Acta Cryst. (1991). C**47**, 2099–2101

Structure of $(+)^{CD}_{580}$-$\Lambda\Lambda$-(Ethylenediaminediacetato)bis(ethylenediamine)-di-μ-hydroxo-dicobalt(III) Chloride Trihydrate

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(*Received* 6 *March* 1991; *accepted* 8 *May* 1991)

Abstract. $[Co_2(C_6H_{10}N_2O_4)(\mu\text{-}OH)_2(C_4H_{16}N_4)]Cl_2.\text{-}3H_2O$, $M_r = 571·19$, orthorhombic, $P2_12_12_1$, $a = 15·534\,(2)$, $b = 14·689\,(2)$, $c = 9·534\,(1)$ Å, $V = 2175·4\,(5)$ Å^3, $Z = 4$, $D_x = 1·744$ g cm^{-3}, λ(Mo $K\alpha$) = 0·70926 Å, $\mu = 17·33$ cm^{-1}, $F(000) = 1184$, room temperature, $R = 0·060$ for 2534 independent reflections $[|F_o| > 3\sigma(|F_o|)]$. The complex cation has a dinuclear structure, two Co atoms being bridged by two OH groups. One Co atom is surrounded octahedrally by ethylenediaminediacetate with the α chelation mode and two μ-OH groups, and the other by two ethylenediamine ligands and two μ-OH groups. Both terminals of the $(+)^{CD}_{580}$ isomer take the Λ configuration.

Introduction. Recently some isomers of $[(L)Co(\mu\text{-}OH)_2Co(en)_2]^{n+}$ [L = ethylenediaminediacetate (edda) or (gly)$_2$, gly = glycinate; en = ethylenediamine] were prepared (Ama, Kawaguchi & Yasui, 1988), and their structures estimated on the basis of the electronic absorption, circular dichroism, and ^{1}H NMR spectra. In order to confirm their structures and to establish systematically their spectral properties, it is necessary to determine the geometry and absolute configuration by the single-crystal X-ray diffraction method. This study was undertaken to establish an accurate structure of the title compound showing a positive CD sign at 580 nm.

Experimental. Preparation and optical resolution for $(+)^{CD}_{580}$-$[(edda)Co(\mu\text{-}OH)_2Co(en)_2]Cl_2.3H_2O$ was conducted according to the methods described in previous papers (Ama, Kawaguchi & Yasui, 1988). The dark violet–red crystals were obtained by slow cooling of a saturated aqueous solution of the complex.

Dark violet–red crystal dimensions 0·15 × 0·18 × 0·25 mm; Rigaku AFC-5 diffractometer with graphite-monochromated Mo $K\alpha$ ($\lambda = 0·70926$ Å) radiation, 50 kV and 150 mA; unit-cell dimensions from 25 reflections (20° < 2θ < 26°); ω–2θ scan, scan rate 3° min^{-1}, scan width $(1·0 + 0·40\tan\theta)$°; three intensity and orientation standards were monitored every 50 scans, the intensities remained constant within experimental error throughout the data collection; 3606 reflections measured in the $2 < 2\theta < 60°$ range ($0 \leq h \leq 21$, $0 \leq k \leq 20$, $0 \leq l \leq 14$); 2534 reflections with $|F_o| > 3\sigma(|F_o|)$ were used for structure determination. Intensities were corrected for Lorentz and polarization effects, but not for absorption. The Co-atom position was determined by the heavy-atom method and other non-H-atom positions were determined by successive difference Fourier syntheses. The H atoms were included in the calculations with a fixed geometrical constraint (C—H = 0·95 Å), except for those of H_2O, OH, NH, and NH_2. The structure was refined by full-matrix least squares using anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms ($U = 0·05$ Å^2); for the $\Lambda\Lambda$ configuration of the complex cation, $R = 0·060$ and $wR = 0·064$, $w = 2·2504/[\sigma^2(F_o) + 0·000886|F_o|^2]$, $S = 2·72$, and for the enantiomeric configuration ($\Delta\Delta$), $R = 0·066$ and $wR = 0·071$, $w = 2·4638/[\sigma^2(F_o) + 0·000970|F_o|^2]$, $S = 3·02$; $(\Delta/\sigma)_{\max} = 0·01$; $|\Delta\rho|_{\max}$ in final difference Fourier map = 0·95 e Å^{-3}. The enantiomeric structure could be rejected at the 0·005 significance level by the Hamilton (1965) test ($\mathscr{R}_{1,2209,0·005} = 1·002$). All calculations were performed with *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1976) on a Facom M-780/20 computer at the Computer Center of the University of Tsukuba. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final atomic parameters are listed in Table 1.†

