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Tetrakis(3-methylpyridine)-1κN,2κN,3κN,4κN-bis(μ_4-pentathio)-1:2$\kappa^2 S^1$,2κS^4,3κS^2,3:4$\kappa^2 S^5$;1$\kappa S^{4'}$,1:3$\kappa^2 S^{1'}$,2:4$\kappa^2 S^{5'}$,4$\kappa S^{2'}$-tetracopper(I) Bis(3-methylpyridine) Solvate

Hongjun Li,[a] Tianlu Sheng,[b] Qun Huang[b] and Xintao Wu[b]

[a]*Department of Chemisty, Fuzhou University, Fuzhou, Fujian 350002, People's Republic of China, and* [b]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China*

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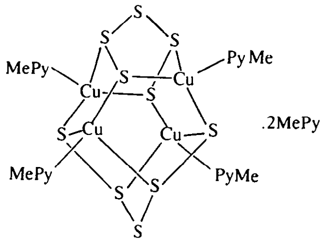
Abstract

The structure of the title compound, $[Cu_4(S_5)_2(C_6H_7N)_4].2C_6H_7N$, consists of a neutral complex molecule $[Cu_4(S_5)_2(CH_3C_5H_4N)_4]$ and two 3-methylpyridine solvent molecules. In the neutral complex molecule, the four Cu atoms are in a distorted tetrahedral arrangement. The non-bonding Cu···Cu distances in the copper tetrahedron range from 3.281 (1) to 3.948 (1) Å and the Cu—S bond lengths vary from 2.255 (2) to 2.397 (3) Å.

Comment

In recent years, since remarkably rich photoluminescence has been found in tetranuclear complexes (Kevin, Chong, John & Peter, 1991) and the cage-type structure with μ_3-S may be potentially used in optical-limiting material (Shi, Ji, Tang, Lang & Xin, 1994), the synthesis of tetranuclear copper(I)–sulfur clusters has attracted attention. To date, a series of tetranuclear copper(I) clusters have been studied (Hathaway, 1987). Herein, a new tetranuclear copper(I) compound, namely, $[Cu_4(S_5)_2(CH_3C_5H_4N)_4].2CH_3C_5H_4N$, (I), is reported.



(I) (MePy = 2-methylpyridine)

The structure of the neutral complex molecule of the title compound is shown in Fig. 1. The neutral molecule is located on a twofold axis which passes through atoms S(3) and S(6). Each Cu atom has distorted tetrahedral geometry and is coordinated by three μ_3-S atoms and an N atom from the pyridine ligand. The four Cu atoms are held together by two pentasulfido S_5^{2-} groups acting as bridging and chelating ligands.

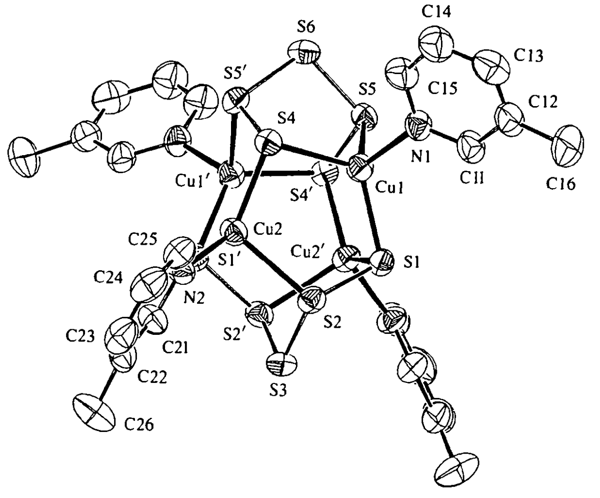


Fig. 1. *ORTEP*II view (Johnson, 1976) of the title compound. Displacement ellipsoids are shown at the 50% probability level.

In the title compound, the four non-bonding Cu···Cu distances are 3.948 (1) [Cu(1)···Cu(1')], 3.312 (2) [Cu(1)···Cu(2)], 3.281 (1) [Cu(2)···Cu(1')] and 3.945 (1) Å [Cu(2)···Cu(2')]. The Cu—S bond lengths vary from 2.255 (2) to 2.397 (3) Å. The S—S bond lengths in the two S_5^{2-} ions vary from 2.062 (3) to 2.076 (5) Å. These distances are close to those found

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in $[Cu_4(S_5)_2(C_5H_5N)_4].1.5C_5H_5N$, where the Cu···Cu distances range from 3.206 (1) to 3.907 (1) Å and the S—S bond lengths from 2.055 (3) to 2.081 (3) Å (Rami, Rauchfuss & Stern, 1990).

Experimental

The title compound was obtained from K_2S, S, Cu and 3-methylpyridine and was crystallized from 3-methylpyridine.

