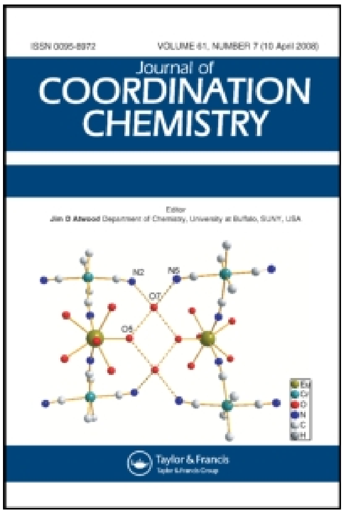

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 50. THE CRYSTALLIZATION BEHAVIOR OF [*trans*-Co(en)$_2$(NO$_2$)$_2$]ClO$_4$ (I), *MESO*-[Co-*trans*-Me-(N-Me-ETHYLENEDIAMINE)$_2$-trans-(NO$_2$)$_2$]ClO$_4$ (II), *K*[*trans*-Co(β-ALANINATO)$_2$(NO$_2$)$_2$] (III) AND THE ISOLATION AND PARTIAL STRUCTURAL DESCRIPTION OF (H$_5$O$_2$)[*trans*-Co(β-ALANINATO)$_2$(NO$_2$)$_2$] (IV)

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To cite this Article Bernal, Ivan , Cai, Jiwen , Somoza, Fernando and Massoud, Salah S.(1999) 'THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 50. THE CRYSTALLIZATION BEHAVIOR OF [*trans*-Co(en)$_2$(NO$_2$)$_2$]ClO$_4$ (I), *MESO*-[Co-*trans*-Me-(N-Me-ETHYLENEDIAMINE)$_2$-trans-(NO$_2$)$_2$]ClO$_4$ (II), *K*[*trans*-Co(β-ALANINATO)$_2$(NO$_2$)$_2$] (III) AND THE ISOLATION AND PARTIAL STRUCTURAL DESCRIPTION OF (H$_5$O$_2$)[*trans*-Co(β-ALANINATO)$_2$(NO$_2$)$_2$] (IV)', Journal of Coordination Chemistry, 46: 4, 533 — 550
To link to this Article: DOI: 10.1080/00958979908054917
URL: http://dx.doi.org/10.1080/00958979908054917

J. Coord. Chem., 1999, Vol. 46, pp. 533–550
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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 50. THE CRYSTALLIZATION BEHAVIOR OF [*trans*-Co(en)$_2$(NO$_2$)$_2$]ClO$_4$ (I), *MESO*-[Co-*trans*-Me-(N-Me-ETHYLENEDIAMINE)$_2$-*trans*-(NO$_2$)$_2$]ClO$_4$ (II), K[*trans*-Co(β-ALANINATO)$_2$(NO$_2$)$_2$] (III) AND THE ISOLATION AND PARTIAL STRUCTURAL DESCRIPTION OF (H$_5$O$_2$)[*trans*-Co(β-ALANINATO)$_2$(NO$_2$)$_2$] (IV)

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(Received 28 April 1997; Revised 29 October 1997; In final form 6 April 1998)

[*trans*-Co(en)$_2$(NO$_2$)$_2$]ClO$_4$ (I) crystallizes, at 22°C, from a deionized water solution, as a racemate, in space group $P\bar{1}$ (No. 2), with lattice constants: $a = 6.581(2)$ Å, $b = 8.274(1)$ Å, $c = 12.660(3)$ Å, $\alpha = 77.28(2)°$, $\beta = 76.58(2)°$, $\gamma = 75.20(2)°$; $V = 638.71$; Å^3 and d(calc; MW $= 370.59, z = 2) = 1.927$ g cm^{-3}. A total of 2233 data were collected over the range of $4° \leq 2\theta \leq 50°$; of these, 1961 (independent and with $I \geq 3\sigma(I)$) were used in the structural analysis. Data were corrected for absorption ($\mu = 15.989$ cm^{-1}) and the relative transmission coefficients ranged from 0.6792 to 0.9874. The final $R(F)$ and $R_w(F)$ residuals were, respectively, 0.0738 and 0.0763. Two half cations are located at inversion centers; the anions are in general positions.

meso-[Co-*trans*-Me-(N-Me-ethylenediamine)$_2$-*trans*-(NO$_2$)$_2$]ClO$_4$ (II) [(N-Meen) = N-methylethylenediamine] crystallizes at 22°C, from a deionized water solution in space group Pbca (No. 61) with lattice constants: $a = 16.882(5)$ Å, $b = 11.990(3)$ Å, $c = 15.017(5)$ Å; $V = 3039.72$ Å^3

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and d (calc; $MW = 398.64, z = 8) = 1.742\,g\,cm^{-3}$. A total of 5281 data were collected over the range of $4° \leq 2\theta \leq 50°$; of these, 1779 (independent and with $I \geq 2.5\sigma(I)$ were used in the structural analysis. Data were corrected for absorption ($\mu = 13.501\,cm^{-1}$ and the transmission coefficients ranged from 0.7956 to 0.9947. The final refinement of the structure (anisotropic thermal parameters for the heavy atoms; idealized hydrogens for the cation) are $R(F) = 0.045$ and $R_w(F) = 0.052$). The $-NO_2$ ligands are *trans* to one another in the axial direction while the N-methyl groups are *trans* to one another across the basal plane. The cations are located in general positions and the torsional angles of the en rings are δ(N1–C1–C2–N2 = 52.0°) and δ(N3–C3–C4–C4 = 51.0°), in contrast with those of (I) which are of opposite helical chirality. This compound is one of two *trans*-Co(III)X_2 cations of which we are aware that, while sitting at a general position of the space group, has two ethylenediamine rings of the same helical chirality.

K[*trans*-Co(β-alaninato)$_2$(NO_2)$_2$] (III) obtained after several batches of crystals of (IV) had separated from the mother liquor (see Syntheses). (III) crystallizes at 22°C, in space group Cc (No. 9) with lattice constants: $a = 12.385(6)\,Å$, $b = 13.109(5)\,Å$, $c = 8.290(5)\,Å$, $\beta = 115.19°$; $V = 1217.97\,Å^3$ and d(calc; $MW = 366.22, z = 4) = 1.997\,g\,cm^{-3}$. A total of 1238 data were collected over the range of $4° \leq 2\theta \leq 50°$; of these, 1016 (independent and with $I \geq 2.5\sigma(I)$ were used in the structural analysis. Data were corrected for absorption ($\mu = 17.90\,cm^{-1}$) and the transmission coefficients ranged from 0.5322 to 0.6627. The final $R(F)$ and $R_w(F)$ residuals were, respectively 0.020 and 0.022. Solution of the structure, using the first batch of crystals, proved that the compound isolated was the $(H_5O_2)^+$ derivative (see below and Discussion). A later batch of crystals contained (III). We have previously observed the precipitation of hydronium salts, trapped by amine carboxylato salts of cobalt (see Discussion). The anions consist of two six-membered rings formed by the metal and two (O,N)-bound β-alaninato ligands; and, both have chair conformations.

