Journal of Organometallic Chemistry, 174 (1979) 121—128
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE CRYSTAL STRUCTURE OF *o*-ANISYLCOPPER(I): AN OCTAMERIC COPPER(I) CLUSTER COMPOUND

A. CAMUS, N. MARSICH, G. NARDIN and L. RANDACCIO
Istituto di Chimica, Università di Trieste, 34127 Trieste (Italy)

(Received February 12th, 1979)

Summary

The cluster structure of *o*-anisylcopper(I), a novel type of organocopper(I) compound, has been established by X-ray crystallographic techniques. The cell constants are a 39.24(1), b 25.91(1), and c 23.57(1) Å; the space group is *Fddd*. The structure was refined by least-squares techniques to a conventional R index of 0.084. The crystals consist of octameric molecules having a distorted square antiprismatic arrangement of copper atoms. Two crystallographically independent molecules, both located at 222 crystallographic sites but differently oriented with respect to the crystallographic axes, have been found. On the basis of these results the structures of related organometallic compounds are discussed.

Introduction

Many alkyl- and aryl-organocopper(I) compounds have been synthesized in recent years, but their solid state structure has been determined in only a few cases [1—5]. In particular, among the simple aromatic organocopper derivatives, a cluster nature has been unambiguously established only in the case of 4-methyl-2-cupriobenzyldimethylamine [4]. Phenylcopper and some substituted phenyl compounds are supposed to be polymeric [6a,b], while others are reported as tetramers [7] or hexamers [8], and a cubic arrangement has been proposed for the octameric (*m*-trifluoromethylphenyl)copper [9]. To obtain further insight into the structural aspects of such kinds of compounds we have carried out the X-ray structural analysis of *o*-anisylcopper(I) (*o*-AnCu).

Results

The crystal consists of octameric molecules $(o\text{-AnCu})_8$, having a distorted copper square antiprismatic arrangement located at 222 crystallographic sites (Fig. 1). Two crystallographically independent octameric molecules, very

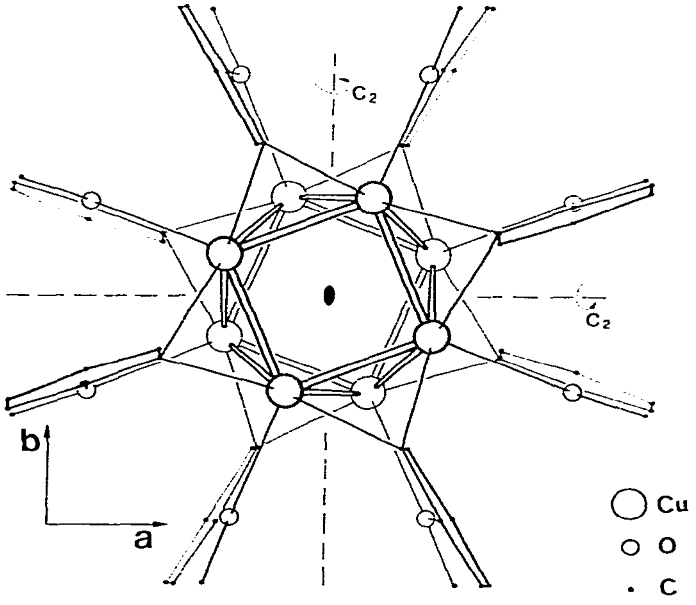

Fig. 1. A view of the octameric molecule (o-AnCu)$_8$.

similar, but differently oriented with respect to the crystallographic axes, are present in the asymmetric unit cell. Distances and angles of interest are reported in Table 1. The numbering scheme for the atoms is shown in Figure 2, and the atomic parameters are listed in Table 2. The edges of the square faces of the

