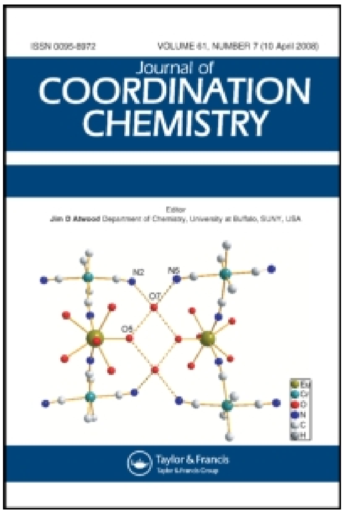

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 48. TWO POLYMORPHS OF RACEMIC TRANS-[CO(2,3,2-TET)$(NO_2)_2$]NO_3 (I AND II)

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 48. TWO POLYMORPHS OF RACEMIC TRANS-[CO(2,3,2-TET)$(NO_2)_2$]NO_3 (I AND II)

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A racemic solution of *trans*-[Co(2,3,2-tet)$(NO_2)_2$]NO_3(I), $CoO_7N_7C_7H_{20}$, crystallizes as a racemate in the centrosymmetric space group, $P2_1/n$ with lattice constants: a = 8.490(2)Å, b = 8.884(2), c = 18.580(2) Å and β = 95.08(1)°; V = 1395.89 Å^3 and d(calc; M.W. = 373.21, Z = 4) = 1.776 g-cm^{-3}. A total of 3489 data were collected over the range of 4° ≤ 2θ ≤ 55°; of these, 2684 (independent and with I ≥ 3s(I)) were used in the structural analysis. Data were corrected for absorption (μ = 12.732 cm^{-1}) and the relative transmission coefficients ranged from 0.7721 to 0.9980. Refinement converged to final residuals of 0.0465 and 0.0541 for $R(F)$ and $R_w(F)$, respectively.

The mother liquor of the same compound, prepared by a different route, produced a second crystalline form of *trans*-[Co(2,3,2-tet)$(NO_2)_2$]NO_3(**II**), $CoO_7N_7C_7H_{20}$, which crystallizes in space group Pn with lattice constants: a = 6.493(5)Å, b = 11.731(4), c = 9.325(4) Å and b = 100.13(9)°; V = 699.21 Å^3 and d(calc; M.W. = 373.21, Z = 2) = 1.773 g-cm^{-3}. A total of 2249 data were collected over the range of 4° ≤ 2θ ≤ 60°; of these, 2012 (independent and with I ≥ 2.5s(I)) were used in the structural analysis. Data were corrected for absorption (μ = 12.732 cm^{-1}) and the relative transmission coefficients ranged from 0.7892 to 0.9345. Refinement converged to final residuals of 0.0301 and 0.0308 for R(F) and R_W(F), respectively.

For (**I**) and (**II**), the central six-membered ring has a chair conformation. The conformational chirality of the two five-membered, outer rings and the asymmetry at the secondary nitrogens, are internally compensated(*meso*) and, with the exception of small deviations at the $-NO_2$ oxygens, the cation has a mirror plane which bisects the central ring. In both cases the asymmetric unit is an ion pair in which nitrate oxygens form bonds with the hydrogens of both terminal $-NH_2$ moieties—the entire array resembling a macrocycle.

The composition of both crystals is identical but while the lattice of both crystals contain racemic pairs, (**I**) is centrosymmetric, while crystals of (**II**) are polar.

Keywords: Conglomerate crystallization; chirality; cobatt complexes; optical activity

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INTRODUCTION

Hereafter, the ligand 1,4,7,10-tetraaminodecane will be referred to as trien, the ligand 1,5,8,12-tetraaminododecane will be referred to as 3,2,3-tet, while the ligand, 1,4,8,11-tetraaminoundecane will be referred to as 2,3,2-tet.

In earlier reports[1–2] derived from our studies on the mechanism of conglomerate crystallization of coordination compounds, and detailing the behavior of *trans*-amine derivatives of Co(III), we suggested that symmetrically substituted, *trans*-compounds such as [*trans*-$Co(en)_2(NO_2)_2$]X (with $X = Cl^-$, I^- and NCS^-)[1], [*trans*-$Co(en)_2(NO_2)_2$][*trans*-$(NH_3)_2Co(NO_2)_2$(oxalato)][2], [*trans*-$Co(en)_2Cl_2$] ClO_4[3a] and [*trans*-$Co(en)_2(NO_2)_2$]ClO_4[3b] crystallize as racemates and the cations are achiral inasmuch as the two five-membered rings are oppositely conformed (*e.g.*, λδ or δλ pairs) in the six examples cited. In fact, the two halides the diniho perchlorate and the oxalato compounds have the cations at crystallographic inversion centers while in the other two compounds they lie at general positions of centrosymmetric space groups. Thus, ring conformations are not the result of the molecule or ion lying at a crystallographic inversion center; rather, it is an inherent property of the molecular system and derived from recognition of the enantiomorphic or centrosymmetric nature of the point group of the ensemble.

At this stage it is useful to point out that in the case of conglomerates of species containing a *trans* pair of en ligands, such as in [*trans*-$Co(en)_2(NO_2)(NCS)$]I, [*trans*-$Co(en)_2(ONO)(NCS)$]I, [*trans*-$Co(en)_2(NO_2)(NCS)$]ClO_4 and [*trans*-$Co(en)_2(ONO)(NCS)$]ClO_4,[4] it has been found that two en rings are in δδ or λλ pairs; *e.g.*, they behave as if they are in an enantiomorphic environment and acquire conformations which render the en rings homochiral. This argument is sound in as much as the species in question lie at general positions of the space group $P2_1$[4] in which neither the symmetry requirements, nor the cell contents, impose any symmetry conditions on the species in question. Thus, the en rings, in theory, acquire conformations attuned to the their environment; *e.g.* they select to be in a δδ or λλ pair when in an enantiomorphic medium and in a δλ or λδ pair when in a centrosymmetric environment, even when located at general positions of the space group. Therefore, it is clear that, in general, the conformation of en rings is acutely sensitive to the enantiomorphic or centrosymmetric properties of the lattice in which they find themselves.

