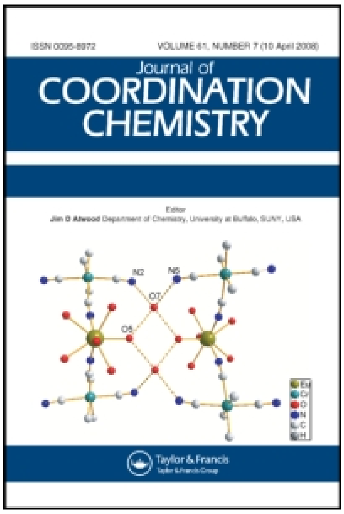

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 47. COUNTERION CONTROL OF THE CRYSTALLIZATION PATHWAY. PART 8. THE CRYSTALLIZATION BEHAVIOR OF [*trans*-Co(3, 2, 3-tet)$(NO_2)_2$] CLO_4 (I), *trans*-Co(3, 2, 3-tet)$(NO_2)_2$] BR · $3H_2O$ (II) AND [*trans*-Co(3, 2, 3-tet)$(NO_2)_2$]I (III)

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 47. COUNTERION CONTROL OF THE CRYSTALLIZATION PATHWAY. PART 8. THE CRYSTALLIZATION BEHAVIOR OF [*trans*-Co(3, 2, 3-tet)(NO$_2$)$_2$] CLO$_4$ (I), [*trans*-Co(3, 2, 3-tet)(NO$_2$)$_2$] BR · 3H$_2$O (II) AND [*trans*-Co(3, 2, 3-tet)(NO$_2$)$_2$]I (III)

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[*trans*-Co(3,2,3-tet)(NO$_2$)$_2$]ClO$_4$ (**I**, $CoClO_8H_6C_8H_{22}$, crystallizes, at 22°C, from a deionized water solution in space group $P2_1/n$ (a variant of No. 14), with lattice constants: a = 10.782(3), b = 9.198(3), c = 17.031(5) Å, β = 105.30(2)°; V = 1629.14 Å^3 and d(calc; MW = 424.69, Z = 4) = 1.731 g-cm^{-3}. A total of 3217 data were collected over the range of $4° \le 2\theta \le 50°$; of these, 2393 (independent and with $\mathbf{I} \ge (2.5\sigma(\mathbf{I}))$ were used in the structural analysis. Data were corrected for absorption (μ = 12.70 cm^{-1}) and the transmission coefficients ranged from 0.9163 to 0.9965. The final R(F) and R$_W$(F) residuals were, respectively 0.043 and 0.045. The cations exist in the lattice as enantiomeric pairs and the conformation of the central, five-membered ring for the molecule described here is δ(N2-C4-C5-N3 = +49.0°). The secondary nitrogens are both R(or S). The ClO$_4^-$ anion forms O....H bonds with a hydrogen of each of the two terminal -NH$_2$ groups, thus rendering those hydrogens different and the terminal nitrogens chiral. In the cation we used as the asymmetric unit, they are both *R*.

[*trans*-Co(3,2,3-tet)(NO$_2$)$_2$]Br · 3H$_2$O (**II**), $BrCoO_7N_6C_8H_{28}$, crystallizes at 22°C, from a deionized water solution in space group $P2_12_12_1$ (No. 19) with lattice constants: a = 18.352(10), b = 14.757(8), c = 6.497(2) Å; V = 1759.46 Å^3 and d(calc; MW = 459.19, Z = 4) = 1.733 g-cm^{-3}. A total of 2917 data were collected over the range of $4° \ge 2\theta \le 60°$; of these, 2175 (independent and with $\mathbf{I} \ge 2.5\sigma(\mathbf{I})$) were used in the structural analysis. Data were corrected for absorption (μ = 32.918 cm^{-1}) and the transmission coefficients ranged from 0.3266 to 0.4783. The final R(F) and R$_W$(F) residuals were,

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respectively 0.056 and 0.061. The cations exist in the lattice pure enantiomers and the conformation of the central ring for the molecule described here is δ(N2-C4-C5-N3 = 47.9°). The chiral, secondary nitrogens are both *R*.

[*trans*-Co(3,2,3-tet)$(NO_2)_2$]I (**III**), $ICoO_4N_6C_8H_{22}$, crystallizes in total darkness, at 22°C, from a deionized water solution in space group $P2_1$ or $P2_1/m$ with lattice constants: $a = 6.451(6)(3)$, $b = 15.253(18)$, $c = 7.859(9)$ Å, $\beta = 97.58(8)°$; $V = 766.59$ Å^3 and *d*(calc; MW = 452.138, $Z = 2$) = 1.959 g-cm^{-3}. A total of 1720 data were collected over the range of $4° \leq 2\theta \leq 60°$; of these, 292 (independent and with $\mathbf{I} \geq 2.5\sigma(\mathbf{I})$) were used in the structural analysis. Data were corrected for absorption ($\mu = 31.306$ cm^{-1}) and the transmission coefficients ranged from 0.1983 to 0.5039. The quality of the crystal was so poor that only 17% of the collected data had $\mathbf{I} \geq 2.5\sigma(\mathbf{I})$; therefore, data processing was abandoned.

Keywords: Conglomerate crystallization; racemates; mechanisms of crystallization; cobalt amines; trans-dinitro cobalt compounds; cobalt perchlorates cobalt halides

INTRODUCTION

Note: The ligand 3,2,3-tet is 1,5,8,12-tetraazadodecane.

