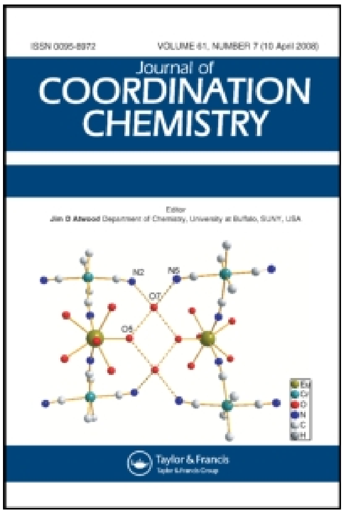

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. XXVI. THE CRYSTAL AND MOLECULAR STRUCTURE OF RACEMIC $NH_4[Cr(EN)_2OX]CL_2·H_2O$ (I) AND ATTEMPTS TO PREPARE $NH_4[Co(EN)_2OX]CL_2·H_2O$ (II)

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. XXVI. THE CRYSTAL AND MOLECULAR STRUCTURE OF RACEMIC $NH_4[Cr(EN)_2OX]CL_2{\cdot}H_2O$ (I) AND ATTEMPTS TO PREPARE $NH_4[Co(EN)_2OX]CL_2{\cdot}H_2O$ (II)

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$NH_4[Cr(en)_2ox]Cl_2{\cdot}H_2O$, $CrCl_2O_5N_5C_6H_{22}$ (I) crytallizes as a racemate in the monoclinic space group $P2_1/c$ (No. 14). The cell constants are $a = 7.386(9)$, $b = 12.138(4)$, $c = 16.999(9)$Å, $\beta = 100.45(10)°$, $V = 1498.55$Å^3, d ($Z = 4$; $M = 367.17$) = 1.627 gm cm^{-3}. A total of 2830 data were collected in the interval $4.0° \leqslant 2\Theta \leqslant 50.0°$ of which 1785 were unique and had intensities greater than $3\sigma(I)$. The data were corrected for absorption using empirical Psi scan curves (five reflections, $\mu = 11.260$ cm^{-1}); the relative transmission coefficients ranged from 0.7849 to 0.9999. Refinement of the structural data leads to final values of $R(F)$ and $R_w(F)$ of 0.050 and 0.063, respectively.

All attempts to prepare the Co analogue of (I) have failed, thus far; instead, crystals of $[Co(en)_2ox]Cl{\cdot}4H_2O$ are obtained, despite changes in crystallization conditions, including the use of a large excess of ammonium chloride.

KEY WORDS: Racemate, chromium(III), 1,2-diaminoethane, oxalic acid, X-ray structure.

INTRODUCTION

It has been known for some time[1–3] that the series $[M(en)_2ox]X$ ($M = Co$, Cr, Rh; $X = Cl^-$, Br^-) crystallize as conglomerates, whereas $[Co(en)_2ox]I$ crystallizes both as a conglomerate and as a racemate 1c. In fact, this observation was used by Shimura, *et al.*[1c] as evidence of the success of their thermodynamic formulation of the condition ($S_r > 1.414S_e$; where S_r is the solubility of the racemate and S_e that of the enantiomer) which defines what crystallization pathway a given substance will prefer—racemate or conglomerate. Relevant crystallization data for these systems are summarized below.

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Compound	*Space Group*	*Ref*
$[Co(en)_2ox]Cl\cdot 4H_2O$ (**III**)	$P2_12_12_1$	1(c), 2
$[Co(en)_2ox]Br\cdot H_2O$ (**IV**)	$P2_12_12_1$	2, 3
$[Co(en)_2ox]I$ (**V**)	?*	1(c)
$[Cr(en)_2ox]Br$	?*	1(a), 4
$[Rh(en)_2ox]Br$	?*	4
$[Rh(en)_2ox]Cl\cdot H_2O$	?*	4

*These substances 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 were reported. See refs. 1(a), 1(c) and 4 for details of the crystallization, seeding and spectroscopic experiments performed on these compounds.