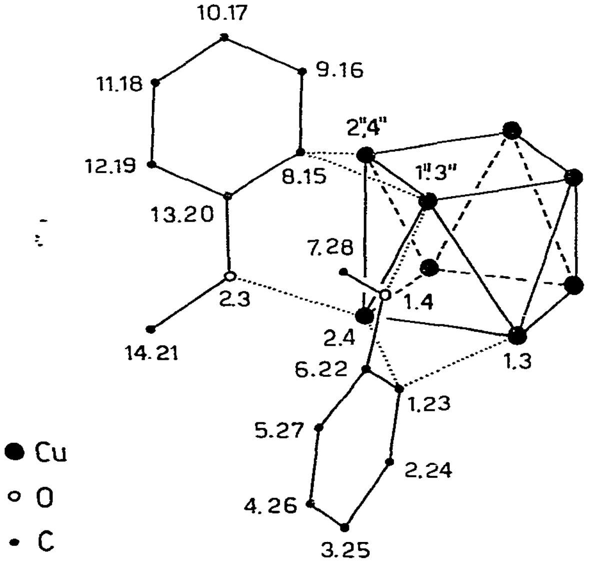

Fig. 2. The numbering scheme for the atoms. The two numbers labeling each atom, refer to the two crystallographically independent molecules.

TABLE 1

SELECTED DISTANCES (Å), AND ANGLES (°) TOGETHER WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Cu(1)—Cu(2)	2.436(5)	Cu(3)—Cu(4)	2.476(4)
Cu(1)—Cu(2′)	2.499(5)	Cu(3)—Cu(4′)	2.480(3)
Cu(1)—Cu(1″)	2.779(4)	Cu(3)—Cu(3″)	2.704(5)
Cu(2)—Cu(1″)	2.745(4)	Cu(4)—Cu(3″)	2.680(5)
Cu(2)—Cu(2″)	2.712(3)	Cu(4)—Cu(4″)	2.775(5)
Cu(1)—C(1)	2.03(2)	Cu(3″)—C(15)	2.06(2)
Cu(2)—C(1)	2.05(2)	Cu(4″)—C(15)	1.99(2)
Cu(1″)—C(8)	2.02(2)	Cu(3)—C(23)	2.07(3)
Cu(2″)—C(8)	2.01(2)	Cu(4)—C(23)	2.08(3)
Cu(1″)—O(1)	2.31(2)	Cu(4)—O(3)	2.38(2)
Cu(2)—O(2)	2.43(2)	Cu(3″)—O(4)	2.37(2)
Cu(2)—Cu(1)—Cu(2′)	89.3(1)	Cu(4)—Cu(3)—Cu(4′)	94.3(1)
Cu(1)—Cu(2)—Cu(1′)	90.6(2)	Cu(3)—Cu(4)—Cu(3′)	85.7(1)
Cu(1)—C(1)—Cu(2)	73.3(8)	Cu(3″)—C(15)—Cu(4″)	75.6(8)
Cu(1″)—C(8)—Cu(2″)	76.7(8)	Cu(3)—C(23)—Cu(4)	73.3(8)
O(1)—Cu(1″)—C(8)	93.9(8)	O(4)—Cu(3″)—C(15)	93.1(8)
O(1)—Cu(1″)—C(1″)	92.4(8)	O(4)—Cu(3″)—C(23″)	88.5(8)
O(2)—Cu(2)—C(1)	92.4(7)	O(3)—Cu(4)—C(15′)	95.7(8)
O(2)—Cu(2)—C(8″)	95.2(8)	O(3)—Cu(4)—C(23)	94.6(8)

Marked atoms are defined as follows:

Cu(1′) $0.25 - x, 0.25 - y, z$
Cu(1″) $0.25 - x, y, 0.25 - z$
Cu(2′) $0.25 - x, 0.25 - y, z$
Cu(2″) $x, 0.25 - y, 0.25 - z$
Cu(3′) $x, 0.25 - y, 0.25 - z$
Cu(3″) $1.25 - x, 0.25 - y, z$
Cu(4′) $x, 0.25 - y, 0.25 - z$
Cu(4″) $1.25 - x, y, 0.25 - z$
C(1″) $0.25 - x, y, 0.25 - z$
C(8″) $x, 0.25 - y, 0.25 - z$
C(15″) $1.25 - x, y, 0.25 - z$
C(23″) $1.25 - x, 0.25 - y, z$

