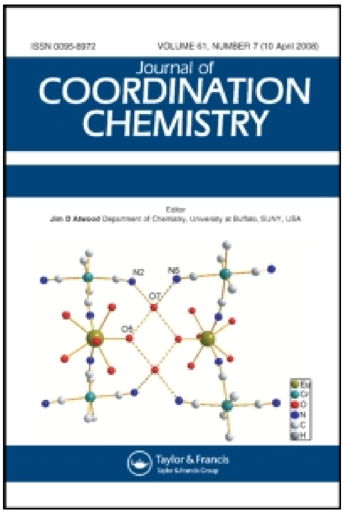

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 42. THE CRYSTALLIZATION MODE AND CONFORMATIONAL AND CONFIGURATIONAL BEHAVIOR OF MER-TRINITRO COBALT TRIAMINES: [MER-Co$(NH_3)_3(NO_2)_3$] (I) AND [MER-Co(DPT)$(NO_2)_3$] (II)

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NOTE

THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. PART 42. THE CRYSTALLIZATION MODE AND CONFORMATIONAL AND CONFIGURATIONAL BEHAVIOR OF MER-TRINITRO COBALT TRIAMINES: [MER-$Co(NH_3)_3(NO_2)_3$] (I) AND [MER-Co(DPT)$(NO_2)_3$] (II)

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KEYWORDS: conformational, configurations, cobalt, triamines, conglomerate

ABBREVIATIONS: dien = diaminoethylamine = H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH_2, dpt = dipropylenetriamine = H_2N-CH_2-CH_2-CH_2-NH-CH_2-CH_2-CH_2-NH_2, trpn = tris(3-aminotripropylamine) = $N(CH_2$-CH_2-CH_2-CH_2-$NH_2)_3$.

The structure of the *fac*-[$Co(NO_2)_3(NH_3)_3$] isomer was determined by B. Nuber, H. Siebert, K. Weidenheimer and J. Weiss, *Acta Crystal.*, **B35**, 1020 (1979). Interestingly, this isomer also crystallizes in the space group $P2_12_12_1$ ($z = 4$), but the volume it occupies is only 782.09 Å^3, whereas the mer-isomer occupies a volume of 816.09 Å^3. Therefore, there is a difference of 34.81 Å^3/4 molecules or a volume difference per molecule, of 8.70 Å^3. If all other factors are equal, this would argue that crystals of the *fac* isomer are thermodynamically more stable since its higher density must be a reflection of its Madelung energy.

INTRODUCTION

Sometime ago, we published[1] comments on the crystallization behavior of [*mer*-Co(dien)$(NO_2)_3$) (III) which, over a wide range of temperatures, crystallizes as a

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racemate in space group Pbca. In that report, we noted that the molecules have a nearly perfect mirror plane passing through the nitrogen of the central -NO_2 ligand, the Co and the secondary amine nitrogen. Moreover, the two five-membered rings have opposite helical chirality at the N-C-C-N fragments; thus, making the possibility of placing the molecules at mirror planes very reasonable. In summary, we proposed that the mesomeric character of the molecule seems to influence the selection of a centrosymmetric space group.

We also pointed out[1] that [*mer*-$Co(NH_3)_3(NO_2)_3$] (**I**) had been observed[2] to crystallize as a conglomerate in space group $P2_12_12_1$. If these molecules recognize their own internal symmetry in the process of selecting a crystallization path (*e.g.*, racemate or conglomerate) then [*mer*-$Co(NH_3)_3(NO_2)_3$] must be sufficiently dissymmetric that it selects a conglomerate crystallization pathway. This, of course, implies that the intramolecular and intermolecular hydrogen bonding between the amines and -NO_2 oxygens is such that the point group symmetry is low enough to render the molecule chiral. However, this concept could not be tested against the structural results of Laing, *et al.*[2] since the quality of their data did not permit an accurate location of the amine hydrogens. Thus, we decided to redetermine the structure at room temperature and at 200 K in order to locate those atoms more precisely.

Finally, the preparation of the [*mer*-$Co(dpt)(NO_2)_3$] (**II**) was carried out for the purpose of testing this idea further. In (**II**), the six-membered rings of the aminopropylamine are likely to have a chair, a twist or a boat conformation but, like the NH_3 ligands of (**I**), the concept of ligand chirality is non-existent since there are no asymmetric centers in dpt. Thus, the only source of chirality would be conformational dissymmetry of one or more of its fragments, as in the case of (**I**). The results of our studies are detailed below.

