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The crystallization behavior of (±)-*cis*-*α*-[Co(dmtrien)$(NO_2)_2$]Cl·$0.5H_2O$ 1 and (±)-*cis*-*α*-[Co(dmtrien)$(NO_2)_2$]I 2 † (dmtrien = 3,6-dimethyl-3,6-diazaoctane-1,8-diamine)

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The compound (±)-*cis*-α-[Co(dmtrien)$(NO_2)_2$]Cl·$0.5H_2O$ **1** has been found to crystallize as a kryptoracemate in the space group *C*2 (*Z* = 4) with a racemic pair as the asymmetric unit, whereas (±)-*cis*-α-[Co(dmtrien)$(NO_2)_2$]I **2** crystallizes as a simple racemate, as expected (dmtrien = 3,6-dimethyl-3,6-diazaoctane-1,8-diamine). For **1** the two cations in the asymmetric unit had the conformations Δ(λδλ), Co(1), and Λ(δλδ), Co(2), and those of the chiral, methylated, nitrogens of Co(1) are (*S*,*S*) while those of Co(2) are (*R*,*R*). Compound **2** crystallizes as a racemate in the space group *Pccn* (*Z* = 8); the anions are in a general position but there are two half cations sitting at two-fold axes of the space group. For **1**, Co(1) and Co(2) cations form separate spiral strings which extend through the length of the *a* axis, and these strings are held together by hydrogen bonds to the anions and waters of crystallization. Each string contains, exclusively, cations of single chirality and layers of homochiral strings define the *ab* plane of the crystals. Each layer is of opposite chirality to the pair of adjacent ones. In **2** the packing is different in that there are strings made exclusively of either Co(1) or Co(2) running along the diagonal of the *bc* plane, as well as [–Co(1)–Co(2)–Co(1)–Co(2)–]$_n$ . . . strings running parallel to the *c* axis.

Introduction

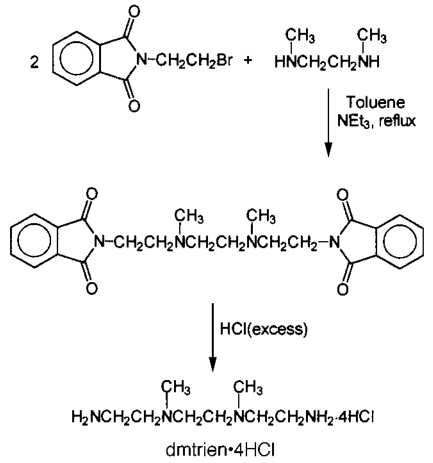
We define the phenomenon of kryptoracemic crystallization as the deposition, from a racemic solution, of enantiomorphic crystals containing racemic pairs of molecules as the asymmetric unit. For such a crystallization mode to occur, the number of molecules in the unit cell, *Z*, must be an even multiple of the number of general positions of the space group and, while some atoms may share a non-crystallographic pseudo-inversion center, the degree to which they conform to such an inversion center varies for different sets of atoms.

This phenomenon appears, at the moment, to be rare and, as such, is currently poorly documented. In Table 1 we list seven cases of such crystallization mode by co-ordination compounds. A list of some two dozen examples of organic compounds crystallizing thus has been published (see ref. 1).

The original purpose of preparing compounds **1** (±)-*cis*-α-[Co(dmtrien)$(NO_2)_2$]Cl·$0.5H_2O$ and (±)-*cis*-α-[Co(dmtrien)-$(NO_2)_2$]I **2** (dmtrien = 3,6-dimethyl-3,6-diazaoctane-1,8-diamine) was to test the validity of a suggestion, proposed by this group,[7] that the conglomerate crystallization mode selected by compounds of the series *cis*-*α*-[Co(trien)$(NO_2)_2$]X·H_2O (X = Cl^-, Br^- or I^-) was determined by specific intra- and intermolecular hydrogen bonded interactions. Moreover, it was proposed[7] that anything disturbing the intramolecular bonds between the NO_2 oxygens (with the axial NH_2 hydrogens) and the intermolecular hydrogen bonds between the halides and the secondary NH hydrogens would alter the crystallization pathway. Evidence that this proposal is reasonable was offered. One way of altering the hydrogen bonds available to the halide is to alkylate the secondary amine nitrogens, which we accomplished recently. The expectation that the result would be a racemate was met, as expected, with the iodide **2** and in a rather extraordinary fashion for the chloride **1**, as we report herein.

