Tetrakis(benzyldiphenylphosphine-κP)tetra-μ_2-sulfido-dicopper(I)molybdenum(VI) tetrahydrate

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Key indicators

Single-crystal X-ray study

$T = 291$ K

Mean σ(C–C) = 0.007 Å

H-atom completeness 90%

Disorder in main residue

R factor = 0.046

wR factor = 0.148

Data-to-parameter ratio = 27.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the crystal structure of the title heterothiolate cluster, [MoCu₂S₄(C₁₉H₁₇P)₄]·4H₂O, the Mo atom lies on a postion of crystallographic site symmetry $\bar{4}$, coordinated by four S atoms in a tetrahedral environment; each pair of S atoms bis-chelates two Cu atoms which are, in addition, coordinated by two phosphine ligands each. The tetrahedrally coordinated Cu atoms lie on positions of site symmetry 2.

Comment

A search of the Cambridge Structural Database (Version 5.27; Allen, 2002) revealed that the trinuclear tetrasulfido-copper(I)molybdenum(VI) cluster, [Mo^{VI}S$_4$Cu$^I_2$], which is a Lewis acidic entity, affords a number of adducts with the donor ligands binding through two Cu atoms. The structures of N-heterocyclic adducts are well known; the structure of tetrapyridyltetra-μ-sulfido-dicoppermolybdenum has been known for 15 years (Lin & Lin, 1986, 1991; Hu, 1999; Ng & Rae, 1999), but phosphine adducts are less common. In the structure of a bis(tri-4-anisylphosphine) adduct in which the Cu atoms are coordinated by only one phosphine ligand, each of the Cu atoms is in a trigonal planar coordination environment (Zheng et al., 2002). The structures of some other phosphine adducts have Cu atoms which have two Cu—P bonds, e.g. the 1,1′-bis(diphenylphosphino)ferrocene and diphenyl(2-pyridyl)phosphine adducts (Niu et al., 2002), and the bis(diphenylphosphino)methane (Lang & Tatsumi, 1998) and bis(dicyclohexylphosphino)methane (Che et al., 2001) adducts, all of which have both Mo and Cu atoms in tetrahedral coordination environments.

(I)
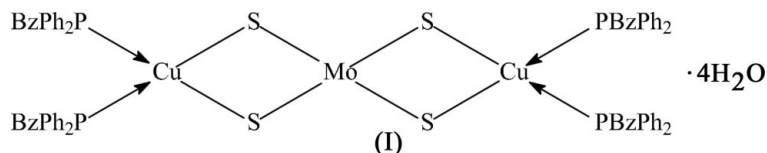
The heptanuclear cluster [Bu₄N]₄[MoS₄Cu₆Br₈] (Lang et al., 1994) has a labile Br atom that can easily be replaced by N-heterocyclic and phosphine ligands (Niu et al., 2002). The title compound, (I), was synthesized by reacting the above cluster compound with benzyldiphenylphosphine. The adduct (Fig. 1) features Mo and Cu atoms in tetrahedral geometries. The Mo atom lies on a special position of site symmetry $\bar{4}$, being tetrahedrally cordinated by four S atoms. Each pair of S atoms bis-chelates a Cu atom, which is also coordinated by two phosphine ligands. The tetrahedrally coordinated Cu atoms lie on positions of site symmetry 2. The bond lengths involving
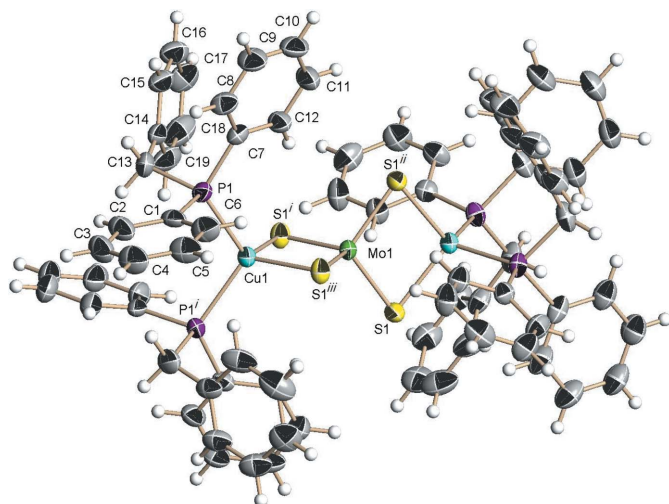
Figure 1
ORTEPII (Johnson, 1976) plot of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are drawn as spheres of arbitrary radii. The disordered uncoordinated water molecule has been omitted and only one component of the disorder is shown. [Symmetry codes: (i) $2 - x, 1 - y, z$; (ii) $\frac{1}{2} + y, \frac{3}{2} - x, \frac{1}{2} - z$; (iii) $\frac{3}{2} - y, x - \frac{1}{2}, \frac{1}{2} - z$.]

