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The Phenomenon of Conglomerate Crystallization. IX. *Clavic* Dissymmetry in Coordination Compounds. VII. An Investigation of the Crystallization Behaviour of [*trans*-Co(en)$_2$(ONO)X]Y, [*trans*-Co(en)$_2$(NO$_2$)X]Y, With (X = NO$_2^-$, NCS$^-$) and (Y = I$^-$, ClO$_4^-$, NO$_3^-$, NCS$^-$) and the Crystal Structures of Racemic [*trans*-Co(en)$_2$(NO$_2$)$_2$]I (VII) and of Racemic [*trans*-Co(en)$_2$(NO$_2$)$_2$]NCS (VIII). Why are some Conglomerates and some Racemic?

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Abstract

The compounds [*trans*-Co(en)$_2$(NO$_2$)$_2$]X (X = I, NCS) will, hereafter, be referred to as **VII** and **VIII**. Compound **VII** crystallizes in space group $C2/c$ with cell constants $a = 10.743(2)$, $b = 9.179(3)$, $c = 13.432(3)$ Å, $\beta = 112.28(2)°$; $V = 1225.56$ Å^3, $d_{calc} = 2.157$ g cm^{-3} and $Z = 4$. Chemical formula for **VII** = C$_4$H$_{16}$N$_6$O$_4$CoI; $M_R = 398.05$ and $\mu = 39.012$ cm^{-1}; absorption corrections were made and the relative values of the transmission coefficients were 99.96 to 77.38. Compound **VIII** crystallizes in the triclinic system, space group $P\bar{1}$, $a = 6.496(2)$, $b = 9.192(3)$, $c = 10.956(8)$ Å, $\alpha = 89.58(5)°$, $\beta = 79.70(5)°$, $\gamma = 75.71(2)°$; $V = 623.26$ Å^3, $d_{calc} = 1.754$ g cm^{-3} and $Z = 2$. Chemical formula for **VIII** = C$_5$H$_{16}$N$_7$O$_4$SCo; $M_R = 329.22$, $\mu = 15.532$ cm^{-1} and transmission coefficients ranged from 99.99 to 73.36. Total data collected for **VII**: 1238 of which 1048 were independent and had $I > 3\sigma(I)$ and **VIII**: 3840 of which 657 were symmetry related forms which were averaged ($R = 0.012$). The remaining 3183 were above $3\sigma(I)$ and were, thus considered observed. Both structures were solved by Patterson methods and refined to R and R_f factors of 0.0284 and 0.0350 for **VII** and 0.0216 and 0.0276 for **VIII**.

Both molecules crystallize in centrosymmetric space groups. The cation of **VII** sits at a crystallographic inversion center while that of **VIII** is located at a general position; nonetheless, it has a nearly perfect, molecular, inversion center. In both compounds, the cations have a λ and a δ conformed ethylenediamine which in the case of **VII** is required by the inversion center. Comparison of the stereochemical parameters of the Co(en)$_2$ fragments in **VII** and **VIII** reveal them to be nearly identical. However, the –NO$_2$ ligands in **VII** are bent towards the terminal –NH$_2$ of the basal plane in what is, obviously, an attempt to form as strong N–H···O–N intramolecular hydrogen bonds as possible. This is not the case with the –NO$_2$ ligands of **VIII** which are almost exactly orthonormal to the CoN$_4$ base. This phenomenological difference in behaviour of the –NO$_2$ ligands is due to the difference in hydrogen bonding ability of the two compensating anions.

Bond lengths and angles compare favorably with literature results on relevant substances.

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, responsible for a newly recognized form of dissymmetry, (*i.e.* –NO$_2$), resemble broad blades or paddles. When these ligands are 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. We now wish to address ourselves to the crystallization behaviour of a series of *trans* compounds – specifically, to the salts of [*trans*-Co(en)$_2$XY]$^{n+}$ ions.

Prior to doing so, we remind readers of an issue raised in our earlier reports [1, 2]; namely, the role played by the counterion in conglomerate crystallization and note here that

(a) Whereas [*cis*-Co(en)$_2$(NO$_2$)$_2$]X (X = Cl, Br) undergo conglomerate crystallization [1, 5] the nitrate was reported [6] to crystallize 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$_3$) moieties which is the suspected mechanism whereby

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the chiral $Co(NO_2)_2$ ensemble seems to enhance the incidence of conglomerate crystallization.

