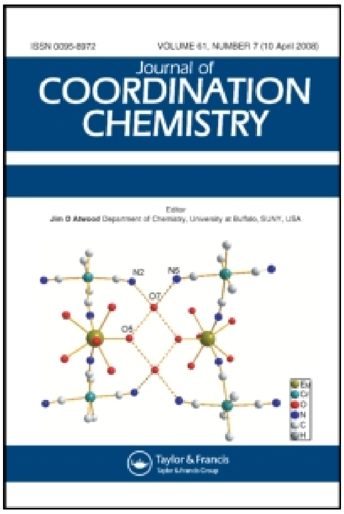

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE PHENOMENON OF KRYPTORACEMIC CRYSTALLIZATION. PART 1. COUNTERION CONTROL OF CRYSTALLIZATION PATHWAY SELECTION. PART 4. THE CRYSTALLIZATION BEHAVIOR OF (/-)-$[Co(tren)(NO_2)_2]Br$(I), (/-)-$[Co(tren)(NO_2)_2]_2Br(ClO_4) \cdot H_2O$(II), (/(-)-$[Co(tren)(NO_2)_2]ClO_4$(III) AND ATTEMPTS TO SOLVE THE STRUCTURE OF (/-)-$[Co(tren)(NO_2)_2]NO_3$(IV)

Ivan Bernal[a]; Jiwen Cai[a]; Salah S. Massoud[b]; Steven F. Watkins[c]; Frank R. Fronczek[c]
[a] Chemistry Department, University of Houston, Houston, TX [b] Department of Chemistry, Faculty of Science, Kuwait University, Safat, Kuwait [c] Chemistry Department, Louisiana State University, Baton Rouge, LA

To cite this Article Bernal, Ivan , Cai, Jiwen , Massoud, Salah S. , Watkins, Steven F. and Fronczek, Frank R.(1996) 'THE PHENOMENON OF KRYPTORACEMIC CRYSTALLIZATION. PART 1. COUNTERION CONTROL OF CRYSTALLIZATION PATHWAY SELECTION. PART 4. THE CRYSTALLIZATION BEHAVIOR OF (/-)-$[Co(tren)(NO_2)_2]Br$(I), (/-)-$[Co(tren)(NO_2)_2]_2Br(ClO_4) \cdot H_2O$(II), (/(-)-$[Co(tren)(NO_2)_2]ClO_4$(III) AND ATTEMPTS TO SOLVE THE STRUCTURE OF (/-)-$[Co(tren)(NO_2)_2]NO_3$(IV)', Journal of Coordination Chemistry, 38: 1, 165 — 181

To link to this Article: DOI: 10.1080/00958979608022702

URL: http://dx.doi.org/10.1080/00958979608022702

J. Coord. Chem., 1996, Vol 38, pp. 165–181
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THE PHENOMENON OF KRYPTORACEMIC CRYSTALLIZATION.
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PART 4. THE CRYSTALLIZATION BEHAVIOR OF (+ / -)-[Co(tren)(NO_2)$_2$]Br(I), (+ / -)-[Co(tren)(NO_2)$_2$]$_2$Br(ClO_4)·H_2O(II), (+ /(-)-[Co(tren)(NO_2)$_2$]ClO_4(III) AND ATTEMPTS TO SOLVE THE STRUCTURE OF (+ / -)-[Co(tren)(NO_2)$_2$]NO_3(IV)

IVAN BERNAL*, JIWEN CAI,

Chemistry Department, University of Houston, Houston, TX 77204-5641

SALAH S. MASSOUD,*

Department of Chemistry, Faculty of Science, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait.

STEVEN F. WATKINS and FRANK R. FRONCZEK

Chemistry Department, Louisiana State University, Baton Rouge, LA 70803-1804

(Received July 26, 1995; in final form November 1, 1995)

Racemic aqueous solutions of (+/–)-[Co(tren)(NO_2)$_2$]Br (**I**), (+/–)-[Co(tren)(NO_2)$_2$]ClO_4 (**III**) and [Co(tren)(NO_2)$_2$]NO_3(**IV**) crystallize as racemates. By contrast, the double salt, (+/–)-[Co(tren)(NO_2)$_2$]$_2$Br(ClO_4)·H_2O(**II**), produces kryptoracemic crystals belonging to the enantiomorphic space group $P2_12_12_1$(No. 19). The former three species crystallize with one molecule in the asymmetric unit; in the latter, a racemic pair is the asymmetric unit, a fact which is hidden by the enantiomorphic nature of its space group — thus the name of the crystallization phenomenon reported. In (**II**) pairs of cations are related by an approximate, non-crystallographic, inversion center. The crystal structure and polarity of (**I**) and the absolute configuration of (**II**) were determined by refinement. The crystalline contents of (**I**) to (**III**) consist of infinite strings of hydrogen bonded cations, the counter ions and (where relevant) waters of crystallization acting as a hydrogen-bonding glue linking the spiral strings

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In (II), the N-CH_2-CH_2-NH_2-Co rings of Co(1) are (δδλ) and those of Co(2) are (λλδ) and adjacent strings are linked by the counter-anions and the water of crystallization. Pairs of Co(1) and of Co(2) cations are hydrogen bonded to one another by two N-O···H-N linkages. Finally, pairs of composition Co(1)-Co(1) as well as of Co(2)-Co(2) share another *pseudo*-inversion center which is

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* Author for correspondence.

approximately valid for the CoN_6 portion of each cation. Since the atoms of the cation are ordered, it is impossible for the *pseudo*-inversion center to be valid for the $-CH_2-CH_2-$ fragment of the Co(1)-Co(1) or of Co(2)-Co(2) pairs. (I) and (III) crystallizes as racemates whose five-membered rings have chiroptical symbols (δδλ), or its enantiomer.

KEYWORDS: Kryptoracemates, racemates, conglomerate crystallization, cobalt(III) amines, Co(III) nitrites, Co(III) halides, Co(III) perchlorates, enantiomorphic lattices.

INTRODUCTION

Abbreviations used in the text:
en = 1,2-diaminoethane; trien = 1,4,7,10-tetraazadecane; edda = ethylenediamine-N,N′-diacetate; tren = tris(2-aminoethyl)amine.

Conglomerate crystallization is defined as the phenomenon whereby solutions of racemates produce a mechanical mixture of enantiomorphic, homochiral, crystals; *e.g.*, each individual crystal contains, exclusively, a single enantiomer or diastereoisomer. Although few in number so far, there are examples in the literature of racemic pairs crystallizing as the asymmetric unit of enantiomorphic crystals, one being $[Co(en)_3]_2[Pb_2Cl_9]Cl \cdot 3H_2O$[1] which crystallizes in space group $P2_1$, $Z = 2$ (or four cations in the unit cell). The asymmetric unit of this substance consists of pairs of Δ(λλδ) and Λ(δδλ) cations which are related to one another by a non-crystallographic, *pseudo*-inversion center; thus; the fact that a substance crystallizes in an enantiomorphic space group does not guarantee its contents are homochiral if the number of molecules in the unit cell is an even multiple of the number of symmetry positions in that space group. Such is the case in $[Co(en)_3]_2[Pb_2Cl_9]Cl \cdot 3H_2O$.[1] Thus far, this crystallization mode has rarely been observed and, thus, the conditions leadign to it are poorly documented inasmuch as the few known species crystalizing as kryptoracemates span a wide variety of substances.