Recently, we reported[1] the conglomerate crystallization of a series of compounds with composition [*trans*-Co(3,2,3-tet)X_2]$Y \cdot n$$H_2O$ (**IV**), $X = NO_2$, $Y = Cl$, $n = 3$; (**V**), $X = Cl$, $Y = NO_3$, $n = 0$; (**VI**), $X = NO_3$, $Y = NO_3$, $n = 0$) and suggested that their crystallization behavior exhibited some reasonable parallels with those of *trans* disubstituted macrocyclic cobalt amines, which also crystallized as conglomerates and share with (**IV**) → (**VI**) a common Co(3,2,3-tet) fragment. However, we had no reasonable explanation for selection of that crystallization pathway since this is only the second[2] family of *trans*-disubstituted compounds observed to behave thus. Moreover, the conglomerate crystallization of the series [*trans*-Co(3,2,3-tet)X_2]$Y \cdot n$$H_2O$ despite changes of axial ligands, and counteranions, was totally new to us.

In order to further probe the effect of counter anions on the crystallization pathway of the [*trans*-Co(3,2,3-tet)$(NO_2)_2$]$^+$ cations, and hoping to understand the crystallization pathway, we have prepared a new group of these species whose structures and crystallization behavior we report herein.

EXPERIMENTAL

Syntheses

Compound (**I**): [Co(3,2,3-tet)CO_3]ClO_4 was prepared according to the procedure given earlier.[3] It was converted to [*trans*-Co(3,2,3-tet)Br_2]ClO_4 by the addition of aqueous HBr (48%; 20 mL) to a solution of the carbonate (1g/40 mL H_2O). The resulting solution was heated in a steam bath (30 min) and allowed to cool to room temperature. After a few days, green crystals were deposited. Compound (**I**) was obtained from [*trans*-Co(3,2,3-tet)Br_2]ClO_4 by the addition of two equivalents of $NaNO_2$, which was then heated in a steam bath (30 min) and allowed to crystallize at room temperature. After 5 days, red-brown crystals suitable for x-ray diffraction were obtained. The compound can also be made by adding the amine ligand to a solution of $Na_3[Co(NO_2)_6]$ and heating in a water bath(30 min) addition of excess $NaClO_4$ causes (**I**) to crystallize.

Compound (**II**) was made from the dichloro chloride by addition of 2 moles of $NaNO_2$[1] followed by addition of excess NaBr to cause the compound to precipitate. The solid bromide was filtered, washed with cold water and ethanol and air dried. A saturated, golden brown solution in deionized water was set aside (22°C) and after some weeks a suitable crop of crystals was obtained.

Compound (**III**) was made from the dichloro chloride by the addition of 2 moles of $NaNO_2$[1] followed by the addition of excess NaI to cause the compound to precipitate. The solid was filtered, washed with cold water and ethanol and air dried. A saturated, golden brown solution in deionized water was set aside (22°C) in total darkness since we have previously observed photochemical decomposition, as well as geometrical rearrangements, of cobalt amine iodides[4–6] in solutions which were exposed to laboratory light. After many failures to obtain useful crystals (see Results) we finally obtained a crystal of (**III**) which produced a reasonable cell. Other crystals tried produced the same values of *a* and *b* but widely different values of *c*, all of which were approximate multiples of the current value of *c*.

Elemental Analyses: Compound (**I**) was analyzed by the analytical laboratory of the University of Kuwait. Theory for $CoClO_8N_6C_8H_{22}$, $C = 22.63$, $H = 5.22$, $N = 19.79$. Found: $C = 22.63$, $H = 5.22$, $N = 19.79$. Compounds (**II**) and (**III**) were analyzed by Galbraith Laboratories.[7] Compound (**II**), theory for $BrCoO_7N_6C_8H_{28}$: $C = 20.93$, $H = 6.15$, $N = 18.30$. Found: $C = 20.87$, $H = 6.18$, $N = 18.27$. Compound (**III**), theory for $ICoO_4N_6C_8H_{22}$: $C = 21.25$, $H = 4.90$, $N = 18.59$. Found $C = 21.32$ $H = 4.92$, $N = 18.63$.

Crystallography

Data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[8] of the SDP-Plus software package.[9] The procedure used for crystal alignment, cell constant determination, space group determination, and data collection were uniform for all three crystals. Processing of the data was carried out with the PC version of the NRCVAX package.[10] Crystals were centered with data in the $20° \leq 2\theta \leq 40°$ range and examination of the cell constants, absences, and Niggli matrix[11] clearly showed (**I**) to crystallize in a primitive, monoclinic lattice whose systematic absences belong to those of the space group $P2_1/n$. Useful crystals of compound (**II**) crystallize in space group $P2_12_12_1$. Finally, many crystals of (**III**) had to be tested prior to finding one that indexed using all 25 reflections in a centered set (see below). For that crystal, systematic absences suggest it crystallizes in space groups $P2_1$ or $P2_1/m$ with cell constants very close to those of the pre-resolved, anhydrous, bromide reported by Payne.[12] Given that information and, since the latter choice implies a disordered system, we assumed the former.

The details of data collection are summarized in Tables 1, 2 and 3, respectively, for compounds (**I**), (**II**) and (**III**). The intensity data sets were corrected for absorption using empirical curves derived from psi scans[8–9] of suitable reflections. The scattering curves were taken from Cromer and Waber's compilation.[13]

TABLE I Summary of Data Collection and Processing Parameters for [*trans*-Co(3,2,3-tet)$(NO_2)_2$]ClO_4 (**I**)

Space Group	$P2_1/n$ (No. 14)
Cell Constants	$a = 10.787(3)$
	Å $= 9.198(3)$
	$c = 17.031(5)$
	$\beta = 105.30(2)°$
Cell Volume	$V = 1629.86$ Å^3
Molecular Formula	$CoClO_8N_6C_8H_{22}$
Molecular Weight	424.69 gm-mole^{-1}
Density (calc; $z = 4$ mol/cell)	1.731 gm-cm^{-3}
Radiation Employed	MoK_α ($\lambda = 0.71073$Å)
Absorption Coefficient	$\mu = 12.645$ cm^{-1}
Relative Transmission Coefficients	0.9163 to 0.9965
Data Collection Range	$4° \leq 2\Theta \leq 50°$
ScanWidth	$\Delta\Theta = 0.95 + 0.35\tan\Theta$
Total Unique Data Collected	3217
Data Used In Refinement*	2389
$R = \Sigma\|\|F_O\| - \|F_C\|\|/\Sigma\|F_O\|$	0.043
$Rw = [\Sigma w(\|F_O\| - \|F_C\|)^2/\Sigma\|F_O\|^2]^{1/2}$	0.045
Weights Used	$w = [\sigma(F_O)]^{-2}$

* The difference between this number and the total is due to subtraction of 828 that were standards, symmetry related or did not meet the criterion that $I \geq 3\sigma$ (I).