Experimental

N-(2-Bromoethyl)phthalimide and *N*,*N′*-dimethylethylenediamine (the Aldrich Chemical Company) were used as received. The NMR spectra were recorded at room temperature with a General Electric QE-300 spectrometer using D_2O as the solvent and $SiMe_4$ as the standard. Elemental analyses were carried out by Galbraith Laboratories (Knoxville, TN). The synthetic procedures for the ligand are depicted in Scheme 1.



Scheme 1

Syntheses

3,6-Dimethyl-1,8-diphthalimido-3,6-diazaoctane. *N*-(2-Bromoethyl)phthalimide (50 g, 0.20 mol) was dissolved in 140 mL toluene and 70 mL of triethylamine, which is the catalyst for this reaction. The resulting solution was distilled at 104 °C and 5–10 mL of moist, turbid fluid were removed. After cooling, the solution was treated with 10 mL of *N*,*N′*-dimethylethylenediamine (0.09 mol), and refluxed for 20 h with the temperature maintained at 110 °C. The solution was allowed to cool and the hydrobromide salt of triethylamine, which had separated in the course of the reaction, was removed by filtration. The filtrate was distilled to strip off the solvent and the crude product, a brown oil, was treated with an excess of concentrated HCl. The white solid was filtered off, washed with

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† The phenomenon of kryptoracemic crystallization, Part 3, and counter ion control of crystallization pathway selection, Part 6.[1]

Table 1 Compounds reported to crystallize as kryptoracemates

Compound	Space group	*Z*	Structure determined?	Ref.
$\{[Co(en)_3][(ox)I]\}_2\cdot 3H_2O$	$P2_12_12_1$	4	Yes	1
$[Co(tren)(NO_2)_2]_2Br[ClO_4]\cdot H_2O$	$P2_12_12_1$	4	Yes	2
$[Co(en)_2(ox)]_2(ox)\cdot 8H_2O$	—	—	No[a]	3
$[Co(en)_2(ox)]F\cdot 11.5H_2O$	$P2_1$	4	Yes	4
$[Fe\{O_2CCH_2N[CH_2\overline{CN(CH_3)CHCHN}]_2\}Cl_2]_2$	$P2_1$	4	Yes	5
$[Co(en)_3]_2[Pb_4Cl_{18}]_{0.5}Cl\cdot 3H_2O$	$P2_1$	2	Yes	6
$[Co(dmtrien)(NO_2)_2]Cl\cdot 0.5H_2O$	*C*2	4	Yes	This study

[a] In an early report[3a] the space group was determined to be $P2_12_12_1$ and the existence of hemihedral faces was postulated; however, no structural analysis was carried out. A later report,[3b] based on a phase diagram study, demonstrated that the previous one was incorrect and suggested that the authors had studied crystals of $[Co(en)_2(ox)]Cl\cdot 4H_2O$, which is a conglomerate and crystallizes in space group $P2_12_12_1$. We have recently indexed crystals of the dimeric oxalate compound [for $C_{14}H_{48}Co_2N_8O_{20}$, $M = 766.477$, $a = 11.612(4)$, $b = 11.834(5)$, $c = 13.458(7)$ Å, $\beta = 110.55(5)°$, $V = 1664.52$ Å^3, $Z = 2$, $D_c = 1.529$ g cm^{-3}, crystal decomposes rapidly due to the loss of waters of crystallization] and found that the correct space group is $P2_1/c$, a centrosymmetric space group incapable of producing hemihedral faces, lending further validity to the data published in ref. 3(*b*) and the suggestions made therein.

cold ethanol and acetone (21.0 g, 55.3%). δ_H 2.896 (6 H, s), 3.452 (4 H, t), 3.584 (4 H, s), 3.982 (4 H, t) and 7.685–7.713 (8 H, m).

dmtrien·4HCl. The above raw product was mixed with 60 mL concentrated HCl and refluxed for 12 h. After cooling to room temperature, the precipitated phthalic acid was removed by filtration and the filtrate evaporated in a roto-evaporator until a light yellow oil was obtained. The oily liquid was treated with 20 mL of concentrated HCl. A white powder thus obtained was washed three times with hot ethanol and then with acetone. The resulting material was dried overnight in an oven set to 85 °C (13.0 g, 44.8%) (Found: C, 29.98; H, 8.05; N, 17.37. $C_8H_{22}N_4\cdot 4HCl$ requires C, 30.02; H, 8.19; N, 17.50%); δ_H 2.976 (6 H, s), 3.481 (4 H, m), 3.574 (4 H, m) and 3.709 (4 H, s); δ_C 34.93, 41.57, 51.57 and 54.15.

