

Fig. 1. The  $\text{Cu}(\text{NO}_3)_2(\text{oaoH}_2)_2$  complex molecule, a perspective view. Thermal ellipsoids are drawn at the 50% probability level.

**Discussion.** Atomic coordinates are listed in Table 1, bond distances and angles in Table 2.\* The centrosymmetric complex molecule is shown in Fig. 1. The coordination around Cu is an elongated square bipyramid with the oxime N atoms of the two neutral

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38371 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$\text{oaoH}_2$  chelate ligands in the plane and O atoms of  $\text{NO}_3^-$  at the apexes. The Cu—O distance is 2.735 (5) Å, the N—Cu—O angles are 88.1 (2) and 85.4 (2)°. As usually found in complexes containing neutral  $\text{oaoH}_2$  chelate ligands, no intramolecular H bridges are formed. This is evident from the long O—O distance, 3.020 (8) Å. In this compound there is no bridging between the Cu ions, contrary to the behavior of nearly all the other Cu— $\text{oaoH}_2$  complexes investigated so far. Hence no magnetic interactions are to be expected. Yet it is interesting to note that in this compound of the general formula  $\text{MX}_2(\text{oaoH}_2)_2$ , X = any anion, the anions are in *trans* positions, whereas in the analogous Ni complexes they are always *cis* (Endres, 1983).

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## Structure of *trans*-Aquabromobis[ethanedial dioximate(1-)-*N,N'*]cobalt(III), $[\text{CoBr}(\text{C}_2\text{H}_3\text{N}_2\text{O}_2)_2\text{H}_2\text{O}]$

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**Abstract.**  $M_r = 330.98$ , orthorhombic, *Pbcn*,  $a = 8.446$  (1),  $b = 11.558$  (2),  $c = 9.922$  (1) Å,  $V = 968.6$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.27$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $F(000) = 648$ ,  $\mu = 58.6$  cm<sup>-1</sup>,  $R(R_w) = 0.068$  (0.082) for 848 observed unique reflections measured at  $295 \pm 2$  K. The coordination around  $\text{Co}^{\text{III}}$  is a distorted tetragonal bipyramid formed by four in-plane oxime N

atoms, and a  $\text{Br}^-$  ion and a water molecule in the axial positions. This coordination is reminiscent of the ligand-field geometry around the central metal in vitamin B<sub>12</sub> and related biological systems.

**Introduction.** Cobaloximes (bis-chelated cobalt oximates carrying variable ligands in the axial positions) are interesting model systems for investigations of the factors and mechanisms that may determine the biological activities of coenzyme vitamin B<sub>12</sub> and

\* Correspondence about preparation and properties should be addressed to M. Mégnamisi-Bélobmé, about the structure to H. Endres.

related natural substances (Hoshino, Konishi, Terai & Imamura, 1982; Schrauzer & Windgassen, 1966; Schrauzer, Lee & Siebert, 1970). Indeed, the close similarity of the coordination around cobalt in cobaloximes and in vitamin B<sub>12</sub> lends strong support to the anticipation that an adequate correlation of relevant chemical and structural parameters in cobaloximes may greatly facilitate the understanding of the pathway of these biological activities.

The few examples of cobaloximes studied earlier (Brown, 1978; Brown, Lyles, Pencovici & Kallen, 1975; Brown & Kallen, 1972; Nishida, Ida & Kida, 1980; Bakač & Espenson, 1980) have been those which were essentially based on butanedione dioximate (or dimethylglyoximate, dmg) as the chelating ligand.

Recently we reported the mixed valence salt, hexa-aquacobalt(II) bis[dibromobis(ethanedial dioximate)cobaltate(III)] acetone solvate (Egharevba, Mégnamisi-Bélombé, Endres & Rossato, 1982) in which the anion is a cobaloxime involving Co<sup>III</sup> in a distorted (4 + 2) octahedral coordination. We have now converted this cobaloxime into the neutral trans-aquabromobis(ethanedial dioximate)cobalt(III) which, like vitamin B<sub>12</sub>, contains Co<sup>III</sup> in tetragonal bipyramidal coordination. We report its preparation and structure in the following.