(H_5O_2) [*trans*-Co(β-alaninato)$_2$(NO_2)$_2$] (IV) is the substance that first crystalized from an aqueous solution of (III) (see Experimental). It crystallizes, at 22°C, in space group Cc (No. 9) or C2/c (No. 15) with lattice constants: $a = 12.389(39)\,Å$, $b = 13.120(11)\,Å$, $c = 8.299(9)\,Å$, $\beta = 115.09(19)°$; $V = 1221.72\,Å^3$ and d(calc; $MW = 364.15, z = 4) = 1.980\,g\,cm^{-3}$. An incomplete data set of 1592 reflections was collected over the range $4° \leq 2\theta \leq 50°$ because the crystal decomposes in air due to rapid loss of water of crystallization, as shown by differential scanning calorimetry. 956 data were independent with $I \geq 2.5\sigma(I)$ and were used in the structural analysis. Data were not corrected for absorption because of decomposition of the crystal. The final $R(F)$ and $R_w(F)$ residuals were, respectively, 0.14 and 0.16. To the precision of such a data set, the anions are identical with those found in (III); however the cation, which sits at an inversion center, consists of a proton sandwiched between the oxygens of two waters thus forming $(H_5O_2)^+$ cations similar to those we have described in the past (see Refs. [15–18]).

Keywords: Conglomerate crystallization; racemates; mechanisms of crystallization; cobalt amines; *trans*-dinitro cobalt compounds; cobalt derivatives of amino acids; hydronium ions

INTRODUCTION

We have studied a wide variety of *trans*-substituted cobalt(III) amines and found that some of them crystallize as conglomerates while others crystallize as racemates.[1–7] For example, a series of compounds of composition [*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), $X = NO_2$, $Y = NO_3$, $n = 0$ crystallize as conglomerates,[5] while closely related compounds crystallize as racemates.[6,7] We suggested that the crystallization behavior seemed to be controlled not only by the chemical nature of the optically active cation, but also by the nature of the counter anion.[1-6] We also noted that, in every case (conglomerate or racemate), the counter anion was achiral. However, we had no reasonable explanation for their selection of the crystallization pathway since the example above[4] is only the second family of *trans*-disubstituted compounds to behave thus. Moreover, the persistence to conglomerate crystallization of the series [*trans*-Co(3,2,3-tet)X_2]$Y{\cdot}n$H$_2$O, despite changes of axial ligands, and of their counteranions, was unprecedented.

Other derivatives of the family [*trans*-Co(3,2,3-tet)(NO$_2$)$_2$]$Y{\cdot}n$H$_2$O, crystallize as both conglomerates and racemates according to the nature of the charge compensating anion;[5] for example, $Y =$ Br, $n = 3$ (**VII**) crystallizes as a conglomerate, while $Y =$ ClO$_4$, $n = 0$ (**VIII**) and $Y =$ I, $n = 0$ (**IX**) crystallize as racemates. Thus far, two polymorphs of family [*trans*-Co(2,3,2-tet)(NO$_2$)$_2$]NO$_3$ crystallize as racemates.[6] Finally, *trans*-(R,S)-[CoCl(2,2,3-tet)(NH$_3$)ZnCl$_4$ crystallizes as a conglomerate.[7] Thus, it has become clear that conglomerate crystallization of *trans*-derivatives of cobalt amines is a pervasive phenomenon and that further structural studies of these substances is warranted.

To provide a clearer picture of the relationship between stereochemistry, counterion composition and conglomerate crystallization, we decided to probe the effect of composition on the crystallization pathway of *trans* species, hoping to obtain clues as to the reasons for the choice of crystallization pathway. We have prepared a new group of these substances whose structures and crystallization behavior we report herein.

EXPERIMENTAL

Syntheses

Compound (I): *trans*-[Co(en)$_2$(NO$_2$)$_2$]ClO$_4$ was prepared by addition of an excess of sodium perchlorate to a solution of the chloride prepared according to the procedure given earlier.[1]

Compound (II): To a 10 mmol solution of Na$_3$[Co(NO$_2$)$_6$] dissolved in water (40 mL), 20 mmol of N-methylethylenediamine (Fluka) in 20 mL of water was added slowly and with stirring. The solution was heated on a water bath for 20 min and filtered while still hot. To the cold solution, 5 mL of saturated NaClO$_4$ were added and the solution was left at room temperature. The precipitate which separated after 4 h was filtered, washed with ethanol and with ether, and air dried. Suitable crystals for X-ray diffraction were obtained by recrystallization upon standing at 22°C.

Compound (III): To a solution of 7.14 g of $CoCl_2{\cdot}6H_2O$ in 100 mL of water were added with stirring 5.35 g of β-alanine and 5.10 g of KNO_2. The solution was aerated for several hours filtered and allowed to crystallize at room temperature. The first two batches of crystals produced were of (IV). On the third batch, the space group and cell constants changed and the crystals produced were those of (III), which was subsequently verified by elemental analysis (see below).

Elemental Analyses

The parent of compound (I) was analyzed previously (see Ref. [1] and the only change made was the counter anion that is verified by the structure reported here. Its crystal structure suffices to identify the product. Compounds (II) and (III) were analyzed by Galbraith Laboratories.[8] Compound (II), theory for $CoClO_8N_6C_6H_{20}$: C = 18.08, H = 5.06, N = 21.08. Found: C = 18.07, H = 5.08, N = 21.04. Compound (III), theory of $CoKO_8N_4C_6H_{12}$: C = 19.68, H = 3.33, N = 15.30. Found C = 19.72, H = 3.30, N = 15.26. (IV) decomposes rapidly by loss of waters of crystallization, a fact verified by differential scanning calorimetry, which gives the correct water content of the lattice (see below) and also by the solution of the structure which shows a nearly identical anion to that found for (III). Finally, a pair of IR peaks found at 3309.6 cm^{-1} are the symmetric and antisymmetric O–H stretching vibrations.

Differential Scanning Calorimetry of (IV)

Measurements were carried out with a TGA V5.1A DuPont 2100: 21.8870 mg of sample, freshly removed from the mother liquor was placed in the sample holder and flooded with dry nitrogen. The sample begins decomposing rapidly near 200°C and precipitously at 240°C, at which point it loses 40.17% of its mass. At 500°C the sample is completely decomposed to Co_2O_3, which is a loss of 54.32% of the original mass. The resting product is Co_2O_3, as verified by its powder diffraction pattern.

