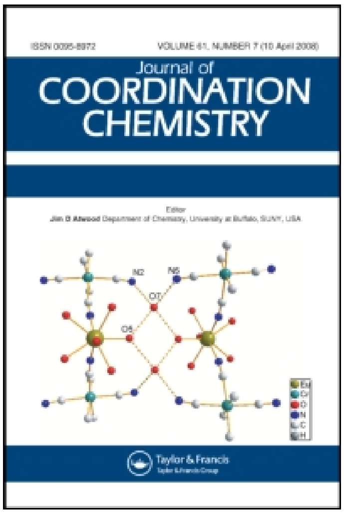

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

The Phenomenon of Conglomerate Crystallization. XXI. Clavic Dissymmetry in Coordination Compounds. XIX. A Topological Investigation of the Conformational and Configurational Characteristics of Racemic [*Cis*-β-Co(trien)(N0$_2$)$_2$][*trans*-Co(NH$_3$)$_2$(No$_2$)$_4$]·H$_2$O

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To cite this Article Bernal, Ivan and Cetrullo, James(1989) 'The Phenomenon of Conglomerate Crystallization. XXI. Clavic Dissymmetry in Coordination Compounds. XIX. A Topological Investigation of the Conformational and Configurational Characteristics of Racemic [*Cis*-β-Co(trien)(N0$_2$)$_2$][*trans*-Co(NH$_3$)$_2$(No$_2$)$_4$]·H$_2$O', Journal of Coordination Chemistry, 20: 3, 237 — 246

To link to this Article: DOI: 10.1080/00958978909408165
URL: http://dx.doi.org/10.1080/00958978909408165

J. Coord. Chem. 1989, Vol. 20. pp. 237–246
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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. XXI.
CLAVIC DISSYMMETRY IN COORDINATION COMPOUNDS. XIX.
A TOPOLOGICAL INVESTIGATION OF THE CONFORMATIONAL AND CONFIGURATIONAL CHARACTERISTICS OF RACEMIC $[cis\text{-}\beta\text{-Co(trien)(NO}_2)_2][trans\text{-Co(NH}_3)_2(\text{NO}_2)_4]\cdot\text{H}_2\text{O}$

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(Received February 27, 1989)

The compound [*cis*-β-Co(trien)$(NO_2)_2$][*trans*-Co$(NH_3)_2(NO_2)_4$].H_2O, (I), crystallizes in the monoclinic system, space group $P2_1/c$, with cell constants $a = 6.536(1)$, $b = 23.168(5)$, $c = 13.670(4)$ Å and $\beta = 92.94°$; $V = 2067.40$ Å^3 and d (calc; $Z = 4$) $= 1.903$ g cm^{-3}. A total of 4065 data were collected in the range of $4° \leqslant 2\theta \leqslant 60°$, of which 2744 were unique, had $I > 3\sigma(I)$ and were used in the refinement of the structural parameters. The refinement converged at values of $R(F) = 0.0308$ and $R_w(F) = 0.0349$. Unlike K[*trans*-Co$(NH_3)_2(NO_2)_4$], NH_4[*trans*-Co$(NH_3)_2$-$(NO_2)_4$], [*cis*-α-Co(trien)$(NO_2)_2$][*trans*-Co$(NH_3)_2$-$(NO_2)_4$] and [*cis*-Co$(en)_2(NO_2)_2$][*trans*-Co$(NH_3)_2(NO_2)_4$], all of which crystallize as conglomerates, (I) crystallizes as a racemate. This behaviour is in accord with observations made in previous studies of salts of the [*cis*-β-Co(trien)$(NO_2)_2$]$^+$ cation.

Keywords: Conglomerate, crystallization, cobalt(III), X-ray structure, hydrogen bonding

INTRODUCTION

We have investigated the crystallization behaviour of K[*trans*-Co$(NH_3)_2(NO_2)_4$],[1] as well as that of a group of salts of the geometrically isomeric cations [*cis*-α-Co(trien)$(NO_2)_2$]$^+$ and [*cis*-β-Co(trien)$(NO_2)_2$]$^+$ with the following results.

