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The Phenomenon of Conglomerate Crystallization.
XI. *Clavic* Dissymmetry in Coordination Compounds.
VIII. An Investigation of the Crystallization, Conformational and Configurational Behaviour of [*mer*-Co(1,5-diamino-3-azapentane)$(NO_2)_3$]

IVAN BERNAL and JAMES CETRULLO

Chemistry Department, University of Houston, Houston, Tex. 77004, U.S.A.

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Abstract

[*mer*-Co(dien)$(NO_2)_3$] does not form conglomerates when crystallized from water at a variety of temperatures; instead, it crystallizes in the racemic space group *Pbca*. Crystals obatined at 21 °C, and studied by X-ray diffraction at 16 °C, crystallize with unit cell parameters of $a = 13.030(3)$, $b = 12.688(2)$ and $c = 13.172(3)$ Å; $V = 2177.66$ Å^3, D(calc; $M = 300.12$ g mol^{-1}; $Z = 8$) = 1.831 g cm^{-3}. Data were collected with Mo Kα ($4° \leqslant 2\theta \leqslant 50°$; 2268 data), corrected for absorption ($\mu = 16.01$ cm^{-1}; relative transmission coefficients range from 0.9026 to 1.0000) producing a reduced set of 1556 reflections for which $I \geqslant 3\sigma(I)$. The structure was solved by the Patterson method and refined to $R(F) = 0.0282$ and $R_w(F) = 0.0330$, using as weights $w = [\sigma(F_o)]^{-2}$.

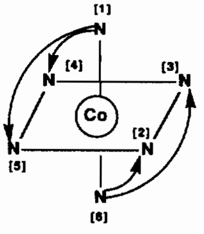
The Co(dien) fragment has the shape of a pleated sheet in which the conformation of the two ($-NH-CH_2-CH_2-NH_2$) fragments are δ and λ or their inverse. The two Co–N(H_2) distances are identical (1.942(1) and 1.944(1) Å) and shorter than the Co–N(H) distance of 1.952(1) Å. The two mutually *trans* Co–N(O_2) bonds are 1.971(1) and 1.931(1) Å, reflecting an interesting molecular asymmetry; the effect in question being the bending of one of the $-NO_2$ ligands towards the $NH_2-Co-NH_2$ edge of the molecule so as to maximize the strength of the O....HN bonds. The bent NO_2(N4) is the one with the long Co–N distance. Finally, the unique Co–N(O_2) distance is 1.914(1) Å, shorter than either of the previous ones and a clear example of the *trans* effect.

The geometry at Co is a distorted octahedron, as expected. The largest distortion being the angle N1–Co–N3(169.9(6)°) defined by the two terminal–NH_2 ligands. Other angular distortions are smaller. The N–C distances range from 1.473(2) to 1.493(2) Å and the two C–C distances are 1.505(2) and 1.498(2) Å. Refined N–H (terminal) distances range from 0.81(2) to 0.88(2) Å and the secondary N–H distance is 0.90(1) Å. C–H distances range from 0.90(2) to 1.05(2) Å.

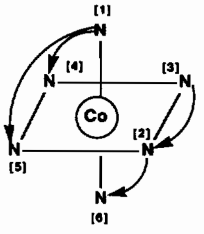
Introduction*

Salient facts, providing a rationale for our carrying out this study are:

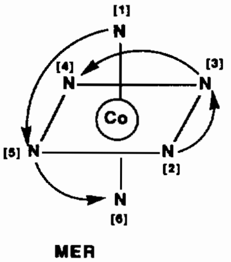
(a) In 1960, Crayton and Mattern [1] prepared a number of cobalt derivatives of dien and argued that the one with composition Co(dien)$(NO_2)_3$ had to be *mer* since the cation Co(dien)$_2^{3+}$ could not be resolved; thus, in their view, the ligands had to be *mer*. Some years later, all three cations of that composition [symmetrical-facial (s-*fac*), unsymmetrical facial (u-*fac*) and *mer*] were described crystallographically by Saito and associates [2–4], the latter two in optically resolved form.



S-FAC



U-FAC



MER

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*The following abbreviations are used in the text: dien = 1,5-diamine-3-azapentane; trien = 1,9-diamine-4,7-diazanonane; [*mer*-Co(dien)$(NO_2)_3$] (I) [*cis*-β-Co(trien)$(NO_2)_2$]-(NO_3) (II) [$\Lambda(\delta\delta\lambda)$-*cis*-$\beta$-chloroaquoCo(trien)]Co]$(ClO_4)_2 \cdot 2H_2O$ (III) $(-)_{589}$-[$\Lambda(\delta\delta\lambda)$-*cis*-$\beta$-Co(trien)(*S*)-Pro]I$\cdot 2H_2O$ (IV) $(-)_{546}$-[$\Lambda(\delta\lambda\delta)$-*cis*-$\beta$-Co(*L*-3,8-dimethyltrien)Co-$(NO_2)_2$](ClO_4) (V) [$\Lambda(\delta\lambda\delta)$-*cis*-$\beta$-Co(2,9-dimethyltrien)Co-$(NO_2)_2$](ClO_4)$\cdot H_2O$ (VI) $(-)_{589}$-[$\Lambda(\delta\lambda\lambda)$-*cis*-$\beta$-Co(*R*-5-methyltrien)Co$(NO_2)_2$]Cl (VII).

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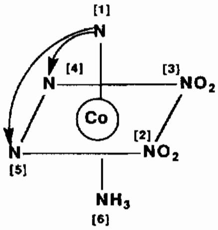
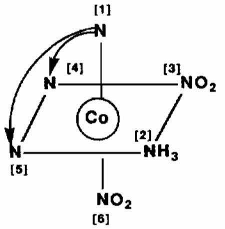
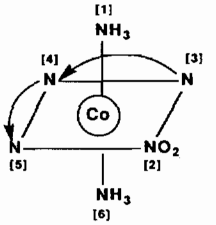
Unlike the chiral *mer*-diene the s-*fac* species is achiral despite the conformational dissymmetry of each of the rings. The molecule can support a center of inversion since each dien is (δ, λ) and the pair of rings spanning positions [1] and [4] and [2] and [6] can have opposite torsional angles; likewise with the other pair of chelate rings. In fact, it sits at a crystallographic inversion center [2], suggesting Crayton and Mattern may have prepared this isomer. Be as it may, the other two species are dissymmetric, as demonstrated by their successful resolution and the determination of their absolute configurations [3, 4].

(b) Both *mer*- [5a] and *fac*-$Co(NH_3)_3(NO_2)_3$ [5b] crystallize as a conglomerate; therefore, to add to our knowledge of the molecular topological factors leading to conglomerate formation, it would be useful to determine the mode of crystallization of *mer*- and *fac*-$Co(dien)(NO_2)_3$.

(c) In 1966, Ablov *et al.* [6] demonstrated that when one reacts the *mer* isomer of $Co(en)(NH_3)(NO_2)_3$ with HCl, one of the mutually *trans*-NO_2 ligands is replaced by Cl^-. They argued [6] this was a natural consequence of the '*trans* effect rule of Chernyaev'. Furthermore, Ablov *et al.* [7, 8] demonstrated this Cl^- can be replaced by nitrogen ligands. For example, NH_3 replaces Cl^- and [*cis*-$(NH_3)_2$-*trans*-$(NO_2)_2$-Co(en)$]^+$ and [Co(en)*cis*-*cis*-$(NH_3)_2(NO_2)_2]^+$ can be isolated; when SCN^- is used, [*cis*-$(NO_2)_2$-$(NH_3)(SCN)Co(en)]^+$ is obtained [9]. Thus, assuming these arguments hold, treatment of [*trans*-$(NH_3)_2Co(NO_2)_4]^-$ with HCl followed by dien (alternatively, use $[dienH_3]Cl_3$), should result in selective replacement, by the dien, of two of the $-NO_2$ ligands, the third binding point for the dien remaining moot for the moment. Assumption of no clearcut further selectivity, three compounds would be expected: the two *fac* geometrical isomers and a *mer* diamine, shown below.







