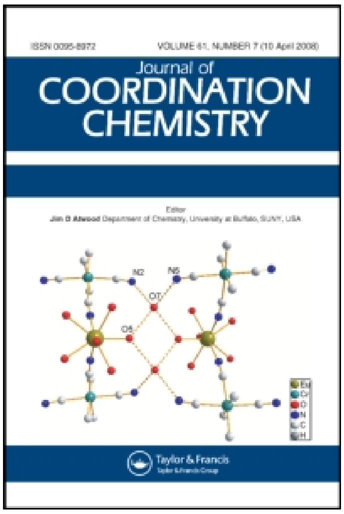

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION. XVI. SPONTANEOUS RESOLUTION IN COORDINATION COMPOUNDS. XIV. THE CONGLOMERATE BEHAVIOUR OF THE COBALT(III) AMINE OXALATES. CRYSTALLOGRAPHIC DATA FOR $NH_4[\textit{trans}\text{-}(NH_3)_2Co(NO_2)_2(\text{oxalato})]$ AND $[\textit{cis}\text{-}\beta\text{-}Co(\text{trien})(NO_2)_2][\textit{trans}\text{-}(NH_3)_2Co(NO_2(\text{oxalato})]$, AND THE CRYSTAL STRUCTURE OF $[\textit{trans}\text{-}Co(\text{en})_2)_2]$ $[\textit{trans}\text{-}(NH_3)_2Co(NO_2)_2(\text{oxalato})]$

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The title compound crystallizes in the triclinic space group $P\bar{1}$ with cell constants $a = 6.534(6)$ $b = 10.922(9)$, $c = 14.905(7)$ Å, $\alpha = 94.44(5)$ $\beta = 94.69(7)$ and $\gamma = 105.41(1)°$, $V = 1016.61$ Å^3 and d(calc; $Z = 2$) = 1.778 g cm^{-3}. A total of 3824 data were collected over the range of $4° \leqslant 2\theta \leqslant 50°$; of these, 2994 were independent and had $I \geq 3\sigma(I)$; these were used in the solution and refinement of the structure. The final $R(F)$ and $Rw(F)$ residuals were 0.072 and 0.108, respectively. The molecule crystallizes with two half cations at inversion centres and the anion in a general position. The two independent Co–N(NO_2) distances of the cations are 1.954(2) and 1.921(2) Å, respectively, while in the anion, they are 1.901(2) and 1.901(2); the Co–N($-NO_2$) distances in the cation, being *trans* to another NO_2, are noticeably longer than those in the anion which are *trans* to oxalato oxygens and thus, we observe a *trans* influence. The Co1–N(NH_2) distances in the cations are 1.956(2) and 1.948(2) Å while those for Co2 are both 1.936(2) Å. For the anion, the Co3–N(NH_3) distances are 1.960(2) and 1.955(2) Å, while the Co3–O(ox) distances are 1.936(2) and 1.932(2) Å. For Co1, the N–O distances are 1.222(3), 1.225(3) Å; for Co2 they are 1.229(3) and 1.215(3) Å, while in the anion they are 1.232(3), 1.214(3), 1.230(3) and 1.236(3) Å, which means that there is no significant variation for the N–O distances between cation and anion. The C–N distances for Co1 are 1.471(3) and 1.474(4) Å; for Co2 they are 1.488(4) and 1.453(4) Å. The C–C bonds for the en ligands in Co1 and Co2 are, respectively 1.501(4) and 1.410(5) Å. The same N of Co2 which has the short Co–N distance is the one with the short N–C bond. We believe this is an artifact due to large thermal motion. The torsional angle N4–C3–C4–N5 (37.2°) is abnormally small, indicating that the ring is flattened by torsional thermal motion. In the anion, the O–C distances are 1.275(3), 1.288(3), 1.216(3) and 1.205(3) Å. The first two belong to the oxygens bound to the Co3 ion; thus it is not surprising the last two are shorter

Keywords: Conglomerates, crystallization, spontaneous resolution, cobalt(III), X-ray structure

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INTRODUCTION

Hereafter, the basal plane of the anion refers to the plane defined by the Co atom the two oxygens of the oxalate ligand and the two other ligands located *trans* to the oxalate oxygens. Abbreviations used in the text are (dien) = 1,5-diamino-3-azapentane, (trien) = 1,8-diamino-3,6-diazaoctane and (ox) = oxalate, with the following complexes indicated in bold roman:

[*trans*-$Co(en)_2(NO_2)_2$][*trans*-$(NH_3)_2Co(NO_2)_2(ox)$]	**(I)**
[*cis*-$Co(en)_2(ox)$]Br	**(II)**
[*cis*-$Co(en)_2(ox)$]Cl	**(III)**
[*cis*-$Co(en)_2(ox)$]$Cl.H_2O$	**(IV)**
[*cis*-$Rh(en)_2(ox)$]Cl	**(V)**
[$Co(dien)(NH_3)(ox)$]PF_6	**(VI)**
[$Co(dien)(NH_3)(ox)$]NO_3	**(VII)**
NH_4[*trans*-$(NH_3)_2Co(NO_2)_2(ox)$]	**(VIII)**
[*cis*-β-$Co(trien)(NO_2)_2$][*trans*-$(NH_3)_2Co(NO_2)_2(ox)$]	**(IX)**
[*cis*-α-$Co(trien)(NO_2)_2$]$Cl.H_2O$	**(X)**
[*cis*-$Co(en)_2(NO_2)_2$]Cl	**(XI)**
K or NH_4[Co-*trans*-$(NH_3)_2(NO_2)_4$]	**(XII)**

In 1899 Alfred Werner[1] reported a substantial solubility difference between the racemate and the enantiomers of the synthesis of [*cis*-$Co(en)_2(ox)$]Br (II). In 1914 he reported[5] (II) and, in effect, documenting the lower solubility of the latter, discovered conglomerate crystallization for this compound. Many years later Yamasaki *et al.*,[2] reported that the analogous chloride [*cis*-$Co(en)_2(ox)$]Cl (III) also undergoes conglomerate crystallization. Finally, Yamanari *et al.*,[3] reported a solubility study of the chloride and demonstrated that this system produces the hydrated conglomerate [*cis*-$Co(en)_2(ox)$]$Cl.H_2O$ (IV) below 36°C and an anhydrous conglomerate, [*cis*-$Co(en)_2(ox)$]Cl (III), above that temperature.

In 1977, Gillard and Tipping[4] demonstrated that the Rh analogue of (III), [*cis*-$Rh(en)_2(ox)$]Cl (V), also undergoes conglomerate crystallization. Presumably, the same is true of the bromide [*cis*-$Cr(en)_2(ox)$]Br, studied by Werner and Bosshart.[5]

In 1975, Couldwell, *et al.*,[6] reported the synthesis of mixed amine–dien complexes, [$Co(dien)(NH_3)(ox)$]X (X = PF_6 (VI) and X = NO_3 (VII). A complete structure determination was carried out on the latter (space group *Cc*; racemic) and the space group of the former was reported as $P2_12_12_1$. The fact that (VII) is racemic while (VI) is a conglomerate is not surprising given our previous discussion[7,8] of the effect the charge compensating anion has on conglomerate crystallization. The interested reader is referred to those papers for details.

Therefore it appears that a sizeable group of metal amine-oxalates undergo conglomerate crystallization and it is important, if possible, to ascertain why. We have shown that *cis*-dinitroamine complexes form conglomerates and provided persuasive evidence that the phenomenon is controlled by hydrogen bonds. The question now is whether similar hydrogen bonded interactions also consistently account for the observations on the oxalates. To address that problem, we have selected a series of compounds designed to probe the role of the amines in this regard.

EXPERIMENTAL

Syntheses

$NH_4[\textit{trans}\text{-}(NH_3)_2Co(NO_2)_2(ox)]$ (VIII)

This compound was prepared according to the procedure of Ito and Shibata.[9]

$[\textit{cis}\text{-}\beta\text{-}Co(trien)(NO_2)_2][\textit{trans}\text{-}(NH_3)_2Co(NO_2)_2(ox)]$ (IX)

The chloride of the cation, prepared as described before,[10] was placed in solution (water) in equimolar proportions with the ammonium salt of the anion (see above) and the resulting solution was allowed to crystallize.

$[\textit{trans}\text{-}Co(en)_2(NO_2)][\textit{trans}\text{-}(NH_3)_2Co(NO_2)_2(ox)]$ (I)

The cation, in the form of the chloride, was prepared according to a literature procedure.[11] Equimolar quantities (water solution) of it and the ammonium salt of the anion (see above) were allowed to crystallize. Tiny, but well formed, crystals of the double salt were filtered and used for the X-ray structure determination.

X-Ray Data Collection and Structure Determination

Data were collected with an Enraf-Nonius CAD-4 diffractometer operating with a Molecular Structure Corporation TEXRAY-230 modification[12] of the SDP-Plus software package.[13] Crystals suitable for X-ray diffraction were mounted on translation heads and centred in the diffractometer using reflections in the $20° \leqslant 2\theta \leqslant 30°$ range. Examination of the cell constants and Niggli matrix[14] showed them to crystallize as follows.

(VIII) crystallizes in the space groups Cc or $C2/c$ with cell constants $a = 8.244(2)$, $b = 18.420(9)$, $c = 7.207(4)$ Å and $\beta = 92.16(3)°$. The crystals are therefore racemic (if the correct space group is $C2/c$) or polar (but not enantiomorphic) if the correct space group is Cc. In either case, the crystals contain enantiomeric pairs.

