The Crystal Structure of Tetraaquabis[(2-methoxyphenoxy)-acetato]copper(II), $[Cu(C_9H_9O_4)_2(H_2O)_4]$

[a]Rolf Stomberg and [b]Knut Lundquist

[a]Department of Inorganic Chemistry and [b]Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

Stomberg, R. and Lundquist, K., 1989. The Crystal Structure of Tetraaquabis[(2-methoxyphenoxy)acetato]copper(II), $[Cu(C_9H_9O_4)_2(H_2O)_4]$. – Acta Chem. Scand. 43: 160–163.

Tetraaquabis[(2-methoxyphenoxy)acetato]copper(II), $[Cu(C_9H_9O_4)_2(H_2O)_4]$, has been synthesized and its structure investigated by single-crystal X-ray diffraction methods. The blue compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.225(3)$, $b = 4.968(1)$, $c = 28.826(9)$ Å, $\beta = 90.16(3)°$ and $Z = 2$. Full matrix least-squares refinement of 194 structural parameters gave $R = 0.044$ for 2004 observed $[I > 3\sigma(I)]$ reflections. Copper is surrounded in a distorted octahedral manner by a centrosymmetric arrangement of four water oxygen atoms and two carboxylate oxygen atoms, one from each of the two monodentate (2-methoxyphenoxy)acetate groups. The two *trans* long bonds are Cu–OH_2 bonds. The monomers are held together in sheets by hydrogen bonds and the sheets are connected by van der Waals forces. The shortest distance between two copper atoms is 4.968(1) Å. The strongest hydrogen bond is intramolecular. Bond distances are: $Cu–O_{acetato}$ 1.942(2), $Cu–O_{aq,equatorial}$ 1.952(2) and $Cu–O_{aq,axial}$ 2.605(3) Å.

A new method for the protection of wood against rotting has recently been developed.[1] In a first step the wood is impregnated with a solution of a lignin derivative, e.g. carboxymethylated kraft lignin. A subsequent treatment with a copper sulfate solution renders the lignin derivative insoluble. Wood treated in this way exhibits good resistance to fungal as well as bacterial attack.

Treatment of wood, impregnated with carboxymethylated lignin, with copper sulfate is expected to result in the formation of copper complexes of aryloxyacetic acid units in the lignin derivative. To gain information about the properties of such complexes we have examined the copper(II) compound of an aryloxyacetic acid, namely (2-methoxyphenoxy)acetic acid. The crystal and molecular structure of this compound is described below. The solubility of the compound was found to be 0.31 g per 100 g H_2O at 21 °C.

Experimental

Blue crystals (whiskers) of tetraaquabis[(2-methoxyphenoxy)acetato]copper(II) were obtained from a mixture of stoichiometric amounts of aqueous solutions of copper sulfate and sodium (2-methoxyphenoxy)acetate on standing at room temperature. The product was recrystallized from water. Besides the whiskers, band-formed crystals were obtained and these were cut to appropriate size for the X-ray work.

Symmetry, conditions for reflections, approximate cell dimensions and information about suitability for single-crystal work were obtained from rotation and Weissenberg photographs (Cu$K\alpha$ radiation).

Crystal data and conditions for the data collection are given in Table 1. Diffracted intensities were measured with a Syntex $P2_1$ X-ray diffractometer (graphite-monochromated Mo$K\alpha$ radiation). Periodic measurement of a test reflection showed no sign of crystal deterioration during the collection of the data. Correction was made for Lorentz and polarization effects. Unit cell dimensions were determined from a least-squares fit of refined diffractometer setting angles for 15 reflections.

Structure determination

The structure was solved by direct methods (MITHRIL[2]) and electron-density calculations. Full-matrix least-squares refinement of positional and isotropic thermal parameters for the non-hydrogen atoms gave an R value of 0.14. With anisotropic thermal parameters for these atoms, R dropped to 0.061. All the hydrogen atoms were located from a subsequent electron density difference map. Inclusion of the hydrogen atoms with isotropic thermal parameters in the refinement reduced R to 0.044.