(d) Since the days of Pasteur's discovery of conglomerate crystallization of $Na(NH_4)Tart \cdot 4H_2O$ there has been a legitimate concern that reports of the phenomenon may not be a true property of the molecular system in question; rather, that chiral material, present as laboratory dust, left from previous work with resolved substances, may act as a seed which induces chiral selectivity, *i.e.* acts as an external resolving agent. Readers interested in this issue are directed to refs. 10* and 11** for illuminating information on this subject. The reason from bringing up this point will become clearer in the 'Discussion'.

Guided by the facts outlined in (a) → (c), interested in contributing to an understanding of the factors controlling conglomerate crystallization and the problems raised in (d), we attempted to make *mer* and *fac* derivatives of Co(dien) in order to establish rational routes for their syntheses, document their crystallization behaviour as well as their molecular conformation and configuration in the solid samples thus obtained.

Experimental

Syntheses

(a) The procedure of Crayton and Mattern [1] was used as follows: 14.6 g (0.05 mol) $Co(NO_3)_2 \cdot 6H_2O$, 15.3 g (0.22 mol) $NaNO_2$, 5.6 g (0.10 mol)

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*Ref. 10 gives two early examples of problems associated with impurities clouding understanding of optical activity. Remember that the seminal papers of van't Hoff and Le Bel were published in 1874. (a) p. 91: in the late 1870s confusion arose as to the validity of van't Hoff's demonstration that all of the known optically active compounds contained asymmetric carbons since among compounds initially reported to be optically active were: styrene, 1-propanol, α-picoline papaverine.... 'Within a decade or so, it was demonstrated that optical activity associated with these compounds was due to the presence of optically active impurities'. (b) p. 135: the initial report of Le Bel that solutions of [(isobutyl)(propyl)(ethyl)NH]Cl (1891) exposed to *Penicillium glaucum* mold gave optical rotation were not confirmed by W. Markwald's study of 1899. In '1912 Pope and Read provided evidence that the optical activity reported by Le Bel was probably due to an impurity in the solution'.

**These authors carried out crystallization experiments using $NaClO_3$ which forms conglomerates of enantiomorphic cubic crystals whose optical rotation can conveniently be measured. After studying thousands of crystals obtained from 46 separate crystallizations, they concluded that: (a) When dealing with enantiomorphic crystals derived from conglomerate crystallizations, an inventory large enough to be statistical produces equal numbers of right and lefthanded crystals. (b) Individual experiments may not give a 50–50 distribution and, in fact, some gave 3:1 or 4:1 ratios favoring, randomly, one or the other species; however, the eventual average was still 1:1. (c) The distribution can be influenced by the addition of chiral material to the solution; however, this preference, though persistent and consistent in favoring a specific enantiomer, produced imbalances no greater than some of the random fluctuations observed in the absence of chiral material. Note further that if the impurity reacts to form an adduct, all bets are off since now (a) we are no longer dealing with the initial compound (b) the new substance is a diastereoisomer and not an enantiomer.

TABLE I. Summary of Data Collection and Processing Parameters for Racemic [*mer*-Co(dien)(NO_2)$_3$]

Space group	*Pbca*
Cell constants	$a = 13.030(3)$ Å $b = 12.688(2)$ Å $c = 13.172(3)$ Å
Cell volume	$V = 2177.66$ Å^3
Molecular formula	$C_4H_{13}N_6O_6Co$
Molecular weight	300.12 g mol^{-1}
Density (calc; $Z = 8$ mol/cell)	1.831 g cm^{-3}
Radiation employed	Mo Kα (λ = 0.71073 Å)
Absorption coefficient	$\mu = 16.010$ cm^{-1}
Transmission coefficients	1.00 to 0.9026
Data collection range	$4° \leqslant 2\theta \leqslant 50°$
Scan width	$\Delta\theta = 1.00 + 0.35 \tan\theta$
Total data collected	2268
Data used in refinement[a]	1556
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$	0.0282
$R_w = [\Sigma w^2(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma \lvert F_o\rvert^2]^{1/2}$	0.0330
Weights used	$w = [\sigma(F_o)]^{-2}$

[a] The difference between this number and the total is due to subtraction of 712 data which either were systematically absent (but collected for verification of space group), were standards or did not meet the criterion that $I \geqslant 3\sigma(I)$.

KOH and 12.1 g (0.20 mol) CH_3CO_2H were dissolved in 20 ml H_2O and the resulting solution placed in a filter flask fitted with a tube reaching near the bottom. 5 ml (99%) dien were dissolved in 20 ml of H_2O. Aeration of the cobalt solution begun and the dien solution slowly added to it. The pH of the solution was checked periodically and kept between 5 and 6. A yellow precipitate begins to appear within 15 min but aeration was continued for one hour, whereupon the solution was filtered. The yellow filtrate, having composition [Co(dien)(NO_2)$_3$], was washed three times with water and ethanol and air dried. Decomposes at 212 °C (uncorr.).

(b) Reaction of equimolar quantities of water solutions of K[*trans*-(NH_3)$_2$Co(NO_2)$_4$], prepared according to the procedure of Schlessinger [12], and (dienH$_3$)Cl$_3$ resulted in exactly the same product as obtained in (a).

(c) The procedure of Hagel and Druding [13] to prepare *fac*-Co(NH_3)$_3$(NO_2)$_3$, using the [Co(CO_3)$_3$]$^{3-}$ anion as an intermediate, was also tried using dien as the amine. However, the Na$_3$[Co(CO_3)$_3$] salt was used as recommended by Bauer and Drinkard [14] who claimed that its purity is higher than that of the potassium analogue. In our hands, the resulting product is the same as that in (a).

Collection and Processing of X-ray Diffraction Data

Selection of crystals

Crystals were obtained from a boiling water saturated solution slowly cooled to room temperature. At various stages, as crystals deposited, they were filtered and examined under the microscope. Eventually, a few were examined in the X-ray diffractometer. After the solution reached room temperature, it was placed in the same area where crystals of other substances [15–18] were found to crystallize as conglomerates. Three of these were examined in the diffractometer and found to give the same space group and cell constants. The most suitable one, a deep yellow crystal, was mounted on a translation head and onto an Enraf-Nonius CAD-4 diffractometer and a set of 25 reflections centered and used to define the primitive cell. Data collection and processing were carried out with the Molecular Structure Corporation TEXRAY-230 Modification [19] of the SDP-Plus [20] Programs. The reader is referred to this manual for the details of the various routines mentioned. The orientation and Niggli [21] matrices indicated the cell is primitive, orthorhombic and a subsequent search for systematic absences revealed the space group is *Pbca*, which is uniquely defined by the systematic absences.

Data were collected using Mo Kα radiation in the range of $4° \leqslant 2\theta \leqslant 50°$ and two reflections were used as intensity standards in order to monitor crystal and electronic stability. Intensity standards were collected every two hours. No decay or systematic variation was observed for this crystal. The scattering curves used were those of Cromer and Waber [22]. Details of data collection and processing are listed in Table I.