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† Lists of structure factors, anisotropic thermal parameters, bond distances and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54244 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/91/102099-03$03.00

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for the non*-H *atoms*

$B_{eq} = (8\pi^2/3)\sum_i\sum_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	B_{eq}
Co(*A*)	0·21951 (7)	0·80555 (8)	0·1817 (1)	1·85 (4)
Co(*B*)	0·32926 (7)	0·72435 (8)	0·3872 (1)	1·95 (4)
O(1)	0·2606 (4)	0·6879 (4)	0·2298 (7)	2·32 (23)
O(2)	0·2870 (4)	0·8425 (4)	0·3404 (6)	2·08 (22)
O(*A*1)	0·3149 (4)	0·8230 (4)	0·0611 (7)	2·66 (25)
O(*A*2)	0·3658 (5)	0·7816 (6)	−0·1468 (8)	4·52 (38)
O(*A*3)	0·1180 (4)	0·7931 (4)	0·2907 (7)	2·39 (24)
O(*A*4)	0·0037 (4)	0·8723 (5)	0·3638 (9)	3·68 (31)
N(*A*1)	0·1587 (4)	0·7622 (5)	0·0184 (8)	2·40 (29)
N(*A*2)	0·1803 (4)	0·9279 (5)	0·1373 (8)	2·09 (27)
N(*B*1)	0·4284 (4)	0·7502 (5)	0·2664 (9)	1·75 (28)
N(*B*2)	0·3971 (5)	0·7738 (6)	0·5396 (8)	2·80 (32)
N(*B*3)	0·3693 (5)	0·5999 (5)	0·4192 (9)	2·84 (33)
N(*B*4)	0·2334 (5)	0·6942 (5)	0·5101 (9)	2·69 (30)
C(*A*1)	0·3089 (6)	0·7832 (7)	−0·0567 (11)	2·95 (38)
C(*A*2)	0·2263 (6)	0·7300 (7)	−0·0826 (10)	3·35 (41)
C(*A*3)	0·0734 (5)	0·8661 (6)	0·3038 (10)	2·46 (34)
C(*A*4)	0·1120 (6)	0·9525 (6)	0·2352 (11)	2·78 (37)
C(*A*5)	0·1039 (6)	0·8367 (6)	−0·0369 (11)	2·97 (39)
C(*A*6)	0·1510 (7)	0·9255 (6)	−0·0096 (11)	2·91 (39)
C(*B*1)	0·5034 (6)	0·7728 (7)	0·3562 (11)	3·34 (41)
C(*B*2)	0·4708 (6)	0·8266 (6)	0·4761 (11)	2·88 (40)
C(*B*3)	0·3029 (6)	0·5480 (6)	0·4916 (12)	3·37 (42)
C(*B*4)	0·2576 (7)	0·6148 (6)	0·5933 (12)	3·69 (45)
Cl(1)	0·3024 (2)	0·0996 (2)	0·1220 (2)	3·24 (10)
Cl(2)	0·4195 (2)	0·5442 (3)	0·0943 (4)	5·35 (16)
O(*W*1)	0·1209 (5)	0·5606 (7)	0·3038 (11)	5·70 (46)
O(*W*2)	0·5199 (5)	0·8703 (6)	0·9251 (10)	4·72 (40)
O(*W*3)	0·4672 (5)	0·9619 (6)	0·1630 (10)	4·96 (42)

Table 2. *Selected bond distances* (Å) *and angles* (°)