In our earlier reports,[1–2] it was suggested that in the *cis*-series there is a direct link between the ability of the oxygens of the *cis*-dinitro pair to form hydrogen bonds with the axial $-NH_2$ hydrogens and the propensity of the substance to form crystalline conglomerates. However, the very same phenomenon forces [1–2] the *trans*-derivatives to align the NO_2 oxygens with the $-NH_2$ hydrogens such that the symmetrically substituted cations, *de facto*, acquire a molecular inversion center if the anion can sit at an inversion center as well. Crystallographically, the decision of placing these ions at a lattice center is dependent on cation-anion packing forces; however, irrespective of the outcome of that issue, the symmetrically substituted ions belong, ideally, to the point group C_i; and, in fact, often crystallize at inversion centers of centrosymmetric space groups.

In order to show the generality of the concepts outlined above, we prepared the compounds *trans*-[Co(3,2,3-tet)(NO_2)$_2$]Cl·3H_2O (**III**), *trans*-[Co(3,2,3-tet)Cl_2]NO_3(**IV**), and *trans*-[Co(3,2,3-tet)(NO_2)$_2$]NO_3 (**V**) in order to ascertain their crystallization behavior. In all three cases, the secondary nitrogens became chiral upon complexation and must be of the same chirality in order for the secondary hydrogen to be at the axial positions. All three crystallize as conglomerates, with ordered and conformationally chiral five-membered rings.[5] The crystallization pathways of (**I**) and (**II**) are important because they have a pair of five-membered rings on opposite sites of the basal plane in a manner analogous to *trans*-bisethylenediamineCo(III) cations. Models show that the secondary nitrogens of (**I**) and (**II**) should be a heterochiral pair, those of (**III**), (**IV**) and (**V**) are a homochiral pair[5] and there are no secondary nitrogens in bisethylenediamineCo(III). Should these factors play a role in the selection of crystallization path? Finding the answer to this question was the motivation for this study.

EXPERIMENTAL

Syntheses

Compound (**I**) was prepared as follows: 0.04 mol of $Na_3[Co(NO_2)_6]$ was dissolved in 100 mL H_2O while heating in a steam bath. The solution was filtered and treated with 0.04 mol of tren(Fluka Chem Co.) dissolved in 60 mL H_2O. The resulting solution was heated in a steam bath at 80°C for 2.5 hrs, during which time the volume was reduced to half. The resulting brown solution was filtered and an orange-brown precipitate was washed with MeOH (100 mL) The crude solid was recrystallized from hot water to produce orange needles of [*trans*-Co(2,3,2-tet)(NO_2)$_2$]NO_2. The nitrite was converted to the nitrate as follows: [*trans*-Co(2,3,2-tet)(NO_2)$_2$]NO_2 (0.34 g, 1 mmol) dissolved in 30–60 mL H_2O by heating in a steam bath, followed by the addition of 1 g of $NaNO_3$ to the cold solution. Upon standing at room temperature for one day, orange-yellow crystals were obtained which were suitable for the structural study.

Using the ligand 2,3,2-tet(Aldrich) and the synthetic procedure of Basolo[6] for the preparation of [*cis*-α-Co(trien)Cl_2]Cl·3H_2O, which was known from the work of Bosnich[6] to result in the *trans* dichloro derivative of 3,2,3-tet, resulted in [*trans*-Co(2,3,2-tet)Cl_2]Cl·0.5H_2O. A solution (1 mmol, 15 mL H_2O) was heated to 80°C whereupon the solution turned red. It was converted to the *trans* dinitro nitrate (**II**) by addition of solid $NaNO_2$ (2:1) and excess $NaNO_3$ and concentrating the solution in a rotary evaporator. On standing, the concentrated solution produces amber, x-ray quality crystals of (**II**).

Crystallography

Data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[7] of the SDP-Plus software package.[8] The procedure used for crystal alignment, cell constant determination, space group determination, and data collection was the same for both crystals. They were centered with data in the $20° \leq 2\Theta \leq 30°$ range and examination of the cell constants, absences, and Niggli matrix[9] clearly showed (**I**) crystallizes in a primitive, monoclinic lattice. Systematic absences clearly show the presence of a two-fold screw axis and an *n*-glide; thus, its space group is unequivocally $P2_1/n$. Compound (**II**) also crystallizes in a primitive, monoclinic space group; however, since the only systematic absences are those of an *n*-glide, the space group is either *Pn* or *P2/n*— a choice which was decided by solution and refinement of the structure (see below). Data processing for (**I**) was carried out with the Nonius package[7,8] while that of (**II**) used the PC version of NRCVAX.[10]

The details of data collection are summarized in Tables I and II for compounds (**I**) and (**II**) respectively. The intensity data sets were corrected for absorption using empirical curves derived from psi scans 7–8 of suitable reflections.