Crystallography

Data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[9] of the SDP-Plus software package.[10] The procedure used for crystal alignment, cell constant determination, space group determination, and data collection were uniform for all four crystals. Processing of the data for (I) was carried with the Nonius package[9,10] while data processing for the other three were carried out with the PC version of the NRCVAX package.[11] Crystals were centered with data in the $20° \leq 2\Theta \leq 40°$ range and examination of the cell constants, absences, and Niggli matrix[12] clearly showed (I) to crystallize in a primitive, triclinic lattice, initially assumed to be $P\bar{1}$ (No. 2). (II) crystallizes in space group Pbca (No. 61) while crystals of (III) and (IV) belong in space groups Cc (No. 9) or C2/c (No. 15). Final assignment of the space groups of these two substances were made during the solution and refinement of the X-ray data (see below). The details of data collection are summarized in Tables I–IV, respectively, for compounds (I), (II), (III) and (IV). The intensity data sets were corrected for absorption using empirical curves derived from Psi scans[9,10] of suitable reflections. The scattering curves were taken from Cromer and Waber's compilation.[13]

The structures of all four compounds were solved from their Patterson maps using their heaviest atom as the initial phasing species for a difference Fourier map. We assumed for (I) that the correct space group was the centric choice. $P\bar{1}$ (No. 2) and refinement showed this was reasonable. There are two independent half cations sitting at inversion centers, and we have remarked in the past that this is a frequent occurrence for *trans*-$Co(en)_2X_2$

TABLE I Summary of data collection and processing parameters for [*trans*-$Co(en)_2(NO_2)_2]ClO_4$ (I)

Space group	$P\bar{1}$ (No. 2)
Cell constants	$a = 6.581(2)$ Å
	$b = 8.274(1)$
	$c = 12.660(3)$
	$\alpha = 77.28(2)°$
	$\beta = 76.58(2)$
	$\gamma = 75.20(2)$
Cell volume	$V = 638.71$ Å^3
Molecular formula	$CoClO_8N_6C_4H_{16}$
Molecular weight	370.59 g mol^{-1}
Density (calc; $z = 2$ mol/cell)	1.927 g cm^{-3}
Radiation employed	MoK$_\alpha$ ($\lambda = 0.71073$ Å)
Absorption coefficient	$\mu = 15.989$ cm^{-1}
Relative transmission coefficients	0.6792–0.9874
Data collection range	$4° \leq 2\Theta \leq 50°$
Scan width	$\Delta\Theta = 0.95 + 0.35 \tan\Theta$
Total unique data collected	2233
Data used in refinement*	1961
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0738
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum\|F_o\|^2]^{1/2}$	0.0763
Weights used	$w = [\sigma(F_o)]^{-2}$

*The difference between this number and the total is due to subtraction of 272 that did not meet the criterion that $I \geq 3\sigma(I)$.

TABLE II Summary of data collection and processing parameters for [*trans*-$(NO_2)_2$Co (*trans*-Meen)$_2$]ClO_4 (II)

Space group	Pbca (No. 61)
Cell constants	$a = 16.882(5)$ Å
	$b = 11.990(3)$
	$c = 15.017(5)$
Cell volume	$V = 3039.72$ Å^3
Molecular formula	$CoClO_8N_6C_6H_{20}$
Molecular weight	398.64 g mol^{-1}
Density (calc; $z = 8$ mol/cell)	1.742 g cm^{-3}
Radiation employed	MoK$_\alpha$ ($\lambda = 0.71073$ Å)
Absorption coefficient	$\mu = 13.501$ cm^{-1}
Relative transmission coefficients	0.7956–0.9947
Data collection range	$4° \le 2\Theta \le 50°$
Scan width	$\Delta\Theta = 0.95 + 0.35 \tan\Theta$
Total data collected	5281
Data used in refinement*	1779
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.045
$R_w = [\sum_w(\|F_o\| - \|F_c\|)^2/\sum\|F_o\|^2]^{1/2}$	0.052
Weights used	$w = [\sigma(F_o)]^{-2}$

*The difference between this number and the total is due to subtraction of 3512 that were standards, symmetry related or did not meet the criterion that $I \ge 2.5\sigma(I)$.

TABLE III Summary of data collection and processing parameters for K[*trans*-Co(β-alaninato)$_2$$(NO_2)_2$] (III)

Space group	Cc (No. 9)
Cell constants	$a = 12.385(6)$ Å
	$b = 13.109(5)$
	$c = 8.290(5)$
	$\beta = 115.19(5)$
Cell volume	$V = 1217.97$ Å^3
Molecular formula	$CoKO_8N_4C_6H_{12}$
Molecular weight	366.22 g mol^{-1}
Density (calc; $z = 4$ mol/cell)	1.997 g cm^{-3}
Radiation employed	MoK$_\alpha$ ($\lambda = 0.71073$ Å)
Absorption coefficient	$\mu = 17.90$ cm^{-1}
Relative transmission coefficients	0.5322–0.6627
Data collection range	$4° \le 2\Theta \le 50°$
Scan width	$\Delta\Theta = 0.95 + 0.35 \tan\Theta$
Total unique data collected	1238
Data used in refinement*	1016
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.020
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum\|F_o\|^2]^{1/2}$	0.022
Weights used	$w = [\sigma(F_o)]^{-2}$

*The difference between this number and the total is due to subtraction of 222 that did not meet the criterion that $I \ge 2.5\sigma(I)$.

cations bearing two identical, monodentate ligands at *trans* positions.[1-7] The perchlorate anion has an ordered Cl and one ordered oxygen (O5), the other three oxygens (O6, O7 and O8) are disordered probably due to hydrogen bond formation with the two half cations present in the asymmetric

TABLE IV Summary of data collection and processing for $(H_5O_2)[trans\text{-}Co(\beta\text{-alaninato})_2(NO_2)_2]$ (IV)

Space group	C2/c (No. 15)
Cell constants	$a = 16.882(5)$ Å $b = 11.990(3)$ $c = 15.017(5)$ $\beta = 115.09(19)$
Cell volume	$V = 1221.72$ Å^3
Molecular formula	$CoO_{10}N_4C_6H_{17}$
Molecular weight	364.15 g mol^{-1}
Density (calc; $z = 4$ mol/cell)	1.980 g cm^{-3}
Radiation employed	MoK$_\alpha$ ($\lambda = 0.71073$ Å)
Data collection range	$4° \leq 2\Theta \leq 50°$
Scan width	$\Delta\Theta = 0.95 + 0.35 \tan \Theta$
Total unique data collected	1592
Data used in refinement*	956
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	Refinement unfinished

unit; their disorder is illustrated by the coordinates listed in Table I, and omitted in the figures in order to avoid cluttering.