(IX) crystallizes in a primitive monoclinic lattice whose systematic absences show it to belong to the space group $P2_1/c$ with cell constants $a = 10.070(2)$, $b = 6.452(5)$, $c = 30.093(15)$ Å and $\beta = 94.97(3)°$. The substance is thus racemic. In comparison, Shintani, Sato and Saito[15] reported a complete structural analysis of the externally resolved species $[(-)_{589}\text{-}\textit{cis}\text{-}Co(en)_2(NO_2)_2][(-)_{589}\text{-}\textit{trans}\text{-}(NO_2)_2Co(NH_3)_2\text{-}(ox)]\cdot H_2O$ (XIII), which crystallizes in the space group $P2_12_12_1$ with cell constants $a = 12.643(2)$, $b = 24.948(2)$, $c = 6.594(1)$ Å.

Compound (I) crystallizes in either $P1$ or $P\bar{1}$ with cell constants $a = 6.534(6)$ Å, $b = 10.922(9)$, $c = 14.905(7)$ Å, $\alpha = 94.44(5)$, $\beta = 94.69(7)$ and $\gamma = 105.41(1)°$, $V = 1016.09$ Å^3, d(calc; $Z = 2$) $= 1.778$ g cm^{-3} and $\mu = 17.028$ cm^{-1} for Mo$K\alpha$.

Intensity data were corrected for absorption using empirical curves derived from Psi scans[12,13] of six reflections. The scattering curves were taken from Cromer and Waber's compilation.[16] Details of data collection and processing parameters are summarized in Table I.

The structure of (I) was solved by assuming the space group to be $P1$ and placing a Co at an arbitrary position in the cell (0.32831, 0.32831, 0.32831); after refining the scale factor, a difference Fourier map readily produced the other two Co atoms as well as a few of the nitrogens, oxygens and carbons of the cations and anions. Heavy atoms were refined isotropically for three cycles and a new difference map computed, whereupon most of the missing O, N and C atoms were found. Repetition of this procedure yielded the rest of the heavy atoms. Hydrogen atoms of the cation were added at idealized positions (N–H and C–H = 0.95 Å) and all heavy atoms allowed to refine (hydrogen positional and thermal parameters fixed, $B = 5.0$ Å^2). A difference Fourier revealed no water molecules present in crystals of (**I**), which accords with the elemental analysis of the crystalline material.

TABLE I

Summary of data collection and processing parameters for [*trans*-$Co(en)_2(NO_2)_2$][*trans*-$(NH_3)_2Co(NO_2)_2(ox)$].

Space Group	$P\bar{1}$
Cell Constants	$a = 6.534(6)$ Å
	$b = 10.922(9)$
	$c = 14.905(7)$
	$\alpha = 94.44(5)°$
	$\beta = 94.69(7)$
	$\gamma = 105.41(1)$
Cell Volume	$V = 1016.09$ Å^3
Molecular Formula	$Co_2O_{12}N_{10}C_6H_{22}$
Molecular Weight	544.17
Density (calc; Z = 2)	1.778 g cm^{-1}
Radiation	Mo$K\alpha$ ($\lambda = 0.71073$ Å)
Absorption Coefficient	$\mu = 17.028$ cm^{-1}
Relative Transmission Coefficients	1.000 to 0.7932
Data Collection Range	$4° \leqslant 2\theta \leqslant 50°$
Scan Width	$\Delta\theta = 1.2 + 0.35\tan\theta$
Total Data Collected	3824
Data Used In Refinement*	2994
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.072
$Rw = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.108
Weights Used	$w = [\sigma(F_o)]^{-2}$

* The difference between this number and the total is due to subtraction of 830 redundant data which were collected to obtain reflections suitable for the absorption correction, were symmetry related, or did not meet the criterion that $1 \geq 3\sigma(I)$.

Given the coordinates of the atoms at this stage, it became clear that the two cations were related by an inversion centre. Thus, the correct space group is $P\bar{1}$ and the cations were located at inversion centres (0.0000, 0.0000, 0.0000 and 0.5000, 0.0000, 0.5000) as shown in Table II. This result is in accord with the NZTEST and the Rogers Plot,[12,13] both of which show a centrosymmetric distribution of intensities. Upon convergence of the isotropic refinement with the correct space group and the shifted coordinates, non-hydrogen atoms were assigned anisotropic motion; hydrogens were refined with fixed thermal parameters ($B = 5.0$ Å^2). The coordinates from the last cycle of refinement are summarized in Table II while bond lengths, angles, torsional angles and hydrogen contacts are reported in Table III. Labelled views of the contents of the asymmetric unit and of the packing diagram are given in Figs. 1 and 2.

