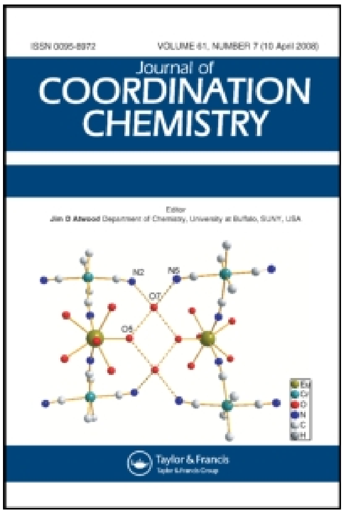

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THE CRYSTALLIZATION BEHAVIOR OF [cis-α-Co(trien)(OX)]Cl $2H_2O$ (I), [cis-α-Co(trien)$(NO_2)_2$]BF_4 (II), [cis-α-Co(trien)$(NO_2)_2$]-(cis-α-Co(trien)(OX)]Cl l/2SiF_6 (III)

Ruiwu Wen[a]; Ivan Bernal[a]
[a] Chemistry Department, University of Houston, Houston, TX, USA

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THE CRYSTALLIZATION BEHAVIOR OF [*cis*-*α*-Co(trien)(OX)]Cl · $2H_2O$ (I), [*cis*-*α*-Co(trien)$(NO_2)_2$]BF_4 (II), [*cis*-*α*-Co(trien)$(NO_2)_2$]-[*cis*-*α*-Co(trien)(OX)]Cl · 1/2SiF_6 (III)

RUIWU WEN and IVAN BERNAL*

Chemistry Department, University of Houston, Houston, TX 77204-5641, USA

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Three new compounds were synthesized and their crystal structures determined. For compound (I), [*cis*-*α*-Co(trien)(OX)]Cl · $2H_2O$, $CoClO_6N_4C_8H_{22}$, triclinic, space group P-1 (No. 2) $a = 6.980(5)$, $b = 8.801(4)$, $c = 12.554(8)$ Å, $\alpha = 89.07(5)°$, $\beta = 75.74(4)°$, $\gamma = 81.44(5)°$, $V = 738.9(8)$ Å^3, cell dimensions were obtained from 24 reflections giving FW = 364.4, $Z = 2$, $F(000) = 380.06$, Dcalc = 1.634 mg · m^{-3}, $\mu = 1.36$ mm^{-1}. A total of 1907 data were collected over the range of $4° \leq 2\theta \leq 45°$; of these, 1647 (independent and $I \geq 3\sigma(I)$) were used in the structure analysis. Data were corrected for absorption; transmission coefficients ranged from 0.51754 to 0.73648. The final RF and Rw residuals were 0.033 and 0.042.

For compound (II), [*cis*-*α*-Co(trien)$(NO_2)_2$]BF_4, $CoN_6C_6O_4BF_4H_{18}$, orthorhombic space group Pbca (No. 61) $a = 12.260(10)$, $b = 12.880(14)$, $c = 17.940(14)$ Å $V = 2833(4)$ Å^3, cell dimensions were obtained from 24 reflections with 2θ in the range of 4.00–45.00 degrees, FW = 383.98, $Z = 8$, $F(000) = 1571.52$, Dcalc = 1.801 mg · m^{-3}, $\mu = 1.28$ mm^{-1}, $\lambda = 0.70930$ Å. A total of 1637 data were collected over the range of $4° \leq 2\theta \leq 45°$; of these, 883 (independent and $I \geq 2.5\sigma(I)$) were used in the structure analysis. The final RF and Rw residuals were 0.122 and 0.132.

For compound (III), [*cis*-*α*-Co(trien)(OX)][*cis*-*α*-Co(trien)$(NO_2)_2$]Cl · 1/2SiF_6, Co_2ClSi-1/2$N_{10}C_{14}F_3O_{12}H_{36}$, orthorhombic, space group Pbca (No. 61) $a = 12.804(10)$, $b = 16.543(10)$, $c = 27.419(23)$ Å, $V = 5808(7)$ Å^3, cell dimensions were obtained from 25 reflections, FW = 760.85, $Z = 8$, $F(000) = 3136.06$, Dcalc = 1.740 mg · m^{-3}, $\mu = 1.34$ mm^{-1}, $\lambda = 0.70930$ Å. A total of 2657 data were collected over the range of $4° \leq 2\theta \leq 40°$; of these, 1902 (independent and $I \geq 2.5\sigma(I)$) were used in the structure analysis. The final RF and Rw residuals were 0.058 and 0.062.

Keywords: Conglomerate; racemate; coordination chemistry of Co(III); trien; dinitro compounds; oxaloto compounds

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* Corresponding author. E-mail: ibernal@uh.edu.

INTRODUCTION

Conglomerate crystallization is the phenomenon whereby a racemic solution produces a mechanical mixture of enantiomorphic crystals, the unit cell of which is homochiral.

In our previous studies of conglomerate behavior of cobalt(III) amine complexes, we found that hydrogen bonding plays an important role in selecting the crystallization pathway. In compounds [*cis*-$Co(en)_2(NO_2)_2$]X ($X = Cl^-, Br^-, I^-$), strong intermolecular hydrogen bonds involving nitro oxygens of one cation and amine hydrogens of an adjacent one helped to hold the cations together.$^{1-3}$ The halides and/or waters of crystallization (where relevant) linked the pair of basal amine hydrogens, thus forming helix-like infinite conglomerate chains.

We have proposed that the charge compensating counter anion is very important in conglomerate crystallization. When halide anions are replaced by powerful hydrogen bonding species such as NO_3^-, or NO_2^-, they successfully compete for the amino hydrogens with the nitro (NO_2) oxygens and racemic crystals were obtained since helix formation is hindered.[4,5]

Compounds $[Co(en)_2(OX)]Cl \cdot 4H_2O$, $[Co(en)_2(OX)]Br \cdot H_2O$, $[Co(en)_2(OX)]I$ are also known to crystallize as conglomerates,[6,7] and exhibit the same infinite helical chain interactions. The hydrogen bonds are between terminal oxalate oxygens and basal plane amino hydrogens of adjacent cations. The helical chains are joined to each other by hydrogen-bonded interactions with the anions and/or the waters of crystallization. $[Co(en)_2(OX)]F \cdot 11.5H_2O$ crystallized as kryptoracemate,^{8} while $[Co(en)_2(OX)]PF_6$ crystallized as a racemate.^{6}