Calculations were carried out on an IBM 3081 computer with programs described in Refs. 3 and 4. Atomic scattering factors were taken from Ref. 5. Further details concerning the refinement are summarized in Table 1.

Results and discussion

Fractional coordinates and thermal parameters are given in Table 2, and bond distances, bond angles, hydrogen bond lengths and other short intermolecular distances in Table 3.

Table 1. Crystal and experimental data for tetraaquabis[(2-methoxyphenoxy)acetato]copper(II). $T = 290$ K.

M_r	497.94
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell dimensions/Å or °	$a = 7.225(3)$ $\beta = 90.16(3)$
	$b = 4.968(1)$ $V = 1034.7(6)$
	$c = 28.826(9)$
Z	2
D_c/g cm^{-3}	1.598
μ(Mo$K\alpha$)/mm^{-1} (no absorption correction)	1.17
Crystal size/mm	0.11×0.19×0.49
No. of reflections for cell determination (θ range/°)	15 ($2.8 < \theta < 11.9$)
Scan mode	ω-2θ
2θ range/°	$3.5 < 2\theta < 60.0$
2θ scan speed/° mm^{-1}	1.5–4.9
Total No. of reflections measured	3362
No. of observed independent reflections [$I > 3\sigma(I)$]	2004
Test reflection (standard deviation/%)	1 1 $\bar{5}$ (1.8)
No. of parameters refined	194
Weights calculated according to	$w = (6+\lvert F_o\rvert+0.015\lvert F_o\rvert^2)^{-1}$
R (R_w)	0.044 (0.051)
Maximum residual electron density/e Å^{-3}	0.38

Table 2. Atomic fractional coordinates and B_{eq} (B_{iso} for H) for tetraaquabis[(2-methoxyphenoxy)acetato]copper(II), $[Cu(C_9H_9O_4)_2(H_2O)_4]$. $T = 290$ K. $B_{eq} = \frac{4}{3}\sum_i \sum_j \beta_{ij}\, \mathbf{a}_i \cdot \mathbf{a}_j$.

Atom	x	y	z	B_{eq}
Cu	1.00000	0.00000	0.50000	2.82(1)
C(1)	0.8196(4)	0.7207(5)	0.34314(9)	2.55(6)
C(2)	0.9669(4)	0.8952(6)	0.3331(1)	2.71(6)
C(3)	0.9521(4)	1.0760(7)	0.2972(1)	3.19(7)
C(4)	0.7904(5)	1.0858(7)	0.2705(1)	3.33(7)
C(5)	0.6477(4)	0.9157(7)	0.2800(1)	3.26(7)
C(6)	0.6590(4)	0.7329(6)	0.3166(1)	3.00(6)
C(7)	1.2452(5)	1.0827(9)	0.3626(2)	4.4(1)
C(8)	0.6957(4)	0.3819(6)	0.3914(1)	2.62(6)
C(9)	0.7451(4)	0.1874(6)	0.42982(9)	2.61(5)
O(1)	1.1188(3)	0.8647(5)	0.36079(8)	3.78(6)
O(2)	0.8465(3)	0.5516(4)	0.37989(7)	2.91(5)
O(3)	0.9073(3)	0.1945(4)	0.44632(7)	3.05(5)
O(4)	0.6186(3)	0.0332(5)	0.44149(9)	4.26(6)
O(5)	0.8893(3)	0.2689(5)	0.54077(8)	3.55(5)
O(6)	1.2978(4)	0.2876(6)	0.4883(1)	4.53(7)
H(C3)	1.054(5)	1.199(8)	0.291(1)	1.7(7)
H(C4)	0.782(5)	1.217(8)	0.246(1)	2.2(8)
H(C5)	0.527(5)	0.930(7)	0.262(1)	1.0(6)
H(C6)	0.556(5)	0.627(7)	0.325(1)	1.1(6)
H1(C7)	1.339(7)	1.03(1)	0.386(2)	4(1)
H2(C7)	1.319(6)	1.108(9)	0.334(2)	2.8(9)
H3(C7)	1.186(6)	1.26(1)	0.370(2)	3(1)
H1(C8)	0.662(4)	0.270(7)	0.363(1)	0.5(6)
H2(C8)	0.593(5)	0.498(8)	0.401(1)	1.9(7)
H1(O5)	0.839(7)	0.40(1)	0.527(2)	4(1)
H2(O5)	0.930(8)	0.26(1)	0.565(2)	7(2)
H1(O6)	1.341(8)	0.23(1)	0.514(2)	6(1)
H2(O6)	1.379(6)	0.24(1)	0.468(2)	3(1)