The phase problem was solved using a Patterson summation from which the positions of the Co atoms were readily extracted. A difference map produced many of the non-hydrogen atoms, and the missing ones were found in subsequent difference maps and

TABLE II. Positional Parameters[a] (e.s.d.s in parentheses)

Atom	x	y	z	B (Å^2)
Co	0.10313(3)	0.10862(3)	0.68722(3)	1.734(7)
O1	0.1733(2)	0.3077(2)	0.7516(2)	5.32(6)
O2	0.2719(2)	0.1861(3)	0.7927(2)	7.95(8)
O3	−0.0187(2)	0.1065(2)	0.8559(2)	5.40(7)
O4	0.1099(3)	0.0106(3)	0.8713(2)	8.03(9)
O5	0.0358(2)	−0.0933(2)	0.6443(2)	5.57(7)
O6	−0.0703(2)	0.0228(2)	0.5999(2)	4.81(6)
N1	−0.0001(2)	0.2179(2)	0.6716(2)	2.47(5)
N2	0.1415(2)	0.1432(2)	0.5479(2)	2.03(4)
N3	0.2182(2)	0.0113(2)	0.6828(2)	3.36(6)
N4	0.1946(2)	0.2153(2)	0.7476(2)	3.00(5)
N5	0.0596(2)	0.0699(2)	0.8209(2)	3.13(6)
N6	0.0119(2)	−0.0001(2)	0.6384(2)	2.80(5)
C1	0.0015(3)	0.2621(3)	0.5666(3)	3.29(7)
C2	0.1089(2)	0.2519(3)	0.5257(2)	3.06(7)
C3	0.2514(2)	0.1166(2)	0.5335(2)	3.10(7)
C4	0.2647(2)	0.0096(3)	0.5797(3)	3.37(7)
H1	0.014(2)	0.268(2)	0.711(2)	2.6(6)*
H2	−0.061(2)	0.195(2)	0.683(2)	4.0(8)*
H3	−0.019(2)	0.336(2)	0.567(2)	3.2(7)*
H4	−0.051(2)	0.218(2)	0.524(3)	5.6(9)*
H5	0.166(2)	0.296(2)	0.561(2)	3.1(7)*
H6	0.111(2)	0.262(2)	0.458(2)	3.0(7)*
H7	0.107(2)	0.099(2)	0.507(2)	2.7(7)*
H8	0.289(2)	0.175(2)	0.571(2)	3.5(7)*
H9	0.266(2)	0.119(2)	0.463(2)	4.2(8)*
H10	0.338(2)	−0.009(2)	0.586(2)	3.7(7)*
H11	0.227(2)	−0.049(2)	0.539(2)	2.6(6)*
H12	0.261(2)	0.032(2)	0.723(2)	4.4(8)*
H13	0.202(2)	−0.053(3)	0.703(2)	5.7(9)*

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

these were refined isotropically till convergence. At this point, the positions of the hydrogen atoms were computed and the structure re-refined using isotropic thermal parameters for the non-hydrogen atoms and holding the positions and thermal parameters (5.0 Å^2) of the hydrogens fixed. Every two cycles of refinement new positions were calculated for hydrogens, added to the list, and the structure refined till convergence. Anisotropic refinement of the heavy atoms, while refining the hydrogens isotropically, converged to the R and R_w factors listed in Table I. The final positional and equivalent (isotropic) thermal parameters are listed in Table II. Bond lengths, angles, torsional angles and selected least-squares planes are listed in Table III. Figures 1 and 2 show the molecular conformation and packing, respectively.

Description of the Molecules

Molecules of **I**, present in the lattice as the racemate of *mer*-Co(dien)$(NO_2)_3$, have with minor distortions a nearly exact, non-crystallographic, mirror plane passing through the Co and secondary NH atoms, bisecting one $-NO_2$ ligand and mirroring the other two $-NO_2$ ligands. Geometrical evidence for the presence of a molecular, pseudo-mirror plane are the torsional angles N1–Co–N4–O1 = −5.9° and N1–Co–N6–O6 = 10.3° and the fact that the dihedral angle between planes N4–O1–O2 and N6–O5–O6 is only 9.7°. Furthermore, the torsional angles with the unique $-NO_2$ ligand (<N4–Co–N5–O4 and <N6–C–N5–O3) are, respectively, −82.5° and −84.1°.

There are two mutually *trans*-NO_2(N4, N6) ligands normal to the basal plane which contains the two (*trans*; N1, N3) terminal $-NH_2$ ligands, the secondary –NH(N2) moiety and the unique $-NO_2$(N5) ligand. The *trans* Co–N4 and Co–N6 distances are, respectively, 1.971(1) and 1.931(1) Å, both longer than Co–N5 = 1.914(1) Å which is *trans* to the secondary NH nitrogen ligand. The environmentally symmetrical pair of Co–N1 and Co–N3 bonds have distances, respectively, of 1.942(1) and 1.944(1) Å. The Co–N2 distance is 1.952(1) Å.

TABLE III. Bond Lengths, Angles, Torsional Angles and Selected Least-squares Planes

Bond distances (A)

Co–N1	1.942(1)	Co–N2	1.952(1)
Co–N3	1.944(1)	Co–N4	1.971(1)
Co–N5	1.914(1)	Co–N6	1.931(1)
O1–N4	1.206(1)	O2–N4	1.226(2)
O3–N5	1.212(2)	O4–N5	1.199(2)
O5–N6	1.226(2)	O6–N6	1.220(2)
N1–C1	1.493(2)	N1–H1	0.84(1)
N1–H2	0.85(2)	N2–C2	1.473(2)
N2–C3	1.482(2)	N2–H7	0.90(1)
N3–C4	1.487(2)	N3–H12	0.81(2)
N3–H13	0.88(2)	C1–C2	1.505(2)
C1–H3	0.98(2)	C1–H4	1.05(2)
C2–H5	1.04(1)	C2–H6	0.90(2)
C3–C4	1.498(2)	C3–H8	1.01(1)
C3–H9	0.95(2)	C4–H10	0.99(2)
C4–H11	1.04(1)		

Hydrogen bonds less than 2.5 A

O1–H1	2.21(1)	O2–H2	2.21(2)
O2–H12	2.17(2)	O6–H7	2.14(1)

Bond angles (°)

N1–Co–N2	85.28(5)	N1–Co–N3	169.92(6)
N1–Co–N4	88.36(6)	N1–Co–N5	94.32(6)
N1–Co–N6	92.77(6)	N2–Co–N3	85.22(5)
N2–Co–N4	94.02(5)	N2–Co–N5	176.86(5)
N2–Co–N6	85.28(5)	N3–Co–N4	88.94(6)
N3–Co–N5	95.34(6)	N3–Co–N6	90.65(6)
N4–Co–N5	89.08(5)	N4–Co–N6	175.61(5)
N5–Co–N6	86.60(5)	Co–N1–C1	110.91(9)
Co–N2–C2	108.87(9)	Co–N2–C3	108.47(9)
C2–N2–C3	117.78(12)	Co–N3–C4	110.53(10)
Co–N4–O1	123.07(10)	Co–N4–O2	118.98(11)
Co–N5–O3	120.03(11)	Co–N5–O4	120.58(12)
Co–N6–O5	120.76(11)	Co–N6–O6	120.57(10)
N1–C1–C2	108.20(12)	N2–C2–C1	106.15(12)
N2–C3–C4	105.42(12)	N3–C4–C3	108.07(13)
Co–N1–H1	109.1(9)	Co–N1–H2	112.7(1.1)
C1–N1–H1	106.4(9)	C1–N1–H2	107.3(1.1)
Co–N2–H7	107.4(9)	C2–N2–H7	108.3(9)
C3–N2–H7	105.6(9)	Co–N3–H12	107.7(1.2)
Co–N3–H13	112.7(1.2)	C4–N3–H12	109.2(1.2)
C4–N3–H13	111.4(1.2)	N1–C1–H5	102.2(7)
N1–C1–H6	109.1(9)	N2–C3–H8	103.5(8)
N2–C3–H9	107.9(9)	N3–C4–H10	109.0(9)
N3–C4–H11	106.6(7)	O1–N4–O2	117.5(1)
O3–N5–O4	119.4(1)	O5–N6–O6	118.7(1)

