

with (I), are taken into account a total of five Co^{II} and Ni^{II} phthalate complexes are known so far. In four of these complexes only monodentate-type coordination is encountered; in all the cases the intramolecular hydrogen bond is also found (as noted above). As pointed out earlier (Poleti, Stojaković, Prelesnik & Herak, 1988), the existence of such hydrogen bonding should markedly diminish the ability of the pht ion to act as a chelate or as a bridging ligand. Further work on this subject is in progress.

This work was supported by the Research Fund of SR Serbia.

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.

ENDRES, K. (1984). *Z. Anorg. Allg. Chem.* **518**, 78–88.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 JOHNSON, J. E. & JACOBSON, R. A. (1973). *Acta Cryst.* **B29**, 1669–1674.
 KOZLOVA, N. P., AGRE, V. M., TRUNOV, V. K., MAKAREVICH, S. S. & BARKHANOVA, N. N. (1982). *Zh. Strukt. Khim.* **23**, 108–113.
 KRSTANOVIĆ, I., KARANOVIĆ, LJ. & STOJAKOVIĆ, DJ. (1985). *Acta Cryst.* **C41**, 43–45.
 MALLINSON, P. R. & MUIR, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.
 NISHIGAKI, S., YOSHIOKA, H. & NAKATSU, K. (1978). *Acta Cryst.* **B34**, 875–879.
 POLETI, D. (1988). PhD Thesis, Univ. of Belgrade, Belgrade, Yugoslavia.
 POLETI, D., STOJAKOVIĆ, D. R., PRELESNIK, B. V. & HERAK, R. M. (1988). *Acta Cryst.* **C44**, 242–245.
 RAY, N. J., HULETT, L., SHEAHAN, R. & HATHAWAY, B. J. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1463–1469.
 ZALKIN, A. (1965). *FORDAP. A Fortran Program for Fourier Calculations*. Univ. of California, Berkeley, USA.

Acta Cryst. (1990). **C46**, 402–404

Structure of Hexa- μ -chloro- μ_4 -oxo-tetrakis[1,2-dimethylimidazolecopper(II)]

BY AHMET ERDONMEZ,* JOHN H. VAN DIEMEN, RUDOLF, A. G. DE GRAAFF AND JAN REEDIJK†

Department of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

(Received 2 December 1988; accepted 6 July 1989)

Abstract. [Cu₄Cl₆(O)(C₅H₈N₂)₄].0.25H₂O, $M_r = 871.90$, monoclinic, $P2_1/c$, $a = 22.582(5)$, $b = 11.829(2)$, $c = 16.114(4)$ Å, $\beta = 128.46(2)^\circ$, $V = 3370.5$ Å³, $Z = 4$, $D_m = 1.744$, $D_x = 1.718$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 30.15$ cm⁻¹, $F(000) = 1746$, $T = 293$ K, final $wR = 0.055$ for 1319 significant reflections. The compound contains a central O atom coordinated tetrahedrally to four Cu atoms, with the metal atoms being bridged in pairs by six Cl atoms. A 1,2-dimethylimidazole (dmim) ligand completes a trigonal-bipyramidal coordination about each of the four Cu atoms. Disordered water molecules which are not bonded to the copper compound are also present in the unit cell.

Introduction. In order to study magnetic superexchange interactions we decided to synthesize compounds with chain structures by established procedures (Van Ooijen, 1979; Van Ooijen, Reedijk

& Spek, 1979). During one of these attempts a tetrameric complex, analysing as [Cu₄Cl₆OL₄].0.25H₂O, where $L = 1,2$ -dimethylimidazole, was obtained instead of a chain compound. The structure determination of this complex was undertaken because of the increasing interest in tetrameric compounds and because such compounds have not previously been reported for imidazole ligands.

Experimental. Crystals were prepared by mixing ethanolic and methanolic solutions of the hydrated copper(II) chloride and ligand in a ratio less than 1:2. An excess of triethyl orthoformate was then added to the solution as a dehydrating agent. Plate-shaped single crystals so obtained were washed with ethanol and diethyl ether and dried at room temperature.

Crystal dimensions approximately $0.3 \times 0.2 \times 0.07$ mm. Density measured by flotation method. Intensities were measured on an Enraf–Nonius CAD-4 four-circle diffractometer (graphite-monochromated Mo $K\alpha$ X-rays). Accurate unit-cell parameters and the orientation matrix determined by

* Present address: Physics Department, Faculty of Sciences and Arts, Ondokuz Mayıs University, Samsun, Turkey.

