Synthesis and Structural Characterisation of a Novel Bimetallic Sulphur Cluster $(PPh_4)_2Cu_3WS_4Cl_3$

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Reaction of $(PPh_4)_2WS_4$ with CuCl in acetonitrile gives the title compound, an *X*-ray analysis of which shows a new type of arrangement of one tungsten and three copper atoms bridged by sulphido-ligands.

Thiometallates can aggregate with closed d shell metals to form complexes having unusual geometry or featuring redox behaviour.[1] In particular, neutral species such as CuCN,[2] or CuCl (this work), can be directly co-ordinated to WS_4^{2-} (or MoS_4^{2-}). Herein, we present the structural characterisation of a new bimetallic compound in which tungsten, copper, and sulphur are present in an unusual arrangement.

$(PPh_4)_2Cu_3WS_4Cl_3$ was isolated as orange crystals after treating $(PPh_4)_2WS_4$ (0.25 mmol) with CuCl (0.75 mmol) in MeCN (25 ml) at room temp. This complex is diamagnetic at 25 °C and reasonably air stable. Its i.r. spectrum contains main absorption bands at 460, 435 (bridging WS groups[3]), and 345 cm^{-1} (solid, KBr pellet). The electronic spectrum (in dimethylformamide solution) is characterised by absorptions at 432 (4350), 308 (11 900), and a shoulder at 330 nm (molecular absorptivities in parentheses).

Crystal Data: $C_{48}H_{40}Cl_3Cu_3P_2S_4W$, $M = 1287$, orthorhombic, $a = 39.142(9)$, $b = 14.816(4)$, $c = 17.322(5)$ Å, $U = 10\,045$ Å^3, space group *Pbca*, $Z = 8$, $D_m = 1.68$ g cm^{-3}, $D_c = 1.70$ g cm^{-3}, μ(Mo-K_α) = 40.5 cm^{-1}. Intensity data were collected on a Philips PW1100 four circle diffractometer with Mo-K_α radiation. An absorption correction was applied. The structure was solved by normal heavy atom Patterson and Fourier procedures and refined by full-matrix least-squares methods to an *R*-value of 0.054 for 2389 reflections [$2\theta < 40°$, with $F_0 > 6\sigma(F_0)$]. All atoms of the bimetallic anion and the phosphorus atoms of the counter anion were refined anisotropically. The phenyl rings of the $(PPh_4)^+$ cation were considered as rigid groups; each individual carbon atom was assigned an isotropic thermal parameter which was allowed to vary during the refinement.†

† 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.

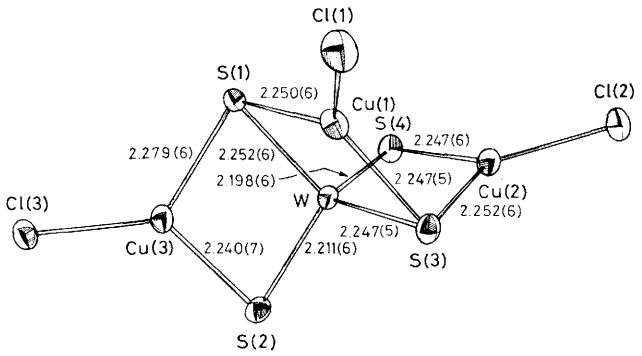

Figure 1. A perspective view of the $[Cu_3WS_4Cl_3]^{2-}$ anion including the atom numbering scheme and some pertinent bond lengths.

The molecular structure of the anion and some important bond lengths are shown in Figure 1. It contains a tetrahedral WS_4 group co-ordinated by three CuCl molecules. All atoms of the anion are distributed in three planar (within 0.09 Å) four-membered rings having the central W atom as common point. Furthermore the Cl(1), Cu(1), Cl(2), Cu(2), Cl(3), Cu(3), and W atoms lie approximatively in one plane. The Cl(2)–Cu(2) . . . W . . . Cu(3)–Cl(3) moiety is nearly linear [Cl(3)–Cu(3) . . . W = 178.4(2)°, Cu(3) . . . W . . . Cu(2) = 173.67(9)°, W . . . Cu(2)–Cl(2) = 175.8(2)°].

The W atom has retained the characteristic geometry of the free WS_4^{2-} ligand with S–W–S angles ranging from 108.2(2)° to 111.8(2)°. The S(2) and S(4) atoms are doubly bridged to tungsten and copper centres, whereas the S(1) and S(3) atoms are triply bridged to tungsten and two copper atoms. The tungsten–sulphur bond lengths are not significantly different. The copper–sulphur distances are comparable with the corresponding values found in other complexes.[4]

The very acute angles about the sulphur atoms bridging copper and tungsten [ranging from 71.4(2)° to 72.9(2)°], together with the short Cu–W separations [2.636(3) to 2.645(3) Å] are suggestive of tungsten–copper bonding. Although no definitive statement can be made about the existence of a bond between copper and tungsten, the observed distances are consistent with a strong attractive interaction between these two atoms as expected when placing two metals with greatly different formal oxidation states Cu^{I} and W^{VI} in close proximity.[5] As previously postulated,[6] Cu^{I} (considered as a soft acid) has a high tendency to form metal–sulphur bonds with MS_4^{2-}, the thiometallate acting preferably as a terdentate or tetradentate ligand.

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