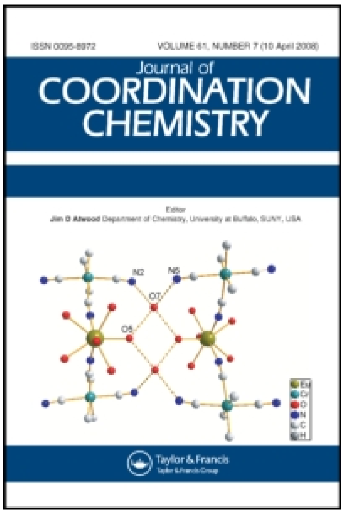

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION VI. HYDRATION POLYMORPHISM. I. THE SYNTHESES, CRYSTAL AND MOLECULAR STRUCTURES OF [cis-α-Co(trien)Cl_2]Cl.nH_2O With n = 3,2

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THE PHENOMENON OF CONGLOMERATE CRYSTALLIZATION VI.
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THE SYNTHESES, CRYSTAL AND MOLECULAR STRUCTURES OF [cis-α-Co(trien)Cl_2]Cl.nH_2O With n = 3,2

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Two hydration polymorphs [*cis*-α-Co(trien)Cl_2]Cl.nH_2O (n = 3, dark blue, IV; n = 2, red-purple, V) were studied by single crystal, X-ray diffraction methods. IV belongs to the triclinic system, crystallizing in the space group $P\bar{1}$ with cell constants of a = 7.216(4), b = 8.474(5), c = 12.348(6) Å, α = 98.96(5), β = 97.18(5) and γ = 94.02(5)°; V = 736.95 Å^3, d(calc; z = 2) = 1.647 gm-cm^{-3}. V is monoclinic, crystallizing in the space group $P2_1/n$ with cell constants of a = 7.323(8), b = 8.330(2), c = 22.648(9) Å, β = 95.94(6)°; V = 1376.30 Å^3, d(calc; z = 4) = 1.677 gm-cm^{-3}. The structural analysis of IV refined to final R and R_w values of 0.0604 and 0.0689, respectively, using 2108 observed data. That of V refined to 0.0323 and 0.0413 with 2070 data.

Despite the difference in the number of waters of hydration and space groups, the two cations are essentially identical and have the *cis*-α geometry. The difference in colour is a solid-state artifact caused by differences in orientation of the cation's axes to the crystallographically developed faces.

The average value of the Co–Cl distances in IV and V are, respectively, 2.265(1) and 2.269(2) Å and the Cl1-Co-Cl2 angles are both 90.9(1)°. In both compounds the *cis* < Cl-Co-N angles are close to 90° while the *cis* < N-Co-N angles range from 85 to 95°. For both compounds, the distances Co–N; (secondary) are somewhat shorter than those between Co and the terminal $-NH_2$ nitrogens. Since the lattices are centrosymmetric, enantiomeric pairs having energy-minima $\Lambda(\delta\lambda\delta)$ and $\Delta(\lambda\delta\lambda)$ configurations are present.

Keywords: Isomerism, hydrates, complexes, cobalt, trien

INTRODUCTION

Studies by Buckingham, Maxwell, Sargeson and Freeman[1-5] of the stereochemical properties of [Co(trien)XY]$^{n+}$ have provided a firm description of the geometry of these substances. In the case of the β-conformer[1-4] the relationship between absolute configuration and optical (CD, ORD) properties have been described in detail.[1-2] A study of the angular strain present in the β-conformer was analyzed[4] as a model for a strain minimization program written to evaluate the experimental data then available.

The structures (and, where relevant, absolute configurations) of racemic [*cis*-α-Co(trien)(NH_3)Cl](NO_3) (I),[5] $(-)_{589}$-[*cis*-α-Co(trien)(NO_2)$_2$]Cl.H_2O (II),[6] and $(-)_{589}$-[*cis*-α-Co(L-3,8-dimethyltrien)(NO_2)$_2$](ClO_4) (II)[7] have been determined†. These three seem at present to be the only structural studies of *cis*-α-Cotrien conformers. Interestingly, the parent of many of those molecules, the [*cis*-α-Co(trien)Cl_2]$^+$ cation, has not been structurally characterized.