† To whom all correspondence should be addressed.

Table 1. Atomic positional parameters [$\times 10^4$ except O(2): $\times 10^3$] and isotropic thermal parameters ($\times 10^2$ for Cu atoms and $\times 10$ for the other atoms)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
O(1)	2329 (5)	735 (8)	-146 (7)	24 (2)
Cu(1)	2157 (1)	42 (2)	759 (2)	315 (8)
Cu(2)	3111 (1)	-33 (2)	-65 (2)	301 (7)
Cu(3)	2624 (1)	2262 (2)	260 (2)	336 (8)
Cu(4)	1397 (1)	678 (2)	-1567 (2)	346 (8)
Cl(1)	3012 (3)	-1427 (4)	959 (4)	61 (2)*
Cl(2)	2201 (3)	-57 (4)	-1962 (4)	50 (2)
Cl(3)	2563 (3)	1811 (3)	1682 (4)	39 (2)
Cl(4)	3880 (2)	1594 (3)	925 (4)	43 (2)*
Cl(5)	1442 (3)	2711 (4)	-1382 (4)	53 (2)
Cl(6)	897 (3)	-326 (4)	-856 (4)	55 (2)
N(11)	2001 (3)	-656 (8)	1701 (6)	31 (2)
N(21)	3902 (1)	-794 (10)	-13 (1)	30 (2)
N(31)	2943 (5)	3832 (6)	595 (8)	38 (3)
N(41)	457 (3)	606 (3)	-3015 (4)	39 (3)
C(11)	1518 (4)	-288 (10)	1859 (8)	39 (4)
C(11A)	999 (5)	672 (11)	1371 (11)	43 (4)
N(12)	1610 (4)	-944 (8)	2613 (7)	39 (3)
C(12)	1219 (7)	-841 (16)	3086 (14)	59 (6)
C(13)	2145 (4)	-1759 (11)	2934 (9)	46 (4)
C(14)	2385 (4)	-1568 (11)	2347 (9)	47 (4)
C(21)	4580 (2)	-1062 (13)	820 (1)	34 (3)
C(21A)	4917 (8)	-976 (15)	1956 (5)	46 (4)
N(22)	4977 (2)	-1539 (11)	528 (1)	49 (3)
C(22)	5768 (2)	-1973 (14)	1228 (11)	57 (5)
C(23)	4521 (2)	-1499 (14)	-553 (1)	54 (4)
C(24)	3850 (2)	-1027 (14)	-906 (2)	43 (4)
C(31)	3241 (6)	4418 (7)	239 (10)	34 (3)
C(31A)	3326 (8)	4041 (15)	-568 (12)	56 (4)
N(32)	3434 (4)	5452 (5)	679 (7)	36 (3)
C(32)	3865 (6)	6294 (14)	561 (14)	60 (5)
C(33)	3247 (7)	5535 (7)	1329 (11)	47 (4)
C(34)	2951 (7)	4527 (7)	1295 (11)	40 (4)
C(41)	153 (4)	-335 (3)	-3538 (6)	33 (3)
C(41A)	413 (8)	-1534 (8)	-3208 (13)	61 (5)
C(42)	-1035 (7)	-967 (15)	-5362 (9)	71 (5)
N(42)	-508 (3)	-127 (3)	-4510 (5)	50 (3)
C(43)	-607 (4)	1024 (3)	-4583 (6)	48 (4)
C(44)	-17 (4)	1490 (3)	-3658 (6)	51 (4)
O(2)	574 (2)	8 (3)	657 (3)	38 (9)

Constraints applied: N(p1)—C(p1) 1.32, N(p4)—C(p4) 1.38, N(p2)—C(p1) 1.34, N(p2)—C(p3) 1.37, C(p3)—C(p4) 1.35, C(p1)—C(p1A) 1.49, N(p2)—C(p2) 1.50 Å, $p = 1-4$.

