X-Ray Crystal and Molecular Structure of $[W_2S_8Ag_4(PPh_3)_4]$, a Compound Having a Novel Metal–Sulphur Cage Fused by Two Connected Six-membered WS_3Ag_2 Rings

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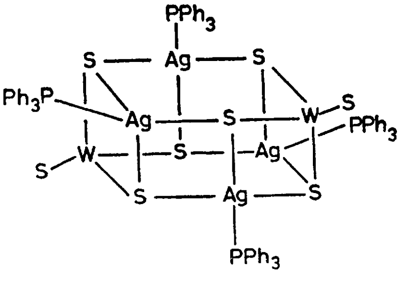
Summary The crystal structure of $W_2S_8Ag_4(PPh_3)_4$ shows that the molecule forms a metal–sulphur cage consisting of two connected six-membered WS_3Ag_2 rings.

Compounds containing metal–sulphur units are interesting because of their bioinorganic relevance. This type of compound can be obtained from thiometallates.[1] Whereas transition metal complexes containing thiometallates as ligands (*e.g.* $[S_2WS_2CoS_2WS_2]^{2-}$) can be classified from the structural point of view according to the rules of classical complex chemistry,[1,2] interesting and unexpected structures were found in the case of compounds containing central metal atoms with closed *d*-shells: *e.g.* $[Sn_2(WS_4)_4]^{4-}$ (novel dimeric structure)[3] or $[Au_2(WS_4)_2]^{2-}$ (ring system).[4] We now report that $[W_2S_8Ag_4(PPh_3)_4]$ (**1**) contains an interesting metal–sulphur cage, formed by two connected six-membered rings. Crystals suitable for an *X*-ray study were obtained by extraction of an aqueous solution of $(NH_4)_2WS_4$ with a solution of Ph_3P and $AgNO_3$ in CH_2Cl_2 (see also ref. 5).



(1)

Crystal data: $C_{72}H_{60}Ag_4P_4S_8W_2$, $M = 2104{\cdot}9$, triclinic, space group $P\bar{1}$, $a = 12{\cdot}245(6)$, $b = 12{\cdot}924(5)$, $c = 13{\cdot}250(6)$ Å $\alpha = 97{\cdot}77(3)$, $\beta = 113{\cdot}35(3)$, $\gamma = 91{\cdot}43(3)°$, ($\lambda = 0{\cdot}7107$ Å for Mo-K_α); $U = 1900{\cdot}1$ Å^3, $Z = 1$, $D_c = 1{\cdot}84$ g cm^{-3}, $\mu = 45{\cdot}1$ cm^{-1} for Mo-K_α. The structure was solved by the heavy-atom method. Least-squares refinements (with the phenyl carbon atoms refined independently) converged at R 0·079 for 7822 independent reflections [$4{\cdot}0° \leqslant 2\theta \leqslant 54°$; $I > 1{\cdot}96\sigma(I)$] measured on a four-circle diffractometer with Mo-K_α radiation.†

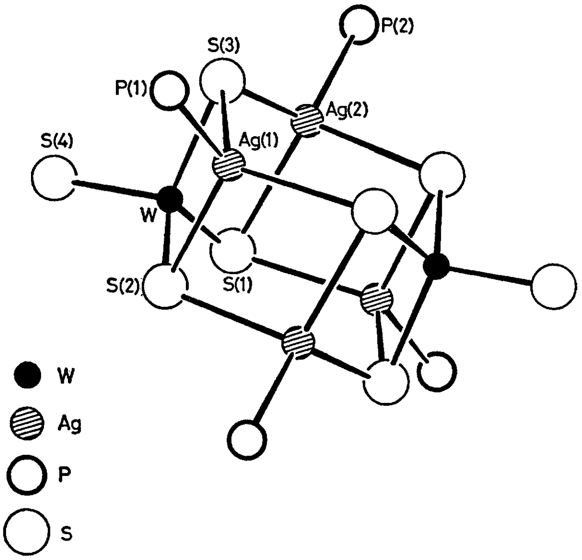


Figure. Molecular structure of $W_2S_8Ag_4(PPh_3)_4$. The phenyl rings have been omitted for the sake of clarity. Bond distances: W–S(1) 2·257(5); W–S(2) 2·208(4); W–S(3) 2·245(6); W–S(4) 2·124(6); Ag(1)–S(1) 2·648(5); Ag(1)–S(2) 2·592(6); Ag(1)–S(3) 2·554(5); Ag(1)–P(1) 2·441(6); Ag(2)–S(1) 2·562(6); Ag(2)–S(2) 2·777(5); Ag(2)–S(3) 2·538(5); Ag(2)–P(2) 2·407(5) Å.

The molecular structure is presented in the Figure. It can formally be described as a cage (with a centre of inversion) composed of two six-membered (SAg_2S_2W) rings, which are connected with metal–sulphur bonds. W [angles in the range 106·07(22)—112·74(18)°] and Ag [distorted, angles varying between 128·29(18) and 92·16(16)°] are tetrahedrally co-ordinated. WS_4^{2-} can be considered as a ter dentate ligand, the terminal WS bonds being significantly shorter than the others. It would be interesting to study the electrochemistry (*e.g.* with cyclic voltammetry) of this and, particularly, the corresponding Mo compound to obtain information about the electron affinity of the core.

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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.

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