Co(*A*)—O(1)	1·899 (6)	Co(*B*)—O(1)	1·917 (6)
Co(*A*)—O(2)	1·919 (6)	Co(*B*)—O(2)	1·908 (6)
Co(*A*)—O((*A*1)	1·893 (7)	Co(*B*)—N(*B*1)	1·960 (7)
Co(*A*)—O(*A*3)	1·898 (6)	Co(*B*)—N(*B*2)	1·937 (8)
Co(*A*)—N(*A*1)	1·929 (7)	Co(*B*)—N(*B*3)	1·954 (7)
Co(*A*)—N(*A*2)	1·945 (7)	Co(*B*)—N(*B*4)	1·945 (7)
Co(*A*)—Co(*B*)	2·858 (2)	N(*A*1)—C(*A*5)	1·484 (11)
N(*A*2)—C(*A*6)	1·472 (12)	C(*A*5)—C(*A*6)	1·519 (13)
O(1)—Co(*A*)—O(2)	83·3 (3)	O(1)—Co(*B*)—O(2)	83·1 (2)
O(*A*1)—Co(*A*)—N(*A*1)	86·4 (3)	N(*B*1)—Co(*B*)—N(*B*2)	86·6 (3)
O(*A*3)—Co(*A*)—N(*A*2)	87·0 (3)	N(*B*3)—Co(*B*)—N(*B*4)	86·4 (3)
N(*A*1)—Co(*A*)—N(*A*2)	88·6 (3)	O(1)—Co(*B*)—N(*B*2)	174·1 (3)
O(*A*1)—Co(*A*)—O(*A*3)	175·1 (3)	O(2)—Co(*B*)—N(*B*3)	175·1 (3)
O(2)—Co(*A*)—N(*A*1)	175·6 (3)	N(*B*1)—Co(*B*)—N(*B*4)	177·6 (3)
O(1)—Co(*A*)—N(*A*2)	177·9 (3)	Co(*A*)—O(1)—Co(*B*)	97·0 (3)
Co(*A*)—O(2)—Co(*B*)	96·6 (3)		

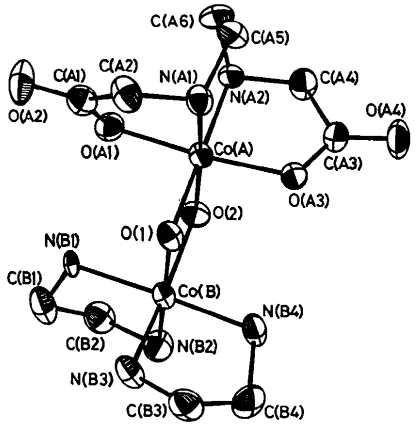
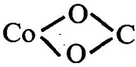


Fig. 1. *ORTEP* drawing of the $(+)^{CD}_{580}$-[(edda)Co(μ-OH)$_2$-Co(en)$_2$]$^+$ cation (50% probability thermal ellipsoids) with the atom-numbering scheme. H atoms are omitted for clarity.

Discussion. An *ORTEP* view of the complex cation and its numbering scheme are given in Fig. 1. Selected bond distances and angles are listed in Table 2.

The complex cation adopts a dinuclear structure bridged by two μ-OH groups. The bridging unit, , is strictly planar; the O—Co—O angles are 83·1 (3) and 83·3 (3)° and the Co—O—Co angles are 96·6 (3) and 97·0 (3)° (sum of these angles is 360°). The Co—Co distance is 2·858 (2) Å and the Co—O distances are 1·899 (6)–1·919 (6) Å (average 1·911 Å). These bond lengths agree well with those of the corresponding ones in [Co$_2$(μ-OH)$_2$(gly)$_2$(en)$_2$]$^{2+}$ [O—Co—O, 82·6 (1); Co—O—Co, 97·4 (2)°; Co—Co, 2·874 (1); and Co—O, 1·908 (3) and 1·917 (3) Å] (Hamada, Ohta, Fujiwara & Ama, 1989).

In the [Co(edda)(μ-OH)$_2$] moiety, the coordination geometry around the Co atom is almost octahedral. The edda ligand coordinates to the Co atom as a quadridentate ligand in the α chelation form. The absolute configuration of this moiety is Λ. The two asymmetric nitrogen donor atoms on the edda ligand adopt an *S* configuration and the N,N-chelate ring adopts the *gauche* form with a λ conformation. The bond distances and angles between the Co atom and the edda ligand are similar to those of *cis*-α-[Co(edda)(en)], except for those around the N(*A*1)—N(*A*2) chelate ring (Das, Sinha, Phulambrikar, Chatterjee & Bohra, 1989). The Co—N [1·929 (7) and 1·945 (7) Å] and C(*A*5)—C(*A*6) [1·519 (13) Å] distances are significantly shorter than those of the en complex [1·976 (6), 1·982 (6) and 1·559 (10) Å, respectively], while the N—C [1·472 (12) and 1·484 (11) Å] distances are longer than those of the en complex [1·439 (9) and 1·444 (11) Å]. The ligands of the remaining two coordination sites, which are occupied by μ-OH groups or en, may be responsible for these effects in the bond lengths.

