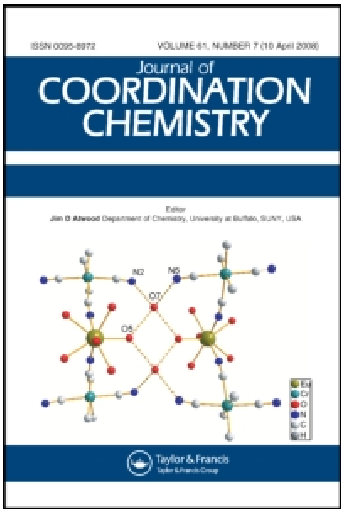

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. XXV. SPONTANEOUS RESOLUTION IN COORDINATION COMPOUNDS. THE CRYSTAL STRUCTURE OF $[\textit{cis}\text{-Co(en)}_2(\text{NH}_3)\text{Br}]\text{Br}_2$

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$Br_3CoN_5C_4H_{19}$, (I), crystallizes in the monoclinic system, space group $C2/c$, with cell constants $a = 24.579(9)$, $b = 8.665(3)$, $c = 14.409(5)$ Å, and $\beta = 92.69(3)°$; $V = 2988.87$ Å^3 and d (MW = 435.875, $Z = 8$) = 2.097 gm cm^{-3}. Data were collected in the range $4° \leqslant 2\theta \leqslant 50°$, for a total of 2823 reflections, of which 1409 were independent and had $I \geqslant 3\sigma(I)$. The structure factors were corrected for absorption ($\mu = 90.882$ cm^{-1}) using psi scan curves obtained from reflections near X = 90°. The transmission coefficients ranged from 0.68 to 0.99. The structure was solved by direct methods and refinement converged to final discrepancy indices of $R(F) = 0.0601$ and $R_w(F) = 0.0663$. The cobalt configuration and chelate ring conformations for (I) were found to be the preferred $(lel)_2$—$\Delta(\delta\delta)$ and $\Delta(\lambda\lambda)$. The Co–N distances to the en rings are 1.961(6), 1.960(6), 1.977(6), 1951(6) Å, while that to the $-NH_3$ ligand is 1.963(6) Å. The C–C distances are 1.52(1) and 1.50(1) Å; finally, the Co–Br distance is 2.403(1) Å.

Keywords: Spontaneous resolution, conglomerates, cobalt complexes, X-ray structure

INTRODUCTION

Twelve years after he predicted[1] that octahedral compounds containing ions such as $[Co(en)_2ox]^+$ should be resolvable into antipodal pairs, Werner was able to announce[2] that he and his student, Victor King, had succeeded in separating the enantiomers of $[\textit{cis}\text{-Co(en)}_2(NH_3)X]^{2+}$ (X = Cl, Br). It is now known[3] that the *cis*-aminobromo derivative is particularly easy to separate due to the insolubility of the (+)-bromocamphorsulfonate ion pair formed by the $(+)_{589}$-cation. Therefore, we decided to examine the crystallization behaviour of $[\textit{cis}\text{-Co(en)}_2(NH_3)X]^{2+}$ cations using related sulfonates in order to determine the extent to which crystallization is affected by the presence of such anionic groups. Elsewhere,[4] we have shown that the use of the tetrathionate anion, $O_3S{-}S{-}S{-}SO_3^{2-}$, leads to conglomerate

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crystallization in which the hydrogen bonded interactions between the amino hydrogens of the cation and the oxygens of the tetrathionate are essentially identical with those found in Werner's resolved bromocamphorsulfonate, suggesting that the specificity of the latter reagent and, concomitantly, the crystallization pathway is influenced by such hydrogen bonds. However, recently the suggestion was made that the parent compound, [*cis*-$Co(en)_2(NH_3)Br]Br_2$ (**I**) may itself have crystallized as a conglomerate and, thereby, influenced the outcome. Here we report the crystallization behaviour of (**I**) using a sample prepared by Werner's method.[5]

EXPERIMENTAL

Syntheses

Unresolved $[Co(en)_2(NH_3)Br]Br_2$ was prepared by the procedure of Werner.[5]

X-ray diffraction

Data for (**I**) were collected with a crystal which came out of the recrystallization procedure.[5] All intensity data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[6] of the SDP-Plus software package.[7] The crystals were centred with data in the $18° \leqslant 2\theta \leqslant 25°$ range and examination of the cell constants and Niggli matrix[8] clearly showed it to crystallize in a primitive, monoclinic lattice whose systematic absences in the case of (**I**) are those expected of a substance crystallizing