Crystal data

$[Cu_4(S_5)_2(C_6H_7N)_4].2C_6H_7N$
$M_r = 1133.58$
Monoclinic
$C2/c$
$a = 27.395 (8)$ Å
$b = 10.804 (3)$ Å
$c = 19.201 (3)$ Å
$\beta = 126.54 (2)°$
$V = 4565.8$ Å^3
$Z = 4$
$D_x = 1.65$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9–14°$
$\mu = 2.32$ mm^{-1}
$T = 296$ K
Prism
0.55 × 0.35 × 0.25 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
5944 measured reflections
5756 independent reflections
3030 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.026$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 32$
$k = -12 \rightarrow 0$
$l = -22 \rightarrow 22$
3 standard reflections monitored every 300 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.049$
$wR = 0.068$
$S = 0.97$
3030 reflections
254 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.020F_o)^2 + 1]$
$(\Delta/\sigma)_{\rm max} = 0.01$
$\Delta\rho_{\rm max} = 0.55$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu(1)	−0.08583 (4)	0.0059 (1)	0.14738 (6)	0.042 (1)
Cu(2)	0.02703 (4)	0.1683 (1)	0.17501 (6)	0.042 (2)
S(1)	−0.10128 (8)	0.1996 (2)	0.1782 (1)	0.039 (2)
S(2)	−0.05235 (9)	0.3019 (2)	0.1482 (1)	0.042 (5)
S(3)	0	0.4230 (3)	1/4	0.049 (1)
S(4)	−0.01191 (8)	−0.0226 (2)	0.1258 (1)	0.037 (9)
S(5)	−0.05119 (8)	−0.1269 (2)	0.2657 (1)	0.040 (7)
S(6)	0	−0.2476 (3)	1/4	0.046 (9)
N(1)	−0.1646 (3)	−0.0749 (7)	0.0427 (4)	0.044 (6)
N(2)	0.0500 (3)	0.2755 (7)	0.1084 (4)	0.045 (8)
N(3)	−0.3693 (5)	0.467 (1)	0.1244 (6)	0.103 (1)
C(11)	−0.2199 (4)	−0.0345 (9)	0.0137 (5)	0.052 (2)
C(12)	−0.2735 (4)	−0.086 (1)	−0.0599 (6)	0.063 (7)
C(13)	−0.2666 (5)	−0.183 (1)	−0.1017 (6)	0.068 (8)
C(14)	−0.2078 (4)	−0.226 (1)	−0.0683 (6)	0.071 (3)
C(15)	−0.1593 (4)	−0.171 (1)	0.0019 (5)	0.058 (6)
C(16)	−0.3347 (5)	−0.035 (1)	−0.0928 (9)	0.098 (1)
C(21)	0.0824 (4)	0.3793 (9)	0.1477 (5)	0.049 (6)
C(22)	0.0937 (4)	0.469 (1)	0.1069 (6)	0.061 (1)
C(23)	0.0703 (4)	0.447 (1)	0.0202 (5)	0.065 (1)
C(24)	0.0386 (4)	0.341 (1)	−0.0181 (5)	0.067 (5)
C(25)	0.0278 (4)	0.2564 (9)	0.0263 (5)	0.050 (9)
C(26)	0.1288 (5)	0.585 (1)	0.1539 (8)	0.095 (5)
C(31)	−0.3505 (5)	0.388 (1)	0.0859 (6)	0.067 (5)
C(32)	−0.2948 (4)	0.335 (1)	0.1317 (5)	0.061 (2)
C(33)	−0.2562 (5)	0.363 (1)	0.2216 (8)	0.096 (8)
C(34)	−0.2718 (5)	0.434 (1)	0.2613 (6)	0.086 (6)
C(35)	−0.3260 (5)	0.490 (1)	0.2149 (7)	0.095 (5)
C(36)	−0.2743 (5)	0.249 (1)	0.0939 (6)	0.082 (7)

Table 2. *Selected geometric parameters (Å, °)*

Cu(1)—S(1)	2.282 (3)	S(2)—S(3)	2.062 (3)
Cu(1)—S(4)	2.317 (3)	S(4)—S(5$^{\rm i}$)	2.076 (5)
Cu(1)—S(5)	2.356 (2)	S(5)—S(6)	2.064 (3)
Cu(1)—N(1)	2.073 (6)	Cu(1)···Cu(1$^{\rm i}$)	3.948 (1)
Cu(2)—S(2)	2.397 (3)	Cu(1)···Cu(2)	3.312 (2)
Cu(2)—S(4)	2.255 (2)	Cu(2)···Cu(1$^{\rm i}$)	3.281 (1)
Cu(2)—N(2)	2.082 (9)	Cu(2)···Cu(2$^{\rm i}$)	3.945 (1)
S(1)—S(2)	2.067 (4)		
S(1)—Cu(1)—S(4)	119.0 (1)	S(4)—Cu(2)—N(2)	119.5 (2)
S(1)—Cu(1)—S(5)	109.8 (1)	Cu(1)—S(1)—S(2)	99.6 (1)
S(1)—Cu(1)—N(1)	113.0 (2)	Cu(2)—S(2)—S(1)	105.9 (1)
S(4)—Cu(1)—S(5)	101.45 (9)	Cu(2)—S(2)—S(3)	98.53 (8)
S(4)—Cu(1)—N(1)	106.7 (3)	S(1)—S(2)—S(3)	106.0 (1)
S(5)—Cu(1)—N(1)	105.5 (2)	Cu(1)—S(4)—Cu(2)	92.8 (1)
S(2)—Cu(2)—S(4)	108.55 (9)	Cu(1)—S(5)—S(6)	99.4 (1)
S(2)—Cu(2)—N(2)	95.8 (2)		

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

The structure was solved by direct methods, the four heavy Cu atoms being located in the E map and the remaining non-H atoms being located in the succeeding Fourier syntheses. H atoms were placed in geometrically calculated positions (C—H 0.95 Å), and not subsequently refined. The structure was refined by a full-matrix least-squares technique, with anisotropic displacement parameters for all non-H atoms.