***cis*-α-[Co(dmtrien)(NO$_2$)$_2$]Cl·0.5H$_2$O 1.** The compound $CoCl_2\cdot 6H_2O$ (0.74 g) was dissolved in 15 mL water and 1 mL 30% H_2O_2 added drop by drop. A 1.0 g amount of dmtrien·4HCl was dissolved in 15 mL water and neutralized with 0.5 g NaOH. The neutralized solution was added to the cobalt solution and 0.45 g of solid $NaNO_2$ was slowly added with stirring. The resulting solution was heated to 60 °C for 0.5 h, and then cooled to room temperature while continuing the stirring (*ca.* 3 h). The solution was transferred to a test-tube and allowed to evaporate at room temperature, whereupon a few crystals suitable for X-ray diffraction were obtained (Found: C, 24.42; H, 6.12; N, 22.01. $C_8H_{23}ClCoN_6O_{4.5}$ requires C, 25.99; H, 6.27; N, 22.73%).

***cis*-α-[Co(dmtrien)(NO$_2$)$_2$]I 2.** This complex was prepared by adding NaI to a saturated aqueous solution of **1** till no more solid precipitated. The solid was filtered off, washed with ethanol and suction-filtered till dryness (Found: C, 21.03; H, 5.20; N, 19.59. $C_8H_{22}CoIN_6O_4$ requires C, 21.25; H, 4.87; N, 18.59%). The same procedure, using NH_4Br, was used to obtain the bromide derivative. The solids thus formed were dissolved in the minimum amount of water at 21 °C and allowed to evaporate. Suitable crystals of the bromide were never obtained from the saturated aqueous solution; instead, occasional bubbling was noted emanating from the solution and, eventually, a gray-green powder precipitated.

Crystallography

For both compounds the intensity data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a TEXRAY 230 modification[8] of the SDP-Plus software package.[9] During data collection intensity and orientation standards were monitored and showed no significant deviations from the initial values. The intensity data of **2** were corrected for absorption using empirical curves derived from ψ scans of suitable reflections. The examination of the cell constants, absences, and Niggli matrix[10] showed **1** to crystallize in one of the space groups *C*2, *Cm* or *C*2/*m*. Compound **2** crystallizes unequivocally in the space group *Pccn* (no. 56). The structures were solved by direct methods using SHELXS 86[12] and refined by full-matrix least squares calculations on F^2 using SHELXL 93.[13] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in their geometrically ideal positions with isotropic thermal parameters 1.2 times those of the attached non-hydrogen atoms. In both refinements, relatively large peaks near the anions (<1.0 Å) were observed in the final difference map; holes were found near cobalts for **1** and near iodide for **2**. Final $R(F^2)$ and $wR(F^2)$ factors are listed in Table 2, which summarizes other details of data collection and processing.

CCDC reference number 186/1207.

Results and discussion

Crystal structures

Initially, we assumed that the correct space group for compound **1** was *C*2/*m* and that the compound, as expected, was a racemate. However, attempts to solve and refine the structure in either *C*2/*m* or *Cm* failed to produce a sensible cation. Instead, we found a smooth solution and refinement of the structure in space group *C*2. Therefore, we thought our previous proposals[1,2,4,7,13–17] may have been faulty, or less general than expected, since the crystals appeared to be those of a conglomerate crystallizing in an enantiomorphic space group. It was, thus, reassuring to find that the asymmetric unit consists of a racemic pair, as we had hoped.[1,2,4,7,13–17] Moreover, this unexpected result taught us an important lesson about the role of the counter ions in the selection of a crystallization pathway, especially that the choice is not limited to conglomerates and racemates; instead, we must include kryptoracemic crystallization as a viable third choice for racemates to select.

When the *R* factor for compound **1** converged the Flack test[18] had a value of 0.02 ± 0.02 which indicates that the assignment of the absolute configuration of the two cations in the asymmetric unit is correct and that the absolute enantiomorphism corresponds to the initial coordinates in the solution of the structure. As shown in Fig. 1, the configuration and conformations at the two cobalt cations of **1** were Δ(λδλ) for Co(1) and Λ(δλδ) for Co(2).