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

Atom	x/a	y/b	z/c	B(Å²)
Co1	0.000	0.000	0.000	1.8
Co2	0.500	0.000	0.500	1.8
Co3	0.6124(2)	−0.4275(1)	0.28920(8)	2.12(2)
O1	−0.431(1)	−0.1143(7)	−0.0351(5)	3.7(2)
O2	−0.301(1)	−0.1716(7)	0.0852(5)	4.6(2)
O3	0.198(1)	−0.2089(7)	0.4117(5)	3.9(2)
O4	0.086(1)	−0.1234(9)	0.5228(6)	5.2(2)
O5	0.412(1)	−0.4212(7)	0.4418(5)	4.2(2)
O6	0.205(1)	−0.5307(9)	0.3314(6)	5.6(2)
O7	0.713(1)	−0.6532(7)	0.2579(6)	4.5(2)
O8	0.407(1)	−0.6615(7)	0.1948(6)	5.0(2)
O9	0.854(1)	−0.3783(6)	0.2199(4)	2.6(1)
O10	0.6733(9)	−0.2466(5)	0.3250(4)	2.4(1)
O11	1.113(1)	−0.2073(6)	0.1999(4)	3.0(1)
O12	0.891(1)	−0.0643(6)	0.2960(5)	3.2(2)
N1	0.120(1)	−0.1456(7)	0.0065(5)	2.3(2)
N2	−0.057(1)	−0.0564(7)	−0.1291(5)	2.4(2)
N3	−0.279(1)	−0.1094(7)	0.0199(5)	2.5(2)
N4	0.633(1)	−0.1373(7)	0.5112(5)	2.4(2)
N5	0.477(1)	−0.0017(7)	0.6288(5)	2.6(2)
N6	0.228(1)	−0.1251(7)	0.4751(5)	2.6(2)
N7	0.417(1)	−0.4048(8)	0.1890(6)	3.6(2)
N8	0.808(1)	−0.4446(7)	0.3909(5)	2.6(2)
N9	0.382(1)	−0.4659(7)	0.3618(6)	2.8(2)
N10	0.571(1)	−0.6005(7)	0.2429(6)	3.0(2)
C1	0.060(2)	−0.2311(9)	−0.0783(7)	3.1(2)
C2	0.068(2)	−0.146(1)	0.1530(7)	3.2(2)
C3	0.598(2)	−0.186(1)	0.6007(8)	5.0(3)
C4	0.585(2)	−0.087(1)	0.6646(8)	5.4(3)
C5	0.948(1)	−0.2591(8)	0.2304(6)	2.3(2)
C6	0.833(1)	−0.1792(8)	0.2895(6)	2.3(2)
H17	0.082	−0.375	0.592	
H18	0.277	−0.479	0.559	
H19	0.109	−0.500	0.643	
H1	0.05(2)	−0.19(1)	0.048(7)	
H2	0.22(2)	−0.14(1)	0.012(7)	
H3	−0.08(2)	−0.28(1)	−0.069(7)	
H4	0.16(2)	−0.28(1)	−0.083(7)	
H5	0.03(2)	−0.17(1)	−0.186(7)	
H6	0.23(2)	−0.09(1)	−0.160(7)	
H7	−0.20(2)	−0.11(1)	−0.138(7)	
H8	−0.02(2)	−0.01(1)	−0.157(7)	
H9	0.78(2)	−0.09(1)	0.485(7)	
H10	0.54(2)	−0.13(1)	0.439(7)	
H11	0.69(2)	−0.21(1)	0.617(7)	
H12	0.43(2)	−0.24(1)	0.605(7)	
H13	0.82(2)	−0.04(1)	0.633(7)	
H14	0.56(2)	−0.10(1)	0.702(7)	
H15	0.55(2)	−0.08(1)	0.641(7)	
H16	0.31(2)	−0.02(1)	0.613(7)	

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[a] Hydrogen atoms were refined isotropically. 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
Selected bond lengths and angles for **I**.