antiprisms, which are bridged by the phenyl groups, are shorter than the others. The mean Cu—Cu distance, is 2.472(5) Å, compared with 2.726(5) Å for the unbridged edges. The ligand is bonded to the copper atoms in such a way that its phenyl groups bridges the side common to the triangular and square faces of the antiprism, whereas the oxygen atom binds the opposite apex. Thus each copper atom is surrounded by two carbon and one oxygen atoms in a distorted pyramidal geometry. The mean Cu—C and Cu—O bond lengths are 2.04 and 2.37 Å, and the C—Cu—C and C—Cu—O angles are 141 and 94.1° respectively. The aryl ligand plane is nearly perpendicular to the Cu—Cu direction, with a mean Cu—C—Cu angle of 74.7°. The copper atoms of the apex of the square faces are coplanar within ±0.03 and ±0.004 Å in the two crystallographically independent molecules. The bridging carbon atoms are displaced above the upper square face of the antiprism and below the lower square face of 0.68 Å (mean) and of 0.62 Å (mean) respectively. The corresponding oxygen atoms are displaced below the upper face and above the lower face (as defined in Fig. 2) of 1.29 Å (mean) and of 1.48 Å (mean), respectively.

The above structure is preserved also in cyclohexane solution, as suggested by osmometric measurements, which show the presence of octomeric species. In toluene, pyridine and chlorinated solvents the cluster breaks down rapidly.

TABLE 2

FRACTIONAL COORDINATES ($\times 10^4$) AND ISOTROPIC THERMAL FACTORS $\AA^2$ ($\times 10^2$) (e.s.d.'s are given in parentheses)

	X	Y	Z	U
Cu(1)	1416(1)	621(1)	729(1)	
Cu(2)	844(1)	986(1)	753(1)	
Cu(3)	6549(1)	1510(1)	595(1)	
Cu(4)	6551(1)	608(1)	941(1)	
O(1)	873(4)	−132(6)	1380(7)	6.5(5)
O(2)	334(5)	655(7)	1210(9)	8.4(6)
O(3)	6280(5)	−150(6)	595(8)	7.7(5)
O(4)	6176(5)	650(8)	−259(8)	8.5(6)
C(1)	981(5)	269(9)	468(10)	5.4(7)
C(2)	953(6)	214(10)	−83(11)	6.4(7)
C(3)	808(7)	−192(13)	−378(14)	9.4(10)
C(4)	670(8)	−590(13)	−28(15)	10.1(11)
C(5)	704(6)	−609(10)	531(11)	5.8(7)
C(6)	847(6)	−162(9)	822(10)	5.3(6)
C(7)	749(8)	−574(12)	1734(14)	9.5(10)
C(8)	623(5)	866(9)	2038(11)	5.7(7)
C(9)	620(7)	882(11)	2647(12)	7.9(9)
C(10)	319(8)	730(12)	2983(14)	9.8(10)
C(11)	50(8)	561(14)	2668(15)	11.1(12)
C(12)	38(7)	519(11)	2085(12)	7.0(8)
C(13)	323(5)	686(8)	1788(9)	4.4(6)
C(14)	47(8)	499(12)	868(14)	9.4(10)
C(15)	5769(6)	285(9)	856(10)	5.7(7)
C(16)	5419(7)	265(10)	857(11)	6.6(8)
C(17)	5223(7)	−165(11)	627(13)	8.2(9)
C(18)	5406(7)	−545(12)	398(14)	8.9(10)
C(19)	5757(7)	−582(12)	350(13)	8.0(9)
C(20)	5946(6)	−171(9)	608(12)	7.0(8)
C(21)	6479(9)	−589(15)	329(18)	12.8(14)
C(22)	6511(6)	703(9)	−323(11)	5.7(7)
C(23)	6702(6)	862(10)	145(11)	5.7(7)
C(24)	7053(7)	917(10)	115(12)	7.0(8)
C(25)	7214(7)	845(11)	−434(13)	8.2(9)
C(26)	7026(8)	706(12)	−883(13)	9.8(11)
C(27)	6668(7)	615(12)	−844(13)	8.7(9)
C(28)	5966(8)	487(12)	−735(14)	9.6(10)
C(29)	7900	1250	1250	6.3
C(30)	8080	850	1020	6.3
C(31)	8430	850	1020	6.3
C(32)	8600	1250	1250	6.3
C(33)	7900	440	800	6.3