The crystallization pathway of compounds with general formula [*cis*-α-$Co(trien)(NO_2)_2]X \cdot H_2O$ are also consistent with this proposal. Compounds [*cis*-α-$Co(trien)(NO_2)_2]X \cdot H_2O$ ($X = Cl^-, I^-$), crystallized as conglomerates,^{1,3} which showed the same hydrogen-bonding pattern discussed above. And, when using a powerful hydrogen-bonding counter anion, such as [*cis*-α-$Co(trien)(NO_2)_2]X$ ($X = NO_3^-$) crystallized as a racemate.[2] However, it should be pointed out that the conglomerate crystallization mechanism for this series of compounds is different from that of [*cis*-$Co(en)_2(NO_2)_2$]X and of $[Co(en)_2(OX)]X$. For the latter case, the cation forms hydrogen bonds with the adjacent cations and forms spiral chains while the halide and water of crystallization stitch the chains together. In the *cis*-α-trien series, a pair of intermolecular hydrogen bonds locks two cations into a close pair, and the halide and water link these pairs together. Further, we reported that when the secondary amine hydrogen is missing, halides would have to go to the terminal $-NH_2$ hydrogens to form hydrogen bonds, destroying the hydrogen bonding pattern necessary for conglomerate crystallization. Such is the case with compounds [*cis*-α-Co(L)$(NO_2)_2$]X (L = 3,6-dithiaoctane-1,8-diamine, X = Cl, Br).[9,10] We also reported that [*cis*-α-Co(L)$(NO_2)_2$]X (L = 3,6-dithiaoctane-1,8-diamine, X = BF_4^-, BF_2O^-) crystallized as racemates, but as conglomerate when X = ClO_4^-, for which we have found no reasonable explanation.[9–11]

To further investigate conglomerate crystallization behavior, we wanted to determine the crystallization behavior of compounds with general formula [*cis*-Co(trien)(OX)]X, and/or [*cis*-Co(tren)(OX)]X. When trying to obtain [*cis*-α-Co(trien)(OX)]X (X = Cl, BF_4^-, $1/2SiF_6^{2-}$), the title compounds were obtained.

EXPERIMENTAL

Preparation of the Compounds

[*cis*-α-Co(trien)$(NO_2)_2$]Cl · H_2O [*cis*-α-Co(trien)$(NO_2)_2$]Cl · H_2O was prepared using the method described earlier,[12] and used in the following steps without further purification.

[*cis*-α-Co(trien)(OX)]Cl · $2H_2O$ (**I**) [*cis*-α-Co(trien)$(NO_2)_2$]Cl · H_2O (1.17 g, 3.3 mmol) was dissolved in 50 ml deionized water. To that solution, HOOC-COOH (0.31 g, 3.3 mmol) was added and the solution was heated to 80°C in a water bath. Soon the solution changed color and in about 40 min, it evaporated to dryness. Deionized water (50 mL) was added, and then heated to dryness again. More deionized water (20 mL) was added, and the solution kept at room temperature; after one day, red crystals suitable for X-ray structure analysis were obtained.

[*cis*-α-Co(trien)$(NO_2)_2$]BF_4 (**II**) and [*cis*-α-Co(trien)$(NO_2)_2$][*cis*-α-Co(trien)(OX)]Cl · $1/2SiF_6$ (**III**) The procedure for synthesizing [*cis*-α-Co(trien)(OX)]Cl · $2H_2O$ (**I**) was repeated. Deionized water (50 mL) was added to the beaker. Then the solution was separated into two parts. A saturated solution of either $NaBF_4$ or Na_2SiF_6 was added to one of the parts. After slow evaporation, compounds (**II**) and (**III**) were obtained. Crystals suitable for X-ray analysis were obtained after recrystallization from water.

X-ray Crystallography

Data were collected with an Enraf-Nonius CAD-4 diffractometer. The procedure used for crystal alignment, cell constant determination, space group determination, and data collection were uniform for all crystals.

A crystal of compound (**I**) was centered in the $4^\circ \leq 2\theta \leq 45^\circ$ range. Cell dimensions were obtained from 24 reflections. A crystal of compound (**II**) was centered in the $4^\circ \leq 2\theta \leq 45^\circ$ range. Cell dimensions were obtained from 24 reflections. A crystal of compound (**III**) was centered in the $4^\circ \leq 2\theta \leq 40^\circ$ range. Cell dimensions were obtained from the fitting of all 24 reflections.

Processing of the data was carried out with the PC version of the NRCVAX package.[13] The structures were solved from the Patterson maps, 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. Most of the hydrogens of compound (**I**) were found in the difference maps. The other hydrogens were added at ideal positions and used for least squares calculations. The details of data collection are summarized in Tables I–III for compounds (**I**), (**II**) and (**III**). These structures are shown in Figures 1–3 and the results from the structure determinations are given in Tables IV–IX.

RESULTS AND DISCUSSION

Compound (**I**) crystallized as a racemate in the primitive triclinic system, whose systemic absences belong to the space group P1 (No. 1) or P-1 (No. 2). Using the space group P-1, the structure was determined and the refinement proceeded smoothly. The compound consists of the complex [*cis*-α-Co(trien)(OX)]$^+$ cation, a Cl^- counter anion and two waters of crystallization. Compound [*cis*-α-Co(trien)(OX)]Cl$\cdot$4.5H_2O was synthesized earlier and found to crystallize as a racemate also.[14] We obtained here the same compound but with different amounts of water of crystallization. Compound [*cis*-α-Co(trien)(OX)]NO_3 was reported to crystallize as a racemate,[14] as well as [*cis*-β-Co(trien)(OX)]Cl$\cdot$3H_2O and [*cis*-β-Co(trien)(OX)]ClO_4.[15]

Compound (**II**) crystallized as a racemate in a primitive orthorhombic space group. Examination of the cell constants, absences and Niggli matrix

TABLE I Summary of data collection and processing parameter for compound (I) [*cis*-α-Co(trien)(OX)]Cl · $2H_2O$

Space group	P-1
Cell constants	$a = 6.980(5)$ $b = 8.801(4)$ $c = 12.554(8)$ $\alpha = 89.07(5)$ $\beta = 75.74(4)$ $\gamma = 81.44(5)$
Cell volume	738.9(8)
Molecular formula	$CoC_8ClH_{22}N_4O_6$
Molecular weight	364.4
$F(000)$	380.06
Density (calc; $z = 2$ mol/cell)	1.634
Radiation employed	MoKα (0.70930 Å)
μ	1.36 mm^{-1}
h(min, max)	−7, 7
k(min, max)	0, 9
l(min, max)	−10, 10
Absorption coefficient	Yes
Relative transmission coefficients	0.51754, 0.73648
Data collection range	4–45
Scan width	$0.70 + 0.35 \tan\theta$
Total data collected	1907
Total unique data collected	1798
Data used in refinement	1647 ($I > 3\sigma(I)$)
Merging R-value	0.025
RF, Rw for significant reflections	0.033, 0.042
RF, Rw for all reflections	0.033, 0.042
GoF	1.01
Max shift/sigma ratio	0.002
Deepest hole (e/A^3)	−0.370
Highest peak (e/A^3)	0.450
Weights used	$w = \sigma[(F_o)]^{-2}$

$RF = \Sigma(F_o - F_c)/\Sigma(F_o)$,
$Rw = [\Sigma(w(F_o - F_c)**2)/\Sigma(wF_o**2)]^{1/2}$,
$GoF = [\Sigma(w(F_o - F_c)**2)/(\text{No. of reflns.} - \text{No. of params.})]^{1/2}$.

clearly showed the compound to crystallize with systematic absences belonging to those of space group Pbca (No. 61). The structure shows that the compound consists of slightly disordered octahedral [*cis*-α-Co(trien)-$(NO_2)_2]^+$ cations and BF_4^- counter anions. The final R factor for this compound is a little bit high; however, the space group is unambiguous and proof, that compound (**II**) crystallized as a racemate, further confirming the role of counter ion for conglomerate crystallization. The [*cis*-α-Co(trien)$(NO_2)_2]^+X$ series of compounds crystallize as conglomerates when $X = Cl^-$ or I^-, and crystallize as racemates when $X = NO_3^-$ or BF_4.