We wish to name the phenomenon described above as kryptoracemic crystallization since crystallization in an enantiomorphic lattice obscures the fact that its contents are racemic pairs and, since the existence of this phenomenon is not widely, known, a name for it has not been assigned.

Another unique, and rare, crystallization mode was described by Albano and associates[2] who determined the structures and absolute configurations of $Cu(PF_3)_3Cl$(or Br), $Pt(CO)(PF_3)_3$ amd of $Ir(NO_2)(PF_3)_3$, and noted that these substances pack in space group $P3$ with $z = 9$, in chiral arrays of composition $\Delta_2\Lambda$ or $\Lambda_2\Delta$, depending on the crystal selected. These compounds crystallize in enantiomorphic lattices with an odd number of chiral species in the asymmetric unit (in their case, three) in which two share the same chirality, while the third is enantiomorphic to them. They refer to this mode of crystallization as unbalanced crystallization.[2]

The phenomenon of kryptoracemic crystallization is quite rare, as exemplified by the search of the Cambridge Crystallographic Data File carried out by Brock *et al.*[3] who found nine examples.[4–12] In addition, we have found the following examples among organic compounds:

(+/−)-o-Tyrosine ($P2_1$, $z = 4$)[13]; (+/−)-erythro-phenylglyceric acid ($P2_1$, $z = 4$)[14]; $C_{13}H_{20}O_3$($P2_1$, $z = 4$)[15]; (+/−)-carvoxime ($P2_1$, $z = 4$)[16], this species forms a series of continuous solid solutions with "unbalanced" amounts of enantiomers.

The degree of disorder depends on the actual composition. That of the nearly (1:1) composition is almost ordered. The same crystalline behavior was found with carvoximebenzene.[17] (2R,4R)-*trans*- and (2S,4S)-*cis*-2-hydroxy-2,4-dimethyl-3,4-dihydro-2H,5H-pyrano[3,2-c][1]benzopyran-5-one($P2_1$, z = 4)[18] Also, 3′-deoxy-3′-fluoro-xylo-Neoplanocin A, $C_{11}H_{12}FN_5O_2$ ($P2_1$, z = 4)[19]; here, the pucker of the cyclopentene differs for the two molecules in the asymmetric unit, one is +36.8° while other one is −12.5°. An extremely interesting, and unusual case, is that of DL-homocystein ($P2_1$, z = 2) studied by Nardelli and associates[20] — the compound is a mesomeric dimer, each molecule has a *pseudo* two-fold axis. If the molecules are viewed as two separate (D or L) halves, then the cell contains four fragments, two of each chirality. Finally, these four segments are then related to one another by a *pseudo* inversion center between fragments of appropriate chirality.

Among coordination compounds, we have found ourselves or reported in the literature are shown in Table 1

Given the wide range of compounds listed in Table 1, it is unreasonable to expect that trends can be deduced from the available data. Therefore, we were delighted to find a series of compounds, differing only by the nature of the counter anion, one of which displays this mode of crystallization while the other three are racemates.

EXPERIMENTAL

Synthesis and Crystallization

$[Co(tren)Cl_2]Cl$ and $[Co(tren)Cl_2]ClO_4$ were prepared according to the literature.[24] To a solution of $[Co(tren)Cl_2]Cl$ were added solid $NaNO_2$ (1:2) and excess NaBr till precipitation of (**I**). $[Co(tren)(NO_2)_2]_2Br(ClO_4)\cdot H_2O$(**II**) was obtained by the addition $NaNO_2$ to a solution of $[Co(tren)Cl_2]ClO_4$ (2:1), followed by the addition of excess NaBr. (**III**) was obtained by the addition (2:1) of $NaNO_2$ to a solution of the dichloro perchlorate. (**IV**) was obtained by displacement of the chlorides from $[Co(tren)Cl_2]Cl$, followed by the addition of excess $NaNO_3$. Crystals of all four were obtained by slow evaporation of water solutions of the racemate standing at ambient (*ca.* 22°C) temperature.

Table 1 Coordination compounds with kryptoracemic crystallization

Compound	*Sp. Gr*	*z*	*Str. Det. ?*	*Ref*
1. $[Co(en)_3]_2[Pb_2Cl_9]Cl\cdot 3H_2O$	$P2_1$	4	Yes	1
2. $[Co(en)_2(Ox)]_2(Ox)\cdot 8H_2O$	–	–	No*	21
3. $[Co(Me_2\text{-}trien)(NO)_2)_2]Cl\cdot H_2O$	$C2$	8	Yes	22
4. $\{[Co(en)_3][(ox)I]\}_2\cdot 3H_2O$	$P2_12_12_1$	4	Yes	23
5. $[Co(tren)(NO_2)_2]_2Br(ClO_4)\cdot 3H_2O$	$P2_12_12_1$	4	Yes	this study

* In an early report,[21(a)] the space group was reported to be $P2_12_12_1$ and the existence of hemihedral faces were described; however, no structural analysis was carried out then. A later report,[21(b)] based on a phase diagram study, demonstrated that the previous report[21(a)] was incorrect and suggested that the authors had studied crystals of $[Co(en)_2Ox]Cl\cdot 4H_2O$, which is a conglomerate and crystallizes in space group $P2_12_12_1$. We have recently indexed crystals of compound 2, 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 21(b) and the suggestions made therein.

Elemental analyses

All elemental analyses were carried out by Galbraith Laboratories, Inc.[25] (**I**): Theory C = 19.11%, H = 4.81%, N = 22.29%; Found: C = 19.09%, H = 4.88%, N = 22.19%. (**II**): Theory for C = 18.20%, H = 4.84%, N = 21.23%; Found: C = 18.13%, H = 4.88%, N = 21.17%. (**III**): Theory for C = 18.93%, H = 4.77%, N = 22.08%; Found:C = 18.80%, H = 4.84%, N = 21.96%. (**IV**): Theory for C = 20.06%, H = 5.05%, N = 27.30%; Found C = 20.08%, H = 5.10%, N = 27.25%.

Crystal data

The crystals used in the structure determinations were randomly selected from material recrystallized from water solutions. (**I**), $BrCoO_4N_6C_6H_{18}$, F(000) = 760, MW = 377.09, orthorhombic, space group $Pca2_1$ (No. 29), a = 12.332(3), b = 8.497(9), c = 12.232(3) Å, V = 1281.64 Å^3, Z = 4, d_c = 1.954 gm-cm^{-3}, λ = 0.71073 Å, μ = 44.416 cm^{-1}, $R(F_o)$ = 0.036, $Rw(F_o)$ = 0.038. For (**II**), $BrCo_2ClO_{13}N_{12}C_{12}H_{38}$, F(000) = 1508, MW = 791.73, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 7.837(2), b = 11.594(6), c = 30.642(7) Å, V = 2784.20 Å^3, Z = 4, d_c = 1.889 gm-cm^{-3}, λ = 0.71073 Å, μ = 27.859 cm^{-1}, $R(F_o)$ = 0.033, $Rw(F_o)$ = 0.036. For (**III**), $CoClO_8N_6C_6H_{18}$, F(000) = 816, MW = 396.63, orthorhombic, space group $Pnma$ (No. 62), a = 12.1753(6), b = 8.5550(3), c = 13.5545(6) Å, V = 1412.0 Å^3, Z = 4, d_c = 1.866 gm-cm^{-3}, λ = 0.71073 Å, μ = 14.40 cm^{-1}, $R(F_o)$ = 0.039, $Rw(F_o)$ = 0.047. For (**IV**), $CoO_7N_7C_6H_{18}$, F(000) = 744, MW = 359.19, orthorhombic, space group $Pna2_1$ (No. 33), a = 20.975(9), b = 7.469(2), c = 8.595(2) Å, V = 1346.51 Å^3, Z = 4, d_c = 1.773 gm-cm^{-3}, λ = 0.71073 Å, μ = 13.17 cm^{-1}, $R(F_o)$ = 0.16, $Rw(F_o)$ = 0.18.