In the case of (II), the choice of space group is unequivocal and its Patterson map easily revealed the positions of the Co ion. After refinement of the scale factor and the positional parameters of the heavier atom, a difference Fourier map produced 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 Table II. In the other three cases, the space groups are very ambiguous.

The systematic absences of the X-ray diffraction patterns of compounds (III) and (IV) demonstrated that they crystallized in either space group Cc or C2/c. Solution of the Patterson functions in both space groups, subsequent refinement of the atoms, and difference maps, readily demonstrate that the former is the correct choice for (III) and the latter was the correct one for (IV). Details are given in Tables III and IV.

RESULTS AND DISCUSSION

Figures 1–3 give labelled views of the asymmetric units found for molecules (I), (II) and (III). Figures 4–6 depict the packing of the ions in their

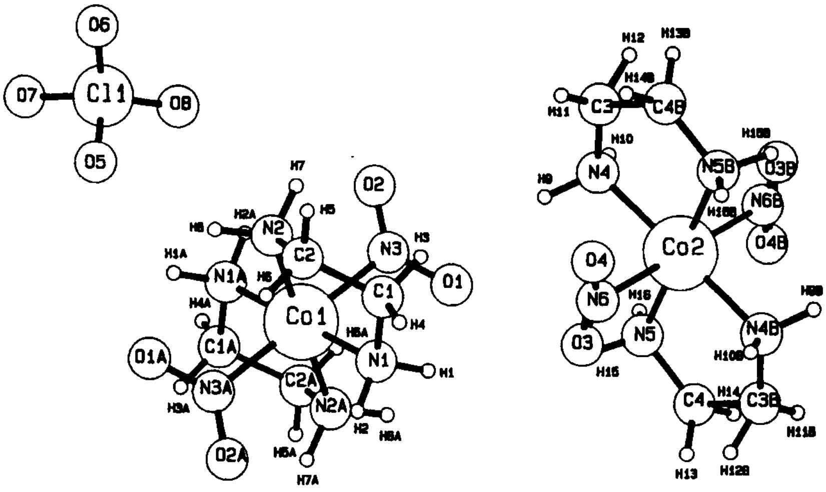

FIGURE 1 The ions in the asymmetric unit of (I); the perchlorate anion is partially disordered, as described by the coordinates of O6′, O7′ and O8′ (see Table V). For clarity, these atoms are omitted from the plots.

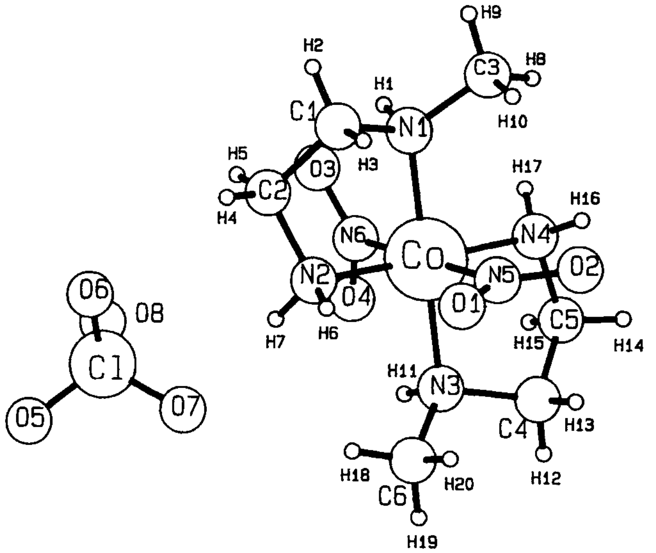

FIGURE 2 The ions in the asymmetric unit of (II); the perchlorate anion of this compound is ordered, as shown. Note the hydrogen bonding between the perchlorate and the hydrogens of N2. Also note that if one looks along the N1–N3 vector, the methyl groups are staggered. This is not always the case, as we have shown separately,[3] where we reported the isolation of both a staggered and an eclipsed cation of similarly alkylated metal amines of Co(III). Finally, note that the planes (ONO) of the two nitro groups are staggered across the N–Co–N vector, whereas those of (III) are eclipsed, or nearly so.

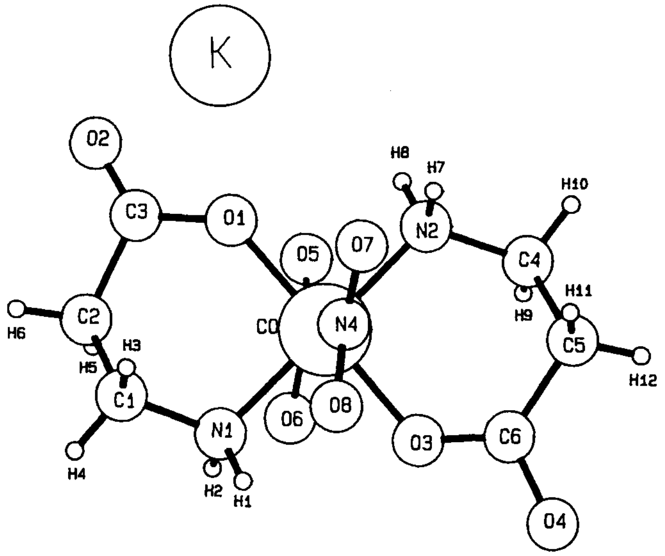

FIGURE 3 The ions in the asymmetric unit of (III); note that the planes (ONO) of the two nitro groups are eclipsed across the N–Co–N vector, whereas those of (II) are almost perfectly staggered. This comes about because of the differing orientations of the amino hydrogens with which the nitro oxygens are intra-molecularly hydrogen bonded. Note the close proximity of the potassium cation to the oxygens of both the carboxylic group and the nitro ligand oxygens. These distances are given in Table X.

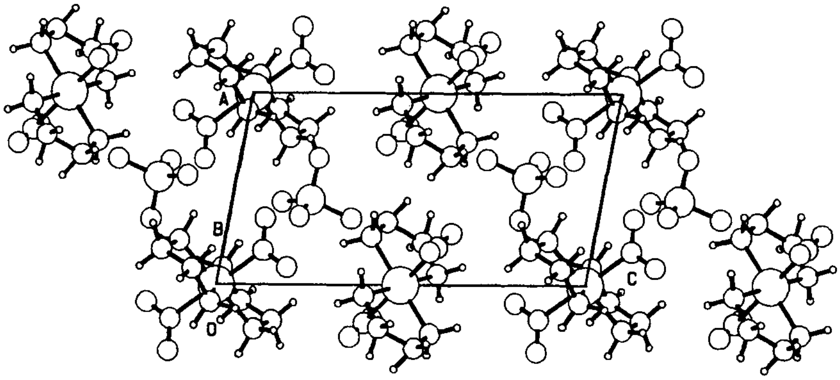

FIGURE 4 The packing of the ions in the unit cell of (I). All nine inversion centers of the *b*-axis projection are readily recognized; the inversion center at 1/2, 1/2, 1/2 is obviously between a pair of perchlorate anions. Cations are linked together by the agency of hydrogen bonds to anions lying 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.