Compound	*Space Group*	*Ref.*
K[*trans*-Co$(NH_3)_2(NO_2)_4$]	$P2_12_12_1$	1
NH_4[*trans*-Co$(NH_3)_2(NO_2)_4$]	$P2_12_12_1$	1
[*cis*-α-Co(trien)$(NO_2)_2$]Cl.H_2O	$P2_12_12_1$	1
[*cis*-Co$(en)_2(NO_2)_2$]Cl	$P2_1$	1
[*cis*-α-Co(trien)$(NO_2)_2$]I.H_2O	$P2_12_12_1$	2
[*cis*-β-Co(trien)$(NO_2)_2$]I	Cc	3
[*cis*-β-Co(trien)$(NO_2)_2$](NO_3)	$P2_1/n$	3
[*cis*-α-Co(trien)$(NO_2)_2$][*trans*-Co$(NH_3)_2(NO_2)_4$]	$P2_12_12_1$	4
[*cis*-Co$(en)_2(NO_2)_2$][*trans*-Co$(NH_3)_2(NO_2)_2$]	$P2_12_12_1$	4

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Thus, whereas the anion [*trans*-$Co(NH_3)_2(NO_2)_4]^-$ forms crystalline conglomerates with K^+, NH_4^+, [*cis*-$Co(en)_2(NO_2)_2]^+$, and [*cis*-α-$Co(trien)(NO_2)_2]^+$ cations, and the chloride and iodide salts of [*cis*-α-$Co(trien)(NO_2)_2]^+$ also conglomerate, the two salts of the [*cis*-β-$Co(trien)(NO_2)_2]^+$ cation previously investigated are racemates. As a result, we decided to use the [*trans*-$Co(NH_3)_2(NO_2)_4]^-$ counter anion in conjunction with the [*cis*-β-$Co(trien)(NO_2)_2]^+$ cation to ascertain their joint crystallization behaviour. The results are given below.

EXPERIMENTAL

Syntheses

The compound was prepared from a water solution of [*cis*-β-Co(trien)-$(NO_2)_2](NO_3)$[3] to which an excess of K[*trans*-$Co(NH_3)_2(NO_2)_4]$ was added. The resulting solution was placed in the refrigerator at *ca* 4°C, from which crystals of [*cis*-β-$Co(trien)(NO_2)_2$][*trans*-$Co(NH_3)_2(NO_2)_4$] suitable for single crystal X-ray diffraction were deposited.

X-Ray Data Collection

Data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[5] of the SDP-Plus software package.[6] The crystal was centred with data in the $18° \leqslant 2\theta \leqslant 25°$ range and examination of the cell constants and Niggli matrix[7] clearly showed it to crystallize in a primitive lattice whose axial relationships and systematic absences showed compound (I) to belong to the racemic space group $P2_1/c$. The intensity data sets were corrected for absorption using empirical curves derived from Psi scans[5,6] of seven reflections. The scattering curves were taken from Cromer and Waber's compilation.[8]

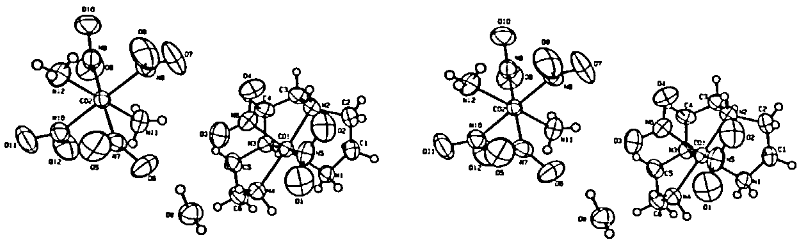

FIGURE 1 A stereoview of the asymmetric unit of compound (I) containing the complex cation, the complex anion, and a water of crystallization.