* These atoms show high thermal anisotropy.

least squares using 24 reflections ($5.3 < \theta < 13.7^\circ$). Pure ω -scan type; $2 < \theta < 19^\circ$; $\mu = 30.15 \text{ cm}^{-1}$; Lorentz and polarization corrections were applied. No correction for absorption; relative transmission-factor range 0.88–1.08. 3019 reflections measured, $R_{\text{int}} = 0.0503$ based on 247 reflections; $h = -20-17$, $k = 0-10$, $l = 0-14$; 1319 reflections with $I > 2\sigma(I)$ considered significant. Standard reflections 404, $1, \bar{2}0, 8$ and $2\bar{4}0$; intensity variation 6.28%.

Position of Cu atoms derived from Patterson synthesis, those of other non-H atoms from subsequent Fourier syntheses. Full-matrix least-squares refinement on F . Anisotropic thermal parameters only for Cu and Cl atoms. Isotropic thermal parameters were used for all other atoms due to the poor quality of data and the very small number of observed reflections. Total number of parameters refined was 212. Waser constraints (Waser, 1963) were applied for the atoms of the imidazole ligands (see Table 1). The H atoms, except those belonging to methyl groups, were located from difference syn-

Table 2. Intramolecular distances (Å) and bond angles ($^\circ$) around Cu with e.s.d.'s in parentheses

O(1)—Cu(1)	1.912 (9)	C(13)—C(14)	1.368 (5)
O(1)—Cu(2)	1.912 (9)	C(14)—N(11)	1.370 (5)
O(1)—Cu(3)	1.895 (9)	N(21)—C(21)	1.298 (3)
O(1)—Cu(4)	1.918 (9)	C(21)—C(21A)	1.487 (3)
Cu(1)—Cl(1)	2.461 (5)	C(21)—N(22)	1.357 (5)
Cu(1)—Cl(3)	2.395 (5)	N(22)—C(23)	1.367 (2)
Cu(1)—Cl(6)	2.415 (5)	C(23)—C(24)	1.362 (5)
Cu(1)—N(11)	1.941 (3)	C(24)—N(21)	1.397 (3)
Cu(2)—Cl(1)	2.439 (5)	N(31)—C(31)	1.319 (7)
Cu(2)—Cl(2)	2.398 (5)	C(31)—C(31A)	1.496 (7)
Cu(2)—Cl(4)	2.412 (5)	C(31)—N(32)	1.342 (4)
Cu(2)—N(21)	1.951 (4)	N(32)—C(32)	1.483 (7)
Cu(3)—Cl(3)	2.440 (5)	N(32)—C(33)	1.353 (6)
Cu(3)—Cl(4)	2.451 (5)	C(33)—C(34)	1.351 (7)
Cu(3)—Cl(5)	2.368 (5)	C(34)—N(31)	1.386 (4)
Cu(3)—N(31)	1.943 (5)	N(41)—C(41)	1.305 (3)
Cu(4)—Cl(2)	2.425 (5)	C(41)—C(41A)	1.500 (5)
Cu(4)—Cl(5)	2.418 (5)	C(41)—N(42)	1.353 (3)
Cu(4)—Cl(6)	2.366 (5)	N(42)—C(42)	1.502 (5)
Cu(4)—N(41)	1.946 (3)	N(42)—C(43)	1.372 (3)
N(11)—C(11)	1.334 (6)	C(43)—C(44)	1.351 (3)
C(11)—C(11A)	1.460 (7)	C(44)—N(41)	1.389 (4)
C(11)—N(12)	1.345 (3)	N(12)—C(12)	1.487 (7)
N(12)—C(13)	1.368 (7)	N(22)—C(22)	1.492 (4)
Cu(1)—O(1)—Cu(2)	111.0 (5)	Cl(4)—Cu(3)—N(31)	93.4 (3)
Cu(1)—O(1)—Cu(3)	109.8 (4)	Cl(5)—Cu(3)—N(31)	93.5 (4)
O(1)—O(1)—Cu(4)	107.7 (4)	O(1)—Cu(4)—Cl(2)	83.3 (3)
Cu(2)—O(1)—Cu(3)	108.6 (4)	O(1)—Cu(4)—Cl(5)	83.5 (3)
Cu(2)—O(1)—Cu(4)	110.1 (4)	O(1)—Cu(4)—Cl(6)	86.4 (3)
Cu(3)—O(1)—Cu(4)	109.5 (4)	O(1)—Cu(4)—N(41)	179.2 (4)
O(1)—Cu(1)—Cl(1)	83.6 (3)	Cl(2)—Cu(4)—Cl(5)	114.0 (2)
O(1)—Cu(1)—Cl(3)	85.3 (3)	Cl(2)—Cu(4)—Cl(6)	127.3 (2)
O(1)—Cu(1)—Cl(6)	85.1 (3)	Cl(2)—Cu(4)—N(41)	95.9 (3)
O(1)—Cu(1)—N(11)	179.0 (4)	Cl(5)—Cu(4)—Cl(6)	115.8 (2)
Cl(1)—Cu(1)—Cl(3)	124.7 (2)	Cl(5)—Cu(4)—N(41)	97.0 (2)
Cl(1)—Cu(1)—Cl(6)	108.3 (2)	Cl(6)—Cu(4)—N(41)	93.9 (4)
Cl(1)—Cu(1)—N(11)	96.0 (2)	Cu(1)—Cl(1)—Cu(2)	80.1 (2)
Cl(3)—Cu(1)—Cl(6)	124.4 (2)	Cu(2)—Cl(2)—Cu(4)	81.2 (2)
Cl(3)—Cu(1)—N(11)	94.1 (4)	Cu(1)—Cl(3)—Cu(3)	80.2 (1)
Cl(6)—Cu(1)—N(11)	95.9 (3)	Cu(2)—Cl(4)—Cu(3)	79.0 (1)
O(1)—Cu(2)—Cl(1)	84.2 (3)	Cu(3)—Cl(5)—Cu(4)	81.2 (2)
O(1)—Cu(2)—Cl(2)	84.1 (3)	Cu(1)—Cl(6)—Cu(4)	80.6 (2)
O(1)—Cu(2)—Cl(4)	85.3 (3)	Cu(1)—N(11)—C(11)	125.2 (3)
O(1)—Cu(2)—N(21)	178.5 (4)	Cu(1)—N(11)—C(14)	126.4 (3)
Cl(1)—Cu(2)—Cl(2)	119.3 (2)	Cl(1)—Cu(2)—Cl(4)	115.0 (2)
Cl(1)—Cu(2)—N(21)	97.2 (3)	Cl(2)—Cu(2)—Cl(4)	123.0 (2)
Cl(2)—Cu(2)—N(21)	94.8 (1)	Cl(4)—Cu(2)—N(21)	94.5 (3)
O(1)—Cu(3)—Cl(3)	84.4 (3)	O(1)—Cu(3)—Cl(4)	84.6 (3)
O(1)—Cu(3)—Cl(5)	85.4 (3)	O(1)—Cu(3)—N(31)	175.4 (3)
Cl(3)—Cu(3)—Cl(4)	104.1 (2)	Cl(3)—Cu(3)—Cl(5)	114.7 (2)
Cl(3)—Cu(3)—N(31)	100.0 (2)	Cl(4)—Cu(3)—Cl(5)	138.7 (2)
Cu(2)—N(21)—C(21)	127.9 (3)	Cu(2)—N(21)—C(24)	123.9 (2)
Cu(3)—N(31)—C(31)	125.5 (2)	Cu(3)—N(31)—C(34)	127.5 (4)