TABLE I
Summary of data collection and processing parameters for [*cis*-$Co(en)_2(NH_3)Br]Br_2$ (**I**)

Space group	*C*2/*c*
Cell constants	$a = 24.579(9)$ Å $b = 8.665(3)$ $c = 14.049(5)$ $\beta = 92.69(5)°$
Cell volume	$V = 2988.87$ Å^3
Molecular formula	$Br_3CoN_5C_4H_{19}$
Molecular weight	435.8 gm mol^{-1}
Density (calc; $Z = 8$ mol/cell)	2.097 g cm^{-3}
Radiation employed	MoK$_\alpha$ ($\lambda = 0.71073$ Å)
Absorption coefficient	$\mu = 90.882$ cm^{-1}
Transmission coefficients	0.6787 to 0.9977
Data collection range	$4° \leqslant 2\theta \leqslant 50°$
Scan width	$\Delta\theta = 1.00 + 0.35 \tan\theta$
Total data collected	2823
Data used in refinement*	1409
$R = \sum \lVert F_0 \rvert - \lvert F_c \rVert / \sum \lvert F_0 \rvert$	0.060
$R_w = [\sum w^2(\lvert F_0\rvert - \lvert F_c\rvert)^2/\sum \lvert F_0\rvert^2]^{1/2}$	0.066
Weights used	$w = [\sigma(F_0)]^{-2}$

* The difference between this number and the total is due to subtraction of 1414 data which either were systematically absent (but collected for verification of space group), redundant data collected to find reflections suitable for the absorption correction, standards, or did not meet the criterion that $I \geqslant 3\sigma(I)$.

in the space groups *Cc* or *C*2/*c*; however, having $Z = 8$, we initially assumed the space group to be *C*2/*c*. This assumption was later found to be correct. The intensity data set was carried for absorption using empirical curves derived from psi scans[6,7] of five reflections. The scattering curves were taken from Cromer and Waber's compilation.[9]

The structure of (**I**) was solved by direct methods. Refinement proceeded smoothly and upon isotropic convergence, the hydrogen atoms of the en rings were computed at idealized positions (N–H, C–H = 0.95 Å). These were added as fixed contributions to the structure factors (B = 4.0 Å^2). After each set of refinement cycles, the hydrogen positions were re-computed, whereupon the structure finally converged to discrepancy indices of $R(F) = 0.060$ and $R_w(F) = 0.066$. Details are summarized in Table I. Final positional and equivalent isotropic thermal parameters are given in Table II; bond lengths, angles and torsional angles are given in Table III. Structure factors are available as Supplementary Material from I.B. upon request.

TABLE II

Positional and equivalent isotropic thermal parameters

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B* (Å^2)
Br1	0.50005(7)	−0.1697(3)	0.1002(1)	2.95(4)
Br2	0.68256(7)	0.2395(3)	−0.1431(1)	2.85(4)
Br3	0.68003(7)	0.2803(2)	0.3136(1)	2.81(4)
Co	0.63874(8)	0.1722(3)	0.1702(2)	1.76(5)
Ow1	0.4658(5)	0.248(2)	0.1200(8)	3.9(3)
Ow2	0.5720(5)	0.537(2)	0.328(1)	4.2(3)
N1	0.6785(5)	0.323(2)	0.096(1)	2.5(3)
N2	0.5810(5)	0.328(2)	0.1644(9)	2.3(3)
N3	0.6995(5)	0.023(2)	0.1683(9)	2.4(3)
N4	0.6104(5)	0.066(2)	0.0557(9)	2.4(3)
N5	0.5936(5)	0.037(2)	0.2489(9)	2.1(3)
C1	0.6511(8)	0.475(2)	0.094(1)	3.6(5)
C2	0.5902(7)	0.443(2)	0.090(1)	3.4(5)
C3	0.6980(7)	−0.059(2)	0.074(1)	3.7(5)
C4	0.6392(7)	−0.081(2)	0.043(1)	3.0(5)
H1	0.6803	0.2854	0.0327	4.0
H2	0.7142	0.3328	0.1239	4.0
H3	0.6610	0.5329	0.0396	4.0
H4	0.6616	0.5333	0.1501	4.0
H5	0.5791	0.4052	0.0295	4.0
H6	0.5709	0.5358	0.1030	4.0
H7	0.5803	0.3778	0.2245	4.0
H8	0.5472	0.2785	0.1504	4.0
H9	0.6963	−0.0513	0.2173	4.0
H10	0.7333	0.0754	0.1771	4.0
H11	0.7159	−0.1554	0.0803	4.0
H12	0.7158	0.0027	0.0286	4.0
H13	0.6240	−0.1591	0.0808	4.0
H14	0.6368	−0.1106	−0.0219	4.0
H15	0.6149	0.1299	0.0019	4.0
H16	0.5726	0.0454	0.0617	4.0

Estimated standard deviations are listed in parentheses. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3) * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) + ab(\cos \text{gamma}) * B(1,2) + ac(\cos \text{beta}) * B(1,3) + bc(\cos \text{alpha}) * B(2,3)]$. Hydrogen atoms are at calculated ideal positions. Their positional and thermal parameters were not refined.