X-Ray Data Collection and Treatment

For all four substances data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[26] of the SDP-Plus software package[27] or an Enraf-Nonius CAD-4 diffractometer controlled by the CAD4.V5 software package.[28] Data were processed with a PC version of the NRCVAX program package[29] or with the Nonius CAD4.V5 software.[28] Examination of the cell constants, Niggli matrix[30] and systematic absences showed (**I**) to crystallize in the space group $Pca2_1$ (No. 29) or $Pbcm$ (No. 57); (**II**) crystallizes in space group $P2_12_12_1$, while (**III**) and (**IV**) crystallize in space group $Pna2_1$ or $Pnam$. (**I**) and (**III**) have z = 4; therefore, the centrosymmetric choice would require the cation to, at least, have one of the three five-membered rings disordered, which is not necessary in the two polar space group choices; therefore, $Pna2_1$ was chosen, and refinement seemed to vindicate its selection. However, with (**III**) the anomalous effect was small and the NRCVAX routine which detects higher symmetry indicated the cation was located at a mirror plane of the centrosymmetric space group. Similar conclusions were reached using a separate and much larger data set processed at Louisiana[28], which is the one submitted with this manuscript. In all cases, the intensity data sets were corrected for absorption using empirical curves derived from Psi scans of suitable reflections.

The scattering curves were taken from Cromer and Waber's compilation.[31] The structures were solved from their Patterson maps, using the Br or Co as the heavy atom. The hydrogens of the cations were added at idealized positions. Heavy atoms were refined anisotropically until convergence, at which point the hydrogens of the water of crystallization of **(II)** were found in a difference map and added as fixed contributions. For **(II)** *R*(F) and *R*w(F) for the original (+++) coordinates were 0.0360 and 0.0443, respectively. For its enantiomorph (−−−) the values were 0.0538 and 0.0606. Thus, the coordinates of the former were assumed correct, and this defined the absolute configuration of the Co cations for our data collection crystal. Finally, for **(III)**, *R*(F) and *R*w(F) were 0.039 and 0.047, respectively. Throughout, $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, and $Rw(F_o) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$ with $w = [\sigma(F_o)]^{-2}$. Final positional and equivalent-isotropic thermal parameters are given in Tables 2, 3 and 4 for (I), (II) and (III), respectively. Distances, angles and selected torsional angles for (I), (II) and (III) are listed in Tables 5, 6 and 7. The contents of the asymmetric units of the three compounds are shown in Figs. 1–3 and their packing diagrams are shown in Figs. 4–7. Two figures are needed for the proper display of the packing features of **(II)** since the packing of this substance is complex, consisting of spiral strings containing either Co1 or Co2 cations which are of opposite chirality (see Figs. 5 and 6 and their captions). The torsional angles, anisotropic thermal parameters of the heavy atoms and Tables of Structure Factors have been deposited as Supplementary Material and can also be obtained from Ivan Bernal in either printed form, or on a PC diskette (send one with the request). Crystals of **(IV)** are very poor quality as may be judged by the fact that out of a total of 2532 unique data collected over the range $4 \leq 2\Theta \leq 55°$ only 713 had $I \geq 3\sigma(I)$. The structure of **(IV)** could readily be solved for the Co cation

Table 2 Positional Parameters and their esd's for **I**

Atom	*x*	*y*	*z*	B(Å^2)
Br	0.2503(2)	0.95184(8)	0.703	2.59(1)
Co	0.86636(5)	0.72275(9)	0.9548(2)	1.41(1)
O1	0.8645(5)	0.4086(8)	0.8705(5)	4.2(2)
O2	0.8582(5)	0.4234(6)	1.0450(5)	4.1(1)
O3	0.6584(4)	0.7034(9)	0.8753(5)	4.2(2)
O4	0.6646(4)	0.7017(8)	1.0471(4)	3.5(1)
N1	1.0243(3)	0.7505(5)	0.9510(9)	1.51(8)
N2	0.8563(3)	0.9531(5)	0.9633(7)	1.56(8)
N3	0.8773(5)	0.7230(8)	0.7921(5)	1.4(1)
N4	0.8796(4)	0.7099(7)	1.1100(4)	2.2(1)
N5	0.8663(4)	0.4889(6)	0.953(1)	2.41(9)
N6	0.7102(3)	0.7078(5)	0.954(1)	1.98(9)
C1	1.0528(4)	0.9227(7)	0.962(1)	2.1(1)
C2	0.9604(5)	1.0266(9)	0.9890(6)	2.5(2)
C3	1.0657(5)	0.670(1)	0.8616(6)	2.2(1)
C4	0.9886(6)	0.732(1)	0.7576(5)	2.3(1)
C5	1.0648(6)	0.6784(9)	1.0659(6)	2.3(1)
C6	0.9983(6)	0.722(1)	1.1460(7)	2.6(1)*

* Hydrogen atoms were added at idealized positions with fixed thermal parameters of 5.0 Å^2. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$(4/3) \times [a^2 \times \beta_{11} + b^2 \times \beta_{22} + c^2 \times \beta_{33} + ab(\cos\gamma) \times \beta_{12} + ac(\cos\beta) \times \beta_{13} + bc(\cos\alpha) \times \beta_{23}]$