Lengths (Å)			
Co1–N1	1.956(2)	Co1–N2	1.948(2)
Co1–N3	1.954(2)	O1–N3	1.222(3)
O2–N3	1.225(3)	N1–C1	1.471(3)
N2–C2	1.474(4)	C1–C2	1.501(4)
Co2–N4	1.936(2)	Co2–N5	1.936(2)
Co2–N6	1.921(2)	O3–N6	1.229(3)
O4–N6	1.215(3)	N4–C3	1.488(4)
N5–C4	1.453(4)	C3–C4	1.410(5)
Co3–O9	1.936(2)	Co3–O10	1.932(2)
Co3–N7	1.960(2)	Co3–N8	1.955(2)
Co3–N9	1.901(2)	Co3–N10	1.901(2)
O5–N9	1.232(3)	O6–N9	1.214(3)
O7–N10	1.230(3)	O8–N10	1.236(3)
C5–C6	1.562(3)	O9–C5	1.275(3)
O10–C6	1.288(3)	O11–C5	1.216(9)
O12–C6	1.205(3)		
Angles (°)			
N1–Co1–N2	84.51(9)	N1–Co1–N3	89.67(8)
N2–Co1–N3	90.18(8)	Co1–N1–C1	110.75(16)
Co1–N2–C2	109.79(16)	Co1–N3–O1	117.80(17)
Co1–N3–O2	121.44(16)	O1–N3–O2	120.76(20)
N1–C1–C2	105.94(21)	N2–C2–C1	106.78(23)
N4–Co2–N5	87.19(9)	N4–Co2–N6	88.92(9)
N5–Co2–N6	90.59(9)	Co2–N4–C3	108.71(16)
Co2–N5–C4	108.58(17)	Co2–N6–O3	119.77(17)
Co2–N6–O4	120.28(18)	O3–N6–O4	119.93(22)
N4–C3–C4	110.07(28)	N5–C4–C3	114.54(28)
N7–Co3–N8	178.12(9)	N7–Co3–N9	89.68(10)
N7–Co3–N10	90.38(9)	N8–Co3–N9	89.97(9)
N8–Co3–N10	91.49(9)	N9–Co3–N10	94.11(9)
O9–Co3–O10	84.56(7)	O9–Co3–N7	91.41(9)
O9–Co3–N8	88.83(3)	O9–Co3–N9	176.39(8)
O9–Co3–N10	89.33(8)	O10–Co3–N7	87.70(8)
O10–Co3–N8	90.46(7)	O10–Co3–N9	92.05(7)
O10–Co3–N10	173.54(8)	Co3–O9–C5	114.11(14)
Co3–O10–C6	113.29(14)	Co3–N9–O5	118.89(16)
Co3–N9–O6	122.04(19)	Co3–N10–O7	119.89(17)
Co3–N10–O8	121.91(18)	O5–N9–O6	119.05(22)
O7–N10–O8	118.15(21)	O9–C5–O11	126.03(22)
O9–C5–C6	113.46(20)	O11–C5–C6	120.50(21)
O10–C6–O12	125.44(22)	O10–C6–C5	114.29(19)
O12–C6–C5	120.20(21)		
Torsional Angles (°)			
Co1–N1–C1–C2	38.2	Co1–N2–C2–C1	40.8
N1–C1–C2–N2	−50.7	Co2–N4–C3–C4	−30.5
Co2–N5–C4–C3	−25.3	N4–C3–C4–N5	37.2
Co3–O9–C5–C6	−5.5	Co3–O10–C6–C5	−3.1
O9–C5–C6–O10	5.9	O9–C5–C6–O12	−171.3
O11–C5–C6–O10	−173.4	O11–C5–C6–O12	9.4
Co3–O9–C5–O11	173.7	Co3–O10–C6–O12	173.9

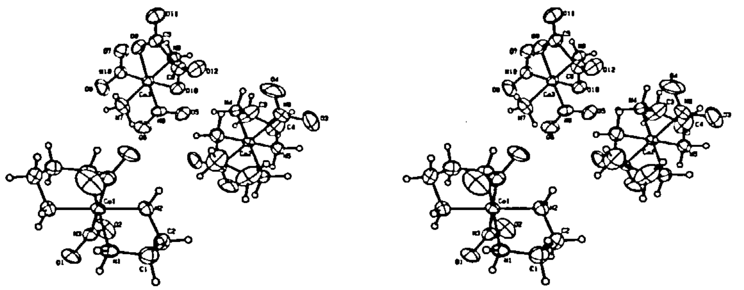

FIGURE 1 An ORTEP stereoview of [*trans*-$Co(en)_2(NO_2)_2$][*trans*-$(NH_3)_2Co(NO_2)_2$(oxalato)] showing the contents of the asymmetric unit.

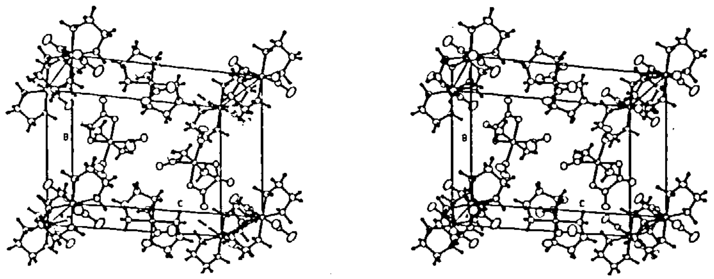

FIGURE 2 Stereoview of the packing of the ions of (I) in the unit cell. Note that the cations and anions are arranged in rows in which cations and anions are intercalated. Each adjacent row is displaced from the previous one by one Co unit such that cation–anion interactions between rows are coulombically feasible.

RESULTS AND DISCUSSION

Before discussing the oxalate results we should like to recall some earlier data and conclusions. Our first observation of conglomerate crystallization in Co(III) compounds was in the case of (X).

