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Acta Cryst. (1992). C**48**, 31–33

Structure of Dichlorobis(1,10-phenanthroline *N*-oxide)copper(II) Dihydrate

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(*Received* 5 *March* 1991; *accepted* 8 *August* 1991)

Abstract. $[CuCl_2(C_{12}H_8N_2O)_2].2H_2O$, $M_r = 562.90$, triclinic, $P\bar{1}$, $a = 8.586\ (6)$, $b = 8.790\ (8)$, $c = 8.770\ (6)$ Å, $\alpha = 68.23\ (6)$, $\beta = 62.42\ (5)$, $\gamma = 86.08\ (7)^\circ$, $V = 540.5\ (8)$ Å^3, $Z = 1$, $D_m = 1.67\ (2)$, $D_x = 1.729$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.30$ mm^{-1}, $F(000) = 287$, $T = 293$ K, final $R = 0.0337$ for 1173 unique reflections with $F > 4\sigma(F)$. The crystal structure consists of $Cu(phenO)_2Cl_2$ (phenO = 1,10-phenanthroline *N*-oxide) and water molecules which are linked *via* hydrogen bonds. The Cu^{II} atom is situated on a centre of symmetry and is octahedrally coordinated by two N and two O atoms of phenO and by two Cl atoms with Cu—N(1) 1.983 (4), Cu—O(1) 1.903 (5) and Cu—Cl 2.899 (4) Å.

Introduction. The title compound is one of a series containing chelating aromatic *N*-oxide ligands. Studies of these complexes are in progress to determine the various bonding modes of the *N*-oxide ligands. 1,10-Phenanthroline *N*-oxide (hereafter phenO) can form six-membered metallocycles containing an aromatic N and *N*-oxygen donor atoms, and it is more rigid than the previously studied 2,2′-bipyridyl *N*,*N*′-dioxide (Baran, Koman, Valigura & Mrozinski, 1991; Koman, Baran & Valigura, 1991) since there is no possibility of rotation of the aromatic rings.

Experimental. Green-brown, well shaped crystals were obtained by slow crystallization from an equimolar ethanolic solution of $CuCl_2$ and phenO; the size of the crystal used was 0.5 × 0.05 × 0.2 mm. D_m was measured by flotation. Crystal system and approximate cell dimensions were determined from Weissenberg and precession photographs. Accurate unit-cell parameters were obtained by a least-squares fit of 15 reflections ($18 < 2\theta < 40^\circ$). Intensity data were measured on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\alpha$ radiation; θ–2θ-scan mode with $(2\theta)_{\max} = 55^\circ$ and index range h −12/12, k −12/12, l 0/12; two standard reflections (212, 201) were measured every 98 reflections, no significant systematic fluctuations were found. 3335 reflections were measured; 1175 unique reflections with $F_o > 4\sigma(F_o)$ were considered observed; $R_{\text{int}} = 0.050$ for 392 unique reflections before absorption correction. Empirical absorption correction based on intensity measurements at different azimuthal angles, transmission range 0.897–0.999. The structure was solved by Patterson methods using *SHELXS86* (Sheldrick, 1990) and refined on F by least squares with *SHELX76* (Sheldrick, 1976). A difference map of the partially refined structure gave the positions of all the H atoms. Refinement continued on all 198 positional and thermal parameters (anisotropic for non-H atoms and isotropic for H atoms). In the final cycle $R = 0.034$ and $wR = 0.029$ for 1173 observed reflections [two of the strongest reflections (010 and $2\bar{1}2$) were thought to be affected by extinction and were excluded from the refinement], $w^{-1} = k\sigma^2(F)$, $k = 0.2763$; maximum $\Delta/\sigma = 0.056$ and maximum and minimum heights in final $\Delta\rho$ map were +0.38 and −0.26 e Å^{-3}. The scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

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Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
Cu	0*	0*	0*	20 (1)
Cl	1338 (2)	3129 (2)	6837 (2)	43 (1)
O(1)	1491 (4)	627 (4)	10789 (4)	35 (2)
O(2)	−1073 (6)	6030 (6)	7004 (7)	57 (3)
N(1)	1944 (4)	−1178 (4)	8783 (5)	28 (2)
N(2)	3142 (4)	1323 (4)	9564 (5)	29 (2)
C(1)	1533 (6)	−2492 (6)	8593 (7)	36 (3)
C(2)	2742 (6)	−3350 (6)	7650 (7)	34 (3)
C(3)	4480 (6)	−2745 (6)	6754 (7)	35 (3)
C(4)	6803 (6)	−684 (6)	5941 (6)	33 (3)
C(5)	7294 (6)	648 (6)	6062 (6)	34 (2)
C(6)	6599 (6)	2687 (6)	7484 (7)	38 (3)
C(7)	5399 (6)	3311 (6)	8711 (7)	39 (3)
C(8)	3671 (6)	2607 (6)	9749 (7)	34 (3)
C(9)	4994 (5)	−1364 (5)	6908 (6)	28 (2)
C(10)	6035 (5)	1358 (5)	7275 (6)	30 (2)
C(11)	4258 (5)	693 (5)	8281 (6)	25 (2)
C(12)	3688 (5)	−636 (5)	8023 (6)	26 (2)