TABLE II Summary of Data Collection and Processing Parameters for [trans-Co(3,2,3-tet)(NO_2)$_2$] Br · $3H_2O$ (**II**)

Space Group	$P2_12_12_1$(No. 19)
Cell Constants	a = 18.352(10) Å
	b = 14.747(8)
	c = 6.497(2)
Cell Volume	V = 1759.46 Å^3
Molecular Formula	$BrCoO_7N_6C_8H_{28}$
Molecular Weight	459.19 gm-mole^{1}
Density (calc; z = 4 mol/cell)	1.733 gm-cm^{-3}
Radiation Employed	MoK$_\alpha$ (λ = 0.71073Å)
Absorption Coefficient	μ = 32.918 cm^{-1}
Relative Transmission Coefficients	0.3266 to 0.4783
Data Collection Range	4° ≤ 2Θ ≤ 60°
ScanWidth	ΔΘ = 0.95 + 0.35tanΘ
Total Unique Data Collected	2917
Data Used In Refinement *	2175
$R = \Sigma\|\|F_O\| - \|F_C\|\|/\Sigma\|F_O\|$	0.056
$Rw = [\Sigma w(\|F_O\| - \|F_C\|)^2/\Sigma\|F_O\|^2]^{1/2}$	0.061
Weights Used	$w = [\sigma(F_O)]^{-2}$

* The difference between this number and the total is due to substraction of 742 that were standards, symmetry related or did not meet the criterion hat I ≥ 2.5σ (I).

TABLE III Summary of Data Collection and Processing Parameters for [trans-Co(3,2,3-tet) (NO_2)$_2$]I (**III**)

Space Group	$P2_1$ (No. 4)
Cell Constants	a = 6.451(6) Å
	b = 15.253(18)
	c = 7.859(9)
	β = 97.58(8)°
Cell Volume	V = 766.59 Å^3
Molecular Formula	$ICoO_4N_6C_8H_{22}$
Molecular Weight	452.138 gm-mole^{-1}
Density (calc; z = 4 mol/cell)	1.959 gm-cm^{-3}
Radiation Employed	MoK$_\alpha$ (λ = 0.71073Å)
Absorption Coefficient	μ = 31.306 cm^{-1}
Relative Transmission Coefficients	0.1983 to 0.5039
Data Collection Range	4° ≤ 2Θ ≤ 60°
ScanWidth	ΔΘ = 1.00 + 0.35tanΘ

TABLE III (*Continued*)

Total Unique Data Collected	1720
Data Used In Refinement	292*
$R = \Sigma \|\|F_O\| - \|F_C\|\|/\Sigma\|F_O\|$	Unfinished(see text)
$Rw = [\Sigma w(\|F_O\| - \|F_O\|)^2/\Sigma\|F_O\|^2]^{1/2}$	Unfinished(see text)

* These are the only data with $I \geq 2.5\sigma(I)$

The structures of (**I**) and (**II**) were solved from their Patterson maps using their heaviest atom as the initial phasing species for a difference Fourier map. For (**III**) the Patterson map is consistent with the positions of Br and Co with Payne's[12] coordinates from the pre-resolved bromide; therefore we used them as trial coordinates and the refinement proceeds isotropically to 36%, but no further progress is made beyond that. Therefore, we suggest that the iodide (**III**) is a conglomerate showing the same crystal quality problems we have often encountered before with cobalt amine iodides. For details of these crystal quality problems encountered here, as well as by others, the reader is referred to our previous publications.[4–6]

In the case of (**I**) and (**II**), the choice of space group is unequivocal and the Patterson maps easily revealed the positions of the heaviest atoms. After refinement of the scale factor and the positional parameters of the heavier atom, a difference Fourier map produced, in the first two cases, most of the non-hydrogen atoms. The remaining ones 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) with fixed thermal parameters. Conversion of the heavy atoms to anisotropic motion resulted in refinement of the overall structure to final R(F) and $R_W(F)$ factors listed in Tables 1 and 2. In the case of (**II**), the absolute configuration of the cations were determined by use of the Flack test (0.008). The hydrogen atoms of the waters of crystallization were located experimentally (in a final difference Fourier map) and fixed where found.

RESULTS AND DISCUSSION

The space groups for compounds (I) and (II) are unambigously determined by their systematic absences. Data collection, structural solution and data refinement proceeded smoothly. The phase diagram of compound (III) may share some common features with that of [*cis*-$Co(en)_2(NO_2)_2$]I published by Yamanari, *et al*,[14] who reported that this iodide can indiscriminately produce racemic and enantiomorphic crystals in the same crystallization batch. We know[15(a)] that crystals of [*cis*-$Co(en)_2(NO_2)_2$]I are mostly of extremely poor quality, and that indexing them present problems. We also know that compounds of composition $[Co(abap)(NO_2)_2]X$ (abap = bis-(2-aminoethyl)aminopropylamine and $X = ClO_4^-$, PF_6^-, Cl are of excellent quality, whereas those with $X = I^-$ are useless for crystallographic purposes.[15(b)] The same can be said of the series $[Co(tren)((NO_2)_2]$ X(tren = tris(aminoethyl)amine and $X = Cl^-$, Br^-, ClO_4(double salt), NO_3^-, BF_4^- which produces excellent specimens for crystallography, while the iodide crystals are useless.[15(c)]

Figures 1and 2 give labeled views of the asymmetric units found for molecules (**I**) and (**II**). 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 4 and 5 and bond length, angles, selected torsional angles and useful hydrogen bonds are listed in Tables 6 and 7.