(b) Literature data on the *trans-* series, given in the table below, shows what appears to be a discrepancy in crystallization behaviour among derivatives of the same cations:

	Compound	Space group	Reference
I	[*trans*-$Co(en)_2(ONO)(NCS)$]I	$P2_1$	7
II	[*trans*-$Co(en)_2(NO_2)(NCS)$]I	$P2_1$	7
III	[*trans*-$Co(en)_2(ONO)(NCS)$]ClO_4	$P2_1$	7
IV	[*trans*-$Co(en)_2(NO_2)(NCS)$]ClO_4	$P2_1$	7
V	[*trans*-$Co(en)_2(NO_2)(NCS)$]NCS	$C2/c$	8
VI	[*trans*-$Co(en)_2(NO_2)_2$](NO_3)	$P2_1/c$	6
VII	[*trans*-$Co(en)_2(NO_2)_2$]I	$C2/c$	this study
VIII	[*trans*-$Co(en)_2(NO_2)_2$]NCS	$P1$	this study

Here we note that

(a) Compounds **II**, **III** and **V** differ only in the nature of the anion. That, apparently, is enough to change the crystallization behaviour from conglomerates (**II** and **III**) to racemic crystals (**V**).

(b) The three *trans*-dinitro compounds (**VI**, **VII** and **VIII**) crystallize as racemates irrespective of the nature of the compensating anion; and, whereas **I** and **II** have one –NCS and either an $-NO_2$ or an –O–NO, **VII** is a *trans*-dinitro cation. All three have iodide compensating anions.

(c) As expected from the above considerations [1–3] the *trans*-nitrate salt (**VI**), like its *cis* analog, was not expected to form conglomerates. The X-ray analysis by Bortin [6] demonstrated that this expectation was met.

One may ask at this point whether there is a rational explanation for the behaviour of these substances insofar as their propensity (or lack thereof) for conglomerate crystallization. Our justification for the difference in crystallization mode (conglomerate *vs.* racemic) exhibited by the series of compounds listed above is the subject of this article.

Experimental

All elemental analyses were performed by Galbraith Analytical Laboratory*. Infrared data were collected from KBr pellets whose spectral characteristics were recorded on a Perkin-Elmer 1330 spectrophotometer.

Preparation of the Compounds

VII [*trans*-$Co(en)_2(NO_2)_2$](NO_3) was prepared in accordance with a standard procedure [9]. 3.6 g of [*trans*-$Co(en)_2(NO_2)_2$](NO_3) were dissolved in the minimum amount of water (21 °C) and 1.95 g freshly recrystallized NaI (20% excess) dissolved in that solution. Upon standing, a small amount of the nitrate crystallizes out. These crystals were filtered and the solution allowed to crystallize further. The second crop of crystals is the desired product. The compound decomposes in the range 209–218 °C.

VIII 11.5 g $Co(NO_3)_2 6H_2O$, 6.0 g $NaNO_2$ and 8.4 g KSCN were dissolved in 30 ml deionized water. 2.5 g of 98% ethylenediamine were mixed with 5 ml of water and partially neutralized with 1.5 ml conc. HNO_3. The two solutions were mixed in a filter bottle through which air could be drawn into the solution via a glass tube fitted through the stopper. Air was passed through the solution for *ca.* 40 min, whereupon a green precipitate formed at the bottom of the solution. The solution was cooled to *ca.* 5 °C and then filtered. The green solid was washed with absolute ethanol and ether, dried in an air current. Melting point (m.p.) 173 °C, dec.

When a portion of this green solid is redissolved in water, the solution rapidly turns amber in color. It was filtered and set aside in a refrigerator (*ca.* 5 °C) and allowed to crystallize. The well-formed crystals of **VIII** melt, with decomposition, at 197–198 °C.

Elemental analysis of the green solid shows it to contain two thiocyanate ions and have the approximate composition $Co(en)_2(NO_2)(NCS)_2$. This substance shows two distinct IR bands in the C=N region (see Fig. 1). Eventually, only one remains and it is identical with that present in compound **VIII**.

Collection and Processing of X-ray Diffraction Data

Data were collected with an Enraf-Nonius CAD-4 diffractometer operating with the Molecular Structure Corporation TEXRAY-230 Modification [10] of the SDP-Plus Programs [11]. The reader is referred to their manuals for details of the various routines mentioned in the text. The scattering curves are those of the International Tables [12].

In both cases, the yellow crystal of **VII** and **VIII** 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 was centered and used to define the orientation and Niggli [13] matrices. The unit cell for **VII** is *C*-centered monoclinic and subsequent examination of the systematic absences revealed a *c*-glide; thus, the space group could be either *Cc* or *C2/c*. The crystal lattice of **VIII** is primitive and triclinic. Examination of the distribution of intensities (NORMAL [10]) suggested crystals of both are centrosymmetric – a fact verified by subsequent solution and refinement of the two crystal structures.