It was thus, at this point, we realized we had a case of kryptoracemic crystallization, with a pair of heterochiral-(racemic) cations in an enantiomorphic lattice, rather than a case of conglomerate crystallization with two homochiral cations as the asymmetric unit. Refinement with the NRCVAX programs[19] and a subsequent test for absolute enantiomorph-

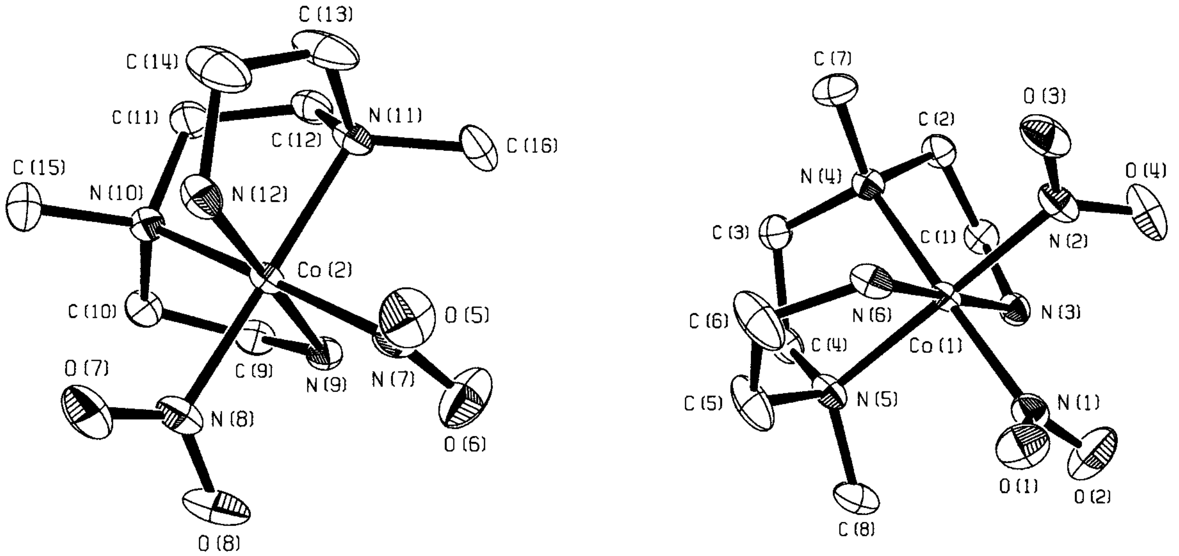

Fig. 1 The two cations in the asymmetric unit of compound **1** drawn at 30% probability level. The anion, water of crystallization and hydrogen atoms have been omitted for clarity. Selected bond lengths and angles: Co(1)–N(1) 1.928(5), Co(1)–N(2) 1.942(5), Co(1)–N(3) 1.966(6), Co(1)–N(4) 2.021(5), Co(1)–N(5) 2.012(5), Co(1)–N(6) 1.941(6), Co(2)–N(7) 1.933(5), Co(2)–N(8) 1.941(5), Co(2)–N(9) 1.974(6), Co(2)–N(10) 2.030(5), Co(2)–N(11) 2.009(5), Co(2)–N(12) 1.962(6) Å; N(1)–Co(1)–N(4) 174.3(3), N(2)–Co(1)–N(5) 175.5(2), N(3)–Co(1)–N(6) 179.3(3), N(7)–Co(2)–N(10) 173.3(3), N(8)–Co(2)–N(11) 176.4(2), N(9)–Co(2)–N(12) 179.1(2)°.

