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The Phenomenon of Conglomerate Crystallization. XII. Spontaneous Resolution in Coordination Compounds. X. The Structure and Absolute Configuration of $\Delta(\lambda\delta\lambda)(+)_{589}$-[*cis*-$\alpha$-Co(trien)$(NO_2)_2$]$Cl\cdot H_2O$ and of $\Lambda(\delta\lambda\delta)(-)_{589}$-[*cis*-$\alpha$-Co(trien)$(NO_2)_2$]$I\cdot H_2O$

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Abstract

Compounds [*cis*-α-Co(trien)$(NO_2)_2$]$X\cdot H_2O$ (with X = I and Cl) are obtained as conglomerates when aqueous solutions of these species are crystallized either by evaporation at room temperature or cooled in a refrigerator at *ca.* 2 °C. Both crystallize in the orthorhombic system, space group $P2_12_12_1$. The chloride crystal examined is the enantiomer of that previously reported and this study merely verifies that the crystalline material obtained consists of a conglomerate; thus, little additional discussion is necessary for this compound.

The cell constants of the iodide are: $a = 8.041(3)$, $b = 13.013(3)$ and $c = 14.169(2)$ Å; $V = 1482.64$ Å^3 and D(calc; $z = 4$) = 1.980 g cm^{-3}. The structure of the iodide was refined with 1536 independent data to final discrepancy indices of $R = 0.027$ and $R_w = 0.026$. The chloride and iodide are isomorphous and nearly isostructural – the halide anions are not placed at the exact same fractional coordinates and this results in a small, but meaningful, difference in the hydrogen bonding between halide and the secondary amino hydrogens with which they interact in the lattice.

The fact that the halides interact in the solid with the secondary nitrogen protons is significant for the mechanism of conglomerate crystallization since in the nitrates, which crystallize as racemates, the NO_3^- anions form strong hydrogen bonds to the terminal-(primary) $-NH_2$ hydrogens. It has been postulated in the past that intramolecular hydrogen bonds between the *cis*-(NO_2) oxygens and the primary $-NH_2$ hydrogens is responsible for the conglomerate crystallization of these compounds.

Finally, solution ^1H NMR studies by Yoneda and associates revealed that the halides of related bis-ethylenediamine species seemed to be associated with the basal plane amino hydrogens *trans* to the *cis*-X_2 moiety. We observe, in the solid state, the same type of preferential interaction between halide and amino hydrogens *trans* to the $-NO_2$ ligands. Thus, the ion pair observed in our solid state studies seems to persist in solution sufficiently to be detectable by NMR measurements – a behaviour never documented previously.

Introduction

In previous communications [1, 2], the spontaneous conglomerate crystallization [3] of [*cis*-α-Co(trien)$(NO_2)_2$]$Cl\cdot H_2O$ (I), [*cis*-Co(en)$_2(NO_2)_2$]Cl (II), K[*trans*-Co$(NH_3)_2(NO_2)_4$] (III) and [*cis*-Co(en)$_2(NO_2)_2$][*trans*-Co$(NH_3)_2(NO_2)_4$] (IV) were reported together with a description of the structures and the absolute configurations of the ions present in crystals of I–IV.

A curious feature revealed at the time [1, 2] was that, whereas the cation of II spontaneously resolves into a crystalline conglomerate as the chloride, the nitrate was reported to crystallize as the racemate [4]. In a series of subsequent papers [5–10], we have suggested reasons for this behavioural difference, which can be summarized as follows. If chemical fragments whose conformation can be the source of molecular dissymmetry can be anchored, by intramolecular interactions into such conformations, the species in question display an enhanced propensity for conglomerate crystallization [5–10]. If this species is charged, the counterion will play a role in the crystallization process [11, 12] such that a given ion, which conglomerates with one or more counterions, may not do so with another counterion that effectively competes with the intramolecular process mentioned [5–12]. In some cases [11, 12], however, ions which do not undergo spontaneous resolution and are difficult to separate by the use of external resolving agents, can sometimes be induced to conglomerate by an appropriate choice of achiral

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counterions which stabilize it in a dissymmetric conformation. Such is the case with the series $[M(en)_3]^{2+}$ with $M = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) whose cations had not been obtained in optically active form till we [11, 12] observed their conglomerate crystallization behaviour as nitrates.

Recently, we became aware of the ^1H NMR study carried out by Yoneda and co-workers [13] on DMSO solutions of compounds [*cis*-$Co(en)_2X_2$]-(halide ($X = CN^-$, NO_2^-, Cl^-, NCS^-, N_3^-). These workers asserted [3] that the halides in those solutions are found closely associated with the basal plane amino protons located *trans* to the X ligands. Note that such molecules contain primary $-NH_2$ only.