Compound	*Space Group*	*Ref.*
[*cis*-α-Co(trien)$(NO_2)_2$] Cl.H_2O (X)	$P2_12_12_1$	7
[*cis*-$Co(en)_2(NO_2)_2$] Cl. (XI)	$P2_1$	7
K or NH_4[*trans*-Co-$(NH_3)_2(NO_2)_4$] (XII)	$P2_12_12_1$	7

At that time[7] we argued that, if conglomerate crystallization was affected by intramolecular interactions, small alterations in the various ligands could provide valuable information about their relative importance to the mechanism of conglomeration. Thus (XI) and (XII) were prepared and found to produce conglomerates, leading, at that time, to the conclusion[7] that compounds containing the fragments [Co-*trans*$(NH_3)_2$-*cis*$(NO_2)_2$] and [Co-*trans*$(-NH_2)_2$-*cis*$(NO_2)_2$] seemed to produce an unusually high proportion of conglomerate crystallizations.

Compound	*Space Group*
[*cis*-Co(en)$_2$(NO$_2$)$_2$][*trans*-Co(NH$_2$)$_2$(NO$_2$)$_4$] (XIV)[17]	$P2_12_12_1$
[*cis*-α-Co(trien)(NO$_2$)$_2$][*trans*-Co(NH$_3$)$_2$(NH$_2$)$_2$(NO$_2$)$_4$] (XV)[17]	$P2_12_12_1$
[*cis*-β-Co(trien)(NO$_2$)$_2$][*trans*-Co(NH$_3$)$_2$(NH$_2$)$_2$(NO$_2$)$_4$] (XVI)[18]	$P2_1/c$
[*trans*-Co(en)$_2$(NO$_2$)$_2$][*trans*-Co(NH$_3$)$_2$(NO$_2$)$_4$] (XVII)[18]	$P\bar{1}$

We have also documented that (XIV) and (XV) are conglomerates[17] while (XVI) and (XVII) are racemates.[18] Moreover, we note that the behaviour of the latter two is fully consistent with our observation[8] that there is no known case of conglomerate crystallization for either of the cations [*cis*-β-Co(trien)(NO$_2$)$_2$]$^+$ or [*trans*-Co(en)$_2$(NO$_2$)$_2$]$^+$, irrespective of the nature of the compensating anion, unless the latter is a chiral species. Compounds (XVI) and (XVII) represent further confirmation of that observation.

In as much as the above strategy of making small changes in a given cation or anion and crystallizing it with a suitable counterion gave us considerable help in establishing the molecular basis of conglomerate behaviour for the nitro compounds, we decided to follow similar strategy for the oxalate derivatives.

The anion with composition [(NH$_3$)$_2$Co(NO$_2$)$_2$(ox)]$^-$ was selected as a trial species because of the following interesting features it possesses.

(a) It can be prepared as two different geometrical isomers,[9] one of which, [*trans*-(NO$_2$)$_2$Co-*cis*-(NH$_3$)$_2$(ox)]$^-$(XIII) was studied in pre-resolved form by Shintani, Sato and Saito.[15] It can also be prepared as the [*trans*-(NH$_3$)$_2$Co-*cis*-(NO$_2$)$_2$(ox)]$^-$ anion, which we have prepared as salts, (I), (VIII), (IX) and (XIV).

(b) We know that salts of the anion of (XII), [*trans*-(NH$_3$)$_2$Co(NO$_2$)$_4$, and of the cation, [*cis*-(NO$_2$)$_2$Co(NH$_3$)$_4$$^+$, undergo conglomerate crystallization.[7] Therefore, it would be useful to establish if substitution of either two –NO$_2$ ligands or two –NH$_3$ ligands by the oxalate oxygens has an effect on the crystallization mode. We have already documented that when the cations, NH$_4$$^+$, K$^+$ and [*cis*-(NO$_2$)$_2$Co(en)$_2$]$^+$ are used as counter ions to [*trans*-(NH$_3$)$_2$Co(NO$_2$)$_4$]$^-$, conglomerate crystallization occurs. However, if the cations [*trans*-(NO$_2$)$_2$Co(en)$_2$]$^+$ or [*cis*-β-(NO$_2$)$_2$Co(trien)]$^+$ are used in conjunction with the anion [*trans*-Co-(NH$_3$)$_2$(NO$_2$)$_4$]$^-$, racemic crystals are obtained. We therefore prepared (I), (VIII), (IX) and (XIV) to determine if the same crystallization pattern as above is followed.

The results are listed below.