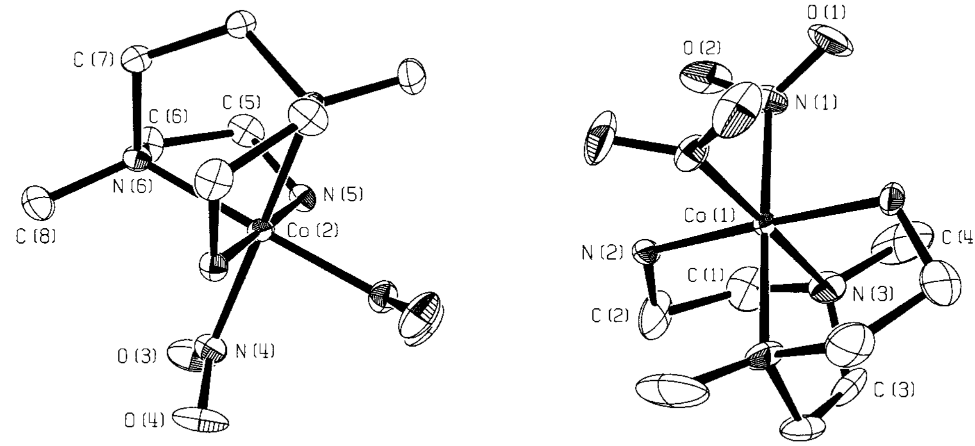

Fig. 2 The two cations in the asymmetric unit of compound **2**. Only unique atoms are labelled and the anion and hydrogen atoms have been omitted for clarity. Selected bond lengths and angles : Co(1)–N(1) 1.931(10), Co(1)–N(2) 1.940(9), Co(1)–N(3) 1.999(10), Co(2)–N(4) 1.929(10), Co(2)–N(5) 1.944(8), Co(2)–N(6) 2.012(8) Å; N(2)–Co(1)–N(2^{I}) 177.8(5), N(1)–Co(1)–N(3^{I}) 176.4, N(5)–Co(2)–N(5^{II}) 179.9(5), N(4)–Co(2)–N(6^{II}) 175.1°. Symmetry relations: I $0.5 - x, 0.5 - y, z$; II $0.5 - x, 1.5 - y, z$.

ism of the lattice gave identical results to those with SHELXL 93. A search for hidden symmetry, using the routine MYSSYM of the NRCVAX program, failed to reveal additional elements of symmetry unless disorder was permitted, and we find no evidence of such disorder in space group *C*2. If the cations are truly disordered, one should see the disorder in either space group.

The crystals of compound **2** we obtained were of lesser quality than those of **1**, inasmuch as a number of peaks whose profile we examined were split. These observations are reinforced by the errors in cell constants of **2** and in the quality of the refinement. Nonetheless, since the systematic absences leave no doubt as to the space group, and the refinement is reasonable enough to show a sensible structure, we are certain of our original postulate[1,2,4,7,13–17] that counter ions exert control of the crystallization pathway selected by solutions of racemates and that interference with helical string formation will, surely, result in racemic crystals.

The stereochemical parameters obtained for compound **2** are similar enough to those obtained with the better ones of **1** that we need not comment further on them. Therefore, in the discussion, we will limit ourselves to commenting on the better results obtained with crystals of **1**. As was found for one of the cations, Co(2) in **1**, both cations present in the asymmetric unit of **2** have chiroptical symbol Λ(δλδ); however, their enantiomers must also be present in that lattice since the iodide is a true racemate. Fig. 2 shows the molecular structure of **2**. Note that only half the atoms of the two cations is required to define the asymmetric unit since they sit at two-fold rotation axes.

In Fig 3, which shows the mode of packing in compound **1**, the entire top row is constituted of Co(1) cations. Rows are held together by the hydrogen bonds between the chlorides and the amino hydrogens and/or by hydrogen bonds between the NO_2 oxygens and the water hydrogens. For details see the hydrogen bonds listed in Table 3.

The packing of the ions for compound **2** is depicted in Fig. 4, where one can see that the cations are also arranged in strings which run both along the *b* and the *c* directions; those zigzagging along the *b* direction are obviously of two types distinguished by their geometrical appearance. The Co(1) ions look like the one at $b = 3/4$, $c = 0.086$ while Co(2) cations look like the one at $b = 3/4$ and $c = 0.34$.

Thus, adjacent zigzagging strings made up exclusively of Co(1) or Co(2) cations run along the diagonal of the *bc* plane, while the strings along the *c* axis are mesomeric since they alternate as $[Co(1)–Co(2)–Co(1)–Co(2)]_n$. . . . In turn, irrespect-

Table 2 Crystal data and structure refinement for {*cis*-α-[Co(dmtrien)(NO_2)$_2$]Cl}$_2$·H_2O **1** and *cis*-α-[Co(dmtrien)(NO_2)$_2$]I **2**