In the [Co(μ-OH)$_2$(en)$_2$] moiety, the Co atom is also octahedrally surrounded by four N atoms of two en ligands and two *cis* O atoms. The absolute configuration of this moiety is Λ. Two en ligands take the *gauche* form with a δ conformation, the C—C bonds being nearly parallel to the pseudo-C_3 axis. The chelate-ring conformation in the [Co(μ-OH)$_2$(en)$_2$] moiety is that expected from intramolecular potential-energy calculations for the bis(ethylenediamine) complex, but differs from that in

$[Co(ox)(en)_2]^+$ (ox = oxalate) which has the $\Delta(\delta\lambda)$ conformation: the oblique-parallel type conformation (Aoki, Matsumoto, Ooi & Kuroya, 1973, and references therein). The bond distances and angles are similar to those of $[Co(ox)(en)_2]^+$, although the Co—N distances [1·937 (8)–1·960 (7) Å, average 1·949 Å] of the present complex are somewhat shorter than those [1·97 (2)–1·99 (2) Å, average 1·983 Å] of the ox complex.

There are some hydrogen bonds between the dicobalt complex cations and/or the water molecules, $N(B2)\cdots O(A2)$ [3·031 (11) Å], $N(B2)\cdots O(A4)$ [2·862 (11) Å], $N(B3)\cdots O(A4)$ [2·966 (11) Å], $O1\cdots O(W1)$ [2·950 (11) Å], $O(A2)\cdots O(W2)$ [2·811 (11) Å], $N(A1)\cdots O(W2)$ [2·954 (11) Å], $O(W1)\cdots O(W2)$ [2·873 (13) Å], and $O(W2)\cdots O(W3)$ [2·761 (13) Å].

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Acta Cryst. (1991). C**47**, 2101–2104

cis/trans Influences on Square-Planar Platinum(II) Complexes. Structure of *cis*-Bis(dimethyl sulfoxide)dinitratoplatinum(II)

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(*Received* 11 *April* 1991; *accepted* 3 *May* 1991)

Abstract. *cis*-$[Pt\{(CH_3)_2SO\}_2(NO_3)_2]$, $M_r = 475{\cdot}36$, monoclinic, $P2_1/c$, $a = 9{\cdot}006\,(1)$, $b = 14{\cdot}209\,(2)$, $c = 10{\cdot}908\,(2)$ Å, $\beta = 117{\cdot}88\,(1)°$, $V = 1233{\cdot}9\,(2)$ Å^3, $Z = 4$, $D_x = 2{\cdot}559$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}7107$ Å, $\mu = 11{\cdot}84$ mm^{-1}, $F(000) = 896$, $T = 293$ K, $R = 0{\cdot}033$ for 1763 unique reflections $[I > 3\sigma(I)]$. The Pt atom coordinates two S atoms from two dimethyl sulfoxide ligands and two O atoms from different nitrate ions in a slightly distorted square-planar geometry (maximal deviation 0·10 Å) in a *cis* arrangement. The compound consists of van der Waals packed molecules appearing in pairs with a Pt—Pt distance of 4·008 (1) Å. The acceptor–donor distances observed are: Pt—S = 2·214 (3), 2·220 (3) and Pt—O = 2·040 (9), 2·059 (9) Å. These are almost the same as the corresponding ones previously found in tetrakis(dimethyl sulfoxide)platinum(II) bis(trifluoromethanesulfonate) where two dimethyl sulfoxide ligands bond to Pt *via* their O atoms, also in a *cis* position. A literature survey of platinum dimethyl sulfoxide compounds shows that the Pt—S distance is significantly affected by both *cis* and *trans* influences.

Introduction. Dimethyl sulfoxide, $(CH_3)_2SO$ = DMSO, possesses two potential donor sites, *i.e.* the S and the O atoms. Hence it can act as an ambidentate ligand in coordinating metal ions (Cotton & Francis, 1960; Davies, 1981). In Pd^{II} and Pt^{II} complexes sulfur bonding is predominant. Recently, the crystal structure of tetrakis(dimethyl sulfoxide)platinum(II) bis(trifluoromethanesulfonate) was determined (Elding & Oskarsson, 1987). The coordination around Pt was found to be distorted square planar with two S- and two O-bonded DMSO ligands in a *cis* arrangement. The cyclic thioether 1,4-thioxane, C_4H_8OS, is also expected to be capable of ambidentate coordination in a similar arrangement. However, the crystal structure determination of tetrakis(1,4-thioxane)platinum(II) bis(trifluoromethanesulfonate) shows this not to be the case. All four thioxane molecules bond to platinum *via* their S atoms (Bugarcic, Norén, Oskarsson, Stålhandske & Elding, 1991). The Pt—S bond length is significantly longer than in the corresponding dimethyl sulfoxide compound. The different coordination ability of these two ambidentate ligands towards Pt^{II} may be

0108-2701/91/102101-04$03.00