Table 3. Distances (Å) and angles (°) in tetraaquabis[(2-methoxyphenoxy)acetato]copper(II).

Distance		*Distance*	
Cu–O(3)	1.942(2) ×2	C(3)–C(4)	1.398(5)
Cu–O(5)	1.952(2) ×2	C(4)–C(5)	1.362(5)
Cu–O(6)	2.605(3) ×2	C(5)–C(6)	1.393(4)
C(1)–C(2)	1.403(4)	C(7)–O(1)	1.418(5)
C(1)–C(6)	1.390(4)	C(8)–C(9)	1.512(4)
C(1)–O(2)	1.365(3)	C(8)–O(2)	1.418(3)
C(2)–C(3)	1.375(4)	C(9)–O(3)	1.264(3)
C(2)–O(1)	1.364(4)	C(9)–O(4)	1.240(4)

Angle		*Angle*	
O(3)–Cu–O(3)^{i}	180	C(1)–C(2)–O(1)	114.8(3)
O(3)–Cu–O(5)	89.90(9)	C(3)–C(2)–O(1)	125.0(3)
O(3)–Cu–O(5)^{i}	90.10(9)	C(2)–C(3)–C(4)	120.0(3)
O(3)–Cu–O(6)	84.65(9)	C(3)–C(4)–C(5)	119.9(3)
O(3)–Cu–O(6)^{ii}	95.35(9)	C(4)–C(5)–C(6)	121.0(3)
O(5)–Cu–O(5)^{i}	180	C(1)–C(6)–C(5)	119.5(3)
O(5)–Cu–O(6)	92.44(10)	C(9)–C(8)–O(2)	111.8(2)
O(5)–Cu–O(6)^{ii}	87.56(10)	C(8)–C(9)–O(3)	118.3(2)
O(6)–Cu–O(6)^{ii}	180	C(8)–C(9)–O(4)	114.9(2)
C(2)–C(1)–C(6)	119.4(3)	O(3)–C(9)–O(4)	126.8(3)
C(2)–C(1)–O(2)	115.7(2)	C(2)–O(1)–C(7)	117.0(3)
C(6)–C(1)–O(2)	124.8(3)	C(1)–O(2)–C(8)	116.1(2)
C(1)–C(2)–C(3)	120.1(3)	Cu–O(3)–C(9)	127.1(2)

O–H···X	O···X	O–H	H···X	∠O–H···X
O(5)–H1(O5)···O(6)^{iii}	2.716(4)	0.84(6)	1.90(6)	165(5)
O(5)–H2(O5)···O(1)^{iii}	2.915(3)	0.75(6)	2.26(6)	146(6)
O(6)–H1(O6)···O(4)^{i}	2.645(4)	0.86(6)	1.84(6)	154(6)
O(6)–H2(O6)···O(4)^{iv}	2.968(4)	0.86(5)	2.16(5)	155(4)

Shortest intermolecular contact distances

H(C4)···H(C5^{v})	2.48(5)	H1(C7)···O(4)^{vi}	2.57(5)
H(C5)···H(C5^{v})	2.60(2) ×2	H(C3)···C(4)^{vii}	2.84(4)

Symmetry codes:

i	(2−x, −y, 1−z)	v	(1−x, ½+y, ½−z)
ii	(1−x, −y, 1−z)	vi	(1+x, 1+y, z)
iii	(2−x, 1−y, 1−z)	vii	(2−x, ½+y, ½−z)
iv	(1+x, y, z)		

Fig. 1 shows a stereoscopic view of the unit cell, and Fig. 2 the complex and the atomic labelling.