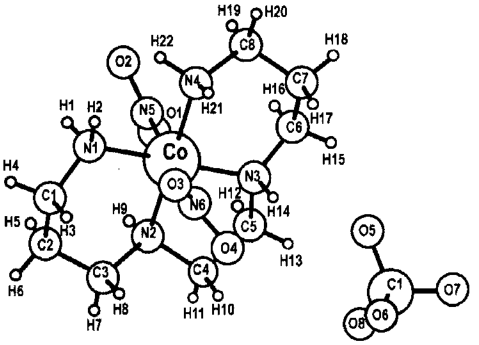

FIGURE 1 The ions in the asymmetric unit of (**I**). The perchlorate anion was placed at that symmetry position in which it forms a hydrogen bond with H14 (2.417 Å) for clarity of depiction. The bonds O6....H22(2.255 Å) and O7....H1 (2.325 Å) are a little shorter (see Discussion and Table 6).

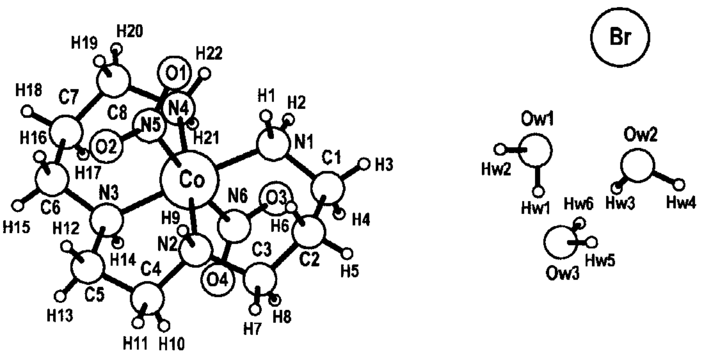

FIGURE 2 The ions and waters of hydration in the asymmetric unit of (**II**). Note the hydrogen-bonded $Br(H_2O)_3$ cluster. Such cluster are hydrogen bonded to the amine hydrogens of the cation, thus linking cations as shown in the packing diagram (Figure 4). For details, see Table 7.

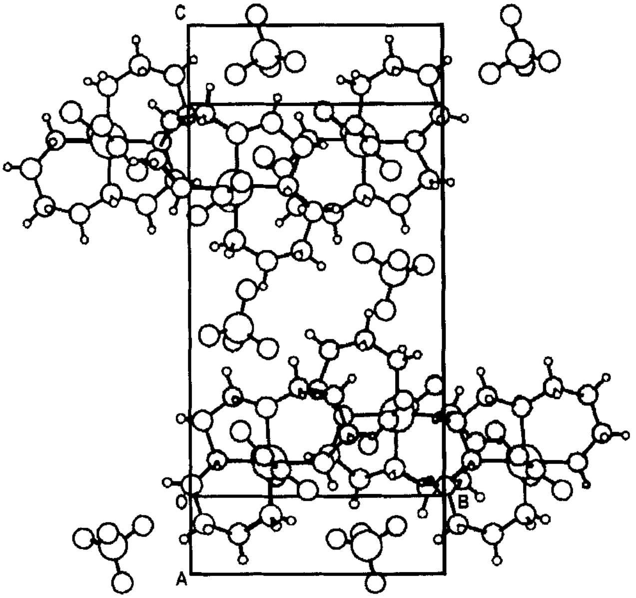

FIGURE 3 The packing of the ions in the unit cell of (**I**). The inversion center is at 1/2, 1/2; cations are held together by the agency of hydrogen bonds to anions lying in between them as depicted in the right side of the figure, near $c = 1/2$, where an oxygen is bonded to a terminal $-NH_2$ hydrogen while another oxygen of the same anion is bonded to a secondary –NH hydrogen of the cation directly above.

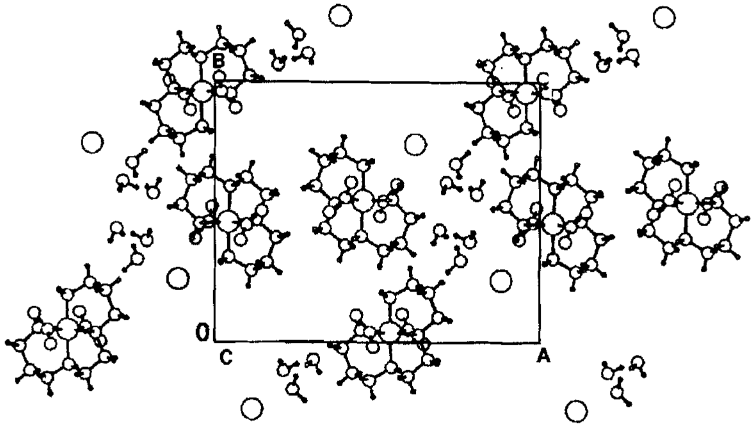

FIGURE 4 The packing of the contents of the unit cell of (**II**). In the region near $a = 0.6$, $b = 0.75$, a bromide anion forms a hydrogen bond with H2 and H22 of terminal $-NH_2$ fragments, then links to Hw2 of the water cluster which, in turn, links to an adjacent cation. Such a hydrogen-bonded web gives rise to a string of cations runing along the a-axis, at approximately $b = 1/2$.

