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The Phenomenon of Conglomerate Crystallization. VII. *Clavic* Dissymmetry in Coordination Compounds. V. An Investigation of the Crystallization Behavior of [*cis*-β-Co(triethylenetetramine)(NO_2)$_2$]X (X = I, NO_3) and the Crystal Structure of Racemic [*cis*-β-Co(trien)(NO_2)$_2$]NO_3*

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Abstract

[*cis*-β-Co(trien)(NO_2)$_2$]X ($X = I^-$, NO_3^-) were prepared and examined crystallographically to ascertain whether or not they undergo conglomerate crystallization. As predicted earlier, the nitrate crystallizes as a racemate: space group $P2_1/n$ with cell constants of $a = 7.604(3)$, $b = 13.019(2)$, $c = 14.472(3)$ Å, $\beta = 98.13(3)°$, $V = 1418.26$ Å^3, $D_c = 1.682$ g cm^{-3}, $Z = 4$. The bonding parameters and overall stereochemistry of the [*cis*-β-Co(trien)] fragment of the cation are essentially identical with that of resolved and racemic salts sharing this common fragment, proving that lattice forces do not play a major role in shaping its geometrical features.

The iodide crystallizes in the monoclinic space group *Cc*, with cell constants of $a = 15.65(1)$, $b = 6.53(3)$, $c = 13.095(7)$ Å, $\beta = 100.59(5)°$, $V = 1314.72$ Å^3, $D_c = 2.142$ g cm^{-3}, $Z = 4$. The crystals of the iodide are not only extremely small but of poor quality, allowing only a qualitative solution of the structure which, nonetheless, is sufficient to establish that this salt also crystallizes as a racemate – a surprise in view of the fact that the α isomer crystallizes as a conglomerate; thus, there is a major difference in the crystallization behaviour of this pair of geometrical isomers.

Introduction

In studies [1–3] preceding this, we reported conglomerate [4] crystallization of *cis*-dinitroamine cobalt coordination compounds belonging to a class we named *clavic* (from the Latin word for paddle or tiller) because some of the ligands (*i.e.*, $-NO_2$) resemble broad blades or paddles. When anchored by the agency of hydrogen bonds to adjacent amine (terminal $-NH_2$ or $-NH_3$) moieties, they impose specific dissymmetric arrangements on the whole. In fact, in one case [*trans*-Co(NH_3)$_2$(NO_2)$_4$]$^-$ a chiral, helix-like, arrangement of a pair of *cis*-NO_2 ligands, anchored into such array by the axial pair of $-NH_3$ moieties, is the source of dissymmetry. Other examples were presented [1], making it clear that a classical chiral backbone such as that present in Co(en)$_2$ fragments is not the source of the effect. Further, it was shown [1–3] that packing forces play no role in dictating these chiral conformations and configurations. Readers are directed to the preceding papers [1–3] for experimental results and details of the arguments.

We noted in our 1985 reports [1–3] that compounds in the inorganic, as well as the organic realm, containing clavic functional groups exhibit an unusually high incidence of conglomerate crystallization (according to the 1981 survey [4], only 248 examples were recorded in the chemical literature, listed in ref. 4). Consequently, since coordination compounds are extremely flexible stereochemical laboratory specimens, we decided to explore more of these geometrically, conformationally and configurationally multi-isomeric compounds hoping to identify the factors responsible for their enhanced propensity for conglomerate crystallization.

One issue raised earlier [1, 2] was the role, if any, of the counter-ion of charged clavic species in enhancing, or reducing, the incidence of conglomerates. The question was prompted by these observations: (a) whereas [*cis*-Co(en)$_2$(NO_2)$_2$]X (X = Cl, Br) undergo conglomerate crystallization [1, 5] the nitrate [6] crystallizes as a racemate. Differences in intra- and intermolecular hydrogen bonding between the halides and the nitrate led to the suggestion [1] that the latter anion disrupted the intramolecular hydrogen bonding needed to anchor the clavic $-NO_2$ groups to the axial $-NH_2$ (or $-NH_3$)

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*In this paper the following abbreviations are used: en = 1,2-diaminoethane; trien = 1,4,7,10-tetraazadecane.

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moieties which appears to be the mechanism whereby the $Co(NO_2)_2$ ensemble is rendered chiral [1–3]; (b) insofar as conglomerate crystallization, the role of the nitrate on hydrogen bonding does not have to always be disruptive. Some years ago [7], we documented the fact that the entire series $M(en)_3(NO_3)_2$, (with $M = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) undergo conglomerate crystallization into massive, hexagonal, crystals some weighing as much as 10 to 20 g. Since all of these cations are labile and crystallize as racemates with other counter anions, the unexpected source of stability was traced [7] to the intricate hydrogen bonding with which the nitrate anions stabilize the system. Consequently, counter ions such as nitrate can play both, positive and negative roles in conglomerate crystallization processes. Thus, for the purpose of understanding conglomerate crystallization at the molecular level, these systems provide interesting testing opportunities since their geometry can readily be altered (*cis vs. trans* isomers; α *vs.* β trien, etc.) and the counter ions can be exchanged in order to ascertain the nature of the successful combinations.