EXPERIMENTAL

Syntheses

(**I**) was prepared according to the literature method.[3]

(**II**) was prepared by chance during an attempt to synthesize [$Co(trpn)(NO_2)_2]NO_3$(**III**) from its carbonato complex, [$Co(trpn)(CO_3)]ClO_4 \cdot H_2O_4$ (**IV**) as follows: 1 mmol of (**IV**) was dissolved in *ca.* 10 mL of water and treated with a few drops of conc. HNO_3 (*ca.* 0.5 mL). The resulting solution was then heated to 60°C for 3 min., followed by addition of two equimolar amounts of $NaNO_2$ and heating was continued for 15 min. at 60°C. The resulting solution was allowed to crystallize at room temperature (20°C). After three weeks, orange crystals separated and were collected by filtration, washed with ethanol and ether and air dried. Our preparation is reproducible and the compound is known.[5-6] Moreover, our accidental preparation of (**II**) is consistent with a previous observation of Massoud and Milbourn, who reported that the attempted preparation of [$Co(trpn)Cl_2]Cl$ by aerial oxidation of an aqueous solution of $CoCl_2$ + trpn + HCl was unsuccessful. Also, attempts to synthesize the dinitro complex of cobalt(III)-trpn, as described for the preparation of [$Co(tren)(NO_2)_2]Cl$ by Collman *et al.*,[8] and then converting it into the dichloro complex by treatment with conc HCl on evaporation, did not lead to the desired product; instead, the yellow crystalline complex Co(dpt)$(NO_2)_3$ was isolated, which had been previously prepared and characterized.

Elemental Analysis

(I) is a known compound whose composition was established by the authors of the original synthetic procedure.[3] Since we expected to have synthesized compound (**III**), compound (**II**) was analyzed by Galbraith.[9] Theory: C = 21.96%, H = 5.22%, N = 25.61%; observed C = 21.88%, H = 5.31%, N = 25.34%; thus, its elemental analysis is in accord with the results obtained by X-ray diffraction (below).

X-Ray Studies

Data were collected at room temperature on (**Ia**) and (**II**) with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[10] of the SDP-Plus software package.[11] The procedure used for crystal alignment, cell constant determination, space group determination, and data collection were uniform for all three determinations. Crystals centered with data in the $20° \leq 2\Theta \leq 35°$ range and examination of the cell constants, absences, and Niggli matrix[12] clearly showed both to crystallize in a primitive, orthorbombic lattice whose systematic absences define the space groups to be $P2_12_12_1$. A low temperature (200 K) data set was collected for compound (**I**) at Brookhaven using an Enraf-Nonius diffractometer and using the same crystal as was used with the room temperature study. This data set is labeled (**Ib**). The details of data collection are summarized in Tables 1, 2 and 3, respectively, for compounds (**Ia**), (**Ib**) and (**II**).

Table 1 Summary of data collection and processing parameters for room temperature study of *mer*-$[Co(NH_3)_3(NO_3)_3]$

Space Group	$P2_12_12_1$
Cell Constants	$a = 6.826\ (2)$ Å
	$b = 10.188\ (1)$
	$c = 11.736\ (1)$
Cell Volume	$V = 816.09$ Å^3
Molecular Formula	$CoO_6N_6H_9$
Molecular Weight	248.04 gm-mole^{-1}
Density (calc; $z = 4$ mol/cell)	2.019 gm-cm^{-3}
Radiation Employed	MoK_α ($\lambda = 0.71073$Å)
Relative Transmission Coefficients	0.7136 to 0.9988
Data Collection Range	$4° \leq 2\Theta \leq 70°$
Scan Width	$\Delta\Theta = 1.0 + 0.35\tan\Theta$
Total Data Collected	2068
Data Used in Refinement*	1497
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.0339
$Rw = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma \lvert F_o \rvert^2]^{1/2}$	0.0377
Weights Used	$w = [\sigma(F_o)]^{-2}$

*The difference between this number and the total is due to subtraction of standards, reflections which are systematically absent, symmetry equivalent collected for absorption correction data, or had $I \geq 3\sigma(I)$.

Table 2 Summary of data collection and processing parameters for (−100°C) study of *mer*-[$Co((NH_3)_3(NO_3)_3]$

Space Group	$P2_12_12_1$
Cell Constants	a = 6.830 (2) Å
	b = 10.070 (2)
	c = 11.680 (2)
Cell Volume	V = 803.4 Å^3
Molecular Formula	$CoO_6N_6H_9$
Molecular Weight	248.04 gm-mole^{-1}
Density (calc; z = 4 mol/cell)	2.051 gm-cm^{-3}
Radiation Employed	MoK_α (λ = 0.71073Å)
Relative Transmission Coefficients	0.7136 to 0.9988
Data Collection Range	$4° \leq 2\Theta \leq 110°$
Scan Width	$\Delta\Theta = 1.0 + 0.14\tan\Theta$
Total Data Collected	12102
Data Used In Refinement*	4925
$R = \Sigma \| \|F_o\| - \|F_c\| \| / \Sigma \|F_o\|$	0.046
$Rw = [\Sigma w(\|F_o\| - \|F_c\|)^2 / \Sigma \|F_o\|^2]^{1/2}$	0.055
Weights Used	$w = [\sigma(F_o)]^{-2}$

*The difference between this number and the total is due to subtraction of standards, reflections which are systematically absent, symmetry equivalent (two equivalent data sets were collected) collected for absorption correction data, or had $I \leq 3\sigma(I)$.