Compound (**III**) also crystallized as a racemate in a primitive orthorhombic space group. Examination of the cell constants, absences and Niggli

TABLE II Summary of data collection and processing parameter for compound (II) [*cis*-α-Co(trien)$(No_2)_2$] · BF_4

Space group	*Pbca*
Cell constants	$a = 12.260(10)$ $b = 12.880(14)$ $c = 17.940(14)$
Cell volume	2833(4)
Molecular formula	$CoBC_6F_4H_{18}N_6O_4$
Molecular weight	383.98
F(000)	1571.52
Density (calc; $z = 8$ mol/cell)	1.801
Radiation employed	MoKα (0.70930 Å)
μ	$1.28\,mm^{-1}$
h(min, max)	0, 13
k(min, max)	0, 13
l(min, max)	0, 14
Absorption coefficient	No
Data collection range	4–45
Scan width	$1.00 + 0.35 \tan\theta$
Total data collected	1637
Total unique data collected	1637
Data used in refinement	883 ($I > 2.5\sigma(I)$)
Merging *R*-value	0.000
RF, Rw for significant reflections	0.122, 0.132
RF, Rw for all reflections	0.122, 0.132
GoF	0.980
Max shift/sigma ratio	0.003
Deepest hole (e/A^3)	−1.060
Highest peak (e/A^3)	0.970
Weights used	$w = \sigma[(F_o)]^{-2}$

$RF = \Sigma(F_o - F_c)/\Sigma(F_o)$,
$Rw = [\Sigma(w(F_o - F_c)**2)/\Sigma(wF_o**2)]^{1/2}$,
$GoF = [\Sigma(w(F_o - F_c)**2)/(\text{No. of reflns.} - \text{No. of params.})]^{1/2}$.

matrix showed that the space group of this substance is also Pbca. There are eight formula units in the unit cell with each molecule consisting of one [*cis*-α-Co(trien)$(NO_2)_2]^+$ cation and one [*cis*-α-Co(trien)(OX)$]^+$ cation in general positions, one Cl^- anion in a general position, and one SiF_6^{2-} in a special position (an inversion center).

In theory, the [Co(trien)$(NO_2)_2]^+$ cation or [Co(trien)(OX)$]^+$ cation can exist as three distinct geometric isomers, symmetrical *cis* (*cis*-α), unsymmetrical *cis* (*cis*-β) and *trans* forms. In all the new compounds discussed here, the cations are in the *cis*-α form.

Following the rule mentioned earlier, if compound [*cis*-α-Co(trien)-(OX)]X could crystallize as a conglomerate, [*cis*-α-Co(trien)(OX)]Cl would have the best chance since Cl is not a powerful hydrogen-bonding counter ion and would not compete for hydrogen bonding with the terminal amine ligands and the oxygens of the OX. For compound (I) possible

TABLE III Summary of data collection and processing parameter for compound (III) [*cis*-α-Co(trien)$(NO_2)_2$][*cis*-α-Co(trien)(OX)]Cl · $1/2SiF_6 \cdot 4H_2O$

Space group	*Pbca*
Cell constants	$a = 12.804(10)$ $b = 16.543(10)$ $c = 27.419(23)$
Cell volume	5808(7)
Molecular formula	$Co_2C_{14}ClF_3H_{44}N_{10}O_{12}Si_{0.5}$
Molecular weight	768.77
$F(000)$	3136.06
Density (calc; $z = 8$ mol/cell)	1.759
Radiation employed	MoKα (0.70930 Å)
μ	$1.34\,mm^{-1}$
h(min, max)	0, 12
k(min, max)	0, 15
l(min, max)	0, 26
Absorption coefficient	No
Data collection range	4–40
Scan width	$0.80 + 0.35 \tan\theta$
Total data collected	2657
Total unique data collected	2657
Data used in refinement	1902 ($I > 2.5\sigma(I)$)
Merging R-value	0.000
RF, Rw for significant reflections	0.058, 0.062
RF, Rw for all reflections	0.058, 0.062
GoF	0.50
Max shift/sigma ratio	0.002
Deepest hole (e/A^3)	−0.620
Highest peak (e/A^3)	1.470
Weights used	$w = \sigma[(F_o)]^{-2}$

$RF = \Sigma(F_o - F_c)/\Sigma(F_o)$,
$Rw = [\Sigma(w(F_o - F_c)**2)/\Sigma(wF_o**2)]^{1/2}$,
$GoF = [\Sigma(w(F_o - F_c)**2)/(\text{No. of reflns.} - \text{No. of params.})]^{1/2}$.

intermolecular hydrogen bonds were calculated, and the results show that the only hydrogen bonds (<2.5 Å) to the oxalato oxygen(s) are O3–H17(N4) = 2.14 Å and O3–H7(N2) = 2.23 Å. These are shown in the packing diagram, Figure 4. Comparing them with the results of compounds [*cis*-Co(en)$_2$(OX)]X (X = Cl, Br, I), one can easily see that the hydrogen bonding pattern which is essential for conglomerate crystallization of [*cis*-Co(en)$_2$(OX)]X compound, is destroyed. As a result compound (I) crystallizes as racemate. Why does [*cis*-α-Co(trien)(OX)]Cl · $2H_2O$ crystallize as a racemate, while [*cis*-Co(en)$_2$(OX)]X (X = Cl, Br, I) and [*cis*-Co(en)$_2$$(NO_2)_2$]X ($X = Cl^-, Br^-, I^-$) crystallize as conglomerates? In [*cis*-Co(en)2$(NO_2)_2$]$^+$ and [*cis*-Co(en)$_2$(OX)]$^+$ cations there are 4 pairs of terminal amine hydrogens each, and the cation can use two pairs to form strong hydrogen bonds and form the conglomerate helix. When using the trien ligand, one