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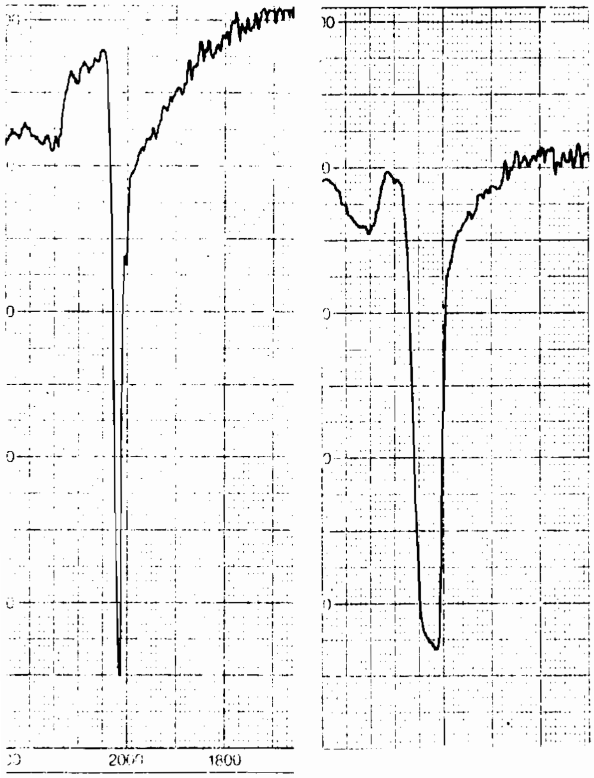

Fig. 1. IR spectrum in the region of the C=N stretch. On the left side of the figure is shown the spectrum of compound **VIII**, on the right side that of the green compound obtained in the synthesis of compound **VIII**. The sharp singlet (*ca.* 2025 cm^{-1}) on the left is due to the $^{-}$NCS anion present in **VIII**, the broad doublet on the right we believe to be due to the kinetic product [*trans*-Co(en)$_2$(NO$_2$)(–SCN)]NCS [20].

For the iodide and thiocyanate crystals data were collected up to $2\theta \leqslant 50°$. These were corrected for Lorentz-polarization effects and for absorption (using the curves obtained from Psi scans [10]). 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. In the final three cycles of refinement, the hydrogens were refined to the final positions given in Tables I and II, respectively. In both cases, the final difference map showed no peaks having meaningful chemical significance, the largest being ripples adjacent to the I or the Co atoms. The results of all these calculations are summarized on Tables III and IV.

TABLE I. Positional Parameters and their Estimated Standard Deviations[a]

Atom	x	y	z	B (Å^2)
I	0.000	0.43004(4)	0.250	2.489(9)
CO	0.000	0.000	0.500	1.40(1)
O1	0.1200(3)	0.0453(4)	0.3546(2)	3.36(8)
O2	0.2397(3)	–0.0885(4)	0.4871(3)	3.72(8)
N1	0.1332(3)	0.0507(4)	0.6406(3)	2.08(7)
N2	–0.0178(3)	0.2100(4)	0.4699(3)	2.16(7)
N3	0.1367(3)	–0.0156(4)	0.4402(3)	1.89(7)
C1	0.1215(4)	0.2098(5)	0.6595(4)	3.0(1)
C2	0.0948(5)	0.2863(5)	0.5549(4)	3.1(1)
H1	0.210(5)	0.026(6)	0.648(4)	4(1)*
H2	0.122(4)	–0.007(5)	0.691(3)	3(1)*
H3	0.201(5)	0.241(6)	0.715(4)	5(1)*
H4	0.027(4)	0.227(5)	0.677(3)	3(1)*
H5	0.177(4)	0.279(5)	0.525(3)	3(1)*
H6	0.088(5)	0.387(6)	0.551(4)	6(1)*
H7	–0.005(5)	0.215(5)	0.403(4)	6(1)*
H8	–0.106(4)	0.246(4)	0.470(3)	2.2(9)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a_2b_{(1,1)} + b_2b_{(2,2)} + c_2b_{(3,3)} + ab(\cos\gamma)b_{(1,2)} + ac(\cos\beta)b_{(1,3)} + bc(\cos\alpha)b_{(2,3)}]$.

Results and Discussion

The structure of the cations are depicted in Figs. 2 and 3 and the packing of the cation and anions are shown in Figs. 4 and 5. Positional parameters, bond lengths, inter- and intramolecular hydrogen bonds, bond angles, torsional angles and least-squares planes are given in Table V.

Description of the Structures

Packing

The packing diagram for **VII** is shown on Fig. 3, from which it is clear the the I$^-$ anions are so distributed about the cations that they form nearest contacts with the hydrogens of both, the –NH$_2$ and the –CH$_2$– fragments. However, as expected, none of those contacts are very significant insofar as a bonding interaction is concerned. The iodide anion forms a symmetrical bridge between two cations having the following characteristics: I···H7 = 2.859 Å, H7···I···H7 = 92.9°. Thus, as expected [1, 2] the iodide anion does not compete effectively with the intramolecular hydrogen bonds between the –NO$_2$ and the terminal –NH$_2$ hydrogens (see below for a discussion of the nature of these bonds).