Torsional angles (°)

N2–Co–N1–C1	3.1	N3–Co–N1–C1	22.7
N4–Co–N1–C1	97.2	N5–Co–N1–C1	−173.8
N6–Co–N1–C1	−87.0	N1–Co–N2–C2	23.8
N3–Co–N2–C2	−152.8	N4–Co–N2–C3	65.1
N5–Co–N2–C2	106.7	N5–Co–N2–C3	−124.0
N6–Co–N2–C2	116.6	N6–Co–N2–C3	−114.1
N1–Co–N3–C4	−24.1	N2–Co–N3–C4	−4.4
N4–Co–N3–C4	−98.5	N5–Co–N3–C4	172.5
N6–Co–N3–C4	85.8	N1–Co–N4–O1	−5.9
N1–Co–N4–O2	166.2	N2–Co–N4–O1	79.2
N2–Co–N4–O2	−108.6	N3–Co–N4–O1	164.4
N3–Co–N4–O2	−23.5	N5–Co–N4–O1	−100.3
N5–Co–N4–O2	71.9	N6–Co–N4–O1	−110.9
N6–Co–N4–O2	61.3	N1–Co–N5–O3	8.4
N1–Co–N5–O4	−170.6	N2–Co–N5–O3	−74.2
N2–Co–N5–O4	106.7	N3–Co–N5–O3	−174.4
N3–Co–N5–O4	6.5	N4–Co–N5–O3	96.7
N4–Co–N5–O4	−82.4	N6–Co–N5–O3	−84.1
N6–Co–N5–O4	96.8	N1–Co–N6–O5	−170.7
N1–Co–N6–O6	10.3	N2–Co–N6–O5	104.0
N2–Co–N6–O6	−75.0	N3–Co–N6–O5	18.8
N3–Co–N6–O6	−160.2	N4–Co–N6–O5	−65.9
N4–Co–N6–O6	115.1	N5–Co–N6–O5	−76.5
N5–Co–N6–O6	104.4	Co–N1–C1–C2	−28.6
Co–N2–C2–C1	−44.7	Co–N2–C3–C4	45.6
Co–N3–C4–C3	31.1	N1–C1–C2–N2	47.2
N2–C3–C4–N3	−49.5		

Least-squares planes and deviations (A) of selected atoms therefrom

(1) Plane defined by N4, O1, O2

$0.5457x + 0.1666y - 0.8213z = -6.2488$

N1 ...... −0.557 N3 ...... 0.438 N6 ...... −0.574

(2) Plane defined by N5, O3, O4

$-0.5169x - 0.7734y - 0.3670z = -5.0566$

N1 ...... −0.328 N2 ...... 0.050 N3 ...... 0.175

(3) Plane defined by N6, O5, O6

$0.4405x + 0.0574y - 0.8959z = -7.4661$

N1 ...... −0.302 N3 ...... 0.669 N4 ...... −0.082

(4) Plane defined by Co, N1, N3, N4, N6

$0.2759x + 0.2467y - 0.9290z = -7.6632$

O1 ...... 0.052 O2 ...... −0.477 O5 ...... −0.385

O6 ...... 0.141

(5) Plane defined by N1, N2, N3, N5

$-0.6203x + -0.6940y - 0.3653z = -5.0988$

Co 0.000

Plane A	Plane B	Angle
Angles between planes (°)		
1	2	96.3
1	3	9.7
1	4	17.3
1	5	98.9
2	3	86.7
2	4	89.6
2	5	7.5
3	4	14.5
3	5	89.2
4	5	90.2

The geometry around the cobalt atom is, as expected, distorted from ideal octahedral coordination. Measures of such deviations are:

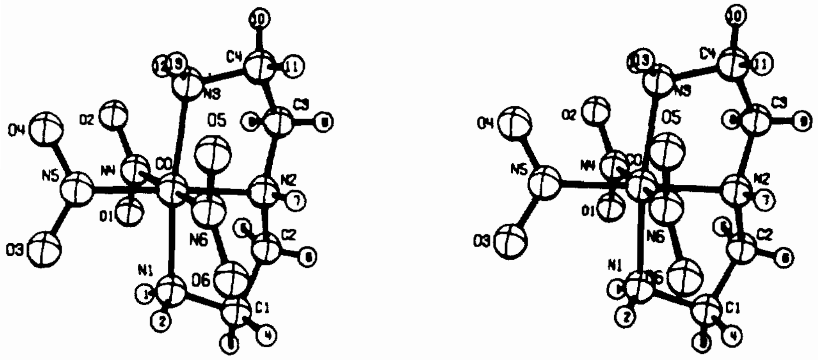


Fig. 1. Stereoview of the molecule showing the molecular conformation and configuration. Note the nearly perfect mirror plane passing through N5, Co, N2, N4 and N6. Also note that all the $-NO_2$ oxygens are oriented such as to form intramolecular bonds with adjacent $-NH_2$ or >NH hydrogens. For numerical details see 'Discussion'.

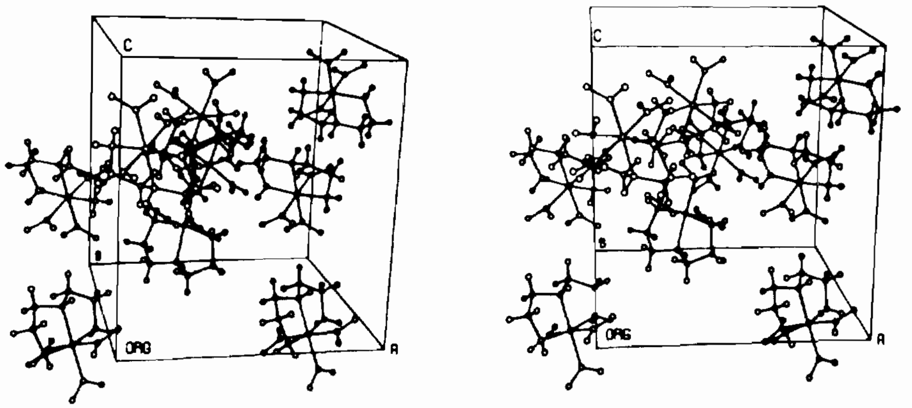


Fig. 2. Packing diagram showing the intermolecular interactions present in the lattice. Note that the $-NO_2$ ligands of a given molecule are closest to the region of the >NH fragment of the dien backbone of another. This relationship is readily apparent in the lower lefthand portion of the diagram.

(a) The angles around the Co differ from the ideal 90°, particularly in those associated with the two five-membered rings. The angles are: N1–Co–N2 = 85.28(5)° and N2–Co–N3 = 85.22(5)° (note the symmetry of these deviations from the ideal 90°).

(b) The angles associated with the monodentate ligands differ, in an interesting fashion, from the ideal, *i.e.* <N2–Co–N6 = 90.31(5)° and <N2–Co–N4 = 94.02(5)°. The reason for such a difference is the bending of the plane of the N4–O1–O2 ligand in the direction of the hydrogens of the terminal N1–H1–H2 and N3–H12–H13 groups. Note (see Table III) that the shortest –NO.....H–N– bonds are O1–H1 (2.21 Å) and O2–H12 (2.17 Å) and that it is this intramolecular pair of hydrogen bonds which causes the plane of the $-NO_2$ ligand to bend in the direction of –N5–O3–O4 and open the N2–Co–N4 angle by 4.02°.

