

Table 3. Distances (Å) and angles (°) in the $B(C_6H_5)_4^-$ ions

E.s.d.'s are given in parentheses.

	[Ni(pssp)Br][BPh ₄]	[Ni(pssp)I][BPh ₄]
B—C(32)	1.66 (3)	1.71 (3)
B—C(38)	1.70 (2)	1.70 (3)
B—C(44)	1.72 (2)	1.71 (3)
B—C(50)	1.76 (3)	1.71 (3)
C(32)—B—C(38)	109 (1)	107 (2)
C(32)—B—C(44)	110 (1)	107 (2)
C(32)—B—C(50)	114 (1)	113 (2)
C(38)—B—C(44)	111 (1)	111 (2)
C(38)—B—C(50)	109 (1)	111 (2)
C(44)—B—C(50)	103 (1)	107 (2)

C(55)—H(6A) 2.35 (3) and 2.29 (3) Å in the Br and I compounds, respectively. These distances are shorter than the sum of van der Waals radii (Br—H 2.95; I—H 3.15; C—H 2.7 Å) (Pauling, 1960; Baur, 1972). The H atoms have, however, been geometrically generated.

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The *catena* Structure and EPR Properties of Bis(oxamide oximato)copper(II)—Oxamide Oxime, $[Cu(C_2H_5N_4O_2)_2] \cdot C_2H_6N_4O_2$

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Abstract. $M_r = 415.83$, monoclinic, $C2/c$, $a = 23.504$ (28), $b = 5.047$ (3), $c = 20.103$ (16) Å, $\beta = 144.03$ (7)°, $V = 1400.7$ Å³, $Z = 4$, $D_x = 1.97$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 16.2$ cm⁻¹, room temperature, $F(000) = 852$, final $R = 0.046$ for 821 observed reflections. The planar centrosymmetric complex molecules form stacks along **b**, the normals of the planes being inclined at $\sim 50^\circ$ to the stacking axis. Close axial interactions between Cu and the amino groups of adjacent complex molecules within a stack, 2.885 (10) Å, result in an elongated square-bipyramidal coordination around Cu. Free oxamide oxime, present in the *s-trans* form, links the stacks into sheets by forming H bridges to the complex molecules. EPR signal intensities follow a Curie–Weiss law in the temperature range 110–400K.

Introduction. Oxamide oxime, $HON=C(NH_2)-C(NH_2)=NOH$ (diaminoglyoxime, oaoH₂) (Ephraim, 1889) forms a variety of complexes with the ions of the Ni triad, depending on crystallization conditions (Endres, 1982). As the structural chemistry of Cu^{II} complexes of α,β -dione dioximes is usually different from that of Ni^{II}, Pd^{II}, Pt^{II}, we started a survey of the structures of Cu complexes of oaoH₂. We were especially interested as to whether the amino groups would coordinate to Cu as well, giving rise to polymeric complexes. Here we report the *catena* structure found in the title compound.

Experimental. The compound was prepared by a diffusion method: A frit was placed inversely in a beaker with ethanol, copper acetate was dissolved outside the frit, and solid oaoH₂ was placed inside the frit. Within a few days brown crystals several mm long

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grew inside the frit. They were filtered off, and unreacted oaoH₂ was removed by treating the residue with hot ethanol. Analysis {% found [calculated for Cu(oaoH)₂.oaoH₂]}: C 17.4 [17.3], H 4.02 [3.88], N 38.1 [40.4], Cu 16.6 [15.3], rest 23.9 [O: 23.1]. Alternatively, the compound may be prepared with the above technique by using an ammoniacal solution of other Cu salts, e.g. CuCl₂ or Cu(NO₃)₂. Lattice parameters derived from the setting angles of 37 reflections centered on a diffractometer (Siemens AED, Zr-filtered Mo K α radiation); data collection (θ - 2θ scans, 'five-value' method, $2\theta \leq 50^\circ$) carried out over half a sphere in reciprocal space; equivalent reflections averaged to give a set of 821 observed independent data with $I > 2.5\sigma(I)$; no correction for absorption. The Patterson synthesis showed that Cu can be placed at the origin of the unit cell, and subsequent Fourier syntheses revealed the positions of the other non-H atoms; refinement of these with anisotropic temperature factors gave $R(R_w) = 0.062$ (0.074); a difference Fourier map revealed the H positions, which were refined with individual isotropic temperature factors lowering $R(R_w)$ to 0.046 (0.059);* $w = 1/\sigma^2(F)$. Calculations were carried out on a Nova 3 computer; plots were drawn on a Tektronix plotter. The SHELXTL program system (Sheldrick, 1981) was applied; this uses scattering factors from *International Tables for X-ray Crystallography* (1974) and takes anomalous dispersion into account. EPR measurements were performed on a Bruker B-ER 418 spectrometer equipped with a Bruker NMR gaussmeter for field calibration and an EIP 351D microwave frequency meter. EPR intensities were obtained by the double integration of the first derivative signal using a Bruker Aspects 2000 Computer and EPR CALL program. The integration range was at least 15 times the peak-to-peak linewidth.