Our crystallization and structural studies[2] of (**III**) and (**IV**) demonstrated that, in both, homochiral cations are present in spiral strings linked by hydrogen bonds spanning from the terminal oxalato oxygens of one cation to the basal plane amines of an adjacent one, each string being an infinite polymer running along the length of the crystal (in ref. 2, we showed strings of cations present in (**III**) and (**IV**) which run along the *b* direction, approximately). Adjacent strings are also homochiral with respect to one another, and are held together by halide anions which are bonded to hydrogens of an axial $-NH_2$ and to a water of crystalization, the latter being bonded to an axial $-NH_2$ hydrogen of a cation beloning to the adjacent string. This stitching together of the strings occurs along the entire length of adjacent spirals.

At the same time we published ref. 2, we suggested that anything that interfered with the orderly formation of the spiral strings and/or of the stitching pattern found in (**III**) and (**IV**) would probably result in the formation of heterochiral crystals (racemates). The availability of (**I**) made it possible to test this hypothesis since it was reasonable to expect that the ammonium cation could alter drastically the hydrogen bond pattern observed in (**III**) and (**IV**).

EXPERIMENTAL

Synthesis

(**I**) was prepared as follows: $[Cr(en)_3]Cl_3$ was synthesized following the procedure of Bailar.[5] It was converted to *cis*$[Cr(en)_2Cl_2]Cl$ by treating the former with NH_4Cl, as described in the same report.[5] The resulting mterial was isolated in crystalline form, redissolved in the minimum amount of water and chromatographed in a column of silica gel. A broad, yellow band was eluted with water and the resulting solution concentrated in a rotary evaporator. The filtered solid was dissolved in the minimum amount of water, reacted with ammonium oxalate (1:) and the product allowed to crystallize in a Petri dish. Golden rods and orange plates were found in the crystalline material wich were separated as carefully as possible under a microscope. Elemental analysis[7] of the orange material was an approximation to the expected results for $NH_4[Cr(en)_2ox]Cl_2\cdot H_2O$ (theory for C, H. N = 19.67, 6.06, 19.13%; observed = 20.22, 5.39, 15.91%). These results are indicative of a mixture of salts such as we observed under the microscope.

$[Co(en)_2ox]Cl{\cdot}4H_2O$ (**III**) was prepared earlier by either of two methods: (a) *cis*-$[Co(en)_2Cl_2]Cl{\cdot}4H_2O$ (**IV**)[8] was reacted (1:1) with solid $(NH_4)_2(C_2O_4){\cdot}H_2O$ in warm water (60°C) and the solution concentrated in a rotary evaporator, and (b) by the more direct method of Jordan.[9] Analyses and the X-ray structure of (**III**) were given in our report on the crystallization behaviour of $[Co(en)_2ox]X{\cdot}nH_2O$ salts, their structure and packing modes.[2] Under the microscope, there is no evidence of the formation of the double chloride salt since the crystals observed are uniform in colour and morphology; moreover, they all effloresce in a few minutes, as noted earlier.[2] Finally, elemental analysis of the crystalline material derived from procedure (a) is identical with that in (b) and both analyses are compatible with the formula $[Co(en)_2ox]Cl{\cdot}4H_2O$ (for details see ref. 2).

Attempts to prepare (**II**) by dissolving (**III**) in a minimum amount of water, adding an excess of NH_4Cl till precipitation occurs, cooling the mixture and filtering, resulted in recovery of (**III**) in fairly high yield, but no evidence of the formation of the desired compound, (**II**). Even allowing the mother liquor, recovered after precipitation of (**III**), to give several further crops of crystals failed produce the double salt.

X-Ray Diffraction

Golden yellow rods

Data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[10] of the SDP-Plus software package.[11] A golden yellow, nearly cylindrical crystal of *ca* 0.3 mm diameter was cleaved to obtain a rod *ca* 0.6 mm in length. The crystal was centered with data in the $22° \leqslant 2\Theta \leqslant 34°$ range and examination of the cell constants and Niggli matrix[12] clearly showed it to crystallize in a primitive, trigonal lattice whose Laue symmetry and systematic absences belong to those of the space group $P\bar{3}c1$ (No. 165). The intensity data set was corrected for absorption using empirical curves derived from Psi scans[10],[11] of five reflections. The scattering curves were taken from Cromer and Waber's compilation.[13] Upon identifying the compound as $[Cr(en)_3]Cl_3{\cdot}3H_2O$ and finding the report of its structure in the literature,[6] we abandoned this study.