In tetraaquabis[(2-methoxyphenoxy)acetato]copper(II), which is centrosymmetric with copper at the centre of symmetry, copper is surrounded by four ligand atoms which almost form a square, at distances of 1.942(2)–1.952(2) Å. These five atoms are coplanar (follows from symmetry). Copper is further coordinated to two water oxygen atoms [O(6) and O(6)′] at 2.605(3) Å, one above and one below the square plane. The angles between the Cu–O_{axial} and Cu–$O_{equatorial}$ bond directions are 84.6(1) and 92.4(1)°, respectively. The coordination is thus distorted octahedral, an arrangement also found in a number of other copper compounds,[6] e.g. $[Cu(HSeO_3)_2(H_2O)_2]_n$, in which the Cu–$O_{equatorial}$ bond distances are 1.986(4) and 1.927(4) Å and the Cu–O_{axial} bond distances are 2.574(5) Å.[7] Only one of the carboxylate oxygen atoms [O(3)] from each of

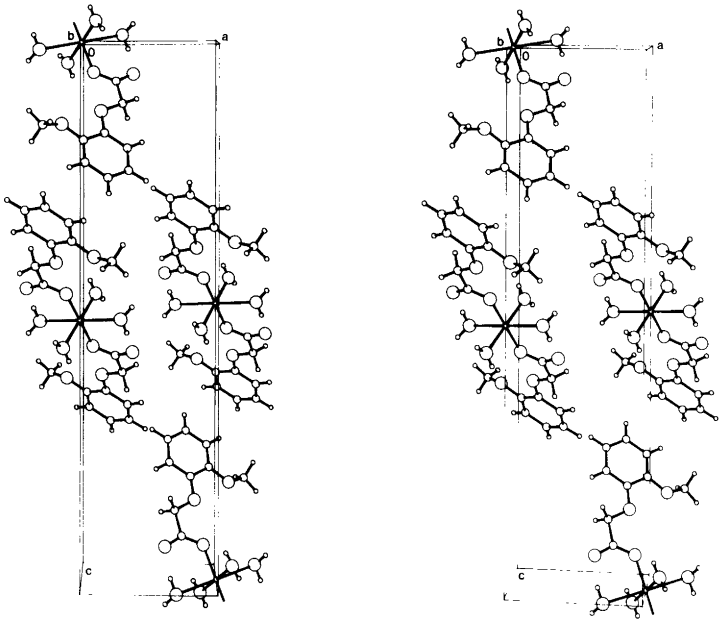

Fig. 1. Stereoscopic view (Ref. 11) of the unit cell of tetraaquabis[(2-methoxyphenoxy)acetato]copper(II).

the two (2-methoxyphenoxy)acetate groups, thus being monodentate, is coordinated to copper. The other [O(4)] forms a rather strong intramolecular hydrogen bond [2.645 (4) Å] with the axial water molecule; this leads to a further stabilization of the complex. Intermolecular hydrogen bonds connect the complexes in the *a* and *b* directions, leading to a layer structure, while only weak van der Waals forces hold these layers together in the *c* direction.

The maximum deviation of the benzene ring carbon atoms from the ring plane is 0.006(2) Å. The methoxy oxygen atom is only 0.026(4) Å out of the plane, while the methoxy carbon atom deviates 0.393(7) Å from the benzene ring plane. The phenoxy oxygen atom, the carbon and oxygen atoms of the acetate group, as well as the copper atom and the apical water oxygen atoms O(6) and O(6)', are also situated near the benzene ring plane. The maximum deviations are shown by O(6) [0.17(1) Å], O(3) [0.16(1) Å] and Cu [0.11(1) Å], while the other atoms are closer than 0.07 Å to the ring plane.

