Crystal and Molecular Structure of a New Type of Tetranuclear Mixed Valence Copper Complex: $Cu_4Ac_6(Ph_3P)_4$ (Ac = O_2CMe)

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The crystal structure of $Cu_4Ac_6(Ph_3P)_4$ comprises centrosymmetrical molecules, each of which consists of a dimeric unit of Cu_2Ac_4, similar to that in the structure of copper(II) acetate monohydrate, with the copper(I) co-ordinated through the oxygen atom of the acetate group in both axial $CuAc(Ph_3P)_2$ units.

The fact that triphenylphosphine (Ph_3P) has a reductive influence on Cu^{II} compounds is well known. Thus Cu^I complexes $CuAc(Ph_3P)_n$ ($n = 2$ or 3)[1] were prepared by the reaction of copper(II) acetate, $CuAc_2$, with Ph_3P. However, in solvents with relatively high concentrations of the Cu_2Ac_4 dimeric species, the copper(II) complex, $Cu_2Ac_4(Ph_3P)_2$, was also prepared and isolated by the reaction of Ph_3P and $CuAc_2$.[2,3] Depending on the experimental conditions a mixed-valence Cu^I–Cu^{II} complex of composition $Cu_2Ac_3(Ph_3P)_2$ was also obtained.[2,4] The electronic, i.r., and e.s.r. spectra, and the magnetic susceptibility measurements indicate the presence of Cu_2Ac_4 units in the structure, thus leading to the molecular formula $Cu_4Ac_6(Ph_3P)_4$.[4] The crystal structure of this complex was solved in order to determine the bonding mode of the ligands to the copper atoms in different oxidation states.

The $Cu_4Ac_6(Ph_3P)_4$ complex was prepared from a saturated solution of $CuAc_2.H_2O$ in ethanol by adding an ethanolic

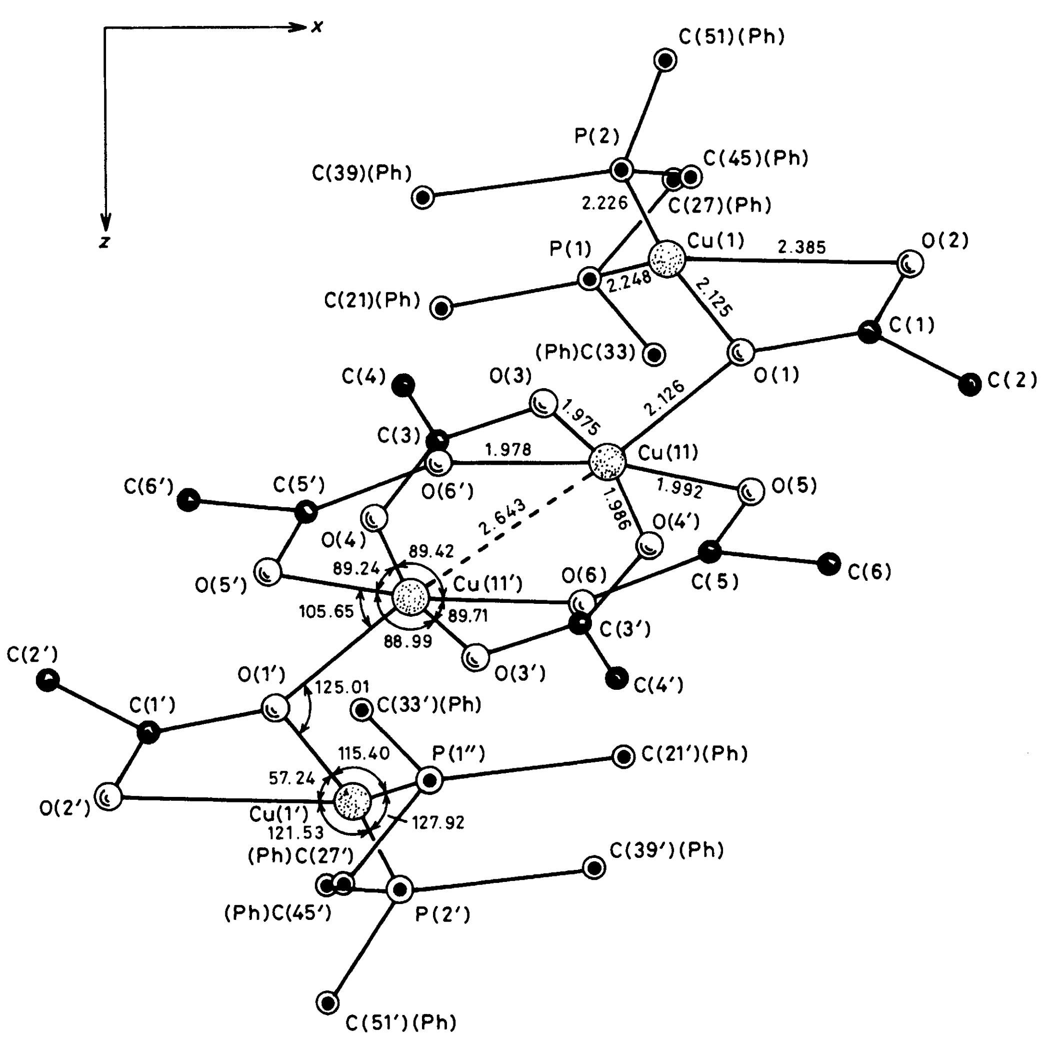

Figure 1. The molecular structure of $Cu_4Ac_6(Ph_3P)_4$ with selected interatomic distances and angles.

solution of the Ph_3P. The mixture was refluxed for 10 minutes, then cooled, and kept for crystallization in a desiccator over anhydrous $CaCl_2$.