As a result of the above observations, we decided to investigate the possibility that the conclusions of Yoneda *et al.* [13] apply to the solid state and to explore the extent to which our conclusions [1, 2, 5–12] are general. In this report, we briefly discuss the structure and absolute configuration of the enantiomer of **I** (hereafter **V**) as well as the structure and absolute configuration of its iodide derivative, [*cis*-α-Co(trien)$(NO_2)_2$]$I\cdot H_2O$ (**VI**), prepared in order to (a) determine the location of the two anions with respect to the common cation and (b) test the effect of changing the halide anion upon the occurrence of conglomerate crystallization. This is not an idle change of anions since it is known from solubility studies [14] that for [Co(en)$_2$(oxalate)]X (X = Cl, Br, I) the former two undergo conglomerate crystallization, whereas, under the same conditions, the latter one crystallizes as a racemate. Clearly, the question is a fundamental one if one addresses the issue of the role played by the counterion in the process of conglomerate crystallization.

Experimental

Syntheses and Conglomerate Crystallization

[*cis*-α-Co(trien)$(NO_2)_2$]$Cl\cdot H_2O$ was prepared by the method of Sargeson and Searle [15]. An equimolar amount of freshly recrystallized NaI was added to a solution of the chloride and placed in a refrigerator at 2 °C, whereupon crystals of the more insoluble iodide precipitated as the monohydrate [*cis*-α-Co(trien)$(NO_2)_2$]$I\cdot H_2O$.

Conglomerate crystallization of [*cis*-α-Co(trien)-$(NO_2)_2$]$Cl\cdot H_2O$ was observed either upon evaporation of a solution at *ca.* 22 °C [1] or by cooling to 2 °C a room temperature-saturated solution, as currently carried out. The same hydration polymorph is obtained at either of these temperatures. At 2 °C and in the presence of large excess of nitrate anions (as added HNO_3), conglomerate crystallization of [*cis*-α-Co(trien)$(NO_2)_2$]$Cl\cdot H_2O$ was also observed. This is in contrast with the *cis*-β derivative [7] for which the nitrate which was obtained from a chloride solution by the addition of excess HNO_3.

X-ray Crystallographic Measurements

Both data sets were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification [16]* of the SDP-Plus software package [17]. The chloride crystal used was a prolate spheroid ground from a large, broken fragment while the iodide crystal was a tiny parallelpiped cut from a longer piece. Both crystals were centered using data in the $20° \leqslant 2\theta \leqslant 30°$ range and examination of the cell constants and Niggli matrix [18] clearly showed them to crystallize in primitive, orthorhombic lattices. Systematic absences showed them to be isomorphous and crystallizing in the space group $P2_12_12_1$. Both intensity data sets were corrected for absorption using empirical curves derived from Psi scans [16, 17] of six reflections. The scattering curves were taken from Cromer and Waber's compilation [19]**. Details of data collection and processing are summarized in Tables I and II.

The structures were solved from Patterson maps; the chloride using the Co as the heavy atom and the iodine with the other. The heavy atoms were refined isotropically till convergence, at which point the hydrogen atoms of the cation were added at idealized

TABLE I. Summary of Data Collection and Processing Parameters for $\Delta(\lambda\delta\lambda)(+)_{589}$-[*cis*-α-Co(trien)$(NO_2)_2$]$Cl\cdot H_2O$

Space group	$P2_12_12_1$
Cell constants	$a = 8.022(4)$ Å $b = 12.435(5)$ Å $c = 13.720(5)$ Å
Cell volume	$V = 1368.49$ Å^3
Molecular formula	$C_6H_{20}N_6O_5CoCl$
Molecular weight	350.65 g mol^{-1}
Density(calc.)	1.702 g cm^{-3}
Z	4 mol/cell
Radiation employed	Mo Kα (λ = 0.71073 Å)
Absorption coefficient	$\mu = 14.73$ cm^{-1}
Transmission coefficients	1.00 to 0.7887
Data collection range	$4° \leqslant 2\theta \leqslant 64°$
Scan width	$\theta = 1.20 + 0.35 \tan\theta$
Total data collected	2706
Data used in refinement[a]	1531
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.035
$R_w = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.046
Weights used	$w = [\sigma(F_o)]^{-2}$

[a] The difference between this number and the total is due to subtraction of 1175 data which either were redundant, systematically absent (but collected for verification of space group), standards or did not meet the criterion that $I \geqslant 3\sigma(I)$.

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*For use with their automation of the CAD-4 diffractometer.