(c) The angle N4–Co–N5 is close to 90° (89.08(5)°) while the angle N5–Co–N6 is only 86.60(5)°, the reason being as follows: when nitro group N4–O1–O2 is bent towards the edge of the dien, it would bring O2 and O4 as well as O1 and O3 closer to each other than is allowed by non-bonded pair repulsions. Thus N5–O3–O4 bends in the same direction while preserving the N4–Co–N5 angle close to 90°. Such bending allows N5–O3–O4 to approximately preserve equally strong intramolecular hydrogen bonds between O3 and O4 with the terminal $-NH_2$ hydrogens of the dien.

Finally, note that the strongest intramolecular hydrogen bond in this molecule is between O6 and H7 (2.14 Å). Given the fact that the Co–N6 geometry is fixed, for O6 to form the strongest hydrogen bond with H7, rotation about the Co–N6 bond is necessary. That is precisely what one observes in Fig. 1 and a measure of this twist is the torsional angle N3–Co–N6–O5 which is 18.8°, rather than 0°.

(d) While it is true that the Co ion lies almost precisely in the basal plane defined by N1, N2, N3 and N5 (see Table III). The same is not true in case of the plane defined by Co, N1, N3, N4, N6, a bad plane (x^2 = 18655), since the Co atom lies above the plane of the nitrogens due to the bending of N1 and N3 and the constraints of the ligand bites (<N1–Co–N3 is only 169.92(6)°).

(e) Despite all those distortions from ideal octahedral geometry, the Co(dien) fragment has the shape of an almost symmetrically pleated sheet with a pseudo mirror plane, as is illustrated by the conformations of the fragments N1–C1–C2–N2 and N2–C3–C4–N4 which are, respectively, δ (torsional angle = 47.2°) and λ (torsional angle = –49.5) and the torsional angles N3–Co–N2–C3 and N1–Co–N2–C2 which are, respectively, 65.1° and 23.8°.

Results and Discussion

Crystallization Results and Implications

The study by Laing *et al.* [5] of *mer*-$Co(NH_3)_3(NO_2)_3$ showed that *mer*-Co(amines) can form conglomerates [23]. On the other hand, our previous study [15] of related substances suggested **I** may not do so. The reason being that while in our early studies [16–18] we reported observing conglomerate crystallization of Werner coordination compounds belonging to this class, recently [15] we noted that geometrical isomers could differ markedly in their crystallization behaviour depending on the maximum symmetry a given conformer can acquire. More explicitly, on whether it can acquire conformations able to support an operation of the second sort (*i.e.* S_n axes). For example, a comparison [15–18] of the crystallization behaviour of the two geometrical series – *cis*-and *trans*-$[Co(en)_2(NO_2)_2]X$ (X = Cl, Br, I) – reveals that, whereas the former compounds crystallize as conglomerates, none of the latter do. These studies documented the fact that in both cases there are intra-ionic hydrogen bonds between the $-NO_2$ oxygens and the terminal $-NH_2$ hydrogens which appear to be somewhat stronger in the case of the *trans* series; but, whereas in the *cis* series the maximum attainable symmetry of the hydrogen-bonded cations is $2(C_2)$, the $-NO_2$ oxygens of *trans* series cations can form very advantageous hydrogen bonds while acquiring a conformation having an S_n ($n = 2$) axis [15]. Thus, while the $Co(NO_2)_2$ moiety of *cis* cations is highly dissymmetric [16–18], in the *trans* series it acquires the high-symmetry conformation, thus rendering the cation achiral. The reader is directed to the originals [15–18] for details of these arguments.

Observations such as those above led to the suggestion [15–18] that, for ligands capable of introducing dissymmetry by virtue of their conformation, their topological distribution around an octahedral Co(III) species appears to have a marked effect on the incidence of conglomerate crystallization, the phenomenon occurring more frequently in the *cis*-$Co(en)_2X_2$ than in the *trans* series. Molecular models of **I** revealed that it shares, with the *trans*-$Co(en)_2(NO_2)_2$ series, the potential of existing as an achiral species whose geometry corresponds, coincidentally, to that for which intramolecular hydrogen bonding is very advantageous (see above) as was the case also for the *trans*-$Co(en)_2(NO_2)_2$ compounds [15].

We have also pointed out in a different report [24] that in the [*cis*-β-Co(trien)XY]Z series there is no example known of a substance undergoing conglomerate crystallization irrespective of the nature of X, Y or Z, providing they are not externally resolved chiral species. For example [24], it is remarkable to observe that for compounds of the two series

Cation	Anion	Conglomerates?
[*cis*-α-$Co(trien)(NO_2)_2$]	Cl	yes
	I	yes
	[*trans*-$(NH_3)_2Co(NO_2)_4$]	yes
[*cis*-β-$Co(trien)(NO_2)_2$]	Cl	no
	I	no
	[*trans*-$(NH_3)_2Co(NO_2)_4$]	no

Models of the *cis*-α and *cis*-β series reveal a major difference in the topology of the surface the two *cis*-dinitro ligands face, the concomitant opportunities for hydrogen bonding they have and the symmetry (or dissymmetry) of the conformations resulting from intramolecular hydrogen bonding of the $-NO_2$ to the amino hydrogens. Furthermore, the middle and one of the outer chelate rings of the *cis*-β series resemble the expected conformation and configuration of the Co(dien) fragment. Thus, once again, analogy would suggest that if [*mer*-$Co(dien)(NO_2)_2X$] compounds behave like those of the [*cis*-β-$Co(trien)(NO_2)_2$] series, they should not undergo conglomerate crystallization.

Nonetheless, the fact remains that the nitroamine derivatives [*mer*-$Co(NH_3)_3(NO_2)_3$] [5], [*trans*-$(NH_3)_4Co(NO_2)_2](NO_3)$ [25] and [*cis*-$(NH_3)_4Co(NO_2)_2](NO_3)$ [36] crystallize in the space group $P2_12_12_1$ – all unambiguous cases of conglomerate crystallization. These compounds are, structurally, the $-NH_3$ analogues of the dien(or dien-like) compounds **I**, **X** and **XIII**. Thus, since all three nitroamines spontaneously conglomerate whereas the polyamines do not, the only conclusions one can reach at this point is that crystallization behaviour may be influenced by the ability of the former to turn the $-NH_3$ ligands into orientations more favorable to the formation of conglomerate-stabilizing [16–18] hydrogen bonds. After all, this requires only torsional motions about the $Co-N(H_3)$ single bond, the barrier for which has been shown in a neutron diffraction study [18] of K[*trans*-$(NH_3)_2Co(NO_2)_4$] to be very low at room temperature.

Regarding the question of seeding [10–11], we can only conclude that either the ‘chiral seeds’ present in our laboratory are not appropriate for the [*mer*-$Co(dien)(NO_2)_3$] or that we had none. In that respect, we remind the reader that

(a) We have observed conglomerate [23] crystallization of [*cis*-$Co(en)_2(NO_2)_2$]X and of [*cis*-α-

Co(trien)$(NO_2)_2$]X (with X = Cl^-, I^-, [*trans*-$(NH_3)_2$-Co$(NO_2)_4$]) as well as of the NH_4^+ and K^+ salts of [*trans*-$(NH_3)_2$Co$(NO_2)_4$]$^-$ in laboratories of two different buildings, sitting on open shelves at room temperature, as well as in closed refrigerators at 2 °C. Finally, since conglomerate crystallization [23] implies crystals of both chiralities are obtained for a given crystallization experiment, we have taken the trouble of verifying this is true and a report on related observations is under preparation [26].

(b) Had 'seeding' with chiral laboratory 'dust' taken place, the resulting first crop of crystals should all be of a single chirality – that favored by the 'seeding' material. We have shown [16] that individual crystals of [*cis*-Co$(en)_2(NO_2)_2$]Cl are chiral; however, when large quantities of those crystals were ground into powders, no net optical rotation was observed in a CD experiment.