TABLE IV Atomic Parameters x,y,z and Biso. E.S.Ds. refer to the last digit printed

	x	*y*	*z*	*Biso*
Br	0.88310(7)	0.24141(7)	0.67507(19)	3.83(5)
Co	0.95812(6)	0.95889(7)	0.03690(17)	1.65(4)
O1	1.0618(4)	0.8965(6)	0.3127(14)	4.7(4)
O2	1.0101(4)	1.0169(5)	0.4201(10)	3.6(3)
O3	0.9206(4)	0.8891(5)	−0.3432(11)	3.3(3)
O4	0.8542(4)	1.0022(5)	−0.2639(12)	4.0(3)
N1	0.9583(4)	0.8253(5)	0.0500(13)	2.5(3)
N2	0.8701(4)	0.9697(6)	0.2148(11)	2.4(3)
N3	0.9530(4)	1.0933(4)	0.0197(12)	2.2(3)
N4	1.0480(4)	0.9532(5)	−0.1318(11)	2.2(3)
N5	1.0196(4)	0.9597(6)	0.2885(11)	2.8(3)
N6	0.9024(4)	0.9480(5)	−0.2206(10)	2.4(3)
C1	0.8868(5)	0.7753(6)	0.0569(16)	3.1(4)
C2	0.8392(6)	0.8063(7)	0.2301(17)	3.1(4)
C3	0.8106(5)	0.9009(8)	0.1979(18)	3.3(4)
C4	0.8405(6)	1.0626(7)	0.1957(18)	3.3(4)
C5	0.9027(6)	1.1282(6)	0.1753(18)	3.3(4)
C6	1.0209(5)	1.1461(6)	0.0240(17)	2.9(4)
C7	1.0738(6)	1.1180(7)	−0.1399(19)	3.4(4)
C8	1.1047(5)	1.0234(7)	−0.1062(16)	3.0(4)
Ow1	0.7860(4)	0.3880(5)	0.9572(14)	4.2(3)
Ow2	0.7570(5)	0.3163(7)	0.3500(16)	5.3(4)
Ow3	0.6936(5)	0.4329(5)	0.6376(13)	4.3(4)
H1	0.984	0.809	0.170	3.3
H2	0.984	0.804	−0.068	3.3
H3	0.896	0.712	0.073	3.9
H4	0.862	0.785	−0.069	3.9
H5	0.799	0.766	0.242	3.9
H6	0.867	0.805	0.354	3.9
H7	0.775	0.913	0.299	4.1
H8	0.789	0.905	0.065	4.1
H9	0.890	0.964	0.349	3.2
H10	0.810	1.066	0.077	4.1
H11	0.813	1.077	0.315	4.1
H12	0.927	1.134	0.303	4.1
H13	0.885	1.186	0.134	4.1
H14	0.931	1.103	−0.111	3.0
H15	1.009	1.208	0.005	3.7
H16	1.043	1.138	0.155	3.7
H17	1.049	1.119	−0.269	4.1
H18	1.113	1.160	−0.142	4.1
H19	1.124	1.020	0.029	3.8
H20	1.143	1.013	−0.203	3.8
H21	1.033	0.955	−0.272	3.0
H22	1.070	0.896	−0.103	3.0
Hw1	0.744	0.412	0.890	4.9
Hw2	0.796	0.423	1.077	4.9
Hw3	0.747	0.365	0.259	6.1
Hw4	0.720	0.272	0.340	6.1
Hw5	0.675	0.385	0.719	5.1
Hw6	0.713	0.410	0.513	5.1

Biso is the Mean of the Principal Axes of the Thermal Ellipsoid

TABLE V Atomic Parameters x,y,z and Biso. E.S.Ds. refer to the last digit printed

	x	*y*	*z*	*Biso*
Co	0.50278(5)	0.81706(6)	0.25904(3)	1.981(24)
Cl	0.72152(13)	0.19303(15)	0.47795(7)	4.28(6)
O1	0.2358(3)	0.7931(4)	0.20157(23)	5.08(19)
O2	0.7618(3)	0.8415(4)	0.33317(22)	5.10(18)
O3	0.2963(3)	0.9653(4)	0.28560(20)	4.56(18)
O4	0.7247(3)	0.7029(4)	0.23162(21)	5.68(21)
O5	0.7723(5)	0.3113(6)	0.4442(3)	9.7(3)
O6	0.5941(4)	0.1735(6)	0.4304(3)	9.0(3)
O7	0.7227(4)	0.2282(5)	0.55836(22)	7.3(3)
O8	0.7962(7)	0.0769(7)	0.4740(3)	16.0(5)
N1	0.5271(3)	0.8198(4)	0.37849(20)	2.90(16)
N2	0.4608(3)	0.6074(4)	0.24914(20)	2.60(16)
N3	0.4836(3)	0.8067(4)	0.14040(19)	2.62(15)
N5	0.3232(3)	0.8620(4)	0.24616(21)	2.84(16)
N4	0.5374(3)	1.0277(4)	0.26592(20)	2.82(16)
N6	0.6848(3)	0.7834(4)	0.27676(21)	2.81(17)
C1	0.5795(5)	0.6918(5)	0.4293(3)	3.78(22)
C2	0.5089(5)	0.5531(5)	0.3965(3)	3.91(22)
C3	0.5259(4)	0.5072(5)	0.3154(3)	3.36(22)
C4	0.4676(4)	0.5518(5)	0.1682(3)	3.42(21)
C5	0.4172(4)	0.6703(5)	0.1068(3)	3.49(21)
C6	0.4292(4)	0.9333(5)	0.0891(3)	3.42(20)
C7	0.5024(4)	1.0699(5)	0.1177(3)	3.56(21)
C8	0.4823(4)	1.1265(5)	0.1961(3)	3.30(22)
H1	0.445	0.839	0.387	3.7
H2	0.583	0.899	0.399	3.7
H3	0.668	0.681	0.431	4.6
H4	0.572	0.708	0.483	4.6
H5	0.420	0.568	0.391	4.8
H6	0.540	0.477	0.435	4.8
H7	0.491	0.412	0.303	4.2
H8	0.615	0.505	0.318	4.2
H9	0.372	0.607	0.248	3.4
H10	0.554	0.530	0.169	4.2
H11	0.416	0.467	0.154	4.2
H12	0.327	0.681	0.098	4.2
H13	0.435	0.647	0.057	4.2
H14	0.570	0.797	0.138	3.4
H15	0.432	0.914	0.035	4.2
H16	0.342	0.946	0.091	4.2
H17	0.591	1.051	0.125	4.4
H18	0.475	1.142	0.077	4.4
H19	0.393	1.136	0.190	4.1
H20	0.522	1.219	0.207	4.1
H21	0.628	1.038	0.278	3.7
H22	0.508	1.063	0.310	3.7

