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Bis(diethylenetriamine-N'-acetato)-di-μ-hydroxo-dicobalt(III) Perchlorate

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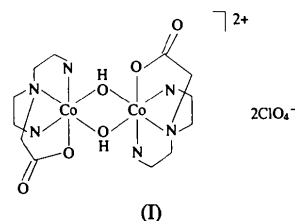(*Received* 1 *February* 1994; *accepted* 21 *November* 1994)

Abstract

The complex cation of the title compound, bis[bis-(2-aminoethyl)aminoacetato]-di-μ-hydroxo-dicobalt(III), $[Co_2(C_6H_{14}N_3O_2)_2(\mu-OH)_2](ClO_4)_2$, has a dinuclear structure, with two OH bridges. Each Co atom is octahedrally surrounded by a bis(2-aminoethyl)aminoacetate tripodal structure and two OH groups. In the crystal structure, intermolecular O—H···O hydrogen bonds form infinite chains of molecules, which significantly stabilizes the dinuclear structure; the Co···Co distance is 2.863 (1) Å.

Comment

The crystal and molecular structure and also the properties of metal–amino acid complexes are of continu-

ing interest to both coordination chemists and molecular biologists. In some cases, these compounds provide adequate model systems for metalloproteins and metalloenzymes (Freeman, 1973). Diethylenetriamine-N'-acetic acid (dtmaH) is a synthetic amino acid having a tripodal structure and studies of its complexes with metal ions (Cu, Zn, Ni) have been helpful in understanding the spectroscopic properties of Cu,Zn-superoxide dismutase and the magnetic properties of μ-carboxylate complexes (Mao, Yu, Chen, Han, Sui & Tang, 1993; Mao, Fu, Hang, Tang & Yu, 1993). In this paper, the structure of the complex [(dtma)Co(μ-OH)$_2$Co(dtma)](ClO$_4$)$_2$, (I), is reported.

(I)

The crystal structure consists of dimeric cations and perchlorate anions. The complex cation has an inversion centre located at the middle of the dimer. The coordination of Co^{III} is roughly octahedral and the bridging unit, Co(OH)Co(OH), is strictly planar with O—Co—O and Co—O—Co angles of 82.43 (8) and 97.57 (8)°, respectively. The Co···Co distance is 2.863 (1) Å and the Co—O distances are 1.902 (3) and 1.904 (2) Å. These bond lengths agree well with corresponding distances in [(edda)Co(OH)$_2$Co(en)$_2$]$^{2+}$ (edda is ethylenediaminediacetate and en is ethylenediamine) (Okamoto, Hidaka, Ama & Yasui, 1991). The fragments N1 N4 O7 O7', N4 N5 O8 O7' and N1 N5 O7 O8 are nearly
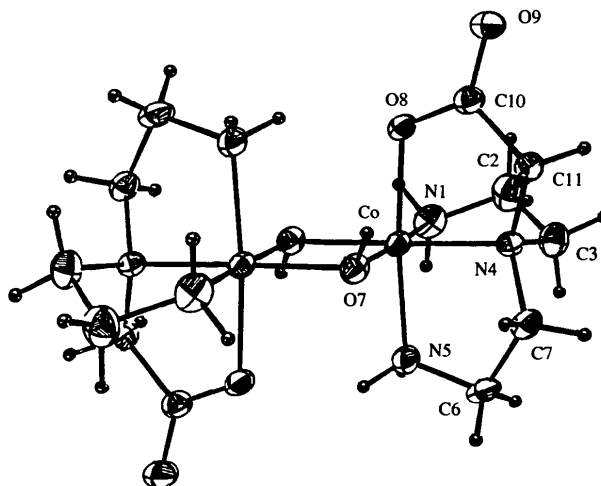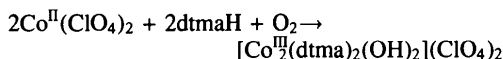

Fig. 1. Displacement ellipsoid representation (*ORTEP*; Johnson, 1965) of the title cation with the atomic numbering scheme. Ellipsoids are plotted at the 50% probability level.

planar with maximum deviations of 0.015 (5), 0.033 (5) and 0.105 (5) Å, respectively. The angles between the plane of the carboxylate group (atoms C10, O8 and O9) and the planes described above are 81.2 (4), 12.2 (18) and 83.6 (4)°, respectively.

In the crystal structure, the complex cations are connected by O7$\cdots$O9($\frac{1}{2}$ + y, 1−x, 1−z) hydrogen bonds [O7—H7 0.719 (2), H7$\cdots$O9 2.030 (2), O7$\cdots$O9 2.737 Å and O7—H7$\cdots$O9 168.6 (2)°] forming infinite chains. Two O atoms of the ClO$_4^-$ groups are disordered.