In previous work [1, 2] we examined only the *cis*-α-conformer of the $[Co(trien)(NO_2)_2]^+$ cation and reported that in two salts, the chloride and the [*trans*-$Co(NH_3)_2(NO_2)_4]^-$, the cation underwent conglomerate crystallization. In this report we document the crystallization behaviour of one halide and the nitrate of a different conformational isomer of the Co(trien) cations – [*cis*-β-$Co(trien)(NO_2)_2]^+$.

Experimental

Preparation of the Compounds

[cis-β-Co(trien)(NO₂)₂]₂(NO₃)

The procedure of Sargeson and Searle [8] was followed for the preparation of [*cis*-α-Co(trien)-$(Cl_2)_2]Cl$ and then the following modified version of their procedure [8] was used to prepare a solution of the carbonato $[Co(trien)CO_3]^+$ cation, from which we prepared the above compound.

55 g of [*cis*-α-Co(trien)$(Cl_2)]Cl$ and 16 g of Li_2CO_3 in 110 ml H_2O were heated to 80 °C, with occasional stirring, for 1 h. The purple color turned to red and when the solution became alkaline (after *ca.* 1 h) the excess of Li_2CO_3 was filtered off and the solution cooled. 2.8 g $CaCl_2$ were stirred in for a few minutes and the solution filtered again. Since the carbonato derivative would not crystallize, as described [8], despite the addition of as much as 1 l of ethanol (others have experienced the same problem*) the solution was evaporated to 200 ml under reduced pressure and 175 ml of 2 M HNO_3 were added. After 25 min, 25 g of solid $NaNO_2$ were stirred into the solution and, 15 min later, yellow and orange crystals began precipitating. The solution was kept at room temperature for one day and then filtered. The crystals were washed with cold 1 M HNO_3, ethanol, air dried, redissolved in warm water (50 °C) and fractionally crystallized at 2 °C. The procedure was repeated three times. The first crop, yellow–orange crystals, was the more insoluble [*cis*-α-Co(trien)-$(NO_2)_2]Cl \cdot H_2O$, as proven by a structural analysis performed here [10]. After it was evident that no more crystals of the α-chloride would be crystallizing out, the solution was concentrated and placed in the refrigerator at 2 °C, whereupon amber–orange crystals of the desired [*cis*-β-$Co(trien)(NO_2)_2]$-(NO_3) precipitated.

[cis-β-Co(trien)(NO₂)₂]I

This salt was prepared by adding an equimolar amount of freshly recrystallized, solid, NaI to a solution of the nitrate. Note that the presence of even small amounts of the I_3^- anion will cause the isomerization of the β to the α form**. Thus, the use of freshly recrystallized NaI is essential to prevent isomerization. All the crystals of [*cis*-β-Co(trien)-$(NO_2)_2]I$ obtained, thus far, are extremely small (see below).

Collection and Processing of X-ray Diffraction Data

All data collection was carried out with an Enraf-Nonius CAD-4 diffractometer operating with the Molecular Structure Corporation TEXRAY-230 Modification [12] of the SDP-Plus Programs [13]. The reader is referred to their manuals for the details of the various routines mentioned. The scattering curves are those of the International Tables [14].

The amber-orange crystals of [*cis*-β-Co(trien)-$(NO_2)_2](NO_3)$ had well defined faces and that selected for data collection was mounted on a translation head and onto the diffractometer. A set of 25 reflections were centered and used to define the orientation and Niggli matrices [15]. The cell is primitive and monoclinic; a subsequent search for

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*Excess $NaClO_4$ added to the solution reliably gave good yields of the carbonate with the perchlorate as the counter-anion [9].

**Initially we used NaI, stored in a brown bottle, directly as it was on the shelf. However, a crystal selected from the recrystallized material was found to have the same space group and identical cell constants as those of [*cis*-α-Co(trien)-$(NO_2)_2]I \cdot H_2O$, whose structure we have recently completed [11]. Thinking we had accidentally selected a crystal of an small impurity, three more, randomly selected crystals, from the same batch were examined and found to be identical with the first one. The NaI used was found to be slightly yellow due to small amounts of I_3^-. Recrystallization eliminated the impurity and the pure NaI readily produced the desired β-isomer.

