Structure of *trans*-Dinitratobis(oxamide oxime)copper(II), [Cu(C₂H₆N₄O₂)₂(NO₃)₂]

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Abstract. $M_r = 423.76$, $P\bar{1}$, $a = 7.269$ (4), $b = 7.392$ (3), $c = 8.098$ (4) Å, $\alpha = 68.45$ (3), $\beta = 67.34$ (3), $\gamma = 64.70$ (3)°, $V = 352.2$ Å³, $Z = 1$, $T = 295$ K, $D_x = 2.00$ g cm⁻³, Mo $K\alpha$ radiation, $\mu = 16.3$ cm⁻¹, $F(000) = 215$, $R(R_w) = 0.060(0.069)$ for 1256 unique observed reflections. Cu has an elongated square bipyramidal coordination and there is no bridging between Cu centers.

Introduction. Previous experience with oxamide oxime ('diaminoglyoxime', oaoH₂) complexes of Cu^II showed that these may form dinuclear or polymeric species in the solid, depending on the anions and on the conditions of preparation (Endres, Genc & Nöthe, 1983*a,b*). Possible magnetic exchange between the paramagnetic Cu^II ions is of primary interest in these compounds. In the nitrate described below unbridged complex molecules have been found.

Experimental. Cu(NO₃)₂ was dissolved in a beaker containing hot ethanol. A frit was placed, inverted, into the beaker, and solid oaoH₂ was put inside the frit. An ethanolic solution of oaoH₂ was then added dropwise into the frit. When all the oaoH₂ had dissolved, a green solution was obtained. Evaporation by standing at room temperature yielded dark-green crystals of the title compound.

Block-like crystal, $0.05 \times 0.05 \times 0.25$ mm; lattice parameters from the setting angles of 32 reflections centered on a diffractometer (Siemens AED, Zr-filtered Mo $K\alpha$ radiation); 'five-value method', θ–2θ scans, $2\theta_{max} = 60°$, 1256 observed unique reflections with $I > 2.5\,\sigma(I)$, 799 unobserved reflections, $\sum w(\Delta F)^2$ minimized, $w = 1/\sigma^2(F)$; as $Z = 1$, Cu can be placed at the origin of the centrosymmetric unit cell, but to check for any error in the assumed composition, a Patterson synthesis was calculated which showed no metal–metal vectors; a Fourier synthesis revealed all the non-H atoms; refinement with isotropic temperature factors resulted in an unweighted $R = 0.155$; refinement with anisotropic temperature factors converged with the

values in the *Abstract*; as not all of the expected H atoms could be found in a difference Fourier map, they were neglected completely; calculations performed on a Nova3 computer, plots drawn on a Tektronix plotter; *SHELXTL* program system (Sheldrick, 1981) was applied, which uses scattering factors from *International Tables for X-ray Crystallography* (1974) and takes anomalous dispersion into account; refinement carried out by 'cascade matrix' least squares.

Table 1. *Atomic coordinates* (× 10⁴) *and isotropic temperature factors* (× 10³) *equivalent to the refined anisotropic values*

U is defined as $U = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$, $\tilde{\mathbf{U}}$ signifying the diagonalized U matrix.

	x	y	z	U (Å²)
N(5)	2739 (8)	8819 (8)	3221 (8)	41 (3)
O(3)	3116 (7)	6953 (6)	3523 (6)	51 (2)
O(4)	2387 (8)	9613 (7)	4494 (8)	62 (3)
O(5)	2677 (10)	9951 (8)	1650 (7)	77 (3)
Cu	0	0	0	41 (1)
N(1)	2104 (9)	−2420 (8)	−963 (7)	43 (3)
N(2)	−908 (8)	−2225 (7)	1962 (7)	42 (3)
N(3)	−82 (9)	−5822 (7)	3061 (7)	43 (3)
N(4)	3433 (8)	−6048 (8)	−236 (7)	43 (3)
O(1)	3836 (8)	−2492 (8)	−2531 (6)	61 (3)
O(2)	−2662 (7)	−2143 (6)	3523 (6)	50 (2)
C(1)	2081 (10)	−4225 (10)	126 (8)	36 (3)
C(2)	286 (10)	−4125 (9)	1836 (8)	32 (3)