In order to prepare [*cis*-α-Co(trien)(NO_2)$_2$]Cl.H_2O for purposes described elsewhere,[6] we synthesized [*cis*-α-Co(trien)Cl_2]Cl which had differently been described in two previous reports.[8,9] Basolo[8] described it as a "dark blue"

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†Abbreviations: trien = 1,4,7,10-tetraazadecane

compound while Sargeson and Searle[9] referred to it as "red purple". In this report, we describe the nature of the two species and show that they were correctly described in both[8,9] reports. The reason for the difference in their colour, melting point, *etc.*, is the subject of this report.

EXPERIMENTAL

Syntheses

The procedure employed here is very similar to that given by Basolo.[8] The blue solution obtained was allowed to cool overnight at room temperature (*ca* 21°C) and filtered. Deep blue crystals were obtained which were washed with ethanol until filtrates were clear. This procedure was repeated until no more crystals deposited. At this point, the solution was concentrated, HCl added and placed in a refrigerator (at *ca* 2°C) whereupon red purple crystals formed. These were also filtered and washed with ethanol. In both cases, examination of the crystals under a binocular microscope revealed them to be highly dichroic, the colour depending on the orientation of the crystals with respect to the illuminating beam. In both cases, the colour ranged from ruby-red to blue. Their composition was eventually found to be $[Co(trien)Cl_2]Cl.nH_2O$ [IV, n = 3; blue; m.p. = 234°C (uncorr) and V, n = 2; red; m.p. = 294°C, (uncorr)]. Upon long standing both samples lose water of hydration, as shown by elemental analyses[10] and by differential scanning calorimetry.[11]

Despite the nearly total loss of water in a sample of IV and the loss of nearly 0.7 H_2O in a sample of V, their colours remained unchanged — IV was still deep blue and V red purple. While there was noticeable dullness on the surface of the crystals, under the microscope one can still see in the partially dehydrated crystals the dichroic behaviour previously described.

X-Ray Data Collection and Processing

Single intensity crystal data sets were collected with an Enraf-Nonius CAD-4 diffractometer operating with the Molecular Structure Corporation TEXRAY-230 modification[12] of the SDP-Plus software package.[13] The crystal of (IV) was nearly cubic, having edges *ca* 0.35 mm, cut from a larger, broken fragment. The data crystal for (V) was a plate of approximate dimensions 0.45 × 0.35 × 0.20 mm. Both were centered using data in the $20° \leqslant 2\theta \leqslant 30°$ range and examination of the cell constants and Niggli matrix[14] clearly showed them to crystallize in primitive lattices; IV was found to be triclinic while (V) is monoclinic. Systematic absences showed that V crystallizes in the space group $P2_1/n$, while IV could be either $P1$ or $P\bar{1}$. Both data sets were corrected for Lorentz-polarization effects but not for absorption. The scattering curves were taken from Cromer and Waber's compilation.[15] All details of data collection and processing are summarized in Tables I and II.

The structures were solved from Patterson maps, using the Co as the heavy atom. The remaining non-hydrogen atoms were found in difference maps computed after a set of cycles of least-squares refinement. After all non-hydrogen atoms were found, they were refined isotropically to convergence, at which point the hydrogen atoms of the cation were added at idealized positions (N-H and C-H = 0.95 Å) and all atoms allowed to refine with hydrogen thermal parameters fixed at 5.0Å^2. Upon convergence, non-hydrogen atoms were assigned anisotropic motion. Hydrogens of IV were refined with an overall, isotropic, thermal

TABLE I

Summary of Data Collection and Processing Parameters for Racemic [*cis*-α-Co(trien)Cl_2]Cl.3H_2O