Data collection and cell refinement were performed using *CAD-4 Software* (Enraf–Nonius, 1989). Molecular graphics were produced using *ORTEP*II (Johnson, 1976). All calculations were performed on a COMPAQ PL4/50 computer using the *MolEN* program package (Fair, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1046). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Triphenylstibine Dihydroxide

Sharma Pankaj, Noe Rosas, Georgina Espinosa-Pérez and Armando Cabrera

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México DF 04510, Mexico. E-mail: georgina@servidor.unam.mx

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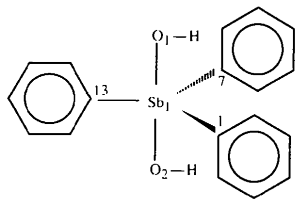
Abstract

Triphenylstibine dihydroxide [alternative name: dihydroxytriphenylantimony(V)], $[Sb(OH)_2(C_6H_5)_3]$, was synthesized by the oxidative hydrolysis of Et_4N^+.-$[PhSbCl_2Br]^-$ in methanol. The dihydroxide was characterized by IR spectroscopy, mass spectrometry and X-ray diffraction. The molecule is monomeric with very slightly distorted trigonal bipyramidal geometry around Sb with two OH groups in axial positions [Sb—O 1.963 (6) and 2.079 (7), Sb—C 2.090 (13)–2.109 (19) Å, O—Sb—O 178.5 (5)°].

Comment

Very few trialkylantimony(V) dihydroxides have been reported in the literature (Long, Doak & Freedman, 1964; Huang, Chen & Shen, 1989), and there had been no report of a triarylantimony(V) dihydroxide until recently; the first triarylantimony(V) dihydroxide, $Mes_3Sb(OH)_2$ (mes = mesityl), was reported by Huber, Westhoff & Preut (1987) and characterized by X-ray crystallography (Huber *et al.*, 1987; Westhoff, Huber, Ruther & Preut, 1988). The title compound, (I), was prepared and characterized by IR, mass spectrometry and X-ray diffraction methods in order to compare its structure with that of $Mes_3Sb(OH)_2$.



(I)

Elemental analysis was in agreement with the formula $Ph_3Sb(OH)_2$. An IR absorption at 507 cm^{-1} indicated the presence of an Sb—O (not an Sb═O) bond, and absorption at 3546 and 3432 cm^{-1} was assigned to ν_{OH}. Since no band that could be attributed to an Sb—O—Sb group was observed, the formation of a dihydroxide during the reaction was inferred. Considering the position and sharpness of the ν_{OH} band, the dihydroxide was inferred to be monomeric in the solid state. The mass spectrum showed a molecular ion peak which confirmed the molecular weight of the compound as 387. The final proof of this composition came from a single-crystal structure determination. $Ph_3Sb(OH)_2$ proved to be monomeric in the solid state and in the molecule Sb is pentacoordinate, two OH groups being in the apical positions and three C(Ph) atoms in the equatorial plane of a trigonal bipyramid.

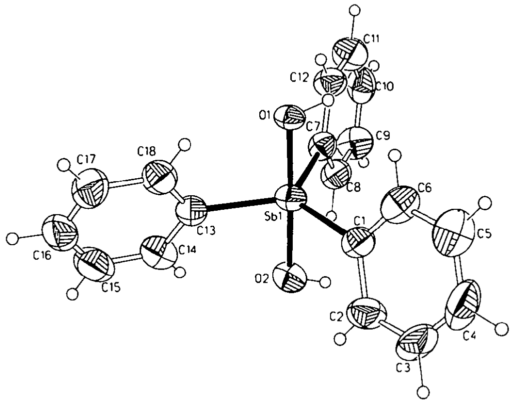


Fig. 1. Molecular structure showing 30% probability displacement ellipsoids.

The two Sb—O distances [1.963 (6) and 2.079 (7) Å] are different from the one type of bond distance found in $Mes_3Sb(OH)_2$ [2.027 (3) Å; Westhoff *et al.*, 1988]. The mean Sb—O bond distance [2.02 (6) Å] corresponds with distances in analogous compounds containing this bond, *e.g.* 2.048 (5) Å in Ph_4SbOH (Beauchamp, Bennett & Cotton, 1969) and 2.033 (8) Å in $Ph_3Sb(OMe)_2$ (Keiweishen, McEwen, La Placa, Hamilton & Wolf, 1968). There is no O—H···O hydrogen bonding; the shortest O···O intermolecular contact is O1···O1($\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$) 4.632 (2) Å. The absence of hydrogen bonding was also inferred from the fact that there is