Orange plates

Using the same procedure outlined above, we collected an intensity data set for this crystal while an elemental analysis on manually separated crystals was being performed (see above). Solution of the structure revealed the presence of a Cr and two chlorides. Eventually, the ammonium ion and the water of crystalization was also found. Details of data collection, processing and refinement are summarized in Table 1. Fractional coordinates are reported in Table 2, together with the isotropic-equivalent thermal parameters. Bond lengths, angles and torsion angles are given in Table 3. The structure factors are submitted as Supplementary Material (see below).

RESULTS

We began our synthetic studies with the published synthesis of *cis*$[Cr(en)_2Cl_2]Cl$[5], planning to convert this salt into $[Cr(en)_2ox]Cl$, followed by metathesis with NaBr and NaI to obtain the respective bromide and iodide—an approach based on our

Table 1 Summary of data collection and processing parameters for racemic $NH_4[Cr(en)_2ox]Cl_2 \cdot H_2O$

Space Group	$P2_1/c$
Cell Constants	$a = 7.386(9)$ Å $b = 12.138(4)$ $c = 16.999(9)$ $\beta = 100.45(10)$
Cell Volume	$V = 1498.55$ Å^3
Molecular Formula	$CrCl_2O_5N_5C_6H_{22}$
Molecular Weight	367.17 gm-mol^{-1}
Density (calc; $Z = 4$ mol/cell)	1.627 gm-cm^{-3}
Radiation Employed	MoKα($\lambda = 0.71073$ Å)
Absorption Coefficient	$\mu = 11.26$ cm^{-1}
Transmission Coefficients	0.7849 to 0.9999
Data Collection Range	$4° \leqslant 2\theta \leqslant 50°$
Scan Width	$\Delta\theta = 1.00 + 0.35\tan\theta$
Total Data Collected	2830
Data Used In Refinement*	1785
$R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$	0.050
$R_w = [\sum_w^2 (\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum \lvert F_o\rvert^2]^{1/2}$	0.063
Weights Used	$w = [\sigma(F_o)]^{-2}$

*The difference between this number and the total is due to subtraction of 1045 data which either were systematically absent (but collected for verification of space group), standards or did not meet the criterion that $I \geqslant 3\sigma(I)$.

