

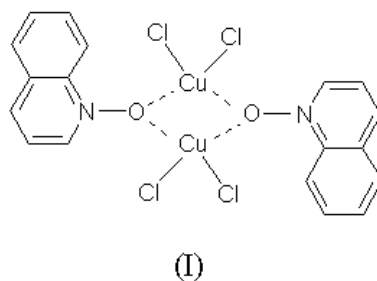
Bis(μ -quinoline *N*-oxide- κ^2 O:O)bis[dichloro-copper(II)], a powder diffraction studySvetlana N. Ivashevskaja,^{a*}
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lana@mainpgu.karelia.ru**Key indicators**Powder X-ray study
T = 293 K
Mean σ (C–C) = 0.04 Å
R factor = 0.064
w*R* factor = 0.081For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of the title compound, [Cu₂Cl₄(C₉H₇NO)₂], has been determined from powder diffraction data. The crystals are built of dinuclear complex molecules, with a central four-membered Cu₂O₂ ring located about a crystallographic inversion centre, which involves two Cu atoms, each carrying two terminal chloro ligands each [Cu–Cl = 2.213 (8) and 2.222 (8) Å] and two O atoms of the quinoline *N*-oxide ligand. The Cu atom has a square-planar coordination, with considerable distortions due to the four-membered ring [O–Cu–O = 78 (1)° and Cl–Cu–Cl = 100.2 (3)°].

Received 6 November 2002
Accepted 11 November 2002
Online 15 November 2002**Comment**

Heteroaromatic *N*-oxides are unique compounds, due to the fact that the N–O group can act either as an electron-acceptor or an electron-donor, depending on the compound structure and conditions. Molecular complexes of heteroaromatic *N*-oxides demonstrate a broad spectrum of biological activity (Ponomarenko, 1999). Moreover, adducts of quinoline *N*-oxide with CuCl₂ have interesting magnetic properties (Whyman *et al.*, 1967).

The electronic spectrum of the title complex, (I), in ethanol is almost identical to the spectrum of quinoline *N*-oxide; however, in CH₂Cl₂, which is not capable of forming donor–acceptor bonds, a new band appears [379 (2.83) nm] and there is a decrease in band intensity. Such an effect is probably caused by symmetrization of the structure of the complex (decreasing log ϵ) and formation of new Cu–O bonds.



The intensities of the N–O bands in the IR spectrum (1310 and 1272 cm^{−1}) are decreased in (I), compared to the spectrum of the parent quinoline *N*-oxide. On the other hand, in agreement with the literature findings (Garvey *et al.*, 1968), a new band at 1175 cm^{−1}, caused by the formation of a donor–acceptor bond between the O atom of quinoline *N*-oxide and a Cu atom, appears; the 343–336 cm^{−1} bands corresponding to the Cu–Cl bonds are also present.

The structure of the dinuclear molecule consists of a central four-membered Cu₂O₂ ring, formed by two Cu atoms and two

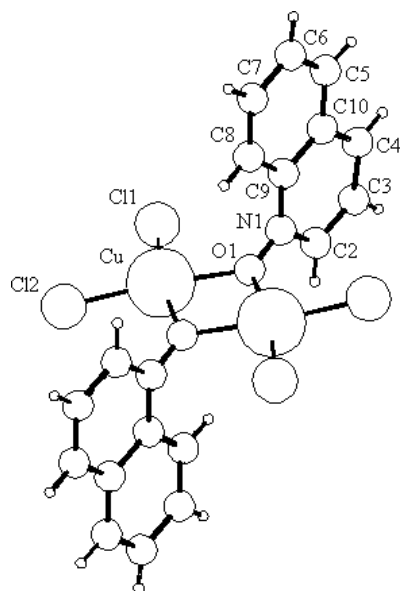


Figure 1
The molecular structure of (I), with the atomic numbering scheme.

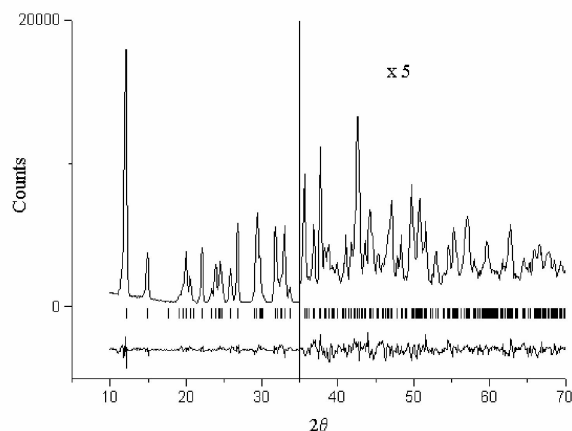


Figure 2
The Rietveld plot for (I), showing the observed and difference profiles. The reflection positions are shown above the difference profile.

quinoline *N*-oxide O atoms (Fig. 1). The structure is similar to that of di- μ -(pyridine *N*-oxide)-bis[dichlorocopper(II)] reported by Sager *et al.* (1967). The Cu atom has a distorted square-planar coordination, formed by two terminal chloro ligands [Cu belonging to quinoline *N*-oxide ligands [Cu—O1 = 2.11 (2) Å and Cu—O1ⁱ 2.00 (2) Å; symmetry code: (i) 1 - x, 1 - y, 1 - z]. The distortions of the coordination are revealed in the O1—Cu—O1ⁱ and Cl1—Cu—Cl2 bond angles [78 (1) and 100.2 (3)°, respectively], which deviate significantly from 90°, as well as in the displacement of the Cu atom from the plane through its four ligands [0.21 (3) Å]. The plane of the Cu₂O₂ ring forms a dihedral angle of 90 (2)° with the quinoline fragment.

