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Aqua(*N*,*N*-dimethylethylenediamine *N*-oxide)oxalatocopper(II) Dihydrate

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Abstract. $[Cu(C_4H_{12}N_2O)(C_2O_4)(H_2O)].2H_2O$, $C_6H_{14}CuN_2O_6.2H_2O$, triclinic, $P\bar{1}$, $Z = 2$, $a = 6\cdot207\,(3)$, $b = 8\cdot960\,(7)$, $c = 11\cdot627\,(12)$ Å, $\alpha = 103\cdot32\,(7)$, $\beta = 94\cdot44\,(7)$, $\gamma = 104\cdot38\,(6)°$, $V = 603\cdot27$ Å^3, $D_m = 1\cdot73$, $D_c = 1\cdot71$ Mg m^{-3}. $R = 0\cdot049$ for 2416 observed reflections. The coordination polyhedron of Cu is a square pyramid whose base is formed by N and O atoms from the diamine *N*-oxide and two O atoms of the oxalate ion. A water molecule is at the apex of the pyramid.

Introduction. Tertiary amine oxides form stable complexes with transition metals. Kida & Oniki (1972) prepared bis complexes of *N*,*N*-dialkylethylenediamine *N*-oxide with Ni and Cu. In connection with our studies on diamine complexes of Cu^{II} carboxylates (Pajunen & Pajunen, 1979) we have prepared a mixed-ligand complex containing *N*,*N*-dimethylethylenediamine *N*-oxide. *N*,*N*-Dimethylethylenediamine *N*-oxide was prepared from the corresponding diamine and hydrogen peroxide (Kida & Oniki, 1972). Crystals of the title compound were obtained from a solution of Cu^{II} oxalate (50 mmol in 200 ml of 50% methanol) treated with slight excess of ligand. Blue-violet crystals were recrystallized from a water–ethanol (1 : 1) mixture.

The unit cell was found to be triclinic. Lattice constants and intensities were determined with a Syntex $P2_1$ automatic diffractometer by the ω-scan technique with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å) and a variable scan range. Of the 3367 independent reflections with $3 < 2\theta < 57°$, 2416 were considered observed by the criterion $I > 3\cdot0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensities were reduced to structure amplitudes by the application of Lorentz and polarization factors; no absorption corrections were applied. The structure was determined with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The refinement of the coordinates and anisotropic temperature factors for non-hydrogen atoms was carried out by the full-matrix least-squares method with XRAY76 (Stewart, 1976). The positions of the H atoms were determined from a difference synthesis and H atoms were included in the refinement with fixed positions and isotropic temperature factors of $U = 0\cdot06$ Å^2. Scattering factors of Cromer & Mann (1968) were used for the non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for H. The refinement converged at $R = 0\cdot049$ with unit weights.* The final atomic coordinates and U_{eq} thermal parameters (Hamilton, 1959) of the non-hydrogen atoms are given in Table 1, and coordinates of the H atoms in Table 2. Bond lengths and angles are listed in Table 3. A

Table 1. *Fractional atomic coordinates* (×10^4) *and* U_{eq} (Å^2 × 10^2) *for the non-hydrogen atoms*

	x	y	z	U_{eq}
Cu	2093 (1)	3283 (1)	3164 (1)	3·2
O(1)	2896 (6)	5448 (4)	4217 (3)	3·7
O(2)	5691 (7)	7706 (4)	4669 (4)	5·5
O(3)	5143 (6)	3933 (4)	2758 (3)	3·8
O(4)	8140 (6)	6066 (5)	3204 (4)	5·2
O(5)	1615 (7)	1220 (4)	2027 (3)	4·4
O(6)	343 (7)	4366 (6)	1653 (4)	6·2
O(7)	5753 (12)	1591 (9)	655 (5)	11·5
O(8)	3889 (14)	5969 (10)	585 (8)	15·3
N(1)	−729 (7)	2709 (5)	3853 (4)	4·2
N(2)	519 (7)	−243 (5)	2247 (4)	3·4
C(1)	4837 (8)	6300 (6)	4139 (4)	3·4
C(2)	6182 (8)	5387 (6)	3287 (4)	3·3
C(3)	−1390 (9)	1040 (6)	3922 (5)	4·7
C(4)	−1630 (10)	−167 (7)	2773 (6)	5·0
C(5)	2096 (10)	−759 (7)	2962 (6)	5·2
C(6)	−204 (11)	−1445 (7)	1051 (6)	5·8

Table 2. *Fractional atomic coordinates* (×10^3) *of the* H *atoms*

	x	y	z		x	y	z
H(N1)	−17	338	467	H(C6)	−101	−261	110
H′(N1)	−195	302	337	H′(C6)	−133	−120	74
H(C3)	−4	83	432	H″(C6)	117	−130	68
H′(C3)	−275	76	429	H(O6)	−77	381	129
H(C4)	−233	−123	290	H′(O6)	−5	497	207
H′(C4)	−283	3	216	H(O7)	451	98	61
H(C5)	273	4	360	H′(O7)	549	239	60
H′(C5)	127	−174	316	H(O8)	401	645	124
H″(C5)	309	−98	251	H′(O8)	275	603	31

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35186 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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perspective drawing of the complex is given in Fig. 1 with the atomic labelling.

Discussion. The structure consists of neutral complexes and water molecules. The Cu coordination polyhedron is a square pyramid whose base is occupied by N and O atoms from the *N,N*-dimethylethylenediamine *N*-oxide and two O atoms of the oxalate ion. The Cu—O and Cu—N distances correspond well to values fround in diamine carboxylato complexes. The four atoms forming the base of the pyramid have a slight tetrahedral distortion, as shown by their displacements from the mean plane through them (Table 4). The Cu atom is displaced 0·060 (1) Å towards the apex of the pyramid, which is occupied by the water O(6). The sixth octahedral site is free. This is undoubtedly due to the steric effect of the methyl groups attached to N(2). The nearest atom in the direction of the sixth coordination position is O(2)($1-x$, $1-y$, $1-z$) at 3·182 (5) Å.