**Scattering factor curves, Table 2.2.8; anomalous dispersion values, Table 2.3.1.

TABLE II. Summary of Data Collection and Processing Parameters for $\Lambda(\delta\lambda\delta)(-)_{589}$-[*cis*-α-Co(trien)$(NO_2)_2$]I·$H_2O$

Space group	$P2_12_12_1$
Cell constants	a = 8.041(3) Å
	b = 13.013(3) Å
	c = 14.169(2) Å
Cell volume	V = 1482.64 $Å^3$
Molecular formula	$C_6H_{20}N_6O_5CoI$
Molecular weight	442.10 g mol^{-1}
Density(calc.)	1.980 g cm^{-3}
Z	4 mol/cell
Radiation employed	Mo Kα (λ = 0.71073 Å)
Absorption coefficient	μ = 32.39 cm^{-1}
Transmission coefficients	1.00 to 0.8314
Data collection range	4° ≤ 2θ ≤ 64°
Scan width	θ = 1.20 + 0.35 tan θ
Total data collected	2487
Data used in refinement[a]	1536
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.027
$R_w = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.026
Weights used	$w = [\sigma(F_o)]^{-2}$

[a] The difference between this number and the total is due to subtraction of 951 data which either were redundant, systematically absent (but collected for verification of space group), standards or did not meet the criterion that $I \geq 3\sigma(I)$.

positions (N–H and C–H = 0.95 Å) and positional parameters for all atoms allowed to refine (heavy atoms isotropic, hydrogen thermal parameters fixed at 5.0 $Å^2$). Upon convergence, non-hydrogen atoms were assigned anisotropic motion; hydrogens were refined with fixed thermal parameters fixed at 5.0 $Å^2$. When the least-squares fitting converged, the absolute configuration was determined by refinement of the data in both absolute configurations. The R and R_w factors for both are listed below:

	V	**VI**	
R =	0.041	0.027	(initial coordinates)
R_w =	0.053	0.026	
R =	0.035	0.028	(inverted coordinates)
R_w =	0.046	0.027	

It is clear the configuration of **V** should be inverted while that of **VI** was correct from the beginning. Thus, the enantiomer of the former was inverted and refinement of both completed. New, ideal, positions for the hydrogens were recomputed and the structures refined (heavy atoms anisotropic; hydrogens isotropic and held fixed at 5.0 $Å^2$) till the final convergence. A summary of the crystallographic results for **V** and **VI** are listed in Tables I and II. In the case of **V** three reflections, severely extincted [(0, 2, 0), (0, 0, 2) and (1, 1, 1)] were removed prior to the final four cycle of refinement. We have shown in two previous papers [1, 2] that, for compounds of this class, refinement accurately reflects the correct absolute configuration, as shown by comparison with Bijvoet [20] pair measurements; thus, through refinement, the correct absolute configurations were determined for both. Coordinates for **VI**, bond lengths, angles and torsional angles are listed in Tables III, IV and V.

Because compound **V** is the enantiomer of **I** there is no need for a detailed discussion of its geometrical parameters since the current and previous [1] sets of coordinates are essentially identical, though inverted. See 'Supplementary Material'.

TABLE III. Positional and Thermal Parameters for Compound **VI**[a]