The structure was solved from the Patterson map, using the Co atoms as the heavy atoms. After refinement of the scale factor and the positional parameters of the Co atoms, a difference Fourier map produced many of the non-hydrogen atoms. The remaining atoms were found in subsequent difference maps. The positions and anisotropic thermal parameters of the heavy atoms, including the water of crystallization, were refined. The hydrogen atoms of the cation were placed at calculated positions (C–H and N–H = 0.95 Å; $B = 5.0$ Å^2) after each set of refinements and not refined. The hydrogens of the anion and those of the water of hydration were found in difference maps. Their positions were refined but their thermal paramaters were fixed at $B = 5.0$ Å^2. At the end of the refinement, the values of $R(F)$ and $R_w(F)$ factors were, respectively, 0.0308 and 0.0349. Details of data collection and processing are summarized in Table I.

TABLE I
Summary of data collection and processing parameters for racemic $[cis\text{-}\beta\text{-Co(trien)(NO}_2)_2][trans\text{-Co(NH}_3)_2(\text{NO}_2)_4]$.

Space Group	$P2_1/c$
Cell Constants	$a = 6.536(1)$ Å $b = 23.168(5)$ $c = 13.670(4)$ $\beta = 92.94(2)$
Cell Volume	$V = 2067.40$ Å^3
Molecular Formula	$C_6H_{26}N_{12}O_{13}Co_2$
Molecular Weight	592.21 gm-mol^{-1}
Density(calc; Z = 4)	1.903 gm-cm^{-3}
Radiation Employed	Mo$K\alpha$($\lambda = 0.71073$ Å)
Absorption Coefficient	$\mu = 16.88$ cm^{-1}
Transmission Coefficients	1.00 to 0.7738
Data Collection Range	$4° \leqslant 2\theta \leqslant 60°$
Scan Width	$\Delta\theta = 0.90 + 0.35\tan\theta$
Total Data Collected	4065
Data Used in refinement*	2744
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0308
$R_w = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.0349
Weights Used	$w = [\sigma(F_o)]^{-2}$

* The difference between this number and the total is due to subtraction of 1321 data which either were systematically absent (but collected for verification of space group), standards, or did not meet the criterion that $I \geq 3\sigma(I)$.

Figure 1 is a stereo view of the two ions present in (I). Figure 2 depicts, in stereo, the packing of the ions in the unit cell. Final values of the fractional coordinates and equivalent isotropic thermal parameters are given in Table II. Bond lengths, angles and torsional angles for (I) are listed in Table III.

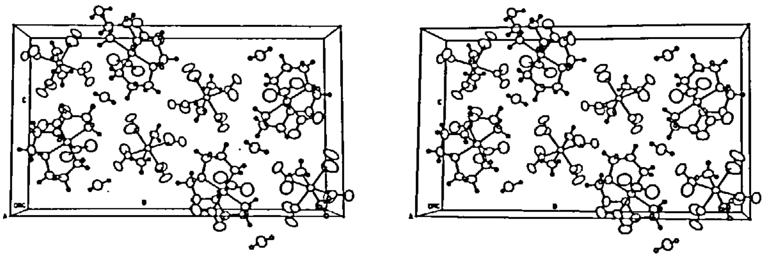

FIGURE 2 A stereoview of the packing diagram of (I) in its crystalline lattice.

TABLE II

Positional parameters[a] and estimated standard deviations for I.