theses and were constrained to ride on the atoms to which they were attached. The H atoms of the methyl groups were also fixed to the adjacent C atom. For all H atoms, C—H = 1.00 Å. B_{iso} is 8.8 Å² for the non-methyl H atoms and 11.3 Å² for the H atoms of the methyl groups. O(2), the water O atom, was assigned a fixed occupancy of 0.25. $wR = 0.055$ ($R = 0.041$), $S = 1.03$, $w = 1/\sigma_F^2$, $\Delta_{\text{max}}/\sigma < 0.020$, minimum and maximum values in final difference synthesis -0.36 and $0.62 \text{ e} \text{ \AA}^{-3}$. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Programs written or modified by Mrs E. W. Rutten-Ceulemans, Dr R. A. G. de Graaff and Mr S. Gorter and the Leiden University IBM 3083 computer was used.

Discussion. The title compound contains the structural unit $[\text{Cu}_4\text{Cl}_6\text{O}]$ in which a central O atom is

coordinated tetrahedrally to four Cu atoms, bridged in pairs by six Cl atoms. Similar structures have been reported previously (Kilbourn & Dunitz, 1967; Barnes, Inman & Hatfield, 1971; Sinn, 1970; Holt, Holt & Vlasse, 1979; Jones, Sams & Thompson, 1983; Guy, Cooper, Gilardi, Flippen-Anderson & George, 1988).