Atom	(x/a)	(y/b)	(z/c)	B ($Å^2$)
I	0.28085(6)	0.56350(3)	0.58444(3)	3.209(7)
Co	0.2560(1)	0.76598(5)	0.20840(5)	1.92(1)
O1	0.2127(7)	0.9742(3)	0.2282(4)	4.7(1)
O2	0.1892(8)	0.9242(4)	0.0859(4)	6.5(1)
O3	0.5552(6)	0.8338(4)	0.1357(4)	5.2(1)
O4	0.4747(7)	0.6921(4)	0.0762(4)	5.2(1)
N1	0.1213(7)	0.7158(4)	0.1042(3)	2.8(1)
N2	0.0492(6)	0.7633(4)	0.2815(3)	2.5(1)
N3	0.3002(7)	0.6267(4)	0.2578(3)	2.4(1)
N4	0.3925(7)	0.8136(4)	0.3131(4)	2.8(1)
N5	0.2133(7)	0.9060(4)	0.1690(4)	3.1(1)
N6	0.4523(7)	0.7637(5)	0.1313(3)	3.1(1)
C1	−0.0464(9)	0.6880(6)	0.1334(4)	2.6(1)
C2	−0.0932(8)	0.7557(6)	0.2147(5)	3.2(1)
C3	0.0592(8)	0.6810(5)	0.3531(4)	2.6(1)
C4	0.1554(8)	0.5893(5)	0.3141(4)	2.8(1)
C5	0.4562(8)	0.6325(5)	0.3134(5)	3.2(1)
C6	0.4569(8)	0.7262(5)	0.3720(4)	3.0(1)
H1	0.132(8)	0.667(5)	0.073(5)	5.0
H2	0.124(8)	0.758(5)	0.058(4)	5.0
H3	−0.045(8)	0.622(5)	0.142(4)	5.0
H4	−0.137(8)	0.703(5)	0.082(4)	5.0
H5	−0.196(8)	0.734(5)	0.244(4)	5.0
H6	−0.097(9)	0.808(5)	0.180(5)	5.0
H7	0.035(9)	0.818(5)	0.325(4)	5.0
H8	−0.018(9)	0.692(5)	0.380(4)	5.0
H9	0.105(8)	0.712(5)	0.416(5)	5.0
H10	0.102(8)	0.545(5)	0.273(5)	5.0
H11	0.188(8)	0.543(5)	0.378(4)	5.0
H12	0.316(8)	0.586(5)	0.212(4)	5.0
H13	0.544(8)	0.640(6)	0.265(5)	5.0
H14	0.476(8)	0.594(5)	0.331(4)	5.0
H15	0.560(9)	0.737(5)	0.403(4)	5.0
H16	0.377(8)	0.731(5)	0.437(4)	5.0
H17	0.474(9)	0.831(5)	0.284(4)	5.0
H18	0.351(8)	0.855(6)	0.344(5)	5.0
Ow	0.2159(8)	0.9051(4)	0.4729(3)	5.3(1)
HA	0.253(9)	0.949(4)	0.428(4)	5.0
HB	0.095(8)	0.926(5)	0.469(4)	5.0

[a] HA and HB belong to the water of hydration(Ow). Heavy atoms refined anisotropically (equivalent Bs listed); hydrogens thermal parameters were fixed at 5.0 $Å^2$.

TABLE IV. Bond Lengths (Å) and Angles (°)

(a) Bond lengths			
Co–N1	1.944(4)	C3–C4	1.525(7)
Co–N2	1.960(4)	C4–N3	1.493(6)
Co–N3	1.975(4)	N3–C5	1.483(7)
Co–N4	1.947(5)	C5–C6	1.475(9)
Co–N5	1.936(4)	C6–N4	1.503(7)
Co–N6	1.920(4)	N1–H1	0.78(6)
N5–O1	1.221(5)	N1–H2	0.86(6)
N5–O2	1.217(5)	N2–H7	0.95(7)
N6–O3	1.233(6)	N3–H12	0.85(5)
N6–O4	1.229(6)	N4–H17	0.80(6)
N1–C1	1.456(8)	N4–H18	0.77(5)
C1–C2	1.497(9)	OW–HA	0.91(5)
C2–N2	1.489(7)	OW–HB	1.01(6)
N2–C3	1.478(7)		
(b) Hydrogen contacts			
O2–H2	2.26(6)	O3–H17	2.21(6)
OW–H18	2.22(6)	I–HB	2.64(6)
(c) Bond angles			
N1–Co–N2	85.6(2)	N1–Co–N3	93.5(2)
N1–Co–N4	178.9(2)	N1–Co–N5	89.9(2)
N1–Co–N6	91.2(2)	N2–Co–N3	87.1(2)
N2–Co–N4	94.7(2)	N2–Co–N5	91.1(2)
N2–Co–N6	176.6(2)	N3–Co–N4	85.5(2)
N3–Co–N5	176.0(2)	N3–Co–N6	92.3(2)
N4–Co–N5	91.1(2)	N4–Co–N6	88.6(2)
N5–Co–N6	89.8(2)	Co–N1–C1	112.5(4)
Co–N2–C2	108.5(3)	Co–N2–C3	109.3(3)
Co–N3–C4	110.4(3)	Co–N3–C5	107.1(3)
Co–N4–C6	112.1(4)	Co–N5–O1	119.1(3)
Co–N5–O2	119.3(3)	Co–N6–O3	120.8(4)
Co–N6–O4	119.6(4)	O1–N5–O2	121.5(4)
O3–N6–O4	119.6(5)	N1–C1–C2	107.8(5)
C1–C2–N2	109.5(4)	C2–N2–C3	115.5(4)
N2–C3–C4	110.3(4)	C3–C4–N3	109.5(4)
C4–N3–C5	113.1(4)	N3–C5–C6	110.1(5)
C5–C6–N4	108.2(4)		