TABLE I. Summary of Data Collection and Processing Parameters for Racemic ([*cis*-β-Co(trien)(NO$_2$)$_2$](NO$_3$)

Space group	$P2_1/n$
Cell constants	$a = 7.604(3)$ Å $b = 13.019(2)$ Å $c = 14.472(3)$ Å $\beta = 98.13(3)°$
Cell volume (V)	1418.26 Å^3
Molecular formula	$C_6H_{18}N_7O_7Co$
Molecular weight	359.184 g mol^{-1}
Density (calc.)	1.682 g cm^{-3}
Z	4 mol/cell
Radiation employed	Mo Kα ($\lambda = 0.71073$ Å)
Absorption coefficient	$\mu = 12.50$ cm^{-1}
Transmission coefficients	1.00 to 0.8412
Data collection range	$4° \leqslant 2\theta \leqslant 60°$
Scan width	$\Delta\theta = 1.20 + 0.35 \tan\theta$
Total data collected	2607
Data used in refinement[a]	1555
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$	0.057
$R_w = [\Sigma w^2(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma \lvert F_o\rvert^2]^{1/2}$	0.068
Weights used	$w = [\sigma(F_o)]^{-2}$

[a] The difference between this number and the total is due to subtraction of 1052 data which either were systematically absent (but collected for verification of space group), standards or did not meet the criterion that $I \geqslant 3\sigma(I)$

systematic absences revealed that for the axes chosen, the space group is $P2_1/n$.

Freshly filtered crystals of [*cis*-β-Co(trien)(NO$_2$)$_2$]I were examined under the microscope and the largest found was a long, extremely thin, blade, *ca* 0.3 X 0.1 X 0.02 mm. Its mosaic spread was very poor and anisotropic, with peaks differing in width by as much as a factor of three. Nonetheless, the 25 reflections found readily gave a Niggli matrix [15] characteristic of monoclinic C-centered cells. The systematic absences noted ($h + k = 2n + 1$ and $h0l$, $l = 2n + 1$) verified the lattice centering and revealed the presence of a c-glide. The space group could, therefore, be either $C2/c$ or Cc at this stage.

For the nitrate, crystal data were collected up to $2\theta \leqslant 60°$. These were corrected for Lorentz-polarization effects and for absorption (using the curves obtained from Psi scans [12]). A Patterson map was computed and the position of the Co atom was found. A series of refinements and of difference Fourier maps produced the positions of all of the non-hydrogen atoms and while hydrogens could be seen in the final difference maps, we opted for placing them at calculated positions which were recomputed after each set of cycles of least-squares refinement. The final difference map showed no peaks having any meaningful chemical significance, the largest two being ripples adjacent to the Co atom. The results of all these calculations are summarized in Table I.

For the iodide, data were collected without programming the expected systematic absences due to the glide plane, to $2\theta \leqslant 40°$ and the resulting data were corrected for absorption, using information from Psi scans [12]. These data indicate that the space group should be either Cc or its centrosymmetric relative, $C2/c$. However, given the molecular weight, cell volume and density, the number of molecules in the unit cell is 4. If the correct space group is $C2/c$, the ions must lie at special positions – which is impossible for the cations, unless they are disordered. Furthermore, an analysis of the data, using both NORMAL [12] and NZTEST [12] suggest that the lattice is non-centrosymmetric. The Patterson function is inconsistent with the Harker sections and lines expected for the centrosymmetric space group; thus, the space group must be Cc. The Patterson function is consistent with this concept, readily yielding the position for the iodide anion. Information concerning the X-ray data collection and processing for this crystal are summarized in Table II.

Results and Discussion

The principal aim of these studies is to determine whether or not a series of substances, carefully selected to meet specific compositional, conformational and configurational requirements undergo conglomerate crystallization Earlier studies [1–3], reinforced by more current structural determinations [10], show that halides of [*cis*-α-Co(trien)(NO$_2$)$_2$]$^+$ do so; however, till now we had not explored the

TABLE II Summary of Data Collection and Processing Parameters for Racemic [*cis*-β-Co(trien)(NO_2)$_2$]I

Space group	*Cc*
Cell constants	a = 15.65(1) Å
	b = 6 53(3) Å
	c = 13 095(7) Å
	β = 100 59(5)°
Cell volume (V)	1314 72 Å^3
Molecular formula	$C_6H_{18}N_6O_4CoI$
Molecular weight	424 09 g mol^{-1}
Density (calc)	2 142 g cm^{-3}
Z	4 mol/cell
Radiation employed	Mo Kα (λ = 0 71073 Å)
Absorption coefficient	μ = 36 44 cm^{-1}
Data collection range	4° ⩽ 2θ ⩽ 40°
Scan width	Δθ = 1 0 + 0.35 tan θ
Total data collected	1170
Data used in refinement[a]	601
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0 20[b]

[a] The difference between this number and the total is due to subtraction of 569 data which either were systematically absent (*h*0*l* data were collected to verify these absences, see text), were standards or did not meet the criterion that $I \geqslant 3\sigma(I)$ [b] No effort was made to refine this structure beyond the point of finding the iodide and the non-hydrogen atoms of the cation The bond lengths and angles were of such low quality it was not worth pursuing the analysis any further

isomeric series containing the [*cis*-β-Co(trien)(NO_2)$_2$]$^+$ cation. In this report, we describe the behaviour of two of them.