The intensity data sets were corrected for absorption using empirical curves derived from Psi scans[10,11] of suitable reflections. The scattering curves were taken from Cromer and Waber's compilation.[13] The data for **(II)** was processed with the NRCVAX package.[14]

After refinement of the scale factor and the positional parameters of the Co, a difference Fourier map produced the remaining non-hydrogen atoms. Heavy atoms were refined isotropically until convergence, at which point all the amine hydrogen atoms of **(Ia)** were found at sensible positions and were added to the refinement at

Table 3 Summary of data collection and processing parameters for *mer*-[Co(dpt)$(NO_2)_3$]

Space Group	$P2_12_12_1$
Cell Constants	a = 7.211 (3)Å
	b = 9.429(4)
	c = 19.021(10)
Cell Volume	V = 1293.22 Å^3
Molecular Formula	$CoO_6N_6C_6H_{17}$
Molecular Weight	328.17 gm-mole^{-1}
Density (calc; z = 4 mol/cell)	1.685 gm-cm^{-3}
Radiation Employed	MoK_α (λ = 0.71073Å)
Relative Transmission Coefficients	0.8565 to 0.9997
Data Collection Range	$4° \leq 2\Theta \leq 52°$
Scan Width	$\Delta\Theta = 0.95 + 0.35\tan\Theta$
Total Data Collected	2409
Data Used In Refinement*	1815
$R = \Sigma \| \|F_o\| - \|F_c\| \| / \Sigma \|F_o\|$	0.0342
$Rw = [\Sigma w(\|F_o\| - \|F_c\|)^2 / \Sigma \|F_o\|^2]^{1/2}$	0.0471
Weights Used	$w = [\sigma(F_o)]^{-2}$

*The difference between this number and the total is due to substraction of data which were standards, reflections which are systematically absent, symmetry equivalent reflections collected to locate absorption correction data, or had $I \leq 3\sigma(I)$.

those positions (fixed) and with fixed thermal parameters. Those in **(Ib)** were likewise found. Positions for the amine hydrogens of **(II)** were calculated and added to the refinement at their idealized positions with fixed thermal parameters. In all cases, heavy atoms were refined anisotropically while the hydrogens were assigned fixed (4.0 Å^2) isotropic thermal parameters and fixed at the positions found (in the case of **I**) or calculated **(II)**. The absolute configuration of the cations in **(Ia,b)** and **(II)** were determined prior to the last cycles of refinement. For set **(Ia)**, the correct enantiomer was determined from the room temperature data set by refinement of the two configurations and the residuals were [(+ + +): $R(F) = 0.0339$, $Rw(F) = 0.0377$; (− − −): $R(F) = 0.0415$, $Rw(F) = 0.0449$]. Thus the former is correct for that crystal. Data set **(Ib)** confirmed these results. The structure and absolute configuration of **(II)** were determined with the Rogers test which gave a refined value of $\varepsilon = +0.95$; therefore, its absolute configuration is also the original one. The final $R(F)$ and $R_w(F)$ factors are listed in Tables 1, 2 and 3 which summarize other details of data collection and processing. Positional and thermal parameters obtained with the three data sets are listed in Tables 4, 5 and 6. The tables in this paper list the stereochemical parameters obtained with data sets **(Ia)** and **(II)**. Those obtained with the data set for **(Ib)** are filed as Supplementary Material since there is no significant difference between sets **(Ia)** and **(Ib)**.

Figures 1 and 2 give labeled views of molecules (I) and (II). Figures 3 and 4 depict the packing of ions in unit cells of (I) and (II).

Table 4 Positional parameters and their estimated standard deviations for compound (I).

Atom	*x*	*y*	*z*	*B*(Å^2)
Co	0.76034(6)	0.81730(4)	0.75712(3)	1.255(6)
O1	0.4205(5)	0.8546(4)	0.6326(3)	3.68(7)
O2	0.5698(5)	0.6754(3)	0.5905(2)	2.81(6)
O3	0.8887(5)	1.0015(3)	0.6003(3)	3.64(7)
O4	0.7184(5)	1.0868(3)	0.7303(3)	2.82(6)
O5	0.9520(5)	0.8202(4)	0.9655(2)	3.41(7)
O6	1.1084(4)	0.9267(4)	0.8383(3)	3.44(7)
N1	0.9538(5)	0.7440(4)	0.6527(3)	2.13(6)
N2	0.7264(5)	0.6432(3)	0.8270(3)	1.93(6)
N3	0.5676(5)	0.8879(3)	0.8639(3)	1.90(6)
N4	0.5572(5)	0.7777(4)	0.6469(3)	1.99(6)
N5	0.7909(5)	0.9882(3)	0.6871(3)	1.68(6)
N6	0.9657(5)	0.8599(3)	0.8661(3)	1.83(6)
H1	0.9746	0.7949	0.5898	4.0
H4	0.7363	0.5859	0.7871	4.0
H7	0.4445	0.8483	0.8457	4.0
H2	0.9099	0.6601	0.6293	4.0
H3	1.0743	0.7354	0.6929	4.0
H5	0.6002	0.6400	0.8603	4.0
H6	0.8233	0.6338	0.8847	4.0
H8	0.5597	0.9805	0.8552	4.0
H9	0.6048	0.8671	0.9394	4.0