Experimental

dtmaH was prepared as described previously (Schneider & Collman, 1968) and the title compound was prepared by mixing aqueous solutions of dtmaH and [Co(ClO$_4$)$_2$].6H$_2$O in a 1:1 molar ratio, followed by addition of a saturated solution of NaClO$_4$. The solution was stirred at about 343 K for 1 h. Brown crystals were obtained by slow cooling in air for a few days. On the basis of the products obtained, the stoichiometry of the reaction was estimated to be:

$$2Co^{II}(ClO_4)_2 + 2dtmaH + O_2 \rightarrow$$
$$[Co_2^{III}(dtma)_2(OH)_2](ClO_4)_2$$

Crystal data

[Co$_2$(C$_6$H$_14$N$_3$O$_2$)$_2$(OH)$_2$]-
(ClO$_4$)$_2$
$M_r = 671.18$
Tetragonal
$P4/ncc$
$a = 14.203$ (6) Å
$c = 22.447$ (4) Å
$V = 4528.18$ Å^3
$Z = 8$
$D_x = 1.969$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 14.5$–$16.0°$
$\mu = 1.783$ mm^{-1}
$T = 293$ (2) K
Rectangular
$0.40 \times 0.25 \times 0.15$ mm
Brown

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.805$, $T_{max} = 0.999$
6790 measured reflections
2363 independent reflections

1550 observed reflections
$[I > 3\sigma(I)]$
$R_{int} = 0.027$
$\theta_{max} = 25°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 33.33 min
intensity decay: 0.1%

Refinement

Refinement on F
$R = 0.047$
$wR = 0.051$
$S = 4.149$
1550 reflections
160 parameters
Only coordinates of H atoms refined
Unit weights applied
$(\Delta/\sigma)_{max} = 0.02$

$\Delta\rho_{max} = 0.97$ (11) e Å^{-3}
$\Delta\rho_{min} = 0.00$ (11) e Å^{-3}
Extinction correction:
$|F_c|(1 + gI_c)^{-1}$ (Zachariasen, 1963)
Extinction coefficient:
1.8819×10^{-8}
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}/B_{iso}
Co	0.50611 (5)	0.46292 (5)	0.55916 (3)	1.45 (1)
Cl1	0.3693 (1)	0.631	3/4	2.68 (3)
Cl2	3/4	3/4	0.2536 (2)	3.39 (4)
Cl3	3/4	3/4	0.4907 (2)	2.99 (5)
O1	0.2837 (7)	0.6192 (7)	0.7769 (4)	10.3 (3)*
O2a †	0.400 (1)	0.546 (1)	0.7261 (7)	6.9 (3)*
O2b †	0.416 (1)	0.644 (1)	0.8042 (7)	7.5 (4)*
O3a †	0.6500 (8)	0.7686 (9)	0.2392 (5)	5.5 (3)*
O3b ‡	0.681 (2)	0.707 (2)	0.224 (1)	5.7 (6)*
O4 ‡	3/4	3/4	0.3160 (6)	5.7 (3)*
O5 †	0.833 (1)	0.750 (1)	0.4558 (6)	7.4 (3)*
O6 †	0.758 (3)	0.671 (1)	0.5288 (8)	13.2 (7)*
O7	0.5874 (3)	0.5124 (3)	0.4995 (2)	1.78 (7)
O8	0.5249 (3)	0.3355 (3)	0.5320 (2)	1.89 (8)
O9	0.6152 (3)	0.2099 (3)	0.5489 (2)	2.74 (9)
N1	0.4156 (4)	0.4147 (4)	0.6161 (2)	2.5 (1)
N4	0.6032 (3)	0.4356 (3)	0.6171 (2)	1.67 (9)
N5	0.5076 (4)	0.5911 (3)	0.5895 (2)	2.06 (9)
C2	0.4661 (5)	0.3572 (5)	0.6616 (3)	2.9 (1)
C3	0.5562 (5)	0.4088 (5)	0.6752 (3)	2.6 (1)
C6	0.5888 (5)	0.6053 (5)	0.6307 (3)	2.7 (1)
C7	0.6577 (4)	0.5238 (4)	0.6240 (3)	2.2 (1)
C10	0.5960 (4)	0.2934 (4)	0.5558 (3)	1.9 (1)
C11	0.6595 (4)	0.3548 (4)	0.5937 (3)	2.1 (1)

* B_{iso}.
† Occupancy factor 0.5.
‡ Occupancy factor 0.25.