Biso is the Mean of the Principal Axes of the Thermal Ellipsoid

TABLE VI Bond Distances (Å) and Angles (°)

A. Bond Distances

Co—N1	1.973(7)	N2—C3	1.494(12)
Co—N2	1.993(7)	N2—C4	1.479(13)
Co—N3	1.988(7)	N3—C5	1.462(13)
Co—N4	1.982(7)	N3—C6	1.471(12)
Co—N5	1.986(7)	N4—C8	1.478(11)
Co—N6	1.967(7)	C1—C2	1.496(15)
O1—N5	1.222(12)	C2—C3	1.506(16)
O2—N5	1.213(11)	C4—C5	1.503(16)
O3—N6	1.225(10)	C6—C7	1.499(16)
O4—N6	1.226(11)	C7—C8	1.523(15)
N1—C1	1.505(12)		

B. Bond Angles

N1—Co—N2	93.2(3)	Co—N3—C5	110.1(6)
N1—Co—N3	177.2(3)	Co—N3—C6	119.2(6)
N1—Co—N4	88.9(3)	C5—N3—C6	109.5(7)
N1—Co—N5	88.3(4)	Co—N4—C8	119.6(6)
N1—Co—N6	87.5(3)	Co—N5—O1	117.5(7)
N2—Co—N3	85.1(3)	Co—N5—O2	120.1(7)
N2—Co—N4	177.1(3)	O1—N5—O2	122.0(8)
N2—Co—N5	89.0(3)	Co—N6—O3	118.0(6)
N2—Co—N6	94.5(3)	Co—N6—O4	121.1(6)
N3—Co—N4	92.9(3)	O3—N6—O4	120.7(8)
N3—Co—N5	93.9(4)	N1—C1—C2	112.4(8)
N3—Co—N6	90.5(3)	C1—C2—C3	112.5(9)
N4—Co—N5	89.0(3)	N2—C3—C2	111.5(8)
N4—Co—N6	87.6(3)	N2—C4—C5	109.0(8)
N5—Co—N6	174.6(4)	N3—C5—C4	108.2(8)
Co—N1—C1	119.4(6)	N3—C6—C7	112.8(8)
Co—N2—C3	119.6(6)	C6—C7—C8	113.1(9)
Co—N2—C4	108.8(6)	N4—C8—C7	111.3(8)
C3—N2—C4	110.9(7)		

C. Torsion angles

N2	Co	N1	C1	35.1(5)	N3	Co	N1	C1	16.6(4)
N4	Co	N1	C1	−146.9(7)	N5	Co	N1	C1	124.1(6)
N6	Co	N1	C1	−59.2(5)	N1	Co	N2	C3	−35.9(5)
N1	Co	N2	C4	−164.8(7)	N3	Co	N2	C3	141.9(7)
N3	Co	N2	C4	13.1(5)	N4	Co	N2	C3	−171.6(7)
N4	Co	N2	C4	59.6(5)	N5	Co	N2	C3	−124.1(6)
N5	Co	N2	C4	107.0(6)	N6	Co	N2	C3	51.8(5)
N6	Co	N2	C4	−77.1(6)	N1	Co	N3	C5	65.1(6)
N1	Co	N3	C6	−167.2(7)	N2	Co	N3	C5	13.3(5)
N2	Co	N3	C6	140.9(6)	N4	Co	N3	C5	−164.6(7)
N4	Co	N3	C6	−36.9(5)	N5	Co	N3	C5	−75.4(6)
N5	Co	N3	C6	52.3(5)	N6	Co	N3	C5	107.7(6)
N6	Co	N3	C6	−124.6(6)	N1	Co	N4	C8	−144.1(6)
N2	Co	N4	C8	−8.4(4)	N3	Co	N4	C8	38.0(5)
N5	Co	N4	C8	−55.8(5)	N6	Co	N4	C8	128.4(6)
N1	Co	N5	O1	31.7(5)	N1	Co	N5	O2	−141.8(7)
N2	Co	N5	O1	125.0(7)	N2	Co	N5	O2	−48.6(5)
N3	Co	N5	O1	−150.0(7)	N3	Co	N5	O2	36.4(5)
N4	Co	N5	O1	−57.2(5)	N4	Co	N5	O2	129.3(7)
N6	Co	N5	O1	−5.7(5)	N6	Co	N5	O2	−179.3(7)

TABLE VI (*Continued*)

N1	Co	N6	O3	−41.6(5)	N1	Co	N6	O4	143.3(7)
N2	Co	N6	O3	−134.6(7)	N2	Co	N6	O4	50.3(5)
N3	Co	N6	O3	140.3(7)	N3	Co	N6	O4	−34.8(5)
N4	Co	N6	O3	47.4(5)	N4	Co	N6	O4	−127.7(7)
N5	Co	N6	O3	−4.1(4)	N5	Co	N6	O4	−179.2(7)
Co	N1	C1	C2	−55.1(6)	Co	N2	C3	C2	55.6(6)
C4	N2	C3	C2	−176.5(11)	Co	N2	C4	C5	−36.3(5)
C3	N2	C4	C5	−169.9(11)	Co	N3	C5	C4	−36.3(5)
C6	N3	C5	C4	−169.2(11)	Co	N3	C6	C7	55.5(6)
C5	N3	C6	C7	−176.5(11)	Co	N4	C8	C7	−56.3(6)
N1	C1	C2	C3	69.3(8)	C1	C2	C3	N2	−69.4(8)
N2	C4	C5	N3	47.9(6)	N3	C6	C7	C8	−67.9(8)
C6	C7	C8	N4	67.8(8)					