TABLE V. Torsional Angles for the Cation of **VI**

N2–Co–N1–C1	–8.4	N3–Co–N1–C1	78.3
N4–Co–N1–C1	94.4	N5–Co–N1–Cl	–99.5
N6–Co–N1–C1	170.7	N1–Co–N2–C2	–15.9
N1–Co–N2–C3	110.8	N3–Co–N2–C2	–109.7
N3–Co–N2–C3	17.0	N4–Co–N2–C2	165.1
N5–Co–N2–C2	73.9	N5–Co–N2–C3	–159.4
N6–Co–N2–C2	–30.6	N6–Co–N2–C3	96.1
N1–Co–N3–C4	–80.2	N1–Co–N3–C5	156.3
N2–Co–N3–C4	5.2	N2–Co–N3–C5	–118.4
N4–Co–N3–C4	100.1	N4–Co–N3–C5	–23.4
N5–Co–N3–C4	67.5	N5–Co–N3–C5	–56.0
N6–Co–N3–C4	–171.5	N6–Co–N3–C5	65.0
N1–Co–N4–C6	–15.5	N2–Co–N4–C6	87.2
N3–Co–N4–C6	0.5	N5–Co–N4–C6	178.3
N6–Co–N4–C6	–91.9	N1–Co–N5–O1	151.0
N1–Co–N5–O2	–29.6	N2–Co–N5–O1	65.5
N2–Co–N5–O2	–115.2	N3–Co–N5–O1	3.2
N3–Co–N5–O2	–177.4	N4–Co–N5–O1	–29.2
N4–Co–N5–O2	150.1	N6–Co–N5–O1	–117.8
N6–Co–N5–O2	61.5	N1–Co–N6–O3	139.2
N1–Co–N6–O4	–40.1	N2–Co–N6–O3	153.9
N2–Co–N6–O4	–25.4	N3–Co–N6–O3	–127.2
N3–Co–N6–O4	53.5	N4–Co–N6–O3	–41.8
N4–Co–N6–O4	138.9	N5–Co–N6–O3	49.3
N5–Co–N6–O4	–130.0	Co–N1–C1–C2	30.5
Co–N2–C2–C1	36.8	C3–N2–C2–C1	–86.2
Co–N2–C3–C4	–35.4	C2–N2–C3–C4	87.2
Co–N3–C4–C3	–25.6	C5–N3–C4–C3	94.4
Co–N3–C5–C6	42.7	C4–N3–C5–C6	–79.1
Co–N4–C6–C5	22.8	N1–C1–C2–N2	–43.6
N2–C3–C4–N3	40.1	N3–C5–C6–N4	–42.8

Results and Discussion

First, let us briefly deal with **V**, for which the following observations merit recording:

(1) This substance was obtained from a solution of the chloride to which a large excess of HNO_3 had been added. Such a procedure was successfully used here [7] to prepare [*cis-β*-Co(trien)$(NO_2)_2$](NO_3) (**VII**) from the chloride; in fact, the sample used for our structural analysis of **VII** was obtained by that method [7].

(2) The order of solubility of the [*cis-α*-Co(trien)-$(NO_2)_2$]X series is $I^- \leqslant Cl^- \leqslant NO_3^-$, whereas in the [*cis-β*-Co(trien)$(NO_2)_2$]X series it is $NO_3^- \leqslant I^- \leqslant Cl^-$. In fact, we found that the most convenient method of preparing the *cis-α* series is to synthesize the Cl^-, add an equimolar amount of NaI (see above) to obtain the iodide. The nitrate is conveniently made by addition of an equimolar amount of $AgNO_3$ to either the Cl^- or I^-. In case of the *cis-β* series, the nitrate was prepared by a local modification [7] of the method of Sargeson and Searle [15]. The iodide is then prepared by addition of an equimolar amount of NaI to the nitrate [7] and the Cl^- was prepared by the addition of an equimolar amount of freshly precipitated AgCl to the iodide and stirred at room temperature for 24 h.

(3) While there may be other and better methods of preparing these substances, we are not aware of them and those described above conveniently produced the desired products for us.

(4) The crystallographic results obtained here produced as an absolute configuration the enantiomer of that found in the previous study [1], showing that this substance crystallizes as a conglomerate – a fact not experimentally proven before.