TABLE I Summary of data collection and processing parameters for racemic *trans*-[Co(2,3,2-tet)$(NO_2)_2$]NO_3 (**I**)

Space Group	$P2_1/n$
Cell Constants	$a = 8.490\ (2)$ Å
	$b = 8.884\ (2)$
	$c = 18.580\ (2)$
	$\beta = 100.13(9)°$
Cell Volume	$V = 1395.89$ Å^3
Molecular Formula	$CoO_7N_7C_7H_{20}$
Molecular Weight	373.21 g-mole^1
Density (calc; $z = 4$ mol/cell)	1.776 g-cm^{-3}
Radiation Employed	MoKα ($\lambda = 0.71073$Å)
Absorption Coefficient	$\mu = 12.732$ cm^{-1}
Relative Transmission Coefficients	0.7821 to 0.9981
Data Collection Range	$4° \leq 2\Theta \leq 55°$
Scan Width	$\Delta\Theta = 1.0 + 0.35\tan\Theta$
Total Data Collected	3489

TABLE I (*Continued*)

Data Used In Refinement*	2684
$R = \Sigma\| \|F_o\| - \|F_c\| \|/\Sigma\|F_o\|$	0.0472
$Rw = [\Sigma w\ (\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.0548
Weights Used	$w = [\sigma(F_o)]^{-2}$

*The difference between this number and the total is due to subtraction of 805 data that were systematically absent reflections, redundant data collected to obtain reflections suitable for the absorption correction, symmetry related, standards or did not meet the criterion that I ≥ 3σ(I).

TABLE II Summary of data collection and processing parameters for racemic *trans*-[Co(2,3,2-tet)(NO_2)$_2$]NO_3 (**II**)

Space Group	Pn (No. 7)
Cell Constants	a = 6.493 (5) Å
	b = 11.731 (4)
	c = 9.325 (4)
	β = 100.13 (9)°
Cell Volume	$V = 699.21 Å^3$
Molecular Formula	$CoO_7N_7C_7H_{20}$
Molecular Weight	373.21 g-mole[1]
Density (calc; z = *2 mol/cell)*	1.773 $g\text{-}cm^{-3}$
Radiation Employed	MoKα (l = 0.71073Å)
Absorption Coefficient	$\mu = 12.732 cm^{-1}$
Relative Transmission Coefficient	0.7892 to 0.9345
Data Collection Range	4° ≤ 2Θ ≤ 60°
Scan Width	ΔΘ = 1.0 + 0.35tanΘ
Total Data Collected	2249
Data Used In Refinement*	2012
$R=\Sigma\| \|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0301
$Rw=[\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.0308
Weights Used	$w = [\sigma(F_o)]^{-2}$

*The difference between this number and the total is due to subtraction of 237 data that were systematically absent reflections, redundant data collected to obtain reflections suitable for the absorption correction, symmetry related, standards or did not meet the criterion that I ≤ 2.5 σ (I).

The structures were solved from their Patterson maps using the Co atom as the heavy atom. For compound (**II**) the solution of the structure was weighed in favor of the *Pn* choice since with $z = 2$ the molecule would be at a special position of the space group *P*2/*n* demanding disorder of the cation. We find no such disorder problem in the lower space group and the refinement was smooth as shown in Table II.

After refinement of the scale factor and the positional parameters of the Co, a difference Fourier map produced, in both cases, most of the non-hydrogen atoms. The remaining atoms were found in subsequent difference maps. Heavy atoms were refined isotropically until convergence, at which point the hydrogen atoms of the cations were added at idealized positions (N-H, C-H = 0.95 Å) and all atoms were allowed to refine with hydrogen thermal parameters fixed. Conversion of the heavy atoms to anisotropic motion and allowing the hydrogens to refine their isotropic thermal parameters resulted in refinement of the overall structure to final *R*(*F*) and $R_w(F)$ factors listed in Tables I and II which summarize other details of the data collection and processing.

Figures 1 and 2 give labeled views of the molecules. Figures 3 and 4 depict the packing of the ions in their respective unit cells. Final positional and equivalent-isotropic thermal parameters are given in Tables III and IV. Bond lengths, angles an other significant data are listed in Tables V and VI.

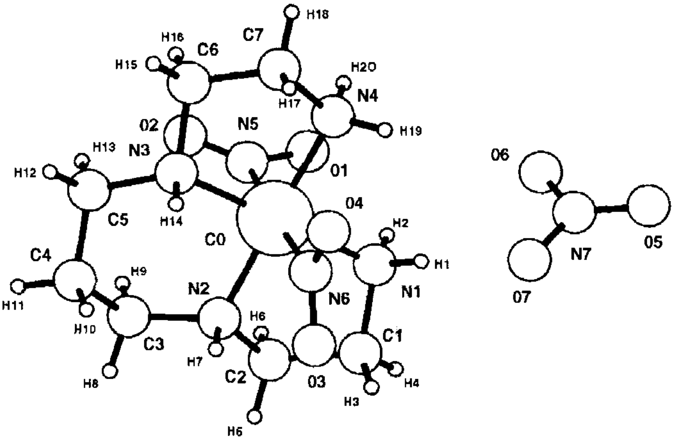

FIGURE 1 A view of the asymmetric unit of (**I**). Note the position of the nitrate anion with respect to the terminal -NH_2 hydrogens of N1 and N4. If the hydrogen bonds (O7...H1 = 2.154 Å and O6...H1 = 2.425 Å, while O19...H6 is larger than 2.50 Å, the limit used) are taken into account, the resulting 'macrocycle' contain chiral centers at N1 and N4, inasmuch as the two hydrogens are now rendered unequal. Both are R, as explained in the text.