Let us, briefly, dispose of the iodide case

(a) First, the space group for this substance is *Cc*, which is a polar, non-enantiomorphic space group, thus the cations are present in the lattice in enantiomeric pairs. On the remote assumption that the space group is, instead, *C*2/*c* the answer is the same inasmuch as the latter space group is centrosymmetric. The conclusion then is clear the iodide of the [*cis*-α-Co(trien)(NO_2)$_2$]$^+$ series crystallizes [10] in conglomerate crystals belonging to the enantiomorphic space group $P2_12_12_1$ while those of the isomeric [*cis*-β-Co(trien)(NO_2)$_2$]$^+$ crystallize as racemates.

(b) The quantity of data obtained was severely limited by the size of the crystal and (see data collection and Table II) as expected in these cases, was mostly low angle data. Consequently, we had neither the number of data points needed to refine the variables (for the 19 non-hydrogen atoms, isotropic refinement requires 77 variables), nor did we have the resolution necessary to place the atoms accurately. Thus, we limit this report on the structure of the iodide to Table II. However, we note that this salt was prepared from the NO_3^- derivative whose structure we report in full below.

The Structure of [cis-β-Co(trien)(NO₂)₂](NO₃)

The structure of the cation is depicted in Fig. 1 and the packing of the cation and anions, together with the hydrogen bonding scheme present in the lattice, is shown in Fig. 2. Bond lengths, inter- and intramolecular hydrogen bonds, bond angles, torsion angles and least-squares planes are listed in Tables III–V.

The enantiomer shown in Fig. 1 has absolute configuration Λ(δδλ), which is the same as that established by Freeman and Maxwell [16] for L(–)$_{589}$-*cis*-β-[Co(trien)(*S*)-Pro]$I_2 \cdot 2H_2O$. Looking down the N–H vector and using the ranking sequence Co > ligand long chain > ligand short chain, one finds in both cases that the absolute configuration at the two central nitrogens is (*R*).

The geometrical parameters obtained in this structural determination agree well with published values [16–19] for *cis*-β-Co(trien)XY complexes and with values obtained here [10] for a series of [*cis*-β-Co(trien)(NO_2)$_2$]$^+$ derivatives. The basic features are (a) the Co–N distances associated with the tetramine ligand are approximately 1.94–1.96 Å while those associated with the Co–NO_2 bonds are about 1.92–1.93 Å; (b) the N–Co–N angles associated with the polyamine ligand cover a broad range of values, the more noticeable features being (1) the angles of the

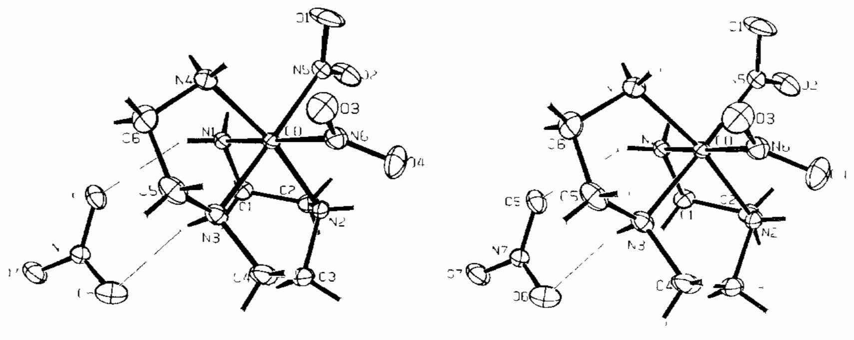

Fig 1 Stereochemistry of the cation and its relationship to the NO_3^- anion

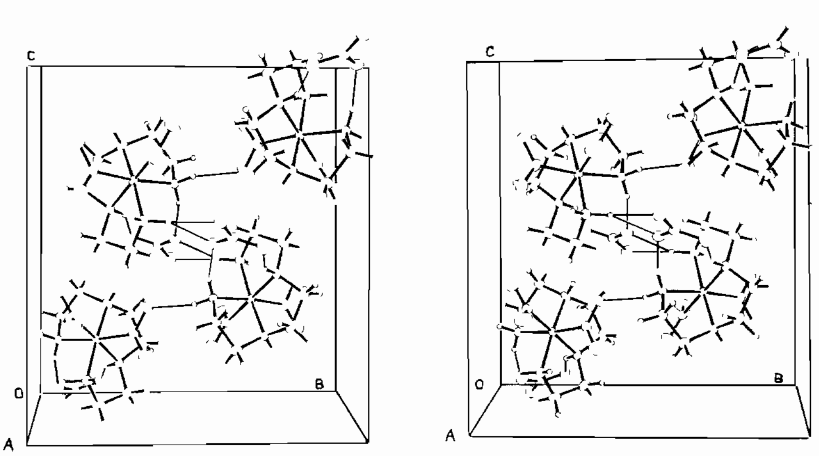

Fig. 2 Packing diagram of the molecule Hydrogen bonds shorter than 2.25 Å are shown as thin lines.