Space group	$P\bar{1}$
Cell Constants	$a =$ 7.216(4) Å
	$b =$ 8.474(5)
	$c =$ 12.348(6)
	$\alpha =$ 98.96(5)°
	$\beta =$ 97.18(5)
	$\gamma =$ 94.02(5)
Cell Volume	$V =$ 736.95 Å^3
Molecular Formula	$C_6H_{24}N_4O_3Cl_3Co$
Molecular Weight	365.575 gm mol^{-1}
Density (calc; z = 2 mol/cell)	1.647 gm cm^{-3}
Radiation Employed	Mo$K\alpha$(λ = 0.71073Å)
Absorption Coefficient	μ = 16.20 cm^{-1}
Data Collection Range	$4° \leqslant 2\theta \leqslant 64°$
Scan Width	$\Delta\theta$ = 1.05 +0.35tanθ
Maximum Scan Time	150 sec
Scan Speed Range	0.65 to 6.70° min^{-1}
Total Data Collected	2651
Data Used in Refinement[†]	2108
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0604
$R_w = \Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.0689
Weights Used	$w = [\sigma(F_o)]^{-2}$

[†] The difference between this number and the total is due to subtraction of 543 data which were standards and others which were redundant, symmetry related or did not meet the criterion that I $\geqslant 3\sigma$(I)

parameter, those of V were refined independently. Lists of thermal parameters and structure factor data are available from the author upon request.

RESULTS AND DISCUSSION

The final positional parameters for IV and V are listed, respectively, in Tables III and IV; bond lengths and angles are given in Table V.

TABLE II

Summary of Data Collection and Processing Parameters for Racemic [*cis*-α-Co(trien)Cl_2]Cl.2H_2O

Space Group	$P2_1/n$
Cell Constants	a = 7.323(8) Å
	b = 8.330(2)
	c = 22.684(9)
	β = 95.94(6)°
Cell Volume	V = 1376.30Å^3
Molecular Formula	$C_6H_{22}N_4O_2Cl_3Co$
Molecular Weight	347.559 gm mol^{-1}
Density (calc; z = 4 mol/cell)	1.677 gm cm^{-3}
Radiation Employed	Mo$K\alpha$(λ = 0.71073Å)
Absorption Coefficient	μ = 17.28 cm^{-1}
Data Collection Range	$4° \leqslant 2\theta \leqslant 60°$
Scan Width	$\Delta\theta$ = 0.95 +0.35tanθ
Scan Speed Range	0.48 to 6.70° min^{-1}
Total Data Collected	4501
Data Used in Refinement[†]	2070
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0323
$R_w = [\Sigma w^2(\|F_o\| - \|F_c\|)^2/\Sigma\|F_o\|^2]^{1/2}$	0.0413
Weights Used	$w = [\sigma(F_o)]^{-2}$

[†] The difference between this number and the total is due to subtraction of 2431 data which were standards and others which were redundant, symmetry related or did not meet the criterion that I $\geqslant 3\sigma$(I)

TABLE III

Atomic Coordinates (x 1000; Co, Cl x 10,000) for the Triclinic Trihydrate with Estimated Standard Deviations in Parentheses.