D. Hydrogen Bond Distances (less than 2.5Å)

Intra-Molecular		***Inter-Molecular***	
H1 to O1	2.13	H9 to O3	2.35
H2 to O3	2.47	H21 to O2	2.24
H9 to O2	2.38	H22 to Br	2.49
H14 to O4	2.28		
H21 to O3	2.33		

Inter-Molecular Bonds of Water	
Hw1 to Ow3	1.91
Hw2 to Ow2	2.48
Hw2 to Ow3	2.17
Hw3 to Ow1	2.12
Hw6 to Ow2	1.92

TABLE VII Bond Distances (Å) and Bond Angles (°)

A. Bond Distances

Co—N1	1.982(3)	O4—N6	1.224(5)
Co—N2	1.978(3)	N1—C1	1.482(6)
Co—N3	1.978(3)	N2—C3	1.482(5)
Co—N5	1.935(3)	N2—C4	1.489(5)
Co—N4	1.971(3)	N3—C5	1.483(5)
Co—N6	1.930(3)	N3—C6	1.481(5)
Cl—O5	1.407(5)	N4—C8	1.490(5)
Cl—O6	1.410(5)	C1—C2	1.515(7)
Cl—O7	1.404(4)	C2—C3	1.502(6)
Cl—O8	1.350(5)	C4—C5	1.509(7)
O1—N5	1.220(5)	C6—C7	1.495(7)
O2—N6	1.215(5)	C7—C8	1.501(7)
O3—N5	1.241(5)		

B. Bond Angles

N1—Co—N2	93.74(14)	Co—N2—C3	119.3(3)
N1—Co—N3	177.45(14)	Co—N2—C4	110.33(25)
N1—Co—N5	88.33(14)	C3—N2—C4	111.2(3)
N1—Co—N4	87.41(14)	Co—N3—C5	110.2(3)
N1—Co—N6	89.32(14)	Co—N3—C6	118.9(3)
N2—Co—N3	84.60(14)	C5—N3—C6	111.2(3)
N2—Co—N5	89.94(14)	Co—N5—O1	123.0(3)
N2—Co—N4	177.61(14)	Co—N5—O3	118.2(3)

TABLE VII (*Continued*)

N2—Co—N6	93.27(14)	O1—N5—O3	118.8(3)
N3—Co—N5	93.60(14)	Co—N4—C8	121.5(3)
N3—Co—N4	94.32(14)	Co—N6—O2	120.4(3)
N3—Co—N6	88.84(14)	Co—N6—O4	120.7(3)
N5—Co—N4	87.99(14)	O2—N6—O4	118.9(4)
N5—Co—N6	176.14(15)	N1—C1—C2	112.1(4)
N4—Co—N6	88.84(14)	C1—C2—C3	113.9(4)
O5—Cl—O6	106.8(3)	N2—C3—C2	112.1(3)
O5—Cl—O7	108.4(3)	N2—C4—C5	107.3(3)
O5—Cl—O8	106.9(4)	N3—C5—C4	107.1(3)
O6—Cl—O7	110.2(3)	N3—C6—C7	112.1(3)
O6—Cl—O8	112.0(4)	C6—C7—C8	113.2(4)
O7—Cl—O8	112.2(3)	N4—C8—C7	112.2(3)
Co—N1—C1	121.1(3)		

C. Torsion angles

N2	Co	N1	C1	33.2(2)	N3	Co	N1	C1	−16.2(2)
N5	Co	N1	C1	123.1(3)	N4	Co	N1	C1	−148.9(3)
N6	Co	N1	C1	−60.0(2)	N1	Co	N2	C3	−35.0(2)
N1	Co	N2	C4	−165.5(3)	N3	Co	N2	C3	143.1(3)
N3	Co	N2	C4	12.5(2)	N5	Co	N2	C3	−123.3(3)
N5	Co	N2	C4	106.2(2)	N4	Co	N2	C3	−153.7(3)
N4	Co	N2	C4	75.8(2)	N6	Co	N2	C3	54.6(2)
N6	Co	N2	C4	−76.0(2)	N1	Co	N3	C5	64.7(2)
N1	Co	N3	C6	−165.3(3)	N2	Co	N3	C5	15.2(2)
N2	Co	N3	C6	145.2(3)	N5	Co	N3	C5	−74.4(2)
N5	Co	N3	C6	55.6(2)	N4	Co	N3	C5	−162.7(3)
N4	Co	N3	C6	−32.7(2)	N6	Co	N3	C5	108.6(3)
N6	Co	N3	C6	−121.4(3)	N1	Co	N5	O1	−129.5(3)
N1	Co	N5	O3	50.1(2)	N2	Co	N5	O1	−35.7(2)
N2	Co	N5	O3	143.9(3)	N3	Co	N5	O1	48.9(2)
N3	Co	N5	O3	−131.5(3)	N4	Co	N5	O1	143.1(3)
N4	Co	N5	O3	−37.3(2)	N6	Co	N5	O1	178.0(3)
N6	Co	N5	O3	−2.4(2)	N1	Co	N4	C8	−152.0(3)
N2	Co	N4	C8	−33.2(2)	N3	Co	N4	C8	29.9(2)
N5	Co	N4	C8	−63.6(2)	N6	Co	N4	C8	118.6(3)
N1	Co	N6	O2	−37.0(2)	N1	Co	N6	O4	142.8(3)
N2	Co	N6	O2	−130.7(3)	N2	Co	N6	O4	49.1(2)
N3	Co	N6	O2	144.8(3)	N3	Co	N6	O4	−35.4(2)
N5	Co	N6	O2	15.5(2)	N5	Co	N6	O4	−164.6(3)
N4	Co	N6	O2	50.5(2)	N4	Co	N6	O4	−129.7(3)
Co	N1	C1	C2	−50.8(2)	Co	N2	C3	C2	55.6(2)
C4	N2	C3	C2	−174.3(4)	Co	N2	C4	C5	−36.9(2)
C3	N2	C4	C5	−171.7(4)	Co	N3	C5	C4	−39.1(2)
C6	N3	C5	C4	−173.1(4)	Co	N3	C6	C7	55.6(2)
C5	N3	C6	C7	−174.9(4)	Co	N4	C8	C7	−48.7(2)
N1	C1	C2	C3	65.9(3)	C1	C2	C3	N2	−69.0(3)
N2	C4	C5	N3	49.0(2)	N3	C6	C7	C8	−71.4(3)
C6	C7	C8	N4	66.8(3)					