Atom	x/a	y/b	z/c	B(Å^2)
Co1	0.47216(8)	0.14781(2)	0.38495(4)	2.12(1)
Co2	−0.02974(8)	0.09862(2)	0.85089(3)	1.886(9)
O1	0.1232(5)	0.2140(2)	0.3651(3)	6.07(9)
O2	0.0840(5)	0.1321(2)	0.3016(2)	5.04(8)
O3	0.3169(6)	0.1324(1)	0.5679(2)	5.29(8)
O4	0.2872(6)	0.0586(1)	0.4799(2)	5.11(8)
O5	−0.3372(5)	0.1827(1)	0.8438(2)	4.99(8)
O6	−0.1096(5)	0.2007(1)	0.7452(2)	4.25(7)
O7	−0.0666(6)	0.0379(1)	0.6775(2)	5.43(8)
O8	−0.3523(5)	0.0547(2)	0.7361(2)	5.25(8)
O9	0.2931(5)	0.0262(1)	0.9052(2)	4.49(8)
O10	0.0086(5)	−0.0174(1)	0.8910(2)	3.97(7)
O11	0.0029(5)	0.1567(1)	1.0290(2)	4.45(7)
O12	0.2865(5)	0.1530(2)	0.9622(2)	4.93(8)
N1	0.5739(5)	0.1861(1)	0.2671(2)	2.83(7)
N2	0.4818(5)	0.0769(1)	0.3087(2)	2.65(7)
N3	0.7444(5)	0.1264(1)	0.4348(2)	2.48(7)
N4	0.5066(5)	0.2167(1)	0.4666(2)	2.90(7)
N5	0.1967(5)	0.1678(2)	0.3435(2)	3.22(8)
N6	0.3477(5)	0.1081(1)	0.4910(2)	2.90(7)
N7	−0.1752(5)	0.1692(1)	0.8089(2)	2.70(7)
N8	−0.1669(6)	0.0588(1)	0.7415(2)	2.94(7)
N9	0.1073(5)	0.0275(1)	0.8875(2)	2.81(7)
N10	0.1038(5)	0.1408(1)	0.9610(2)	2.76(7)
N11	0.1979(5)	0.1183(2)	0.7721(2)	3.16(8)
N12	−0.2489(5)	0.0782(1)	0.9334(2)	2.85(7)
C1	0.6171(7)	0.1426(2)	0.1901(3)	3.27(9)
C2	0.4745(7)	0.0926(2)	0.2020(3)	3.17(9)
C3	0.6732(7)	0.0428(2)	0.3388(3)	3.27(9)
C4	0.7608(7)	0.0633(2)	0.4358(3)	3.24(9)
C5	0.7888(7)	0.1571(2)	0.5276(3)	3.36(9)
C6	0.7168(7)	0.2176(2)	0.5146(3)	3.7(1)
OW	0.2408(5)	0.2597(1)	0.6430(2)	4.09(7)
H1W	0.109	0.227	0.666	
H2W	0.109	0.287	0.615	
H19	0.292	0.092	0.788	
H20	0.178	0.117	0.714	
H21	0.243	0.150	0.792	
H22	−0.223	0.437	0.486	
H23	−0.334	0.439	0.396	
H24	−0.389	0.410	0.437	
H1	0.6953	0.2069	0.2851	
H2	0.4719	0.2127	0.2422	
H3	0.7544	0.1298	0.1977	
H4	0.5934	0.1591	0.1266	
H5	0.5171	0.0606	0.1641	
H6	0.3386	0.1031	0.1803	
H7	0.3667	0.0531	0.3201	
H8	0.7725	0.0473	0.2907	
H9	0.6393	0.0028	0.3434	

Table II (*continued*)

Atom	x/a	y/b	z/c	B(Å^2)
H10	0.9008	0.0519	0.4437	
H11	0.6863	0.0472	0.4867	
H12	0.8496	0.1385	0.3944	
H13	0.9320	0.1564	0.5445	
H14	0.7182	0.1392	0.5794	
H15	0.8069	0.2379	0.4736	
H16	0.7143	0.2367	0.5758	
H17	0.4890	0.2502	0.4274	
H18	0.4108	0.2164	0.5160	

[a] Hydrogen atoms thermal parameters were fixed at B = 5.0Å2.

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 gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)].

