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$\{Cu_4W_2S_6\}(PPh_3)_4O_2$, a Compound with a Metal Sulfur Cage generated by the WOS_3^{2-} Ligand. Preparation, Crystal and Molecular Structure

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$\{Cu_4W_2S_6\}(PPh_3)_4O_2$ has been prepared by the reaction of an aqueous solution of Cs_2WOS_3 with a mixture of $CuCl_2 \cdot 2H_2O$ in H_2O and $P(C_6H_5)_3$ in CH_2Cl_2. The structure was determined from single crystal X-ray diffractometer data and was refined by least-squares methods to R = 0.071 for 5869 independent data. The compound crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the unit cell (a = 12.432(4), b = 12.567(2), c = 13.123(4) Å, α = 93.02(2), β = 117.43(2), γ = 95.05(2)°, V = 1803.4 Å^3, d_{calcd} = 1.75 g/cm^3). The structure can be described as a cage (with a centre of inversion), fused by two six-membered SCu_2S_2W rings. W(107.53(33)–113.52(12)°) and Cu (distorted, angles varying between 102.16(13) and 121.08(13)°) are tetrahedrally coordinated.

Introduction

In recent years considerable interest has been shown in finding synthetic routes for compounds containing different transition metal atoms linked by sulfur because of the bioinorganic relevance of this problem [1]. Using tetrathiometalate ligands like MoS_4^{2-} or WS_4^{2-}, interesting ring and cage compounds such as $[Au_2(WS_4)_2]^{2-}$ [2], $\{Ag_4Mo_2S_6\}(PPh_3)_4S_2$ [3]* and $(PPh_3)_3Ag_2WS_4$ [4] could be obtained. In such compounds the thiometalate ligands act as bi-, ter- or tetradentate ligands [3]. Whereas tetrathioanions can act as tetradentate ligands, trithioanions like $MoOS_3^{2-}$ or WOS_3^{2-} should preferably act as terdentate ligands towards soft acids such as Ag^I and Cu^I. Following this idea, a compound with a cubane type structure $\{Cu_3WS_3Cl\}(PPh_3)_3O$ could intentionally be obtained [5]. Now we report $\{Cu_4W_2S_6\}(PPh_3)_4O_2$, a cage compound fused by two six-membered metal–sulfur rings, which is formed as a by-product of $\{Cu_3WS_3Cl\}(PPh_3)_3O$.

*The atoms in the cage are listed in the first bracket.

Experimental

Synthesis

A solution of 0.5 g Cs_2WOS_3 in 80 ml H_2O was extracted with a thoroughly shaken mixture of 0.17 g $CuCl_2 \cdot 2H_2O$ in 5 ml H_2O and 0.4 g $P(C_6H_5)_3$ in 25 ml CH_2Cl_2. Topping the organic phase with a mixture of acetone (10 ml) and n-pentane (50 ml) and keeping the two-phase system for 5–6 days yields red crystals (~0.04 g) of the title compound and yellow-orange crystals of $\{Cu_3WS_3Cl\}(PPh_3)_3O$ in a ratio of 4:6, which have to be separated mechanically. $\{Cu_3WS_3Cl\}(PPh_3)_3O$ can be obtained without by-product by another method [5]. The compound, which is sparingly soluble in organic solvents such as dichloromethane, acetone and nitromethane, shows characteristic ir bands at 937 [$\nu(W{-}O)_t$] and 438 cm^{-1} [$\nu(W{-}S)_{br}$]. The infrared spectra (KBr, solid) were measured with a Perkin-Elmer Model 180 spectrophotometer.

X-Ray Structure Determination [6]

The molecular structure of $\{Cu_4W_2S_6\}(PPh_3)_4O_2$ was determined from a single crystal X-ray structure analysis. A summary of the crystal data and details concerning the intensity data collection are given in Table I. The unit cell parameters were obtained at 22 °C by a least squares refinement of the angular settings of 9 high-angle reflections. Intensity data were collected on a Syntex $P2_1$ four-circle diffractometer. An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. The W and Cu atoms were located from a three-dimensional Patterson synthesis. The positional parameters of the remaining non-hydrogen atoms were deduced from successive difference-Fourier syntheses. Several cycles (with the carbon atoms being refined independently) converged at $R = \Sigma\|F_o|-|F_c\|/\Sigma|F_o| = 0.071$ and $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.076$ ($1/w = \sigma^2(F_o)^2$). The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$.

