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Complexes of *Meso* Bidentate Ligands. The Crystal Structure of the Racemic Modification of *Cis*-C_2-*anti*-[oxalatobis(2*R*,4*S*-diaminopentane)cobalt(III)] Perchlorate

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The crystal structure of racemic cis-C_2-*anti-[oxalatobis(2*R*,4*S*-diaminopentane)cobalt(III)] perchlorate has been determined by diffractometric methods. The salt crystallizes in the triclinic space group* $P\bar{1}$, *with unit cell constants* $a = 11.005(3)$, $b = 11.863(3)$, $c = 7.626(2)$ Å, $\alpha = 103.36(1)$, $\beta = 90.09(1)$, *and* $\gamma = 74.00(1)^\circ$, *and* $Z = 2$. *Full-matrix least-squares refinement on F utilizing 3478 reflections with* $F_o^2 > 3\sigma(F_o^2)$ *converged at a conventional agreement factor of 0.052. The inner sphere coordination geometry of the cobalt atom is octahedral, and the cation possesses pseudo* C_2 *symmetry. The 2,4-diaminopentane rings adopt the chair conformation. The perchlorate ion is disordered and has been refined as two rigid, tetrahedral groups.*

Introduction

Transition metal compounds containing the 2,4-diaminopentane ligand (2,4-dmtn) have been studied by both proton magnetic resonance and circular dichroism techniques [1–4]. The β-diamine ligand exhibits stereoisomerism and can exist in three isomeric forms, *RR*-, *SS*-, and *RS*-2,4-dmtn. Both the Λ and the Δ isomer of the tris(2*R*, 4*R*-dmtn)Co(III) cation have been studied by Kobayashi *et al.* [5, 6], who found that the six membered chelate rings adopted twist-boat conformations. In each isomer the conformations could be designated λ, and the methyl groups were in equatorial positions with respect to the average planes of the chelate rings.

Saito *et al.* have shown that the favoured conformation of the chelate ring formed by a 2*R*,4*S*-dmtn ligand is chair, rather than a δ or λ twist-boat [7]. If a chair conformation is assumed, there are three geometrical isomers of the oxalatobis(2*R*,4*S*-dmtn)Co(III) cation [8], which differ in the relative orientations of the chelate rings. The first has *cis*-C_1 symmetry. The other two each possess two-fold rotation axes which pass through the Co atom and the mid-point of the oxalate ligand, but are distinguished by the spatial dispositions of the chelate rings relative to the axis. One has the rings well separated, and is designated *cis*-C_2-anti. In the other, the rings approach much more closely, leading to the classification *cis*-C_2-syn. We undertook a single crystal X-ray analysis of one of the C_2 isomers in order to distinguish between the syn and anti geometries, and report here the structure of the *cis*-C_2-anti isomer. This isomer has subsequently been resolved, and the crystal structure and absolute configuration reported by Saito *et al.* [7].

Experimental

Wine red crystals of the two *cis*-C_2 isomers of [oxalatobis(2*R*,4*S*-dmtn)Co(III)] perchlorate were kindly supplied by H. Boucher and B. Bosnich of the

TABLE I. Crystal Data.

$C_{12}H_{28}ClCoN_4O_8$	Formula weight 450.8
a = 11.005(3) Å	α = 103.36(1)°
b = 11.863(3) Å	β = 90.09(1)°
c = 7.626(2) Å	γ = 74.00(1)°
Cell volume 995.6 Å^3	μ = 10.52 cm^{-1} (MoKα)
Density[a] (obsvd) 1.63(1) g cm^{-3}	Density (calcd) 1.614 g cm^{-3}

[a] By neutral buoyancy in 1,2-$C_2H_4Br_2$ and CCl_4.

TABLE II. Experimental Conditions.

Radiation:	Mo Kα, λ (Kα_1) 0.70926 Å
Filter:	Nb foil, 0.07 mm prefilter
Aperture:	5 × 5 mm, 30 cm from the crystal
Scan:	θ–2θ at 1° min^{-1}
Range:	1.2° symmetric, with α_1–α_2 dispersion correction
Background:	stationary crystal, stationary counter measured at scan limits. 10s for $2\theta < 40°$ 20s thereafter
Standards:	Six, recorded every 200 observations, 002, 300, 00$\bar{2}$, 0$\bar{2}$0, $\bar{3}$00, and 020

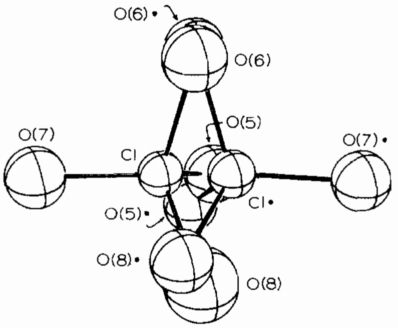

Figure 1. The disordered perchlorate anion.