TABLE III

Bond lengths (Å) and angles (°)

A. Bond Lengths for the Cation and Water

Co1–N1	1.983(2)	C3–C4	1.496(3)
Co1–N2	1.947(2)	C4–N3	1.465(3)
Co1–N3	1.937(2)	N3–C5	1.471(3)
Co1–N4	1.954(2)	C5–C6	1.486(3)
Co1–N5	1.916(2)	C6–N4	1.492(3)
Co1–N6	1.931(2)	N1–H1	0.95
N5–O1	1.216(3)	N1–H2	0.95
N5–O2	1.229(3)	N2–H7	0.95
N6–O3	1.218(2)	N3–H12	0.95
N6–O4	1.220(2)	N4–H17	0.95
N1–C1	1.494(3)	N4–H18	0.95
C1–C2	1.501(3)	Ow–H1w	1.206(2)
C2–N2	1.502(3)	Ow–H2w	1.119(2)
N2–C3	1.519(3)		

B. Bond Lengths for the Anion

Co2–N7	1.963(2)	Co2–N8	1.938(2)
Co2–N9	1.930(2)	Co2–N10	1.962(2)
Co2–N11	1.935(2)	Co2–N12	1.927(2)
N7–O5	1.224(2)	N7–O6	1.230(2)
N8–O7	1.220(3)	N8–O8	1.214(3)
N9–O9	1.226(3)	N9–O10	1.226(2)
N10–O11	1.223(2)	N10–O12	1.226(3)
N11–H19	0.89	N11–H20	0.80
N11–H21	0.83	N12–H22	0.82
N12–H23	0.84	N12–H24	0.96

C. Hydrogen Bonding Contacts (Less than 2.40 Å and with N-H...O angles greater than 140°) for Cation and Anion

O6–H1w	1.93	O11–H2w	1.87
O2–H12	2.04	O3–H20	2.26
O5–H17	2.27	O10–H22	2.37
Ow–H2	2.08		

TABLE III (*continued*)

D. Bond Angles for the Cation and Water

N1–Co1–N2	85.45(8)	N1–Co1–N3	93.42(8)
N1–Co1–N4	93.74(8)	N1–Co1–N5	90.06(8)
N1–Co1–N6	173.85(9)	N2–Co1–N3	85.29(8)
N2–Co1–N4	171.26(9)	N2–Co1–N5	95.79(9)
N2–Co1–N6	91.52(8)	N3–Co1–N4	86.07(8)
N3–Co1–N5	176.44(8)	N3–Co1–N6	91.67(8)
N4–Co1–N5	92.91(9)	N4–Co1–N6	90.06(8)
N5–Co1–N6	84.91(8)	Co1–N1–C1	110.7(1)
Co1–N2–C2	108.4(1)	Co1–N2–C3	110.1(1)
Co1–N3–C4	108.9(2)	Co1–N3–C5	108.5(2)
Co1–N4–C6	109.8(1)	Co1–N5–O1	121.2(2)
Co1–N5–O2	120.5(2)	Co1–N6–O3	121.5(2)
Co1–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)	C2–N2–C3	111.9(2)
N2–C3–C4	110.3(2)	C4–N3–C5	117.5(2)
C3–C4–N3	106.5(2)	N3–C5–C6	107.7(2)
C5–C6–N4	108.7(2)	Hw1–Ow–Hw2	84.6(1)

E. Bond Angles for the Anion

N7–Co2–N8	88.46(8)	N7–Co2–N9	177.56(8)
N7–Co2–N10	89.96(8)	N7–Co2–N11	90.92(9)
N7–Co2–N12	90.68(9)	N8–Co2–N9	89.10(8)
N8–Co2–N10	178.38(9)	N8–Co2–N11	91.19(9)
N8–Co2–N12	90.38(9)	N9–Co2–N10	92.48(8)
N9–Co2–N11	89.17(9)	N9–Co2–N12	89.30(8)
N10–Co2–N11	89.17(9)	N10–Co2–N12	89.30(8)
N11–Co2–N12	177.79(8)	Co2–N7–O5	121.0(2)
Co2–N7–O6	121.3(2)	Co2–N8–O7	119.9(2)
Co2–N8–O8	120.3(2)	Co2–N9–O9	121.0(2)
Co2–N9–O10	119.8(2)	Co2–N10–O11	119.8(2)
Co2–N10–O12	121.3(2)	O5–N7–O6	117.7(2)
O7–N8–O8	119.8(2)	O9–N9–O10	119.2(2)
O11–N10–O12	118.9(2)		