Table 2. *Selected geometric parameters* (Å, °)

Co—O7	1.902 (3)	N4—C3	1.514 (4)
Co—N1	1.939 (2)	N5—C6	1.491 (1)
O8—C10	1.289 (4)	Co—O8	1.929 (2)
C2—C3	1.507 (5)	Co—N5	1.944 (2)
N4—C11	1.494 (4)	N1—C2	1.491 (4)
Co—O7′	1.904 (2)	N4—C7	1.482 (4)
Co—N4	1.934 (2)	C6—C7	1.523 (4)
O9—C10	1.228 (3)		
O7—Co—O7′	82.43 (8)	O7—Co—O8	92.32 (9)
O7—Co—N1	175.8 (2)	O7—Co—N4	96.58 (9)
O7—Co—N5	83.9 (1)	O7′—Co—O8	92.91 (8)
O7′—Co—N1	93.4 (2)	O7′—Co—N4	178.3 (1)
O7′—Co—N5	94.45 (9)	O8—Co—N1	88.2 (2)
O8—Co—N4	85.7 (1)	O8—Co—N5	171.2 (1)
N1—Co—N4	87.7 (2)	N1—Co—N5	96.2 (1)
N4—Co—N5	86.8 (1)	Co—O7—Co	97.57 (8)
Co—O8—C10	114.4 (2)	Co—N1—C2	109.1 (3)
Co—N4—C3	108.4 (2)	Co—N4—C7	105.9 (2)
Co—N4—C11	107.5 (2)	C3—N4—C7	110.6 (2)
C3—N4—C11	110.2 (2)	C7—N4—C11	114.0 (2)
Co—N5—C6	110.7 (2)	N1—C2—C3	106.3 (3)
N4—C3—C2	108.8 (2)	N4—C7—C6	108.5 (2)
O8—C10—O9	124.7 (3)	O8—C10—C11	115.6 (2)
O9—C10—C11	119.6 (3)	N4—C11—C10	108.7 (2)
N5—C6—C7	109.5 (2)		

Symmetry code: (′) $1 - x, 1 - y, 1 - z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Program used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program used to refine structure: *SDP-Plus* (B. A. Frenz & Associates, Inc, 1983). Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: AB1161). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(ethanol)-1κO,4κO-hexakis(μ-propionato)-1κO:2κO';2κ⁴O:3κ⁴O';3κO:4κO'-tetrakis(triphenylphosphine)-1κ²P,4κ²P-tetracopper(I,II), [Cu₄(C₃H₅O₂)₆(C₂H₆O)₂(C₁₈H₁₅P)₄]

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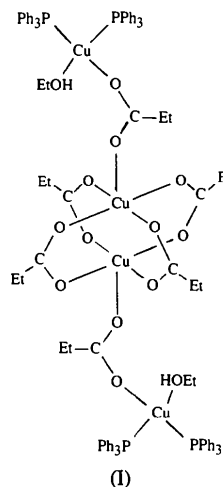*(Received 21 July 1993; accepted 30 August 1994)*

Abstract

The crystal structure of the title compound is formed by centrosymmetric [Cu₄(prop)₆(Ph₃P)₄(EtOH)₂] (prop = $CH_3CH_2CO_2^-$) molecules which contain a din-

uclear $Cu_2(\mu\text{-prop})_4$ unit similar to those found in tetrakis(μ-acetato)copper(II) complexes. Both axial positions of this unit are occupied by an O atom of the propionate group of a Cu(prop)(Ph₃P)₂(EtOH) moiety.

Comment

The crystal structure of the title compound, (I), consists of centrosymmetric [Cu₄(prop)₆(Ph₃P)₄(EtOH)₂] molecules (Fig. 1). The two centrosymmetrically related Cu^{II} atoms [Cu(1)] are linked by four bridging propionate groups, this motif being similar to those of copper acetate monohydrate (Meester, Fletcher & Skapski, 1973), [Cu₄Ac₆(Ph₃P)₄] (Ac = acetate) (Koman, Valigura, Ďurčanská & Ondrejovič, 1984) and [Cu₂Ac₄(Ph₃P)₂] (Koman, Valigura & Ondrejovič, 1988). Each Cu^{II} atom forms a further axial coordination bond with the O atom of a propionate group which forms a bridge to the Cu^I atom [Cu(2)]. The Cu^{II} coordination polyhedron is thus a distorted tetragonal pyramid with O atoms at the vertices. The Cu^I coordination polyhedron is a distorted tetrahedron formed by an ethanol O atom, a propionate O atom and two P atoms from the Ph₃P ligands.

(I)

The basal Cu^{II}—O [average 1.971 (9) Å] and apical Cu^{II}—O [2.092 (8) Å] bond lengths are close to those found in [Cu₄Ac₆(Ph₃P)₄]. The $Cu^{II}\cdots Cu^{II}$ distance is 2.624 (4) Å. The Cu^I—O(8) bond length of 2.075 (8) Å to the propionate ligand is significantly shorter than the Cu^I—O(9) distance of 2.183 (7) Å to the ethanol group. The remaining distances, including those in the Ph₃P ligand, are not significantly different from values found in [CuAc(Ph₃P)₂] (Drew, Othman, Edwards & Richards, 1975).

The large U_{eq} parameter for C(11) may indicate disorder. The crystals decompose in the X-ray beam at room temperature and lose ethanol at 353 K.