

Horst Puschmann,^a Judith A. K. Howard,^a Bernardino Soto,^b Raul Bonne^b and Oscar Au-Alvarez^{b*}^aDepartment of Chemistry, University of Durham, Durham DH1 3LE, England, and
^bDepartment of Chemistry, Faculty of Science, University of Oriente, Santiago de Cuba 90500, CubaCorrespondence e-mail:
oscar.au-alvarez@durham.ac.uk

Key indicators

Single-crystal X-ray study
T = 100 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.042
wR factor = 0.098
Data-to-parameter ratio = 21.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Di- μ -chloro-bis{chloro[2-(4-methylphenylamino)-1,2-diphenylethanoximato]copper(II)}

The title compound, $[\text{Cu}_2\text{Cl}_4(\text{C}_{42}\text{H}_{40}\text{N}_4\text{O}_2)]$, is a binuclear molecule bridged by two Cl atoms. The bridging unit Cu_2Cl_2 is almost planar and the Cu^{II} ions are coordinated by two N and three Cl atoms forming a square pyramid. There are two bifurcated hydrogen bonds.

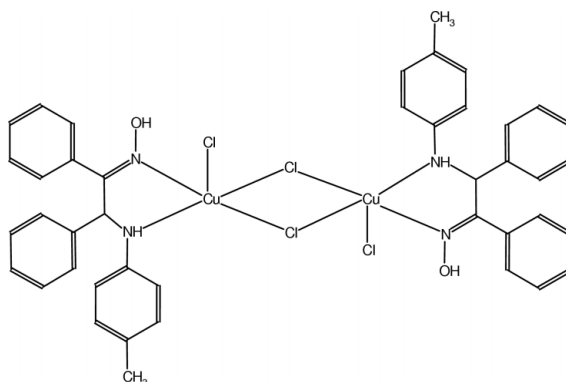
Received 7 November 2001

Accepted 9 November 2001

Online 17 November 2001

Comment

During our study of the formation of $\text{Cu}_2\text{Cl}_4\text{N}_4$ compounds *via* the reaction of Cu^{II} salts with different $-\text{N}-\text{C}-\text{C}=\text{N}-$ ligands, we found that the best results were obtained by the reaction of 1,2-diphenyl-2-(4-*X*-phenylamino)-ethanoxime (*X* = H, Cl, CH_3) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in ethanol. This reaction is successful if the ethanol solution of the oxime is added to the ethanol solution of CuCl_2 and unsuccessful if added *vice versa*. Recently we reported the structures of di- μ -chloro-bis{chloro[1,2-diphenyl-2-(phenylamino)ethanoximato]copper(II)}, (II) (Puschmann, Batsanov *et al.*, 2001) and di- μ -chloro-bis{chloro[1,2-diphenyl-2-(4-chlorophenylamino)ethanoximato]copper(II)}, (III) (Puschmann, Howard *et al.*, 2001), where *X* = H and Cl, respectively. In this paper, we describe the structure of the title compound, (I), which is chemically related to (II) and (III), with *X* = CH_3 .



(I)

There is one independent molecule per asymmetric unit (Fig. 1) and, like (II) and (III), compound (I) is a binuclear molecule bridged by two Cl atoms. The two Cu^{II} ions are surrounded by a square-pyramidal environment achieved by two N atoms and three Cl atoms. There are four short bonds to two N atoms, a terminal Cl atom and a bridging Cl atom. The long apical bond involves the other bridging Cl atom.