F. Hydrogen Bond Angles (N–H...O or O–H...O angles)

Ow–Hw1...O6	154.3	Ow–H2w...O11	149.9
N3–H12...O2	158.4	N11–H20...O3	145.1
N4–H17...O5	142.9	N12–H22...O10	155.4
N1–H2...Ow	153.9		

G. Torsional Angles for the Cation

N2–Co1–N1–C1	−4.2	N3–Co1–N1–C1	80.8
N4–Co1–N1–C1	167.1	N5–Co1–N1–C1	−100.0
N6–Co1–N1–C1	−64.9	N1–Co1–N2–C2	−22.0
N1–Co1–N2–C3	100.7	N3–Co1–N2–C2	−115.8
N3–Co1–N2–C3	6.9	N4–Co1–N2–C2	−107.1
N5–Co1–N2–C2	67.6	N5–Co1–N2–C3	−169.7
N6–Co1–N2–C2	152.6	N6–Co1–N2–C3	−84.7
N1–Co1–N3–C4	−115.5	N1–Co1–N3–C5	115.4
N2–Co1–N3–C4	−30.4	N2–Co1–N3–C5	−159.4
N4–Co1–N3–C4	151.0	N4–Co1–N3–C5	21.9

TABLE III (*continued*)
Bond lengths (Å) and angles (°)

N5–Co1–N3–C4	77.5	N5–Co1–N3–C5	−51.5
N6–Co1–N3–C4	61.0	N6–Co1–N3–C5	−68.0
N1–Co1–N4–C6	−89.4	N2–Co1–N4–C6	−5.0
N3–Co1–N4–C6	3.8	N5–Co1–N4–C6	−179.6
N6–Co1–N4–C6	95.5	N1–Co1–N5–O1	−87.1
N1–Co1–N5–O2	99.3	N2–Co1–N5–O1	−172.5
N2–Co1–N5–O2	13.9	N3–Co1–N5–O1	79.9
N3–Co1–N5–O2	−93.7	N4–Co1–N5–O1	6.7
N4–Co1–N5–O2	−166.9	N6–Co1–N5–O1	96.5
N6–Co1–N5–O2	−77.1	N1–Co1–N6–O3	−125.0
N1–Co1–N6–O4	50.8	N2–Co1–N6–O3	174.6
N2–Co1–N6–O4	−9.6	N3–Co1–N6–O3	89.2
N3–Co1–N6–O4	−94.9	N4–Co1–N6–O3	3.2
N4–Co1–N6–O4	179.0	N5–Co1–N6–O3	−89.7
N5–Co1–N6–O4	86.1	Co1–N1–C1–C2	29.4
Co1–N2–C2–C1	43.9	C3–N2–C2–C1	−77.7
Co1–N2–C3–C4	17.4	C2–N2–C3–C4	138.1
Co1–N3–C4–C3	46.4	C5–N3–C4–C3	170.2
Co1–N3–C5–C6	−43.1	C4–N3–C5–C6	−167.1
Co1–N4–C6–C5	−28.6	N1–C1–C2–N2	−47.3
N2–C3–C4–N2	−40.9	N3–C5–C6–N4	46.6

