Synthesis and Structural Characterization of a Large Molybdenum–Copper–Sulphur Cluster Compound $[Bu^n{}_4N]_4[Cu_{12}Mo_8S_{32}]$

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Reaction of $[NH_4]_2[MoS_4]$, CuCN and $[Bu^n{}_4N]Br$ in the solid state produced the mixed-metal sulphur cluster anion $[Cu_{12}Mo_8S_{32}]^{4-}$; an X-ray analysis of $[Bu^n{}_4N]_4[Cu_{12}Mo_8S_{32}]$ shows that the anion forms a cubane-like $[Cu_{12}Mo_8]$ bimetallic cage through μ_1-S, μ_2-S, μ_3-S and μ_4-S atoms.

The $[MoS_4]^{2-}$ anion is the most effective antagonist of copper metabolism[1,2] and a common ligand in copper complexes.[3–7] About sixty Mo–Cu–S cluster compounds have been reported. A few bigger cluster compounds containing molybdenum, copper and sulphur, *e.g.* $[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9]$ $(p\text{-}MeC_6H_4SO_3)_8\cdot 12H_2O$[8] and $[NEt_2]_2[(\mu_6\text{-}S)Cu_6S_6(S_2)_6\text{-}Mo_6O_6]\cdot$dmf (dmf = dimethylformamide),[9] have been prepared in the last few years. Here, we report the synthesis and characterization of $[Bu^n{}_4N]_4[Cu_{12}Mo_8S_{32}]$, a rare example of an Mo–Cu–S cluster involving twenty bimetal atoms.

The title compound was obtained by heating $[NH_4]_2[MoS_4]$ (1 mmol), CuCN (2 mmol) and $[Bu^n{}_4N]Br$ (3 mmol) in the solid state at 90 °C for 10 h, extracting the product with CH_2Cl_2 (40 ml), and filtering the deep-red coloured extract. Slow diffusion of a mixture of acetone (20 ml) and n-pentane (20 ml) into this solution yielded dark-red rhombic crystals.

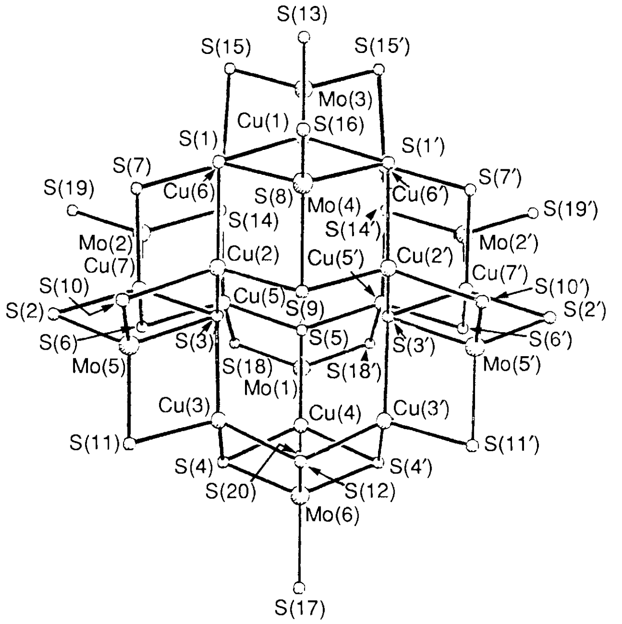

Fig. 1 Structure of the anion $[Cu_{12}Mo_8S_{32}]^{4-}$

This complex is air-sensitive. Its IR spectrum contains main absorption bands at 518, 482, 447 and 405 cm^{-1} (solid, KBr pellet) and it gave satisfactory elemental analyses for $C_{64}H_{144}N_4Mo_8Cu_{12}S_{32}$. Its crystal structure has been determined (Fig. 1).†

The elemental analyses indicated that the title compound contains four $[Bu^n{}_4N]$ cations. The positions of eight of the C atoms of this compound could not be determined by the X-ray single crystal analysis owing to intersite interference from the metal atoms, but this does not affect our understanding of the structure of the cluster anion.

The anion has a very high degree of symmetry with six mirror planes, and four three-fold and three two-fold rotation axes. Its structure can formally be described as a cage containing a pseudo-cubane type $[Mo_8Cu_{12}]$ core, in which the metal atoms are connected through bridging sulphur atoms and the Mo–Cu distances [2.688(10)–2.570(10) Å] show significant interactions between heteronuclear metallic atoms. Each unit consisting of a copper atom and the two nearest neighbour molybdenum atoms is nearly linear [angles in the range 175.5(4)–178.2(3)°] and the angles about molybdenum atoms bonding the two copper atoms vary between 84.3(3) and 90.3(2)°.

The X-ray data indicate that there are four classes of sulphur atoms in this complex. This is the first example of a Mo–Cu–S cluster involving μ_1-S, μ_2-S, μ_3-S and μ_4-S in one complex. The S(16), S(17), S(19) and S(19′) atoms may be regarded as terminal sulphur atoms connected to one molybdenum atom, whereas S(2), S(2′), S(10), S(10′), S(11), S(11′), S(13), S(15), S(15′), S(18), S(18′) and S(20) are doubly bridging sulphur atoms bound to a molybdenum and a copper atom; the S(1), S(1′), S(4), S(4′), S(6), S(6′), S(7), S(7′), S(9), S(12), S(14) and S(14′) atoms are triply bridged to a molybdenum atom and two copper atoms; the S(3), S(3′), S(5) and S(8) atoms are quadruply bridged to a molybdenum atom and three copper atoms. The Cu–S–Cu angles vary between 105.8(6) and 115.5(7)°, while the Cu–S–Mo angles lie in the range 71.4(7)–76.5(6)°. There are two classes of molybdenum atoms in this molecule, Mo(2), Mo(2′), Mo(4) and Mo(6) atoms being bound to a terminal sulphur atom and three triply bridging sulphur atoms, and the others to a quadruply bridging sulphur atom and three doubly bridging sulphur atoms. The local coordination sphere around each molybdenum atom approaches a tetrahedron [106.7(5)–112.2(7)] and the Mo–S bond distances vary between 2.065(29) and 2.301(17) Å.

All copper atoms are coordinated by a μ_4-S, a μ_2-S and two μ_3-S atoms with a distorted tetrahedral geometry [101.9(7)–116.0(6)] and the Cu–S bond distances range from 2.264(31) to 2.362(19) Å.

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† *Crystal data*: $[Bu^n{}_4N]_4[Cu_{12}Mo_8S_{32}]$, M = 3526.11, monoclinic space group $C2/m$, a = 22.627(3), b = 21.628(5), c = 26.259(6) Å, β = 101.66(1)°, V = 12585.1 Å^3, Z = 4, D_c = 1.86 g cm^{-3}, $F(000)$ = 7008, Mo-Kα radiation, λ = 0.71069 Å, μ = 32.81 cm^{-1}. Data were collected on an R3M/E four-circle diffractometer using the ω-2θ scan mode with 2θ in the range $2° \leqslant 2\theta \leqslant 50°$; of 6465 independent reflections corrected for Lorentz–polarisation and for empirical absorption based on the scans, 2453 with $I \geqslant 3\sigma(I)$ were used for structure determination by Patterson and Fourier methods. Full-matrix least-squares refinement with anisotropic thermal parameters for all atoms of the anion gave a final R of 0.083; R_w = 0.090. 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.