The bridging Cu_2Cl_2 unit is almost planar with a maximum deviation of atoms of 0.0042 \AA . The $\text{Cu}-\text{Cl}$ distances are not equal: there are two larger distances [$\text{Cu}1-\text{Cl}4$ $2.6919(8) \text{ \AA}$ and $\text{Cu}2-\text{Cl}3$: $2.6589(8) \text{ \AA}$] and two shorter [$\text{Cu}1-\text{Cl}3$

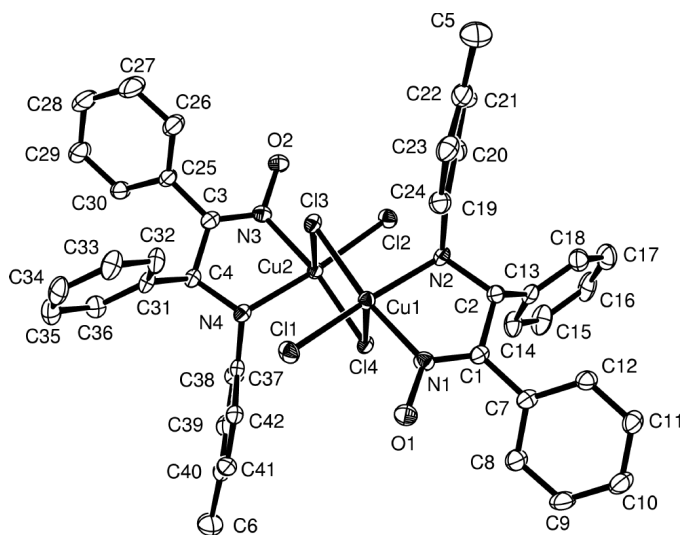


Figure 1
The molecule of (I) showing the atomic labelling. Displacement ellipsoids are drawn at the 50% probability level.

2.2485 (7) Å and Cu2—Cl4 2.2326 (7) Å]. Just as in (II) and (III), the larger distances correspond to the Cl atoms in the apex of the square pyramid and the smaller ones to the basal Cl atoms. Now if we compare the mean of each of these two values (2.2406 and 2.6754 Å) with those found for (II) [2.2814 (4) and 2.6582 (4) Å] and for (III) [2.2454 (3) and 2.6624 (4) Å], we conclude that the short mean distance in (I) is the shortest of the three compounds while the mean larger distance is the largest. When analysing the angles of the bridging unit we found that the Cl3—Cu1—Cl4 angle [95.24 (3)°] and the Cl4—Cu2—Cl3 angle [96.54 (3)°] are larger than the corresponding ones in (II) and (III) [89.528 (15) and 94.306 (11)°, respectively] while the Cu1—Cl3—Cu2 angle [84.34 (2)°] and the Cu2—Cl4—Cu1 angle [83.87 (2)°] are smaller than those of (II) and (III) [90.472 (15) and 85.694 (11)°, respectively].

The Cu1—Cu2 distance in (I) is smaller than the values found in (II) and (III) [3.3087 (5) versus 3.5172 (4) and 3.3514 (3) Å] and it is also the smallest Cu—Cu distance found up to now in any of the di- μ -chloro pentacoordinated Cu^{II} complexes reported in the Cambridge Structural Database (Allen & Kennard, 1993).

The general layout of the groups within the molecule of (I), and especially the position of the —OH group with respect to the terminal Cl, is similar to that of the Cl derivative (III), so it seems that the substitution of the Cl atom of the phenylamino group by a CH₃ group in (I) has no steric effect. Really the position of the OH group and the terminal Cl in (I) and (III) is different from that in compound (II). In (I) and (III), these two groups point approximately in the same direction, and they can form an intramolecular hydrogen bond, but in (II) they point in opposite directions and the formation of this type of hydrogen bond is not possible.

All hydrogen bonds in (I) are intramolecular and bifurcated (Jeffrey *et al.*, 1985). Atom Cl1 acts as a bifurcated acceptor to O1—H1 and N4—H4, and Cl2 acts as a bifurcated acceptor to O2—H2A and N2—H2A. The packing interactions in (I) are mainly van der Waals in nature.