D. Hydrogen Bond Distances (Å)

Intra-Molecular	***Inter-Molecular***		
H1 to O2	2.33	H1 to O7	2.32
H9 to O1	2.26	H9 to O2	2.19
H14 to O4	2.16	H21 to O4	2.23
H14 to O5	2.47	H22 to O6	2.25

TABLE VII (*Continued*)

H21 to O3	2.35
H22 to O2	2.38

Compound (**I**) is the first derivative of the class [*trans*-Co(3,2,3-tet)X_2] $Y \cdot n H_2O$ to crystallize as a racemate which emphasizes the control counter ions exert in the mode of crystallization selected by a chiral cation. This is interesting in view of the fact that [*trans*-Co(3,2,3-tet)X_2]$Y \cdot nH_2O$ (**IV**), $X = NO_2$, $Y = Cl$, $n = 3$; (**V**), $X = Cl$, $Y = NO_3$, $n = 0$; (**VI**), $X = NO_2$, $Y = NO_3$, $n = 0$), as well as (**II**), crystallize as conglomerates. In fact (**VI**) differs from (**I**) only by a change from NO_3^- to ClO_4^- which is a rather subtle change since as both contain oxo-anions as their counter ion. In fact, the difference is a reduction in hydrogen bonding power in the case of the perchlorate, suggesting that this diminishing power to link cations is the origin of the change in crystallization pathway. If this is, indeed, the origin of the change, it would be surprising to find that the chloride (**V**), bromide (**II**) and iodide (**III**) are also conglomerates since their anions are not particularly powerful hydrogen-bonding species; this is specially true of the last two examples cited above.

If not hydrogen-bonding power, what causes the change in crystallization mode? A comparison of the packing features of (**I**) and (**II**) show that, whereas the latter has cations linked into an infinite string with spiraling O_2N-Co-NO_2 vectors, the former does not. In fact, such a spiraling string has been observed in every case of conglomerate crystallization we have studied, irrespective of the nature of the compound. Aside from the multitude of charged coordination compounds we have studied, we observed the same phenomenon in neutral ones[16], as well as in organometallic compounds[17] and organic compounds.[18] These spiraling strings are not always aligned along screw axes of the space group in question, as was noted recently.[16] Thus, while is most cases the spiraling strings formed by intermolecular interactions adapt themselves to the packing forces of screw axes in a harmonic fashion, molecules explore the Sohncke space groups and select that which allows them to interact in the energetically most desirable mode. If the two do not coincide, molecular interactions appear to take precedence, at least in some cases.[16]

Finally, concerning the stronger hydrogen bonds in (**I**) (see Table 6) there are seven intramolecular hydrogen bonds between terminal and secondary hydrogens and the $-NO_2$ oxygens, four inter-ionic hydrogen bonds between the various amino hydrogens and the oxygens of the perchlorate anions, and only two inter-ionic hydrogen bonds between adjacent cations (H9....O2 = 2.26 Å and H21....O4 = 2.23 Å). In (**II**) there are six intramolecular hydrogen bonds between $-NO_2$ oxygens and amino hydrogens, three to the bromide anions and four between adjacent cations (H9....O3 = 2.35 Å, H9....O4 = 2.66 Å, H21....O1 = 2.88 Å and H21....O2 = 2.24 Å).

The central row of cations (Figure 4, near b = 1/2), indicates that there is a spiraling motion of these ions as exemplified by the N-N vector of the two *trans*-NO_2 ligands. Note that the mode of linkage of these strings is a little different from that normally observed for conglomerate crystals of the *cis*-dinitro species in which the spiraling string is formed exclusively by cations, while the anions (and, where relevant, waters of crystallization) link adjacent strings into a three dimensional array. In the case of (**II**), the hydrogen-bonded strings are aligned along the diagonal of the *a* and *b* axes and the cations are linked to one another by hydrogen bonds with the bromide and the waters of crystallization. The strings running parallel to the *b* axis are not hydrogen bonded to one another; in fact, the closest contacts appear to be between pairs of cations whose aliphatic CH_2 moieties face each other. Then, pairs of cations are linked to one another by hydrogen bonds to the bromide and the waters as described in the figure caption. Thus, the packing in (**II**) is similar to that observed in (**IV**) → (**VI**), despite differences in space groups and decidedly different from the packing mode observed in (**I**), once more demonstrating the effect of the counter ion in influencing the crystallization mode.

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SUPPLEMENTARY MATERIAL AVAILABLE:

Compound (**I**): Anisotropic thermal parameters (1 page), structure factor table (13 pages). Compound (**II**): Anisotropic thermal parameters (1 page), structure factor table (13 pages). These can be obtained directly from I. Bernal in printed or diskette form.