H. Torsional Angles for the Anion

N8–Co2–N7–O5	94.0	N8–Co2–N7–O6	−84.2
N9–Co2–N7–O5	93.2	N9–Co2–N7–O6	−85.1
N10–Co2–N7–O5	−85.6	N10–Co2–N7–O6	96.1
N11–Co2–N7–O5	−174.8	N11–Co2–N7–O6	6.9
N12–Co2–N7–O5	3.7	N12–Co2–N7–O6	−174.6
N7–Co2–N8–O7	117.9	N7–Co2–N8–O8	−61.9
N9–Co2–N8–O7	−62.2	N9–Co2–N8–O8	118.0
N10–Co2–N8–O7	129.9	N10–Co2–N8–O8	−49.9
N11–Co2–N8–O7	27.0	N11–Co2–N8–O8	−152.8
N12–Co2–N8–O7	−151.5	N12–Co2–N8–O8	28.7
N7–Co2–N9–O9	131.8	N7–Co2–N9–O10	−46.4
N8–Co2–N9–O9	130.9	N8–Co2–N9–O10	−47.2
N10–Co2–N9–O9	−49.4	N10–Co2–N9–O10	132.5
N11–Co2–N9–O9	39.7	N11–Co2–N9–O10	−138.4
N12–Co2–N9–O9	−138.7	N12–Co2–N9–O10	43.2
N7–Co2–N10–O11	69.7	N7–Co2–N10–O12	−108.3
N8–Co2–N10–O11	57.7	N8–Co2–N10–O12	−120.3
N9–Co2–N10–O11	−110.2	N9–Co2–N10–O12	71.7
N11–Co2–N10–O11	160.7	N11–Co2–N10–O12	−17.4
N12–Co2–N10–O11	−20.9	N12–Co2–N10–O12	161.0
N7–Co2–N11–H19	173.1	N7–Co2–N11–H20	−68.7
N7–Co2–N11–H21	59.2	N8–Co2–N11–H19	−98.4
N8–Co2–N11–H20	19.8	N8–Co2–N11–H21	147.7
N9–Co2–N11–H19	−9.3	N9–Co2–N11–H20	108.9
N9–Co2–N11–H21	−123.3	N10–Co2–N11–H19	83.1
N10–Co2–N11–H20	−158.6	N10–Co2–N11–H21	−30.8

RESULTS AND DISCUSSION

The cation depicted in the figures has configuration and conformation described as Δ(λλδ); the torsional angles for the three rings of the trien ligand are: N1–C1–C2–N2 = −47.3°, N2–C3–C4–N3 = −40.9° and N3–C5–C6–N4 = +46.6°. In the case of the [*cis*-β-Co(trien)(NO_2)$_2$](NO_3) derivative,[3] these values are +47.1°, +39.8° and −49.4°, respectively, for the species describing the asymmetric unit reported. Thus, the cations of the nitrate have configuration Λ(δδλ). The major discrepancy between the two results is the *ca* 3° difference in the last ring. This is the result of significant hydrogen bonding involving H17 and H18 in compound (**I**) as compared with the [*cis*-β-Co(trien)(NO_2)$_2$](NO_3) derivative,[3] in which there are no significant hydrogen bonds to these $-NH_2$ hydrogens. In (**I**), H18 forms an intramolecular hydrogen bond, N4–H18–O3 = 2.17 Å, with one oxygen of a nitro group bound to the same cobalt centre. Also, H17 forms a hydrogen bond, N4–H17–O5 = 2.27 Å, to an $-NO_2$ oxygen of the charge compensating anion.

Aside from that small difference in ring torsional angles of the Co(trien) backbone, the stereochemistry of this fragment of the cations of (I) and [*cis*-β-Co(trien)-(NO_2)$_2$](NO_3) are quite similar. Such is not the case for the Co(NO_2)$_2$ fragment, as exemplified by the following comparison of Ni–Co–N5–O2 and N2–Co–N6–O2 torsional angles

Angle	*Compound* (I)	[cis-*β*-Co(*trien*)(*NO_2*)$_2$](2NO_3)
N1–Co–N5–O1	−87.1°	125.0°
N1–Co–N5–O2	+99.3°	−54.4°
N1–Co–N6–O3	−125.0°	+136.8°
N1–Co–N6–O4	+50.8°	−39.8°
N2–Co–N5–O1	−172.5°	−150.6°
N2–Co–N5–O2	+13.9°	+29.9°
N2–Co–N6–O3	+174.6°	−162.4°
N2–Co–N6–O4	−9.6°	+21.1°

When one realizes that in the two cations in question the Co(trien) backbones are enantiomorphic to one another, the difference in torsional angles would be even worse if one were to compare the correct enantiomorphic pair. This state of affairs is brought about by the major difference in hydrogen bonding between the ion pairs present in the two lattices in question. Moreover, it lends factual credibility to the point we have made in previous publications (such as refs. 1 to 3 and 9 to 12) that the stereochemistry of the $-NO_2$ ligands is intimately tied to the nature of the hydrogen bonded interactions present in the compounds in question. In particular, there is a fine balance between the compounds of the Co–NO_2 fragment and the nature of the counter anion. If the latter is a weak hydrogen bonding species, the major interactions involving the $-NO_2$ oxygens will be intramolecular (with the axial $-NH_2$ hydrogens) and/or intercationic. This point is discussed in detail in the three preceding papers of this series (refs. 13 to 15).