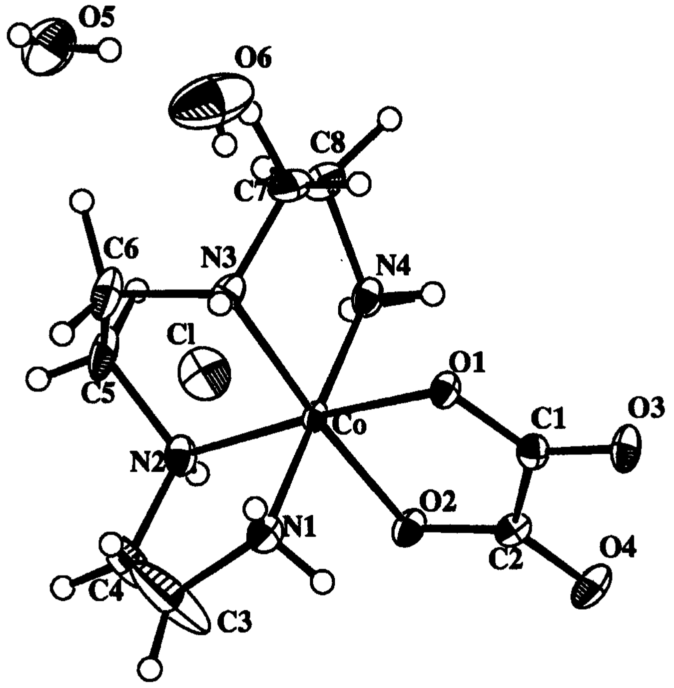

FIGURE 1 ORTEP view of the molecular structure of compound (I) [*cis*-α-Co(trien)(OX)]Cl · $2H_2O$. Thermal ellipsoids are drawn at 30% probability level.

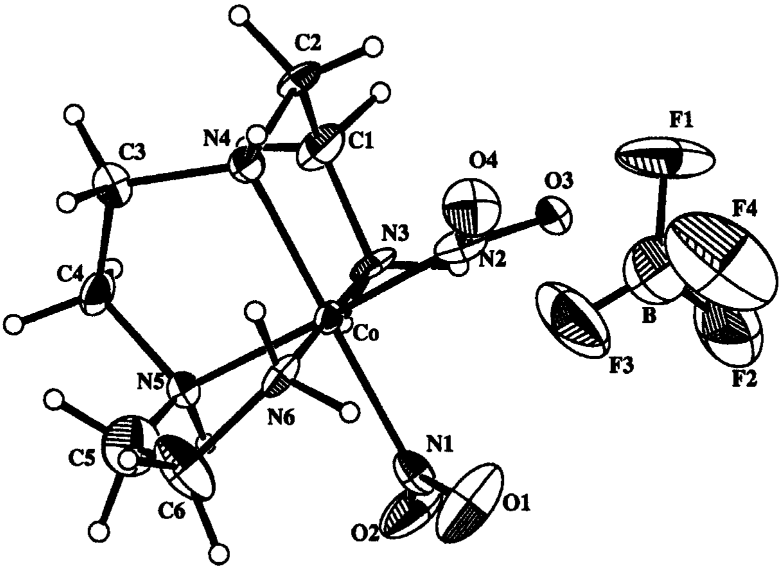

FIGURE 2 ORTEP view of the molecular structure of compound (II) [*cis*-α-Co(trien)-$(NO_2)_2$]BF_4. Thermal ellipsoids are drawn at 30% probability level.

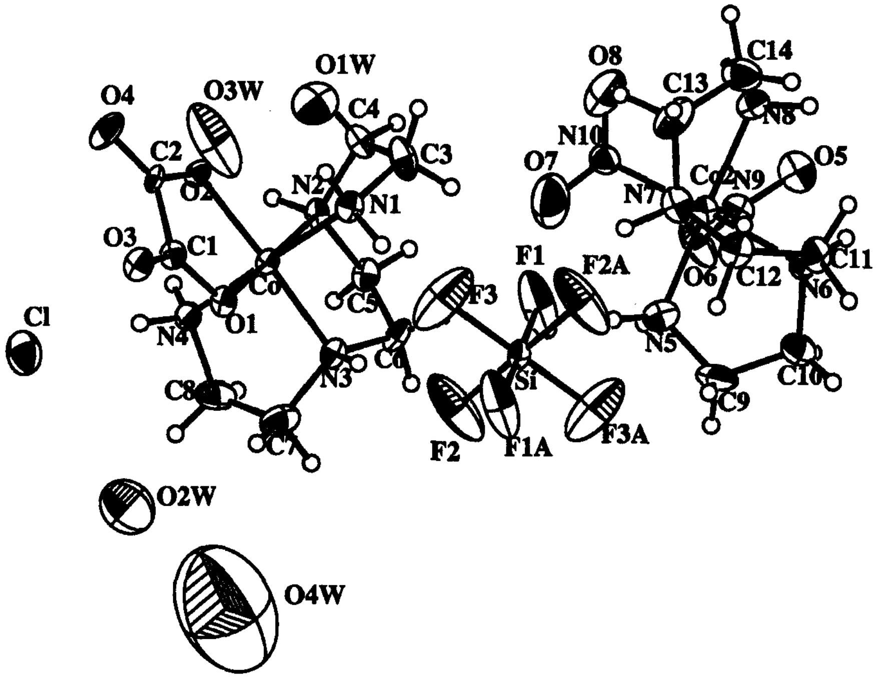

FIGURE 3 ORTEP view of the molecular structure of compound (III) [*cis*-α-Co(trien)-$(NO_2)_2$][*cis*-α-Co(trien)(OX)]Cl · $1/2SiF_6 \cdot 4H_2O$. Thermal ellipsoids are drawn at 30% probability level. Note the SiF_6^{2-} counter anion is on a special position (an inversion center).

pair of basal plane hydrogens is eliminated and the two additional CH_2 moieties make access to the secondary amine hydrogens much more difficult with much less chance for *cis*-α-trien to undergo conglomerate crystallization by using the mechanism proposed for *cis*-$(en)_2$ compounds. Thus, if a *cis*-α-trien compound crystallizes as a conglomerate, it must choose an alternative way, such as for the dinitro halide compound. However, why does [*cis*-α-Co(trien)$(NO_2)_2$]X crystallize as a conglomerate while compound (I) crystallizes as racemate? Since the oxalato ligand is flat and rigid, it does not have the necessary flexibility required to form the "desired" hydrogen bond pattern with the hydrogens of trien, while each nitro ligand has two oxygens pointing in opposite directions and rotation around the Co–N(O_2) bond is possible. Thus, the *cis*-dinitro cations have a considerable advantage over the oxalato counterparts when it comes to their ability to form the "desired" hydrogen-bond interaction.