Atom	*x/a*	*y/b*	*z/c*
Co	.3544(1)	.2048(1)	.3567(1)
CL1	.2918(3)	.2569(2)	.5338(2)
CL2	.6668(3)	.2285(3)	.4163(2)
CL3	.4275(3)	.1579(3)	−.1372(2)
01	−.0260(9)	.5043(7)	.3407(7)
02	.1766(9)	.6766(9)	.0243(7)
03	.1231(10)	.3998(9)	.8653(7)
N1	.3626(9)	.4351(7)	.3489(6)
N2	.3930(9)	.1776(8)	.2026(6)
N3	.0876(8)	.1616(8)	.3033(6)
N4	.3503(8)	−.0258(7)	.3617(6)
C1	.3868(12)	.4676(10)	.2381(8)
C2	.4815(12)	.3322(10)	.1810(9)
C3	.2162(11)	.1163(10)	.1271(8)
C4	.0498(11)	.1690(10)	.1849(7)
C5	.0180(10)	.0066(9)	.3321(8)
C6	.1641(11)	−.1115(9)	.3129(8)
H1	.479(1)	.497(1)	.407(1)
H2	.233(1)	.479(1)	.370(1)
H3	.252(1)	.475(1)	.192(1)
H4	.472(1)	.579(1)	.245(1)
H5	.629(1)	.345(1)	.213(1)
H6	.465(1)	.334(1)	.093(1)
H7	.487(1)	.086(1)	.185(1)
H8	.215(1)	.165(1)	.051(1)
H9	.207(1)	−.013(1)	.109(1)
H10	−.074(1)	.091(1)	.149(1)
H11	.027(1)	.291(1)	.174(1)
H12	.011(1)	.253(1)	.344(1)
H13	−.004(1)	.023(1)	.418(1)
H14	−.113(1)	−.039(1)	.280(1)
H15	.162(1)	−.151(1)	.225(1)
H16	.136(1)	−.214(1)	.353(1)
H17	.380(1)	−.043(1)	.447(1)
H18	.456(1)	−.075(1)	.316(1)
HW1	.059(12)	.431(11)	.571(8)
HW2	.081(12)	.470(11)	.735(9)
HW3	.154(14)	.470(12)	.899(9)
HW4	.196(14)	.332(12)	.845(9)
HW5	.745(13)	.315(12)	.915(8)

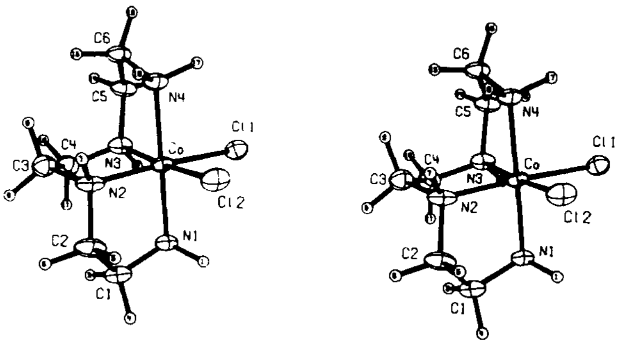

FIGURE 1 The stereochemistry of both cations (IV and V) are illustrated with this stereo plot. The numbering system is common to both since they are essentially identical (see Discussion and Figure 4).

TABLE IV

Atomic Coordinates (x 1000; Co. Cl x 10,000) for the Monoclinic Dihydrate with Estimated Standard Deviations in Parentheses.

Atom	*x/a*	*y/b*	*z/c*
Co	.36918(4)	.25986(4)	.92213(1)
CL1	.67249(8)	.25799(8)	.95415(3)
CL2	.29612(9)	.25005(8)	1.01674(3)
CL3	.88599(12)	.06827(9)	.69662(4)
01	−.0735(4)	−.1786(3)	.8040(1)
02	−.0162(3)	−.0451(3)	.9163(1)
N1	.3682(3)	.0232(3)	.9193(1)
N2	.4190(3)	.2475(3)	.8395(1)
N3	.1093(3)	.2841(3)	.8933(1)
N4	.3745(3)	.4957(3)	.9227(1)
C1	.3945(4)	−.0382(3)	.8596(1)
C2	.5010(4)	.0874(3)	.8293(1)
C3	.2497(4)	.2853(3)	.7991(1)
C4	.0793(4)	.2453(3)	.8288(1)
C5	.0488(4)	.4491(3)	.9088(1)
C6	.1975(4)	.5663(3)	.8968(1)
H1	.470(5)	−.006(4)	.946(2)
H2	.268(4)	−.021(4)	.935(1)
H3	.270(4)	−.053(4)	.837(1)
H4	.461(5)	−.134(5)	.864(2)
H5	.627(5)	.106(5)	.848(2)
H6	.509(5)	.075(4)	.787(2)
H7	.495(4)	.320(4)	.833(1)
H8	.253(5)	.387(5)	.790(2)
H9	.246(5)	.231(4)	.762(1)
H10	−.025(5)	.303(5)	.809(2)
H11	.056(4)	.134(4)	.825(1)
H12	.046(4)	.220(4)	.910(1)
H13	.031(4)	.446(4)	.950(1)
H14	−.066(4)	.471(4)	.886(1)
H15	.180(5)	.662(5)	.917(1)
H16	.208(5)	.571(5)	.851(2)
H17	.470(5)	.537(5)	.903(2)
H18	.397(4)	.521(4)	.959(1)
H19	.035(5)	.085(5)	.114(2)
H20	.084(6)	.076(6)	.061(2)
H21	.155(6)	.238(4)	.196(2)
H22	.104(5)	.121(6)	.227(2)