Discussion. Atomic coordinates are listed in Table 1, bond distances and angles in Table 2. Fig. 1 shows the centrosymmetric Cu(oaoH)₂ molecule and the two uncoordinated oaoH₂ molecules which are connected *via* H bonds (Table 2) to the complex species. The uncoordinated oaoH₂ molecules adopt the *s-trans* configuration and are bisected by a crystallographic twofold axis.

The molecules are stacked along **b** in a way similar to the structure of Ni(oaoH)₂.oaoH₂, which was first reported to be triclinic (Endres, Jannack & Prickner, 1980), but was then shown to crystallize in space group C2/c (Herbstein & Marsh, 1982), and to the structure of Co(oaoH)₂.oaoH₂ (Bekaroglu, Sarisaban, Koray &

Ziegler, 1977). The plane of the complex molecule (defined as the plane through Cu and the four oxime N atoms) is inclined at 50 (1) $^\circ$ to **b**, resulting in an interplanar distance of 3.26 (1) Å. A perpendicular projection of two adjacent complex molecules of a stack onto each other is shown in Fig. 2. Cu lies nearly perpendicularly above and below the amino N atoms of adjacent complex species, at a Cu-N distance of 2.885 (10) Å. Hence the coordination polyhedron around Cu is an elongated square bipyramid with angles N(basal)-Cu-N(apical) of 90.2 (4) and 93.5 (4) $^\circ$. A similar environment of the metal atom was found in the Co analogue, with an apical distance of 2.639 (5) Å. In the corresponding Ni compound the distance is much longer, 3.04 (1) Å. Fig. 3 shows a side view of a stack.

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

U_{eq} is defined as $U_{eq} = \frac{1}{3} \text{trace } \bar{U}$, \bar{U} signifying the diagonalized U matrix.

	x	y	z	U_{eq} or $U(\text{\AA}^2)$
Cu	0	0	0	25 (1)
O(1)	-1024 (3)	481 (9)	-2243 (3)	19 (5)
O(2)	1614 (4)	3473 (11)	1999 (4)	23 (6)
N(1)	-320 (4)	1415 (11)	-1169 (4)	17 (6)
N(2)	979 (4)	2737 (11)	888 (4)	17 (6)
N(3)	112 (5)	4667 (16)	-1542 (5)	23 (8)
N(4)	1417 (5)	6559 (14)	734 (5)	25 (8)
C(1)	199 (5)	3428 (14)	-868 (5)	14 (7)
C(2)	925 (5)	4297 (13)	327 (6)	14 (7)
O(3)	2439 (4)	1749 (12)	907 (5)	27 (6)
N(5)	2904 (4)	-317 (13)	989 (4)	18 (6)
N(6)	1356 (5)	-675 (13)	-958 (6)	21 (7)
C(3)	2313 (5)	-1367 (14)	18 (5)	14 (7)
H(1)	147 (5)	225 (14)	216 (5)	15 (21)
H(2)	-43 (4)	439 (12)	-219 (4)	10 (16)
H(3)	40 (5)	614 (14)	-132 (6)	11 (19)
H(4)	153 (4)	701 (13)	51 (5)	0 (19)
H(5)	168 (6)	684 (21)	121 (7)	40 (40)
H(6)	112 (3)	-86 (10)	-151 (4)	0 (15)
H(7)	129 (3)	84 (10)	-84 (4)	0 (15)
H(8)	275 (5)	244 (14)	137 (5)	0 (22)

Table 2. Bond distances (Å) and angles ($^\circ$), including some H-bonding interactions