The packing of the cations and anions in **VIII** is completely different (see Fig. 5). Here, the N and S

TABLE II. Positional Parameters and Their Estimated Standard Deviations[a]

Atom	x	y	z	B (Å^2)
CO	0.21870(2)	0.26412(2)	0.24298(1)	1.384(3)
S	0.64361(7)	−0.21006(5)	0.37611(4)	2.871(8)
O1	−0.2132(2)	0.3984(1)	0.2543(1)	2.91(2)
O2	−0.1298(2)	0.3629(2)	0.4336(1)	3.70(3)
O3	0.5739(2)	0.1663(2)	0.0551(1)	4.79(3)
O4	0.6490(2)	0.1277(1)	0.2350(1)	3.08(2)
N1	0.1240(2)	0.1284(1)	0.1409(1)	1.92(2)
N2	0.2295(2)	0.1076(1)	0.3645(1)	1.87(2)
N3	0.2038(2)	0.4207(1)	0.1212(1)	1.97(2)
N4	0.3144(2)	0.4005(1)	0.3439(1)	1.78(2)
N5	−0.0765(2)	0.3530(1)	0.3200(1)	2.01(2)
N6	0.5153(2)	0.1743(1)	0.1677(1)	2.06(2)
N7	0.8096(3)	−0.2766(2)	0.1244(1)	3.85(4)
C1	0.1598(2)	−0.0232(2)	0.1942(1)	2.37(3)
C2	0.1066(2)	0.0006(2)	0.3331(1)	2.25(3)
C3	0.3260(2)	0.5280(2)	0.1519(1)	2.35(3)
C4	0.2749(2)	0.5522(2)	0.2908(1)	2.23(3)
C5	0.7406(2)	−0.2483(2)	0.2280(1)	2.43(3)
H1	0.183(3)	0.127(2)	0.070(2)	3.1(4)*
H2	−0.015(2)	0.164(2)	0.138(1)	2.2(3)*
H3	0.301(2)	−0.069(2)	0.169(1)	2.1(3)*
H4	0.068(2)	−0.079(2)	0.166(1)	2.5(3)*
H5	0.144(2)	−0.095(2)	0.371(1)	2.8(3)*
H6	−0.046(2)	0.043(1)	0.356(1)	1.9(3)*
H7	0.360(3)	0.056(2)	0.368(2)	3.0(4)*
H8	0.176(3)	0.148(2)	0.438(1)	3.0(4)*
H9	0.071(2)	0.468(2)	0.121(1)	2.1(3)*
H10	0.249(3)	0.384(2)	0.048(1)	2.8(4)*
H11	0.292(3)	0.619(2)	0.112(1)	3.1(4)*
H12	0.478(2)	0.483(2)	0.125(1)	2.4(3)*
H13	0.129(2)	0.597(2)	0.315(1)	2.2(3)*
H14	0.363(2)	0.609(2)	0.320(1)	2.7(3)*
H15	0.254(3)	0.408(2)	0.417(2)	3.2(4)*
H16	0.461(3)	0.373(2)	0.344(1)	2.7(4)*

[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 III. Summary of Data Collection and Processing Parameters for Racemic [*trans*-Co(en)$_2$(NO$_2$)$_2$]I

Space group	$C2/c$
Cell constants	a = 10.743(2) Å b = 9.179(3) Å c = 13.432(3) Å β = 112.28(2)°
Cell volume	V = 1225.56 Å^3
Molecular formula	$C_4H_{16}N_6O_4CoI$
Molecular weight	398.05 g mol^{-1}
Density (calc; Z = 4)	2.157 g cm^{-3}
Radiation employed	Mo Kα (λ = 0.71073 Å)
Absorption coefficient	μ = 39.012 cm^{-1}
Transmission coefficients	1.00 to 0.7738
Data collection range	4° $\leqslant 2\theta \leqslant$ 50°
Scan width	$\Delta\theta = 0.95 + 0.35 \tan\theta$
Total data collected	1238
Data used in refinement[a]	1048
$R = \Sigma \|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0284
$R_w = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.0350
Weights used	$w = [\sigma(F_o)]^{-2}$

[a] The difference between this number and the total is due to subtraction of 190 data which either were systematically absent (but collected for verification of space group), were standards or did not meet the criterion that $I \geqslant 3\sigma(I)$.

TABLE IV. Summary of Data Collection and Processing Parameters for Racemic [*trans*-Co(en)$_2$(NO$_2$)$_2$]NCS

Space group	$P\bar{1}$
Cell constants	a = 6.496(2) Å b = 9.192(3) Å c = 10.956(8) Å α = 89.58(5)° β = 79.70(2)° γ = 75.71(2)°
Cell volume	V = 623.26 Å^3
Molecular formula	$C_5H_{16}N_7O_4SCo$
Molecular weight	329.22 g mol^{-1}
Density (calc; Z = 4)	1.754 g cm^{-3}
Radiation employed	Mo Kα (λ = 0.71073 Å)
Absorption coefficient	μ = 15.532 cm^{-1}
Transmission coefficients	1.00 to 0.7336
Data collection range	4° $\leqslant 2\theta \leqslant$ 50°
Scan width	$\Delta\theta = 1.00 + 0.35 \tan\theta$
Total data collected	3840
Data used in refinement[a]	3183
$R = \Sigma[\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0216
$R_w = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.0276
Weights used	$w = [\sigma(F_o)]^{-2}$

[a] The difference between this number and the total is due to subtraction of 657 data which either symmetry related, were standards or did not meet the criterion that $I \geqslant 3\sigma(I)$.

of the $^{-}$NCS anions interact with the terminal $-NH_2$ hydrogens of the ethylenediamine ligands, a fact amply demonstrated by the N7···H hydrogen bonds in this lattice (N7···H10 = 2.27 Å) which are comparable in length with the shortest O···H hydrogen bond (O1···H16 = 2.24 Å). To bring this point into perspective, one should recall that N–H···N bonds are expected to be inherently weaker [14] than N–H···O bonds.