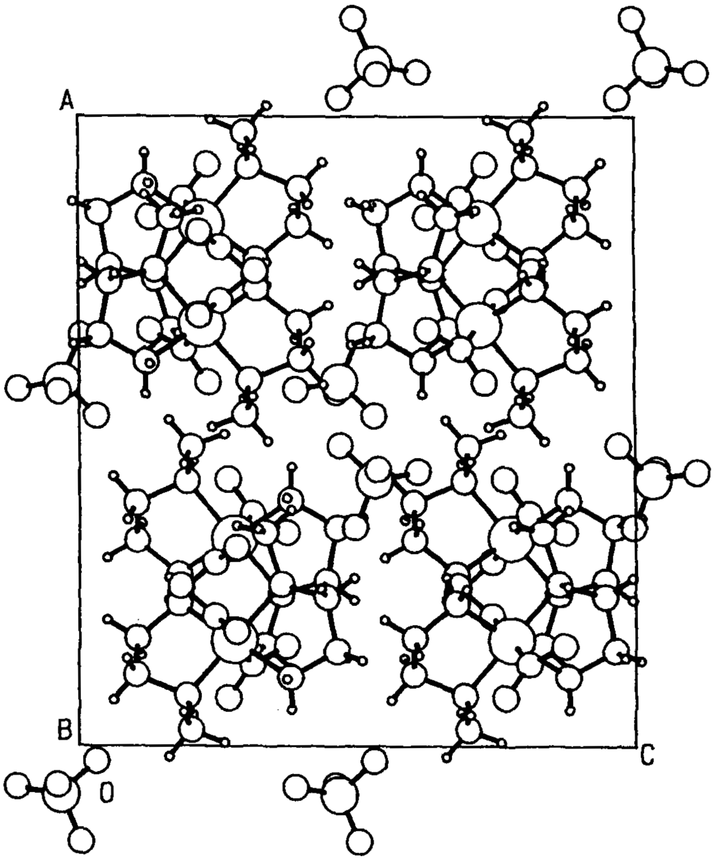

FIGURE 5 The packing of the contents of the unit cell of (II). As in the case of (I), the cations are linked to one another by anions to which they are hydrogen bonded. The packing mode is obviously centrosymmetric, as is most obvious in the region of 1/2, 1/2, 1/2.

respective unit cells. Final positional and equivalent-isotropic thermal parameters are given in Tables V–VII and bond lengths are listed in Tables VIII–X.

Since *trans* compounds crystallize in both centrosymmetric crystals and enantiomorphic crystals,[1–6] depending on the counter ion, we decided to explore the effect of counter anion in the dinitro bis-ethylenediamine series. As for previous compounds, crystals of compound (I) are centrosymmetric, and the cation is an internal mesomer (the two independent cations in the asymmetric unit sit at inversion centers; therefore, they contain en ligands of opposite helical chirality). This is frequently the case with

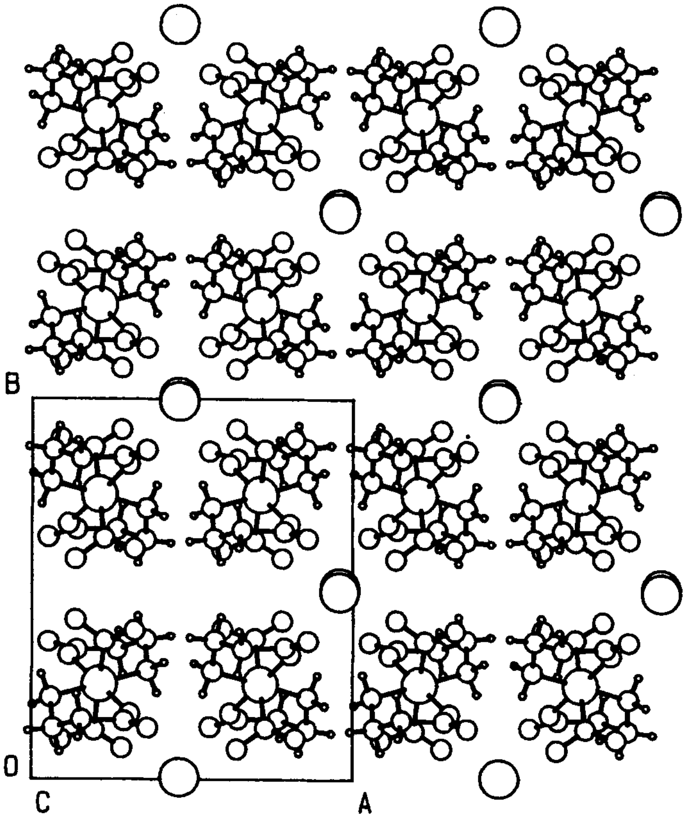

FIGURE 6 The packing of the contents of the unit cell of (III). Note that the anions are mostly intra-molecularly hydrogen bonded and that they brought together primarily by potassium cations which link them *via* K···O bonds, readily seen everywhere in this *c*-axis projection.

trans-[Co(en)$_2$(X_2)]Y complexes.[1,3] Finally, the *trans* dichloro compound *trans*-[Co(en)$_2$Cl$_2$]ClO$_4$ is isomorphous and nearly isostructural[14] with (I). Therefore, we have not yet found a counteranion which will produce conglomerate crystals of *trans*-[Co(en)$_2$(X_2)]$^+$, but it will certainly be useful, and revealing, to do so since its packing diagram would show us the desired properties for achiral anions required to so crystallize.

Comparison of the packing of *trans*-[Co(en)$_2$(X_2)]Y complexes reveal that none of them form the infinite helical strings associated with conglomerate crystallization. This is certainly not the case with (I) as can readily be ascertained by referring to Figure 4, which illustrates the packing.