	1	**2**
Empirical formula	$C_{16}H_{46}Cl_2Co_2N_{12}O_9$	$C_8H_{22}CoIN_6O_4$
Formula weight	739.41	452.15
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2	*Pccn*
a/Å	16.133(4)	9.053(10)
b/Å	17.649(3)	13.446(10)
c/Å	13.215(2)	25.487(12)
β/°	127.80(5)	
V/Å^3	2973.1(3)	3102.4(4)
D_c/g cm^{-3}	1.652	1.936
μ/mm^{-1}	1.361	3.118
F(000)	1544	1792
θ Range/°	2.0 to 30.0	2.0 to 25.0
Index ranges (h, k, l)	−22 to 17, 0 to 24, 0 to 18	0 to 9, 0 to 18, 0 to 35
Reflections collected	4620	2570
Independent reflections	4454 (R_{int} = 0.0437)	2570 (R_{int} = 0.0000)
Observed reflections [$I > 2\sigma(I)$]	3507	1780
Data/restraints/parameters	4454/1/372	2570/0/182
Goodness of fit on F^2	1.227	1.157
$R(F^2)$, $wR(F^2)$ [$I > 2\sigma(I)$]	0.0540, 0.1315	0.0778, 0.2223
(all data)	0.0887, 0.1600	0.1146, 0.2720
Flack x parameter	0.02(2)	
Extinction coefficient	0.028(2)	
Largest difference peak, hole/e Å^{-3}	1.528, −2.027	1.446, −2.049

Details in common: 293(2) K, λ 0.71073 Å, Z = 4 for **1**; Z = 8 for **2**.

Table 3 Hydrogen bonds shorter than 2.5 Å in compounds **1** and **2**

1[a]		**2**[b]	
N(3)–H(3A)···O(4)	2.212(9)	N(9)–H(9A)···Cl(2^{II})	2.429(6)
N(3)–H(3A)···O(5^I)	2.466(9)	N(9)–H(9B)···O(8)	2.212(9)
N(3)–H(3B)···Cl(1)	2.438(6)	N(9)–H(9B)···O(1^{III})	2.465(9)
N(6)–H(6A)···O(1)	2.130(9)	N(12)–H(12A)···O(7)	2.341(9)
N(6)–H(6B)···O(3)	2.362(9)	N(12)–H(12B)···O(5)	2.128(9)
N(2)–H(2A)···O(1^I)	2.464(16)	N(2)–H(2B)···N(1)	2.496(14)
N(2)–H(2B)···O(2)	2.095(15)	N(5)–H(5B)···O(3)	2.255(14)

[a] Symmetry relations: I 0.5 − x, 0.5 + y, 1 − z; II 0.5 − x, y − 0.5, 1 − z; III −x, y, 1 − z. [b] Symmetry relation: I 0.5 − x, 0.5 − y, z.

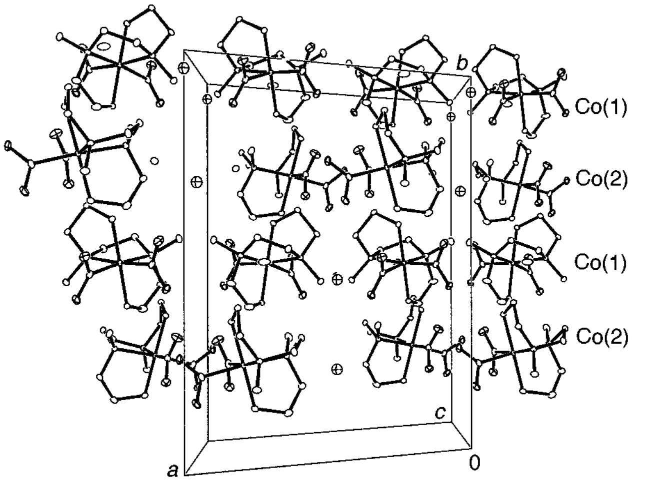

Fig. 3 Perspective view showing the packing of ions and water molecules of compound **1**. Principal and boundary ellipses represent oxygen atoms. Each string running parallel to the *a* axis of the unit cell contains exclusively either Co(1) or Co(2) cation as labelled on the right-hand side.

ive of the direction chosen (*b* or *c*) adjacent strings are stitched together by the iodide anions. There are no very significant hydrogen bonds between cations, as shown by the data in Table 3, where the strongest intermolecular hydrogen bonds are listed.

