The Synthesis and Characterisation of two Novel Heterometallic Trinuclear Incomplete Cubane-like Clusters $[Et_4N](M_2AgS_4)(S_2C_2H_4)_2(PPh_3)\cdot CH_2Cl_2$ (M = Mo, W)

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Two new members of the heterometallic trinuclear incomplete cubane-like cluster family, with the core $[M_2AgS_4]^{3+}$ (M = Mo, W), were synthesized and characterised; the Mo–Mo [W–W] bond was found to be 2.881(4) [2.874(1)] Å and two Mo–Ag [W–Ag] non-bonding distances 3.010(4) and 3.117(4) [3.112(2), 3.055(2)] Å.

There is extensive interest in trinuclear triangular metal clusters.[1] Trimolybdenum clusters with the incomplete cubane-like cluster core $[Mo_3S_4]^{4+}$ [2] have attracted much interest, not only because the $[Mo_3S_4]^{4+}$ aquo ion has especial stability,[3] but also because it may be employed as a starting material in reactions with many metals, *e.g.*, Fe,[4] Cu[5,6] Ni[7] *etc.*, to form cubane-like clusters, or to dimerize to form an Mo_6S_8 cluster.[8] Tritungsten clusters with the incomplete cubane-like cluster core $[W_3S_4]^{4+}$ [9] can also react with a copper atom to form cubane-like clusters.[10] However, research on heterometallic trinuclear incomplete cubane-like clusters is just beginning, for only two clusters, $[Et_4][M_2CuS_4(edt)_2(PPh_3)]$[11] (M = Mo, W; edt = ethane-1,2-dithiolato), have recently been reported by our group. The two heterometallic incomplete cubane-like clusters can react further with another $CuPPh_3^+$ group to form a cubane-like cluster, $[M_2Cu_2S_4(edt)_2(PPh_3)_2]$[12] (M = Mo, W). Herein the synthesis and characterisation of two novel heterometallic trinuclear clusters with incomplete cubane-like cores $[M_2AgS_4]^{3+}$ (M = Mo, W), are described.