Since (I) does not crystallize as a conglomerate despite having a counter anion which seems to display some tendency towards forming conglomerates, it is interesting to explore the stereochemistry of the counter anion in (I) *vs* K[*trans*-$(NH_3)_2(NO_2)_4$, as we have done for the cation.

Torsional Angle Comparison

Compound (I)		K[trans-$(NH_3)_2(NO_2)_4$	
N11-Co2-N7-O5	−174.8°	N1-Co-N5-O5	12.5°
N11-Co2-N7-O6	6.9°	N1-Co-N5-O6	−174.8°
N12-Co2-N7-O5	3.7°	N2-Co-N5-O5	−167.3°
N12-Co2-N7-O6	−174.6°	N2-Co-N5-O6	5.4°
N11-Co2-N10-O11	160.7°	N1-Co-N6-O7	168.4°
N11-Co2-N10-O12	−17.4°	N1-Co-N6-O8	−9.9°
N12-Co2-N10-O11	−20.9°	N2-Co-N6-O7	−12.5°
N12-Co2-N10-O12	161.0°	N2-Co-N6-O8	169.2°
N11-Co2-N8-O7	27.0°	N1-Co-N4-O3	39.7°
N11-Co2-N8-O8	−152.8°	N1-Co-N4-O4	−140.2°
N12-Co2-N8-O7	−151.5°	N2-Co-N4-O3	−139.4°
N12-Co2-N8-O8	28.7°	N2-Co-N4-O4	40.7°
N11-Co2-N9-O9	39.7°	N1-Co-N3-O1	−136.5°
N11-Co2-N9-O10	−138.4°	N1-Co-N3-O2	41.4°
N12-Co2-N9-O9	−138.7°	N2-Co-N3-O1	43.3°
N12-Co2-N9-O10	43.2°	N2-Co-N3-O2	−138.8°

The torsional angles listed above are superficially similar, as they must be in order to maintain proper inter O...O contacts, which we have shown before[1–3,9] to be about 3.2 Å. However, there are noticeable differences and these are responsible for the fact that the intramolecular O...H distances are larger in compound (I) than in K[*trans*-$Co(NH_3)_2(NO_2)_4$]. Furthermore (see Table III) the shortest intermolecular hydrogen bonds for the anion (I) are with the water of hydration (O6...H1w = 1.93 and O11...H2w = 1.87 Å), whereas the two shortest intramolecular hydrogen bonds in the anion of (I) are O9...H19 = 2.21 Å and O12...H21 = 2.33 Å. The observation that the torsional angles change when intermolecular or interionic hydrogen bonds are stronger than intramolecular or intraionic ones and that conglomerate crystallization occurs when the latter is true has already been documented for four different salts of the anion.[1–3,10] This is the first one which does *not* undergo conglomerate crystallization; however, we have already suggested that salts of the cation of (I) do not undergo conglomerate crystallization with any counter anion. Moreover, we have provided a plausible reason for this behaviour. For relevant arguments see refs. 3, 11, 12. Thus, compound (I) seems to follow the pattern observed in the past and lends some credence to the arguments we have put forward in preceding papers.[1–3,9–15]

ACKNOWLEDGEMENTS

We thank the Robert A. Welch Foundation for support of this research (Grant E-592 to I. Bernal) and for a fellowship granted to J. Cetrullo.

SUPPLEMENTARY MATERIAL

Full lists of bond lengths and angles, anisotropic thermal parameters and observed and calculated structure factors are available from the authors upon request.

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