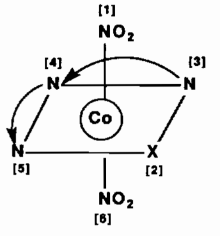
(c) Crystals of [*mer*-Co(dien)$(NO_2)_3$] used in this study were grown in the same room where we observed conglomerate crystallization of a variety of classes of Co(III) compounds, including the entire series of compounds [M$(en)_3$]$(NO_3)_2$, with M = Mn, Fe, Co, Ni, Cu and Zn [27].

(d) At the same laboratory where conglomerate crystallization has been observed for all the above, we have been unable to obtain conglomerates of [*cis*-*β*-Co(trien)$(NO_2)_2$]X (with X = Cl^-, I^-, [*trans*-$(NH_3)_2$-Co$(NO_2)_4$], NO_3^- and [*trans*-$(NH_3)_2$-*cis*-$(NO_2)_2$Co-(oxalate)]) or of [*trans*-Co$(en)_2(NO_2)_2$]X (with X = Cl^-, I^-, SCN^-, NO_3^-).

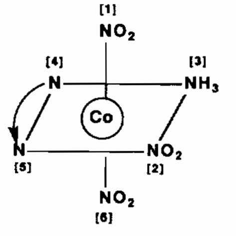
As has carefully been documented by Jacques, Collet and Wilen [23], the phenomenon is traceable to solubility differences between racemate and enantiomer and has been documented for coordination compounds since the days of Werner, who observed the phenomenon [23] in salts of [Co$(en)_2$-(oxalate)]$^+$. The present challenge is to find a molecular cause for such fine selectivity difference in crystallization behaviour not only between obviously differentiable geometrical isomers (*i.e.* [*cis*-*α*-Co(trien)$(NO_2)_2$]X and [*cis*-*β*-Co(trien)$(NO_2)_2$]X) but between species as similar as [*mer*-Co$(NH_3)_3$-$(NO_2)_3$] and [*mer*-Co(dien)$(NO_2)_3$].

Structural Comparisons with other Nitro mer-Cobalt Dienes or Dien-like Systems

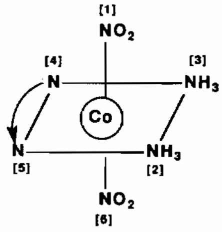
In what follows, we will limit ourselves to comparisons of the stereochemical behaviour of **I** with those of other *mer*-Co(dien) derivatives available in the literature; among them, we will include compounds which are [*mer*-Co(dien)-like], such as those in which an ethylenediamine and an NH_3 ligand constitute the grouping [*mer*-Co(en)(NH_3)]. However, we will not go into a detailed numerical comparison of geometrical parameters since the precision and accuracy of the various structures available in the literature differ enough to render such comparisons less effective than one would wish. Some useful ones to consider are given below



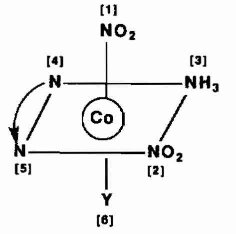
X = NO_2 (I); NH_3 (VIII)



[IX]



[X]



Y = NCS(XI); Cl (XII)
NH_3 (XIII)

The arrows, in the above diagrams, stand for either of two bidentate species, the ligand fragment $NH_2-CH_2-CH_2-NH-$ or $NH_2-CH_2-CH_2-NH_2$.

Compounds **I** and [(**VIII**)(BF_4)] [28] are both *mer*-Co(dien) systems; the other ones are dien-like sharing the common feature of a meridional (ethylenediamine + NH_3)Co fragment. **IX** [28] and **X** [7] were studied as the nitrates while **XI** [9] and **XII** [6] are neutral. **XI** was made from **XII** [6]; however, while **XI** [9] exists as two crystallographic morphs [one orthorhombic, **XI**, **a** and another monoclinic **XI**, **b**], **XII** [6] is known in only one crystalline form. Finally, **XIII** [8] was also obtained from **XII** [6] by reaction with NH_3 and was found as a single morph. The relevant space groups are listed below

Compound	Space group	Reference
I	*Pbca*	this study
VIII	$P2_1/n$	28
IXa; brown	$P2_1/c$	29
IXb; yellow	$P2_1/c$	29
X	$P\bar{1}$	7
XIa	*Pbca*	9
XIb	$P2_1/c$	9
XII	$P2_1/c$	6
XIII	*Pbca*	8

Let us enumerate some general facts concerning crystallization behaviour and molecular conformational phenomena observed for this series of dien or dien-like substances:

(1) All the above substances crystallize as racemates whose space groups are not even polar.

(2) Charge does not seem to play a major role in their crystallization behaviour since some are neutral while others are ions.

(3) Within a given class, crystallization behaviour seems to be relatively insensitive to changes in substituents at a given position (in this case [6], see diagrams above) of a class of geometrical isomers. For instance, note that **XI** and **XII** differ only by exchange of a pseudo-halide (NCS^-) for a halide (Cl^-). The former crystallizes in two different racemic morphs, the latter in only one, racemic as well. However, the conformation and configuration of **XII** is very close to that of the brown isomer **IXa**, implying that interchange of a Cl^- for NO_2^- has little effect on the conformation and configurational features of these molecules. In fact, to the extent of the precision of the two structural determinations, they are nearly isomorphous and isostructural compounds. An obvious conclusion is that the substituent at this position plays no major role in the crystallization behaviour of these *mer* or *mer*-like species. See also the next entry.

(4) Mazus *et al.* [9] remarked that one of the two molecules present in the asymmetric unit of orthorhombic **XIa** is identical in conformation and configuration with that found for the same compound in the monoclinic modification **XIb**. Also, that the major difference between the two molecules in the asymmetric unit of **XIa** is "a rotation of the plane of the NO_2 group *cis* to the NCS about the Co–N bond by an angle of 28°. A similar difference in the structure of complexes due solely to the orientation of the planes of nitro groups has been observed in two modifications of trinitro(ethylenediamine)ammine cobalt(III) [7]. In this work it was found that different isomers were formed depending on the method of preparation..." (ref. 7 in their paper is our ref. 29). However, as Mazus *et al.* [9] noted further on "both conformation isomers of our rhombic isothyocyanatodinitro(ethylenediamine)amminecobalt(III) are formed in the same synthesis".

(5) Substitution at this position [6] by an ammonia, leading to formation of a cation, also results in a racemic lattice. Compound **XIII**, crystallized by Neverov *et al.* [8] as the nitrate shows a configuration similar with that of the yellow form of **IX**.

(6) Compound **X**, which is the *trans*-dinitro geometrical isomer of **XIII** crystallizes in the triclinic system as the nitrate and, as the authors comment [7], "a similar orientation of the two *trans*-nitro groups have been observed in the brown isomer of trinitro(ethylenediamine)amminecobalt(III) [15]." (note their ref. 15 is our ref. 29).

The structural studies of the above compounds provide further insight into the matter of the conglomerate crystallization problem. **IX** and **XI** are isolable in more than one crystalline form in which the difference between conformers present in the lattices is primarily in the orientation of the *clavic* $-NO_2$ ligand oxygens with respect to the hydrogens of the available amino ligands. **IX** and **XI** are dimorphic and since **XIa** contains two independent molecules in the asymmetric unit surrounded by different environments, it is clear that these substances can be fairly flexible as to the environment they solidify in and, thus, there seem to be no obvious reason for them to exclusively pack in centrosymmetric space groups. Suggesting, therefore, that unlike related systems described in earlier reports [15–18] in which specific hydrogen bonded intramolecular interactions caused well-defined chiral conformations and configurations to be preferred, these systems do not share that property inasmuch as the *clavic* ($-NO_2$) groups seem to form equally stable hydrogen bonded systems in more than one conformation, thus appearing to become more fluxional. In fact, it seems that unlike those compounds [15–18] which conglomerate and seem to have a single, highly favored (low, single-well potential; LS-WP) those of the current group appear to have more than one, energetically-equally-acceptable, conformation (equivalently low multi-well potentials, or ELM-WP).