TABLE III. Table of Positional Parameters and their Estimated Standard Deviations

Atom	x	y	z	B (Å^2)[a]
Co	0.17967(7)	0.18985(4)	0.18355(4)	2.388(9)
O1	0.5094(4)	0.1208(3)	0.2570(3)	6.9(1)
O2	0.3199(4)	0.0743(3)	0.3381(2)	5.47(9)
O3	0.4249(4)	0.3456(3)	0.1642(3)	5.33(8)
O4	0.3130(5)	0.3536(3)	0.2897(2)	5.40(8)
O5	0.3078(4)	0.4445(2)	0.4906(2)	4.15(7)
O6	0.1581(4)	0.3038(2)	0.4907(2)	5.06(8)
O7	0.0473(4)	0.4347(3)	0.4137(2)	5.05(8)
N1	0.0445(4)	0.0621(2)	0.1676(2)	2.54(7)
N2	0.0163(4)	0.2249(3)	0.2729(2)	3.17(8)
N3	0.0089(5)	0.2624(3)	0.0935(2)	3.30(8)
N4	0.3054(4)	0.1614(3)	0.0787(2)	3.18(8)
N5	0.3569(4)	0.1201(3)	0.2702(2)	3.20(8)
N6	0.3209(4)	0.3116(3)	0.2150(2)	3.61(8)
N7	0.1698(4)	0.3935(3)	0.4649(2)	3.24(8)
C1	−0.1124(5)	0.0646(3)	0.2191(3)	3.28(9)
C2	−0.0650(5)	0.1300(4)	0.3034(3)	3.7(1)
C3	−0.1216(6)	0.3000(4)	0.2309(3)	4.2(1)
C4	−0.0688(6)	0.3457(3)	0.1436(4)	4.6(1)
C5	0.0988(7)	0.2907(4)	0.0123(3)	4.7(1)
C6	0.2014(6)	0.1974(4)	−0.0097(3)	4.4(1)
H1	0.098(5)	0.005(3)	0.191(3)	3.6(9)*
H2	0.015(5)	0.047(3)	0.111(2)	3.7(9)*
H3	−0.147(5)	−0.002(2)	0.233(2)	3.0(9)*
H4	−0.202(5)	0.098(3)	0.177(2)	3.2(9)*
H5	0.007(5)	0.097(3)	0.353(3)	4(1)*
H6	−0.162(5)	0.146(3)	0.331(2)	3.4(9)*
H7	0.064(4)	0.252(2)	0.317(2)	1.7(7)*
H8	−0.132(5)	0.354(3)	0.277(3)	4(1)*
H9	−0.220(5)	0.257(3)	0.212(3)	4(1)*
H10	0.010(5)	0.401(3)	0.151(3)	5(1)*
H11	−0.164(6)	0.372(3)	0.109(3)	7(1)*
H12	−0.087(5)	0.218(3)	0.071(3)	4(1)*
H13	0.184(5)	0.353(3)	0.031(3)	4(1)*
H14	0.034(6)	0.314(4)	−0.033(3)	7(1)*
H15	0.273(5)	0.214(3)	−0.051(3)	4(1)*
H16	0.121(6)	0.134(3)	−0.033(3)	6(1)*
H17	0.392(5)	0.195(3)	0.092(2)	3.3(9)*
H18	0.315(6)	0.086(3)	0.076(3)	5(1)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

TABLE IV. Geometrical Parameters. Lengths (Å) and Angles (°)

Bond lengths

Co–N1	1.951(2)	C3–C4	1.501(5)
Co–N2	1.969(2)	C4–N3	1.474(4)
Co–N3	1.949(2)	N3–C5	1.487(4)
Co–N4	1.939(2)	C5–C6	1.502(5)
Co–N5	1.932(2)	C6–N4	1.482(4)
Co–N6	1.932(2)	N1–H1	0.89(3)
N5–O1	1.202(3)	N1–H2	0.84(3)
N5–O2	1.217(3)	N2–H7	0.78(2)
N6–O3	1.235(3)	N3–H12	0.95(2)
N6–O4	1.221(3)	N4–H17	0.79(3)
N1–C1	1.495(3)	N4–H18	0.98(3)
C1–C2	1.489(4)	O5–N7	1.253(3)
C2–N2	1.476(4)	O6–N7	1.233(3)
N2–C3	1.499(3)	O7–N7	1.229(3)

Hydrogen contacts

O4–H1	2.09(6)	O5–H2	2.18(3)
O6–H12	2.13(3)		

Bond angles

N1–Co–N2	84.54(9)	N1–Co–N3	92.5(1)
N1–Co–N4	93.1(1)	N1–Co–N5	89.1(1)
N1–Co–N6	173.1(1)	N2–Co–N3	84.5(1)
N2–Co–N4	169.8(1)	N2–Co–N5	97.4(1)
N2–Co–N6	92.1(1)	N3–Co–N4	85.7(1)
N3–Co–N5	177.6(1)	N3–Co–N6	93.2(1)
N4–Co–N5	92.4(1)	N4–Co–N6	91.2(1)
N5–Co–N6	85.4(1)	Co–N1–C1	111.5(2)
Co–N2–C2	109.4(2)	Co–N2–C3	110.8(2)
Co–N3–C4	107.6(2)	Co–N3–C5	108.1(2)
Co–N4–C6	110.7(2)	Co–N5–O1	119.6(2)
Co–N5–O2	122.3(2)	Co–N6–O3	122.4(2)
Co–N6–O4	118.7(2)	O1–N5–O2	118.1(2)
O3–N6–O4	118.8(2)	N1–C1–C2	107.6(2)
C1–C2–N2	107.3(2)	C2–N2–C3	111.6(2)
N2–C3–C4	110.2(2)	C3–C4–N3	107.2(2)
C4–N3–C5	117.9(3)	N3–C5–C6	106.1(3)
C5–C6–N4	107.6(3)		