Hydrogen atoms were not refined. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab (cos γ) *B (1,2) + ac (cos β)*B(1,3) + bc(cos α)*B(2,3)]

Table 5 Atomic Parameteers x,y,z and Biso. For Compound (II) E.S.Ds. refer to the last digit printed.

	x	*y*	*z*	Biso
Co	0.12292(18)	0.07292(13)	0.12932(6)	2.01(5)
N1	0.1325(13)	0.0940(9)	0.0259(3)	3.5(4)
N2	0.3849(12)	-0.0024(8)	0.1315(4)	3.0(3)
N3	0.0874(11)	0.0694(9)	0.2320(4)	2.7(3)
N4	0.0159(12)	-0.1153(9)	0.1217(5)	3.4(4)
N5	-0.1284(12)	0.1514(8)	0.1243(5)	3.0(3)
N6	0.222(11)	0.2670(8)	0.1387(4)	2.8(4)
O1	-0.0946(12)	-0.1408(9)	0.0752(5)	6.0(5)
O2	0.0591(15)	-0.2084(9)	0.1635(5)	6.3(5)
O3	-0.2303(12)	0.1524(12)	0.1747(5)	6.4(5)
O4	-0.1888(14)	0.1990(14)	0.0711(5)	9.2(7)
O5	0.1663(12)	0.3473(8)	0.1840(4)	5.0(4)
O6	0.3430(12)	0.3094(8)	0.0981(4)	5.0(4)
C1	0.2227(22)	-0.0118(16)	-0.0209(6)	5.6(7)
C2	0.4203(19)	-0.0365(14)	0.0005(6)	5.1(6)
C3	0.4389(16)	-0.1034(13)	0.0721(7)	4.6(6)
C4	0.4507(16)	-0.0628(14)	0.2008(7)	4.7(6)
C5	0.4169(17)	0.0349(16)	0.2617(6)	5.1(7)
C6	0.2224(22)	0.0319(16)	0.2853(6)	5.9(7)
H1	0.192	0.182	0.017	4.3
H2	0.007	0.099	0.011	4.3
H3	-0.013	0.006	0.239	3.6
H4	0.049	0.163	0.244	3.6
H5	0.157	-0.098	-0.019	6.3
H6	0.222	0.024	-0.068	6.3
H7	0.475	-0.099	-0.033	5.8
H8	0.484	0.051	0.001	5.8
H9	0.361	-0.184	0.075	5.3
H10	0.564	-0.131	0.079	5.3
H11	0.580	-0.081	0.197	5.6
H12	0.386	-0.149	0.209	5.6
H13	0.448	0.129	0.248	5.7
H14	0.493	0.006	0.300	5.7
H15	0.210	0.097	0.323	6.5
H16	0.195	-0.061	0.301	6.5
H17	0.456	0.081	0.124	3.9

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

RESULTS AND DISCUSSION

Figure 1 shows the molecule described by the coordinates (**Ia**). Note that despite the fact that the Co-N bond is expected to be a single bond, and thus allow free rotation of the H_3N- fragment about the Co-N bond, all H-N-H angles are very close to the ideal tetrahedral value (see Table 7). Therefore, we must conclude that the hydrogen-bonding scheme described in Table 7 represents a sufficiently sturdy set of intra- and intermolecular hydrogen bonds to restrain the amine ligands from rotation or having high amplitude librational motions. There are three relatively strong intramolecular hydrogen bonds to hydrogens 1, 6 and 8, which means all three amino ligands are restrained by those bonds into a more rigid conformation. Also, there are five intermolecular hydrogen bonds binding the oxygens of each of