the metal atoms are similar to those found in the reported phosphine adducts listed above. As the space group is non-centrosymmetric, the compound has been investigated for non-linear optical behaviour (Niu, 2006).

Experimental

A solution of the heptanuclear cluster [Bu4N]4[MoS4Cu6Br8], which was synthesized using a literature method (Lang *et al.*, 1994) (1.107 g, 0.5 mmol), in acetonitrile (5 ml) was mixed with a dimethyl-formamide solution (15 ml) of benzyldiphenylphosphine (0.819 g, 3.0 mmol). Dark-red crystals separated from the solution after the solvent was allowed to evaporate over a few days. The crystals were washed with acetonitrile and then dried under vacuum (50% yield).

Crystal data

[MoCu₂S₄(C₁₉H₁₇P)₄]·4H₂O	Mo $K\alpha$ radiation
$M_r = 1528.51$	Cell parameters from 3407
Tetragonal, $I\bar{4}$	reflections
$a = 13.777 (1)$ Å	$\theta = 2.7–25.7°$
$c = 22.995 (2)$ Å	$\mu = 0.83$ mm⁻¹
$V = 4364.3 (4)$ Å³	$T = 291 (2)$ K
$Z = 2$	Plate, red
$D_x = 1.163$ Mg m⁻³	$0.39 \times 0.28 \times 0.06$ mm

Data collection

Bruker APEX-II area-detector diffractometer	4886 independent reflections
	3959 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.017$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 27.5°$
	$h = -17 \rightarrow 15$
$T_{min} = 0.831$, $T_{max} = 0.952$	$k = -17 \rightarrow 7$
9215 measured reflections	$l = -25 \rightarrow 29$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0923P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.148$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.11$	$\Delta\rho_{max} = 0.79$ e Å⁻³
4886 reflections	$\Delta\rho_{min} = -0.25$ e Å⁻³
180 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	2328 Friedel pairs
	Flack parameter: 0.00 (2)

Table 1
Selected geometric parameters (Å, °).

Mo1—S1	2.205 (1)	Cu1—S1	2.306 (1)
Cu1—P1	2.298 (1)		
S1—Mo1—S1ⁱ	107.62 (6)	P1—Cu1—S1ⁱ	114.77 (4)
S1—Mo1—S1ⁱⁱ	110.40 (3)	S1—Cu1—S1ⁱ	101.04 (6)
P1—Cu1—P1ⁱ	111.05 (6)	Mo1—S1—Cu1	75.67 (3)
P1—Cu1—S1	107.51 (5)		

Symmetry codes: (i) $-x + 2, -y + 1, z$; (ii) $y + \frac{1}{2}, -x + \frac{3}{2}, -z + \frac{1}{2}$.

The phenyl ring which includes atoms C1–C6 is disordered over two sites and was refined as two rigid hexagons with C—C bond lengths of 1.39Å. The P—C bond distances were restrained to be within 0.01Å of each other, and anisotropic displacement parameters of the disorder components were restrained to be equal. In addtion, the P···C_ortho distances were also restrained to within 0.01Å of each other. Owing to the large number of restraints, the occupancies of the disorder components could not be refined and they were set to be equal. The other phenyl rings, C7–C12 and C14–C19, were also refined as rigid hexagons.

The uncoordinated water molecule is disordered over two sites; these disorder components were also assumed to have equal occupancy. The H atoms of the water molecule were not located nor included in the refinement. The C-bound H atoms were positioned geometrically (C—H = 0.93 and 0.97Å), and were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$. Fairly large voids in the structure are suspected to have initially contained acetonitrile solvent molecules. Athough these were not visible in difference Fourier maps, this solvent may have evaporated from the crystal structure during the course of the experiment.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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