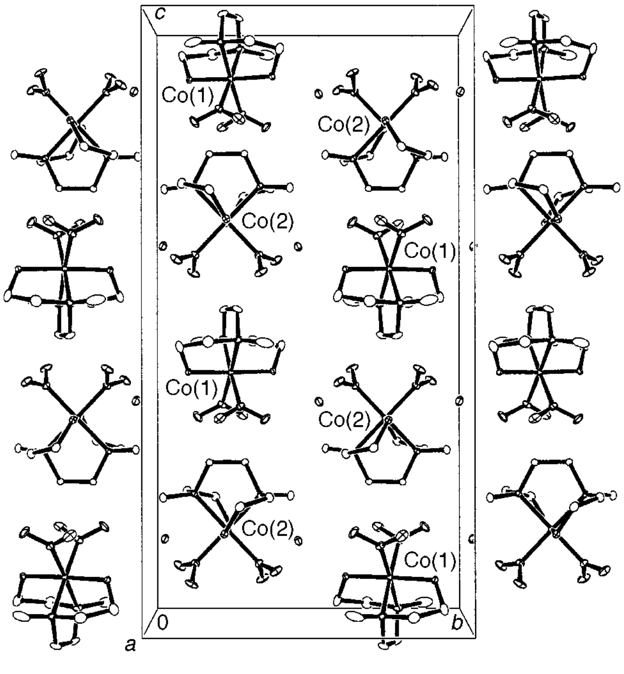

Fig. 4 The packing of ions in the unit cell of compound **2**.

Crystallization pathway and cationic conformation

The motivating force behind this study was the following: in previous papers detailing the crystallization behavior of cobalt cations of *cis*-α-[Co(trien)(NO_2)$_2$]X·H_2O (X = Cl^-[7a] or I^-[7b]) and of *cis*-[Co(en)$_2$(NO_2)$_2$]X (X = Cl^-,[7a] Br^-,[13] I^-,[14] NO_2^-[15] or NO_3^-[20]) we reported that the halides crystallize as conglomerates (homochiral crystals); however, if the counter anion is a powerful hydrogen bonding species, such as NO_2^- or NO_3^-, the compounds crystallize as racemates(heterochiral crystals). We also pointed out[1,2,4,7,13–17] that, whether racemic or conglomerate crystallization is the selected mode, these conglomerates form infinite helical strings in which the constituent cations of a given string are hydrogen bonded to one another and are of a single chirality. In turn, adjacent helices are held together by hydrogen bonded anions and waters (if present). Sometimes

Table 4 Selected torsional angles (°) for *cis*-*α*-[Co(trien)$(NO_2)_2$]X·H_2O (X = $Cl^{-\,7a}$ or $I^{-\,7b}$), **1** and **2**

	Ref. 7(*a*)	7(*b*)	
N(1)–Co–N(5)–O(1)	−143.1	−135.0	
N(1)–Co–N(5)–O(2)	39.4	44.9	
N(1)–Co–N(6)–O(3)	−144.9	−169.2	
N(1)–Co–N(6)–O(4)	33.3	12.6	
1		**2**	
N(3)–Co(1)–N(1)–O(1)	178.5	N(2)–Co(1)–N(1)–O(1)	175.1
N(3)–Co(1)–N(1)–O(2)	−0.9	N(2)–Co(1)–N(1)–O(2)	3.4
N(3)–Co(1)–N(2)–O(3)	156.1	N(5)–Co(2)–N(4)–O(3)	−22.2
N(3)–Co(1)–N(2)–O(4)	−27.8	N(5)–Co(2)–N(4)–O(4)	152.8

racemates also form infinite helical strings. The difference introduced by changing the anions is a change in the mode of binding the helical strings together; in the case of many of the halides, adjacent strings are of the same chirality. In the case of the nitrites and nitrates quoted above, adjacent strings are of opposite chirality.

In the halides the anions are located near the basal plane NH_2 (or NH) hydrogens and do not interfere with either the intra- or the inter-molecular hydrogen bonds present within a string. These intramolecular bonds are formed by the NO_2 oxygens and the axial NH_2 hydrogens. If, on the other hand, there are no basal plane amino hydrogens, the expectation was the halides would form hydrogen bonds with the axial amine moieties, and one way of forcing this issue is to methylate the secondary hydrogens of the trien ligand.