TABLE V Positional and equivalent isotropic thermal parameters for compound (I)

	x	*y*	*z*	*Biso*
Co1	0.0000	0.0000	0.0000	2.09(2)
Co2	0.0000	0.0000	−0.5000	2.18(3)
Cl1	−0.5580(3)	0.3880(3)	0.2118(2)	4.35(5)
O1	−0.094(1)	−0.0671(9)	−0.1818(5)	6.6(2)
O2	−0.3467(9)	0.0903(9)	−0.0985(5)	6.6(2)
O3	0.269(2)	0.010(1)	−0.3877(8)	11.8(3)
O4	0.173(2)	0.210(2)	−0.437(1)	17.2(5)
O5	−0.340(1)	0.378(1)	0.2126(6)	7.6(2)
O6	−0.643(2)	0.560(2)	0.189(1)	8.9(4)
O7	−0.654(2)	0.338(2)	0.331(1)	9.2(4)
O8	−0.567(2)	0.290(2)	0.134(1)	9.7(4)
O6′	−0.598(3)	0.222(2)	0.261(1)	8.5(5)
O7′	−0.728(3)	0.496(3)	0.263(2)	10.5(6)
O8′	−0.605(3)	0.409(3)	0.105(2)	9.9(5)
N1	0.2309(8)	0.0487(7)	−0.1220(4)	2.7(1)
N2	−0.0915(8)	0.2462(7)	−0.0069(4)	2.8(1)
N3	−0.1797(8)	0.0086(7)	−0.1091(4)	2.6(1)
N4	−0.2535(8)	0.0885(8)	−0.3971(4)	3.1(1)
N5	0.0564(9)	−0.2228(8)	−0.4074(5)	3.4(1)
N6	0.1971(6)	0.0862(5)	−0.4194(3)	0.82(9)
C1	0.186(1)	0.236(1)	−0.1665(6)	3.9(2)
C2	0.084(1)	0.3280(9)	−0.0730(6)	3.7(2)
C3	−0.328(2)	0.265(1)	−0.432(1)	7.9(4)
C4	0.222(2)	−0.339(1)	−0.462(1)	10.9(4)
H1	0.2387	−0.0129	−0.1784	5*
H2	0.3629	0.0165	−0.0966	5*
H3	0.0921	0.2600	−0.2174	5*
H4	0.3159	0.2692	−0.2024	5*
H5	0.0285	0.4437	−0.0999	5*
H6	0.1861	0.3209	−0.0289	5*
H7	−0.2141	0.2872	−0.0403	5*
H8	−0.1253	0.2718	0.0655	5*
H9	−0.2187	0.0704	−0.3260	5*
H10	−0.3629	0.0306	−0.3938	5*
H11	−0.3047	0.3509	−0.4003	5*
H12	−0.4375	0.3110	−0.4741	5*
H13	0.3678	−0.3612	−0.4550	5*
H14	0.1999	−0.4246	−0.4941	5*
H15	0.0964	−0.2110	−0.3425	5*
H16	−0.0703	−0.2661	−0.3879	5*

Biso is the Mean of the Principal Axes of the Thermal Ellipsoid.
*Isotropic thermal parameter was fixed at this value.

Compound (**II**) is best described as *meso*-[Co-*trans*-Me-(N-Me-ethylene-diamine$_2$-*trans*-(NO$_2$)$_2$]Cl (**I**) where the *meso* refers to the fact that the two chiral, methylated amine ligand atoms are an (R,S) pair, N1 is R and N3 is S for the anion whose coordinates are listed in Table III. The *trans* appelatives refer to the locations of the two $-NO_2$ ligands and the *trans* pair of methylated amine nitrogens. We have recently[3] described the structures of both, the

TABLE VI Positional and equivalent isotropic thermal parameters for compound (II)

	x	*y*	*z*	*Biso*
Co	0.33100(5)	0.39299(6)	0.27865(5)	2.12(3)
Cl	0.57739(12)	0.21554(14)	0.96742(14)	4.26(8)
O1	0.3168(3)	0.6254(3)	0.2826(3)	4.00(22)
O2	0.2449(3)	0.5531(4)	0.1828(3)	4.19(21)
O3	0.3403(3)	0.1918(4)	0.3730(3)	4.50(23)
O4	0.4235(3)	0.2016(4)	0.2679(4)	5.8(3)
O5	0.6518(3)	0.1956(5)	1.0037(5)	7.9(4)
O6	0.5235(5)	0.1730(8)	1.0307(7)	12.6(6)
O7	0.5653(5)	0.1526(8)	0.8890(5)	11.4(5)
O8	0.5616(5)	0.3276(5)	0.9620(5)	10.2(5)
N1	0.2424(3)	0.3748(4)	0.3633(3)	3.33(22)
N2	0.3903(3)	0.4562(4)	0.3799(4)	3.47(24)
N3	0.4203(3)	0.4098(4)	0.1944(3)	3.24(22)
N4	0.2729(3)	0.3257(4)	0.1800(3)	3.02(22)
N5	0.2930(3)	0.5414(4)	0.2447(3)	2.68(20)
N6	0.3693(3)	0.2444(4)	0.3111(4)	3.18(23)
C1	0.2624(5)	0.4417(6)	0.4452(5)	4.5(4)
C2	0.3480(5)	0.4290(6)	0.4638(5)	4.8(4)
C3	0.1602(4)	0.3972(6)	0.3344(5)	4.4(3)
C4	0.3860(4)	0.3990(7)	0.1021(4)	4.3(3)
C5	0.3279(5)	0.3058(6)	0.1037(5)	4.3(3)
C6	0.4743(4)	0.5051(6)	0.2018(5)	4.3(3)
H1	0.246	0.298	0.379	4.1
H2	0.233	0.415	0.494	5.3
H3	0.250	0.518	0.435	5.3
H4	0.364	0.479	0.510	5.6
H5	0.359	0.355	0.481	5.6
H6	0.394	0.535	0.373	4.3
H7	0.442	0.425	0.381	4.3
H8	0.149	0.354	0.283	5.2
H9	0.125	0.377	0.381	5.2
H10	0.155	0.474	0.321	5.2
H11	0.451	0.344	0.205	4.0
H12	0.427	0.383	0.061	5.1
H13	0.360	0.466	0.086	5.1
H14	0.299	0.304	0.049	5.1
H15	0.355	0.237	0.112	5.1
H16	0.232	0.375	0.162	3.8
H17	0.251	0.257	0.199	3.8
H18	0.495	0.509	0.261	5.1
H19	0.517	0.496	0.161	5.1
H20	0.446	0.572	0.188	5.1

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

meso and racemic derivatives of this cation but in the form of the *meso*-[Co-*trans*-Me-(N-Me-ethylenediamine)$_2$-*trans*-$(NO_2)_2$]Cl (X) and of racemic-[Co-*trans*-Me-(N-Me-ethylenediamine)$_2$-*trans*$(NO_2)_2$]Cl · $2H_2O$ (XI). We have discussed the stereochemistry of both molecules and have made comparisons of their geometrical and packing relationships and differences.