Description of the Cations

Cation of VII

Stereo Figs. 2 and 3 clearly show that the cation of **VII** has two oppositely conformated en ligands: one λ, the other δ. Interestingly, the planes of the nitro groups are bent such that the oxygens can approach closer to the terminal $-NH_2$ hydrogens.

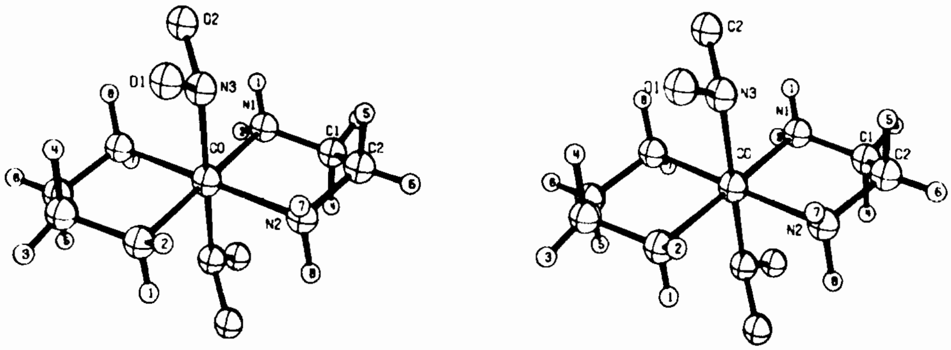

Fig. 2. The cation of **VII**. Note that although the general orientation of the $-NO_2$ ligands is between en ligands, each of them is bent such that its oxygens approach more closely the $-NH_2$ ends of the diamines. This does not happen with the $-NO_2$ ligands on **VIII**. Also note that the en ring on the left is λ while the one on the right is δ.

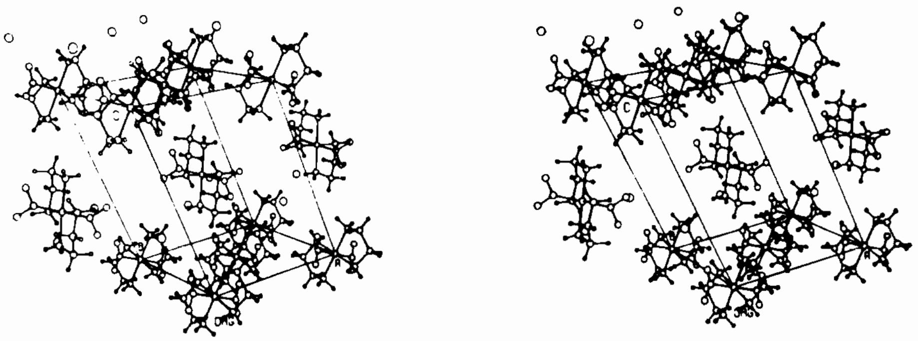

Fig. 3. The packing of the ions in compound **VII**. The larger open circles are the iodide anions.

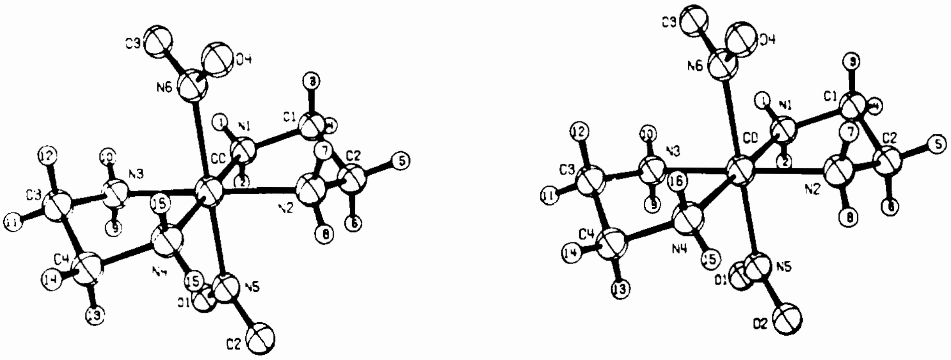

Fig. 4. The cation of compound **VIII** showing the nitro groups nearly perpendicular to the basal plane and also in an orientation bisecting the angle between the two en rings. Also note that the en ring on the left is δ while the one on the right is λ.