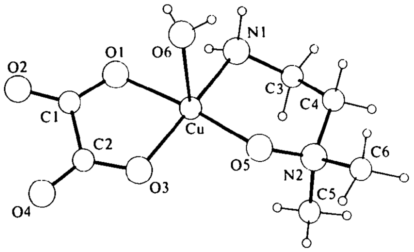

Fig. 1. A view of the complex showing the atom numbering.

Table 3. *Bond lengths* (Å) *and angles* (°)

Cu–N(1)	1·984 (5)	C(2)–O(3)	1·282 (5)
Cu–O(1)	1·960 (4)	C(2)–O(4)	1·239 (6)
Cu–O(3)	1·965 (4)	N(1)–C(3)	1·472 (8)
Cu–O(5)	1·947 (4)	C(3)–C(4)	1·484 (8)
Cu–O(6)	2·495 (6)	N(2)–C(4)	1·519 (8)
C(1)–C(2)	1·562 (7)	N(2)–C(5)	1·462 (8)
C(1)–O(1)	1·279 (6)	N(2)–C(6)	1·506 (7)
C(1)–O(2)	1·227 (6)	N(2)–O(5)	1·410 (6)
N(1)–Cu–O(1)	90·9 (2)	O(2)–C(1)–C(2)	119·6 (4)
N(1)–Cu–O(3)	170·4 (2)	O(3)–C(2)–C(1)	115·2 (4)
N(1)–Cu–O(5)	96·1 (2)	O(3)–C(2)–O(4)	125·2 (5)
O(1)–Cu–O(3)	84·1 (1)	O(4)–C(2)–C(1)	119·5 (4)
O(1)–Cu–O(5)	173·0 (2)	Cu–N(1)–C(3)	113·6 (4)
O(3)–Cu–O(5)	89·2 (2)	Cu–O(5)–N(2)	123·7 (3)
O(6)–Cu–N(1)	93·2 (2)	N(1)–C(3)–C(4)	115·0 (5)
O(6)–Cu–O(1)	86·7 (2)	C(3)–C(4)–N(2)	116·5 (4)
O(6)–Cu–O(3)	94·7 (2)	C(4)–N(2)–C(5)	114·1 (5)
O(6)–Cu–O(5)	92·1 (2)	C(4)–N(2)–C(6)	105·8 (4)
Cu–O(1)–C(1)	113·8 (3)	C(4)–N(2)–O(5)	111·7 (4)
Cu–O(3)–C(2)	112·8 (3)	C(5)–N(2)–C(6)	108·4 (5)
O(1)–C(1)–C(2)	114·0 (4)	C(5)–N(2)–O(5)	109·8 (4)
O(1)–C(1)–O(2)	126·4 (5)	C(6)–N(2)–O(5)	106·7 (4)

Table 4. *Description of the best planes*

(*a*) Equations of planes with reference to the cell axes.

Plane (I): $2{\cdot}464X - 5{\cdot}568Y + 9{\cdot}573Z = 1{\cdot}717$
Plane (II): $2{\cdot}890X - 5{\cdot}615Y + 9{\cdot}118Z = 1{\cdot}706$
Plane (III): $3{\cdot}257X - 5{\cdot}559Y + 8{\cdot}710Z = 1{\cdot}613$
Plane (IV): $2{\cdot}498X - 5{\cdot}279Y + 9{\cdot}701Z = 1{\cdot}905$

(*b*) Deviations of atoms (10^{-3} Å) from the mean plane. Atoms with an asterisk were used to define the plane.

Plane (I)		Plane (II)		Plane (III)		Plane (IV)	
Cu*	0	Cu	−60 (1)	Cu*	0	Cu	−46 (1)
O(1)*	0	O(1)*	−84 (4)	O(5)*	0	O(1)*	33 (4)
O(2)	−136 (4)	O(3)*	86 (4)	N(1)*	0	O(2)*	−22 (4)
O(3)*	0	O(5)*	−77 (4)	N(2)	649 (4)	O(3)*	−22 (4)
O(4)	−22 (4)	N(1)*	75 (6)	C(3)	773 (6)	O(4)*	34 (4)
C(1)	−71 (6)			C(4)	364 (6)	C(1)*	−8 (6)
C(2)	−46 (6)					C(2)*	−16 (6)

Table 5. *Interatomic distances* (Å) *between* O *atoms less than* 3 Å

Symmetry code
(i) $-1+x$, y, z
(ii) $1-x$, $1-y$, $-z$
(iii) $1-x$, $-y$, $-z$

O(6)–H′(O6)···O(4)^{i}	2·755 (7)*	O(6)···O(8)	2·850 (10)
O(7)–H′(O7)···O(8)^{ii}	2·857 (13)*	O(7)···O(7)^{ii}	2·789 (10)
O(3)···O(7)	2·950 (8)	O(8)···O(8)^{iii}	2·675 (13)

* Hydrogen bonding.

The five-membered Cu–oxalate ring is almost planar and the six-membered Cu–diamine *N*-oxide ring is in the chair configuration.

The complexes and water molecules are connected by hydrogen bonds and van der Waals contacts (Table 5). There are three water molecules per asymmetric unit. One of these [O(6)] is coordinated to Cu and forms an O—H···O hydrogen bond to O(4)($-1+x,y,z$). This hydrogen bond serves to join the complexes in chains parallel to **a**. Two other water molecules [O(7) and O(8)] form chains parallel to **b**.

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