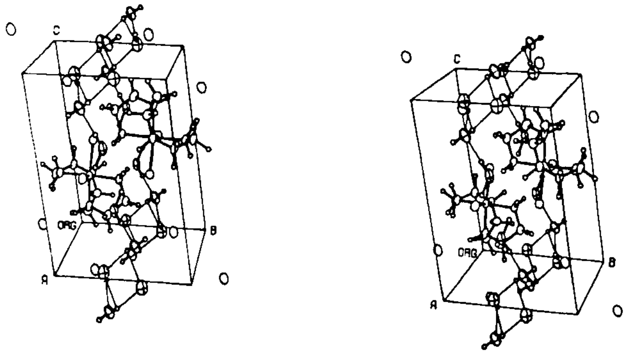

FIGURE 2 Packing of the ions and the three waters of hydration in compound IV. Note the strings ....Cl....H_2O....H_2O....H_2O....Cl.... running through the lattice.

TABLE V

Bond Lengths (Å) and Angles (°) With Estimated Standard Deviations in Parentheses.

Bond Distances

	IV	V
Co-Cl1	2.270(2)	2.264(1)
Co-Cl2	2.267(2)	2.266(1)
Co-N1	1.972(2)	1.950(2)
Co-N2	1.939(7)	1.950(2)
Co-N3	1.945(6)	1.958(2)
Co-N4	1.963(6)	1.965(2)
N1-C1	1.465(10)	1.480(4)
C1-C2	1.504(11)	1.511(4)
N2-C2	1.493(9)	1.490(4)
N2-C3	1.492(10)	1.496(3)
C3-C4	1.530(11)	1.515(4)
N3-C4	1.465(10)	1.492(3)
N3-C5	1.484(9)	1.497(3)
C5-C6	1.518(10)	1.508(4)
N4-C6	1.490(8)	1.488(3)

Bond Angles

	IV	V
N1-Co-Cl1	90.7(2)	90.2(1)
N1-Co-Cl2	90.0(2)	89.7(1)
N1-Co-N2	85.4(3)	85.2(1)
N1-Co-N3	94.9(3)	95.3(1)
N1-Co-N4	178.6(3)	178.2(1)
N2-Co-Cl1	92.5(2)	91.9(1)
N2-Co-Cl2	174.3(2)	174.2(1)
N2-Co-N3	86.8(3)	87.5(1)
N2-Co-N4	93.3(3)	93.1(1)
N3-Co-Cl1	174.3(2)	174.4(1)
N3-Co-Cl2	90.4(2)	90.2(1)
N3-Co-N4	85.8(3)	85.3(1)
N4-Co-Cl1	88.7(2)	89.2(1)
N4-Co-Cl2	91.3(2)	92.1(1)
Co-N1-C2	112.2(5)	112.0(2)
N1-C1-C2	108.2(7)	107.4(2)
C1-C2-N2	108.5(7)	108.3(2)
C2-N2-C3	111.7(5)	114.5(2)
C3-N2-Co	111.7(5)	110.6(2)
N2-C3-C4	108.6(7)	110.5(2)
C3-C4-N3	110.2(7)	110.1(2)
C4-N3-Co	110.9(5)	110.2(2)
C4-N3-C5	114.3(2)	113.6(7)
C5-N3-Co	109.3(4)	108.5(1)
N3-C5-C6	108.3(6)	108.4(2)
C5-C6-N4	107.2(6)	106.8(2)
C6-N4-Co	111.4(5)	112.1(2)