Table 2. *Bond distances* (Å) *and angles* (°)

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N(5)–O (3)	1.232 (7)	N(5)–O(4)	1.259 (10)
N(5)–O(5)	1.246 (7)	Cu–N(1)	1.979 (5)
Cu–N(2)	1.966 (5)	Cu–N'(1)	1.979 (5)
Cu–N'(2)	1.966 (5)	N(1)–O(1)	1.400 (6)
N(1)–C(1)	1.304 (8)	N(2)–O(2)	1.405 (6)
N(2)–C(2)	1.316 (7)	N(3)–C(2)	1.340 (7)
N(4)–C(1)	1.343 (8)	C(1)–C(2)	1.492 (7)
N'(2)–Cu	1.966 (5)		
O(3)–N(5)–O(4)	120.7 (5)	O(3)–N(5)–O(5)	120.2 (7)
O(4)–N(5)–O(5)	119.0 (6)	N(1)–Cu–N(2)	79.9 (2)
N(1)–Cu–N'(1)	180.0	N(2)–Cu–N'(1)	100.1 (2)
N(1)–Cu–N'(2)	100.1 (2)	N(2)–Cu–N'(2)	180.0
N'(1)–Cu–N'(2)	79.9 (2)	Cu–N(1)–O(1)	128.8 (4)
Cu–N(1)–C(1)	116.3 (4)	O(1)–N(1)–C(1)	114.1 (5)
Cu–N(2)–O(2)	130.6 (4)	Cu–N(2)–C(2)	116.7 (4)
O(2)–N(2)–C(2)	112.7 (5)	N(1)–C(1)–N(4)	125.4 (5)
N(1)–C(1)–C(2)	113.7 (5)	N(4)–C(1)–C(2)	120.8 (5)
N(2)–C(2)–N(3)	124.6 (5)	N(2)–C(2)–C(1)	113.1 (5)
N(3)–C(2)–C(1)	122.3 (5)		
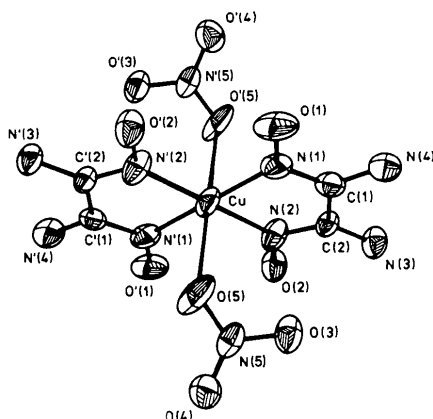
Fig. 1. The $Cu(NO_3)_2(oaoH_2)_2$ complex molecule, a perspective view. Thermal ellipsoids are drawn at the 50% probability level.

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.

$oaoH_2$ chelate ligands in the plane and O atoms of 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 $oaoH_2$ 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 $Cu-oaoH_2$ 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 $MX_2(oaoH_2)_2$, $X =$ any anion, the anions are in *trans* positions, whereas in the analogous Ni complexes they are always *cis* (Endres, 1983).

References

ENDRES, H. (1983). *Z. Anorg. Allg. Chem.* Submitted.
ENDRES, H., GENC, N. & NÖTHE, D. (1983a) *Acta Cryst.* B39, 701–703.
ENDRES, H., GENC, N. & NÖTHE, D. (1983b). *Z. Naturforsch. Teil B*, 38, 90–95.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
SHELDRICK, G. M. (1981). *SHELXTL. An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.

Structure of *trans*-Aquabromobis[ethanedial dioximato(1—)-N,N']cobalt(III), [CoBr(C2H3N2O2)2H2O]

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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^3, $Z = 4$, $D_x = 2·27$ g cm^{-3}, Mo $K\alpha$ radiation, $F(000) = 648$, $\mu = 58·6$ cm^{-1}, $R(R_w) = 0·068$ (0·082) for 848 observed unique reflections measured at 295 ± 2K. The coordination around Co^{III} is a distorted tetragonal bipyramid formed by four in-plane oxime N atoms, and a 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_{12} and related biological systems.

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

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_{12} and