The pale blue-green crystals of $Cu_4C_{84}H_{78}O_{12}P_4$ are triclinic, space group $P\bar{1}$, with $a = 10.898(8)$, $b = 12.850(4)$, $c = 19.877(8)$ Å, $\alpha = 121.03(2)$, $\beta = 90.14(5)$, $\gamma = 117.98(4)°$, $D_m = 1.376$ g cm^3 (at 20 °C), $D_c = 1.38$ g cm^3 for $Z = 1$. Experimental intensity data were collected on a four-circle computer-controlled Syntex $P2_1$ diffractometer using monochromated Cu-K_α radiation. The structure was solved by the heavy atom technique and was refined by full-matrix least-squares methods to $R = 0.056$ for 2227 reflections [$I \geq 1.96\,\sigma(I)$].†

The crystal structure consists of $Cu_4Ac_6(Ph_3P)_4$ molecules held together by van der Waals interactions and weak hydrogen bonds. The $Cu_4Ac_6(Ph_3P)_4$ molecule is centrosymmetrical; the centre of the symmetry lies between the two Cu^{II} atoms. The two Cu^{II} atoms are bridge-bonded by four acetate groups (Figure 1) as in copper acetate monohydrate, and in another dimeric Cu^{II} carboxylate complex.[5] Each Cu^{II} atom forms a further axial co-ordination bond with the oxygen atom from another acetate group thus forming the bridging donor atom between the Cu^{II} and Cu^{I} atoms. The other oxygen atom of this acetate group is co-ordinated to the Cu^{I} atom. The third and the fourth co-ordination sites of Cu^{I} are occupied by Ph_3P molecules.

The co-ordination polyhedron of the Cu^{II} atom is a distorted tetragonal pyramid with the oxygen atoms in the corners. The Cu^{II} atom is displaced from the basal plane by about 0.2 Å towards the apical oxygen atom. The co-ordination polyhedron of Cu^{I} is a *cis*-distorted tetrahedron similar to that of Cu^{I} in the $CuAc(Ph_3P)_2$ complex.[6]

The Cu^{II}–O(basal) distances are significantly longer (average value 1.983 Å) than they are in other acetate complexes with oxygen donor atoms in the apical position (1.969, 1.971, and 1.966 Å for $CuAc_2.H_2O$,[7] $CuAc_2.HAc$,[8] and $CuAc_2.MeOH$,[8] respectively). The Cu^{II}–O(apical) distance in the structure of the $Cu_4Ac_6(Ph_3P)_4$ complex is shorter (2.126 A) than those found for the compounds discussed above (2.156, 2.195, and 2.159 Å for $CuAc_2.H_2O$,[7] $CuAc_2.HAc$,[8] and $CuAc_2.MeOH$,[8] respectively). There are also differences in the Cu^{II}–Cu^{II} distance, which is 2.643 Å in the $Cu_4Ac_6(Ph_3P)_4$ complex and 2.616, 2.582, and 2.597 Å for $CuAc_2.H_2O$,[7] $CuAc_2.HAc$,[8] and $CuAc_2.MeOH$,[8] respectively.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The co-ordination polyhedron of Cu^I in $Cu_4Ac_6(Ph_3P)_4$ shows significant differences in Cu^I–O distances in comparison with those found for $CuAc(Ph_3P)_2$.[6] The Cu^I–O(1) distance is shorter (2.125 Å) and the Cu^I–O(2) distance is longer (2.385 Å) than the analogous distances in $CuAc(Ph_3P)_2$[6] (2.162 and 2.257 Å, respectively). The remaining distances including the bond lengths in the Ph_3P ligand are not significantly different from those in the $CuAc(Ph_3P)_2$ complex.[6]

The complex $Cu_4Ac_6(Ph_3P)_4$ represents a new structural type among mixed valence Cu^{II}–Cu^I carboxylates. It involves the neutral Cu^I carboxylate complex as a terminal ligand of each Cu^{II} atom in contrast to other mixed valence copper carboxylates[9,10] in which the copper(I) complex is the bridging ligand between each of the two dimeric $Cu_2(RCO_2)_4$ units thus forming polymeric chains.

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References

1 B. Hammond, F. H. Jardine, and A. G. Vohra, *J. Inorg. Nucl. Chem.*, 1971, **33**, 1017.
2 G. Ondrejovič, D. Valigura, M. Máriássy, and J. Mroziński, *Chem. Zvesti,* in the press.
3 T. Tokii, T. Ikeda, and Y. Muto, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 3925.
4 D. Valigura, G. Ondrejovič, and M. Máriássy, Proc. 9th Conf. Co-ord. Chem., Smolenice-Bratislava, 1983, p. 437.
5 M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.
6 M. G. B. Drew, A. H. bin Othman, D. A. Edwards, and R. Richards, *Acta Crystallogr., Sect. B,* 1975, **31**, 2695.
7 P. de Meester, S. R. Fletcher, and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1973, 2575.
8 V. M. Rao and H. Manohar, *Inorg. Chim. Acta,* 1979, **34**, L213.
9 R. L. Beddoes, J. A. Connor, D. Dubowski, A. C. Jones, O. S. Mills, and R. Price, *J. Chem. Soc., Dalton, Trans.*, 1981, 2119.
10 T. Glowiak and H. Kozlowski, *Inorg. Chim. Acta,* 1980, **46**, L65.