This fact is clearly shown in Fig. 2, for which the observer's line of sight was selected to emphasize this point. Like the two en ligands, the nitro groups are identical and are bent in opposite directions as demanded by the crystallogrphic inversion center at which the cation is located.

Cation of VIII

As in the case of **VII**, this cation has two oppositely conformated en rings (*i.e.*, one λ, the other δ) despite the fact that the ion sits at a general position of the space group. However, the plane of the nitro groups is almost exactly orthonormal to the plane

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

A. Bond lengths for the cation of **VII**

Co–N1	1.945(1)	Co–N2	1.964(1)
Co–N3	1.928(1)	N1–C1	1.496(2)
C1–C2	1.497(3)	C2–N2	1.486(2)
N3–O1	1.228(2)	N3–O2	1.241(2)

B. Bond lengths for the cation of **VIII**

Co–N1	1.957(1)	Co–N2	1.950(1)
Co–N3	1.952(1)	Co–N4	1.958(1)
Co–N5	1.927(1)	Co–N6	1.932(1)
N5–O1	1.234(1)	N5–O2	1.229(1)
N6–O3	1.221(1)	N6–O4	1.233(1)
N1–C1	1.488(1)	C1–C2	1.503(1)
C2–N2	1.488(1)	N3–C3	1.485(1)
C3–C4	1.504(1)	C4–N4	1.487(1)
N1–H1	0.80(1)	N1–H2	0.89(9)
C1–H3	0.90(8)	C1–H4	0.97(8)
C2–H5	0.97(8)	C2–H6	0.96(8)
N2–H7	0.87(1)	N2–H8	0.86(9)
N3–H9	0.86(8)	N3–H10	0.84(9)
C3–H11	0.94(9)	C3–H12	0.96(8)
C4–H13	0.93(8)	C4–H14	0.96(8)
N4–H15	0.82(1)	N4–H16	0.92(9)

C. Bond lengths for the anion of **VIII**

C5–N7	1.150(1)	C5–S	1.639(1)

D. Hydrogen contacts (less than 2.50 Å)

Compound **VII**		Compound **VIII**	
O1–H2	2.24(2)	O1–H9	2.36
O1–H2	2.46(2)	O1–H16	2.24
O2–H8	2.26(2)	O2–H8	2.44
O2–H8	2.32(2)	O4–H7	2.39
		O4–H16	2.48
		N7–H10	2.27

E. Bond angles for the cation of **VII**

N1–Co–N2	86.76(6)	N1–Co–N3	88.47(6)
Co–N1–C1	108.7(1)	Co–N2–C2	108.5(1)
Co–N3–O1	119.5(1)	Co–N3–O2	120.1(1)
O1–N3–O2	120.4(1)	N1–C1–C2	107.3(1)
C1–C2–N2	108.1(1)		

F. Bond angles for the cation of **VIII**

N1–Co–N2	84.45(8)	N1–Co–N3	93.42(8)
N1–Co–N4	93.74(8)	N1–Co–N5	90.06(8)
N1–Co–N6	173.85(9)	N2–Co–N3	84.29(9)
N2–Co–N4	171.26(9)	N2–Co–N5	95.79(9)
N2–Co–N6	91.52(8)	N3–Co–N4	86.07(8)
N3–Co–N5	176.44(8)	N3–Co–N6	91.67(8)
N4–Co–N5	92.4(1)	N4–Co–N6	90.06(8)
N5–Co–N6	84.91(8)	Co–N1–C1	110.7(1)
Co–N2–C2	108.4(1)	Co–N3–C3	108.9(2)
Co–N4–C4	108.5(2)	Co–N5–O1	121.2(2)
Co–N5–O2	120.5(2)	Co–N6–O3	121.5(2)
Co–N6–O4	120.0(2)	O1–N5–O2	118.1(2)
O3–N6–O4	118.4(2)	N1–C1–C2	107.7(2)
C1–C2–N2	107.6(2)	N3–C3–C4	110.3(2)
C3–C4–N4	106.5(2)		

(continued)

TABLE V. *(continued)*

G. Bond angle for the anion of **VIII**

C5–N7–S	178.99(3)

H. Torsional angles for the cation of **VII**

N2–Co–N1–C1	15.1	N3–Co–N1–C1	105.9
N1–Co–N2–C2	12.2	N3–Co–N2–C2	–79.3
N1–Co–N3–O1	–131.8	N1–Co–N3–O2	49.3
N2–Co–N3–O1	–45.0	N2–Co–N3–O2	136.1
Co–N1–C1–C2	–39.0	Co–N2–C2–C1	–37.0
N1–C1–C2–N2	49.8		