Table 3 Positional parameters and their esd's for **II**

Atom	*x*	*y*	*z*	B(Å^2)
Br	-0.2069(1)	0.17031(8)	0.69614(3)	3.25(2)
Co1	0.6487(1)	0.46511(9)	0.53587(3)	2.03(2)
Co2	0.6456(1)	0.61623(8)	0.32957(3)	1.67(2)
Cl	0.2820(3)	0.4214(2)	0.67910(7)	2.74(4)
Ow	0.6152(9)	0.8279(6)	0.5524(2)	5.8(2)
O1	0.7204(9)	0.2864(5)	0.4774(2)	5.2(2)
O2	0.8839(8)	0.4279(5)	0.4681(2)	4.5(2)
O3	0.418(1)	0.4424(8)	0.4699(3)	11.6(3)
O3	0.402(1)	0.592(1)	0.4966(4)	11.9(3)
O5	0.719(1)	0.6329(6)	0.4193(2)	6.1(2)
O6	0.283(1)	0.7183(6)	0.6146(2)	6.1(2)
O7	0.3501(8)	0.6780(6)	0.3691(2)	5.1(2)
O8	0.3907(8)	0.7682(6)	0.3108(2)	4.8(2)
O9	0.3094(9)	0.3765(6)	0.6367(2)	5.4(2)
O10	0.237(1)	0.3342(5)	0.7090(2)	6.4(2)
O11	0.148(1)	0.5038(7)	0.6771(3)	8.1(2)
O12	0.4261(9)	0.4821(8)	0.6942(3)	7.8(2)
N1	0.8277(8)	0.4374(5)	0.5791(2)	2.3(1)
N2	0.5274(9)	0.5454(6)	0.5820(2)	3.0(2)
N3	0.5576(9)	0.3163(6)	0.5535(2)	3.1(2)
N4	0.7722(9)	0.6061(6)	0.5203(2)	3.2(2)
N5	0.7693(9)	0.3852(6)	0.4885(2)	3.1(2)
N6	0.462(1)	0.4967(6)	0.4957(2)	3.6(2)
N7	0.8494(8)	0.5223(5)	0.3180(2)	2.1(1)
N8	0.5651(8)	0.4853(5)	0.3635(2)	2.0(1)
N9	0.5545(8)	0.5566(5)	0.2750(2)	2.1(1)
N10	0.7626(8)	0.7389(5)	0.2985(2)	2.3(1)
N11	0.7296(8)	0.6837(5)	0.3848(2)	2.5(1)
N12	0.4374(8)	0.7010(5)	0.3378(2)	2.1(1)
C1	0.775(1)	0.4871(8)	0.6224(3)	3.2(2)
C2	0.645(1)	0.5818(7)	0.6158(3)	3.2(2)
C3	0.849(1)	0.3138(7)	0.5830(3)	3.3(2)
C4	0.671(1)	0.2615(7)	0.5859(3)	3.3(2)
C5	0.986(1)	0.4967(9)	0.5618(3)	3.6(2)
C6	0.938(1)	0.6131(8)	0.5451(3)	3.2(2)
C7	0.868(1)	0.4389(7)	0.3548(3)	2.3(2)
C8	0.690(1)	0.3906(7)	0.3639(3)	2.6(2)
C9	0.824(1)	0.4554(7)	0.2759(3)	2.7(2)
C10	0.698(1)	0.5157(7)	0.2467(3)	2.6(2)
C11	0.996(1)	0.6060(7)	0.3147(3)	3.1(2)
C12	0.942(1)	0.7071(7)	0.2879(3)	2.9(2)

* Hydrogen atoms were added at idealized positions with fixed thermal parameters of 5.0 Å^2. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:
$(4/3) \times [a^2 \times \beta_{11} + b^2 \times \beta_{22} + c^2 \times \beta_{33} + ab(\cos\gamma) \times \beta_{12} + ac(\cos\beta) \times \beta_{13} + bc(\cos\alpha) \times \beta_{23}]$

and nearly all the heavy atoms found in difference maps, including the nitrate anion, properly identified the compound. However, refinement gave a distorted pair of ions and, given the quality of the stereochemical data, the structural details are not worth reporting any further (see below). The Co is located at (0.1282, 0.1108, 0.0662) and the nitrate nitrogen is at (0.1693, 0.0074, 0.3459).

Table 4 Coordinates for $[Co(tren)(NO_2)_2]ClO_4$

Atom	x	y	z	$B_{eq}(Å^2)$
Co	0.19631(2)	1/4	0.34383(2)	1.887(4)
Cl	-0.06095(5)	3/4	0.20772(5)	3.05(1)
O1	-0.0162(1)	0.1281(2)	0.3441(1)	5.01(4)
O2	0.1810(2)	0.1284(3)	0.1583(1)	7.43(6)
O3	-0.1712(2)	3/4	0.2455(2)	5.27(6)
O4	0.0166(2)	3/4	0.2866(2)	5.34(5)
O5	-0.0473(2)	0.6145(2)	0.1477(1)	6.24(5)
N1	0.2141(2)	1/4	0.4878(1)	2.26(3)
N2	0.3568(2)	1/4	0.3373(2)	3.82(5)
N3	0.1911(1)	0.0223(2)	0.3534(1)	3.10(3)
N4	0.0341(2)	1/4	0.3470(1)	2.40(3)
N5	0.1856(2)	1/4	0.2029(1)	2.95(4)
C1	0.3333(2)	1/4	0.5152(2)	4.77(8)
C2	0.4070(3)	1/4	0.4318(2)	5.63(9)
C3	0.1593(2)	0.1048(2)	0.5240(1)	2.82(3)
C4	0.1929(2)	-0.0295(2)	0.4583(1)	3.71(4)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$

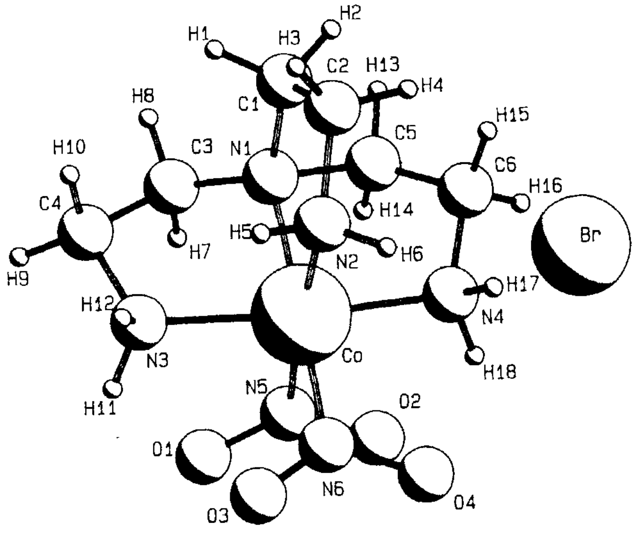

Figure 1 The contents of the asymmetric unit in (I). Note that the conformations of N1-C1-C2-N2, N1-C3-C4-N3 and N1-C5-C6-N4 are λ, λ and δ, respectively, with torsional angles of -19.7, -47.4 and 42.6° which are similar in magnitude to those observed in (III) but markedly different from those present in the two independent cations of (II). See Fig. 2 for details. The bromide anion is at the position at which the shortest hydrogen bond is formed with the cation.