* Parameter fixed.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and hydrogen-bond geometries* (Å, °) *with e.s.d.'s in parentheses*

Cu—Cl	2.899 (4)	C(3)—C(9)	1.392 (8)
Cu—O(1)	1.903 (5)	C(4)—C(5)	1.327 (9)
Cu—N(1)	1.983 (4)	C(5)—C(10)	1.423 (7)
O(1)—N(2)	1.326 (4)	C(6)—C(7)	1.362 (8)
N(1)—C(1)	1.319 (8)	C(7)—C(8)	1.367 (6)
N(1)—C(12)	1.361 (5)	C(9)—C(12)	1.405 (6)
N(2)—C(8)	1.334 (8)	C(10)—C(11)	1.393 (6)
N(2)—C(11)	1.372 (6)	C(11)—C(12)	1.426 (8)
C(2)—C(3)	1.356 (7)		

Cl—Cu—O(1)	87.8 (1)	C(6)—C(7)—C(8)	119.6 (6)
Cl—Cu—N(1)	94.7 (1)	N(2)—C(8)—C(7)	120.8 (5)
O(1)—Cu—N(1)	86.7 (2)	C(3)—C(9)—C(4)	120.9 (5)
Cu—O(1)—N(2)	120.2 (3)	C(3)—C(9)—C(12)	118.8 (5)
Cu—N(1)—C(1)	118.4 (4)	C(4)—C(9)—C(12)	120.3 (5)
Cu—N(1)—C(12)	123.2 (4)	C(5)—C(10)—C(6)	119.7 (5)
O(1)—N(2)—C(8)	115.3 (4)	C(5)—C(10)—C(11)	119.7 (5)
O(1)—N(2)—C(11)	122.5 (5)	C(6)—C(10)—C(11)	120.6 (5)
N(1)—C(1)—C(2)	124.8 (6)	N(2)—C(11)—C(10)	116.8 (5)
C(1)—C(2)—C(3)	117.7 (6)	N(2)—C(11)—C(12)	122.9 (5)
C(2)—C(3)—C(9)	120.0 (5)	C(10)—C(11)—C(12)	120.2 (5)
C(5)—C(4)—C(9)	121.0 (5)	N(1)—C(12)—C(9)	120.1 (5)
C(4)—C(5)—C(10)	120.5 (5)	N(1)—C(12)—C(11)	122.1 (5)
C(7)—C(6)—C(10)	119.3 (5)	C(9)—C(12)—C(11)	117.8 (5)

X—H···*Y*	*X*···*Y*	H···*Y*	*X*—H···*Y*
O(2)—H(11)···Cl	3.175 (6)	2.24 (6)	171 (6)
O(2)—H(12)···Cl^{i}	3.284 (7)	2.72 (9)	139 (8)
C(6)—H(6)···O(2^{ii})	3.452 (9)	2.78 (6)	123 (4)
C(7)—H(7)···O(2^{ii})	3.356 (8)	2.60 (4)	128 (4)
C(8)—H(8)···O(2^{iii})	3.287 (8)	2.27 (5)	168 (4)

Symmetry code: (i) $-x, 1-y, 1-z$; (ii) $1+x, y, z$; (iii) $-x, 1-y, 2-z$.

Discussion. Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1 and bond lengths and angles (Nardelli, 1983) in Table 2.* The molecular structure with atom numbering is shown in Fig. 1 (*ORTEP*II; Johnson, 1971).

The unit cell contains a molecule of [Cu(phenO)$_2$Cl$_2$], with the Cu atom lying on a centre of symmetry, and two water molecules. The coordination polyhedron of the Cu^{II} atom is an elongated quasi-tetragonal bipyramid with an equatorial plane formed by the O and N atoms of two bidentate phenO ligands and with Cl ions in the axial sites. The observed Cu—O and Cu—N bond lengths of 1.903 (5) and 1.983 (4) Å agree well both with values found for O and N donors in equatorial positions in Cu^{II} complexes (Gažo, Bersuker, Garaj, Kabešová, Kohout, Langfelderová, Melník, Serátor & Valach, 1976) and also with those of 1.953 (4) and 1.999 (4) Å in bis[2-(methylaminoethyl)pyridine 1-oxide]copper(II) diperchlorate (Pavkovic & Brown, 1982). Elongation of the square bipyramid is typical for Cu^{II} complexes showing 4 + 2 coordination and the Cu—Cl distance is within the interval from 2.845 (4) Å (Nardelli, Fava, Boldrini & Giraldi, 1965) to 2.916 (2) Å (Stephens, Vagg & Williams, 1977) found for analogous [CuN$_2$O$_2$Cl$_2$] chromophores.