TABLE IV Atomic parameters *x*, *y*, *z* and Biso for compound (I), [*cis*-α-Co(trien)(OX)]Cl · $2H_2O$. E.S.Ds. refer to the last digit printed

	x	*y*	*z*	*Biso*
Co	0.25768(9)	0.86163(7)	0.30894(5)	1.44(3)
O1	0.5135(4)	0.8906(3)	0.3270(3)	1.98(15)
O2	0.1669(4)	1.0630(3)	0.3720(3)	2.19(15)
O3	0.6576(5)	1.0640(4)	0.3922(3)	2.75(16)
O4	0.2744(5)	1.2420(4)	0.4558(3)	3.14(17)
N1	0.3244(7)	0.9474(6)	0.1634(4)	2.44(23)
N2	0.0036(7)	0.8421(5)	0.2784(4)	2.27(20)
N3	0.3476(6)	0.6498(4)	0.2583(4)	2.20(18)
N4	0.1962(8)	0.7734(5)	0.4549(4)	2.18(21)
C1	0.5114(7)	1.0211(5)	0.3727(4)	1.97(21)
C2	0.3030(7)	1.1209(5)	0.4044(4)	2.12(22)
C3	0.1531(12)	0.9726(15)	0.1180(9)	10.6(7)
C4	−0.0140(10)	0.9234(9)	0.1765(6)	5.0(4)
C5	−0.0160(8)	0.6764(7)	0.2764(6)	3.5(3)
C6	0.1867(8)	0.5855(7)	0.2215(6)	3.4(3)
C7	0.4155(9)	0.5651(6)	0.3481(5)	3.0(3)
C8	0.2592(9)	0.6052(6)	0.4534(5)	3.0(3)
H1	0.409(9)	0.901(7)	0.130(5)	3.2(17)
H2	0.363(8)	1.035(7)	0.171(5)	3.8(14)
H3	0.165(8)	1.036(6)	0.053(5)	4.0(13)
H4	0.196	0.866	0.075	12.9
H5	−0.138(8)	0.923(6)	0.158(4)	3.4(12)
H6	−0.055	1.028	0.218	6.6
H7	−0.082(8)	0.885(6)	0.321(4)	2.3(13)
H8	−0.077(9)	0.637(7)	0.372(5)	5.2(15)
H9	−0.101(9)	0.669(7)	0.240(5)	4.2(15)
H10	0.186(8)	0.465(7)	0.253(5)	4.2(13)
H11	0.214(7)	0.595(5)	0.144(5)	2.1(12)
H12	0.446(8)	0.643(6)	0.201(5)	3.0(13)
H13	0.540(9)	0.597(6)	0.356(4)	3.6(13)
H14	0.449(7)	0.451(6)	0.338(4)	2.8(11)
H15	0.304(8)	0.576(6)	0.529(5)	4.0(13)
H16	0.148(8)	0.561(6)	0.455(4)	3.3(12)
H17	0.257(7)	0.807(5)	0.489(4)	0.8(11)
H18	0.090(9)	0.788(6)	0.481(5)	2.7(15)
Cl	0.68970(22)	0.67872(19)	0.03369(13)	4.19(7)
O5	0.5119(9)	0.2276(7)	0.1629(6)	6.0(3)
H19	0.597(8)	0.180(6)	0.101(4)	1.7(12)
H20	0.627(14)	0.253(10)	0.160(8)	9.1(29)
O6	0.8673(10)	0.3572(8)	0.1181(8)	8.5(4)
H21	0.845(9)	0.418(6)	0.114(5)	1.0(14)

Biso is the mean of the principal axes of the thermal ellipsoid.

In our experience, the incidence of conglomerate crystallization of coordination compounds with composition A_2B or AB_2 is very small compared with those of composition of AB or neutral species. Yet, we reported that [*cis*-Co(tren)$(NO_2)_2]_2SiF_6$ crystallized as a conglomerate[12] and that [cis-Co(tren)$(NO_2)_2]_2BrClO_4$, crystallized as a kryptoracemate,[16] while

TABLE V Atomic parameters x, y, z and Biso for compound (**II**) [*cis*-α-Co(trien)(NO$_2$)$_2$]BF$_4$. E.S.Ds refer to the last digit printed

	x	y	z	*Biso*
Co	0.6401(3)	0.3017(3)	0.15806(24)	2.71(17)
N1	0.6166(20)	0.4552(22)	0.1616(16)	3.8(14)
N2	0.7899(21)	0.3131(19)	0.1737(13)	3.6(13)
N3	0.6076(20)	0.2951(17)	0.2658(15)	4.2(12)
N4	0.6544(19)	0.1519(17)	0.1666(15)	3.4(5)
N5	0.4848(19)	0.2834(19)	0.1355(17)	4.3(15)
N6	0.6638(21)	0.3110(18)	0.0527(14)	4.3(13)
O1	0.6805(25)	0.4993(21)	0.1274(16)	9.6(19)
O2	0.5504(24)	0.4845(18)	0.2013(19)	9.0(20)
O3	0.8211(20)	0.3428(16)	0.2466(17)	6.8(14)
O4	0.8625(20)	0.2869(22)	0.1348(14)	7.2(15)
C1	0.608(3)	0.188(3)	0.2927(20)	6.2(22)
C2	0.677(3)	0.1238(20)	0.2453(20)	4.2(16)
C3	0.5471(23)	0.1010(25)	0.1399(16)	3.5(15)
C4	0.4539(24)	0.1731(21)	0.1508(22)	4.7(17)
C5	0.479(3)	0.290(4)	0.057(3)	8.1(28)
C6	0.561(4)	0.328(4)	0.0097(20)	8.7(31)
H1	0.53443	0.32390	0.27433	5.0
H2	0.65706	0.33871	0.29281	5.0
H3	0.53688	0.15234	0.29621	6.4
H4	0.64556	0.18146	0.34450	6.4
H5	0.75430	0.13620	0.25714	5.4
H6	0.65769	0.04923	0.25185	5.4
H7	0.71592	0.13220	0.13286	5.2
H8	0.53323	0.03387	0.16375	3.9
H9	0.55234	0.08610	0.08184	3.9
H10	0.43040	0.16766	0.20371	6.3
H11	0.39070	0.15334	0.11744	6.3
H12	0.44296	0.33551	0.16378	5.8
H13	0.41164	0.33600	0.04205	8.5
H14	0.46105	0.21867	0.03511	8.5
H15	0.56602	0.28953	−0.04132	9.1
H16	0.55201	0.40465	−0.00440	9.1
H17	0.70027	0.24973	0.03412	4.3
H18	0.71421	0.36897	0.04171	4.3
F1	0.7294(22)	0.375(3)	0.474(3)	24.6(43)
F2	0.678(3)	0.528(4)	0.4789(20)	16.5(30)
F3	0.629(4)	0.440(4)	0.3893(25)	21.0(36)
F4	0.794(4)	0.480(4)	0.4001(22)	21.6(43)
B	0.704(6)	0.447(6)	0.428(5)	8.7(17)

Biso is the mean of the principal axes of the thermal ellipsoid.

[*cis*-Co(tren)(NO$_2$)$_2$]X (X = Cl$^-$, Br$^-$, I$^-$), ClO$_4^-$, NO$_3^-$, BF$_4^-$ crystallized as racemates.[12,16,17] Compound (**III**), [*cis*-α-Co(trien)(NO$_2$)$_2$][*cis*-α-Co(trien)(OX)]Cl · 1/2SiF$_6$, crystallized as a racemate; which, given the above, is not a surprise.