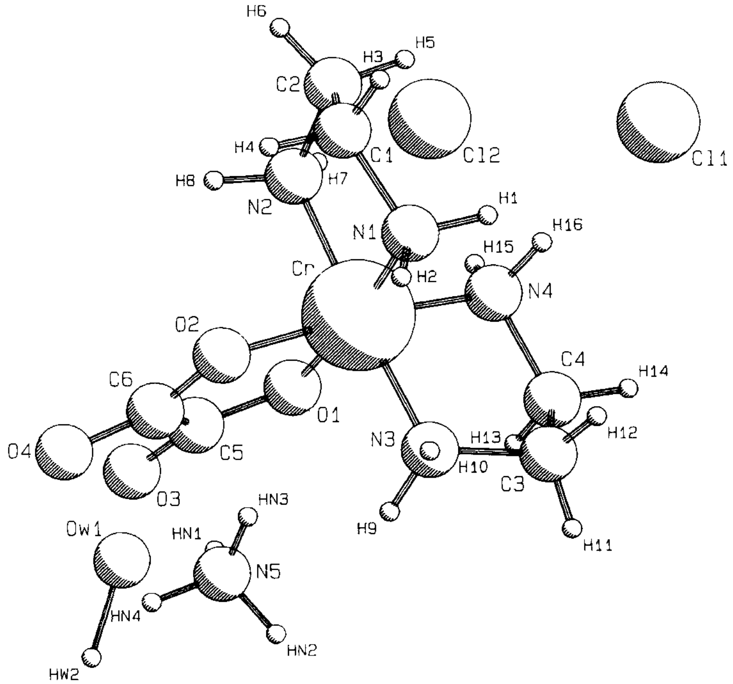

Figure 1 A view of the contents of the asymmetric unit. Note the position of the NH_4^+ cation, blocking access to O3 of the oxalato ligand. Also, note the position of the chloride anions which effectively block access to the $-NH_2$ hydrogens in the equatorial plane. These hydrogen bonded interactions effectively eliminate all chances of forming the spiral strings of cobalt cations found (see ref. 2) in the series of $[Co(en)_2Ox]X$ ($X = Cl$, Br, I) and whose formation was postulated as the origin of conglomerate crystallization.

Table 2 Positional parameters and esd's

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(Å^2)
Cr	0.2196(1)	0.20239(7)	0.19678(5)	1.21(1)
Cl1	−0.1727(4)	0.4571(2)	0.1171(1)	5.99(2)
Cl2	−0.3066(3)	0.0692(2)	0.1045(1)	4.01(4)
O1	0.2558(6)	0.0569(4)	0.1597(3)	2.8(1)
O2	0.4091(6)	0.1661(4)	0.2862(3)	3.0(1)
O3	0.4213(7)	−0.0933(4)	0.1987(3)	3.3(1)
I4	0.6048(7)	0.0286(4)	0.3266(3)	4.0(1)
N1	0.1796(7)	0.3420(4)	0.2446(3)	2.7(1)
N2	0.0276(8)	0.1454(5)	0.2500(3)	2.9(1)
N3	0.4029(8)	0.2657(5)	0.1412(3)	3.2(1)
N4	0.0470(7)	0.2285(5)	0.0996(3)	2.9(1)
N5	−0.381(2)	0.1736(6)	−0.0564(4)	8.8(4)
C1	0.086(1)	0.3221(6)	0.3135(4)	3.7(2)
C2	−0.062(1)	0.2373(6)	0.2855(5)	3.8(2)
C3	0.310(1)	0.3100(7)	0.0628(5)	4.5(2)
C4	0.148(1)	0.2391(8)	0.0328(5)	4.8(2)
C5	0.3765(9)	0.0041(5)	0.2068(4)	2.6(1)
C6	0.473(1)	0.0696(6)	0.2794(4)	2.9(1)
Ow1	−0.2900(9)	0.3567(5)	−0.0468(3)	5.8(2)
HN1	−0.2961	0.2292	−0.0380	5*
HN2	−0.4347	0.1469	−0.0119	5*
HN3	−0.3258	0.1143	−0.0783	5*
HN4	−0.4796	0.2028	−0.0952	5*
Hw1	−0.2207	0.4335	0.0000	5*
Hw2	−0.4453	0.3847	−0.0371	5*
H1	0.1046	0.3873	0.2063	5*
H2	0.2944	0.3773	0.2625	5*
H3	0.0323	0.3883	0.3282	5*
H4	0.1711	0.2947	0.3578	5*
H5	−0.1561	0.2686	0.2465	5*
H6	−0.1128	0.2115	0.3294	5*
H7	−0.0617	0.1078	0.2122	5*
H8	0.0801	0.0957	0.2910	5*
H9	0.4885	0.2104	0.1328	5*
H10	0.4658	0.3236	0.1724	5*
H11	0.3928	0.3089	0.0260	5*
H12	0.2708	0.3834	0.0691	5*
H13	0.1874	0.1688	0.0179	5*
H14	0.0727	0.2725	−0.0120	5*
H15	−0.0367	0.1685	0.0896	5*
H16	−0.0192	0.2945	0.1044	5*

*Hydrogen atoms of the Cr cation were added at idealized positions (see text). Hydrogen atoms of the water of crystallization and of the ammonium cation were found experimentally. All hydrogen atoms were assigned fixed thermal parameters of 5.0Å^2. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)^*[a^{2*}\beta_{11} + b^{2*}\beta_{22} + c^{2*}\beta_{33} + ab(\cos\gamma)^*\beta_{12} + ac(\cos\beta)^*\beta_{13} + bc(\cos\alpha)^*\beta_{23}]$.