RESULTS

Let us first comment on the structure of (IV): it crystallizes in space group $Pna2_1$. It cannot crystallize in the centrosymmetric space group $Pnma$(No. 62) with z = 4, unless it is disordered. Moreover, attempts to solve the structure in the higher

Table 5 Bond distances (Å) and angles (°) for I

A) Distances

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co	N1	1.963(2)	O2	N5	1.528(9)	N3	C4	1.438(12)
Co	N2	1.964(2)	O3	N6	1.153(12)	N4	C6	1.533(13)
Co	N3	1.995(7)	O4	N6	1.275(12)	C1	C2	1.479(5)
Co	N4	1.908(6)	N1	C1	1.511(4)	C3	C4	1.673(13)
Co	N5	1.987(3)	N1	C3	1.387(11)	C5	C6	1.330(14)
Co	N6	1.929(2)	N1	C5	1.612(11)			
O1	N5	1.220(9)	N2	C2	1.462(4)			

B) Angles

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N1	Co	N2	86.8(1)	N4	Co	N5	87.3(4)	Co	N5	O1	124.6(7)
N1	Co	N3	84.8(4)	N4	Co	N6	95.0(5)	Co	N5	O2	115.7(6)
N1	Co	N4	86.9(4)	N5	Co	N6	86.2(1)	O1	N5	O2	119.4(3)
N1	Co	N5	96.9(1)	Co	N1	C1	110.2(2)	Co	N6	O3	124.1(8)
N1	Co	N6	176.4(2)	Co	N1	C3	108.9(5)	Co	N6	O4	115.9(7)
N2	Co	N3	93.2(4)	Co	N1	C5	104.0(5)	O3	N6	O4	119.9(3)
N2	Co	N4	90.6(3)	C1	N1	C3	117.5(8)	N1	C1	C2	114.7(3)
N2	Co	N5	175.6(3)	C1	N1	C5	102.7(7)	N2	C2	C1	111.9(3)
N2	Co	N6	90.2(1)	C3	N1	C5	112.7(3)	N1	C3	C4	103.6(7)
N3	Co	N4	170.7(1)	Co	N2	C2	112.4(2)	N3	C4	C3	107.6(7)
N3	Co	N5	89.5(4)	Co	N3	C4	110.9(6)	N1	C5	C6	110.2(8)
N3	Co	N6	93.5(4)	Co	N4	C6	111.3(6)	N4	C6	C5	111.0(9)

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

C) Selected List of Hydrogen Bonds

Br-H5	2.59	N2-H5 ··· Br	169.7	
Br-H6	2.43	N2-H6 ··· Br	155.0	
Br-H12	2.41	N3-H12 ·· Br	175.2	
Br-H17	2.54	N4-H17 ·· Br	169.7	
O1-H11	2.29	N3-H11 ·· O1	116.5	N3 at 1/2 - x, y, 1 - z
O2-H18	1.94	N4-H18 ·· O2	122.2	N4 at x, y - 1, z

* No esd's are shown since hydrogen atoms were not refined.

symmetry space group fail to give a reasonable solution. However, in either case, the crystals are racemic, as expected.

Figures 1, 2 and 3 give, respectively, labelled overviews of the contents of the asymmetric units of (**I**), (**II**) and (**III**). For (**I**) the chiroptical symbol of the cation described by the coordinates (Table 2) is (λλδ; with torsional angles of -19.7, -47.4 and 42.6°) as shown in Fig. 1. The absolute configuration of the two independent cations in (**II**) were (δδλ; with torsional angles of 40.7, 43.5, -41.5°) and (λλδ; with torsional angles of -44.0, -42.1, 39.5°) as shown in Fig. 2. for (**III**) they were (δδλ; with torsional angles of 11.4, 49.3, -35.0°) as shown in Fig. 3. Note that, like (**I**), but unlike (**II**), (**III**) has one ring which is nearly flat; however the effect is more pronounced in the latter case. We attribute these changes in ring helicity to differences in the strength of the intra- and inter-molecular hydrogen-bonded interactions, as has been documented and remarked upon in previous publications.[32-36]

Table 6 Bond distances (Å) and angles (°) for **II**

A) distances

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co1	N1	1.955(3)	C1	O12	1.409(4)	N2	C2	1.447(5)
Co1	N2	1.942(3)	O1	N5	1.255(4)	N3	C4	1.474(5)
Co1	N3	1.944(4)	O2	N5	1.200(4)	N4	C6	1.509(5)
Co1	N4	1.959(3)	O3	N6	1.067(5)	N7	C7	1.493(5)
Co1	N5	1.965(4)	O4	N6	1.200(6)	N7	C9	1.520(5)
Co1	N6	1.947(4)	O5	N11	1.214(4)	N7	C11	1.507(5)
Co2	N7	1.965(3)	O6	N11	1.211(4)	N8	C8	1.473(5)
Co2	N8	1.946(3)	O7	N12	1.208(4)	N9	C10	1.495(5)
Co2	N9	1.946(3)	O8	N12	1.195(4)	N10	C12	1.488(5)
Co2	N10	1.942(3)	N1	C1	1.506(5)	C1	C2	1.512(6)
Co2	N11	1.976(3)	N1	C3	1.449(5)	C3	C4	1.528(6)
Co2	N12	1.921(3)	N1	C5	1.511(5)	C5	C6	1.409(7)
C1	O9	1.415(3)				C7	C8	1.527(6)
C1	O10	1.409(3)				C9	C10	1.507(5)
C1	O11	1.421(4)				C11	C12	1.494(6)

B) Angles

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N1	Co1	N2	86.4(1)	N10	Co2	N12	95.2(1)	Co2	N7	C11	106.0(2)
N1	Co1	N3	86.0(1)	N11	Co2	N12	88.2(1)	C7	N7	C9	108.9(3)
N1	Co1	N4	87.0(1)	O9	C1	O10	111.8(2)	C7	N7	C11	113.1(3)
N1	Co1	N5	94.4(1)	O9	C1	O11	108.6(3)	C9	N7	C11	111.8(3)
N1	Co1	N6	176.5(2)	O9	C1	O12	111.3(2)	Co2	N8	C8	111.7(2)
N2	Co1	N3	92.4(2)	O10	C1	O11	109.1(3)	Co2	N9	C10	109.6(2)
N2	Co1	N4	91.1(2)	O10	C1	O12	110.1(3)	Co2	N10	C12	111.8(3)
N2	Co1	N5	179.1(1)	O11	C1	O12	105.7(2)	Co2	N11	O5	122.1(3)
N2	Co1	N6	90.2(2)	Co1	N1	C1	109.6(3)	Co2	N12	O6	120.0(3)
N3	Co1	N4	171.9(2)	Co1	N1	C3	107.7(3)	O5	N11	O6	117.6(4)
N3	Co1	N5	88.0(2)	Co1	N1	C5	106.1(2)	Co2	N12	O7	118.2(3)
N3	Co1	N6	93.8(2)	C1	N1	C3	109.7(3)	Co2	N12	O8	120.2(3)
N4	Co1	N5	88.6(2)	C1	N1	C5	111.1(3)	O7	N12	O8	121.4(4)
N4	Co1	N6	93.5(2)	C3	N1	C5	112.5(4)	N1	C1	C2	110.3(3)
N5	Co1	N6	89.0(2)	Co1	N2	C2	110.5(3)	N2	C2	C1	108.1(3)
N7	Co2	N8	85.8(1)	Co1	N3	C4	110.4(3)	N1	C3	C4	106.8(4)
N7	Co2	N9	86.9(1)	Co1	N4	C6	110.4(3)	N3	C4	C3	110.1(3)
N7	Co2	N10	86.2(1)	Co1	N5	O1	118.9(3)	N1	C5	C6	109.1(3)
N7	Co2	N11	95.9(1)	Co1	N5	O2	123.4(3)	N4	C6	C5	109.9(4)
N7	Co2	N12	175.8(1)	O1	N5	O2	117.7(4)	N7	C7	C8	106.6(3)
N8	Co2	N9	93.6(1)	Co1	N6	O3	126.7(4)	N8	C8	C7	109.5(3)
N8	Co2	N10	170.7(1)	Co1	N6	O4	117.0(4)	N7	C9	C10	110.7(3)
N8	Co2	N11	87.6(1)	O3	N6	O4	115.7(5)	N9	C10	C9	107.3(3)
N8	Co2	N12	93.1(1)	Co2	N7	C7	107.6(2)	N7	C11	C12	108.9(3)
N9	Co2	N10	90.7(1)	Co2	N7	C9	109.3(2)	N10	C12	C11	110.0(4)
N9	Co2	N11	177.0(1)	N9	Co2	N12	89.0(1)	N10	Co2	N11	88.5(1)

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

Table 6 Continued.