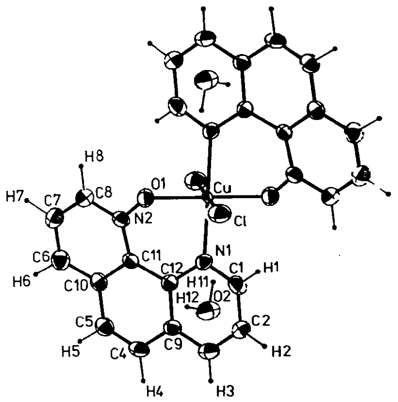

Fig. 1. The molecular structure of dichlorobis(1,10-phenanthroline *N*-oxide)copper(II) dihydrate with atom numbering.

The phenO ligand atoms exhibit unusually large deviations from planarity, those for O(1) and N(1) [−0.226 (4) and 0.255 (4) Å, respectively] being the largest. The dihedral angles between the *N*-oxide ring plane [defined by the N(2), C(6), C(7), C(8), C(10) and C(11) atoms] and the other rings of the phenO ligand [5.08 (15) and 10.26 (14)°, respectively] characterize the twisted ligand structure.

In contrast to phenanthroline complexes the Cu^{II} atom is displaced from the mean plane of the phenO ligand by as much as 0.206 (2) Å. The donor O atom

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54486 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0249]

lies on the opposite side of the mean phenO plane from the Cu atom. The displacement of the Cu atom from the ligand plane, together with the strict planarity of the equatorial CuN_2O_2 unit, leads to the adoption of a 'stepped' structure (Holm & O'Connor, 1971) characterized by the angle θ between the planes of the ligand and the chromophore of 33.77 (14)° and/or by the step s (defined as the distance between the ligand planes) of 1.570 (4) Å.

The complex and water molecules are held together by van der Waals interactions and hydrogen bonds (see Table 2). There are intermolecular Cl···H (water) contacts involving H(11) and H(12) of 2.24 (6) and 2.72 (9) Å and between the water oxygen O(2) and H(6), H(7) and H(8) atoms [O(2)···H 2.78 (6), 2.60 (4) and 2.27 (5) Å respectively]. Other contacts correspond to the sum of the van der Waals radii for the atoms involved.

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Acta Cryst. (1992). **C48**, 33–35

Structure of an Aminodicarbonyldiiodo(triphenylphosphine)osmium Complex

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(*Received* 3 *June* 1991; *accepted* 24 *July* 1991)

Abstract. $[OsI_2(CO)_2(C_3H_9N)(C_{18}H_{15}P)]$, $M_r = 821.4$, monoclinic, $P2_1/n$, $a = 15.011$ (3), $b = 11.316$ (4), $c = 16.155$ (2) Å, $\beta = 106.55$ (1)°, $V = 2630$ (1) Å^3, $Z = 4$, $D_x = 2.07$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 7.25$ mm^{-1}, $F(000) = 1528$, $T = 298$ K, $R = 0.058$, $wR = 0.051$ for 2432 observed reflections. The Os atom is six coordinate in a slightly distorted octahedral geometry. Two I ligands and two CO groups are mutually in a *cis* form. The Os—C(2) bond length [1.75 (2) Å] is significantly shorter than that of Os—C(1) [1.82 (2) Å]. Two Os—I bond distances [2.698 (2), 2.705 (3) Å] are among the shortest Os—I bond lengths reported in the literature.

Introduction. In the previous paper (Lu, Chen, Lin & Peng, 1988) we reported the synthesis of (μ-I)$Os_2(CO)_6$(μ-OCNHCHMe$_2$)I_2, (1). Since halides have been employed as promoters in many catalytic (Dombek, 1981) or stoichiometric reactions (Morrison, Geoffroy & Rheingold, 1985), we were interested in the chemical behavior of the cluster in the presence of halogen. In this work, the crystal structure of the product, $Os(CO)_2[NH_2CH(CH_3)_2](PPh_3)I_2$, (2), from the reaction of (1) with PPh_3 is determined.

Experimental. Synthesis of the title compound was achieved by reacting the carboxamidotriiododiosmium complex (μ-I)$Os_2(CO)_6$(μ-OCNHCHMe$_2$)I_2 with PPh_3 in refluxing chloroform solution. Crystals of the yellow complex were grown by slow evaporation of a saturated dichloromethane solution of the complex at room temperature. CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$. Crystal 0.20 × 0.20 × 0.30 mm. Unit-cell parameters from 24 reflections with $18.78 < 2\theta < 24.72$°, data collected by $\omega/2\theta$-scan method with scan width of $2(1.0 + 0.35\tan\theta)$° and variable scan speed of 20/2–20/

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0108-2701/92/010033-03$03.00