TABLE VII Positional and equivalent isotropic thermal parameters for compound (**III**)

	x	*y*	*z*	*Biso*
Co	0.70923	0.75003(18)	0.48720	1.220(19)
K	0.9581(4)	0.50572(6)	0.7357(6)	1.98(9)
O1	0.8031(8)	0.6725(7)	0.6923(13)	1.8(4)
O2	0.8594(9)	0.3647(11)	0.4725(15)	2.4(4)
O3	0.6137(8)	0.8268(7)	0.2795(11)	1.8(4)
O4	1.0507(9)	0.6378(10)	0.4925(15)	2.5(4)
O5	0.8201(9)	0.8923(8)	0.7520(14)	3.0(4)
O6	0.6350(9)	0.9205(8)	0.6164(14)	2.8(4)
O7	0.7786(11)	0.5821(9)	0.3516(18)	3.8(6)
O8	0.5893(10)	0.6047(10)	0.2237(17)	4.0(4)
N1	0.5585(8)	0.7159(10)	0.4978(14)	1.9(5)
N2	0.8588(8)	0.7863(8)	0.4819(14)	1.5(4)
N3	0.7251(9)	0.8651(8)	0.6316(15)	2.3(4)
N4	0.6925(9)	0.6287(7)	0.3345(12)	1.5(4)
C1	0.5657(12)	0.6344(10)	0.6224(19)	2.1(5)
C2	0.6538(12)	0.6571(10)	0.7965(16)	2.0(5)
C3	0.7860(10)	0.6535(9)	0.8361(17)	1.9(5)
C4	0.8553(12)	0.8688(12)	0.3570(19)	2.1(5)
C5	0.7648(9)	0.8416(11)	0.1583(15)	2.3(5)
C6	0.6391(11)	0.8414(9)	0.1490(15)	1.5(4)
H1	0.503	0.695	0.382	2.5
H2	0.530	0.776	0.532	2.5
H3	0.586	0.572	0.583	3.2
H4	0.490	0.627	0.626	3.2
H5	0.638	0.724	0.824	3.0
H6	0.643	0.610	0.875	3.0
H7	0.889	0.727	0.450	2.3
H8	0.912	0.807	0.599	2.3
H9	0.831	0.930	0.392	2.7
H10	0.933	0.878	0.362	2.7
H11	0.783	0.776	0.127	3.0
H12	0.770	0.891	0.079	3.0

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

Therefore, since the cations present in (**II**) and (**X**) are very similar, we refer the reader to the published comparison.[3] The two most important results obtained here are: (a) it is notable that the helical chirality of the ethylenediamine N–C–C–N rings is the same in (**II**) and (**X**) (both are δδ *or* λλ). In previous examinations of the helical chirality of *trans*-bis-ethylenediamine metal complexes, we observed that all compounds crystallizing as racemates had, till recently, exhibited pairs of ethylenediamine rings of opposite chirality, whether the ions sat at general or special positions. Interestingly, both (**II**) and (**X**) crystallize with both en rings of the same chirality (b) neither the chloride (**X**) nor the perchlorate (**II**) crystallize as conglomerates despite

TABLE VIII Bond lengths and angles for compound (I)

A. Bond distances (Å)			
Co1-N1	1.951(2)	Cl1-O8′	1.426(7)
Co1-N2	1.959(2)	O1-N3	1.179(2)
Co1-N3	1.996(2)	O2-N3	1.129(2)
Co2-N4	1.950(2)	O3-N6	0.777(3)
Co2-N5	1.952(2)	O4-N6	0.979(5)
Co2-N6	2.154(1)	N1-C1	1.501(3)
Cl1-O5	1.415(2)	N2-C2	1.482(3)
Cl1-O6	1.384(5)	N4-C3	1.417(4)
Cl1-O7	1.506(5)	N5-C4	1.413(4)
Cl1-O8	1.426(5)	C1-C2	1.485(3)
Cl1-O6′	1.445(6)	C3-C4	1.442(5)
Cl1-O7′	1.370(2)		
B. Bond angles (°)			
N1-Co1-N1	179.98(8)	O7-Cl1-O8	118.5(3)
N1-Co1-N2	86.21(7)	O5′-Cl1-O6	105.8(2)
N1-Co1-N2	93.79(7)	O5′-Cl1-O7	125.4(3)
N1-Co1-N3	89.09(7)	O5′-Cl1-O8	114.1(3)
N1-Co1-N3	90.91(7)	O6′-Cl1-O7′	103.8(4)
N2-Co1-N2	179.97(8)	O6′-Cl1-O8′	102.2(4)
N2-Co1-N3	90.78(7)	O7′-Cl1-O8′	102.9(4)
N2-Co1-N3	89.22(7)	Co1-N2-C2	109.3(1)
N3-Co1-N3	179.98(7)	Co1-N3-O1	115.3(2)
N4-Co2-N4	179.98(9)	Co1-N3-O2	117.7(2)
N4-Co2-N5	94.04(8)	Co1-N1-C1	108.8(1)
N4-Co2-N5	85.96(8)	Co2-N4-C3	110.4(2)
N4-Co2-N6	90.11(6)	Co2-N5-C4	111.8(2)
N4-Co2-N6	89.89(6)	Co2-N6-O3	111.2(3)
N5-Co2-N5	179.97(8)	Co2-N6-O4	109.3(3)
N5-Co2-N6	89.58(6)	O1-N3-O2	126.9(2)
N5-Co2-N6	90.42(6)	O3-N6-O4	139.4(4)
N6-Co2-N6	179.97(2)	N1-C1-C2	108.5(2)
O5-Cl1-O6	104.4(2)	N2-C2-C1	107.3(2)
O5-Cl1-O7	104.3(2)	N4-C3-C4	116.6(3)
O5-Cl1-O8	108.3(2)	N5-C4-C3	114.4(3)
O6-Cl1-O7	103.9(3)		
O6-Cl1-O8	116.0(3)		

having homochiral cations. These are the only two examples of *trans*-bis-ethylenediamine compounds crystallizing at a general position while having a pair of homochiral rings. We suspect this is the result of having N-methylated amino groups requiring the hydrogens to be in the axial position. It is equally notable that a geometrical isomer of (**II**) and (**X**) crystallizes with a pair of N-Meen rings of opposite helical chirality; thus, the presence of N-Meen rings is not the only factor affecting the outcome.