experience of the solubility order for many of the relevant Co(III) (Cl > Br > I). Much to our astonishment, crystallization of the chromatographed "$[Cr(en)_2ox]Cl$" gave crystals of $[Cr(en)_3]Cl_3 \cdot H_2O$ and $NH_4[Cr(en)_2ox]Cl_2 \cdot H_2O$ in an approximate ratio of 50:50. The orange crystals turned out to be $NH_4[Cr(en)_2ox]Cl_2 \cdot H_2O$—a heretofore unreported double salt. The contents of the asymmetric unit are shown in Figure 1, where one observes that the water of crystallization is hydrogen bonded to the

Table 3 Bond distances (Å) and angles (°)

A) Distances

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Cr	O1	1.910(2)	N4	C4	1.475(5)
Cr	O2	1.921(2)	N5	HN1	0.934(5)
Cr	N1	1.925(3)	N5	HN2	0.971(5)
Cr	N2	1.943(3)	N5	HN3	0.936(5)
Cr	N3	1.944(3)	N5	HN4	0.960(6)
Cr	N4	1.922(3)	C1	C2	1.513(5)
O1	C5	1.260(4)	C3	C4	1.485(6)
O2	C6	1.277(4)	C5	C6	1.533(5)
O3	C5	1.241(3)	Ow1	Hw1	1.272(3)
O4	C6	1.245(4)	Ow1	Hw2	1.236(4)
N1	C1	1.483(5)			
N2	C2	1.478(5)			
N3	C3	1.483(5)			

Number in parentheses are estimated standard deviations.

B) Angles

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O1	Cr	O2	85.6(1)	N3	C3	C4	108.1(3)
O1	Cr	N1	173.9(1)	N4	C4	C3	106.0(3)
O1	Cr	N2	89.0(1)	O1	C5	O3	125.9(3)
O1	Cr	N3	93.1(1)	O1	C5	C6	114.9(3)
O1	Cr	N4	88.8(1)	O3	C5	C6	119.2(3)
O2	Cr	N1	90.7(1)	O2	C6	O4	124.6(3)
O2	Cr	N2	92.2(1)	O2	C6	C5	114.9(3)
O2	Cr	N3	90.2(1)	O4	C6	C5	120.5(3)
O2	Cr	N4	173.1(1)	Hw1	Ow1	Hw2	89.6(2)
N1	Cr	N2	86.3(1)	HN1	N5	HN2	109.1(3)
N1	Cr	N3	91.8(1)	HN1	N5	HN3	112.1(7)
N1	Cr	N4	95.1(1)	HN1	N5	HN4	110.0(4)
N2	Cr	N3	176.9(1)	HN2	N5	HN3	108.8(4)
N2	Cr	N4	91.9(1)	HN2	N5	HN4	106.9(7)
N3	Cr	N4	85.9(1)	HN3	N5	HN4	109.8(3)
Cr	O1	C5	112.7(2)				
Cr	O2	C6	111.6(2)				
Cr	N1	C1	108.6(2)				
Cr	N2	C2	109.8(2)				
Cr	N3	C3	109.3(2)				
Cr	N4	C4	109.0(2)				
N1	C1	C2	106.0(3)				
N2	C2	C1	107.0(3)				

Numbers in parentheses are estimated standard deviations.

C) Torsion Angles

Atom 1	Atom 2	Atom 3	Atom 4	Angle	Atom 1	Atom 2	Atom 3	Atom 4	Angle
O2	Cr	O1	C5	0.9	N3	Cr	N4	C4	20.9
N1	Cr	O1	C5	−52.4	Cr	O1	C5	O3	176.9
N2	Cr	O1	C5	−91.3	Cr	O1	C5	C6	−3.5
N3	Xr	O1	C5	90.9	Cr	O2	C6	O4	175.5
N4	Cr	O1	C5	176.8	Cr	O2	C6	C5	−4.5
O1	Cr	O2	C6	2.2	Cr	N1	C1	C2	−43.3
N1	Cr	O2	C6	177.4	Cr	N2	C2	C1	−34.6
N2	Cr	O2	C6	91.0	Cr	N3	C3	C4	−33.0