TABLE III Positional Parameters and Their esd's for I

Atom	*x*	*y*	*z*	*B*($Å^2$)
Co	0.33952(5)	0.18361(5)	0.12460(2)	1.611(7)
O1	0.3266(5)	0.0979(6)	−0.0180(2)	7.4(1)
O2	0.5185(5)	0.2300(5)	0.0072(2)	6.9(1)
O3	0.1626(5)	0.2634(4)	0.2383(2)	5.64(8)
O4	0.3158(4)	0.0890(4)	0.2651(2)	5.64(8)
O5	−0.1159(4)	−0.3251(4)	0.1482(2)	6.5(1)
O6	0.0401(4)	−0.2076(4)	0.0824(2)	5.15(8)
O7	−0.0240(5)	−0.1088(4)	0.1807(2)	5.20(8)
N1	0.1265(4)	0.1278(4)	0.0854(2)	2.71(6)
N2	0.2658(3)	0.3915(3)	0.1134(1)	1.84(5)
N3	0.5506(3)	0.2400(3)	0.1695(2)	2.03(5)
N4	0.4133(4)	−0.0267(3)	0.1365(2)	2.55(6)
N5	0.4084(4)	0.1778(3)	0.0233(2)	2.14(5)
N6	0.2624(3)	0.1776(3)	0.2214(2)	2.07(5)

TABLE III (*Continued*)

Atom	*x*	*y*	*z*	*B(Å^2)*
N7	-0.0350(4)	-0.2153(4)	0.1371(2)	3.21(7)
C1	0.0207(5)	0.2616(5)	0.0819(2)	3.30(9)
C2	0.1197(5)	0.3932(5)	0.0636(2)	2.87(8)
C3	0.3778(5)	0.5109(4)	0.0942(2)	2.74(7)
C4	0.5221(5)	0.5177(4)	0.1473(2)	2.98(8)
C5	0.6293(4)	0.3812(4)	0.1467(2)	2.67(7)
C6	0.6584(4)	0.1086(4)	0.1648(2)	2.79(8)
C7	0.5679(5)	-0.0314(4)	0.1802(2)	2.90(8)
H1	0.0856	0.0537	0.1156	4 *
H2	0.1306	0.0878	0.0382	4 *
H3	-0.0204	0.2771	0.1271	4 *
H4	-0.0640	0.2478	0.0455	4 *
H5	0.0633	0.4841	0.0694	4 *
H6	0.1457	0.3852	0.0150	4 *
H7	0.2490	0.4209	0.1613	4 *
H8	0.3253	0.6054	0.0937	4 *
H9	0.4098	0.4903	0.0474	4 *
H10	0.4881	0.5275	0.1944	4 *
H11	0.5818	0.6039	0.1364	4 *
H12	0.7207	0.3988	0.1788	4 *
H13	0.6594	0.3675	0.0991	4 *
H14	0.5298	0.2661	0.2173	4 *
H15	0.7470	0.1189	0.1994	4 *
H16	0.6935	0.1030	0.1177	4 *
H17	0.5517	-0.0355	0.2300	4 *
H18	0.6255	-0.1176	0.1674	4 *
H19	0.3380	-0.0830	0.1601	4 *
H20	0.4243	-0.0691	0.0902	4 *

* Hydrogen atoms were added at idealized positions with fixed thermal parameters of 4.0 Å^2. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) * [$a^2*\beta_{11}+b^2*\beta_{22}+c^2*\beta_{33}+ab(\cos\gamma)*\beta_{12}+ac(\cos\beta)*\beta_{13}+ bc(\cos\alpha)*\beta_{23}$

TABLE IV Atomic parameters *x*, *y*, *z* and biso. for compound II E.S.Ds. refer to the last digit printed

	x	*y*	*z*	*Biso*
Co	0.25000	0.20969(4)	0.25000	1.260(15)
O1	-0.1620(8)	0.2078(4)	0.1197(7)	3.42(20)
O2	-0.0715(7)	0.3748(4)	0.1919(6)	4.08(19)
O3	0.6668(8)	0.1876(5)	0.3859(7)	3.60(21)
O4	0.5377(7)	0.0323(4)	0.2954(6)	4.64(21)
O5	0.1290(7)	0.8747(4)	0.2129(6)	4.16(20)
O6	0.1402(9)	0.6923(4)	0.1860(6)	4.98(21)
O7	0.4064(7)	0.7789(5)	0.3028(6)	4.94(24)
N1	0.2181(6)	0.1156(4)	0.0748(5)	2.13(14)
N2	0.4047(6)	0.3169(3)	0.1440(4)	1.72(12)
N3	0.2973(6)	0.3007(4)	0.4305(4)	1.91(13)
N4	0.1136(6)	0.0988(3)	0.3577(5)	2.11(15)
N5	-0.0236(6)	0.2758(4)	0.1778(4)	2.05(14)
N6	0.5172(6)	0.1326(4)	0.3194(4)	2.03(13)
N7	0.2235(9)	0.7822(4)	0.2345(7)	2.47(20)
C1	0.3531(9)	0.1588(5)	-0.0249(7)	2.26(20)

TABLE IV (*Continued*)

	x	*y*	*z*	*Biso*
C2	0.3564(12)	0.2862(6)	−0.0132(9)	2.50(22)
C3	0.3898(8)	0.4409(4)	0.1700(6)	2.49(19)
C4	0.4519(8)	0.4702(4)	0.3286(6)	2.67(19)
C5	0.3023(8)	0.4265(4)	0.4242(6)	2.60(19)
C6	0.1512(11)	0.2587(7)	0.5238(8)	2.6(3)
C7	0.1498(10)	0.1294(6)	0.5148(8)	2.82(23)
H1	0.076	0.118	0.027	2.9
H2	0.256	0.039	0.101	2.9
H3	0.491	0.129	0.002	3.0
H4	0.298	0.137	−0.122	3.0
H5	0.224	0.316	−0.056	3.3
H6	0.461	0.316	−0.062	3.3
H7	0.546	0.296	0.178	2.5
H8	0.480	0.480	0.116	3.3
H9	0.250	0.465	0.137	3.3
H10	0.586	0.438	0.363	3.4
H11	0.459	0.551	0.337	3.4
H12	0.166	0.453	0.386	3.4
H13	0.345	0.455	0.520	3.4
H14	0.433	0.277	0.476	2.7
H15	0.197	0.282	0.622	3.4
H16	0.015	0.288	0.490	3.4
H17	0.041	0.099	0.560	3.6
H18	0.280	0.100	0.562	3.6
H19	0.170	0.025	0.346	2.9
H20	−0.032	0.098	0.321	2.9