TABLE VI Atomic parameters x, y, z and Biso for compound (III) [*cis*-α-Co(trien)(NO$_2$)$_2$]-[*cis*-α-Co(trien)(OX)]Cl · 1/2SiF$_6$ · 4H$_2$O. E.S.Ds refer to the last digit printed

	x	y	z	*Biso*
Co	0.38866(11)	0.48061(10)	0.17864(6)	1.97(7)
Co2	0.14137(12)	0.65292(10)	−0.04727(6)	2.28(7)
O1	0.5326(6)	0.4478(5)	0.1831(3)	2.6(4)
O2	0.4168(6)	0.5440(4)	0.2353(3)	2.5(4)
O3	0.6742(7)	0.4745(5)	0.2275(3)	3.3(4)
O4	0.5489(7)	0.5724(6)	0.2853(3)	4.6(5)
O5	−0.0577(7)	0.6917(6)	−0.0745(4)	4.6(5)
O6	−0.0537(7)	0.5867(7)	−0.0301(4)	5.8(6)
O7	0.1434(12)	0.6051(10)	0.0465(4)	9.1(9)
O8	0.0885(12)	0.7203(9)	0.0407(4)	9.0(9)
N1	0.4305(8)	0.5700(6)	0.1367(3)	3.0(5)
N2	0.2486(6)	0.5231(6)	0.1723(3)	2.2(5)
N3	0.3587(7)	0.4105(6)	0.1245(3)	2.6(5)
N4	0.3441(8)	0.3911(6)	0.2201(3)	2.9(5)
N5	0.1578(9)	0.5363(7)	−0.0429(4)	4.3(6)
N6	0.1595(8)	0.6375(6)	−0.1179(4)	3.3(5)
N7	0.2937(7)	0.6714(7)	−0.0444(4)	3.7(6)
N8	0.1300(8)	0.7699(6)	−0.0534(4)	3.3(5)
N9	−0.0076(8)	0.6418(7)	−0.0520(4)	3.1(5)
N10	0.1244(9)	0.6617(8)	0.0244(5)	3.7(6)
C1	0.5820(11)	0.4818(7)	0.2179(5)	2.7(6)
C2	0.5107(10)	0.5375(7)	0.2509(5)	2.2(6)
C3	0.3411(11)	0.6223(9)	0.1230(5)	4.3(7)
C4	0.2575(10)	0.6099(8)	0.1605(5)	3.4(6)
C5	0.1871(9)	0.4721(8)	0.1374(4)	3.0(6)
C6	0.2595(10)	0.4361(8)	0.0997(4)	3.4(7)
C7	0.3611(12)	0.3268(9)	0.1424(5)	5.0(8)
C8	0.3128(12)	0.3202(8)	0.1907(6)	5.2(8)
C9	0.1769(17)	0.4998(9)	−0.0906(6)	7.2(11)
C10	0.1397(12)	0.5504(9)	−0.1295(6)	4.8(8)
C11	0.2620(11)	0.6679(9)	−0.1337(5)	3.9(7)
C12	0.3400(10)	0.6556(9)	−0.0929(5)	3.8(7)
C13	0.3087(11)	0.7560(11)	−0.0265(5)	5.1(8)
C14	0.2317(12)	0.8103(9)	−0.0509(6)	5.3(8)
H1	0.462	0.550	0.107	3.6
H2	0.483	0.603	0.153	3.6
H3	0.314	0.609	0.091	4.8
H4	0.361	0.679	0.122	4.8
H5	0.275	0.641	0.189	4.1
H6	0.192	0.631	0.149	4.1
H7	0.219	0.518	0.205	3.0
H8	0.151	0.430	0.155	3.8
H9	0.134	0.505	0.122	3.8
H10	0.275	0.475	0.075	4.4
H11	0.228	0.390	0.085	4.4
H12	0.417	0.419	0.102	3.4
H13	0.326	0.292	0.119	5.5
H14	0.432	0.308	0.145	5.5
H15	0.236	0.321	0.186	5.9
H16	0.329	0.271	0.206	5.9
H17	0.286	0.408	0.241	3.6
H18	0.400	0.376	0.242	3.6

TABLE VI (*Continued*)

	x	*y*	*z*	*Biso*
H19	0.216	0.524	−0.021	4.8
H20	0.096	0.513	−0.028	4.8
H21	0.254	0.494	−0.096	8.1
H22	0.149	0.447	−0.094	8.1
H23	0.065	0.541	−0.131	5.2
H24	0.170	0.536	−0.160	5.2
H25	0.105	0.670	−0.133	3.9
H26	0.285	0.638	−0.164	4.5
H27	0.258	0.728	−0.142	4.5
H28	0.402	0.693	−0.099	4.6
H29	0.367	0.598	−0.095	4.6
H30	0.321	0.633	−0.021	4.6
H31	0.297	0.757	0.011	5.6
H32	0.383	0.774	−0.032	5.6
H33	0.257	0.825	−0.084	6.3
H34	0.224	0.864	−0.031	6.3
H35	0.097	0.783	−0.084	4.1
H36	0.087	0.791	−0.027	4.1
Cl	0.5215(3)	0.3238(3)	0.29318(15)	5.98(21)
Si	1/2	1/2	0	2.39(22)
F1	0.3819(7)	0.5370(7)	0.0102(4)	9.7(6)
F2	0.4661(8)	0.4202(7)	0.0300(5)	11.4(8)
F3	0.5451(9)	0.5331(9)	0.0516(4)	12.5(9)
O1W	0.5907(8)	0.6818(6)	0.1621(4)	6.6(6)
O2W	0.5566(12)	0.2180(9)	0.1984(6)	11.1(10)
O3W	0.7727(13)	0.6372(10)	0.1972(6)	14.3(12)
O4W	0.542(4)	0.154(4)	0.1204(21)	50.9(65)

Biso is the mean of the principal axes of the thermal ellipsoid.