C) Selected list of hydrogen bonds				
Br-H24	2.46	N8-H24 ··· Br	154.0	
Br-H29	2.50	N9-H29 ··· Br	174.8	
Br-H35	2.49	N10-H35 ··· Br	148.8	
Ow-H18	2.10	N4-H18 ··· Ow	164.0	
O1-H12	2.09	N3-H12 ··· O1	119.6	
O2-H17	2.28	N4-H17 ··· O2	110.3	
O4-H5	2.33	N2-H5 ···· O4	113.8	
O5-H17	2.26	N4-H17 ··· O5	152.5	N4 at 1/2 + x, 1/2 − y, 1 − z
O5-H23	2.14	N8-H23 ··· O5	116.6	
O6-H5	2.36	N2-H5 ··· O6	119.3	N2 at x + 1, y − 1, z
O6-H36	2.14	N10-H36 ··· O6	117.2	N10 at −1/2 + x, 3/2 − y, 1 − z
O7-H3	2.42	N2-H3 ···· O7	162.9	N2 at x, y − 1, z
O8-H30	2.48	N9-H30 ··· O8	112.6	
O9-H6	2.17	N2-H6 ···· O9	164.0	
O9-H11	2.48	N3-H11 ··· O9	141.5	
O10-H30	2.46	N9-H30 ··· O10	147.2	N9 at 1 − x, y + 1/2, z
O11-H1	2.49	N1-H1 ···· O11	123.1	N1 at x − 1, y, z
O11-H36	2.39	N10-H36 ··· O11	143.3	N10 at −1/2 + x, 3/2 − y, 1 − z
O12-H4	2.40	N2-H4 ···· O12	110.1	
O12-H26	2.47	N7-H26 ··· O12	136.4	N7 at x − 1, 1/2 + y, z

* No esd's are shown since hydrogen atoms were not refined.

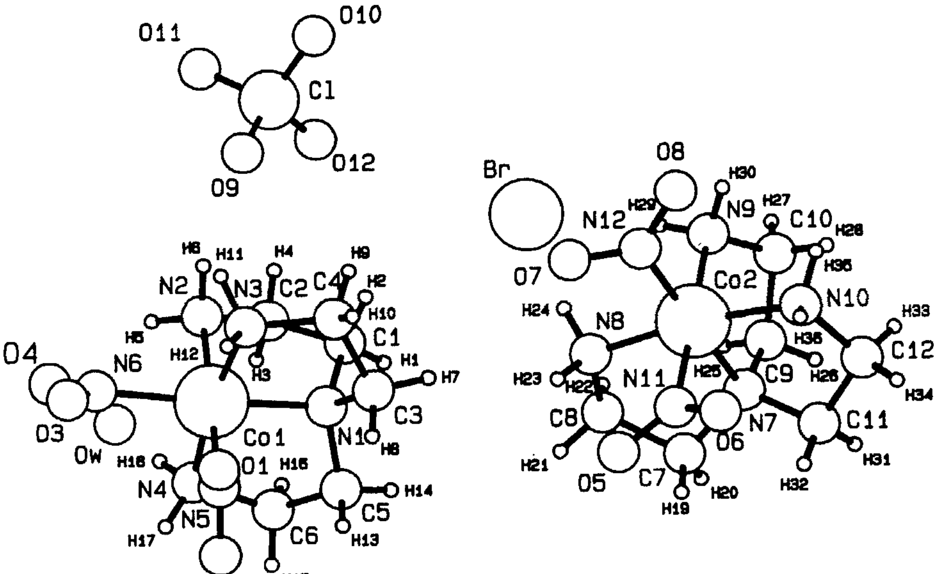

Figure 2 The contents of the asymmetric unit in (**II**). Note that the conformations of the three en rings in Co1 are δδλ (torsional angles of 40.7, 43.5, −41.5°) while conformations of those in Co2 are λλδ (torsional angles of −44.0, −42.1, 39.5°). Thus, the two independent Co cations constitute a racemic pair except for minor deviations in the values of the torsional angles of the five-membered rings.

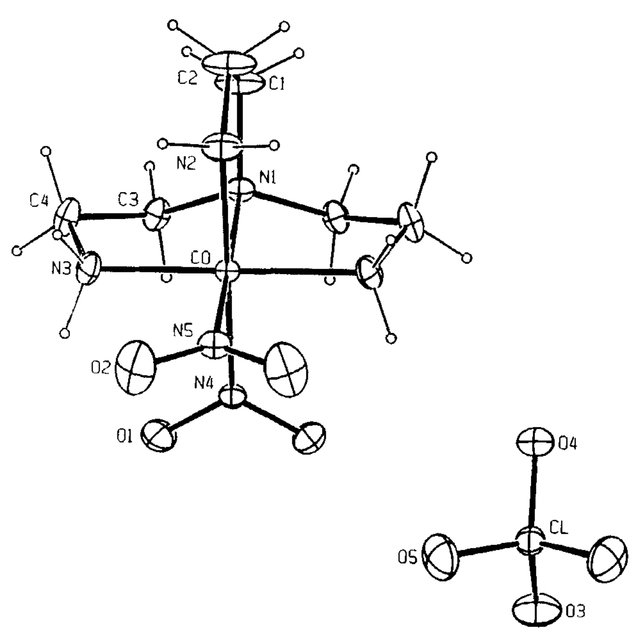

Figure 3 The contents of the asymmetric unit in (**III**). The cation and anion are located at symmetry positions which allows them to be as close as possible. Note that the torsional angles of the five-membered rings differ markedly, that of N1-C1-C2-N2 being only 11.4° while the other two are 49.3° and -35.0°. Also, note that the mirror plane bisects the -NO_2 ligands as well as the ellipsoids of C1 and C2.

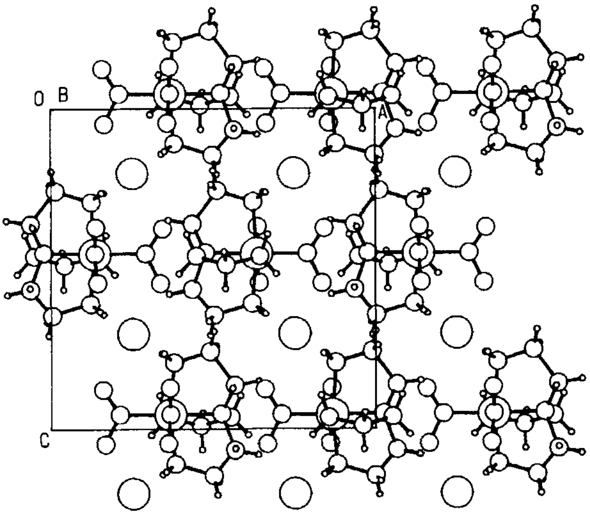

Figure 4 A B-projection of the contents of one layer of the unit cell in (**I**). Note there are helical strings running parallel to the *c* axis and approximately normal to *b* = 0, 1/2 and 1. The cations on adjacent pairs of strings are of opposite chirality since they are related to one another by the mirror planes at *a* = 1/4 and 3/4 (approximately along the two perpendicular rows of Br anions, whose x coordinate is 0.2503).