Biso is the mean of the principal axes of the thermal ellipsoid

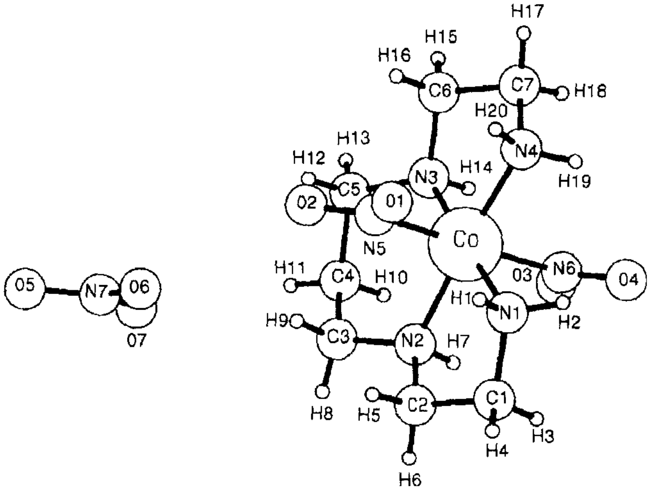

FIGURE 2 A view of the asymmetric unit of (**II**). The position of the anion can be switched by a symmetry operation such that it has the same relative position with respect to the terminal NH_2 moieties as in the case of (**I**), see Discussion. Thus, the same comments concerning the chirality of N1 and N4 made in the caption of Figure 1 apply here; however, they are an RS pair in this case (see text).

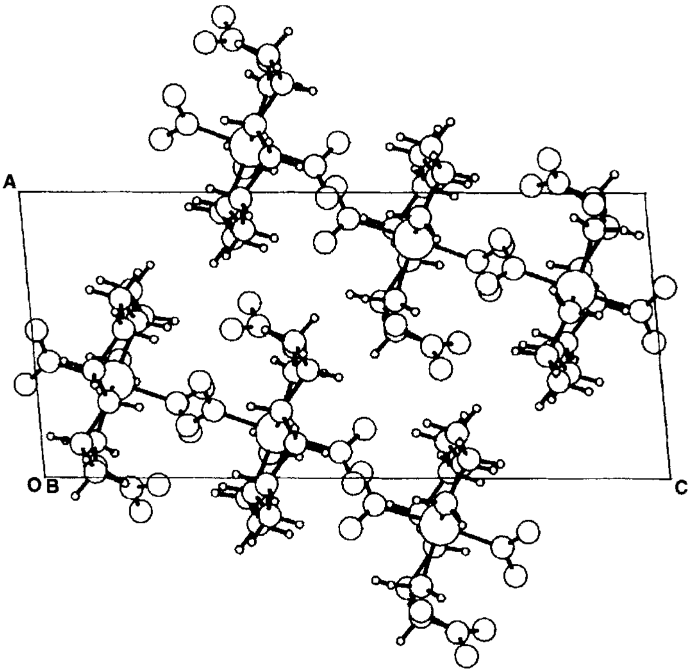

FIGURE 3 A view down the *b*-direction displaying the packing of the ions and waters in the unit cell of (**I**). The inversion center at 1/2, 1/2, 1/2 is evident. Note the direction of the Co-N(O$_2$) vectors, which differ from the direction of those vectors in (**II**), and the hydrogen bonds between -NO$_2$ oxygens and terminal amino hydrogens, as well as hydrogen bonds between nitrate anion oxygens and amino hydrogens.

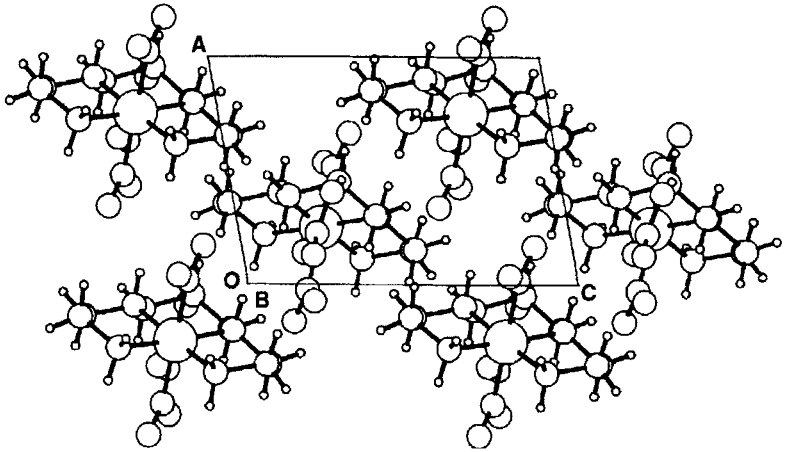

FIGURE 4 A view of the packing of the ions in the unit cell of (**II**). As in the case of (**I**), this is an [010] projection showing the hydrogen bonds between -NO$_2$ oxygens and amino hydrogens. However, note that the direction of the Co-NO$_2$ vectors is different in the two cases.