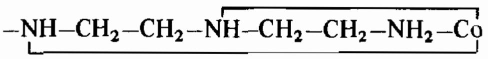
Two final comments on the conformational and configurational behaviour of the above molecules and their relationship to their crystallization preferences (racemates *versus* conglomerates) are in order:

(a) Among the interesting observations made by Jensen *et al.* [29] on compound **IX** is its existence in two different crystalline morphs, one brown **IXa**, the other one yellow **IXb**, both monoclinic (both space group $P2_1/c$). Within experimental error, the observed densities were the same, suggesting equally efficient packing. Thus, molecular-bulk packing considerations provide no suitable answer to the need for dimorphic crystallization and, thus, seems not unreasonable to attribute the phenomenon to an intra-molecular cause. Jensen *et al.* describe [29] the stereochemical difference between the molecules present in the two crystalline morphs as consisting of a change in relative orientation of the planes of the nitro groups. In both cases, however, the resulting conformations are those in which the nitro groups strike the best compromise between having (a) their oxygens oriented towards amino hydrogens and forming N–O....H–N bonds of *ca.* 2.2 Å and (b) adjacent nitro oxygens canted so as to minimize O....O non-bonded pair repulsions. Finally, the brown and yellow species constitute examples of atropisomers frozen in different, but apparently energetically similar, conformations in crystalline lattices.

(b) In a similar vein, Mazus *et al.* [9] described two morphs of compound **XI**; however, in this case, one is orthorhombic and the other one monoclinic, suggesting somewhat larger molecular conformational differences reflecting in the choice of two different systems. The orthorhombic **XIa** form contains two independent molecules in the asymmetric unit, of which one is identical in conformation and configuration to that present in its monoclinic **XIb**. The second molecule in the asymmetric unit of **XIa** differs from its companion by a rotation of one of the nitro groups about the Co–N(NO_2) axis, as in the above case.

Stereochemical Comparison of mer-Dienes with cis-β-Trienes

As expected, the [*cis*-β-Co(trien)XY] systems share many of the stereochemical features of the *mer*-Co(dien) described above. This is certainly the case for the *mer*-shaped fragment since it also suffers from



$-NH-CH_2-CH_2-NH-CH_2-CH_2-NH_2-Co$

the same angular strains imposed by having two fused five-membered rings, with similarly narrow ligand bites, sharing a common plane. For example, in the case of [*cis*-β-Co(trien)(NO_2)$_2$](NO_3) (**II**) [24], the two relevant N–Co–N angles are 84.5(1)° and 85.7(1)°, which are close to those given above for **I**. However, we note a somewhat larger dissymmetry in *cis*-β-trienes than in **I** which is caused by the strain of the third ring, extending from the *mer*-plane to an axial position of the Co atom. Thus, *mer*-dienes and *cis*-β-triene systems cannot have exactly the same stereochemistry for this fragment since the pleated sheet of the *mer*-dien systems contains two nearly identical N–C–C–N torsional angles of *ca.* 48° whereas *cis*-β-trienes have torsional angles at these fragments of *ca.* 40 and 50°. Furthermore, the former have two terminal, primary, $-NH_2$ and one secondary –NH ligands associated with this pleated sheet; the latter systems have two secondary –NH– amino ligands and only one terminal $-NH_2$ within the relevant fragment. Thus, for the dinitro derivatives, the hydrogen-bonded interactions between the $-NO_2$ ligands and the amino hydrogens can never be the same.

The similarity in stereochemistry between **I** and **II** is a general feature of such systems and not an accidental, solid state, artifact created by packing forces present in crystals of those two species. Note in that regard that **I** crystallizes in the orthorhombic space group *Pbca* (racemic), **II** [24] crystallizes in the monoclinic, racemic space group $P2_1/n$, while related derivatives of [*cis*-β-Co(trien)XY]$^+$ cations [30, 31] behave similarly despite the fact the first [30] crystallizes in the polar (non-enantiomorphic) space group $Pna2_1$ while the latter [31], being a resolved chiral species, crystallizes in the enantiomorphic space group $P2_12_12_1$. Thus, this is a common stereochemical feature of nitro polyamines of Co containing a *mer*-conformated, pleated-sheet fragment and, qualitatively, its conformation is largely invariant to changes of compensating anions (if any present) and variations in space group. It appears to be associated with the energetically advantageous opportunity for the $-NO_2$ oxygens to form intramolecular bonds with specific amino hydrogens, as described above.

Comparisons between **I** and *cis*-β-trienes are most meaningful when the latter are not methylated; otherwise, additional conformational problems maybe introduced. For example, the configurations of the five-membered rings in the compounds **II** [24], **III** [30], **IV** [31], **V** [32], **VI** [33] and **VII** [34] are as follows: the two Freeman and Maxwell compounds [30, 31] are non-methylated and have configurations Λ(δδλ) as is the case with **II** [24]; however, methylated derivatives such as **V** [32] and **VI** [33] were found to be Λ(δλδ) while **VII** [34] was assigned the chiral symbol Λ(δλλ). Thus, to simplify the comparisons in this report we limit ourselves to unsubstituted *mer*-dienes and unsubstituted β-trienes. In all such cases there is a pair of fused five-membered rings having conformations λδ or δλ, depending on the enantiomer in question. The important point is that both classes of compounds have an approximate mirror plane passing through the metal, the secondary NH jointly shared by the two rings and the monodentate ligand *trans* to the secondary NH. Thus, nucleophilic groups, such as $-NO_2$, seeking to make hydrogen bonds with the amino hydrogens acquire related conformations in both systems and those suggestions [24] made to justify the absence of conglomerate crystallization in the case of [*cis*-β-Co(trien)(NO_2)$_2$]$^+$ cations are relevant to the *mer*-dien complexes. Moreover, those as **I** able to strongly hydrogen bond with the amino moieties while, coincidentally, acquiring or nearly acquiring conformations supporting S_n symmetry, appear unlikely candidates for conglomeration. Thus, they also resemble the behaviour of *trans* compounds [15], as shown in the next paragraph.

Stereochemical Comparison with trans-Dinitro Polyamines

Surprising at first, compounds such as **I** share many of the stereochemical features of [*trans*-Co(en)$_2$(NO_2)$_2$]Y (Y = Cl, Br, I) complexes, discussed earlier [15]. Specifically, we refer to the fact that in both systems the nitro groups can form significant hydrogen bonds with the N–H basal plane hydrogens while, concurrently, acquiring an achiral conformation. That the hydrogen bonds are, indeed, significant [15] is demonstrated by the bending of the –N4–O1–O2 plane observed in both systems (see ref. 16 and the above discussion of this phenomenon in **I**). Such behaviour has been shown earlier [15] to be a common feature of *trans*-bisethylenediamines symmetrically substituted by nitro ligands, provided the counter anion is not a potent hydrogen bonding species such as NO_2^-, NO_3^-, NCS^-, etc. Compound I, having no counter anion to compete for the hydrogens and sharing the possibility of forming favorable, intramolecular hydrogen bonds while acquiring high symmetry (*i.e.*, a mirror plane), does so, as suggested earlier [15]. Also, we note that the lack of conglomeration, occurring in association with the feature of acquiring maximum molecular symmetry while $-NO_2$ oxygens form advantageous hydrogen bonds, is also present in a related species, [*trans*-Co(1,3-diaminopropane)$_2$(NO_2)$_2$]NO_2 [35] which contains six-membered chelate rings. Here, as in [*trans*-Co(en)$_2$(NO_2)$_2$]I [15], the molecule sits at a crystallographic inversion center. Thus, at least for racemates, no special significance seems to be associated with the size (five or six) of the chelate ring.