TABLE VII Bond distances, selected bond angles for compound (**I**) [*cis*-*α*-Co(trien)(OX)]-$Cl\cdot 2H_2O$

Co–O1	1.908(3)	N4–H18	0.73(6)
Co–O2	1.906(3)	C1–C2	1.546(7)
Co–N1	1.941(5)	C3–C4	1.344(10)
Co–N2	1.937(4)	C3–H3	0.98(6)
Co–N3	1.941(4)	C3–H4	1.052(14)
Co–N4	1.952(5)	C3–H6	1.683(11)
O1–C1	1.289(6)	C4–H5	0.95(6)
O2–C2	1.292(6)	C4–H6	1.033(8)
O3–C1	1.219(6)	C5–C6	1.522(8)
O4–C2	1.219(6)	C5–H8	1.23(7)
N1–C3	1.434(9)	C5–H9	0.84(6)
N1–H1	0.71(6)	C6–H10	1.12(6)
N1–H2	0.87(6)	C6–H11	0.94(6)
N2–C4	1.478(8)	C7–C8	1.501(8)
N2–C5	1.486(7)	C7–H13	0.98(6)
N2–H7	0.75(5)	C7–H14	1.00(5)
N3–C6	1.500(7)	C8–H15	1.09(6)
N3–C7	1.478(7)	C8–H16	0.91(6)

TABLE VII (*Continued*)

N3-H12	0.86(6)	O5-H19	0.92(5)
N4-C8	1.479(7)	O5-H20	0.86(9)
N4-H17	0.76(5)	O6-H21	0.54(5)
O1-Co-O2	85.75(14)	Co-N2-C5	108.7(3)
O1-Co-N1	89.30(18)	C4-N2-C5	114.4(5)
O1-Co-N2	174.87(17)	Co-N3-C6	110.7(3)
O1-Co-N3	93.47(16)	Co-N3-C7	107.1(3)
O1-Co-N4	89.75(20)	C6-N3-C7	114.4(5)
O2-Co-N1	90.32(20)	Co-N4-C8	113.0(4)
O2-Co-N2	93.66(17)	O1-C1-O3	124.3(4)
O2-Co-N3	174.76(18)	O1-C1-C2	114.2(4)
O2-Co-N4	90.31(17)	O3-C1-C2	121.5(4)
N1-Co-N2	85.60(20)	O2-C2-O4	124.6(4)
N1-Co-N3	94.85(22)	O2-C2-C1	113.6(4)
N1-Co-N4	178.83(22)	O4-C2-C1	121.8(4)
N2-Co-N3	87.57(19)	N1-C3-C4	116.9(6)
N2-Co-N4	95.35(22)	N2-C4-C3	115.7(6)
N3-Co-N4	84.51(20)	N2-C5-C6	108.9(5)
Co-O1-C1	113.0(3)	N3-C6-C5	109.5(4)
Co-O2-C2	113.1(3)	N3-C7-C8	108.3(4)
Co-N1-C3	110.9(4)	N4-C8-C7	106.9(4)
Co-N2-C4	109.8(4)		

TABLE VIII Selected bond distances, selected bond angles for compound (II) [*cis*-α-Co(trien)$(NO_2)_2$]BF_4

Co-N1	2.00(3)	N5-C4	1.50(4)
Co-N2	1.86(3)	N5-C5	1.40(6)
Co-N3	1.98(3)	N6-C6	1.49(5)
Co-N4	1.943(22)	C1-C2	1.45(5)
Co-N5	1.960(24)	C3-C4	1.49(4)
Co-N6	1.92(3)	C5-C6	1.41(6)
N1-O1	1.15(4)	F1-B	1.29(8)
N1-O2	1.14(4)	F2-F3	2.05(5)
N2-O3	1.42(4)	F2-F4	2.10(6)
N2-O4	1.18(3)	F2-B	1.42(10)
N3-C1	1.47(4)	F3-F4	2.10(7)
N4-C2	1.48(4)	F3-B	1.16(9)
N4-C3	1.55(4)	F4-B	1.28(9)
N1-Co-N2	93.4(10)	Co-N3-C1	111.2(19)
N1-Co-N3	89.0(11)	Co-N4-C2	109.5(18)
N1-Co-N4	173.0(12)	Co-N4-C3	108.6(17)
N1-Co-N5	89.2(10)	C2-N4-C3	110.6(22)
N1-Co-N6	89.5(11)	Co-N5-C4	108.8(18)
N2-Co-N3	93.1(10)	Co-N5-C5	104.4(23)
N2-Co-N4	88.7(10)	C4-N5-C5	103(3)
N2-Co-N5	175.9(12)	Co-N6-C6	113.1(21)
N2-Co-N6	89.6(10)	N3-C1-C2	110(3)
N3-Co-N4	84.2(10)	N4-C2-C1	108(3)
N3-Co-N5	90.1(12)	N4-C3-C4	110.4(24)

TABLE VIII (*Continued*)

N3–Co–N6	176.9(11)	N5–C4–C3	112.0(24)
N4–Co–N5	89.2(10)	N5–C5–C6	126(4)
N4–Co–N6	97.2(11)	N6–C6–C5	103(3)
N5–Co–N6	87.2(12)	F1–B–F2	99(6)
Co–N1–O1	112.0(23)	F1–B–F3	121(7)
Co–N1–O2	116.6(22)	F1–B–F4	106(6)
O1–N1–O2	130(3)	F2–B–F3	105(6)
Co–N2–O3	115.3(17)	F2–B–F4	102(6)
Co–N2–O4	129.1(23)	F3–B–F4	118(8)
O3–N2–O4	114(3)		

TABLE IX Bond distances, selected bond angles for compound (III) [*cis*-α-Co(trien)-$(NO_2)_2$]·[*cis*-α-Co(trien)(OX)]Cl·1/2SiF_6·$4H_2O$

Co–O1	1.926(7)	N8–H35	0.960(10)
Co–O2	1.908(8)	N8–H36	0.964(10)
Co–N1	1.948(10)	C1–C2	1.580(18)
Co–N2	1.933(8)	C3–C4	1.498(19)
Co–N3	1.923(10)	C3–H3	0.960(14)
Co–N4	1.952(10)	C3–H4	0.974(14)
Co2–N5	1.944(11)	C4–H5	0.971(13)
Co2–N6	1.967(10)	C4–H6	0.964(13)
Co2–N7	1.976(10)	C5–C6	1.511(17)
Co2–N8	1.947(10)	C5–H8	0.964(12)
Co2–N9	1.921(10)	C5–H9	0.965(12)
Co2–N10	1.982(13)	C6–H10	0.954(13)
O1–C1	1.276(16)	C6–H11	0.958(13)
O2–C2	1.280(16)	C7–C8	1.464(22)
O3–C1	1.216(16)	C7–H13	0.971(15)
O4–C2	1.210(16)	C7–H14	0.968(16)
O5–N9	1.215(15)	C8–H15	0.995(15)
O6–N9	1.239(16)	C8–H16	0.945(15)
O7–N10	1.141(21)	C9–C10	1.437(22)
O8–N10	1.163(19)	C9–H21	0.999(21)
N1–C3	1.483(17)	C9–H22	0.947(17)
N1–H1	0.971(9)	C10–H23	0.973(15)
N1–H2	0.969(10)	C10–H24	0.942(16)
N2–C4	1.477(16)	C11–C12	1.513(19)
N2–C5	1.499(15)	C11–H26	1.019(13)
N2–H7	0.976(9)	C11–H27	1.018(14)
N3–C6	1.501(16)	C12–H28	1.018(13)
N3–C7	1.470(19)	C12–H29	1.011(14)
N3–H12	0.973(9)	C13–C14	1.492(23)
N4–C8	1.478(17)	C13–H31	1.034(15)
N4–H17	0.973(10)	C13–H32	1.008(13)
N4–H18	0.973(9)	C14–H33	0.997(17)
N5–C9	1.461(20)	C14–H34	1.037(15)
N5–H19	0.971(12)	H18–Cl	2.259(4)
N5–H20	0.964(11)	H30–F1	1.965(9)
N6–C10	1.497(18)	Si–F1	1.655(8)
N6–C11	1.470(17)	Si–F1a	1.655(8)