**Experimental.** Hexa-aquacobalt(II) bis[dibromobis(ethanedial dioximate)cobaltate(III)] acetone solvate (Egharevba, Mégnamisi-Bélombé, Endres & Rossato, 1982) was dissolved to saturation in *ca* 353 K warm water (100 ml). The red-brown solution was filtered while hot into a beaker which was loosely covered and allowed to stand undisturbed on a warmed electric plate (*ca* 313 K). Within two days single crystals suitable for X-ray diffraction had grown. The brown crystals were separated by filtration, washed with a little acetone and dried. M.p. 457–458 K (vigorous decomposition). The compound is moderately soluble in water. The microanalysis was consistent with the formulated composition: % found (calculated) C 14.85 (14.08), H 2.28(2.34), N 16.99 (16.44), Br 23.8 (23.44).

Block-like crystal; Weissenberg photographs showed it to be orthorhombic; accurate lattice parameters from an orientation matrix derived from the setting angles of 25 reflections centered on a diffractometer (Syntex R3, monochromatic Mo K $\alpha$  radiation). Data collection ( $\theta$ - $2\theta$  scans background-peak-background,  $2\theta \leq 60^\circ$ ) yielded 848 observed independent reflections with  $I > 2.5 \sigma(I)$ ; empirical absorption correction ( $\psi$  scans) applied (minimum transmission factor 0.55, taking maximum transmission as unity). The positions of Co and Br from a Patterson synthesis, other non-H atoms from Fourier maps; refinement by 'cascade matrix' least squares [anisotropic temperature factors,  $\sum w(\Delta F)$  minimized] converged with  $R(R_w) = 0.068$  (0.082);  $w = 1/\sigma^2(F)$ . H positions could not be identified in a difference Fourier map; largest features +2.1 and

-1.67 e  $\text{\AA}^{-3}$ , close to the heavy-atom positions. Nova 3 computer, plots drawn on a Tektronix plotter; SHELXTL program system (Sheldrick, 1981), which uses scattering factors from *International Tables for X-ray Crystallography* (1974) and takes anomalous dispersion into account.

**Discussion.** Atomic coordinates are listed in Table 1,\* bond distances and angles in Table 2. A view of the complex molecule is shown in Fig. 1. Co, Br, and the water molecule are on a crystallographic twofold axis. Although the H atoms could not be detected, it appears reasonable to assume that each ethanedial dioxime, H<sub>2</sub>(g), molecule has lost a proton to become a uni-negative chelating ligand, as is commonly the case in bis( $\alpha,\beta$ -dione dioximate)metal complexes. Usually the two dioximate ligands are connected to each other by intramolecular O-H-O bridges, with typical O-O separations of 2.4–2.7  $\text{\AA}$ . In the present case, the O(2)-O'(3) distance of 2.53 (2)  $\text{\AA}$  lies well within this range. The composition CoBr(H<sub>2</sub>O)(H(g))<sub>2</sub> implies, therefore, the presence of Co<sup>III</sup>. The coordination around Co has the shape of a tetragonal bipyramid with the four oxime N atoms in the basal plane, and Br<sup>-</sup> and H<sub>2</sub>O in the axial positions. The axial Co-OH<sub>2</sub> and the

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Table 1. Atomic coordinates ( $\times 10^4$ ) and isotropic temperature factors ( $\times 10^3$ ) equivalent to the refined anisotropic values