University of Toronto. One sample crystallized as well-formed equidimensional blocks, the other in needle form. The equidimensional sample was chosen for a structural analysis. A preliminary photographic examination showed that the crystals belonged to the triclinic system. The reduced cell shown in Table I was chosen. The density of the crystals, calculated for two formula units per cell, is in good agreement with the value determined by flotation in a mixture of chloroform and 1,2-dibromoethane. This fact, together with the centrosymmetric habit of the crystals, led us to choose P$\bar{1}$ (C_i^1 No. 2) [9] as the space group. Crystal data are summarised in Table I.

The experimental conditions under which data were collected are outlined in Table II. The crystal chosen had eight faces, which were identified as the forms {100}, {010}, {110} and {011} by optical goniometry. Its dimensions, 0.34 × 0.34 × 0.20 mm, were measured using a microscope fitted with a filar eyepiece. ω scans of intense, low-angle reflections had a mean width at half-height of 0.11°. Intensity data were collected on a Picker FACS-1 automatic four-circle diffractometer, with the ϕ axis approximately collinear with the long dimension of the crystal [01$\bar{1}$]. An orientation matrix and the cell constants and their estimated standard deviations were determined at 21 °C by a least-squares refinement of the angular settings for 24 carefully centered reflections ($14 < 2\theta < 35°$) in all regions of reciprocal space [10]. All reflections in the hemisphere with indices ±h, ±k and $l > 0$ were collected in three shells to a 2θ maximum of 55°. Six standard reflections were recorded at intervals throughout data collection to monitor crystal and electronic stability. They remained steady over the period of 16 days, showing only random fluctuations. Copper foil attenuators were used to minimise coincidence losses for strong reflections.

A total of 4722 reflections was measured, and the intensities corrected for background, polarization and Lorentz effects. A standard deviation was assigned to each reflection as detailed elsewhere [11]. A value of 0.02 was chosen for p, the ignorance factor, though it was later reduced to 0.01 [12]. An absorption correction was applied to the data; transmission coefficients varied from 0.71 to 0.81 [10]. Of the 4722 observations recorded, 3478 had $I > 3\sigma(I)$ and were used for the solution and refinement of the structure.

Structure Solution and Refinement

The position of the Co atom was located from a three dimensional Patterson synthesis. Two cycles of least-squares refinement on F, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors respectively, and the weight w is given by $4F_o^2/(\sigma(F_o^2))^2$, gave agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.56$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2} = 0.58$. Scattering factors for Co, Cl, C, N and O were taken from Cromer and Waber [13] while those for H were from Stewart, Davidson and Simpson [14]. Anomalous dispersion corrections were applied for Co, and were those of Cromer and Libermann [15].

The remaining non-H atoms were located from a difference Fourier synthesis. Least-squares refinement, with all atoms assigned anisotropic thermal parameters, converged at $R_1 = 0.087$ and $R_2 = 0.105$ (235 variables, 3679 observations). A difference Fourier synthesis revealed residual electron density in the region of the perchlorate ion, and the Cl atom showed pronounced anisotropic thermal motion. A disorder model was formulated to account for the remaining electron density. Good agreement was obtained with the inclusion of two rigid, tetrahedral groups, Figure 1. The group origin and orientation angles were refined for each group, and individual isotropic thermal parameters varied for the atoms of the dominant group [16]. An overall group parameter was varied for the less common orientation. The multiplicity parameter refined to a value of 70.1(4)%.

All 28 H atoms of the cation were located from a difference Fourier synthesis. Their contributions

TABLE III. Atomic Positional and Thermal Parameters (×10^4).