The two cations are essentially identical (*vide infra*); therefore, since the same numbering system was used for both, only one of them is shown (ORTEP[16] stereo plot, Figure 1). Separate packing diagrams (Figures 2 and 3) are given for both and a stereo (BMFIT[17]) comparison is presented in Figure 4 in which the two cations are superimposed. BMFIT[17] finds the best least-squares fit for the two molecules and generates an ORTEP[16] coordinate file. For the purpose of observing the effect of packing forces on the stereochemistry of these cations, Figure 5 was plotted. In this BMFIT[17] stereo plot, we compare the cation of V with that of II. The rationale, behind this plot is the following: II crystallizes in the non-centrosymmetric space

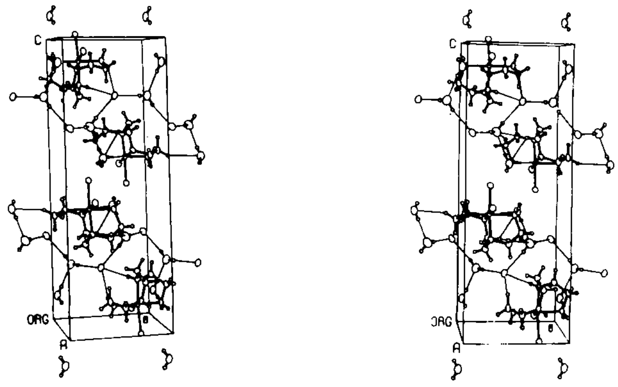

FIGURE 3 Packing of the ions and the two waters of hydration in compound V. Note the strings ....Cl....H_2O....H_2O....Cl.... running through the lattice. One is particularly clear in the lower left side of the cell near the label ORG.

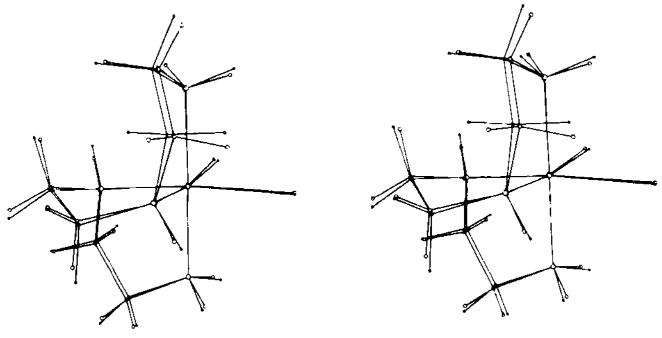

FIGURE 4 A BMFIT[17] comparison of the two [*cis*-α-Co(trien)Cl_2]$^+$ cations (IV and V). The cation IV was used as the standard and V was least-squares fitted to it; the criterion used was minimizing distances between the Co, N1, N2, N3 and N4 atoms.

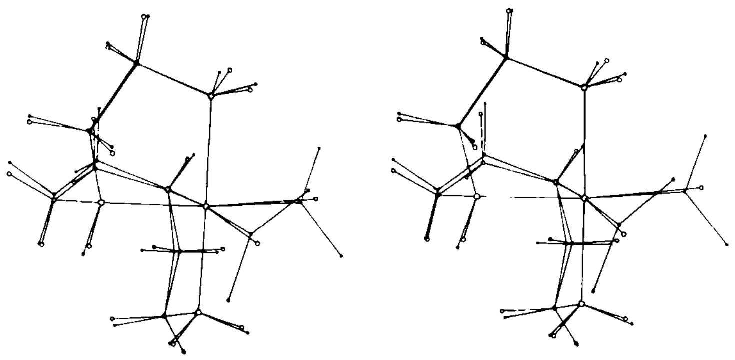

FIGURE 5 A BMFIT[17] comparison of [*cis*-α-Co(trien)Cl_2]$^+$ and [*cis*-α-Co(trien)$(NO_2)_2$]$^+$ (cations IV and II). The cation IV was used as the standard and II was least-squares fitted to it; the criterion used was minimizing distances between the Co, N1, N2, N3 and N4 atoms.

group $P2_12_12_1$ while IV and V crystallize in the centrosymmetric space groups $P\bar{1}$ and $P2_1/n$. Therefore, if packing has a significant effect on the geometry of these cations, we should see them in these comparisons.