Table 3 *Continued*

C) Torsion Angles, *continued*

Atom 1	Atom 2	Atom 3	Atom 4	Angle	Atom 1	Atom 2	Atom 3	Atom 4	Angle
N3	Cr	O2	C6	−90.8	Cr	N4	C4	C3	−43.7
N4	Cr	O2	C6	−34.9	N1	C1	C2	N2	50.4
O1	Cr	N1	C1	−19.1	N3	C3	C4	N4	49.6
O2	Cr	N1	C1	−72.3	O1	C5	C6	O2	5.5
N2	Cr	N1	C1	19.9	O1	C5	C6	O4	−174.5
N3	Cr	N1	C1	−162.5	O3	C5	C6	O2	−174.8
N4	Cr	N1	C1	111.5	O3	C5	C6	O4	5.2
O1	Cr	N2	C2	−175.1					
O2	Cr	N2	C2	99.3					
N1	Cr	N2	C2	8.7					
N3	Cr	N2	C2	−42.8					
N4	Cr	N2	C2	−86.3					
O1	Cr	N3	C3	95.5					
O2	Cr	N3	C3	−178.9					
N1	Cr	N3	C3	−88.1					
N2	Cr	N3	C3	−36.7					
N4	Cr	N3	C3	6.9					
O1	Cr	N4	C4	−72.3					
O2	Cr	N4	C4	−35.3					
N1	Cr	N4	C4	112.3					
N2	Cr	N4	C4	−161.2					

D) Selected List of Hydrogen Bonds

Cl1-Hw1	1.978	Ow1-Hw1...Cl1	135.5	
Cl1-H16	2.305	N4-H16...Cl1	178.5	
Cl2-HN2	2.242	N5-HN2...Cl2	131.3	
Ow1-HN1	1.556	N5-HN1...Ow1	135.8	
Cl1-H8	2.313	N2-H8...Cl1	171.3	N2 at $-x$, $1/2+y$, $1/2-z$
O3-HN3	2.055	N5-HN3...O3	113.5	N5 at $-x$, $-y$, $-z$
O3-HN4	2.306	N5-HN4...O3	95.1	N5 at $-x$, $-y$, $-z$
O3-H2	2.114	N1-H2...O3	162.7	N1 at $1-x$, $1/2+y$, $1/2+z$

No esd's are given since hydrogen were not refined

ammonium cation (Ow...HN1 = 1.556Å), which, in turn, is hydrogen bonded to the oxalato ligand (O3...HN3 = 2.055Å and O3...HN4 = 2.306Å). $\mathrm{Cl1}^-$ is bonded to a hydrogen of N4: (Cl1...H16 = 2.305Å) and, although not obvious in the view shown, $\mathrm{Cl1}^-$ is also bonded to H8 of N3 ($\mathrm{Cl1}^-$...H8 = 2.313Å) and to (water ($\mathrm{Cl2}^-$...Hw1 = 1.978Å), while $\mathrm{Cl2}^-$ is hydrogen bonded to the ammonium cation ($\mathrm{Cl2}^-$...HN2 = 2.242Å). The remaining hydrogen bonds of the chlorides to the amino hydrogens of the cation are too long (>2.40Å) to be considered very significant. Nonetheless, their geometrical arrangement in the lattice of (**I**) is such that the chlorides are adjacent to, and sterically block access of other particles to the hydrogens on nitrogens N1 and N4, as can be noted in the packing diagram, Figure 2. This latter observation is significant with respect to the crystallization pathway of this substance (see Discussion, below).