Compound	*Space Group*
NH$_4$[*trans*-(NH$_3$)$_2$Co(NO$_2$)$_2$(ox)] (VIII)	$C2/c$
[*cis*-β-Co(trien)(NO$_2$)$_2$][*trans*-(NH$_3$)$_2$Co(NO$_2$)$_2$(ox)] (IX)	$P2_1/c$
[*cis*-Co(en)(NO$_2$)$_2$][*trans*-(NH$_3$)$_2$Co(NO$_2$)$_2$(ox)] (XVIII)	$P2_1/c$
[*trans*-Co(en)$_2$(NO$_2$)$_2$][*trans*-(NH$_3$)$_2$Co(NO$_2$)$_2$(ox)] (I)	$P\bar{1}$

Inasmuch as there is no known case of conglomerate crystallization for any salt of either of the cations, [*cis*-β-Co(trien)(NO$_2$)$_2$]$^+$ or [*trans*-Co(en)$_2$(NO$_2$)$_2$], we were not surprised that neither of them produced a conglomerate with [*trans*-(NH$_3$)$_2$Co-(NO$_2$)$_2$(ox)]. However, since conglomerate crystallization occurs for the anion [*trans*-Co(NH$_3$)$_2$(NO$_2$)$_4$]$^-$ with both NH$_4$$^+$, K$^+$ and [*cis*-Co(en)$_2$(NO$_2$)$_2$]$^+$, the replacement of two $-NO_2$ ligands by oxalate appears to cause these salts to crystallize as racemates, despite the fact the fragment [Co-*trans*-$(NH_3)_2$-*cis*-$(NO_2)_2$] is still common to all of them.

In that regard we note an interesting topological feature of the [*trans*-$(NH_3)_2Co(NO_2)_2$] fragment, namely the torsional angles N–Co–N–O by way of comparison with those in K[*trans*-$(NH_3)_2Co(NO_2)_4$] (XII) as shown below.

[*trans*-$(NH_3)_2Co(NO_2)_2(ox)$]		[*trans*-$(NH_3)_2Co(NO_2)_4$]	
N7–Co–N9–O5	−138.6°	N1–Co–N5–O5	12.5°
N7–Co–N9–O6	39.9°	N1–Co–N5–O6	−174.8°
N8–Co–N9–O5	39.6°	N2–Co–N5–O5	−167.3°
N8–Co–N9–O6	−142.0°	N2–Co–N5–O6	5.4°
N8–Co–N10–O7	28.2°	N1–Co–N6–O7	168.4°
N8–Co–N10–O8	154.5°	N1–Co–N6–O8	− 9.9°
N9–Co–N10–O7	−118.2°	N2–Co–N6–O7	− 12.5°
N9–Co–N10–O8	64.4°	N2–Co–N6–O8	169.2°

The nitrogens and oxygens of the $-NO_2$ ligands in the latter are those which form the shortest intramolcular hydrogen bonds (ranging from 2.03 Å to 2.06 Å). In the former, not only are the torsional angles very different but, as expected from that observation, the intramolecular hydrogen bonds were found to be longer than 2.30 Å. In fact, in (I) the shortest hydrogen bonds for the anion are interionic, as shown in Table III. This behaviour is typical of racemates in which interionic hydrogen bonds are stronger than the intramolecular ones.[7,8,10]

The stereochemistry of the Co(oxalate) group

Because the projection chosen by Shintani, Sato and Saito[15] to display the anion [*cis*-$(NH_3)_2$-Co-*cis*-$(NO_2)_2(ox)]^-$ does not properly show the stereochemistry we are about to discuss, we show their anion below (Fig. 3).

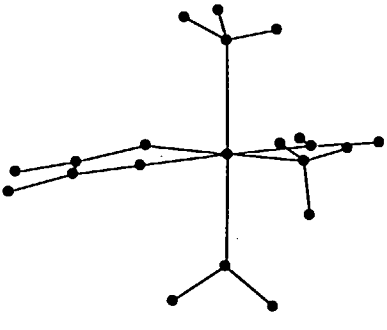

FIGURE 3 The structure of the anion [*cis*-$(NH_3)_2$-Co-*cis*-$(NO_2)_2(ox)]^-$ of Shintani, *et al.*,[15] drawn in such a projection as to show the folding of the oxalate ligand along the line of the two oxygens bound to the cobalt atom.

Comparison of their results with those of ours (see Figs. 1 and 2) reveal that our anion contains a non-planar oxalate fragment, which is readily proven by the torsional angles as follows.

Torsional Angle	*Anion of* (I)	[*cis*-$(NH_3)_2$-*Co*$(NO_2)_2$(ox)]$^-$
Co3–O9–C5–C6	−5.5°	8.1°
Co3–O10–C6–C5	−3.1°	−8.5°
O9–C5–C6–O10(chelate)	5.9°	−2.1°
O11–C5–C6–O12	9.4°	0.5°

As pictorially shown in the figures, and demonstrated by the torsional angular data, the oxalate ligand in [*cis*-$(NH_3)_2$-Co$(NO_2)_2$(ox)]$^-$ remains almost exactly-planar but it is folded along the vector of the two oxygen ligands such that the O–Co–O plane does not coincide with the plane of the oxalate ligand. This is not the case with the anion of (I) which is best described as having a nearly planar Co–O–C–C–O fragment with a slightly twisted (−2.88°) O–C–C–O fragment for the chelated side of the oxalate.