chelate rings have average values close to 85° (in the current case, they are 84.5, 84.5 and 85.7°) and (2) the fact that the *trans* angle (N2–Co–N4) is only 169.8(1)°. While it is true that similar deviations from the ideal (90°) are found for the angles of the chelate rings of the α-conformer of Co(trien), such a large compression in *trans* angles is not present in the later cations [1, 2] where all three *trans* angles are uniformly *ca* 176°; (c) the torsion angles, 47.1, 39.8 and −49.4°, show a distinct compression at the middle ring not present in the α conformer, where they tend to be more uniform and have values clustered about |40°| – typical values [1] found in Λ(δλδ)[*cis*-α-Co(trien)$(NO_2)_2$]Cl·H_2O, are 42.59, −40.39 and 39.31°; (d) finally, the angles at the aliphatic C and N atoms of the polyamine should, ideally be about 109.47°. This is not the case with the current cation, where the range, 106.1–117.9° is larger than that found in Λ(δλδ)[*cis*-α-Co(trien)$(NO_2)_2$]Cl·H_2O, whose angular values ranged from 107.8 to 115.0°. Note, however, that the averages (β-av. = 109.54°; α-av. = 110.39°) are not that different and that the former is closer to the ideal even though the spread of angles is larger for the β conformer.

TABLE V. Geometrical Parameters Torsion Angles and Least-squares Planes

Torsion angles

N2–Co–N1–C1	6.4	N2–Co–N6–O3	−162.4
N3–Co–N1–C1	−77.8	N2–Co–N6–O4	21.1
N4–Co–N1–C1	−163.7	N3–Co–N6–O3	−77.7
N5–Co–N1–C1	104.0	N3–Co–N6–O4	105.7
N6–Co–N1–C1	67.6	N4–Co–N6–O3	8.0
N1–Co–N2–C2	20.1	N4–Co–N6–O4	−168.5
N1–Co–N2–C3	−103.4	N5–Co–N6–O3	100.4
N1–Co–N3–C4	116.9	N5–Co–N6–O4	−76.2
N1–Co–N3–C5	−114.7	Co–N1–C1–C2	−31.2
N1–Co–N4–C6	86.3		
N1–Co–N5–O1	125.0	Co–N2–C2–C1	−42.2
N1–Co–N5–O2	−54.4	C3–N2–C2–C1	80.7
N2–Co–N5–O1	−150.6	Co–N2–C3–C4	−13.9
N2–Co–N5–O2	29.9	C2–N2–C3–C4	−136.1
N3–Co–N5–O1	−6.3	Co–N3–C4–C3	−47.7
N3–Co–N5–O2	174.3	C5–N3–C4–C3	−170.3
N4–Co–N5–O1	32.0	Co–N3–C5–C6	44.3
N4–Co–N5–O2	−147.5	C4–N3–C5–C6	166.5
N6–Co–N5–O1	−59.1	Co–N4–C6–C5	32.1
N6–Co–N5–O2	121.5	N1–C1–C2–N2	47.1
N1–Co–N6–O3	136.8	N2–C3–C4–N3	39.8
N1–Co–N6–O4	−39.8	N3–C5–C6–N4	−49.4

Least-squares planes

(1) Plane defined by Co, N5, N6
$0.6383x - 0.1952y - 0.448z - 1.8087 = 0$

(2) Plane defined by N5, O1, O2
$-0.0807 - 0.8341y - 0.5757z - 3.5912 = 0$

(3) Plane defined by N6, O3, O4
$-0.6601x + 0.6076y - 0.4416z - 0.2159 = 0$

Angles between planes

Plane 1	Plane 2	Angle (°)
1	2	58.8
1	3	102.2

Conglomerate Crystallization and Intra- and Intermolecular Interactions

In an earlier contribution [1], it was reported that the compounds [*cis*-α-Co(trien)$(NO_2)_2$]Cl·H_2O (**I**), [*cis*-Co$(en)_2(NO_2)_2$]Cl (**II**) and K[*trans*-Co$(NH_3)_2(NO_2)_4$]$_4$ (**III**) undergo conglomerate crystallization and that intramolecular hydrogen bonding between the oxygens from *cis* pairs of $-NO_2$ ligands with the hydrogens of a pair of mutually *trans* $-NH_2$ or $-NH_3$ moieties was probably responsible for the unusually high incidence [4] of such a phenomenon in this class of compounds. The proposal was then made [1] that such hydrogen bonding lends additional stereochemical rigidity to specific conformations of broad, paddle-like (*clavic*) groups such as $-NO_2$ which confer additional dissymmetry for these ions. Thus, while it is true that the Co(trien) fragment of **I** is chiral, the presence of the middle ring of the trien ligand is not necessary or sufficient to cause conglomerate crystallization. This is obvious since in neither of the hydrates of [*cis*-α-Co(trien)Cl_2]Cl· nH_2O (**IV**, **V**) (**IV**, $n = 2$, **V**, $n = 3$) studied here [20] crystallizes as a conglomerate. Furthermore, the $Co(en)_2$ fragment of **II** contains no middle ring; yet, **II** forms a crystalline conglomerate. Finally, **III** contains no chelate rings at all; nonetheless, it also crystallizes as a conglomerate.