Finally, we note (see Figure 2) that only one of the terminal oxygens of oxalato forms an intermolecular hydrogen bond with an amino hydrogen of an adjacent cation (O3...H2). This, and other longer bonds, are listed in Table 3(D). O4 does not have bonds as short as those of O3 and those hydrogen contacts found exceed 2.5Å. Nonetheless, even if they are labelled “long contacts”, O4 is close to H2, H10, H12

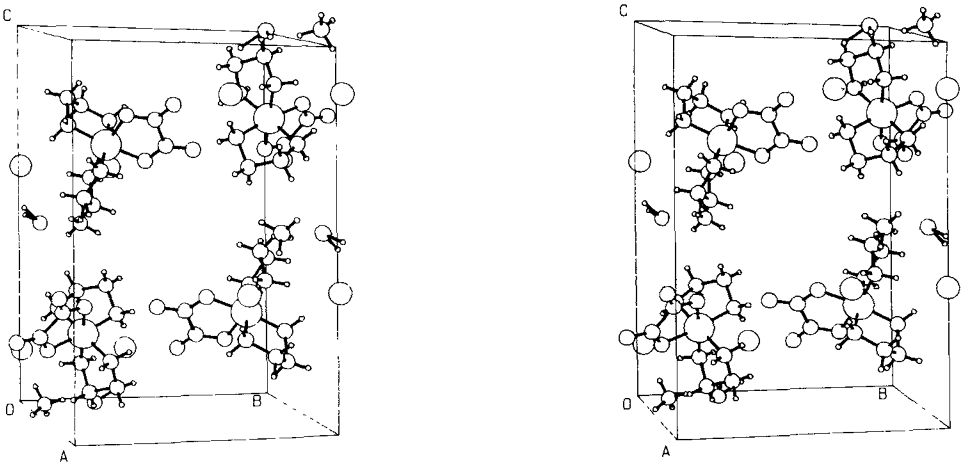

Figure 2 A stereo view of the unit cell contents. Here, one may see the approach between chromium cations blocked by the NH_4^+ cation and the chlorides. Only one oxalato oxygen can approach the $-NH_2$ moiety in the basal plane. For details see Results and Discussion, as well as numerical data in Table 3(D).

and Hw2, which effectively block access to this oxygen, and prevent chromium cations from forming the spiral strings found in the case in the $[Co(en)_2ox]X$ series,[2] and mentioned in the Introduction.

It is unfortunate that we have been unable to isolate the cobalt analogue, thus far.

DISCUSSION

From the outset, we acknowledge that the synthesis of (I) was an accident caused, apparently, by our inability to reproduce previous published work,[5] the lack of success for which we blame ourselves. However, this was a fortunate bit of clumsiness since it provided us with an additional piece of the puzzle we mentioned in the Introduction; namely, the ammonium cation was bound to form hydrogen bonds with the oxalato oxygens, with the anions and with the water of crystallization. Therefore, it would be expected to alter the nature of the packing by (a) intercalating between Cr cations and modifying or destroying the spiral strings, or by (b) upsetting the nature of the bridges between adjacent strings, or both. Despite the outcome, it seemed useful to observe whether the outcome was conglomerate or racemic crystallization. We now know it was the latter, and below we attempt to justify this result.

First, Figure 1 shows that $Cl1^-$ and $Cl2^-$ are located in the region of the equatorial $-NH_2$ ligands (N1 and N4) and that irrespective of the strength of their hydrogen bonds, they present a steric barrier to the approach of a second chromium cation. Consequently, the onset of the formation of a spiral string is obviously hopelessly compromised. Secondly, on the other side of the Cr cation, terminal oxygen O3 is strongly hydrogen bonded to the ammonium cation and O4 has a weak, but sterically demanding, contact with Ow (*via* Hw2). Again, the possibility of retaining the spiral string geometry observed in previous cases is seriously impaired on the other side of the Cr cation.