The aromatic C–C bond distances are normal [mean value 1.387(14) Å; r.m.s. deviation is given in parenthesis]. The $C(sp^3)$–O_{ether} bond distances agree well with those observed in a series of lignin-related compounds,[8] as do the $C(sp^2)$–O_{ether} bond distances. There is a slight difference between the C–$O_{carboxylate}$ bond lengths, that involving the coordinated carboxyl oxygen atom being the longer one.

The related monomeric aryloxyacetates triaquabis(phenoxyacetato) copper(II)[9] and diaquabis (phenoxyacetato)-copper(II)[10] exhibit different coordination patterns, which also differ from that of tetraaquabis[(2-methoxyphenoxy)-acetato] copper(II). In triaquabis (phenoxyacetato) copper(II), square pyramidal five-coordination was observed with the phenoxyacetate groups acting as monodentate ligands as also found in the compound examined in this work. In diaquabis(phenoxyacetato)copper(II) the copper coordination is distorted octahedral, as in tetraaquabis-[(2-methoxyphenoxy)acetato]copper(II). The phenoxyacetate group in the former compound is, however, bidentate with one short bond (1.94 Å) between copper and one carboxylate oxygen atom, and one long bond (2.50 Å) to the phenoxy oxygen atom. In all these structures the monomeric complexes are held together by hydrogen bonds in sheets.

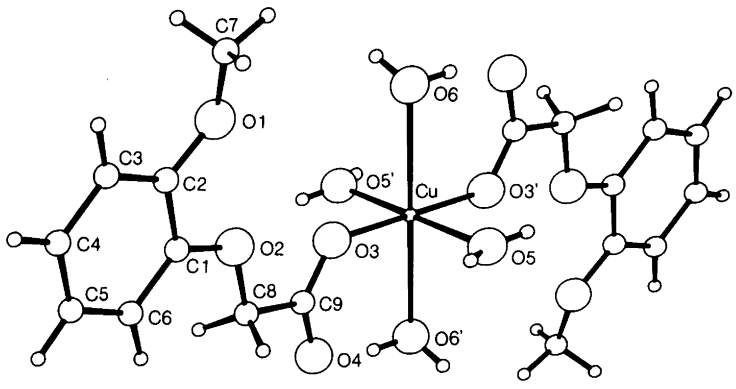

Fig. 2. The molecule tetraaquabis[(2-methoxyphenoxy) acetato]copper(II).

Acknowledgement. We wish to express our gratitude to Mrs. S. Olson for drawing the figures.

References

1. Simonson, R. and Lundquist, K. *U.S. Pat.* 4, 752, 509 (1988).
2. Gilmore, C. J. *J. Appl. Crystallogr. 17* (1984) 42.
3. Lindgren, O. *An Integrated Set of Crystallographic Programs.* In: *On the Oxygen Coordination of Cerium in Some Sulfates and Chromates, Thesis,* Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, Göteborg, Sweden 1977.
4. Andersen, L. *An Integrated Set of Crystallographic Programs.* In: *Structure Determination of Some Symmetrical Oxoanions of Sulfur(IV), Selenium (IV) and Tellurium (IV) and Implementation of a General Set of Programs for Crystallographic Computing, Thesis,* Chalmers University of Technology and University of Göteborg. Göteborg, Sweden 1985.
5. *International Tables for X-Ray Crystallography,* Kynoch Press, Birmingham 1974, Vol. IV.
6. Wells, A. F. *Structural Inorganic Chemistry,* 5th ed., Clarendon Press, Oxford 1984.
7. Hiltunen, L., Leskelä, M., Niinistö, L. and Tammenmaa, M. *Acta Chem. Scand., Ser. A 39* (1985) 809.
8. Stomberg, R. and Lundquist, K. *Acta Chem. Scand., Ser. B 41* (1987) 610 and references therein.
9. Goebel, C. V. and Doedens, R. J. *Inorg. Chem. 10* (1971) 2607.
10. Prout, C. K., Armstrong, R. A., Carruthers, J. R., Forrest, J. G., Murray-Rust, P. and Rossotti, F. J. C. *J. Chem. Soc. A* (1968) 2791.
11. Johnson, C. K. *ORTEP*: Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN 1965.

Received May 17, 1988.