It has been suggested [1–3, 10, 20] that the common thread, inducing high incidence of conglomerate crystallization in all of these compounds, is the intramolecular hydrogen bonding interaction of the $-NO_2$ oxygens with the $-NH_2$ or $-NH_3$ hydrogens. It was shown [1–3, 10, 20] that so long as *clavic* moieties are present which can be locked into dissymmetric arrangements by the agency of either hydrogen bonding, steric hindrance or both, the incidence of conglomerate crystallization is markedly enhanced. This observation is general and not restricted to specialized series of compounds such as octahedral cobalt coordination compounds. The reader is urged to peruse the lists of such substances given in ref. 1.

Bortin [6] reported that, unlike **II**, [*cis*-$Co(en)_2$-$(NO_2)_2$](NO_3) crystallizes as a racemate and noted that the hydrogen bonding between the hydrogens on the $-NH_2$s and the oxygens of the NO_3^- anion were markedly stronger than the intramolecular hydrogen bonds. It was, therefore, suggested [1] that such intraionic bonds interfered with the mechanism giving rise to conglomerate crystallization in compounds such as **I**, **II** and **III**. To test this hypothesis, we prepared the α(**VI**) and β(**VII**) nitrates of the [*cis*-Co(trien)$(NO_2)_2$]$^+$ cation. In a separate report [10], we discuss the very complex crystallization behaviour of the former substance – a racemate in which the asymmetric unit consists of clusters of three cations heavily hydrogen bonded by the $-NO_3^-$ anions. Each cluster consists of [2Λ(δδλ) + 1Δ(λλδ)] or its enantiomeric counterpart, the overall lattice being $P2_1/c$, with $Z = 12$ molecules. Aside from the very unusual and interesting crystallization behaviour of α(**VI**), the most important feature of this substance, insofar as this report is concerned, is that it does not, as predicted [1, 2], form conglomerates since a strong network of hydrogen bonds with the anion interferes with the intramolecular interactions needed to induce conglomeration.

Now, we come to β(**VII**) which, as predicted [1, 2], is also a racemate, crystallizing in space group $P2_1/n$ which is merely a different setting of the space group, $P2_1/c$, in which α(**VI**) crystallizes. Let us examine the inter- and intramolecular interactions present in the nitrate:

(a) Figure 1 shows the stereochemistry of the cation and an adjacent anion as well as some of the hydrogen bonding scheme present. Figure 2 shows the latter features in more detail.

(b) It is clear that the strongest three hydrogen bonds (O4–H1 = 2.09(6) Å, O5–H2 = 2.18(3) Å and O6–H12 = 2.13 Å) are intermolecular. These are shown in Fig. 2. They are all relatively weak [1–3]; however, the strongest one is between an oxygen (O4) on an $-NO_2$ ligand and a hydrogen(H1) of a terminal $-NH_2$ of an adjacent cation. The other hydrogen of this same terminal $-NH_2$ moiety is engaged in bonding with a nitrate oxygen. Thus, the entire $-NH_2$ fragment is blocked from further access to meaningful intramolecular hyrogen bonding, as is clearly shown in the center of the packing diagram (Fig. 2).

(c) The third strongest hydrogen bond (O6–H12) is between another oxygen of the nitrate and the hydrogen of a middle –N3H12– moiety. Such an arrangement is illustrated in both Figs. 1 and 2. Here, the nitrate anion is, effectively, acting as a bidentate ligand to a cation by binding one hydrogen of a terminal $-NH_2$ to a hydrogen of a secondary (–NH–) while preventing access of these hydrogens to the *clavic* $-NO_2$ oxygens. In view of previous remarks [1–3, 10, 20], it is not surprising that these nitrates crystallize in racemic form; thus, our results for the α(**VI**) and β(**VII**) nitrates of the [*cis*-Co(trien)-$(NO_2)_2$]$^+$ cations provide firmer support for our earlier suggestions. Obviously, in neither case is the chiral Co(α- or β-trien) backbone nor the *clavic* $Co(NO_2)_2$ fragments, nor (apparently) the combination of both able to cause conglomerate recrystallization in the presence of nitrate anions.