TABLE V Bond Distances (Å) and Angles (°) for I

A) Distances

Atom1	*Atom2*	*Distance*	*Atom1*	*Atom2*	*Distance*	*Atom1*	*Atom2*	*Distance*
Co	N1	1.953(1)	O3	N6	1.202(2)	N3	C5	1.500(2)
Co	N2	1.956(1)	O4	N6	1.191(2)	N3	C6	1.490(2)
Co	N3	1.973(1)	O5	N7	1.222(2)	N4	C7	1.482(2)
Co	N4	1.976(1)	O6	N7	1.248(2)	C1	C2	1.496(2)
Co	N5	2.020(1)	O7	N7	1.243(2)	C3	C4	1.505(2)
Co	N6	1.968(1)	N1	C1	1.487(2)	C4	C5	1.517(2)
O1	N5	1.217(2)	N2	C2	1.480(2)	C6	C7	1.503(2)
O2	N5	1.107(2)	N3	C3	1.489(2)			

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	85.58(5)	N4	Co	N6	90.01(5)	Co	N6	O3	121.4(1)
N1	Co	N3	176.86(5)	N5	Co	N6	176.03(5)	Co	N6	O4	120.2(1)
N1	Co	N4	94.35(5)	Co	N1	C1	110.44(9)	O3	N6	O4	118.4(1)
N1	Co	N5	88.94(5)	Co	N2	C2	108.56(9)	O5	N7	O6	121.2(2)
N1	Co	N6	87.80(5)	Co	N2	C3	119.54(8)	O5	N7	O7	120.5(2)
N2	Co	N3	94.34(5)	C2	N2	C3	111.1(1)	O6	N7	O7	118.3(1)
N2	Co	N4	179.63(4)	Co	N3	C5	120.22(9)	N1	C1	C2	106.6(1)
N2	Co	N5	92.38(4)	Co	N3	C6	108.45(9)	N2	C2	C1	107.9(1)
N2	Co	N6	89.63(5)	C5	N3	C6	110.3(1)	N2	C3	C4	111.8(1)
N3	Co	N4	85.72(5)	Co	N4	C7	110.18(9)	C3	C4	C5	114.6(1)
N3	Co	N5	94.19(5)	Co	N5	O1	114.0(1)	N3	C5	C4	112.6(1)
N3	Co	N6	89.07(5)	Co	N5	O2	124.2(1)	N3	C6	C7	108.1(1)
N4	Co	N5	87.98(5)	O1	N5	O2	121.5(2)	N4	C7	C6	108.4(1)

C) Torsional Angles

Atom 1	*Atom 2*	*Atom 3*	*Atom 4*	*Angle*	*Atom 1*	*Atom 2*	*Atom 3*	*Atom 4*	*Angle*
N2	Co	N1	C1	−10.4	N2	Co	N5	O1	−109.7
N3	Co	N1	C1	78.1	N2	Co	N5	O2	77.6
N4	Co	N1	C1	169.2	N3	Co	N5	O1	155.8
N5	Co	N1	C1	−102.9	N3	Co	N5	O2	−16.9
N6	Co	N1	C1	79.4	N4	Co	N5	O1	70.2
N1	Co	N2	C2	−17.2	N4	Co	N5	O2	−102.5
N1	Co	N2	C3	−146.0	N6	Co	N5	O1	10.6
N3	Co	N2	C2	165.9	N6	Co	N5	O2	−162.1
N3	Co	N2	C3	37.1	N1	Co	N6	O3	−64.1
N4	Co	N2	C2	−95.2	N1	Co	N6	O4	116.8
N4	Co	N2	C3	136.0	N2	Co	N6	O3	21.5
N5	Co	N2	C2	71.6	N2	Co	N6	O4	157.6
N5	Co	N2	C3	−57.3	N3	Co	N6	O3	115.8
N6	Co	N2	C2	−105.0	N3	Co	N6	O4	−63.3
N6	Co	N2	C3	126.1	N4	Co	N6	O3	−158.4
N1	Co	N3	C5	−122.6	N4	Co	N6	O4	22.5
N1	Co	N3	C6	109.3	N5	Co	N6	O3	−98.8
N2	Co	N3	C5	−34.3	N5	Co	N6	O4	82.1
N2	Co	N3	C6	−162.5	Co	N1	C1	C2	35.2
N4	Co	N3	C5	146.1	Co	N2	C2	C1	41.2
N4	Co	N3	C6	17.9	C3	N2	C2	C1	174.6
N5	Co	N3	C5	58.4	Co	N2	C3	C4	−56.2
N5	Co	N3	C6	−69.8	C2	N2	C3	C4	176.1
N6	Co	N3	C5	−123.9	Co	N3	C5	C4	50.2

TABLE V (*Continued*)

N6	Co	N3	C6	108.0	C6	N3	C5	C4	177.5
N1	Co	N4	C7	-168.5	Co	N3	C6	C7	-40.2
N2	Co	N4	C7	-90.6	C5	N3	C6	C7	-173.8
N3	Co	N4	C7	8.3	Co	N4	C7	C6	-32.6
N5	Co	N4	C7	102.7	N1	C1	C2	N2	-49.5
N6	Co	N4	C7	-80.7	N2	C3	C4	C5	67.2
N1	Co	N5	O1	-24.2	C3	C4	C5	N3	-64.1
N1	Co	N5	O2	163.2	N3	C6	C7	N4	47.7

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

TABLE VI Bond distances (Å) and bond angles (°)

A. Bond distances

Co—N1	1.953(4)	O7—N7	1.245(7)
Co—N2	1.979(4)	N1—C1	1.475(8)
Co—N3	1.972(4)	N2—C2	1.488(9)
Co—N4	1.949(4)	N2—C3	1.480(6)
Co—N5	1.946(4)	N3—C5	1.477(7)
Co—N6	1.963(4)	N3—C6	1.480(8)
O1—N5	1.252(6)	N4—C7	1.486(8)
O2—N5	1.216(6)	C1—C2	1.499(9)
O3—N6	1.238(7)	C3—C4	1.503(8)
O4—N6	1.209(6)	C4—C5	1.518(8)
O5—N7	1.246(6)	C6—C7	1.519(11)
O6—N7	1.233(6)		