TABLE III
Bong lengths, bond angles and torsional angles

(A) Bond distances in Å

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Co	Br3	2.403(1)	Co	N1	1.961(6)
Co	N2	1.960(6)	Co	N3	1.977(6)
Co	N4	1.951(6)	Co	N5	1.984(6)
N1	C1	1.481(9)			
			N2	C2	1.464(9)
N3	C3	1.499(9)			
			N4	C4	1.475(9)
C1	C2	1.52(1)	C3	C4	1.50(1)

Bond angles in °

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Br3	Co	N1	89.2(2)	Br3	Co	N2	92.5(2)
Br3	Co	N3	88.7(2)	Br3	Co	N4	174.0(2)
Br3	Co	N5	89.3(2)	N1	Co	N2	84.1(3)
N1	Co	N3	91.9(3)	N1	Co	N4	92.3(3)
N1	Co	N5	174.2(3)	N2	Co	N3	175.8(3)
N2	Co	N4	93.5(3)	N2	Co	N5	90.4(3)
N3	Co	N4	85.5(3)	N3	Co	N5	93.7(3)
N4	Co	N5	89.7(3)	Co	N1	C1	111.4(5)
Co	N2	C2	111.1(4)	Co	N3	C3	109.5(5)
Co	N4	C4	110.5(5)	N1	C1	C2	106.4(7)
N2	C2	C1	106.6(7)	N3	C3	C4	107.4(6)
N4	C4	C3	108.3(7)				

(C) Hydrogen bonds (distances in Å, angles in °)

O–H distance			N–H · · · O angle	
Ow1	H8	2.04	N2–H8 · · · Ow1	160.3
Ow2	H7	2.02	N2–H7 · · · Ow2	163.0
O2	H1	2.18	N1–H1 · · · O2	167.9
O3	H10	2.31	N3–H10 · · · O3	151.5
O3	H16	2.14	N4–H16 · · · O3	159.3
O4	H9	2.04	N3–H9 · · · O4	168.8
O5	H8	2.07	N2–H8 · · · O5	153.9
O6	H18	2.17	N5–H18 · · · O6	175.1

(D) Torsional angles in °

Atom 1	Atom 2	Atom 3	Atom 4	Angle
Br3	Co	N1	C1	−80.4
N5	Co	N4	C4	−80.1
N2	Co	N1	C1	12.1
Co	N1	C1	C2	−36.3
N3	Co	N1	C1	−169.1
N4	Co	N1	C1	105.4
N5	Co	N1	C1	−5.6
Co	N2	C2	C1	−39.8
Br3	Co	N2	C2	105.1
N1	Co	N2	C2	16.2
N3	Co	N2	C2	−0.4

TABLE III *Continued*

(D) Torsional angles in ° *continued*

Atom 1	Atom 2	Atom 3	Atom 4	Angle
Co	N3	C3	C4	−35.9
N4	Co	N2	C2	−75.8
N5	Co	N2	C2	−165.6
Br3	Co	N3	C3	−168.5
Co	N4	C4	C3	−37.0
N1	Co	N3	C3	−79.3
N2	Co	N3	C3	−62.8
N4	Co	N3	C3	12.9
N1	C1	C2	N2	48.5
N5	Co	N3	C3	102.3
Br3	Co	N4	C4	0.4
N1	Co	N4	C4	105.3
N3	C3	C4	N4	47.2
N2	Co	N4	C4	−170.6
N3	Co	N4	C4	13.5

Standard deviations are given in parentheses.