ANISOTROPIC THERMAL PARAMETERS U_{ij} ($\times 10^4$) TOGETHER WITH THEIR E.s.d. IN PARENTHESES

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
Cu(1)	529(13)	322(12)	655(17)	−8(11)	−39(13)	−54(12)
Cu(2)	555(18)	307(15)	711(23)	−4(14)	−33(19)	49(16)
Cu(3)	631(19)	315(15)	556(22)	1(14)	43(17)	−35(15)
Cu(4)	618(19)	364(16)	561(21)	58(15)	−50(17)	−37(15)

Discussion

The mode of bonding found in this compound is similar to that in bis(2-dimethylamino)phenylcopper cuprous bromide [5], and seems to be general for oligomeric arylcopper(I) compounds. According to previous suggestions [10], our results confirm that substituted aryl ligands having *o*-hetero-atoms as N or O act virtually as tridentate bridging ligands, requiring a nearly regular triangular arrangement of copper atoms. When the heteroatom is not directly bonded to the phenyl group, as in benzyldimethylamine [4], the ligand bridges only two copper atoms, one of which is further coordinated to the heteroatom.

The structure of *o*-AnCu shows that the number of methyl groups on the hetero-atom may play a decisive role in determining the geometrical arrangement of the copper atoms. In fact inspection of models shows that octameric species similar to that found for *o*-AnCu are ruled out in the case of 2-dimethylaminophenyl)copper because of the steric hindrance of *N*-bonded methyl groups. The hexameric species having an octahedral arrangement of copper atoms, with the tridentate bridging $Me_2NC_6H_4$ ligand bonded to its six adjacent faces, appears sterically more probable, although in conflict with its insolubility. However the polymeric structure (Fig. 3a) suggested for this compound by van Koten et al., [6b], is unlikely, in view of the known geometrical requirements for coordination of aryl ligand to copper ((Cu)C—Cu angle of about 75°, Cu—C distance of about 2.1 Å, tridentate bridging ability of the *o*-aryl ligands). The only way to build up polymeric species preserving such features is to assume a rotation around the C_5H_4C—X bond, increasing the "triangular bite" of the ligand. A hypothetical arrangement is shown in Fig. 3b.

The general tendency of copper(I) centers to cluster together has recently caused an increasing interest in the possible presence of direct Cu—Cu interactions in this type of compound [11,12]. While it may be reasonable to rule

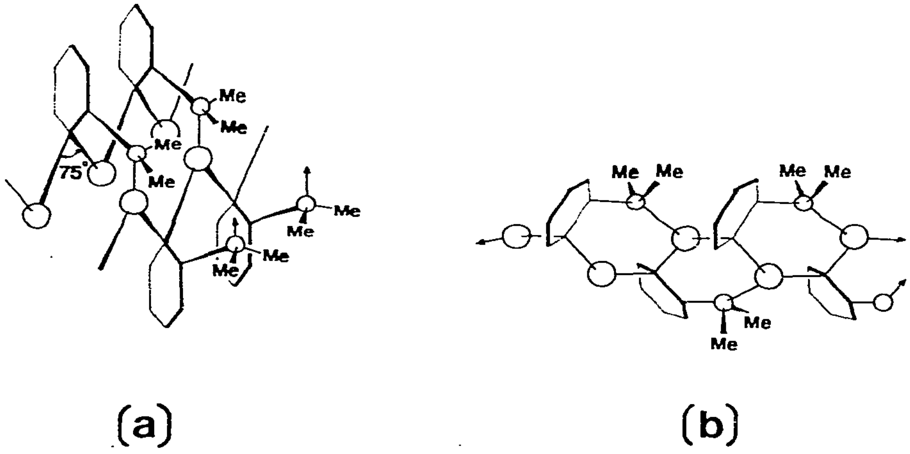

Fig. 3. The polymeric structure proposed for (2-dimethylaminophenyl)copper in ref. 6b (a) and in the present work (b).