B. Bond angles

N1—Co—N2	85.98(17)	Co—N3—C6	107.5(4)
N1—Co—N3	176.85(16)	C5—N3—C6	112.2(5)
N1—Co—N4	93.62(19)	Co—N4—C7	109.9(3)
N1—Co—N5	88.84(19)	Co—N5—O1	116.0(4)
N1—Co—N6	88.43(19)	Co—N5—O2	125.3(3)
N2—Co—N3	93.77(17)	O1—N5—O2	118.5(4)
N2—Co—N4	176.46(16)	Co—N6—O3	119.7(4)
N2—Co—N5	94.98(16)	Co—N6—O4	120.5(3)
N2—Co—N6	87.74(16)	O3—N6—O4	119.8(4)
N3—Co—N4	86.44(18)	O5—N7—O6	120.9(5)
N3—Co—N5	94.30(18)	O5—N7—O7	120.5(5)
N3—Co—N6	88.43(18)	O6—N7—O7	118.6(5)
N4—Co—N5	88.52(17)	N1—C1—C2	107.4(5)
N4—Co—N6	88.74(17)	N2—C2—C1	108.1(5)
N5—Co—N6	176.00(18)	N2—C3—C4	111.8(4)
Co—N1—C1	110.2(3)	C3—C4—C5	114.3(4)
Co—N2—C2	107.5(4)	N3—C5—C4	112.4(4)
Co—N2—C3	119.3(3)	N3—C6—C7	107.4(5)
C2—N2—C3	113.0(4)	N4—C7—C6	107.1(5)
Co—N3—C5	120.5(3)		

C. Torsion angles

N2	Co	N1	C1	11.0(3)	N3	Co	N1	C1	-74.5(3)
N4	Co	N1	C1	-165.5(4)	N5	Co	N1	C1	106.1(3)
N6	Co	N1	C1	-76.8(3)	N1	Co	N2	C2	16.4(3)

TABLE VI (*Continued*)

N1	Co	N2	C3	146.6(3)	N3	Co	N2	C2	–166.8(4)
N3	Co	N2	C3	–36.5(2)	N4	Co	N2	C2	100.0(3)
N4	Co	N2	C3	–129.8(3)	N5	Co	N2	C2	–72.1(3)
N5	Co	N2	C3	58.1(2)	N6	Co	N2	C2	105.0(3)
N6	Co	N2	C3	–124.8(3)	N1	Co	N3	C5	120.2(3)
N1	Co	N3	C6	–109.5(4)	N2	Co	N3	C5	34.9(2)
N2	Co	N3	C6	165.2(4)	N4	Co	N3	C5	–148.7(3)
N4	Co	N3	C6	–18.4(3)	N5	Co	N3	C5	–60.4(3)
N5	Co	N3	C6	69.9(3)	N6	Co	N3	C5	122.5(3)
N6	Co	N3	C6	–107.2(4)	N1	Co	N4	C7	167.1(4)
N2	Co	N4	C7	83.7(3)	N3	Co	N4	C7	–9.7(3)
N5	Co	N4	C7	–104.2(3)	N6	Co	N4	C7	78.8(3)
N1	Co	N5	O1	41.2(3)	N1	Co	N5	O2	–143.0(4)
N2	Co	N5	O1	127.1(4)	N2	Co	N5	O2	–57.1(3)
N3	Co	N5	O1	–138.7(4)	N3	Co	N5	O2	37.0(3)
N4	Co	N5	O1	–52.4(3)	N4	Co	N5	O2	123.4(3)
N6	Co	N5	O1	–5.7(3)	N6	Co	N5	O2	170.1(4)
N1	Co	N6	O3	142.2(4)	N1	Co	N6	O4	–36.5(3)
N2	Co	N6	O3	56.1(3)	N2	Co	N6	O4	–122.6(3)
N3	Co	N6	O3	–37.7(3)	N3	Co	N6	O4	143.6(4)
N4	Co	N6	O3	–124.2(4)	N4	Co	N6	O4	57.1(3)
N5	Co	N6	O3	–170.9(4)	N5	Co	N6	O4	10.4(3)
Co	N1	C1	C2	–35.8(3)	Co	N2	C2	C1	–40.2(3)
C3	N2	C2	C1	–173.9(7)	Co	N2	C3	C4	55.7(3)
C2	N2	C3	C4	–176.6(6)	Co	N3	C5	C4	–51.8(3)
C6	N3	C5	C4	–180.0(6)	Co	N3	C6	C7	42.0(3)
C5	N3	C6	C7	176.8(7)	Co	N4	C7	C6	35.0(3)
N1	C1	C2	N2	49.9(4)	N2	C3	C4	C5	–67.6(4)
C3	C4	C5	N3	65.4(4)	N3	C6	C7	N4	–50.5(4)

RESULTS AND DISCUSSION

From the outset, it should be clear that the contents of the asymmetric unit need not be chiral in order for a substance to crystallize in an enantiomorphic lattice (for example, $NaClO_3$ crystallizes from water in space group $P2_13$), and within the class of compounds under consideration, there is ample documentation that this needs not always be the case. For example, the double salt {[Δ-Co(en)$_2$(ox)][Λ-Co(en)$_2$(ox)]}(ox) was studied by Fuyuhiro, *et al.*[13] who demonstrated it crystallizes in an undisclosed enantiomorphic space group (hemihedral faces are clearly developed) but containing **two** cations in the asymmetric unit, enantiomorphically related to one another (for details, [13]). Thus, the asymmetric unit is a racemate whose structure is under investigation here. We have observed similar examples[14–16] of enantiomorphic lattices whose asymmetric units are racemic pairs and, since we have completed their crystal structures already, we can categorically state the pair of cations present in ours are racemic pairs related to one another by imperfect, non-crystallographic inversion centers.

