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A novel tetranuclear copper(I) sulfanide complex with bis(diphenylphosphino)amine

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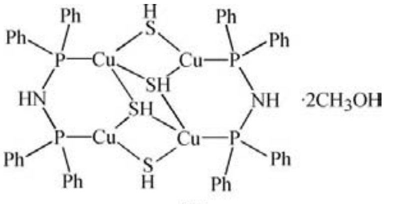
The title novel mixed μ_2-SH- and μ_3-SH-bridged tetranuclear copper(I) complex, *cyclo*-bis[μ_2-bis(diphenylphosphino)amine]di-μ_3-sulfanido-di-μ_2-sulfanido-tetracopper(I) methanol disolvate, $[Cu_4(SH)_4(C_{24}H_{21}NP_2)_2]\cdot 2CH_3OH$, has crystallographically imposed centrosymmetry and affords a neutral Cu_4S_4 core with a distorted step-like structure. The distances of 2.8458 (16) and 2.8179 (16) Å between copper(I) centres indicate the presence of ligand-supported Cu$\cdots$Cu interactions. Strong N—H$\cdots$O and O—H$\cdots$S hydrogen bonds between the tetranuclear cluster and methanol solvent molecules result in a two-dimensional hydrogen-bonded supramolecular network. This complex is the first example of a coinage tetranuclear metal complex with mixed μ_2-SH- and μ_3-SH-bridged chromophores.

Comment

The design of luminescent polynuclear d^{10} metal complexes with various molecular motifs has attracted increasing attention in recent years due to their potential applications in materials science, such as photoactive reagents, optical sensors, light-emitting devices and photovoltaic fabrication (Yam *et al.*, 2003; Chen *et al.*, 2008; Henkel & Krebs, 2004). This stems from the tendency of these metal ions to form clusters and aggregates as a result of weak metal–metal interactions. In this area, polynuclear copper(I)–chalcogenide species are attracting considerable interest because of their rich photophysical properties and structural diversity (Henkel & Krebs, 2004; Brown *et al.*, 2005; Lee *et al.*, 2006). Many novel structures have been discovered in the synthesis of Cu^I aggregates of high nuclearity based on metal diphosphine building blocks and using the S^{2-} ion, monothiolates, 1,1-dithiolates or 1,2-dithiolates as the bridging ligands (Yam *et al.*, 2003). However, in only a few cases were they derived from self-assembly with a capped sulfanide (SH^-) ion (Han *et al.*, 2003; Chen *et al.*, 2004).

To investigate new structural and functional motifs, we are currently interested in developing luminescent molecular materials formed by self-assembly occurring between metal diphosphine and chalcogenide components, where the former possesses labile solvate sites while the latter show versatile bridging characteristics. Recently, the first example of a copper(I) sulfanide complex with a diphosphine as co-ligand, namely $[Cu_3(\mu_2\text{-}Ph_2PNHPPh_2)_3(\mu_3\text{-}SH)_2]^+$, which displays an unprecedented trigonal bipyramid geometry comprising a triangular Cu^I_3 core dicapped with μ_3-SH, has been isolated *via* the disruption of a C—S bond from the reaction between $[Cu_2(Ph_2PNHPPh_2)_2(MeCN)_2](BF_4)_2$ and the sodium salt of mercaptoacetic acid ($HSCH_2COONa$) (Han *et al.*, 2003). We report here the synthesis and crystal structure of the title novel neutral tetranuclear copper(I) sulfanide complex, $[Cu_4(\mu_2\text{-}SH)_2(\mu_3\text{-}SH)_2(\mu_2\text{-}Ph_2PNHPPh_2)_2]\cdot 2CH_3OH$, (I), which is considerably different from the complex mentioned above in terms of structural and functional motifs. To our knowledge, (I) is the first example of a coinage tetranuclear metal complex with mixed μ_2-SH- and μ_3-SH-bridged chromophores.