The Structure of [cis-α-Co(trien)$(NO_2)_2$]I·H_2O

The cation of **VI** is depicted in Fig. 1 and its packing diagram is shown in Fig. 2. The coordinates of **V** and **VI** show that the two cations crystallize in

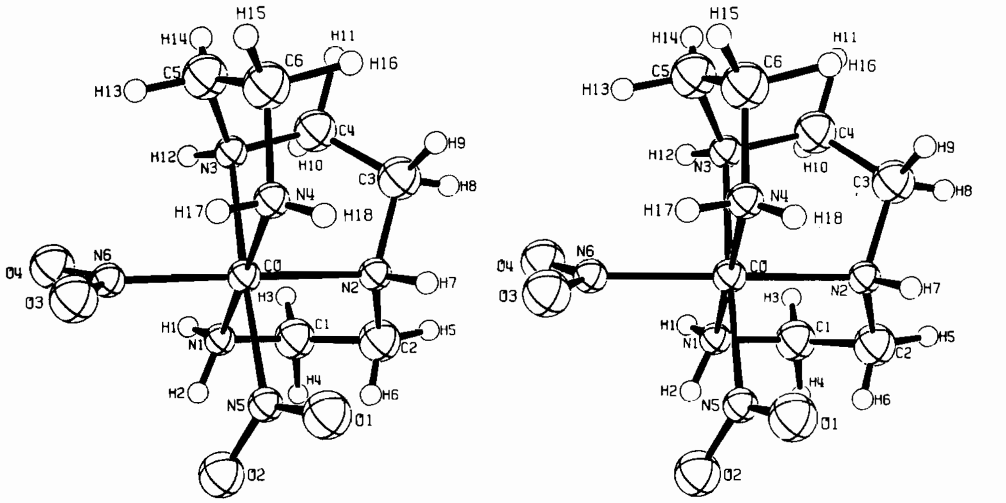

Fig. 1. Stereoview of the cation of compound **VI**. Note the orientation of the oxygens of the two $-NO_2$ ligands which are oriented towards the terminal $-NH_2$s of the trien ligands in such a way that their non-bonded pairs point towards the hydrogens.

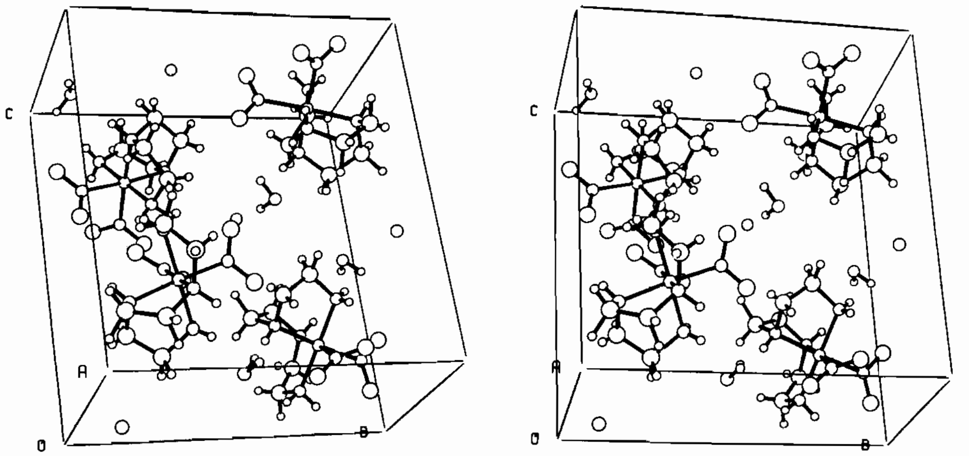

Fig. 2. Packing diagram for compound **VI**. Note the position of the charge compensating iodides with respect to the secondary hydrogens of the trien ligands.

isomorphous and nearly isostructural lattices. The fractional values of the coordinates are not exactly the same, reflecting the radius ratio differences between cation/Cl^- and cation/I^-. Nonetheless, the relative positions of the anions with respect to the cations are sufficiently similar that they obviously interact in the same manner, as shown in Fig. 2. To summarize, the closest contacts between the halide anion and the cation hydrogens are in the region of the central ring, which is located *trans* to the two $-NO_2$. This is readily demonstrated by the fact that the I–H7 (2.86 Å) and I–H12 (2.77 Å) are the shortest hydrogen bonds in the iodide lattice while the shortest Cl–H contact in the chloride is Cl–H7 (2.42 Å). In the latter lattice, Cl–H12 (2.54 Å) and Cl–H18 (2.52 Å) contacts are essentially the same length, within the estimated experimental error. Nonetheless, it is clear that these halides are preferentially linked to the cation through hydrogen bonds of the secondary amino moieties located *trans* to the *cis*-X_2 pair.

Thus, our conclusion is that the observations of Yoneda *et al.* [3] seem to be born out by structural studies in the solid state. Moreover, it seems that their observations are equally valid for Co(trien)X_2 derivatives – a non-trivial fact inasmuch as in trien derivatives there are primary as well as secondary nitrogens. Thus, the *trans* effect noted by the Japanese workers [13] is more general than may have been previewed by them. This observation is the more interesting in that there is no reason why a solvated anion in DMSO has to interact with an equally solvated cation as they do in a water solution such as those from which our crystals grew. Nor are the interionic packing interactions in the solid necessarily comparable with those observed by Yoneda *et al.* [3], [13], yet, our crystallographic results seem to indicate that these interionic interactions are similar enough to produce fully compatible results in the two experiments.