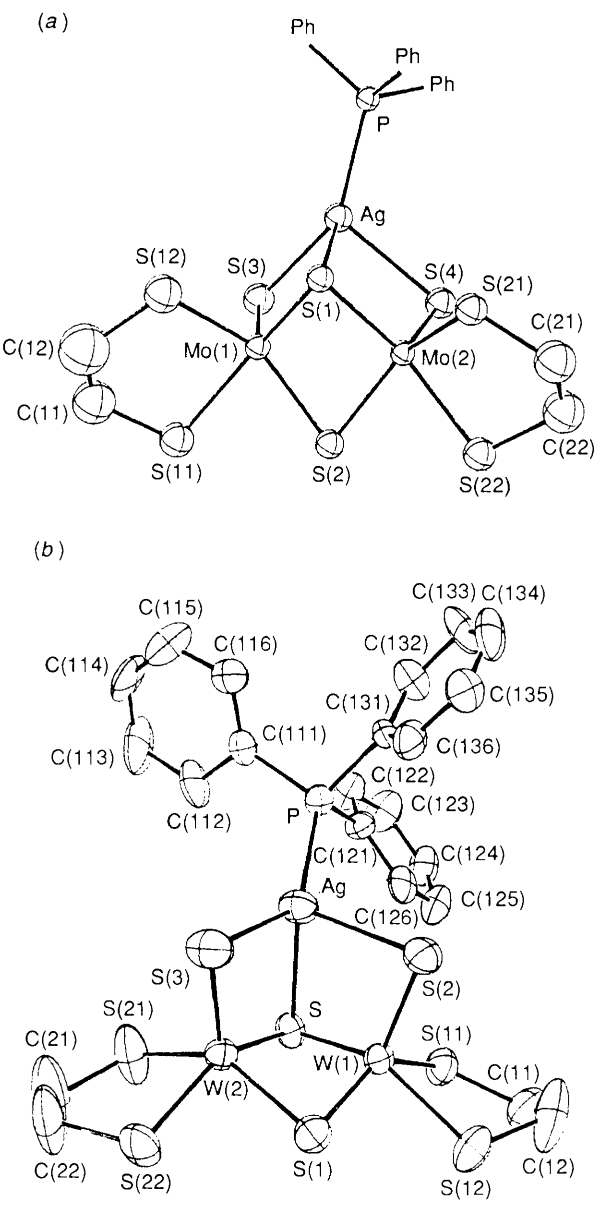

Fig. 1 (*a*) Structure of the $Mo_2AgS_4(edt)_2(PPh_3)^-$ anion and selected bond lengths (Å); Mo(1)–Mo(2) 2.881(4), Mo(1)–Ag 3.010(4), Mo(2)–Ag 3.117(4), Mo(1)–S(1) 2.346(8), Mo(2)–S(1) 2.36(1), Mo(1)–S(2) 2.33(1), Mo(2)–S(2) 2.336(9), Mo(1)–S(3) 2.16(1), Mo(2)–S(4) 2.15(1), Ag–S(1) 2.55(1), Ag–S(3) 2.587(9), Ag–S(4) 2.71(1), Ag–P 2.405(8), C(11)–C(12) 1.26(7), C(21)–C(22) 1.44(6). (*b*) Structure of the $W_2AgS_4(edt)_2(PPh_3)^-$ anion and selected bond lengths (Å); W(1)–W(2) 2.874(1), W(1)–Ag 3.112(2), W(2)–Ag 3.055(2), W(1)–S 2.300(4), W(1)–S(1) 2.303(4), W(1)–S(2) 2.200(4), W(2)–S 2.370(4), W(2)–S(1) 2.394(4), W(2)–S(3) 2.195(4), Ag–P 2.398(4), Ag–S 2.568(4), Ag–S(2) 2.720(5), Ag–S(3) 2.573(4).

The number of Mo–Ag–S and W–Ag–S complexes, which are formed from the reaction of MS_4^{2-} (M = Mo, W) anions with the soft cation Ag^+ in the presence of PPh_3 or $S_2CN(CH_2CH_3)_2^-$ ligands, is limited. One type is the linear di- or tri-nuclear compounds of composition $[Pr^i{}_4N]_2[(CN)AgS_2MS_2]$[13] or $(PR_3)_nAg_2MS_4$[14] (M = Mo, W; R_3 = Ph_3, $MePh_2$; n = 3, 4). The second type is the species with cages fused by two six-membered metal–sulphur rings of the formula $(Ag_4M_2S_6)(PR_3)_4S_2$[15] (M = Mo, W; R_3 = Ph_3, $MePh_2$). The third type is the recently reported compound $[Bu_4N]_2\{M_2Ag_3(\mu_3\text{-}S)_2(\mu_2\text{-}S)_4(S)_2[S_2CNEt_2]\}$,[16] in which the structure contains two butterfly-fragments $(S)M(\mu_2\text{-}S)_2(\mu_3\text{-}S)Ag_2$ sharing one Ag atom and two Ag atoms being bridged by a bidendate $S_2CNEt_2^-$ ligand while the five metal atoms form a normal five-membered ring. Both compounds **1** and **2** were synthesized by the unit-construction method,[17] a convenient method that uses reactive fragments as building blocks to obtain clusters.

The dinuclear compounds $[Et_4N]_2Mo_2S_4(edt)_2$ **3** and $[Et_4N]_2W_2S_4(edt)_2$ **4** were prepared under a dinitrogen atmosphere according to the procedure of Stiefel *et al.*[18] Both compounds reacted with the silver complex $Ag(PPh_3)_3NO_3$ under a dinitrogen atmosphere. Dark-red crystals of **1** and orange-red crystals of **2** were obtained respectively from CH_2Cl_2–MeCN by gaseous diffusion of diethyl ether at room temperature. Satisfactory elemental analyses were obtained.†

$[Et_4N][Mo_2AgS_4(edt)_2(PPh_3)]\cdot CH_2Cl_2$	**1**
$[Et_4N][W_2AgS_4(edt)_2(PPh_3)]\cdot CH_2Cl_2$	**2**
$[Et_4N]_2[Mo_2S_4(edt)_2]$	**3**
$[Et_4N]_2[W_2S_4(edt)_2]$	**4**

X-Ray structure analysis‡ revealed the existence of an incomplete cubane-like core of $[M_2AgS_4]^{3+}$ (M = Mo, W) which is completed by two edt ligands and one PPh_3 ligand as shown in Fig. 1(*a*) and 1(*b*). Crystals of the two complexes are isomorphous.

Each Mo(W) atom displays tetragonal-pyramidal (TP) coordination geometry by the five sulphur atoms; one μ_2-sulphido atom occupies the axial position of each TP and the remaining four sulphido atoms are equatorial. In both structures the Mo(W) atom is an average of 0.75(0.698) Å out of the basal plane. The Ag atom sits in a distorted tetrahedral environment; for compound **1** (or **2**) the angles P–Ag–S and S–Ag–S are in the wide range of 89.9(3) to 136.5(3)° [89.3(1) to 137.0(1)°]. Except for slight changes, the bond lengths and bond angles of the $M_2S_4(edt)_2$ (M = Mo, W) moiety in the trinuclear clusters are almost the same as in the isolated dinuclear complexes.[19] Only the Mo=S (W=S) double bond lengths elongate from an average of 2.10 to 2.16 Å (av. 2.144 to av. 2.198 Å), when the terminal S atoms become μ_2-S atoms. The C–C distances of the edt ligands are unrealistically short for single bonds because of thermal motion.[19]

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† *Spectroscopic data* for **1**: IR (KBr pellet): ν/cm^{-1}: δ(C–H, PPh_3) 750s, 740s, 695s; ν(Ag–P) 516m, 505m; $\nu(Mo\text{–}\mu_2\text{-}S_t)$ (S_t = terminal sulphido) 490m; $\nu(Mo\text{–}\mu_2\text{-}S)$ and $\nu(Mo\text{–}\mu_3\text{-}S)$ 460w, 430w; $\nu(Mo\text{–}\mu_2\text{-}S)$ 320w; $\lambda(Mo\text{–}S_{edt})$ 345m, 305w; λ_{max}/nm 460, 255, 235.