If one inquires as to the location of the non-bonded pairs of the oxalate oxygen ligands in [*cis*-$(NH_3)_2$-Co-*cis*$(NO_2)_2$(ox)]$^-$, it is clear they are pointing in the direction of the amine hydrogens, the O ... H distance (shortest one) being 2.69 Å. However, since the non-bonded lobes of the oxygens must have a reasonable spatial extension (say, 0.5 Å), the distance between the centre of electron density of the non-bonded lobe and the hydrogen must be shorter and therefore may constitute a non-trivial hydrogen-bonded interaction.

In the anion of (I), the two $-NH_3$ ligands are *trans* to each other and symmetrically distributed with respect to the oxalate moiety. Thus, whatever interaction occurs with one axial $-NH_3$ is balanced by an approximately equal, and opposite, interaction with the other one. The result is a more twisted oxalate ligand.

Such observation is significant and revealing since it demonstrates the stereochemical role played by the non-bonded electron pair of oxalate ligands in metal complexes of the type under consideration. This role is similar to that we have attributed[7,8,10,17] to the non-bonded pairs of oxygens present in other ligands, such as $-NO_2$, in that they are obviously affected by the proximity of hydrogens on axial $-NH_3$ or $-NH_2$ ligands. Thus, the fact that compounds such as (II) to (VI) conglomerate while (I) does not constitutes a significant observation towards an eventual understanding of the molecular basis underlying conglomerate crystallization.

In the former compounds ((II) to (VI)) the oxalate oxygens share the octahedral array of the metal with four $-NH_2$ ligands of the ethylenediamines; two located in the axial direction and two in the basal plane. Thus, since the fragment [*cis*-Co$(en)_2$XY] is expected to have a two-fold axis of symmetry, the oxalate should sense a symmetrical environment (*i.e.*, an $-NH_2$ above and below the basal plane). This is indeed the case, as demonstrated by the structural results obtained with the externally resolved compounds $\Delta(\lambda\delta)](-)_{589}$-Co$(en)_2$(ox)]Br.$H_2O$[19] (XIX) and $\Lambda(\lambda\delta)](+)_{589}$-Co$(en)_2$(ox)][(*R*,*R*)tartH].$H_2O$[20] (XX) in which the oxalate ligand was found[19,20] to be planar and symmetrically distributed between the two axial $-NH_2$ terminal moieties. In (I) there are two $-NH_3$ ligands in the axial positions; consequently, one would expect a planar, symmetrically distributed oxalate ligand as experimentally found here.

Evidence for the interaction of the $-NH_3$ ligand or the terminal $-NH_2$ group of en ligands with the oxalate oxygen non-bonded pairs comes from another observation, namely, that the conformation of the en ligands in (XIX) and (XX) is not the lowest energy one. In each of these substances one of the en rings has the conformation opposite to that expected, given the configuration of the bidentate en ligands about the central Co atom. This change in conformation has previously been documented,[21] for the case of [*cis*-$Co(en)_2(NO_2)_2]^+$ derivatives, to be due to intramolecular hydrogen bonds between $-NO_2$ oxygens with amine hydrogens which are enhanced in strength by the inversion of the en ring torsional angle. Given the observation above, a similar phenomenon is probably responsible for such inversion in (XIX) and (XX).

It has recently been shown[22,23] that in the series, *cis*- or *trans*-$[Co(NH_3)_4(NO_2)_2]X$, only the nitrate derivative forms conglomerates and that this is due to the fact that the nitrate anion helps the $-NO_2$ ligands lock the amines in a dissymmetric conformation. Intramolecular hydrogen bonds from the $-NO_2$ oxygens of only a pair of $-NO_2$ ligands are not capable of doing this by themselves.[22,23] In the oxalate series[23], $[Co(NH_3)_4(oxalato)]X$, X = I, NO_3, only the nitrate forms a conglomerate. The role of the nitrate anion in this compound is similar to that described above.

These results, when viewed together, indicate that with a pair of *trans* $-NH_3$ ligands, conglomerate crystallization is not induced by a pair of nitro groups *cis* or *trans* if the remaining two ligands are $-NH_3$, an oxalato and two $-NO_3$ ligands, or an oxalato and two $-NH_2$ ligands. However, the nitrate anion is capable of synergistically interacting with a number of those groups to induce conglomerate crystallization. Finally, it has recently been demonstrated by Urland and Niketic[24] that the orientation of non-bonded pairs of oxygen atoms in bidentate ligands can play a crucial role in the determination of the size of the crystal field around a central ion. This effect has been demonstrated, experimentally, to be as large as *ca* $2000\,cm^{-1}$. Thus it is expected that details of the stereochemistry of the non-bonded pair of bidentate ligands would affect not only the crystal field of the central ion but the stereochemistry of $-NH_2$ or $-NH_3$ ligands located in the axial positions.

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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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