Atom	x	y	z	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	2687.9(5)	1741.5(5)	1576.2(7)	249(3)	208(2)	210(3)	−78(2)	−39(2)	54(2)
O(1)	4097(2)	1282(2)	−166(3)	302(14)	313(14)	261(14)	−114(12)	−41(11)	71(11)
O(2)	1695(2)	1596(2)	−491(3)	300(14)	367(16)	282(14)	−118(12)	−83(11)	121(12)
O(3)	4528(3)	688(3)	−3142(4)	442(18)	535(20)	301(16)	−36(15)	48(13)	90(14)
O(4)	1933(3)	1080(3)	−3510(4)	554(20)	585(21)	304(16)	−221(16)	−170(14)	117(14)
C(1)	3783(4)	1058(3)	−1817(5)	348(21)	245(19)	269(20)	−70(16)	−13(16)	68(16)
C(2)	2352(4)	1263(3)	−2011(5)	392(22)	271(20)	270(20)	−125(17)	−73(17)	79(16)
N(10)	2986(3)	21(3)	1534(4)	311(18)	278(18)	355(19)	−98(14)	−69(14)	96(14)
N(11)	1188(3)	2102(3)	3204(4)	324(18)	315(18)	309(18)	−96(15)	−16(14)	93(14)
C(10)	1934(4)	−541(4)	1061(5)	341(22)	313(21)	354(22)	−154(17)	−101(17)	102(17)
C(11)	851(4)	66(4)	2465(6)	353(22)	372(23)	412(24)	−206(18)	−93(18)	145(19)
C(12)	246(4)	1404(4)	2638(6)	253(20)	398(23)	397(23)	−130(17)	−50(17)	157(19)
C(13)	−883(4)	1878(5)	4013(7)	362(25)	555(31)	652(33)	−116(22)	98(23)	208(26)
C(14)	2398(5)	−1896(4)	879(7)	553(29)	316(24)	553(30)	−182(21)	−154(23)	134(21)
N(20)	2433(3)	3453(3)	1606(4)	378(19)	265(17)	336(18)	−99(15)	−60(15)	98(14)
N(21)	3755(3)	1937(3)	3622(4)	307(17)	302(18)	288(17)	−135(14)	−45(13)	84(14)
C(20)	3564(4)	3913(4)	1571(6)	532(28)	317(23)	426(25)	−231(20)	−89(21)	121(19)
C(21)	4360(4)	3703(4)	3156(6)	476(26)	354(23)	427(25)	−241(20)	−93(20)	87(19)
C(22)	4839(4)	2427(4)	3376(5)	316(21)	390(23)	333(22)	−157(18)	−55(17)	75(18)
C(23)	5667(4)	2366(4)	4962(6)	413(26)	585(31)	454(27)	−249(23)	−162(21)	134(23)
C(24)	3144(6)	5254(5)	1626(7)	991(44)	384(28)	648(36)	−376(29)	−298(32)	209(25)

[a] The thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. $U_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*)$Å^2. [b] Estimated standard deviations in this and other tables are given in parentheses, and refer to the least significant digit(s).

TABLE IV. Group Parameters.

Group	x_c[a]	y_c	z_c	δ	ϵ	η
1	0.1730(2)	0.48537(14)	−0.2866(2)	−2.132(6)	2.065(3)	−1.223(6)
2	0.1155(4)	0.4585(3)	−0.2850(5)	0.744(8)	−3.859(8)	−0.937(8)

Derived Group Atom Parameters

	Atom	x	y	z	B(Å^2)
Group 1	Cl	1730(2)[b]	4854(1)	−2866(2)	3.37(4)
	O(5)	603(2)	5640(3)	−1877(5)	6.6(2)
	O(6)	1487(4)	4499(4)	−4712(3)	6.5(2)
	O(7)	2685(3)	5462(4)	−2717(6)	6.5(2)
	O(8)	2145(4)	3814(3)	−2160(6)	8.7(2)
Group 2	Cl*	1155(4)	4586(3)	−2850(5)	3.78(10)
	O(5)*	900(9)	5663(6)	−1457(11)	5.78(10)
	O(6)*	1211(10)	4868(10)	−4554(8)	5.78(10)
	O(7)*	176(7)	4024(8)	−2784(12)	5.78(10)
	O(8)*	2333(6)	3786(7)	−260(2)	5.78(10)

[a] x_c, y_c and z_c are the coordinates of the group origin. δ, ϵ and η (radians) are the group orientation angles, see ref. 16. [b] Positional parameters have been multiplied by 10^4.

were included in F_c thereafter, assuming ideal geometries with C–H 1.00 Å, N–H 0.95 Å, and sp^3 hybridization at the C and N atoms. No hydrogen atom parameters were refined. With all non-perchlorate atoms assigned anisotropic thermal parameters, the refinement converged at R_1 = 0.052 and R_2 = 0.057 (3478 observations and 209 variables). The error on an observation of unit weight was 1.69 electrons. There was no evidence for secondary extinction. An examination of the structure factors in

TABLE V. Hydrogen Atom Positional (X10^4) and Thermal Parameters.