out Cu—Cu bonding in many copper polynuclear species containing phosphines and halogens, where Cu—Cu distances are about 3.0 Å [13], it is difficult to exclude direct bonding interactions in *o*-AnCu and some other organocopper compounds where the distances are below the value of 2.6 Å found in metallic copper, Furthermore Hoffmann et al. have shown by molecular calculations that in a d^{10}—d^{10} system [14] and particularly in copper(I) clusters of any size [12], closed shell repulsions between the d^{10} centers may be converted into weak attractive interactions by mixing of metal *s* and *p* orbitals into the molecular orbitals primarily composed of *d* functions. On this basis we propose for *o*-AnCu a simple qualitative model which takes into account direct metal—metal bonds in addition to the 2*e*—3*c* bonds previously suggested to explain the formation of polynuclear arylcopper derivatives [4,5]. Considering the octameric molecule as built up by two copper squares with an edge of 2.47 Å, bridged by the organic ligand, we assume for each copper atom the following qualitative hybridization scheme: two half-empty s^nd $(0 < n < 1)$ hybrid orbitals directed along the edges of the square; two empty sp^m $(1 < m < 2)$ hybrid orbitals, lying in a plane perpendicular both to the copper square and its diagonal; the last empty *p* orbital directed along the above diagonal. In this way the s^nd hybrids may overlap forming four Cu—Cu bonds, whilst each of the two sp^m hybrids participates to a 2*e*—3*c* bond with the filled orbital of the bridging carbon atom, and the empty *p* orbital overlaps with the filled orbital of the coordinated oxygen. Such a model is in agreement with the observation that a square arrangement of copper atoms is common in clusters [15]. Furthermore it allows us to rationalize the values of the bond angles around copper, the C—Cu—C angles being expected to be between 180 and 120° (found 141°) and the C—Cu—O angles nearly 90° (found 94°).

Experimental

Orange crystals of *o*-anisylcopper, C_7H_7CuO containing toluene as crystallization solvent were obtained by concentrating the solution obtained by treatment of cuprous bromide with *o*-anisyllithium in toluene [16]. (Found: C, 51.7; H, 4.33; Cu, 34.6; anisole, 58.7; toluene 6.5; $(C_7H_7CuO)_8 \cdot C_7H_8$ calcd.: C, 51.91; H, 4.42; Cu, 34.88; anisole 59.36; toluene, 6.32%. Mol. wt. in cyclohexane: found: 1435 (0.4% w/w); 1480 (0.6% w/w); $(C_7H_7CuO)_8 \cdot C_6H_{12}$ calcd. 1449.5). Anisole and toluene were determined by GLC after hydrolysis; mol. wt. by osmometry at 37°C under nitrogen.

Crystal data. The crystals are orthorhombic, with *a* 39.24(1), *b* 25.91(1), *c* 23.57(1) Å, space groups *Fddd* with 128 (*o*-AnCu · 1/8 PhMe) units in the cell; $\mu(\text{Mo-}K_\alpha)$ 29.4 cm^{-1}. The unit cell dimensions were determined from Weissenberg photographs and refined by using 15 carefully centered reflections. Intensity data were collected on a Siemens AED automated diffractometer in the θ—2θ scan mode out to 2θ 46° with Mo-K_α radiation. The quality of intensity data was affected by a slow decomposition of the crystal accompanied by gradual darkening, eventhough it was immersed in Nujol and enclosed in a thin glass capillary tube. The intensities of two check reflections were monitored every 50 reflections, showing a significant lowering of the intensity during data collection. Reflections having $I_0 \leqslant 3\sigma(I_0)$ were rejected, the remainder were corrected for the Lorentz polarization factor. A total of 1372 independent reflections were used in the subsequent calculations. No absorption correction was applied owing to the poor quality of the collected set of data.