Such a mode of crystallization has been labeled[14–16] 'kryptoracemic crystallization'. A summary is given below:

Compound	Sp.Group(z)	Reference
$\{[CO(en)_3](ox)I\}_2 \cdot 3H_2O$	$P2_12_12_1(8)$	14
$[CO(tren)(NO_2)_2]_2(ClO_4)Br$	$P2_12_12_1(8)$	15
[*cis*-Co(4,7-dimethyltrien(N0$_2$)$_2$]Cl	C2(8)	16

Therefore, momentarily ignoring the, thus far rare form of kryptoracemic crystallization, and taking only into account the information provided in the Introduction, it seems that some *trans*-[Co(en)$_2$XY]Z systems are capable of crystallizing in enantiomorphic space groups and that the conformation of the en rings reflect the homo- or hetero-chiral nature of the lattice. That is, those crystallizing in centrosymmetric space groups invariably have a pair of δλ conformed en rings, while those selecting enantiomorphic space groups have δδ (or λλ) rings. That a pair of δλ rings are present in the cations crystallizing at inversion centers of a centrosymmetric space group occur is easily understood; however, comparison of the crystallization behavior of [*trans*-Co(en)$_2$(NO$_2$)$_2$]X (with X = Cl$^-$, I$^-$ and NCS$^-$)[1] reveals the two halides place the cations and anions at inversion centers while the latter, not being able to place the anions thus, crystallizes as a racemate (space group $P\bar{1}$ (No. 2) with both ions at general positions of the space group, and each cation has a pair of δλ rings. Since it is crystallographically possible to have a pair of δδ and λλ cations related by an inversion center of space group $P\bar{1}$, we find it interesting that such a situation seems not to have been observed despite the observations made above about kryptoracemic crystallization. Likewise, the *trans*-bis(en)$_2$Co(III) compounds crystallizing in enantiomorphic space groups, with cations at general positions invariably have a pair of equally conformed (δδ or λλ) en rings, despite the fact that in space groups such as $C2$, $P2_1$, $P2_12_12_1$, *etc*... cations, related exclusively by a screw axis, could contain opposite conformed en rings without violations of crystallographic principles. The suggestion is, therefore, that these rings are acutely aware of enantiomorphism (or lack thereof) of the space groups into which they crystallize, and *vice-versa*.

We selected compound (**I**) without expecting that the two synthetic procedures devised (for (**I**) in Alexandria, that for (**II**) in Houston) would give rise to two different crystalline phases of the same compound, whose structures we now discuss. This is a rare opportunity to observe the difference in packing phenomena in polymorphic phases of coordination compounds of identical composition.

Compound (**I**) crystallizes in a centrosymmetric crystal lattice in which pairs of enantiomers are related to one another by inversion centers, there being two pairs of the same chirality in this case. From Figure 1, one can see that if the entire ion pair is assumed to be a single entity in the solid state, it resembles a macrocycle. The same, applies to the ion pair present in (**II**); therefore, comments made earlier[17–18] concerning the crystallization pathway selected by macrocycles and 'macrocycle-like' species and how the chiral nature of the ligand nitrogens and the chiral conformation of the five-membered rings influence such a selection applies here also. Briefly, in (**I**) and (**II**), the central ring is achiral, its two secondary nitrogens are a heterochiral (RS) pair and the, outer, five-membered rings are oppositely conformed; therefore, under the rules suggested previously,[17–18] both these compounds are likely to crystallize as racemates. Interestingly, (**I**) and (**II**) have identical compositions and differ exclusively in the nature of the mother liquor from which they were crystallized (with possibly a small different in temperature during crystallization); yet, the contents of both lattices are racemic pairs.

Concerning the chirality at the terminal amino nitrogens: in the case of (**I**), the relevant (2.50 Å, or less) hydrogen bonds to the nitrate oxygens are H1 ... O7, H1 ... O6 and H19...O6, while in the case of (**II**) they are H2...O5, H19...O5. The asymmetry (in length) of those hydrogen bonds render the terminal nitrogens chiral centers, thus: if we define the priority sequence of the fragments bound to the terminal amino nitrogens as Co > carbon fragment > HX(bonded to nitrate) > HY(long or no hydrogen bond), the chirality at the terminal nitrogens of (**I**) is RR, while in (**II**) they are a mesomeric (RS) pair. On the other hand, the secondary nitrogens are a mesomeric (RS) pair in both compounds; therefore, chirality at the terminal nitrogens seems to be of little or no consequence in selecting the crystallization pathway while the earlier suggestion[17–18] that homochirality at the secondary nitrogens may be decisive appears to hold out with (**I**) and (**II**).

The packing differs qualitatively in the two polymorphs in the sense of relative orientation of Co-N(O_2) vectors with respect to the axes of the crystalline cell. Yet, not much can be made of that inasmuch as the two calculated densities are the same within a very tiny difference (0.004 gm-cm^{-3}, see Tables I and II).

In conclusion: (a) the *trans*-cations in (**I**) and (**II**) behave as the majority of *trans*-dinitro cobalt amines mentioned in the Introduction, namely they tend to crystallize as racemates[1–4] (b) the suggested rules of behavior for the selection of crystallization mode[17–18] are also capable of predicting the crystallization behavior of (**I**) and (**II**) (c) this study clearly demonstrates that chirality at the terminal amine nitrogens is not a decisive factor in the selection of the crystallization mode—otherwise, (**I**) and (**II**) would crystallize differently; while, in fact, both are racemates even though (**I**) is a centrosymmetric lattice while (**II**) is polar. Finally, we expect to examine a few more derivatives of (2,3,2-tet)Co cations to determine if any of them crystallize as conglomerates, as observed for a number of (3,2,3-tet)Co amine cations.[17–18] If so, we will attempt to ascertain why and how those differ in the crystallization and packing behavior from the current molecules.

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SUPPLEMENTARY MATERIAL AVAILABLE:

The original CAD4.DAT;1 file, anisotropic thermal parameters and structure factor tables for both compounds are available in hard copy or PC diskette format from I. Bernal.

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