The stereochemical parameters of the cation of **VI** are listed in Tables IV and V. The results are sufficiently similar to those of the analogous chloride (**I**) that no further comments are necessary since the current study produced steric data which are not only in full accord with the results for **I** but, in fact, strengthens the conclusions reached before [1, 2].

Why Do Some Conglomerate and Others Do Not?

At the moment that question cannot be answered satisfactorily; however, we can summarize the results of many experiments [1, 2, 6–12] by some general observations:

(1) A cation, such as [*cis*-α-Co(trien)$(NO_2)_2]^+$ in which the $-NO_2$ ligands can be locked into a dissymmetric conformation by the agency of a stereochemical phenomenon such as intramolecular (in this case hydrogen) bonds appear to exhibit a pronounced tendency to form crystalline conglomerates, provided the compensating anion does not interfere with this process.

(2) When the charge-compensating anion is a halide, or some other relatively poor hydrogen bonding species, cations such as [*cis*-α-Co(trien)$(NO_2)_2]^+$ form conglomerates. However, if the compensating anion is a powerful hydrogen bonding species, such as NO_3^-, they tend to crystallize as racemates. At least, that is the experience so far. Detailed analyses of the effect of compensating anions on the phenomenon of conglomerate crystallization have been published by us before [1, 2, 7, 9, 11, 12].

(3) An independent, little noticed and extremely elegant demonstration of the role of the anion in controlling the process of conglomerate crystallization is an observation made by Kaki *et al.* [21] who, upon determining the solubility diagrams of $[Co(en)_2(glycine^-)]XY$ (with X = Y = acetate; X = Y = ClO_4^- and X = acetate, Y = ClO_4^-) noted that while the former two crystallize as racemates, the latter conglomerates. At the moment, not knowing the structures of any of these substances, it is impossible to ascertain the reason for this behaviour; however, we are planning to investigate this report at the molecular level.

(4) Charged or neutral species such as [*cis*-β-Co(trien)$(NO_2)_2]X$ and *mer*-Co(dien)$(NO_2)_3$ crystallize exclusively (thus far) [7, 10] as racemates. Suggestions were made [7, 10] for this behaviour which, briefly stated are as follows: (a) if the groups which can be anchored into dissymmetric conformations are given the opportunity to form equally meaningful intramolecular interactions with more than one set of stereochemically differently disposed moieties, they will attempt to do so; however, (b) since in order to do so, the dissymmetry-inducing groups have to rotate about the Co–N bond, the overall effect is to average out the dissymmetry. Under those circumstances, the species in question will crystallize predominantly as racemates.

(5) The $-NO_2$ oxygens of species such as [*trans*-$Co(en)_2(NO_2)_2]X$ can form very advantageous hydrogen bonds with the basal–NH_2 moieties. If the charge compensating anion is a poor hydrogen bonding species (*i.e.* I^-) the $-NO_2$ ligands interact so strongly with the amino hydrogens that the $-NO_2$ ligands are bent towards the basal plane [22]. If, however, the compensating anion is a powerful hydrogen bonder (*i.e.* SCN^- or NO_3^-) the basal plane amino hydrogens form better hydrogen bonds with them and the $-NO_2$ ligands are no longer bent towards the base. Despite this difference, the best conformation for each cation has an inversion center and the molecules crystallize as racemates. The conclusion drawn then [22] was that if, as a result of intramolecular interactions, a species can acquire a very advantageous conformation which imposes upon it symmetry elements which render it achiral, it will crystallize as racemates. Evidence that this is not limited to ionic species is the fact that neutral ones, such as *mer*-Co(dien)$(NO_2)_3$, crystallize as racemates. The reader is referred to the original [10] for a detailed analysis of the stereochemistry and crystallization behaviour of *mer* compounds.

(6) Let us compare two species, [*cis*-α-Co(trien)-$(NO_2)_2]Cl\cdot H_2O$ (**I**) and [*cis*-$Co(en)_2(NO_2)_2]Cl$ (**II**), both of which undergo conglomerate crystallization. It is clear the water of hydration is not essential since **II** has none. We have demonstrated [1, 2], however, that their cations are similarly conformated and intramolecularly hydrogen bonded. Why should this contribute to enhancement of conglomerate crystallization? Let us suggest some possible reasons:

(a) Solvents, such as water, are able to form a solvation cage around a solute probably similar to those clathrate-hydrate cages described by Jeffrey and McMullan [23]. The cage in question has to be large enough to accommodate the solute and, among those of favorable size, that giving the thermodynamically most favorable solute–(solvent cage) interactions will be selected.