I. Torsional angles for the cation of **VIII**

N2–Co–N1–C1	–12.7	N3–Co–N1–C1	168.0
N4–Co–N1–C1	139.4	N5–Co–N1–C1	–101.7
N6–Co–N1–C1	77.7	N5–Co–N1–C1	–101.7
N1–Co–N2–C2	–16.0	N3–Co–N2–C2	34.8
N4–Co–N2–C2	164.2	N5–Co–N2–C2	74.7
N1–Co–N2–C2	–105.7	N1–Co–N3–C3	–163.9
N2–Co–N3–C3	145.3	N4–Co–N3–C3	15.9
N5–Co–N3–C3	105.5	N6–Co–N3–C3	–74.1
N1–Co–N4–C4	41.5	N2–Co–N4–C4	–166.5
N3–Co–N4–C4	12.9	N5–Co–N4–C4	–77.5
N6–Co–N4–C4	103.1	N1–Co–N5–O1	–51.3
N1–Co–N5–O2	127.7	N2–Co–N5–O1	–136.8
N2–Co–N5–O2	42.2	N3–Co–N5–O1	42.7
N3–Co–N5–O2	–138.3	N4–Co–N5–O1	128.3
N5–Co–N5–O2	–52.7	N6–Co–N5–O1	–171.6
N6–Co–N5–O2	7.6	N1–Co–N6–O3	54.1
N1–Co–N6–O4	–127.7	N2–Co–N6–O3	139.6
N2–Co–N6–O4	–42.2	N3–Co–N6–O3	–39.9
N3–Co–N6–O4	138.3	N4–Co–N6–O3	–125.5
N4–Co–N6–O4	52.7	N5–Co–N6–O3	174.4
N5–Co–N6–O4	–7.5	Co–N1–C1–C2	38.1
Co–N2–C2–C1	40.7	Co–N4–C4–C3	–38.4
N1–C1–C2–N2	–50.9	N3–C3–C4–N4	51.3

J. Least-squares planes for **VII**

Plane 1. Defined by N3, O1, O2

$$-0.2933x - 0.8153y - 0.4992z = -2.3874$$

Distance (Å) of other atoms from plane 1

Co	0.032	N1	–1.429	N2	–1.342

K. Least-squares planes for **VIII**

Plane 1. Defined by N5, O1, O2

$$-0.4244x - 0.9055y - 0.0047z = -3.1381$$

Distance (Å) of other atoms from plane 1

Co	0.028	N1	1.566	N2	1.349
N3	–1.283	N4	–1.519	N6	0.059
O3	0.027	O4	0.077		

Plane 2. Defined by N6, O3, O4

$$-0.4240x - 0.9052y - 0.0308z = -3.1244$$

Distance (Å) of other atoms from plane 2

Co	–0.052	N1	1.513	N2	1.235
N3	–1.328	N4	–1.626	N6	–0.102
O1	–0.084	O4	–0.134		

Angle between Planes 1 and 2 = 1.5°

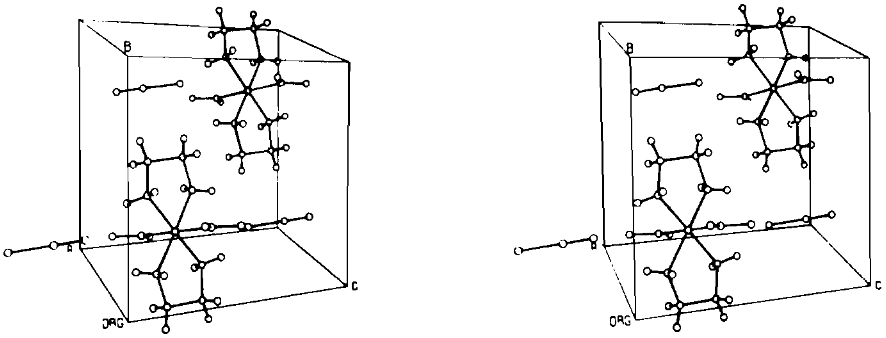

Fig. 5. Packing of cations and anions in compound **VIII**. The close proximity of the $^{-}$NCS to the amine hydrogens is evident from this diagram.

defined by the four basal plane nitrogens. In fact, the plane of the nitro groups almost exactly bisect the angles N1–Co–N3 and N2–Co–N4, as can be seen in Fig. 4.

Description of the Anions

The I$^-$ ions of **VII** occupy inversion centers of its lattice and their location can readily be ascertained from the packing diagram (Fig. 3) already discussed above. In the case of **VIII**, the $^{-}$NCS anions are essentially linear (N–C–S = 178.99(3)°; see Table VG.) and have normal dimensions (see refs. 7 and 8 for details).

Discussion

A. Symmetrically Substituted [trans-Co(en)$_2$X$_2$] Species

It is interesting to note that compounds **V** to **VIII** as well as [*trans*-Co(en)$_2$(NO$_2$)$_2$]Cl (**IX**)* and [*trans*-Co(en)$_2$Cl$_2$]Cl (**X**) [15] which crystallize as racemates in a variety of space groups all have a pair of δ and λ conformated ethylenediamine ligands. Note that this is true irrespective of

(a) the nature of the ligands in the axial positions,

(b) the nature of the compensating anion present in those lattices and

(c) of whether the cations sit at special lattice positions (*i.e*, inversion centers) or not.

