# Crystal and Molecular Structure of the Adduct between Dichlorodiaquacopper(II) and Triphenylphosphine Oxide

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*Summary* The *X*-ray crystal structure of $Cu(OPPh_3)_4(H_2O)_2Cl_2$ shows that the compound is an adduct of dichlorodiaquacopper(II) and triphenylphosphine oxide; the adduct unit is formed by one $CuCl_2(H_2O)_2$ square-planar complex unit and four molecules of triphenylphosphine oxide which are bonded to the complex unit by hydrogen bonds.

We have prepared previously compounds of the type $Cu(OPPh_3)_4(H_2O)_2X_2$ ($X = Cl^-$, $Br^-$).[1] In view of the unusually large number of possibilities for co-ordination of ligands to the central $Cu^{II}$ atom several methods have been used (i.r., electronic, and e.s.r. spectra, magnetic measurements,[1] and thermal decomposition studies[1,2]) to establish their structure. We now report the *X*-ray crystal structure determination for the chloride complex.[3]

The dark blue crystals of $Cu(OPPh_3)_4(H_2O)_2Cl_2$ are monoclinic, space group $P2_1/c$ with $a = 14{\cdot}038(4)$, $b = 9{\cdot}826(2)$ $c = 27{\cdot}544(9)$ Å, $\beta = 122{\cdot}540(1)°$, $D_m = 1{\cdot}385(2)$ g cm$^{-3}$ (by immersion, at 18 °C); $D_c = 1{\cdot}396$ g cm$^{-3}$ for $Z = 2$. Unit cell parameters were obtained by least-squares treatment of the powder data. Experimental intensity data were collected on a four-circle computer-controlled Syntex $P2_1$ diffractometer using monochromated Mo-$K_\alpha$ radiation. The structure was solved by the heavy-atom technique and was refined by full-matrix least-squares to $R = 0{\cdot}093$ for 3412 independent non-zero reflections. Hydrogen atoms were not included in the refinement.†

The crystal structure consists of the adduct units $\{[CuCl_2(H_2O)_2](OPPh_3)_4\}$ (Figure) which are held together by van der Waals interactions. One adduct unit is formed by one *trans* square-planar $CuCl_2(H_2O)_2$ complex unit and

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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.

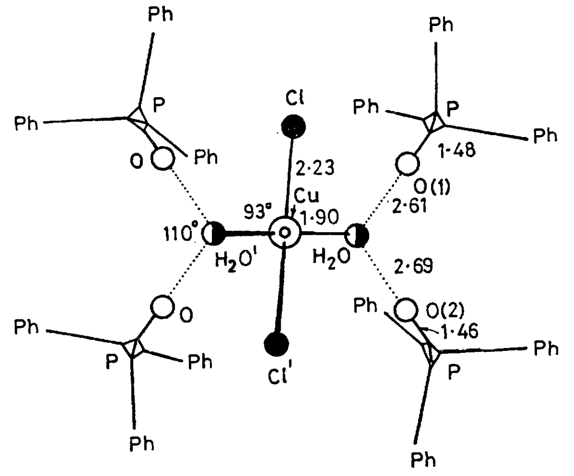

FIGURE. The molecular structure of the adduct unit $\{[CuCl_2(H_2O)_2](OPPh_3)_4\}$, with selected bond lengths (Å) and angles (°). The angle between the O(1), $H_2O$, O(2) and Cu, Cl, Cl′, $H_2O$, $H_2O'$ planes is 34°.

four molecules of triphenylphosphine oxide. The triphenylphosphine oxide molecules are bonded by hydrogen bonds to each hydrogen atom of the complex unit. This adduct unit is centrosymmetric, the $Cu^{II}$ atom being at the centre of symmetry. Additional co-ordination, completing the square-planar arrangement to the usual octahedral co-ordination for $Cu^{II}$ is not observed. The nearest atom in the axial direction is the phenyl ring carbon atom from the triphenylphosphine oxide molecule of the neighbouring adduct unit at a distance 4·00 Å. The Cl–Cu–C and $H_2O$–Cu–C angles are 65 and 76°, respectively. The geometry of the $OPPh_3$ molecule remains almost the same as it is in the unbonded molecule.

TABLE. E.s.r. and electronic spectral data for $Cu(OPPh_3)_4(H_2O)_2X_2$; X = Cl (**1**), Br (**2**).

| | E.s.r. | | | | Electronic |
|---|---|---|---|---|---|
| Complex | $g_\perp$ | $g_\parallel$ | $A_\perp \times 10^{-4}$ /cm$^{-1}$ | $A_\parallel \times 10^{-4}$ /cm$^{-1}$ | ν/cm$^{-1}$ |
| (**1**) | 2·06 | 2·26 | — | 120 | 14,400, 17,400sh, 34,000sh, 37,400 |
| (**2**) | 2·08 | 2·38 | 30 | 85 | 10,000sh, 14,200, 17,000sh, 26,000, 30,000, 37,500 |

This crystallographic result leads to a possible interpretation of the data obtained by other methods[1,2] (Table) and can be utilised to elucidate the structure of $Cu(OPPh_3)_4(H_2O)_2Br_2$. Some structural differences would be expected between the chloride and bromide compounds on the basis of their different magnetic moments and electronic absorption spectra. The higher value of the magnetic moment ($\mu_{eff}$ 2·06 B.M.) for the bromide compared with that for the chloride ($\mu_{eff}$ 1·83 B.M.) as well as the band observed at *ca.* 10,000 cm$^{-1}$ in the electronic spectrum of the bromide indicates a tetrahedral or distorted tetrahedral co-ordination of $Cu^{II}$ in $Cu(OPPh_3)_4(H_2O)_2Br_2$.

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[2] D. Makáňová, G. Ondrejovič, and J. Gažo, *Chem. Zvesti*, 1976, **30**, 81.

[3] M. Dunaj-Jurčo, J. Kožíšek, A. S. Ancyškina, G. Ondrejovič, D. Makáňová, and J. Gažo, Proc. XIXth I.C.C.C., Prague, Czechoslovakia, Sept. 4—8th, 1978, II, 36.