(d) At this point it is important to bring forth a major difference in crystallization behaviour of the α- and the β-isomers which is emphasized by the data below:

Anion	Space group for	
	[*cis*-α-Co(trien)$(NO_2)_2$]$^+$	[*cis*-β-Co(trien)$(NO_2)_2$]$^+$
NO_3^-	$P2_1/c$ [10]	$P2_1/n$ (this study)
I^-	$P2_12_12_1$ [10]	*Cc* (this study)
$[Co(NH_3)_2(NO_2)_4]^-$	$P2_12_12_1$ [2]	$P2_1/c$ [11]

The difference is the following. the nitrates of both are racemic, as expected, however, the other two salts are conglomerates in the case of the *cis*-α but, again, racemic, in the case of all the *cis*-β isomers.

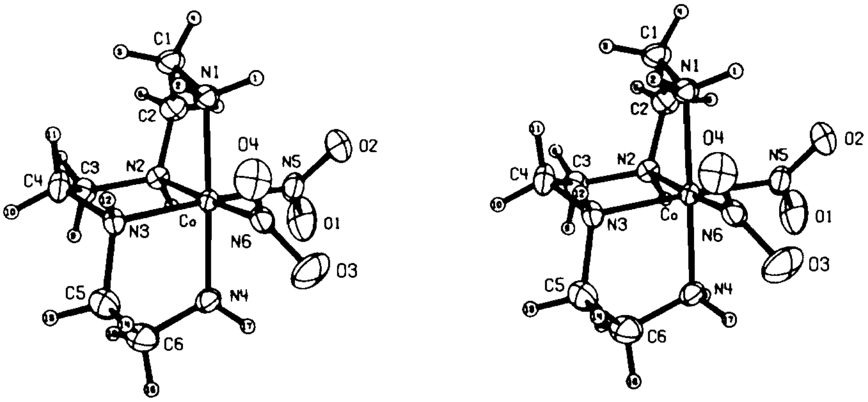

Fig 3 The stereochemistry of the $[cis\text{-}\alpha\text{-}Co(trien)(NO_2)_2]^+$ cation, as described in ref 3

We are currently investigating the structures of the $[Co(NH_3)_2(NO_2)_4]^-$, Cl^- .... derivatives of the *cis*-α and β isomers in order to ascertain the degree to which the conformations of the *clavic* $-NO_2$ ligands are affected by the presence or absence of weakly and strongly hydrogen bonding anions.

(e) On the assumption that the overall conformation of the *cis*-β cation is not too severely altered by the intermolecular bonds described above, we can already see some of the reasons for major differences in the conformational behaviour of α and β cations (1) for the convenience of the reader we reproduce, as Fig. 3, a stereo picture of the cation in $[cis\text{-}\alpha\text{-}Co(trien)(NO_2)_2]Cl \cdot H_2O$ (**I**). Note that in this geometrical isomer there is a terminal(axial) $-NH_2$ ligand above and below the basal plane defined by Co, N2, N3, N5 and N6. Given the geometry of this $-NH_2$ fragment, each of the $-NO_2$ ligands can be anchored by a relatively strong hydrogen bond while, at the same time, minimizing O....O repulsions. It is this geometry, common to the cobalt ions of **I**, **II** and **III**, which enhances the incidence of conglomerate crystallization as discussed earlier (in order to avoid repetition of lengthy geometrical details and arguments, the unfamiliar reader is referred to refs. 1–3). (2) comparison of the above conformational details with those of the cation in Figs 1 and 2 show that in the latter the $-NO_2$ groups face an entirely different topological situation, which is as follows

(a) the oxygens of N5 and N6 have no problem staying out of each other's way; however,

(b) oxygens O1 and O2 view a planar face bearing three different hydrogens located on N1, N4 and N2. It is impossible for the oxygens of a flat $-NO_2$ to effectively hydrogen bond with all three of them. Nonetheless, it appears attempting it and in the process forming weaker contacts. A situation very similar to this one was already described in our neutron diffraction study [3] of **III** in which disorder occurred as a result of having an $-NH_3$ ligand attempting hydrogen bond with too many $-NO_2$ oxygens. Again, the reader is referred to the original [3] for details. Finally, neither O1 nor O2 form neither inter- or intramolecular hydrogen bonds of any significance (*i e* , shorter than 2.25 Å)

(c) O3 and O4 attempt, likewise to form bonds with the hydrogens of N2 and N4. Note, however, that the shortest hydrogen bond (2.09 Å) formed by this species is an intermolecular bond, clearly shown in the packing diagram (Fig. 2). It is the bond between the upper left and the upper right cations, shown as a thinner line Again, no meaningful intramolecular bonds are formed by this $-NO_2$ ligand.

Conclusions

The nitrates of neither the α- nor the β-$[cis\text{-}Co(trien)(NO_2)_2]^+$ cations crystallize as conglomerates. This observation reinforces previously made suggestions [1] as to the negative effect the NO_3^- anion has on conglomerate crystallization of these species. However, it appears that the $[cis\text{-}\beta\text{-}Co(trien)(NO_2)_2]^+$ cations behave totally differently from their α brethren, which is a most important chemico-topological observation in need of further exploration and currently under study here.

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