Atom	x	y	z	B(Å^2)
H1N(10)	3680	−420	682	3.43
H2N(10)	3215	−74	2704	3.43
H1C(10)	1638	−396	−129	3.52
H1C(11)	178	−355	2167	3.76
H2C(11)	1171	−37	3662	3.76
H1C(12)	−52	1527	1439	3.62
H1N(11)	1472	1958	4331	3.46
H2N(11)	755	2934	3360	3.46
H1N(20)	1981	3600	581	3.53
H2N(20)	1924	3915	2674	3.53
H1C(20)	4092	3472	423	4.13
H1C(21)	5116	3999	3036	4.12
H2C(21)	3836	4201	4283	4.12
H1C(22)	5359	1915	2253	3.66
H1N(21)	3229	2469	4633	3.27
H2N(21)	4092	1167	3873	3.27
H1C(13)	−1195	2777	4229	5.07
H2C(13)	−1572	1513	3537	5.07
H3C(13)	−619	1651	5169	5.07
H1C(14)	1744	−2278	308	4.61
H2C(14)	3208	−2235	105	4.61
H3C(14)	2543	−2057	2103	4.61
H1C(23)	6022	1503	5016	4.63
H2C(23)	6375	2719	4803	4.63
H3C(23)	5145	2835	6105	4.63
H1C(24)	3906	5533	1468	5.92
H2C(24)	2572	5394	630	5.92
H3C(24)	2681	5708	2818	5.92

terms of Miller indices, $|F_o|$, λ^{-1} sinθ and the diffractometer setting angles χ and ϕ showed no unusual trends, and indicated a suitable weighting scheme. A final difference Fourier synthesis contained no peak higher than 0.88(11)eÅ^{-3}, and that was associated with the disordered perchlorate anion. The atomic positional and thermal parameters are given in Table III, and group parameters in Table IV. A table of observed and calculated structure amplitudes is available [17]. The hydrogen atom parameters are listed in Table V.

Structure Description

A view of the cation, showing the atom labelling scheme, is given in Figure 2. Atoms are drawn as 50% probability ellipsoids [10]. A number of weak hydrogen bonds hold the structure together. On the cation at 1 − x, $\bar{y}$, $\bar{z}$, atom H1N(10) approaches O(1) at 2.37 Å, while O(3) is 2.25 Å from H2N(21) and 2.43 Å from H2N(10). Comparable interactions occur with the H atoms on the cation at x, y, z − 1, for H1N(11) approaches O(4) at 2.13 Å, and H2N(21) is 2.49 Å distant from O(3). There is only one nonbonding interaction between cations less than 2.5 Å, namely 2.38 Å between H2C(13) and H2C(23) on the cation at x − 1, y, z; both atoms are methyl group hydrogens. There are few hydrogen bonds to the anion less than 2.5 Å, and the disorder observed may be due to this. The shortest interaction is 2.1 Å between O(6)/O(6)* and H2N(20) on the cation at x, y, z − 1.

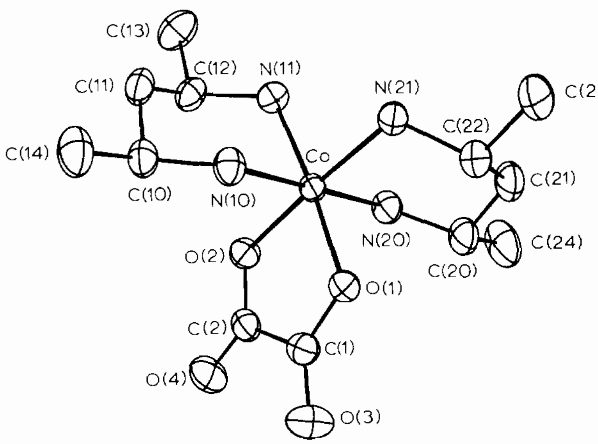

Figure 2. The complex cation, showing the atom numbering scheme.