The atomic coordinates and equivalent isotropic thermal parameters of the non-H atoms are listed in Table 1. Bond distances and angles are given in Table 2.* An ORTEP drawing (Johnson, 1965) of the molecule with the atomic numbering scheme is shown in Fig. 1. All H atoms have been omitted for clarity. Cu—O, Cu—Cl and Cu—N distances are in the ranges 1.895 (9)–1.918 (9), 2.366 (5)–2.461 (5) and 1.941 (3)–1.951 (4) Å, respectively. Cu—O—Cu, O—Cu—Cl, Cl—Cu—Cl, Cl—Cu—N, Cu—Cl—Cu

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52398 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and O—Cu—N angles are in the ranges 107.7 (4)–111.0 (5), 83.3 (2)–86.4 (3), 104.1 (2)–138.7 (2), 93.4 (3)–100.0 (2), 79.0 (1)–81.2 (2) and 175.4 (3)–179.2 (4)°, respectively.

From the observed bond distances and angles we may conclude that the tetrahedron formed by the four Cu atoms with the O atom at its centre is regular within experimental error, but the octahedron of Cl atoms deviates from regularity due to variations in the Cl—Cu—Cl angles [104.1 (2)–138.7 (2)°]. Cu...Cu and O...Cl distances are in the ranges 3.092 (3)–3.152 (3) and 2.91 (1)–2.95 (1) Å, respectively. The atoms of the dmim ligands are planar to within 0.02 Å, except for those of the ligand attached to Cu(3) which is planar only to within 0.06 Å. The unit cell also contains disordered solvate water molecules. Packing is determined by van der Waals contacts and some weak hydrogen bonds to Cl.

The authors are grateful to Dr Gert Admiraal for collection of data. One of the authors (AE) is indebted to the governments of the Netherlands and Turkey for a fellowship for advanced studies at Leiden University.

References

- BARNES, J. A., INMAN, G. W. JR & HATFIELD, W. E. (1971). *Inorg. Chem.* **10**, 1725–1727.
- GUY, J. T., COOPER, J. C., GILARDI, R. D., FLIPPEN-ANDERSON, J. L. & GEORGE, C. F. JR (1988). *Inorg. Chem.* **27**, 635–638.
- HOLT, E. M., HOLT, S. L. & VLASSE, M. (1979). *Cryst. Struct. Commun.* **8**, 767–770.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- JONES, D. H., SAMS, J. R. & THOMPSON, R. C. (1983). *Inorg. Chem.* **22**, 1399–1401.
- KILBOURN, B. T. & DUNITZ, J. D. (1967). *Inorg. Chim. Acta*, **1**, 209–216.
- SINN, E. (1970). *Coord. Chem. Rev.* **5**, 313–343.
- VAN OOIJEN, J. A. C. (1979). PhD Thesis. Delft Univ. of Technology, The Netherlands.
- VAN OOIJEN, J. A. C., REEDIJK, J. & SPEK, A. L. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1183–1186.
- WASER, J. (1963). *Acta Cryst.* **16**, 1091–1094.

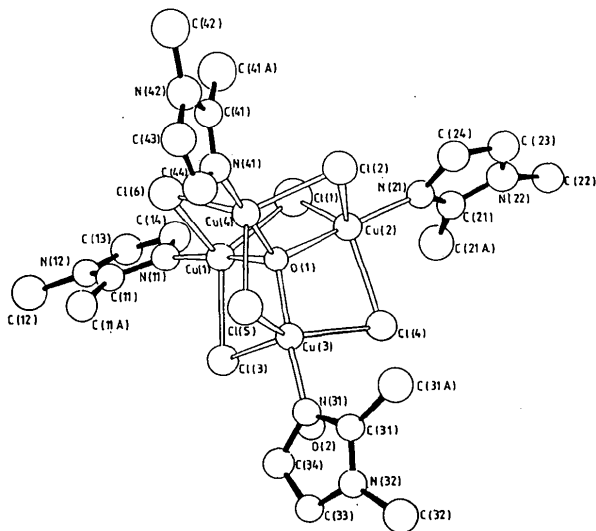


Fig. 1. ORTEP drawing of [Cu₄Cl₆O(dmim)₄] showing the atomic numbering scheme.