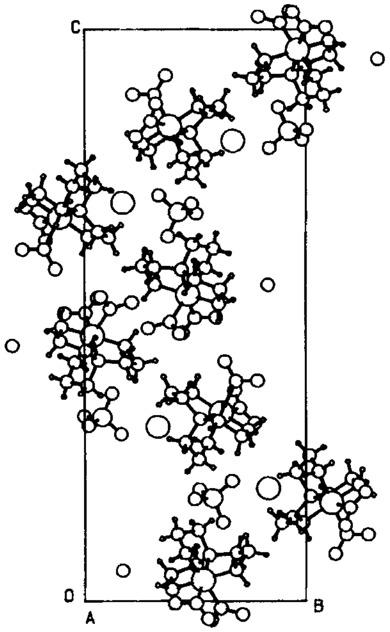

Figure 5 The contents of one layer of the unit cell in (**II**). This projection shows cations of both kinds of Co, both of which form helical strings running parallel to one another along the *z*-axis as well as at angles to the axis. In order to separate the strings made up of only Co1 from those of Co2, Fig. 6 was plotted showing strings containing only Co2 cations.

Fig. 4 depicts the contents of the unit cell of (**I**). Figs. 5 and 6 depict the packing of the unit cell of (**II**). Fig. 5 shows the entire contents of the unit cell of (**II**), while Fig. 6 shows only the packing of Co2 cations. As may be observed at *ca.* $C = 1/2$ and $B = 1/4$, there is a pair of cations sharing a *pseudo*-inversion center between pairs of Co2 cations. The same inversion center is shared by pairs of Co1 cations located at *ca.* $C = 0.7$, $B = -0.15$ and at $C = 0.33$ and $B = 0.6$, as may be verified by reference to Fig. 5. The anions and the water of crystallization also share this *pseudo*-inversion center. Obviously, since both cations of a given pair have the same chiroptical symbol, it is impossible for them to be related by a true inversion center. Finally, it is clear from the pair depicted in Fig. 6, that they are bonded to one another by two hydrogen bonds, one each from the oxygen of one $-NO_2$ ligand to a hydrogen on the axial $-NH_2$ fragment of the adjacent one. The anions and water hydrogen bond the cations in a complex scheme described by the data in Table 6

The packing of the perchlorate (**III**) is depicted in Fig. 7 which is a *b*-projection selected to depict the nature of the interactions between cations and anions present therein. Note that there is an inversion center which divides the lattice in two equal halves, relating pairs of enantiomeric cations as best shown at 1/2, 1/2, 1/2. We are depositing the bond lengths, angles, torsional angles and Structure Factor Tables for this compound since the streochemistry of the cation and anion are no different than those described for these same ions found in compounds (**I**) and (**II**).

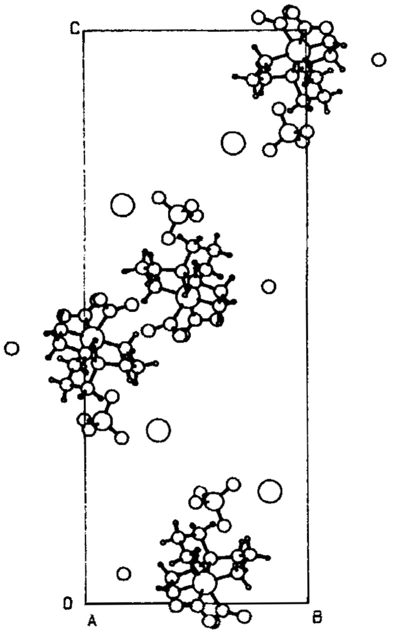

Figure 6 This layer contains exclusively strings made up of Co(2) cations which, in Fig. 5, run parallel to the *c*-axis and consist of alternating Co1 and Co2 cations, related to one another by the *pseudo*-inversion center shown at *ca.* $c = 1/2$, $b = 1/4$. This *pseudo*-inversion center also relates pairs of perchlorates, bromides and waters. The reason for the failure of the *pseudo*-inversion center to become a true inversion center is that it is located between pairs of cations of the same chirality, *e.g.*, Co1 with Co1 and Co2 with Co2.

DISCUSSION

Sometime ago, we described the crystallization behavior of compounds [*cis*-α-Co(trien)$(NO_2)_2$]X · H_2O(V) (X = Cl,[32] I[33]), [*cis*-Co$(en)_2(NO_2)_2$]X (X = Cl,[32] Br,[34] I[35]) all of which crystallize as conglomerates. In the case of K[*cis*-α-Co(edda)$(NO_2)_2$] · nH_2O[36] we found for $n = 0$, a conglomerate while for $n = 1$, a racemate. In these series of conglomerates the exact same pattern of hydrogen-bonded attachments are formed between their transition metal ions, leading to the formation of polymeric, spiral strings resembling helical polypeptides. In all these substances, a three-point attachment between adjacent chiral ions hold the components of the strings together and is reminiscent of the chiral recognition three-point attachment postulated in enzymatic recognition and catalysis. The reader is directed to the original papers for details of the crystallization patterns observed in the aforementioned systems.[32–36]

In the course of analyzing and reporting our results, we provided evidence that the formation of such three-point hydrogen-bonded spiral strings could not be interfered with; otherwise, the crystallization pathway would be altered to that of a racemate.[32–36] Likewise, the nature of the linkages between helices determines whether helices of the same, or opposite, chirality will be used in crystallization.

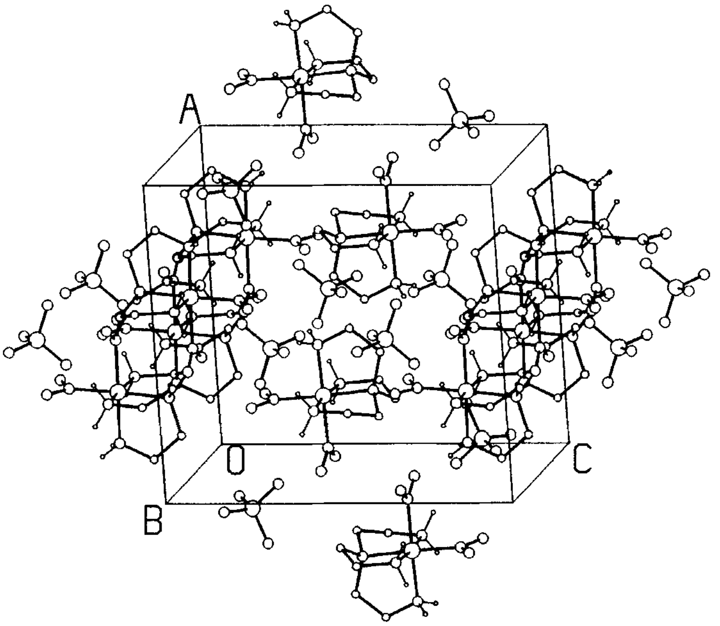

Figure 7 The packing of the ions in **(III)**. Note the that cations are linked to one another by the agency of hydrogen bonds between amine hydrogens of the cations to oxygens of the perchlorate anions.