Experimental

Compound (I) was prepared in polycrystalline form, by mixing saturated ethanol solutions of quinoline *N*-oxide dihydrate (0.181 g, 1 mmol) and CuCl₂·2H₂O (0.171 g, 1 mmol). A yellow precipitate, which quickly turned black, was washed with ethanol and diethyl ether. It was then dried in air (yield: 58%). The electronic spectra of (I) in ethanol and in CH₂Cl₂ were recorded using a Specord UV-Vis spectrometer. The IR spectra were measured in KBr using a Specord M-80 spectrometer.

Crystal data

[Cu ₂ Cl ₄ (C ₉ H ₇ NO) ₂]	$\lambda = 1.93728 \text{ \AA}$
$M_r = 559.02$	Cell parameters from 66 reflections
Monoclinic, $P2_1/n$	$\theta = 4.8\text{--}26.3^\circ$
$a = 11.780 (3) \text{ \AA}$	$\mu = 7.32 \text{ mm}^{-1}$
$b = 14.872 (5) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 6.061 (2) \text{ \AA}$	Black
$\beta = 98.27 (2)^\circ$	Specimen shape: flat sheet
$V = 1050.8 (6) \text{ \AA}^3$	12 × 12 × 2 mm
$Z = 2$	Particle morphology: no specific habit
$D_x = 1.767 \text{ Mg m}^{-3}$	
Fe $K\alpha$ radiation	

Data collection

Burevestnic (Saint Petersburg)	$\theta_{\max} = 35.0^\circ$
X-ray powder diffraction system	$h = 0 \rightarrow 6$
DRON-4.07	$k = 0 \rightarrow 8$
Specimen mounting: the powder was sprinkled on the sample holder.	$l = -3 \rightarrow 3$
Specimen mounted in reflection mode	$2\theta_{\min} = 10.00, 2\theta_{\max} = 70.00^\circ$
	Increment in $2\theta = 0.1^\circ$

Refinement

Refinement on I_{net}	$w = 1/Y_{\text{meas}}^2$
$R_p = 0.064$	$(\Delta/\sigma)_{\max} = 0.02$
$R_{\text{wp}} = 0.081$	$\Delta\rho_{\max} = 0.52 \text{ e \AA}^{-3}$
$R_{\text{exp}} = 0.029$	$\Delta\rho_{\min} = -0.48 \text{ e \AA}^{-3}$
$S = 2.80$	Preferred orientation correction: spherical harmonics expansion (Ahtee <i>et al.</i> , 1989) up to the 6th order
Profile function: split-type pseudo-Voigt (Toraya, 1986)	
77 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Cu—O1	2.11 (2)	Cu—Cl2	2.213 (8)
Cu—O1 ⁱ	2.00 (2)	Cu—Cl1	2.222 (8)
O1 ⁱ —Cu—O1	78 (1)	Cl2—Cu—Cl1	100.2 (3)
O1—Cu—Cl2	168.8 (5)	Cu ⁱ —O1—Cu	101.8 (1)
O1—Cu—Cl1	91.1 (5)	N1—O1—Cu	126.3 (15)
Cl1—Cu—O1—N1	20 (2)	Cu—O1—N1—C2	-100 (2)

Symmetry code: (i) 1 - x, 1 - y, 1 - z.

X-ray powder diffraction patterns were obtained with two X-ray powder instruments, *viz.* a Guinier-de Wolff camera and a DRON-4.07 diffraction system equipped with a standard resolution goniometer GUR-9 and scintillation counter. The first pattern was used for indexing and the second pattern was measured for structure solution and refinement. The powder was sprinkled on the sample holder to avoid preferred orientation. During the exposures, the specimen was spun in its plane to improve particle statistics. The unit-cell dimensions were determined using the indexing program *TREOR* (Werner

et al., 1985) with $M_{20} = 39$ and $F_{29} = 59$ (0.0076, 65), using the positions of the first 66 peaks.

The correct solution was found in monoclinic space group $P2_1/n$. The structure was determined using the *MRIA* program (Zlokazov & Chernyshev, 1992), using grid search (Chernyshev & Schenk, 1998) and simulated annealing (Zhukov *et al.*, 2001) techniques. The strength of the restraints was a function of the interatomic separation and, for intramolecular bond lengths, corresponds to an r.m.s. deviation of 0.03 Å. An additional restraint was applied to the planarity of the quinoline *N*-oxide fragment. Isotropic atomic displacement parameters were refined for Cu and Cl, and an overall U_{iso} parameter was used for the remaining non-H atoms. H atoms were placed in geometrically calculated positions and allowed to refine using bond restraints, with a common isotropic displacement parameter $U_{\text{iso}}(\text{H})$ fixed at 0.051 Å². The diffraction profiles are shown in Fig. 2.

Data collection: local program; cell refinement: *LSPAID* (Visser, 1986); data reduction: local program; program(s) used to solve structure: *MRIA* (Zlokazov & Chernyshev, 1992); program(s) used to refine structure: *MRIA*; molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *MRIA*, *SHELXL97* (Sheldrick, 1997) and *PARST* (Nardelli, 1983).

This work has been supported by the Russian Federation Educational Program 'Integration' (project No. 1.5-100).

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