Originally, the principal aim of this study was to establish the geometrical parameters for the cation [*cis*-α-Co(trien)Cl_2]$^+$ a species which has played a fundamental role in the syntheses and in kinetic and spectral studies of the *cis*-α geometrical isomers of Co(trien). The fact that the chloride was reported to exist in two different coloured forms provided additional impetus for the study of these species. In retrospect, we found that the problem arose probably as a result of the fact that previous investigators[8,9] followed the traditional method of *drying* their samples prior to submission for elemental analysis, *thereby eliminating the difference between these two hydration polymorphs.*

A few final comment on the effect of the lattice forces and of changes of the XY ligands on the stereochemistry of the *cis*-α-Co(trien) fragments of [cis-α-Co(trien)XY] are in order.

1) As is visually displayed in Figures 4 and 5, neither changes in the nature of the lattice forces, nor XY ligand changes, have much of an effect on the geometrical parameters of the [*cis*-α-Co(trien)] skeleton.

2) The [*cis*-α-Co(trien)XY] moieties have a nearly perfect two-fold axis of symmetry, present even though it is not crystallographically required. This point was raised previously[6,18] while discussing the geometry of the [*cis*-α-Co(trien)$(NO_2)_2$]$^+$ cation in two totally different environments — both chiral. Here, we compare the stereochemistry of the [*cis*-α-Co(trien)Cl_2]$^+$ cation in two different centrosymmetric environments. We also compare them with the [*cis*-α-Co(trien)$(NO_2)_2$]$^+$ cation as found in a chiral environment.[6]

3) Quantitatively, these observations can be summarized by the information given below, which was computed with BMFIT.[17]

Compd. IV Atom 1	Compd. V Atom 2	Compd. II Atom 3	Dist.2-1(Å)—Dist.2-3(Å)	
Co	Co	Co	0.025	0.010
Cl	Cl		0.116	not relevant
Cl	Cl		0.113	not relevant
N1	N4	N1	0.035	0.026
N2	N3	N2	0.020	0.011
N3	N2	N3	0.041	0.020
N4	N1	N4	0.029	0.002
C1	C6	C1	0.147	0.081
C2	C5	C2	0.137	0.058
C3	C4	C3	0.084	0.103
C4	C3	C4	0.059	0.160
C5	C2	C5	0.100	0.121
C6	C1	C6	0.144	0.038

It is worth remarking that using BMFIT, the same comparison can be made between IV and V as described by the crystallographic data and by rotating one of the molecules about the axis bisecting the Cl1-Co-Cl2 angle. This was done in the current case and one of the two is listed above. Furthermore, there is an equally good, if not better, fit between the [*cis*-α-Co(trien)$(NO_2)(NO_2)_2$]$^+$ cation II and one of the [*cis*-α-Co(trien)Cl_2]$^+$ cations V as there is between cations IV and V. Consequently, it is clear that neither the packing forces nor the change of XY = Cl_2 to XY = $(NO_2)_2$ has a significant effect in the overall geometrical features of the

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*Note that the reference atom, for all these comparisons, is the relevant atom in compound V [*cis*-α-Co(trien)XY] moiety. In fact, one of the most important differences between the [*cis*-α-Co(trien)(NO_2)$_2$]$^+$ cation II and the [*cis*-α-Co(trien)Cl_2]$^+$ cations IV and V is that, in the former, the N-Co-N angle is[6,18] *ca* 88.5° whereas in the two *cis*-dichloro cations this angle is *ca* 91°.

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11. I thank Dr. Michael W. Creswick of the Dow Chemical Corporation, Freeport, Texas for the differential scanning calorimetric measurements. This method gave approximate values of 2.5% and 7% loss of weight in the range of 100 to 200°C for these samples.
12. *TEXRAY-230* is a modification of the SDP-Plus[13] set of X-ray crystallographic programs distributed by Molecular Structure Corporation, 3304 Longmire Dr., College Station, TX 77840 for use with their automation of the CAD-4 diffractometer.
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