TABLE IX (*Continued*)

N6–H25	0.974(10)	Si–F2	1.615(9)
N7–C12	1.479(17)	Si–F2a	1.615(9)
N7–C13	1.497(20)	Si–F3	1.622(11)
N7–H30	0.973(11)	Si–F3a	1.622(11)
N8–C14	1.465(19)		
O1–Co–O2	85.5(4)	O2–Co–N2	92.8(4)
O1–Co–N1	89.4(4)	O2–Co–N3	176.1(4)
O1–Co–N2	174.8(4)	O2–Co–N4	89.9(4)
O1–Co–N3	94.0(4)	N1–Co–N2	85.8(4)
O1–Co–N4	91.6(4)	N1–Co–N3	93.3(4)
O2–Co–N1	90.6(4)	N1–Co–N4	178.9(4)
N2–Co–N3	88.0(4)	Co2–N8–C14	112.5(8)
N2–Co–N4	93.3(4)	Co2–N9–O5	119.6(9)
N3–Co–N4	86.2(4)	Co2–N9–O6	120.7(9)
N5–Co2–N6	85.3(5)	O5–N9–O6	119.6(10)
N5–Co2–N7	92.5(5)	Co2–N10–O7	116.3(11)
N5–Co2–N8	177.6(4)	Co2–N10–O8	119.1(11)
N5–Co2–N9	90.9(5)	O7–N10–O8	124.3(14)
N5–Co2–N10	91.3(5)	O1–C1–O3	126.8(12)
N6–Co2–N7	86.7(5)	O1–C1–C2	113.5(11)
N6–Co2–N8	93.0(4)	O3–C1–C2	119.7(11)
N6–Co2–N9	92.2(5)	O2–C2–O4	126.9(11)
N6–Co2–N10	176.7(5)	O2–C2–C1	113.6(11)
N7–Co2–N8	85.6(4)	O4–C2–C1	119.4(12)
N7–Co2–N9	176.3(5)	N1–C3–C4	107.3(10)
N7–Co2–N10	93.3(5)	N2–C4–C3	109.7(10)
N8–Co2–N9	90.9(5)	N2–C5–C6	109.6(9)
N8–Co2–N10	90.3(5)	N3–C6–C5	108.7(9)
N9–Co2–N10	88.0(5)	N3–C7–C8	111.3(11)
Co–O1–C1	113.4(8)	N4–C8–C7	108.6(11)
Co–O2–C2	113.8(7)	N5–C9–C10	111.6(13)
Co–N1–C3	112.4(7)	N6–C10–C9	110.3(12)
Co–N2–C4	107.6(7)	N6–C11–C12	109.0(10)
Co–N2–C5	109.9(7)	N7–C12–C11	112.1(10)
C4–N2–C5	116.6(9)	N7–C13–C14	109.3(11)
Co–N3–C6	110.4(7)	N8–C14–C13	109.5(12)
Co–N3–C7	107.8(8)	F1–Si–F1a	179.9
C6–N3–C7	115.8(10)	F1–Si–F2	88.3(5)
Co–N4–C8	111.3(8)	F1–Si–F2a	91.7(5)
Co2–N5–C9	111.9(9)	F1–Si–F3	93.1(6)
Co2–N5–H19	109.3(8)	F1–Si–F3a	86.9(6)
Co2–N5–H20	109.8(8)	F1a–Si–F2	91.7(5)
C9–N5–H19	109.4(12)	F1a–Si–F2a	88.3(5)
C9–N5–H20	109.7(12)	F1a–Si–F3	86.9(6)
H19–N5–H20	106.6(11)	F1a–Si–F3a	93.1(6)
Co2–N6–C10	108.3(8)	F2–Si–F2a	180.0
Co2–N6–C11	110.6(8)	F2–Si–F3	85.8(8)
C10–N6–C11	114.7(10)	F2–Si–F3a	94.2(8)
Co2–N7–C12	109.5(8)	F2a–Si–F3	94.2(8)
Co2–N7–C13	106.5(8)	F2a–Si–F3a	85.8(8)
C12–N7–C13	114.1(10)	F3–Si–F3a	180.0

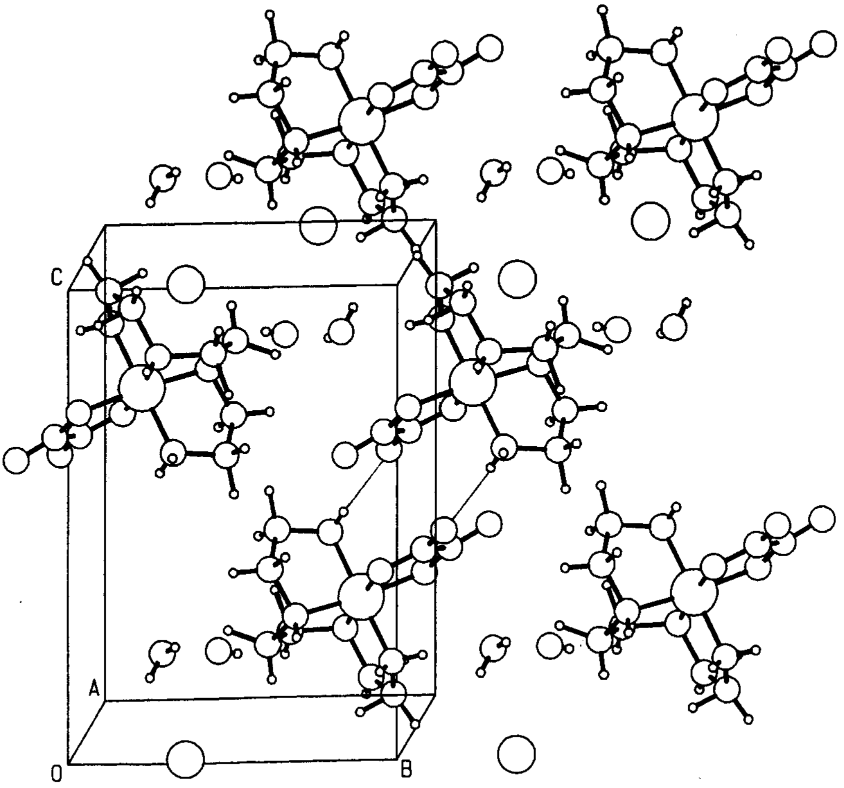

FIGURE 4 Packing diagram of compound (I) [*cis*-α-Co(trien)(OX)]Cl · H_2O.

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Supplementary Material Available

Torsion angles, anisotropic thermal parameters, structure factor tables and packing diagrams for the two compounds are available in hard copy or PC diskette format from I. Bernal.

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