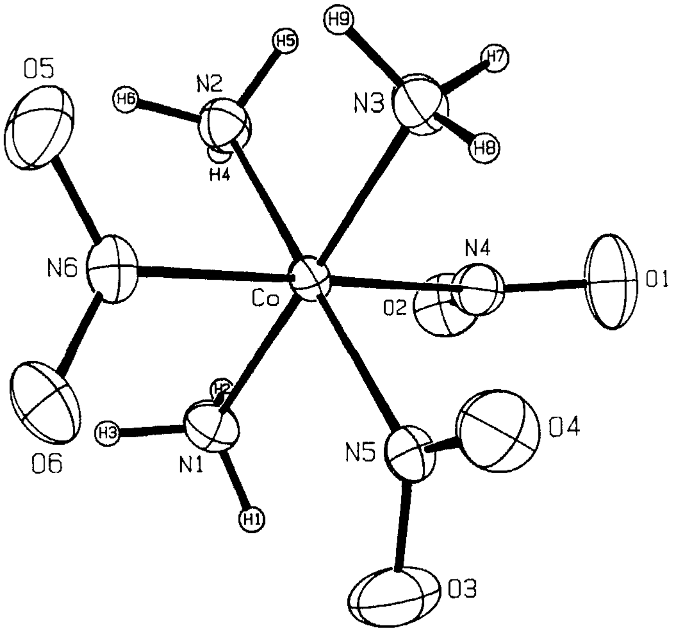

Figure 1

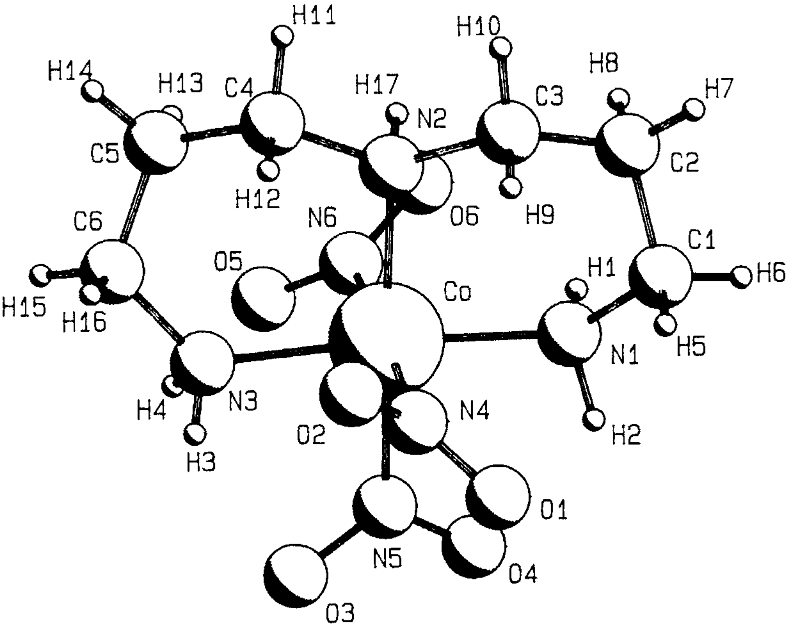

Figure 2

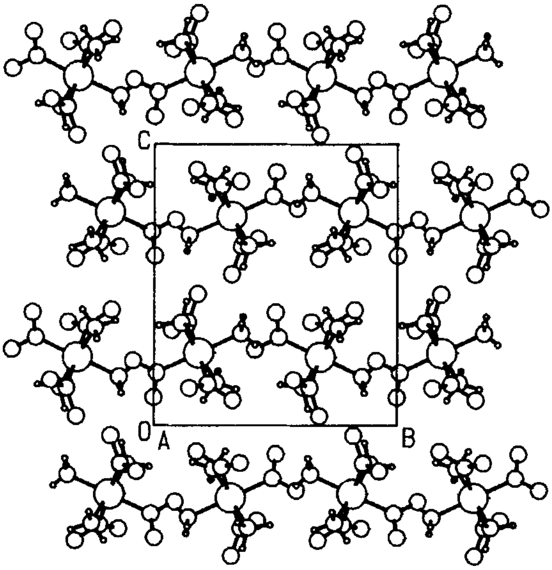

Figure 3

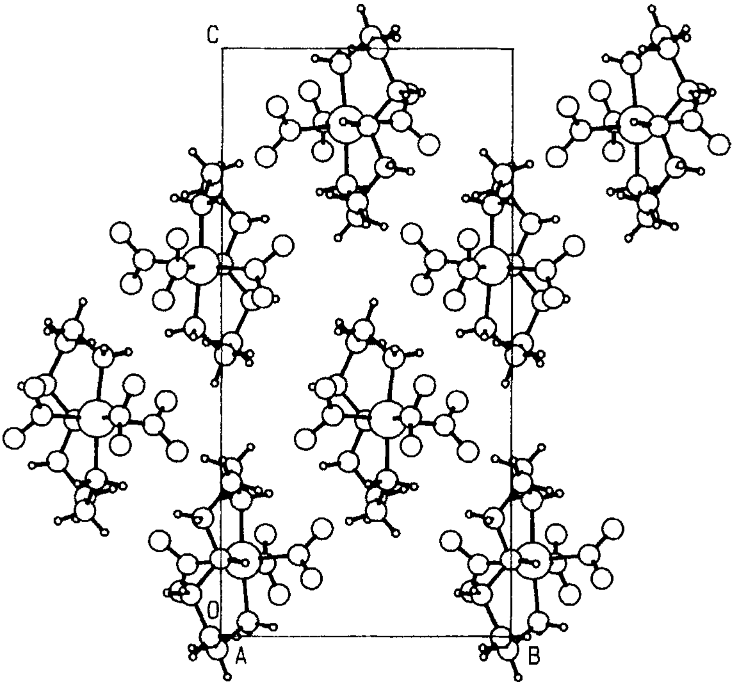

Figure 4

Table 6

a) Bond distances in angstroms for (I)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co	N1	1.950(2)	Co	N2	1.968(2)
Co	N3	1.954(2)	Co	N4	1.939(2)
Co	N5	1.937(2)	Co	N6	1.947(2)
O1	N4	1.229(3)	O2	N4	1.237(3)
O2	N4	1.237(3)	O3	N5	1.226(2)
O4	N5	1.229(2)	O5	N6	1.238(3)
O6	N6	1.232(3)	N1	H1	0.913(2)
N1	H2	0.946(2)	N1	H3	0.953(2)
N2	H4	0.750(2)	N2	H5	0.947(2)
N2	H6	0.953(2)	N3	H7	0.956(2)
N3	H8	0.951(2)	N3	H9	0.946(2)

b) Bond angles in degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N1	Co	N2	89.78(9)	N1	Co	N3	178.84(9)
N1	Co	N4	89.18(8)	N1	Co	N5	90.27(9)
N1	Co	N6	90.60(9)	N2	Co	N3	89.17(9)
N2	Co	N4	90.36(9)	N2	Co	N5	179.26(8)
N2	Co	N6	90.69(9)	N3	Co	N4	91.31(9)
N3	Co	N5	90.79(8)	N3	Co	N6	88.92(8)
N4	Co	N5	88.90(9)	N4	Co	N6	178.93(9)
N5	Co	N6	90.05(9)	Co	N4	O1	120.1(2)
Co	N4	O2	118.8(2)	Co	N5	O3	120.7(2)
Co	N5	O4	121.1(1)	Co	N6	O5	119.4(2)
Co	N6	O6	121.2(2)	O1	N4	O2	121.1(2)
O3	N5	O4	118.2(2)	O5	N6	O6	119.4(2)
Co	N1	H1	113.3(2)	Co	N1	H2	108.3(2)
Co	N1	H3	108.0(2)	H1	N1	H2	109.1(2)
H1	N1	H3	108.6(2)	H2	N1	H3	109.6(2)
Co	N2	H4	115.5(2)	Co	N2	H5	108.0(1)
Co	N2	H6	107.7(2)	H4	N2	H5	108.3(2)
H4	N2	H6	107.7(2)	H5	N2	H6	109.5(2)
Co	N3	H7	107.1(2)	Co	N3	H8	109.6(2)
Co	N3	H9	109.7(2)	H7	N3	H8	110.2(2)