Experimental

Compound (I) was obtained by slow addition of 30 ml of an absolute ethanol solution (0.001 M) of 1,2-diphenyl-2-(4-methylphenylamino)ethanoxime to 30 ml of an absolute ethanol solution (0.001 M) of CuCl₂·2H₂O. The resulting green precipitate was left overnight, filtered and washed several times with water, followed by ethanol and ether. Recrystallization from absolute ethanol after drying in vacuum gave crystals suitable for X-ray structural analysis. Melting point: 446–448 K.

Crystal data

[Cu₂Cl₄(C₄₂H₄₀N₄O₂)]
M_r = 901.66
 Monoclinic, *P*2₁/*c*
a = 14.8811 (5) Å
b = 12.9287 (4) Å
c = 21.7718 (6) Å
 β = 101.569 (1)°
V = 4103.6 (2) Å³
Z = 4

D_x = 1.459 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 4690 reflections
 θ = 2.4–28.1°
 μ = 1.34 mm⁻¹
T = 100 (2) K
 Irregular, dark green
 0.18 × 0.10 × 0.08 mm

Data collection

Bruker SMART 1K diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
*T*_{min} = 0.709, *T*_{max} = 0.898
 48138 measured reflections
 10377 independent reflections

6753 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.083
 θ _{max} = 28.5°
h = -19 → 19
k = -17 → 17
l = -28 → 29

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.042
wR(*F*²) = 0.098
S = 1.02
 10377 reflections
 489 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 2.4175P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.50 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.39 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu1—N1	1.987 (2)	Cu2—N3	1.984 (2)
Cu1—N2	2.036 (2)	Cu2—N4	2.068 (2)
Cu1—Cl3	2.2485 (7)	Cu2—Cl4	2.2326 (7)
Cu1—Cl1	2.2552 (8)	Cu2—Cl2	2.2852 (8)
Cu1—Cl4	2.6919 (8)	Cu2—Cl3	2.6589 (8)
Cu1—Cu2	3.3087 (5)		
N1—Cu1—N2	80.65 (10)	N3—Cu2—Cl4	171.22 (7)
N1—Cu1—Cl3	170.92 (8)	N4—Cu2—Cl4	90.98 (7)
N2—Cu1—Cl3	92.04 (7)	N3—Cu2—Cl2	92.80 (7)
N1—Cu1—Cl1	92.44 (8)	N4—Cu2—Cl2	172.36 (7)
N2—Cu1—Cl1	167.64 (7)	Cl4—Cu2—Cl2	95.33 (3)
Cl3—Cu1—Cl1	93.76 (3)	N3—Cu2—Cl3	86.50 (7)
N1—Cu1—Cl4	90.61 (7)	N4—Cu2—Cl3	91.82 (7)
N2—Cu1—Cl4	93.62 (7)	Cl4—Cu2—Cl3	96.54 (3)
Cl3—Cu1—Cl4	95.24 (3)	Cl2—Cu2—Cl3	91.75 (3)
Cl1—Cu1—Cl4	96.71 (3)	Cu1—Cl3—Cu2	84.34 (2)
N3—Cu2—N4	80.68 (9)	Cu2—Cl4—Cu1	83.87 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...Cl1	0.84	2.31	2.996 (2)	140
O2—H2...Cl2	0.84	2.36	3.041 (2)	139
N2—H2A...Cl2	0.93	2.79	3.649 (2)	154
N4—H4...Cl1	0.93	2.87	3.723 (3)	153

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular

graphics: *ORTEP-3* for Windows (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
- Bruker (1998). *SMART-NT* and *SAINT-NT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Jeffrey, G. A., Maluszynska, H. & Mitra, J. (1985). *Int. J. Biol. Macromol.* **7**, 336–348.
- Puschmann, H., Batsanov, A. S., Howard, J. A. K., Soto, B., Bonne, R. & Au-Alvarez, O. (2001). *Acta Cryst.* **E57**, m524–m526.
- Puschmann, H., Howard, J. A. K., Soto, B., Bonne, R. & Au-Alvarez, O. (2001). *Acta Cryst.* **E57**, m551–552.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELX97*. University of Göttingen, Germany.