iodide, $[Co(NH_3)_4Ox]I\cdot H_2O$[1], crystallized as a racemate, it was concluded[1] that the nitrate played a crucial role since any potential cation-cation interaction was still possible in the iodide complex, as well as in the nitrate complex. That observation, coupled with our observation[20] that the tetrathionate anion forms a tight ion pair with its cation in the conglomerate salt [*cis*-$Co(en)_2(NH_3)Br]S_4O_6$, led to our testing the crystallization behavior of (**I**). Therefore, the failure of this compound to crystallize as a conglomerate was a disappointment.

CHOICE OF SPACE GROUP AND PACKING CONSIDERATIONS

The β angle of the monoclinic cell is very close to 90°; consequently, we checked the Laue symmetry very carefully and oriented the crystal several times, using high angle data, in order to ascertain our assignment. The Niggli matrix[23] of the cell described in Table II is

60.220	101.586	891.918
0	−3.697	0

Consequently, there is no higher system to which this crystal can belong. Program Tracer [22–23] also produced no higher crystal system for this compound if the range of error is properly restricted. Therefore, once the crystal had been centered to our satisfaction, we checked for systematic absences and found that they correspond to those expected for space group $P2_1/c$, whose systematic absences are unmistakable. Finally, data were collected without any systematic absence constraints, and the total data set searched for those absences. Again, the space group consistent with the data was $P2_1/c$.

Interestingly, the relationship between cations present in the asymmetric unit (see also Figure 1) indicates that the difference in fractional coordinates between their constituent atoms constitutes the trace of a straight line approximately through (0, 1/4, z); *e.g.* a *pseudo* two-fold axis. The presence of a *pseudo* two-fold axis between cations is very suggestive in that one generates a species of somewhat higher symmetry than can occur in the case of the nitrate by having two cations forming an ion pair with the two symmetrical ends of a divalent anion. Perhaps we did two things which cancelled each other by choosing this cation-anion combination. On the one hand, we produced a powerful hydrogen-bonding anion which could lock the cations into rigid, dissymmetric, species; however, by having a 2:1 combination, we introduced an overall symmetry impossible in the nitrate.

This prompted us to check the possibility of additional, non-crystallographic, symmetry elements using the ‘missing symmetry’ routine of the NRCVAX program.[25] Interestingly, three approximate mirror planes were found linking cation pairs, as follows (Note: in the standard setting of the space group $P2_1/c$, the mirrors perpendicular to the *b*–axis are located at 0 1/4 0 and 0 3/4 0):

[0 1 0]	perpendicular mirror plane through	0.0000	0.405	0.0000
[1 0 0]	perpendicular mirror plane through	0.359	0.000	0.0000
[0 0 1]	perpendicular mirror plane through	0.0000	0.000	−0.280

We accidentally selected a counteranion which arrayed cation pairs in nearly enantiomorphic pairs. In order to test this idea, we are exploring the crystallization behavior of the $[Co(NH_3)_4Ox]^+$ cation with thiosulfate as the counter anion.

Acknowledgments

We thank the Robert A. Welch Foundation for a grant (E-594, to IB) and for a fellowship to J. Cetrullo. The structural work was carried out with a diffractometer purchased with funds provided by the National Science Foundation whom we also thank.

References

[1] I. Bernal and J. Cetrullo, *Struct. Chem.*, **1**, 235 (1990).

[2] Y. Komiyama, *Bull. Chem. Soc. Japan*, **31**, 26 (1958).

[3] Y. Tanito, Y. Saito and H. Kuroya, *Bull. Chem. Soc. Japan*, **26**, 420 (1953).

[4] Alfed Werner, was the first to establish a large solubility difference between the racemate and the enantiomers of the Co and Cr compounds, see A. Werner, *Chem. Ber.*, **47**, 2171 (1914). Further work in this area was done by K. Yamasaki, H. Igarishi, Y. Yoshikawa, *Inorg. Nuclear Chem. Letters*, **4**, 491 (1968) and for a more quantitative description of the phase diagram of this substance see K. Yamanari, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Japan*, **46**, 3724 (1972). For the crystal structure of this compound, determined from crystals of pre-resolved material, see ref. 3.

[5] T. Aoki, K. Matsumoto, S. Ooi and H. Kuroya, *Bull. Chem. Soc. Japan*, **46**, 159 (1973).

[6] For solubility data on these compounds, see ref. 4.; for the structures of the chloride, bromide and iodide, see I. Bernal, J. Cetrullo, J. Myrczek and S.S. Massoud, *J. Coord. Chem.*, **30**, 29 (1993).

[7] R.D. Gillard, and L.H.R. Tipping, *J. Chem. Soc.*, Dalton Trans., 1241 (1977).

[8] M.C. Couldwell, D.A. House and B.R. Penfold, *Inorg. Chim. Acta*, **13**, 61 (1975).

[9] I. Bernal, *Inorg. Chim. Acta*, **96**, 99 (1985).

[10] I. Bernal, *Inorg. Chim. Acta*, **101**, 175 (1985).

[11] I. Bernal, C.K. Fair and E.O. Schlemper, *Inorg. Chim. Acta*, **115**, 25 (1986).

[12] I. Bernal and J. Cetrullo, *Inorg. Chim. Acta*, **120**, 109 (1986).

[13] I. Bernal and J. Cetrullo, *Inorg. Chim. Acta*, **122**, 213 (1986).

[14] I. Bernal, *J. Coord. Chem.*, **15**, 337 (1987).

[15] I. Bernal and J. Cetrullo, *Inorg. Chim. Acta*, **131**, 201 (1987).

[16] I. Bernal and J. Cetrullo, *Inorg. Chim. Acta*, **134**, 105 (1987).

[17] I. Bernal and J. Cetrullo, *Inorg. Chim. Acta*, **144**, 227 (1988).

[18] M. Kuramoto, Y. Kushi and H. Yoneda, *Bull Chem. Soc. Japan*, **51**, 3196 (1978).

[19] A. Werner, *Chem. Ber.*, **44**, 1887 (1911) and *Chem. Ber.*, **44**, 3279 (1911).

[20] I. Bernal and J. Cetrullo and W.G. Jackson, *Inorg. Chem.*, **32**, 4098 (1993).

[21] TEXRAY-230 is a modification of the SDP-Plus[22] 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.

[22] 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.

[23] R.B. Roof, "A Theoretical Extension of the Reduced Cell Concept in Crystallography", Report LA-4038, Los Alamos Scientific Laboratory, 1969.
[24] D.T. Cromer and J.T. Waber, "International Tables for X-Ray Crystallography", The Kynoch Press, Birmingham, England, 1975; vol. IV, Tables 2.2.8 and 2.3.1, respectively, for the scattering factor curves and the anomalous dispersion values.
[25] 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, N.C., 27599-3290.