RESULTS AND DISCUSSION

One of the two enantiomorphic cations present in the lattice of (**I**), depicted in Figure 1, is in the $\Lambda(\delta\delta)$ configuration (the relevant torsional angles are N1–C1–C2–N2 = +49.1° and N3–C3–C4–N4 = +49.9°); as shown, the $Br3^-$ anions are bonded to the Co cation while $Br2^-$ is a bridge between cations, hydrogen bonded to H1 (2.503 Å) of one and to H9 (2.572 Å) of another. $Br1^-$ seems to be bonded to the amine hydrogens and to H7 and H8 (see Figure 1); however, the distances between those atoms are so large that this bromine is unlikely to be bonded

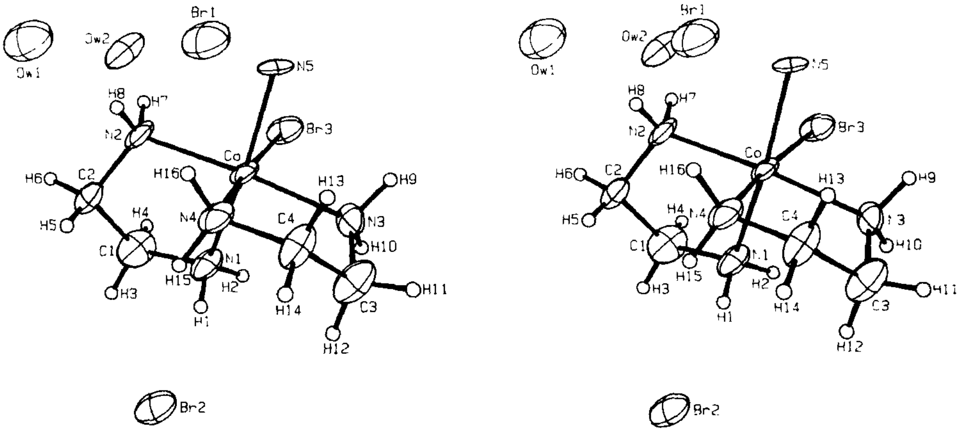

FIGURE 1 Stereoview of the ion-pair present in $[cis\text{-}Co(en)_2(NH_3)Br]Br_2$. Note the interaction between the bromide anions and the $-NH_2$ hydrogens of the en ligands. Note also that the conformation (δ) of both en ligands is the correct one for the Λ configuration at the Co cation.

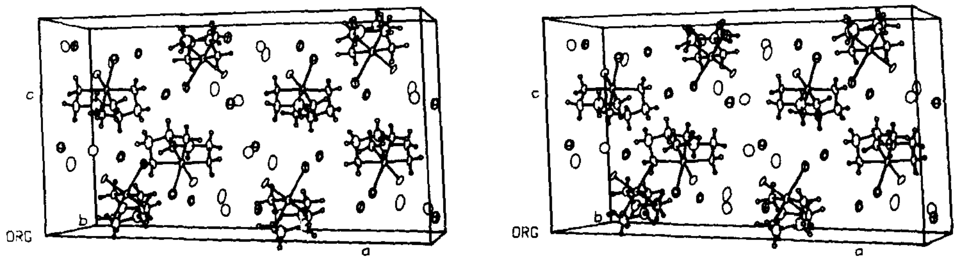

FIGURE 2 Packing diagram for [*cis*-Co(en)$_2$(NH$_3$)Br]Br$_2$. Note the interactions between the cations and anions in the unit cell; this is a stereo pair.

to anything in the lattice and appears to be, strictly, a charge compensating species. Significantly, this anion has higher thermal parameters than the other two bromides. These cation-anion relationships are very obvious in the packing diagram shown in Figure 2. Since (**I**) is a racemate, cations of the opposite configuration are also present in the lattice (Figure 2). The main object of determining the crystal structure of (**I**) was to prove it crystallized as a racemate, *inter alia* demonstrating our conglomerate crystallization results with $(+)_{589}$-[*cis*-$\Lambda(\delta\lambda)$Co(en)$_2$(NH$_3$)Br]·S$_4$O$_6$ (**II**) were not vitiated by accidentally having a chiral starting material as the source for the preparation of (**II**). Thus, since the source material, [*cis*-Co(en)$_2$(NH$_3$)Br]Br$_2$, was found to crystallize in the centrosymmetric space group $C2/c$, it is clear that the resolved crystals of (**II**) found in our previous study arose as a result of conglomerate crystallization.

One additional point concerning the cations present in (**I**) is important for our discussion[4] of the stereochemistry of the species present in (**II**): despite some hydrogen bonding between the Br$^-$ anion and the amine hydrogens (*vide supra*) the conformation and configuration of the Co(en)$_2$ fragment is either $\Lambda(\delta\delta)$ or $\Delta(\lambda\lambda)$, which is the expected, lowest energy conformation of this cation, (*lel*)$_2$.[10] Thus, the weak hydrogen bonding between the components of the ion pair is insufficiently strong to affect the normal stereochemistry of the cation. This observation is in accord with the fact that, unlike[4] the case of (**II**), we could not find the hydrogens of the -NH$_3$ ligand in (**I**), which we infer to be freely rotating in the lattice.

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