Structure determination. Owing to the particular arrangement of the four crystallographically independent copper atoms in the cell we were not able to solve the structure by the heavy-atom method. However, an E map calculated from one of the best solutions obtained by using 205 E values (>1.7) in the Germain et al. program [17], clearly revealed the four copper atoms. The positions of all other non-hydrogen atoms (excluding toluene molecules) were determined by successive Fourier syntheses. After several cycles of block diagonal least-squares refinement (R = 0.096), with anisotropic temperature factors for copper atoms, a Fourier difference synthesis was calculated to locate the molecules of crystallization solvent. The ΔF map showed positive electron density arranged along the C_2 axis parallel to a. The peaks were not well resolved, but in agreement with the elemental analysis, half a molecule of toluene, crystallographically independent, fitted well into the electron density distribution, assuming the benzene ring to be located on the binary axis and the methyl group to occupy two positions defined by the symmetry axis (see atomic coordinates). The atomic parameters of the toluene atoms were not refined. The final refinement, with the contribution of toluene atoms held constant, gave a conventional R value of 0.084. In the least-squares refinement * the function minimized was $\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2$, where $w = 1/(A + |F_0| + B|F_0|^2 + C|F_0|^3)$, with $A = 250$, $B = 0.0006$ and $C = 0.5 \times 10^{-6}$. Atomic scattering factors were calculated according to ref. [18].

Acknowledgement

This work was partially supported by C.N.R., Rome.

References

1 J.A.J. Jarvis, B.T. Kilbourn, R. Pearce and M.F. Lappert, J. Chem. Soc. Chem. Commun., (1973) 475; J.A.J. Jarvis, R. Pearce and M.F. Lappert, J. Chem. Soc. Dalton Trans., (1977) 999.

2 A. Camus, N. Marsich, G. Nardin and L. Randaccio, J. Organometal. Chem., 60 (1973) C39.

3 G. Nardin, L. Randaccio and E. Zangrando, J. Organometal. Chem., 74 (1974) C23.

4 G.M. Guss, R. Mason, I. Sotofte, G. Van Koten and J.G. Noltes, J. Chem. Soc. Chem. Commun., (1972) 446.

5 G.M. Guss, R. Mason, K.M. Thomas, G. van Koten and J.G. Noltes, J. Organometal. Chem., 40 (1972) C79.

6 (a) G. Costa, A. Camus, N. Marsich and L. Gatti, J. Organometal. Chem., 8 (1967) 339; A. Camus and N. Marsich, ibid., 21 (1970) 249; (b) G. Van Koten, A.J. Leusink and J.G. Noltes, ibid., 85 (1975) 105.

7 A. Cairncross, H. Omura and W.A. Sheppard, J. Amer. Chem. Soc., 93 (1971) 248; G. Van Koten and J.G. Noltes, J. Organometal. Chem., 84 (1975) 129, 419; G. Van Koten, J.T.B.H. Jastrzebski and J.G. Noltes, ibid., 42 (1977) 2047.

8 G. Van Koten and J.G. Noltes, J. Chem. Soc. Chem. Commun., (1974) 575; R.W.M. ten Hoedt, G. Van Koten and J.G. Noltes, J. Organometal. Chem., 133 (1977) 113.

9 A. Cairncross and W.A. Sheppard, J. Amer. Chem. Soc., 93 (1971) 247.

10 G. Van Koten, R.W.M. ten Hoedt,and J.G. Noltes, J. Organometal. Chem., 42 (1977) 2705.

11 A. Avdeef and J.P. Fackler, Jr., Inorg. Chem., 17 (1978) 2182.

---

* Supplementary material available: a listing of observed and calculated structure factors.

12 P.K. Mehrotra and R. Hoffmann, Inorg. Chem., 17 (1978) 2187.
13 A. Camus, G. Nardin and L. Randaccio, Inorg. Chim. Acta, 12 (1975) 23.
14 A. Dedieu and R. Hoffmann, J. Amer. Chem. Soc., 100 (1978) 2074.
15 A. Camus, N. Marsich, G. Nardin and L. Randaccio, Inorg. Chim. Acta, 23 (1977) 131.
16 A. Camus and N. Marsich, J. Organometal. Chem., 14 (1968) 441.
17 G. Germain, P. Main and M.M. Woolfson, Acta Cryst. A, 27 (1971) 368.
18 F.H. Moore, Acta Cryst., 16 (1963) 1169.