H7	N3	H9	110.5(2)	H8	N3	H9	109.7(2)

c) Selected torsional angles in degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle
N1	Co	N4	O1	-141.7
N1	Co	N4	O2	37.1
N1	Co	N5	O3	8.0
N1	Co	N5	O4	-169.6
N1	Co	N6	O5	-126.1
N1	Co	N6	O6	54.6
N2	Co	N4	O1	128.5
N2	Co	N4	O2	-52.7
N2	Co	N5	O3	-86.1
N2	Co	N5	O4	96.2
N2	Co	N6	O5	-36.3
N2	Co	N6	O6	144.4
N3	Co	N4	O1	39.3

Table 6 — (*Continued*)

Atom 1	Atom 2	Atom 3	Atom 4	Angle
N3	Co	N4	O2	-141.8
N3	Co	N5	O3	-172.4
N3	Co	N5	O4	9.9
N3	Co	N6	O5	52.9
N3	Co	N6	06	-126.5
N4	Co	N5	O3	-81.1
N4	Co	N5	O4	101.2
N4	Co	N6	O5	155.6
N4	Co	N6	O6	-23.7
N5	Co	N4	O1	-51.4
N5	Co	N4	O2	127.4
N5	Co	N6	O5	143.6
N5	Co	N6	O6	-35.7
N6	Co	N4	O1	-63.4
N6	Co	N4	O2	115.5
N6	Co	N5	O3	98.6
N6	Co	N5	O4	-79.0

d) Hydrogen bonds (distances in Å, angles in °)

O3-H1	2.188	N1-H1...O3	117.4	
O4-H8	2.120	N3-H8...O4	123.5	
O5-H6	2.296	N2-H6...O5	118.5	
O2-H1	2.235	N1-H1...O2	152.6	O2 at 1/2 + x, 3/2 - y, 1 - z
O2-H8	2.265	N3-H8...O2	149.6	O2 at 1 - x, 1/2 + y, 3/2 - z
O3-H9	2.314	N3-H9...O3	129.8	O3 at 3/2 - x, 2 - y, 1/2 + z
O4-H3	2.260	N1-H3...O4	143.1	O4 at 2 - x, -1/2 + y, 3/2 - z
O5-H5	2.316	N2-H5...O5	139.2	O5 at -1/2 + x, 3/2 - y, 2 - z

Numbers in parentheses are estimated standard deviations in the least significant digits.

the three -NO_2 ligands to adjacent molecules. Thus the entire ensemble of hydrogen bonds fixes the molecule into a rigid and distinctly asymmetric entity.