(I)

Complex (I) is composed of two $[Cu_2(Ph_2PNHPPh_2)]$ units linked together by two μ_2-SH and two μ_3-SH chromophores. The complex is located on a crystallographic centre of inversion (Fig. 1; selected bond angles in Table 1). In (I), the Cu and S atoms are alternately bonded to form an eight-membered ring in which two S atoms further bridge two Cu atoms to form a distorted stepladder arrangement or a distorted chair-like conformation. Each Cu atom is bonded to one P atom of a

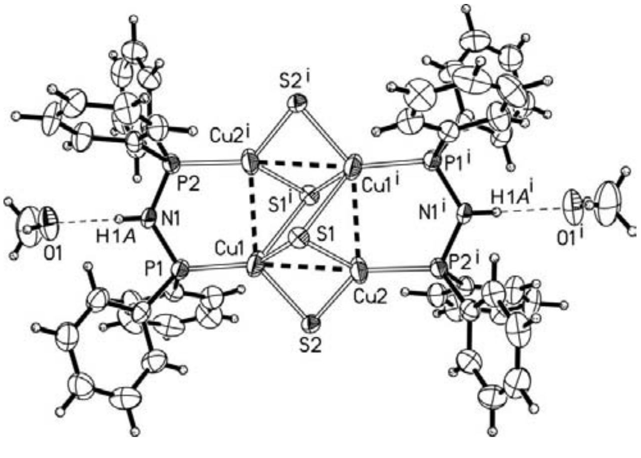


Figure 1
A perspective view of complex (I), showing selected atom labels. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown as thin dashed lines and Cu$\cdots$Cu interactions as thick dashed lines. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

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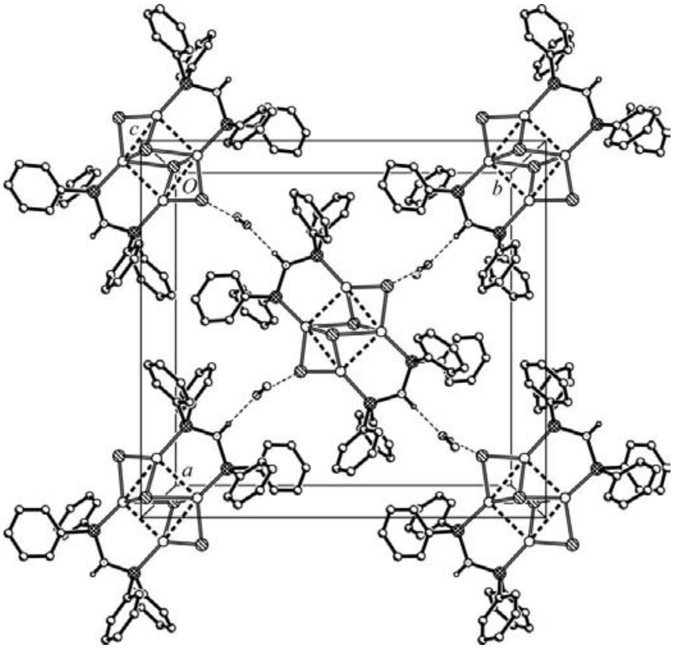

Figure 2
A packing diagram for (I), showing the two-dimensional hydrogen-bonded network. Hydrogen bonds are shown as thin dashed lines and Cu$\cdots$Cu interactions as thick dashed lines.

bis(phosphine) ligand in such a way that two Cu atoms have approximate $CuPS_2$ trigonal planar geometry and the other two have $CuPS_3$ tetrahedral coordination geometry. There are two types of bridging SH groups present, namely μ_2-SH and μ_3-SH. This structural feature is similar to the tetramer $[(\mu_2\text{-}X)_2(\mu_3\text{-}X)_2(CuPPh_3)_4]$ (X is Cl, Br, I or SPh) reported in the literature (Camus *et al.*, 1975; Fu *et al.*, 2004; Ganesamoorthy *et al.*, 2007; Dance *et al.*, 1985). The Cu—S bond distances at the trigonal Cu1 centre [2.298 (2) and 2.366 (2) Å)] are slightly shorter than the corresponding distances at the tetrahedral Cu2 centre [2.351 (2), 2.370 (2) and 2.805 (2) Å]. The Cu—S bond distances observed here are comparable with the corresponding distances observed in the copper thiolate tetramer (Dance *et al.*, 1985). The Cu—P bond distances are normal. The distances between the two Cu centres are Cu1$\cdots$Cu2 = 2.8456 (16) Å and Cu1$\cdots$Cu2^{i} = 2.8179 (16) Å [symmetry code: (i) $1 - x$, $1 - y$, $1 - z$], which indicates the presence of weak ligand-supported Cu$\cdots$Cu interactions in complex (I). Such metallophilic interactions between formally closed-shell metal centres are well documented and are due to the combination of correlation and relativistic effects with added ionic contributions (Pyykko, 1997).

