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Synthesis and Characterisation of $[VS_4(CuPPh_3)_5(CuCl)Cl_2]{\cdot}CH_2Cl_2$; a Compound containing a Tetrahedral V^VS_4 Core Encapsulated by an Octahedral Array of Copper(I) Atoms

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Reaction between $[NH_4]_3[VS_4]$, $[NEt_4]Cl$, CuCl, and PPh_3 in CH_2Cl_2 has led to the formation of $[VS_4(CuPPh_3)_5(CuCl)Cl_2]$ which contains a hitherto unrecognised type of mixed metal sulphur cluster, consisting of a tetrahedral V^VS_4 core bound to an octahedral array of Cu^I atoms.

The tetrathiometallate anions of several of the early d-transition metals have been shown to act as ligands to a wide variety of metal ions.[1] Research in these laboratories has led to the characterisation of a large number of compounds in which an $[MS_4]^{2-}$ (M = Mo or W) anion binds one, two, three, or four copper(I) atoms.[2—6] Also, three copper(I) atoms have been shown to bind to $[ReS_4]^{-}$ [7] and $[VS_4]^{3-}$,[8] and five copper(I) atoms to $[ReS_4]^{-}$.[9] In each case, the tetrathiometallate anion acts as a bidentate ligand to copper(I) and this common structural feature leads to a considerable versatility in molecular structure. As a novel extension of this research herein we report the synthesis, structure, and selected properties of $[VS_4(CuPPh_3)_5(CuCl)Cl_2]$, the first example of a mixed metal sulphur cluster to involve six copper(I) atoms bound to a tetrathiometallate anion.

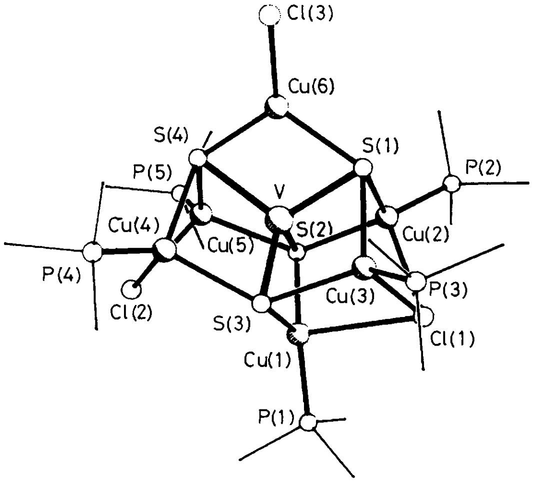

Figure 1. Structure of $[VS_4(CuPPh_3)_5(CuCl)Cl_2]$. Selected dimensions: V–S(1) 2.218(3), V–S(2) 2.208(3), V–S(3) 2.222(2), V–S(4) 2.208(3) Å; S–V–S range 108.0(1)–110.3(1)°; V–Cu range 2.596(3)–2.680(2), Cu–S range 2.238(3)—2.344(3), Cu–P range 2.212(2)—2.239(3) Å; Cu(6)–Cl(3) 2.144(5), Cu(4)–Cl(2) 2.494(3), Cu(5)–Cl(2) 2.454(3), Cu(1)–Cl(1) 2.815(3), Cu(2)–Cl(1) 2.592(3), Cu(3)–Cl(1) 2.518(3) Å. Only the α-carbon atoms of the phenyl rings are shown.

The title compound was obtained by reacting $[NH_4]_3[VS_4]$, $[NEt_4]Cl$, CuCl, and PPh_3 in CH_2Cl_2; the deep red coloured solution was filtered and evaporated to dryness, and the solid dissolved in CH_2Cl_2. Slow diffusion of hexane into this solution yielded dark red crystals, individuals of which when mounted in a Lindemann tube containing the mother liquor, permitted *X*-ray crystallographic examination.† A satisfactory elemental analysis was obtained.

The structure of $[VS_4(CuPPh_3)_5(CuCl)Cl_2]$ is shown in Figure 1. This aggregate possesses a central VS_4 moiety with a distorted tetrahedral geometry; each copper atom is bound across an edge of this tetrahedron and these six atoms form a distorted octahedron. Each copper atom is bound to a terminal ligand: five of these are PPh_3 molecules and one [for Cu(6)] a chlorine atom. There are two additional bridging

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† $C_{91}H_{77}Cl_5Cu_6P_5S_4V$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 13.901(1)$, $b = 15.105(2)$, $c = 22.949(2)$ Å, $\alpha = 92.635(7)$, $\beta = 98.889(8)$, $\gamma = 107.288(8)°$, $U = 4524.2$ Å^3, $D_c = 1.514$ g cm^{-3}, $F(000) = 2088$, Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 5.79 mm^{-1}, crystal size 0.10 × 0.20 × 0.35 mm. The structure was solved by normal heavy-atom methods [phenyl groups were treated as rigid hexagons (C–C = 1.395 Å) with no inclusion of hydrogen atoms], and refined by weighted least-squares [$w^{-1} = \sigma^2(F)$]. Anisotropic thermal parameters were used for all included atoms. The refinement converged with $R = 0.084$ and $R_w = 0.060$ for 7543 observed reflections with $F_o \geqslant 4\sigma(F_o)$; these were corrected for a steady decay and were semi-empirical absorption-corrected. Data were collected on a Siemens AED2 diffractometer with a graphite monochromator. An ω/θ scan was employed for 2θ = 3—120°. Analysis and refinement was accomplished using the SHELXTL[10] programs and complex scattering factors were taken from reference 11.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

chlorine atoms: Cl(2) is a μ_2-atom linking Cu(4) and Cu(5) to form a six-membered (CuClCuSCuS) ring with the boat conformation; Cl(1) is a μ_3-atom which leads to the formation of a distorted cubane-like (VS_3Cu_3Cl) framework.

This structure is unprecedented and extends the structural versatility of metal–sulphur cluster frameworks. The compound is the first mixed-metal–sulphur cluster based on a tetrathiometallate (MS_4) anion which has a stoicheiometry M : M′ : S of 1 : 6 : 4, and it is the first such species to involve a MS_4 moiety completely enveloped by metal atoms. Four v(V–S) stretching modes are manifest in the i.r. spectrum [at 478, 459, 443, and 437(sh) nm], indicating that the irregular atomic arrangement on the periphery of the cluster results in a significant lowering of the symmetry of the VS_4 unit. The u.v.–visible spectrum is unusual for a metal–sulphur cluster based on a tetrathiometallate anion, in that there is no apparent correlation with the bands of the parent anion; rather, a general increase in absorbance is seen with increasing energy, upon which features at 420, 332, and 258 nm are observed. ^{31}P N.m.r. spectra recorded for the title compound dissolved in CD_2Cl_2, alone, and in the presence of added PPh_3, are consistent with phosphine dissociation and exchange occurring at room temperature; at *ca.* 173 K, this exchange appears to cease and the compound exhibits two resonances at +3.4 and +6.4 p.p.m., with relative intensities of 4 : 1, as expected from retention of the solid state structure. Analogues of this compound should be possible, varying the central metal, the peripheral metal atoms, and their ligands.

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