Conclusions

(1) Compound I is produced either exclusively or as the largely predominant species by a variety of synthetic procedures reasonably expected to yield other compounds. There is also no evidence for the presence of the *fac* derivative under the conditions described. If it is produced, it must be a minor component requiring careful chromatographic procedures to isolate it from the main product, I.

(2) Under a variety of crystallization conditions described above, the only morph of I thus far obtained is a racemate crystallizing in the orthorhombic space group *Pbca*. These conditions include proximity to solutions of other species undergoing conglomerate crystallization.

(3) Molecular comparisons of I with related substances such as [*mer*-Co(dien-like)XYZ] species provide persuasive evidence that the $-NO_2$ groups of these molecules are exposed to a molecular topology in which hydrogen-bonding multiwell potentials of equal or similar depth may be present. This results in lack of stereochemical rigidity needed to clamp the *clavic*$-NO_2$ ligands in a single, well-defined dissymmetric conformation. In such instances, the molecules may be trapped, as shown above, in polymorphic crystalline species or in lattices containing more than one molecule in the asymmetric unit. In either case differing conformations of comparable stability have been observed. In other cases, as in [*cis*-β-Co(trien)(NO_2)$_2$]$^+$ derivatives, the $-NO_2$ groups can interact with a multiplicity of amino hydrogens located at widely different angular positions of the surface this ligand faces. Since both oxygens are chemically equivalent and located 180° from each other, attempts of both to form the most advantageous hydrogen bonds appear to lead to fluxionality, thereby averaging the dissymmetry needed to induce conglomerate crystallization. In other words, the potentially dissymmetry-inducing $-NO_2$ ligands become spherically averaged and behave as a Cl^- anion, whose diameter is similar. In that context, the reader is reminded that while [*cis*-α-Co(trien)(NO_2)$_2$]X salts (see above and refs. 15–18) form conglomerates, two hydration polymorphs of [*cis*-α-Co(trien)Cl_2]Cl·nH_2O ($n = 2, 3$) are known to crystallize as racemates [37].

Structural studies of molecules such as those derived from [*trans*-Co(en)$_2$(NO_2)$_2$]$^+$ show that the most favorable hydrogen bonding scheme appears to attach the $-NO_2$ ligands in a symmetric arrangement in which the molecules have a molecular inversion center; thus, they are achiral and not expected to undergo conglomerate crystallization.

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References

1 P. H. Crayton and J. A. Mattern, *J. Inorg. Nucl. Chem., 13,* 248 (1960); 'Inorganic Syntheses', Vol. 7, McGraw-Hill, New York, 1963, p. 209.

2 M. Kobayashi, F. Marumo and Y. Saito, *Acta Crystallogr., Sect. B, 28,* 470 (1972).

3 M. Kono, F. Marumo and Y. Saito, *Acta Crystallogr., Sect. B, 29,* 739 (1973).

4 K. Okiyama, S. Sato and Y. Saito, *Acta Crystallogr., Sect. B, 35,* 2389 (1979).

5 (a) M. Laing, S. Baines and P. Sommerville, *Inorg. Chem., 10,* 1057 (1971); (b) B. Nuber, H. Siebert, K. Weidenheimmer, J. Weiss and M. L. Ziegler, *Acta Crystallogr., Sect. B, 35,* 1020 (1979).

6 V. N. Biyushkin, A. V. Ablov and N. V. Belov, *Doklady Akad. Nauk. SSSR, English Translation, 169–171,* 1031 (1976).

7 V. A. Neverov, A. V. Ablov, V. M. Golyshev, A. I. Andronov, E. V. Popa, F. M. Gal'perin and V. N. Biyushkin, *Doklady Akad. Nauk SSSR, English Translation, 223–225,* 613 (1975).

8 V. A. Neverov, A. V. Ablov, E. V. Popa, V. N. Biyushkin, A. P. Gulya and T. I. Malinovskii, *Doklady Akad. Nauk SSSR, English Translation, 238–243,* 424 (1978).

9 M. D. Mazus, A. V. Ablov, V. N. Biyushkin and T. I. Malinovskii, *Doklady Akad. Nauk SSSR, English Translation, 214–219,* 262 (1974).

10 O. B. Ramsay, 'Stereochemistry', Hayden, London, 1981, p. 91, 135.

11 F. S. Kipping and W. J. Pope, *J. Chem. Soc., Trans., 73,* 606 (1898).

12 C. G. Schlessinger, 'Inorganic Syntheses', Vol. 9, McGraw-Hill, New York, 1967, p. 170.

13 R. B. Hagel and L. F. Druding, *Inorg. Chem., 9,* 1496 (1967).

14 H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc., 82,* 5031 (1960).

15 I. Bernal and J. Cetrullo, *Inorg. Chim. Acta,* in press.

16 I. Bernal, *Inorg. Chim. Acta, 96,* 99 (1985).

17 I. Bernal, *Inorg. Chim. Acta, 101,* 175 (1985).

18 I. Bernal, C. K. Fair and E. O. Schlemper, *Inorg. Chim. Acta, 115,* 25 (1986).

19 'TEXRAY-230', a modification of the SDP-Plus [20] set of X-ray crystallographic programs, Molecular Structure Corporation, 3304 Longmire Dr., College Station, Tex. 77840, for use with their automation of the CAD-4 diffractometer.

20 'SDP-Plus', the Enraf-Nonius Corporation X-ray diffraction data processing programs, B. A. Frenz & Associates, College Station, Tex. 77840.

21 R. B. Roof, 'A Theoretical Extension of the Reduced Cell Concept in Crystallography', *Report LA-4038,* Los Alamos Scientific Laboratory, 1969.

22 D. T. Cromer and J. T. Waber, 'International Tables for X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham, U.K., 1975, Tables 2.2.B and 2.3.1, respectively, for the scattering factor curves and the anomalous dispersion values.

23 J. Jacques, A. Collet and S. H. Wilen, 'Enantiomers, Racemates and Resolutions', Wiley-Interscience, New York, 1981.

24 I. Bernal and J. Cetrullo, *Inorg. Chim. Acta, 120,* 109 (1986).

25 I. Oonishi, F. Muto and Y. Komiyama, *Bull. Chem. Soc. Jpn., 42,* 2791 (1969).

26 I. Bernal and J. Cetrullo, in preparation.

27 I. Bernal and R. A. Palmer, *Inorg. Chem., 20,* 295 (1981).

28 M. D. Mazus, V. N. Biyushkin, E. V. Popa, A. V. Ablov, T. I. Malinovskii and V. T. Tkachev, *Doklady Akad. Nauk SSSR, English Translation, 229–231,* 591 (1976).

29 K. G. Jensen, H. Soling and N. Thorup, *Acta Chem. Scand., 24,* 908 (1970).

30 H. C. Freeman and I. A. Maxwell, *Inorg. Chem., 8,* 1293 (1969).

31 H. C. Freeman and I. A. Maxwell, *Inorg. Chem., 9,* 649 (1970).

32 M. Ito, F. Marumo and Y. Saito, *Acta Crystallogr., Sect. B, 26,* 1408 (1970).

33 I. Bernal and R. Job, to be published.

34 K. Tanaka, F. Marumo and Y. Saito, *Acta Crystallogr., Sect. B, 29,* 733 (1973).

35 I. Krstanovic and M. Celap, *Cryst. Struct. Commun., 6,* 171 (1977).

36 I. Oonishi, H. Fujimaki, F. Muto and Y. Komiyama, *Bull. Chem. Soc. Jpn., 43,* 733 (1969).

37 I. Bernal, *J. Coord. Chem., 15,* 337 (1987).