(b) Note that the water cages described by Jeffrey and McMullan [23] are highly symmetric and that if a solute advantageously interacts with a portion of that cage, it will be able to interact equally well with a symmetry related portion of that cage. Thus, there is an inherent degeneracy to such interactions. The interested reader should refer to Section VI (p. 87) of ref. 23 since these authors give useful description of the orientational disorder of guest-in-cage present in clathrate solvates.

(c) Now, assume that enantiomeric molecules are placed in a solvent. If those enantiomers have stronger ligand–(solvent cage) interactions than intramolecular ones and the ligands in question (*i.e.* $-NO_2$) can easily acquire, by torsional motions and angle deformations, conformations which maximize solute–(solvent cage) interactions, they will do so in the manner described in (b), *i.e.* equally well in several orientations with respect to the atoms of the cage. As a consequence (1) the highly dissymmetric, intramolecularly-bonded, conformation is no longer possible and (2) as a result of torsional motion of the ligands in question (*i.e.* $-NO_2$ about the Co–N bond) and of the tumbling motion of solute-in-(solvent cage) there is an increase in the number of solute–(solvent interactions), presumably, thermodynamically desirable. However, such ligand torsional motions and those desirable solute–solvent interactions lead to an effective time-averaging of the molecular dissymmetry – the phenomenon is no different than the acquisition of higher symmetry (on the average) by the rotation of the $-NO_2$ group, about the C–N bonds, of nitrobenzene.

(d) Let us now consider the case when there are stronger intramolecular interactions within the solvent molecules than those which can take place between solute and any available solvent cage. Then, the enantiomers will be relatively less soluble in this particulat solvent medium. But, the gross thermodynamic criterion [3] for deciding whether a molecule will crystallize as a racemate or a conglomerate is that the solubility of the latter be less, by a well-defined amount, than the racemate. Thus, under such conditions, one would expect conglomerate crystallization to occur.

(e) Finally, prior studies [1, 2, 4, 7] of nitrates of cations which form conglomerates as halides have shown that the $-NO_3^-$ oxygens form stronger hydrogen bonds with the terminal $-NH_2$ hydrogens than do the *cis* pair of $-NO_2$ ligands. This is not only due to the ability of the ionic nitrate to approach the $-NH_2$s as closely as needed, but also to its ability to approach them at the most advantageous angular orientation (*i.e.* $<$N–H....O as close to 180° as possible). The acquisition of that advantageous angular orientation is, of course, impossible for the bound $-NO_2$ ligand. Consequently, $-NO_3^-$ anions interfere with the process described in (d) and racemate crystallization occurs.

If the $-NO_2$ ligands are no longer able to form strong hydrogen bonds with the terminal $-NH_2$ hydrogens, they now become available for hydrogen bond formation with the water cage and the situation described in (b) and (c) will prevail.

Conclusions

The most important results derived from this study are:

(a) [*cis*-α-Co(trien)$(NO_2)_2$]I·H_2O crystallizes, as does its chloride analogue [1] in the optically active space group $P2_12_12_1$.

(b) We have experimentally verified that the chloride derivative, [*cis*-α-Co(trien)$(NO_2)_2$]Cl·H_2O, forms a conglomerate.

(c) ^1H NMR experiments in DMSO solutions, by Yoneda *et al.* [13], suggested that the ionic halide of compounds [*cis*-Co(en)$_2$X$_2$](halide) (X = CN^-, NO_2^-, Cl^-, NCS^-, N_3^-) are located closest to the amino hydrogens *trans* to the X ligands. Our crystallographic studies of single crystals of the [*cis*-α-Co(trien)-$(NO_2)_2$](halide)·H_2O (halide = Cl^-, I^-) are in accord with their suggestion. In fact the I^- herein reported is closer, by about 0.2 Å, to hydrogens of both secondary nitrogens than to any other hydrogen, except those of the water of crystallization (see Table V). However, the difference in Cl–H distance between the shortest secondary and primary amino hydrogens is only 0.1 Å, which is not as mathematically significant as in the case of the iodide.

Nonetheless, it is highly satisfying that the model they [13] used to interpret their ^1H NMR data adequately describes the cation–anion interactions in the trien series as solids. This suggests that the results obtained in either the solid state or in solution are reasonable models for interionic interactions in either medium, implying that our earlier conclusions [1, 2, 6–12], derived from solid state measurements, reasonably describe their expected behaviour in solution just prior to crystallization.

Supplementary Material

The results obtained with **V** are available from the authors.

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