For **2**: IR (KBr pellet): ν/cm^{-1}: δ(C–H, PPh_3) as for **1**; ν(Ag–P) 520m, 508m; $\nu(W\text{–}\mu_2\text{–}S_t)$ 490m, sh; $\nu(W\text{–}\mu_2\text{-}S)$ and $\nu(W\text{–}\mu_3\text{-}S)$ 484s, 467m, 443w, 422w, 344w; $\nu(W\text{–}S_{edt})$ 355m, 310m; λ_{max}/nm 405, 270, 235.

‡ *Crystal data* for compound **1**, $C_{31}H_{45}Cl_2PNAgS_8Mo_2$, M_r = 1087.8, orthorhombic, space group $Pna2_1$, a = 25.45(2), b = 11.151(8), c = 15.03(1) Å, U = 4266(10) $Å^3$; Z = 4; D_c = 1.69 g cm^{-3}; μ = 15.80 cm^{-1}; T = 296 K; λ(Mo-Kα) = 0.71069 Å, $2\theta_{max}$ = 50°. Rigaku AFC5R diffractometer, $\omega/2\theta$ scan, 2213 unique reflections with $I > 3\sigma(I)$ were used in the refinement. The last successful full-matrix least-squares refinement with anisotropic thermal parameters for Mo, Ag, S, P atoms, isotropic thermal parameters for all N, C atoms (240 variables) converged to R 0.075, R_w = 0.096, S = 1.97. (Hydrogen atoms were placed geometrically in calculated positions and were included in the calculation of the R-factor).

For compound **2**, $C_{31}H_{45}Cl_2PNAgS_8W_2$, M_r = 1265.6, orthorhombic, space group $Pna2_1$, a = 25.396(5), b = 11.146(5), c = 14.994(4) Å, U = 4244(4) $Å^3$; Z = 4; D_c = 1.98 g cm^{-3}; μ = 65.45 cm^{-1}; T = 296 K; λ(Mo-Kα) = 0.71069 Å, $2\theta_{max}$ = 50.1°. Rigaku AFC5R diffractometer, $\omega/2\theta$ scan. 3441 unique reflections with $I > 3\sigma(I)$ were used in the refinement. The last successful full-matrix least-squares refinement with anisotropic thermal parameters for all atoms (414 variables) converged to R = 0.036, R_w = 0.048, S = 1.34. (Hydrogen atoms were placed geometrically in calculated positions and were included in the calculation of the R-factor). Both structures were solved by direct methods and Fourier synthesis using the TEXSAN program package. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.

The structures of the heterometallic core $[M_2AgS_4[^{3+}$ and homometallic $[M_3S_4]^{4+}$ core (M = Mo, W) are very different; the $[M_3S_4]^{4+}$ core has approximately C_{3v} symmetry and the heterometallic trinuclear cluster core $[M_2AgS_4]^{3+}$ has no symmetry because of extreme distortion. The M–Ag bond lengths are too long for effective bonding [3.010(4) and 3.117(4) Å for compound **1** and 3.112(2) and 3.055(2) Å for compound **2**]. The two bonds are much longer than either of the Mo–Mo or the W–W bond length. As shown previously,[11] the $[M_2CuS_4]^{3+}$ core has three metal–metal bonds, but the title compounds have only one metal–metal bond between the two Mo (or W) atoms. So the three types of incomplete cubane-like clusters each have some differences.

For compound **1**, the Ag-μ_3-S has a bond length of 2.55(1) Å, but the two Ag–μ_2-S bond lengths are significantly different, one being 2.587(9) Å and the other 2.71(1) Å. For compound **2**, the Ag–μ_3-S bond length is 2.568(4) Å and the two Ag–μ_2-S bond lengths are 2.573(4) and 2.740(4) Å, respectively. It is exceptional that the Ag–μ_3-S bond is shorter than the Ag–μ_2-S bond. To rationalise the bond lengths of compound **2**, the $[AgPPh_3]^+$ group can clearly withdraw electrons through the W=S double bonds to make all the bonds to the W atoms shorter (or stronger). Comparing the bonds to the two W atoms, the stronger the Ag–μ_2-S bond is, the shorter the bonds to the corresponding W atom are.

It has already been shown that the cores of the compounds $[M_2AgS_4]^{3+}$ and $[M_2CuS_4]^{3+}$ have the same symmetry and they may have similar reactivity, *e.g.* to combine with a metal atom to form a cubane-like cluster. These complexes may be precursors for cubane-type structures; we have obtained cubane-type clusters from reactions between $[M_3S_4]^{4+}$ or $[M_2CuS_4]^{3+}$ (M = Mo, W) with copper complexes.

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