The packing diagram of the molecules in (**I**) is shown in Figure 3, which is an *a*-axis projection. Note that there are infinite hydrogen-bonded strings of molecules running along the *b*-direction. The hydrogen-bonding scheme linking the elements of the four strings in Figure 3 are rather obvious; their nature is quantified by the data in Table 7. Careful examination of those strings shows that they describe helical arrays of molecules in which the positions of the -NH_3 ligands spiral as one moves along the length of the strings. Note also that a hydrogen of one of the -NH_3 groups bonds to the oxygen of an -NO_2 on an adjacent string, as is obvious by looking at the leftmost pair of molecules of the two lowest strings. This, then, is a case of supramolecular assembly in which a chiral object, far more complex than its component elements, is created by hydrogen-bonded interactions. It is of exactly the same type we have observed in a wide variety of other systems crystallizing as conglomerates and containing amines and nitro groups.[15]

Figure 2 shows molecule (**II**) in its correct absolute configuration. The -NO_2 oxygens are engaged in a variety of intramolecular hydrogen bonds whose lengths are listed in Table 8, the principal ones being O3...H3, O3...H4, O4...H2, O5...H4, O6...H1 and O6...H17. As in the case of (**I**), these hydrogen bonds determine the orientation of the O-N-O planes and, in the solid state, lower the point group of the

Table 7 Bond distances (Å) and angles (°) for compound (II)

a) Bond distances

Co-N1	1.979(7)	N4-O1	1.214(14)
Co-N2	2.018(8)	N4-O2	1.225(14)
Co-N3	1.970(7)	N5-O3	1.208(12)
Co-N4	1.941(8)	N5-O4	1.190(12)
Co-N5	1.960(9)	N6-O5	1.216(12)
Co-N6	1.973(8)	N6-O6	1.231(11)
N1-C1	1.486(16)	C1-C2	1.500(22)
N2-C3	1.528(14)	C2-C3	1.505(19)
N2-C4	1.513(14)	C4-C5	1.501(19)
N3-C6	1.450(16)	C5-C6	1.473(21)

b) Angles

N1-Co-N2	91.3(4)	C3-N2-C4	109.2(9)
N1-Co-N3	172.7(4)	Co-N3-C6	127.6(8)
N1-Co-N4	91.8(4)	Co-N4-O1	119.7(8)
N1-Co-N5	86.9(4)	Co-N4-O2	120.4(8)
N1-Co-N6	89.1(4)	O1-N4-O2	119.8(9)
N2-Co-N3	95.5(3)	Co-N5-O3	121.8(7)
N2-Co-N4	93.0(3)	Co-N5-O4	121.5(8)
N2-Co-N5	177.7(3)	O3-N5-O4	116.8(9)
N2-Co-N6	89.1(3)	Co-N6-O5	121.4(7)
N3-Co-N4	90.4(4)	Co-N6-O6	120.1(7)
N3-Co-N5	86.2(4)	O5-N6-O6	118.5(8)
N3-Co-N6	88.5(4)	N1-C1-C2	110.9(10)
N4-Co-N5	88.5(4)	C1-C2-C3	113.3(10)
N4-Co-N6	177.7(4)	N2-C3-C2	112.6(10)
N5-Co-N6	89.4(3)	N2-C4-C5	113.0(9)
Co-N1-C1	122.9(8)	C4-C5-C6	112.2(11)
Co-N2-C3	116.3(7)	N3-C6-C5	114.9(10)
Co-N2-C4	116.3(6)		

c) Selected hydrogen bonds

O2 - H3	2.56	N3-H3...O2	105.6	
O2 - H4	2.26	N3-H4...O2	140.5	N3 at -x, y-1/2, 1/2-z
O3 - H3	2.45	N3-H3...O3	92.6	
O3 - H4	2.42	N3-H4...O3	94.8	
O3 - H17	2.53	N2-H17...O3	129.4	N2 at 1-x, y, z
O4 - H1	2.19	N1-H1...O4	139.7	N1 at x-1/2, 1/2-y, -z
O4 - H2	2.07	N1-H2...O4	119.7	
O5 - H3	2.34	N3-H3...O5	148.7	N3 at -x,y+1/2,1/2-z
O5 - H4	2.25	N3-H4...O5	119.3	
O6 - H1	2.26	N1-H1...O6	124.5	
O6 - H2	2.53	N1-H2...O6	134.8	N1 at x+1/2, 1/2-y, -z
O6 - H17	2.35	N2-H17...O6	126.7	