The complex cation has pseudo C_2 symmetry, and the unit cell contains pairs of enantiomers related by the center of symmetry. Coordinates are listed for the Δ isomer. Bond distances and bond angles are summarised in Table VI. The Co atom has a slightly distorted octahedral coordination geometry, for the mean N–Co–N angle is 88.61(1), and the O–Co–O angle 84.8(1)°. Both 2,4-dmtn ligands have chair conformations, with the substituent methyl groups in equatorial dispositions with respect to the average plane of the ligand. The average torsion angles within the 2,4-dmtn chelates are Co–N–C–C 62(1) and N–C–C–C 61(1)°. Molecular dimensions in the 2,4-dmtn ligands are normal [5, 6], as are those within the oxalate ligand, which shows only slight deviations from planarity, Table VII.

One of the enantiomers studied here has been independently examined, as $(+)_{510}$-oxalatobis-(2*R*,4*S*-dmtn)cobalt(III) perchlorate monohydrate [7]. The probability plot method of de Camp [18] has been used to compare dimensions within the complex cations which possess the same absolute configurations. The analysis showed that the geometry of the oxalate ligand is very similar in both structures. In contrast, the dimensions of the 2,4-dmtn ligands show significant differences, and reflect the different environments for the cation in the two crystalline forms.

TABLE VI. Selected Intramolecular Dimensions.

At the Cobalt Atom

Bond	Distance (Å)	Atoms	Angle (deg.)
Co–O(1)	1.917(3)	O(1)–Co–O(2)	84.8(1)
Co–O(2)	1.919(3)	O(1)–Co–N(10)	88.3(1)
Co–N(10)	1.969(3)	O(1)–Co–N(11)	174.7(1)
Co–N(11)	1.955(3)	O(1)–Co–N(20)	90.6(1)
Co–N(20)	1.966(3)	O(1)–Co–N(21)	92.9(1)
Co–N(21)	1.961(3)	O(2)–Co–N(10)	91.5(1)
		O(2)–Co–N(11)	91.1(1)
		O(2)–Co–N(20)	89.1(1)
		O(2)–Co–N(21)	176.8(1)
		N(10)–Co–N(11)	88.5(1)
		N(10)–Co–N(20)	178.7(1)
		N(10)–Co–N(21)	90.6(1)
		N(11)–Co–N(20)	92.7(1)
		N(11)–Co–N(21)	91.3(1)
		N(20)–Co–N(21)	88.8(1)
The oxalate ligand			
C(1)–O(1)	1.292(4)	O(1)–C(1)–O(3)	124.8(4)
C(1)–O(3)	1.218(4)	O(1)–C(1)–C(2)	114.3(3)
C(2)–O(2)	1.287(5)	O(3)–C(1)–C(2)	120.9(4)
C(2)–O(4)	1.227(4)	O(2)–C(2)–O(4)	125.7(4)
C(1)–C(2)	1.538(6)	O(2)–C(2)–C(1)	113.6(3)
		O(4)–C(2)–C(1)	120.6(4)

The 2*R*,4*S*-dmtn ligands[a]

Bond	Distances (Å)	
	Ring 1	Ring 2
N(10)–C(10)	1.492(5)	1.493(5)
N(11)–C(12)	1.501(5)	1.494(5)
C(10)–C(14)	1.519(6)	1.520(6)
C(12)–C(13)	1.518(6)	1.517(6)
C(10)–C(11)	1.504(6)	1.519(6)
C(12)–C(11)	1.517(6)	1.508(6)

Atoms	Angles (deg.)	
	Ring 1	Ring 2
N(10)–C(10)–C(14)	110.5(3)	109.9(4)
N(11)–C(12)–C(13)	109.2(4)	109.9(3)
N(10)–C(10)–C(11)	109.0(3)	111.0(3)
N(11)–C(12)–C(11)	110.5(3)	110.4(3)
C(11)–C(10)–C(14)	112.3(4)	109.6(4)
C(11)–C(12)–C(13)	110.6(4)	111.2(3)
C(10)–C(11)–C(12)	116.4(3)	117.9(3)

The perchlorate ion

Cl–O	1.420 Å	O–Cl–O	109.46°

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[a] Ring 2 contains N(20), N(21), C(20), C(21), C(22), C(23) and C(24).

TABLE VII. Weighted Least-Squares Plane and Atom Displacements (Å).

Plane equation: $-1.921x - 11.80y + 1.966z = -2.322$

O(1)	−0.010(3)	C(2)	−0.015(4)
O(2)	0.017(3)	O(3)	0.023(3)
C(1)	−0.010(4)	O(4)	−0.014(3)

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Supplementary Material Available

A table of observed and calculated structure amplitudes is available (from N.C.P.).

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