Cu-N(1)	1.934 (10)	N(1)-C(1)-N(3)	124.8 (7)
N(2)	1.934 (6)	C(2)	113.5 (10)
N''(4)	2.885 (10)	N(3)-C(1)-C(2)	121.7 (8)
N(1)-Cu-N(2)	81.9 (3)	C(2)-N(4)	1.333 (10)
N''(4)	90.2 (3)	N(2)-C(2)-N(4)	124.0 (8)
N(2)-Cu-N''(4)	93.5 (3)	C(1)	113.6 (6)
N(1)-O(1)	1.355 (7)	N(4)-C(2)-C(1)	122.2 (10)
C(1)	1.300 (11)	O(3)-N(5)	1.420 (13)
Cu-N(1)-O(1)	125.4 (6)	N(5)-C(3)	1.278 (10)
C(1)	115.3 (6)	O(3)-N(5)-C(3)	110.1 (6)
O(1)-N(1)-C(1)	119.3 (9)	N(6)-C(3)	1.374 (8)
N(2)-O(2)	1.399 (9)	C(3)-C'(3)	1.479 (20)
C(2)	1.296 (15)	N(5)-C(3)-N(6)	125.1 (10)
Cu-N(2)-O(2)	126.7 (7)	C'(3)	116.2 (6)
C(2)	115.2 (4)	N(6)-C(3)-C'(3)	118.5 (8)
O(2)-N(2)-C(2)	117.1 (6)	O(1)-O(2)	2.696 (10)
C(1)-N(3)	1.349 (17)	O(3)-O(1)	2.663 (10)
C(2)	1.495 (11)		

* Lists of structure factors, anisotropic thermal parameters, and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38406 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

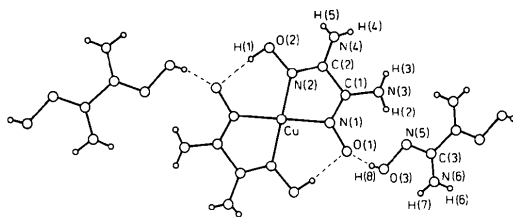


Fig. 1. The $\text{Cu}(\text{oaoH})_2$ complex molecule and two H-bonded oaoH_2 molecules with the numbering scheme.

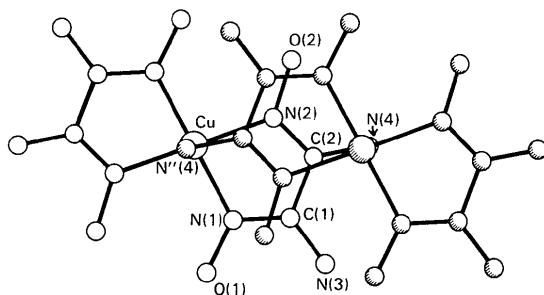


Fig. 2. Perpendicular projection of two adjacent complex molecules of a stack onto each other.

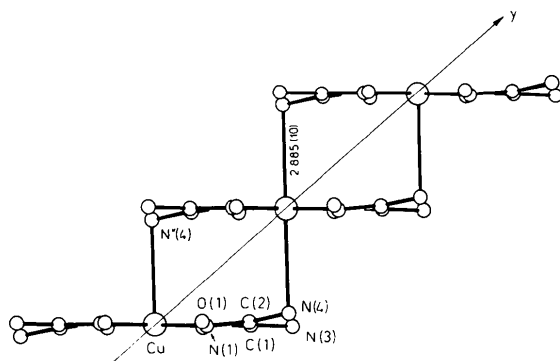


Fig. 3. Side view of the stack of complex molecules showing the axial Cu–N interaction. The distance between adjacent Cu atoms is 5.047 (3) Å.

It is especially impressive to see how the amino N(4) atoms are bent out of the molecular plane [by 0.38 (1) Å] to come in close contact with the adjacent Cu atom.

The stacks are linked along z by intermolecular H bridges from the uncoordinated oaoH_2 molecules. Thus, sheets of alternating $[\text{Cu}(\text{oaoH})_2]$ and oaoH_2 piles are formed parallel to the xz plane. Comparable sheets exist in the Ni and Co analogues.

The powder EPR spectrum consists of a single, slightly asymmetric line at $g = 2.07$ and a peak-to-peak width of 103 Gauss (10.3 mT). The g value is thus in the range usual for Cu complexes with similar ligands (Nonaka, Tokii & Kida, 1974). The rather strong interaction between monomers of a chain as indicated by the out-of-plane bending of N(4) (Fig. 3) could cause coupling between the unpaired electrons of adjacent Cu^{2+} ions. Yet the temperature dependence of the EPR intensity between 110 and 400 K follows a Curie law or at most a Curie–Weiss law with a Weiss constant < 10 K. The magnetic behavior in the indicated temperature range thus resembles that of many other ligand-bridged Cu^{II} complexes (Hatfield, 1974). Yet measurements of the static susceptibility at very low temperatures could possibly indicate spin–spin interactions.

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