d) Torsion angles

N2	Co	N1	C1	39.7(6)	N3	Co	N1	C1	-160.8(8)
N4	Co	N1	C1	-53.3(7)	N5	Co	N1	C1	-141.7(8)
N6	Co	N1	C1	128.8(8)	N1	Co	N2	C3	-39.5(6)
N1	Co	N2	C4	-170.4(8)	N3	Co	N2	C3	143.0(7)
N3	Co	N2	C4	12.1(5)	N4	Co	N2	C3	52.4(6)
N4	Co	N2	C4	-78.5(6)	N5	Co	N2	C3	-77.6(6)
N5	Co	N2	C4	151.5(7)	N6	Co	N2	C3	-128.6(7)

Table 7 — (*Continued*)

N6	Co	N2	C4	100.5(7)	N1	Co	N3	C6	-155.7(8)
N2	Co	N3	C6	3.7(6)	N4	Co	N3	C6	96.7(8)
N5	Co	N3	C6	-174.8(8)	N6	Co	N3	C6	-85.3(7)
N1	Co	N4	O1	-36.5(6)	N1	Co	N4	O2	143.4(8)
N2	Co	N4	O1	-127.9(8)	N2	Co	N4	O2	52.0(6)
N3	Co	N4	O1	136.5(8)	N3	Co	N4	O2	-43.5(6)
N5	Co	N4	O1	50.3(6)	N5	Co	N4	O2	-129.7(8)
N6	Co	N4	O1	76.3(7)	N6	Co	N4	O2	-103.7(7)
N1	Co	N5	O3	170.9(8)	N1	Co	N5	O4	-8.2(6)
N2	Co	N5	O3	-151.0(8)	N2	Co	N5	O4	29.9(6)
N3	Co	N5	O3	-11.4(5)	N3	Co	N5	O4	169.4(9)
N4	Co	N5	O3	79.0(7)	N4	Co	N5	O4	-100.2(8)
N6	Co	N5	O3	-99.9(7)	N6	Co	N5	O4	80.9(7)
N1	Co	N6	O5	140.9(7)	N1	Co	N6	O6	-38.9(5)
N2	Co	N6	O5	-127.8(7)	N2	Co	N6	O6	52.4(5)
N3	Co	N6	O5	-32.3(5)	N3	Co	N6	O6	147.9(7)
N4	Co	N6	O5	28.0(5)	N4	Co	N6	O6	-151.8(8)
N5	Co	N6	O5	54.0(6)	N5	Co	N6	O6	-125.8(7)
Co	N1	C1	C2	-55.3(7)	Co	N2	C3	C2	59.6(7)
C4	N2	C3	C2	-166.3(13)	Co	N2	C4	C5	-50.4(7)
C3	N2	C4	C5	175.5(13)	Co	N3	C6	C5	17.8(6)
N1	C1	C2	C3	65.0(10)	C1	C2	C3	N2	-70.0(10)
N2	C4	C5	C6	78.3(11)	C4	C5	C6	N3	-58.3(9)

two molecules to C_1. There are also intermolecular hydrogen bonds which link the molecules together in the fashion displayed in Fig. 4. The shortest of those bonds are O2...H4, O4...H1 and O5...H3. Two longer intermolecular hydrogen bonds, also linking the molecules in spiraling strings can be observed in Fig. 4 where the leftmost molecule is obviously hydrogen bonded to the one near the origin which, in turn, is bonded to the one near (0, 1/2, 1/3), etc... Thus, a string runs at nearly 45° to the *b*-direction. A similar string is above the one just described. Adjacent strings are also linked to one another by hydrogen bonds, as is obvious by looking at the orientation of the -NO_2 and -NH_2 fragments on the two long strings displayed in Figure 4.

Interestingly neither (**I**) nor (**II**) contain any chiral centers and, in the solid state, both are conformationally chiral due to the orientation of its component groups which lower their symmetry to C_1. This observation is interesting but far from new, with similar examples in the case of K[*trans*-Co$(NH_3)_2(NO_2)_4$] whose structure was determined both by X-ray and neutron diffraction.[15(a), 15(c)] The anion of this compound is an example of helical chirality trapped rigidly in the solid state.

In conclusion, we point out that the ability to form supramolecular, helical assemblies of chiral or non-chiral molecules seems to be a required condition for compounds to crystallize as conglomerates. We have pointed this out before[15] and our current results agree nicely with that suggestion.

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SUPPLEMENTARY MATERIAL

Table of anisotropic thermal parameters for (I) and (II). Structure factor tables and a complete data set for **(Ib)** and for **(II)** are available from Ivan Bernal.

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