Compound (**III**) and (**IV**) are also racemates despite the change of counter cation. The fact that (**IV**) came out of solution first was a surprise of us. In retrospect, however, this is not so novel since we isolated using a variety of

TABLE IX Bond lengths and angles for compound (**II**)

A. Bond distances (Å)			
Co–N1	1.975(5)	O2–N5	1.243(7)
Co–N2	1.972(5)	O3–N6	1.225(7)
Co–N3	1.978(5)	O4–N6	1.233(8)
Co–N4	1.952(5)	N1–C1	1.507(9)
Co–N5	1.959(5)	N1–C3	1.478(9)
Co–N6	1.957(5)	N2–C2	1.485(9)
Cl–O5	1.390(6)	N3–C4	1.508(9)
Cl–O6	1.410(10)	N3–C6	1.466(8)
Cl–O7	1.413(9)	N4–C5	1.494(9)
Cl–O8	1.373(7)	C1–C2	1.479(13)
O1–N5	1.224(6)	C4–C5	1.487(11)
B. Bond angles (°)			
N1–Co–N2	86.06(24)	O7–Cl–O8	116.5(5)
N1–Co–N3	179.40(20)	Co–N1–C1	107.2(4)
N1–Co–N4	93.56(23)	Co–N1–C3	120.1(4)
N1–Co–N5	91.11(20)	C1–N1–C3	110.7(5)
N1–Co–N6	89.42(22)	Co–N2–C2	109.0(4)
N2–Co–N3	93.83(23)	Co–N3–C4	106.7(4)
N2–Co–N4	178.18(20)	Co–N3–C6	120.3(4)
N2–Co–N5	91.02(21)	C4–N3–C6	112.0(5)
N2–Co–N6	89.42(21)	Co–N4–C5	109.6(4)
N3–Co–N4	86.53(22)	Co–N5–O1	121.3(4)
N3–Co–N5	89.48(20)	Co–N5–O2	120.7(4)
N3–Co–N6	89.99(22)	O1–N5–O2	118.0(5)
N4–Co–N5	90.77(21)	Co–N6–O3	121.7(4)
N4–Co–N6	88.79(21)	Co–N6–O4	119.5(4)
N5–Co–N6	179.32(22)	O3–N6–O4	118.8(5)
O5–Cl–O6	104.9(5)	N1–C1–C2	108.6(6)
O5–Cl–O7	111.4(5)	N2–C2–C1	106.7(6)
O5–Cl–O8	111.6(4)	N3–C4–C5	107.6(5)
O6–Cl–O7	106.0(6)	N4–C5–C4	107.6(5)
O6–Cl–O8	105.6(6)		

TABLE X Bond distances and bond angles for compound (**III**)

A. Bond distances (Å)			
Co–O1	1.896(9)	O5–N3	1.228(14)
Co–O3	1.909(9)	O6–N3	1.291(14)
Co–N1	1.957(10)	O7–N4	1.185(15)
Co–N2	1.930(9)	O8–N4	1.255(15)
Co–N3	1.884(11)	N1–C1	1.462(18)
Co–N4	1.988(9)	N2–C4	1.486(18)
K–O1	2.830(9)	C1–C2	1.422(20)
K–O2	2.721(12)	C2–C3	1.528(17)
K–O4	3.216(14)	C3–O2a	1.134(17)
K–O7	3.171(14)	C4–C5	1.589(18)
O1–C3	1.320(15)	C5–C6	1.527(17)
O3–C6	1.263(15)		
B. Bond angles (°)			
O1–Co–O3	179.4(4)	K–O1–C3	95.8(7)
O1–Co–N1	94.0(4)	Co–N1–C1	115.3(8)

TABLE X (*Continued*)

O1–Co–N2	85.6(4)	Co–N2–C4	116.9(8)
O1–Co–N3	90.0(5)	Co–N3–O5	123.6(9)
O1–Co–N4	90.0(4)	Co–N3–O6	122.4(8)
O3–Co–N1	85.6(4)	O5–N3–O6	113.9(11)
O3–Co–N2	94.7(4)	Co–N4–O7	119.5(9)
O3–Co–N3	90.5(5)	Co–N4–O8	117.7(8)
O3–Co–N4	89.5(4)	O7–N4–O8	122.8(11)
N1–Co–N2	178.5(5)	N1–C1–C2	110.7(11)
N1–Co–N3	89.9(5)	C1–C2–C3	120.0(11)
N1–Co–N4	90.1(5)	N2–C4–C5	110.9(11)
N2–Co–N3	88.6(4)	C4–C5–C6	107.9(10)
N2–Co–N4	91.3(4)	O3–C6–C5	125.3(10)
N3–Co–N4	179.9(4)	O2–K–O7	61.7(3)
O1–K–O2	112.0(3)	Co–O1–K	130.7(5)
O1–K–O7	58.7(3)	Co–O1–C3	129.7(8)

metal amine carboxylates as hydronium ion traps, the following hydronium ions:

Compound	*Ref.*
$(H_3O)[Co(en)_2(oxalato)]Cl_2$	[15]
$(H_5O_2)[\textit{cis}\text{-}\alpha\text{-}Co(edda)_2(oxalato)]$*	[16]
$K(H_5O_2)[Co(pddpda)]_2 \cdot 4H_2O$*	[17]
$K(H_9O_4)[Co(\textit{trans}\ N,N\text{-}glycinato)_2(\textit{cis}\text{-}NO_2)_2]_2$	[18]

* edda = N,N′-ethylenediamine diacetic acid and pddpda = N,N′-propylenediamine dipropionic acid.

CONCLUSIONS

None of the four compounds selected for this study crystallize as conglomerates which is helpful in narrowing the search for those that do. However, we have also found some interesting and unexpected results, namely: (1) Compound (**III**) is another hydronium ion trap whose aqueous solution produces crystals of (**IV**) first. (2) That crystals of (**IV**) are produced from a deionized aqueous solution of (**III**) is remarkable since the concentration of hydrogen ion in deionized water is 1×10^{-7} while that of K^+ is several orders of magnitude higher. Thus, the solubility difference is enormous. (3) When hydrogen ions are sufficiently depleted, one obtains the expected potassium salt. (4) Finally, it is remarkable that the nature of the hydronium ion trapped by these amine carboxylates is so sensitive to the nature of the compound doing the trapping; thus far, we have trapped three of the four known hydronium ions, the only one we have not yet trapped is $H_7O_3^+$.

Supplementary Material Available

Anisotropic thermal parameters and structure factor tables for the three compounds. These can be obtained directly from I. Bernal in printed or diskette form.

Acknowledgements

We thank the Robert A. Welch Foundation for support of this research (Grant E-592 to I. Bernal) and for fellowships granted to J. Cai and F. Somoza. We thank the National Science Foundation for the funds used in purchasing the diffractometer. S.S. Massoud thanks Kuwait University for Grant # SC 073 extended to him while he was a Visiting Professor there.

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