However, in the case of compounds **I** to **IV**, all of which crystallize as conglomerates, each cation contains solely [7] $\lambda\lambda$ or $\delta\delta$ conformated rings.

Thus far, the normal expectation [16] has been that each [*trans*-Co(en)$_2$XY] cation has one λ and one δ conformated ring since enthalpy differences are insignificant and the 'meso form is preferred statistically over the chiral isomer by a factor of two' [16]. However (1) this expectation seems only to be met in the case of substances crystallizing in centrosymmetric space groups and it is true, independently of the nature of the space group, so long as it is a centrosymmetric one; and (2) it is not obeyed for *trans* compounds crystallizing in enantiomorphic space groups. This observation is very general since it is obeyed not only for conglomerates of ethylenediamine, such as compounds **I** to **IV**, but is also obeyed in the case of chiral species resolved by external agents such as [(–)$_{589}$-*trans*-dichlorobis(R-propylenediamine)Co[Cl·HCl·2H$_2$O (**XI**) [17] and [(–)$_{589}$-*trans*-dichlorobis(N-Me-ethylenediamine)Co]ClO$_4$·1/2H$_2$O (**XII**) [18]. In the former species, **XI**, both chelate rings adopt the λ conformation whereas in the latter, **XII**, both rings are δ. Obviously, their enantiomorphs crystallize oppositely.

B. Unsymmetrically Substituted [trans-Co(en)$_2$X$_2$] Species

The species [*trans*-Co(en)$_2$X$_2$] whose conglomerate crystallization behaviour and crystal and molecular structures have been described above (Part 'A') share a common characteristic; namely, that in all of them the two substituents, X, are identical. However, when we consider compounds [*trans*-Co(en)$_2$-(ONO)(NCS)]I (**I**), [*trans*-Co(en)$_2$(NO$_2$)(NCS)]I (**II**), [*trans*-Co(en)$_2$(ONO)(NCS)]ClO$_4$ (**III**) and [*trans*-Co(en)$_2$(NO$_2$)(NCS)]ClO$_4$ (**IV**) one notes that

(a) Either non-bonding pairs of oxygens in nitrogen bound (**II**, **IV**) or the nitrogen non-bonded pair of oxygen bound nitrito (**I**, **III**) point directly at hydrogens of terminal –NH$_2$ groups of the en ligands (the reader is referred to Figs. 1a–1d, ref. 7).

(b) All four cations have very low symmetry: the two nitro cations, **II** and **IV**, have approximately C_2 symmetry while the other two have only the

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*I. Bernal and J. Cetrullo determined the space group and lattice constants of [*trans*-Co(en)$_2$(NO$_2$)$_2$]Cl as follows: $P2_1/c$; a = 6.571(26), b = 12.674(6), c = 14.037(32) Å, β = 96.98(26). V = 1160.30 Å^3, D(calc; Z = 4 and M_R = 307.57 g mol^{-1}) = 1.76 g cm^3.

identity element (C_1 symmetry). (See Figs. 1a–1d, ref. 7.)

(c) Species **I**–**IV** have compensating anions which are known to be poor hydrogen bonders and, as demonstrated earlier [1–3] do not interfere with the anchoring of the $-NO_2$ or $-O-NO$ ligands which introduce disymmetry either directly or by inducing the pair of en ligands to acquire a dissymmetric $\delta\delta$ or $\lambda\lambda$ conformation, or both.

(d) An independent piece of evidence which lends support to these arguments is the fact that compound V, [*trans*-Co(en)$_2$(NO$_2$)(NCS)]NCS, which contains the exact same cation as **II** and **IV** crystallizes in the centrosymmetric space group $C2/c$ while the latter two crystallize in the enantiomorphic space group $P2_1$.

(e) We pointed out earlier [1–3] the ability of the nitrate anion to break up the intramolecular N–O•••H–NH hydrogen bonds and, effectively, interfere with conglomerate crystallization. Now, we note that the $^-$NCS anion is equally capable of causing similar disruption. This is evident by comparison of the crystallization behaviour of compound **V** with that of **II** and **IV**.

Conclusions

We can summarize the expected crystallization behaviour of compounds having the general formula [*trans*-Co(en)$_2$XY]Z thus

(1) If X, Y and Z are neither chiral nor dissymmetric themselves and if X = Y, irrespective of the nature of Z these substances will not crystallize as conglomerates.

(2) If X and Y are different and one or both are *clavic* (*i.e.*, groups such as $-NO_2^-$, ^-O-NO, $-SO_2$, etc.) and Z is a weak hydrogen acceptor such as Cl^-, Br^-, I^-, ClO_4^-, etc. it is expected that the incidence of conglomerate crystallization will be high for these species.

(3) If either X or Y are *clavic*, but Z is a powerful hydrogen bonding anion such as NO_3^- or ^-NCS, the compounds are expected to crystallize in centrosymmetric or polar (but non-enantiomorphic) space groups such as $Pna2_1$, Cc, etc. In either case, the lattice will consist of enantiomeric pairs related by an operation of the second sort.

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