Equivalent isotropic  $U$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	$x$	$y$	$z$	$U(\text{\AA}^2)$
Br	0	1581 (1)	7500	20 (1)
Co	0	3626 (2)	7500	27 (1)
O(1)	0	5318 (9)	7500	49 (4)
N(1)	-2257 (9)	3653 (7)	7553 (13)	36 (3)
N(2)	-414 (11)	3622 (8)	5604 (9)	27 (3)
O(2)	-3115 (9)	3687 (15)	8732 (9)	48 (4)
O(3)	751 (10)	3593 (8)	4709 (8)	40 (3)
C(1)	-3008 (14)	3719 (19)	6409 (13)	31 (5)
C(2)	-1889 (15)	3681 (11)	5246 (12)	35 (4)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Br-Co	2.364 (2)	Co-O(1)	1.955 (11)
Co-N(1)	1.908 (8)	Co-N(2)	1.914 (9)
N(1)-O(2)	1.377 (15)	N(1)-C(1)	1.302 (17)
N(2)-O(3)	1.325 (12)	N(2)-C(2)	1.297 (15)
C(1)-C(2)	1.492 (17)		
Br-Co-O(1)	180.0	Br-Co-N(1)	90.9 (3)
O(1)-Co-N(1)	89.1 (3)	Br-Co-N(2)	89.8 (3)
O(1)-Co-N(2)	90.2 (3)	N(1)-Co-N(2)	81.0 (3)
N(1)-Co-N'(1)	178.2 (5)	N(2)-Co-N'(2)	179.7 (6)
Co-N(1)-C(1)	117.6 (9)	Co-N(1)-O(2)	123.3 (8)
Co-N(2)-O(3)	121.5 (7)	O(2)-N(1)-C(1)	118.9 (9)
O(3)-N(2)-C(2)	122.1 (9)	Co-N(2)-C(2)	116.4 (8)
N(2)-C(2)-C(1)	113.5 (10)	N(1)-C(1)-C(2)	111.3 (10)

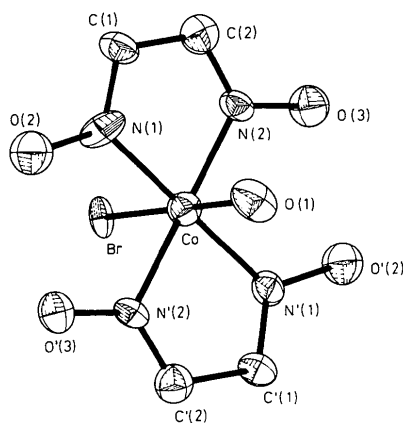


Fig. 1. A perspective view of the  $\text{CoBr}(\text{H}_2\text{O})[\text{H}(\text{g})]_2$  complex molecule. Thermal ellipsoids are drawn at the 50% probability level.

equatorial Co—N distances are virtually identical while the Co—Br separation is considerably larger, of course.

The complexes are linked by intermolecular H bridges *via* the  $\text{H}_2\text{O}$  ligands. This is indicated by a short O(3)—O''(1) distance of 2.60 (2) Å, where O''(1) is related to the O(1) position of Table 1 by the symmetry operation  $-x, 1-y, 1-z$ .

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## Structure of Di- $\mu$ -chloro-bis[chloro(1,2-cyclohexanedione dioxime- $N,N'$ )copper(II)], [ $\text{Cu}_2(\text{C}_6\text{H}_{10}\text{N}_2\text{O}_2)_2\text{Cl}_4$ ]

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(Received 15 December 1982; accepted 8 February 1983)

**Abstract.**  $M_r = 553.22$ , monoclinic,  $P2_1/n$ ,  $a = 6.957(2)$ ,  $b = 19.161(4)$ ,  $c = 7.660(2)$  Å,  $\beta = 93.34(2)^\circ$ ,  $V = 1019.4$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.80$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $F(000) = 556$ ,  $\mu = 26.5$  cm<sup>-1</sup>,  $R(R_w) = 0.028(0.032)$  for 1786 observed independent reflections measured at  $295 \pm 2$  K. Monomers are linked into discrete, centrosymmetric dimers by two Cl

\* Correspondence about preparation and properties should be addressed to M. Mégnamisi-Bélobmé, about the structure to H. Endres.

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bridges. The coordination around Cu is a distorted square pyramid. The cyclohexane rings adopt a twisted conformation.

**Introduction.** The title compound was prepared in the course of research which aims to provide more examples of magnetic coordination compounds suitable for investigation of superexchange (Andoseh, Douglas, Egharevba & Mégnamisi-Bélobmé, 1982). So far, our interest has focused on the synthesis, structural and