There are two unique hydrogen-bond interactions between the neutral tetranuclear cluster and the methanol solvent molecules. As shown in Fig. 2, each tetranuclear cluster molecule links to four methanol molecules through two N—H$\cdots$O and two O—H$\cdots$S hydrogen bonds. Each of these four methanol molecules further links to another tetranuclear cluster unit through N—H$\cdots$O or O—H$\cdots$S hydrogen bonds. Details of the hydrogen-bond geometry are listed in Table 2. Consequently, a two-dimensional hydrogen-bonded supramolecular network of (I) is formed in the *ab* plane.

Table 1
Selected bond angles (°).

P1—Cu1—S1	133.94 (10)	P2^{i}—Cu2—S2	127.12 (9)
P1—Cu1—S2	119.99 (9)	P2^{i}—Cu2—S1	130.38 (9)
S1—Cu1—S2	97.92 (8)	S2—Cu2—S1	99.54 (8)
P1—Cu1—S1^{i}	116.40 (9)	Cu1—S1—Cu2	74.20 (7)
S1—Cu1—S1^{i}	86.14 (8)	Cu1—S1—Cu1^{i}	93.86 (8)
S2—Cu1—S1^{i}	90.32 (8)	Cu2—S1—Cu1^{i}	65.40 (6)
Cu2^{i}—Cu1—Cu2	96.28 (5)	Cu2—S2—Cu1	75.11 (7)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$O1	0.86	2.04	2.895 (9)	177
O1—H1$\cdots$S2^{ii}	0.82	2.35	3.152 (7)	166

Symmetry code: (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

In conclusion, a novel tetranuclear copper(I) sulfanide complex supported by $Ph_2PNHPPh_2$ ligands has been successfully prepared. The molecular structure has an interesting $Cu_4(\mu_2\text{-SH})_2(\mu_3\text{-SH})_2$ core with a distorted stepladder motif and exhibits ligand-supported Cu$\cdots$Cu interactions.

Experimental

The synthesis of (I) was carried out under a dry nitrogen atmosphere using standard Schlenk and vacuum-line techniques. A methanol solution (5 ml) of Li_2S (23 mg, 0.50 mmol) was added to a dichloromethane solution (10 ml) of $[Cu_2(Ph_2PNHPPh_2)_2(MeCN)_2](BF_4)_2$ (148 mg, 0.13 mmol). After stirring for 8 h at room temperature, the solvents were removed and the residue dissolved in dichloromethane (5 ml). Diethyl ether was layered on to this solution and the product, (I), was obtained after a few days as well-shaped yellow crystals in a yield of about 48%.

Crystal data

$[Cu_4(SH)_4(C_{24}H_{21}NP_2)_2]\cdot 2CH_4O$
$M_r = 1221.23$
Orthorhombic, *Pbca*
$a = 17.0144$ (8) Å
$b = 18.2738$ (9) Å
$c = 17.1713$ (9) Å
$V = 5338.9$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.89$ mm^{-1}
$T = 298$ (2) K
$0.30 \times 0.24 \times 0.24$ mm

Data collection

Siemens SMART CCD diffractometer
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 2001)
$T_{\min} = 0.586$, $T_{\max} = 0.636$
15623 measured reflections
4726 independent reflections
2983 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.071$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.086$
$wR(F^2) = 0.174$
$S = 1.21$
4726 reflections
300 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.76$ e Å^{-3}
$\Delta\rho_{\min} = -0.99$ e Å^{-3}

All H atoms on C and N atoms were positioned geometrically and allowed to ride on their respective parent atoms, with C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for phenyl, C—H = 0.96 Å and $U_{\rm iso}$(H) =

$1.5U_{eq}$(C) for methyl, and N—H = 0.86 Å and U_{iso}(H) = $1.2U_{eq}$(N) for amine H atoms. Atom H1 on the methanol O1 atom was located and then allowed for with calculated geometry but allowed rotational freedom. Not all H atoms on S atoms were included because of the poor diffraction of compound (I).

Data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM3015). Services for accessing these data are described at the back of the journal.

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