Thirdly, as one may note in Figure 2 (especially the lower half), the crystallization behaviour of (**I**) can be accounted for by the intra- and intermolecular interactions described above (see Results) and depicted in this figure; e.g., the shortest hydrogen bonds to chromium cations are those from the ammonium hydrogens to O3, a terminal oxalato oxygen which bonds to HN3 and HN4. The lower half of Figure 2 also shows this single-oxygen attachment, while the upper half clearly shows the steric effect of the chloride anion between adjacent chromium cations. Therefore, it seems that blocking access to the formation of infinite homochiral strings of cations in lattices in which halides, and/or waters, are linking adjacent strings is a necessary packing formula for conglomerate crystallization of these metal(en)$_2$oxalates, as suggested elsewhere.[2] Such inter-cationic hydrogen bonds are impossible with the hydrated ammonium double salt (**I**) herein reported; as described above, only one such oxalato oxygen...H_2N- hydrogen bond can be formed due to the presence of the NH_4^+ cation, as well as te additional chloride. This observation strengthens our previously derived conclusions as to why and how the halides of the $[Co(trien)_2(NO_2)_2]^+$, $[Co(en)_2(NO_2)_2]^+$ and $[Co(en)_2ox]^+$ cations undergo conglomerate crystallization.[2,14-17] Therefore, there appears to be consistency in our crystallization mechanistic conclusions, even when we compare members of different series of cations—a fact which is greatly satisfying to us.

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Supplementary Material

Compound (**I**): Anisotropic thermal parameters (1 page), structure factor table (10 pages). Available from IB upon request.

References

1. (a) Alfred 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); (b) further work in this area was done by K. Yamasaki, H. Igarishi and Y. Yoshikawa, *Inorg. Nuclear Chem. Letters*, **4**, 491 (1968); (c) 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 (1973); (d) for the crystal structure of $[Co(en)_2ox]Br{\cdot}H_2O$, determined from crystals of pre-resolved material, see ref. 3. However, that structural study (ref. 3) was carried out with a very limited set of film data; consequently, it lacks precision and no hydrogen atom positions were given for either the cation or the water of crystallization.
2. Using crystals from conglomerate crystallization experiments, we have determined the crystals structures of $[Co(en)_2ox]Br{\cdot}H_2O$ and $[Co(en)_2ox]Cl{\cdot}4H_2O$. In general, the former agrees with the results given in ref. 3; the latter is a new structural analysis. A detailed description and comparson of both will be published elsewhere (I. Bernal, J. Cetrullo, J. Myrczek, and S.S. Massoud, to be published). Both compounds crystallize in the enantiomorphic space group $P2_12_12_1$ with $Z=4$.
3. T. Aoki, K. Matsumoto, S. Ooi and H. Kuroya, *Bull. Chem. Soc. Japan*, **46**, 159 (1973).
4. R.D. Gillard and L.H.R. Tipping, *J. Chem. Soc., Dalton Trans.*, 1241 (1977).
5. J.C. Bailar, Jr., "Inorganic Syntheses", (McGraw-Hill, New York, 1946), Vol. 2, p. 198.
6. A. Whuler, C. Brouty, P. Spinat and P. Herpin, *Acta Cryst.*, **B31**, 2069 (1975).

7. Galbraith Laboratories, Inc., P.O. Box 51610, Knoxville, TN, 37950-1610.
8. J.C. Bailar, Jr., "Inorganic Syntheses", (McGraw-Hill, New York, 1946), Vol. 2, p. 222.
9. W.T. Jordan and L.R. Froebe, "Inorganic Syntheses", (McGraw-Hill, New York, 1978), Vol. XVIII, p. 96.
10. TEXRAY-230 is a modification of the SDP-Plus[11] set of X-ray crystallographic programs distributed by Molecular Structure Corporation, 3200 Reseaarch Forest Dr., The Woodlands, TX 77386 for use with their automation of the CAD-4 diffractometer.
11. SDP-Plus is the Enraf-Nonius Corporation X-ray diffraction data processing programs distributed by B.A. Frenz and Associates, 1140 East Harvey Road, College Station, TX, 77840.
12. R.B. Roof, "*A Theoretical Extension of the Reduced Cell Concept in Crystallography*", Report LA-4038, Los Almos Scientific Laboratory, 1969.
13. 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.
14. I. Bernal, *Inorg. Chim. Acta*, **96**, 99 (1985).
15. I. Bernal and J. Cetrullo, *Inorg. Chim. Acta*, **144**, 227 (1988).
16. I. Bernal and J. Cetrullo, *Inorg. Chim. Acta*, **150**, 75 (1988).
17. I. Bernal, S. Berthane and J. Cetrullo, *Struct. Chem.*, **1**, 361 (1990).