Recently, we also tested the above hypothesis in a different way, closely related in nature to the current one; namely, we prepared the 3,6-dithia analogue of trien and obtained salts of *cis*-*α*-(1,8-diamino-3,6-dithiaoctane)dinitrocobalt(III) (X = Cl^-, ClO_4^-;[16] BF_4^-, OBF_2^- [17]). In these salts there are no HN amino nitrogens to bond with the counter anions. All four of them were found to be racemates with the counter anions hydrogen bonded to the axial H_2N hydrogens, and preventing the intramolecular NO···HN hydrogen bonds from being formed. Similar results were recently reported by Toscano, *et al.*,[21] who reported *cis*-*α*-(1,8-diamino-3,6-dithiaoctane)-dinitrocobalt(III) bromide to crystallize as a racemate as well.

Therefore, if our conclusions of the past are correct and general, the expectation was that compound **1** would crystallize as a racemate. This expectation was met in a rather unexpected, if welcomed, manner. Moreover, we can demonstrate vividly the effect of such methylation by a comparison of the torsional angles found earlier in the conglomerates *cis*-*α*-[Co(trien)-$(NO_2)_2$]X·H_2O (X = $Cl^{-\,7a}$ or $I^{-\,7b}$) with those currently reported for **1**. These are listed in Table 4.

As the above data illustrate, there is a marked change in the conformation of the NO_2 groups. The first two compounds (both conglomerates) have torsional angles clearly different from those present in **1** and **2**, and the latter values are suggestive of a completely different intramolecular hydrogen bonding pattern, as we expected. Also note that in both cases there is one(outer) ring with a markedly smaller torsional angle than the other two. This has been noted in the structures of other *cis*-*α*-$[Co(trien)(NO_2)_2]^+$ cations[7] and attributed to hydrogen bonded interactions which attempt to coerce the relevant ring into a conformation which allows enhancement of the strength of the hydrogen bonds in question. It is, thus, not only a well documented phenomenon but our current data lend further evidence that its origin is as attributed earlier. To avoid repetition, the interested readers are directed to the original papers.[7] The structures of **1** and **2** show another interesting aspect of the hydrogen bonded interactions of the contents of the asymmetric unit; namely, the location of the chlorides with respect to the amine cations. As mentioned above, in *cis*-*α*-[Co(trien)-$(NO_2)_2$]X·H_2O (X = Cl^- or I^-), the halides are near the hydrogens of the secondary (basal plane) nitrogens. In **1** and **2** however they are clearly associated with the primary NH_2 hydrogens of the axial amine moieties, as was the case for the dithia complexes[16,17] cited earlier. Thus, one can readily understand the changes in the torsional angles of the NO_2 ligands of **1** and **2** since its chlorides are competing for the hydrogen bonds which normally anchor the NO_2 oxygens into the positions exhibited by the *cis*-*α*-[Co(trien)$(NO_2)_2$]X·H_2O (X = Cl^- or I^-) compounds.

Kryptoracemic and other unusual modes of crystallization

In view of the unexpected crystallization pathway selected by compound **1**, we decided to research other possible modes of crystallization obtained from racemic solutions. We found an additional, and equally interesting one, in the reports by Albano *et al.*[22] who discovered what they refer to as "unbalanced" crystallization; *e.g.* compounds crystallizing in enantiomorphic lattices but with an odd number of chiral species in the asymmetric unit (in their case, three of them). In those compounds there are two moieties of the same chirality, while the third is enantiomorphic to the homochiral pair. The reader is referred to their papers for further details.

After our experience with the crystallization behavior of compound **1** and the work of Albano *et al.*[22] it is clear that when racemic solutions crystallize, as ordered crystals in enantiomorphic space groups, and *Z* is a multiple of the number of general positions of the space group, the following situations may arise.

(a) *Z* is an even multiple of the general positions of the space group. Then, the contents of the asymmetric unit can be (1) homochiral, and the crystals constitute a true case of conglomerate crystallization, or (2) if they are present in pairs of enantiomeric species the crystallization pathway is that of a kryptoracemate, as found here.

(b) *Z* is an odd multiple of the general positions of the space group, then the contents of the asymmetric unit can be (1) homochiral and the crystals constitute a true case of conglomerate crystallization, or (2) pairs of enantiomeric species, plus an additional species of one or the other chirality, and the substance has selected an "unbalanced" crystallization pathway as was discovered by Albano *et al.*

The case of chiral species crystallizing in enantiomorphic space groups but with random occupancy of sites by either enantiomer is well documented, and has been described by Kitaigorodskii[23] and by Jacques *et al.*[24] The interested reader is referred to these sources and to the originals cited therein.

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