Interestingly, the linking of spiral strings of equal or opposite chiralities is controlled by achiral species such as halides, potassium ions on where relevant, waters of crystallization.[32–36]

The choice of cations of the compounds comprising the subject of this paper was dictated by our desire to modify the amine system of [*cis*-α-Co(trien)(NO_2)$_2$]$^+$ such that, while much of the system is kept intact, there is either no equatorial -NH hydrogens left in the modified cation, or one of the equatorial positions contains a quaternary nitrogen. The simplest way to block both of the amine equatorial sites of trien is to synthesize a 4,7-N,N′-dimethyltrien ligand.[23] Briefly, the resulting (+/−)-{[*cis*-α-Co(4,7-di-N,N′-methyltrien)(NO_2)$_2$]Cl·H_2O(**VI**) crystals are also examples of kryptoracemates, crystallizing in space group *C*2 ($z = 8$) while those of the iodide (+/−)-{[*cis*-α-Co(4,7-di-N,N′-methyltrien)(NO_2)$_2$]I (**VII**) are true racemates, space group *P*ccn($z = 8$), as we had expected.[23] Thus, the validity of our proposal is demonstrated with the results obtained for (**VII**) while (**VI**) represents an unexpected, variant of our proposed racemate crystallization pathway selection.

Methylating only one of the trien secondary nitrogens is not simple as we learned by methylating both of them, which is a simpler task. An equally effective way of eliminating only one of the equatorial -NH moieties present in the basal plane of the metal, yet making use of a tetradentate amine capable of forming three five-membered rings is using of the ligand tren. The tren ligand should produce racemic crystals irrespective of the counteranion. The results with the bromide(**I**), perchlorate(**III**) and nitrate(**IV**) vindicate our expectations. We also know that crystals of the iodide are racemates(unpublished results).

A sensible suggestion as to why (II) crystallizes as a kryptoracemate with a non-crystallographic, approximate, inversion center between homochiral pairs of cations, while (I), (III) and (IV) are racemates, is based on the following observations: (a) intermolecular interactions between cations of compounds (I) through (IV) cannot have the stereochemistry observed to lead to conglomerates as described earlier,[32–36] It was in order to demonstrate then that the current series of compounds was prepared and, unexpectedly, produced the kryptoracemate (II), but also produced racemates (I), (III) and (IV) (b) the intramolecular hydrogen bonded interactions among cations of all four compunds should be the same were it not for the differing strength and number of the hydrogen bonds from their anions and (c) it is, therefore, these that force the torsional angles of the (amine)N-Co-N-O fragments to differ significantly, as may be appreciated by comparison of their observed values: In (I) these are N1-Co-N5-O1(-89.8), N1-Co-N5-O2 (96.5), N1-Co-N6-O6(60.5) and N1-Co-N6-O3(-119.9); in (II), N1-Co-N5-O1(104.2°), N1-Co-N5-O2(-78.9°), N1-Co-N6-O3(-140.2), N1-Co-N6-O4(48.9), N7-Co-N11-O5(104.2°), N7-Co-N11-O6(102.9°), N7-Co-N12-O7(98.8°) and N7-Co-N12-O8(-75.6°); and, in (III), they are N1-Co-N5-O1 (-93.2), N1-Co-N5-O2 (92.2), N1-Co-N6-O6(92.4) and N1-Co-N6-O3(-88.2). Such changes in torsional angles of the $-NO_2$ ligands force the cations to interact at differing orientations within a string leading to differing probabilities of being able to sustain an inversion center(centrosymmetric structures) or not(polar or enantiomorphic space groups). Finally, the magnitudes of the torsional angles of the N-C-C-N rings also differ by substantial amounts, as documented in the data presented above. Thus, while it appears all these substances seek to crystallize as true racemates, the combination of ions and waters of crystallization present in (II) are thwarted in their attempts to do so by the better intra- and inter-molecular hydrogen-bond patterns offered by an enantiomorphic lattice. The lattice is almost centrosymmetric — witness the *pseudo*-inversion center present which, if perfect, would lead to space group *P*bca or *P*nma. However, the optimal hydrogen bonded interactions lead to positioning the *pseudo*-inversion center between pairs of Co1-Co1 and of Co2-Co2 cations facing a partner of the same chirality, instead of the other way around, as shown with Figs. 5 and 6. Thus, the phenomenon seems to be driven by packing forces between the constituent cations, anions and waters of crystallization, the latter two acting as the hydrogen bonding glue between adjacent sets of cations. A very similar pattern was observed in the crystalline lattices of the other two kryptoracemates studied here; namely, in $[Co(Me_2\text{-trien})(NO_2)_2]Cl \cdot H_2O$[22] and $\{[Co(en)_3][(ox)I]\}_2 \cdot 3H_2O$[23] as well as in $[Co(en)_3]_2[Pb_2Cl_9]Cl \cdot 3H_2O$.[1]

CONCLUSIONS

Two totally different methods of blocking hydrogen bonding from the basal plane of the *cis*-dinitro cations present in (V) lead to the same kryptoracemic crystallization mode. However, it is equally true that not all derivatives of those new cations produce kryptoracemic crystals as shown here and elsewhere.[22,23] Thus, it seems that for each cation there appears to be a very specific glue that leads to racemates, to true enantiomorphs or to kryptoracemates. If this observation is generally valid, simple lattice binding agents, K^+, Br^-, *etc*... (and where relevant, waters of crystallization), are playing a crucial role in processes of chiral discrimination and self-assembly, in spite of the fact that they themselves are achiral. If correct, such a conclusion is rather startling.

The phenomenon is rare enough that, in spite of having several documented examples of cobalt amine cations that crystallize as kryptoracemates, we need more examples before it is possible to guess at the molecular design characteristics which can be expected to produce kryptoracemic crystals. We have not yet seen the master plan that would allows us to predict with any degree of certainty which coordination compounds are reasonable candidates for kryptoracemic crystallization — an obvious conclusion dictated by the fact that each case seems to occur specifically with a given pair of counterions. So far, each example seems to be unique and leaves us, for the moment, unable to generalize on the nature of new potential candidates. As for the organic compounds that share this mode of crystallization,[3] the collection is so eclectic as to be of little use in providing a reasonable basis for identifying the source of this interesting mode of crystallization.

Supplementary Material: H-atom coordinates, thermal parameters and Structure Factor tables for compounds (**I**) and (**II**). Tables of bond lengths, angles, trosional angles and the Structure Factor Table for compound (**III**) are available from Ivan Bernal in hard copy form. The original CAD4.DAT;1 and PSI.DAT;1 files, as well as the Structure Factor tables are also available from Ivan Bernal in PC 3.5″ diskette form (send a double sided, double density one if you wish to receive a copy).

Acknowledgements

We thank the Robert A. Welch Foundation for support of this investigation through Grant E-594 and for Fellowships for Jiwen Cai. We also thank the US National Science Foundation for the funds used to purchase the diffractometers at the University of Houston and at Louisiana State University.

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