TABLE I. Summary of Crystal Data and Intensity Collection for $\{Cu_4W_2S_6\}(PPh_3)_4O_2$.

a, A 12.432(4)	Crystal-system triclinic
b, A 12.567(2)	Space group $P\bar{1}$
c, A 13.123(4)	Crystal dimensions, mm 0.3 x 0.35 x 0.5
α, deg 93.02(2)	Absorption coefficient 48.6
β, deg 117.43(2)	μ(Mo-Kα), cm^{-1}
γ, deg 95.05(2)	F_w 1895.4
V, A^3 1803.4	Empirical formula $C_{72}H_{60}Cu_4O_2P_4S_6W_2$
d_{calc}, g/cm^3 1.75	
Z 1	
F(000), electrons 928	
Radiation	Graphite monochromated Mo-Kα (λ = 0.71069 A)
Data collection	2θ: θ mode, 2θ range 4–50°, scan from 1° below $K\alpha_1$ to 1° above $K\alpha_2$ in 2θ, scan speed 3.45–29.3°/min, background scantime ratio 0.75, reference reflection every 50 reflections
Number of measured reflections ($(\sin\theta)/\lambda < 0.60$ A^{-1})	6349
Number of observed reflections ($I \geq 1.96\sigma(I)$)	5869
Number of variables	226

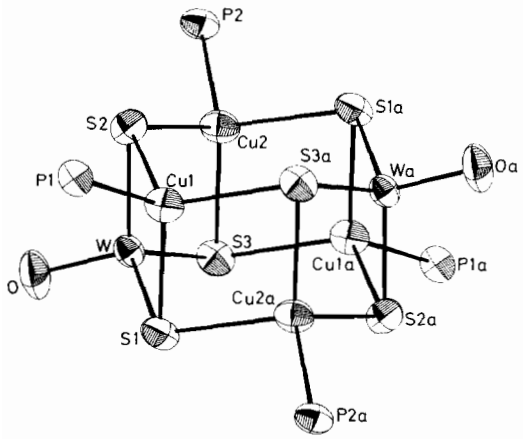

Fig. 1.The heavy atom skeleton of $\{Cu_4W_2S_6\}(PPh_3)_4O_2$ (ORTEP plot, 50% atomic vibration ellipsoids). The index a refers to the transformation $\bar{x}, \bar{y}, \bar{z}$.

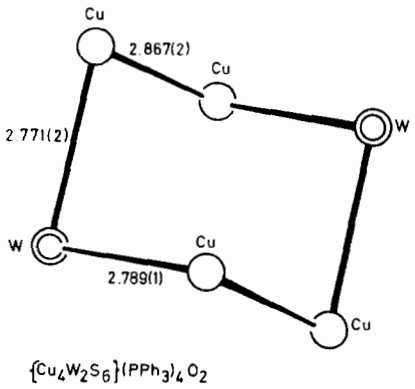

Fig. 2. The array of the metal atoms in $\{Cu_4W_2S_6\}(PPh_3)_4O_2$.

During the last cycles of refinement the temperature factors of all atoms (except for the carbon atoms) were treated in the anisotropic form. In the final stage of refinement, no parameter shifted more than 0.06σ, where σ is the standard deviation of the parameter. The atomic scattering factors for W, Cu, S, P, O and C were taken from ref. 7. Anomalous dispersion corrections were applied to the W, Cu and S atoms. The final ΔF map contained no significant peaks.

The final positional and thermal parameters are given in Table II. A list of observed and calculated structure factors has been deposited with the Editor.

Results and Discussion

The crystal structure consists of one molecule $\{Cu_4W_2S_6\}(PPh_3)_4O_2$ per unit cell having the site-symmetry 1. The interatomic distances are given in Table III. Bond angles are collected in Table IV. Figure 1 shows the heavy atom skeleton of the molecular structure, consisting of a cage fused by two six-

TABLE II. Positional and Thermal (A^2)[a] Parameters for $\{Cu_4W_2S_6\}(PPh_3)_4O_2$ with Standard Deviations.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	0.1062(0)	0.3943(0)	0.1485(0)	2.09(2)	1.86(2)	2.37(2)	0.28(1)	0.67(1)	0.38(1)
Cu1	0.0762(1)	0.6090(1)	0.1785(1)	2.83(6)	2.31(6)	3.23(6)	−0.03(5)	1.30(5)	−0.43(5)
Cu2	−0.1418(1)	0.3484(1)	−0.0006(1)	2.34(6)	2.71(6)	3.38(6)	−0.24(5)	1.21(5)	−0.28(5)
S1	0.2332(3)	0.5364(2)	0.1554(3)	2.15(12)	2.72(12)	3.66(13)	0.32(10)	1.06(11)	0.63(10)
S2	−0.0457(3)	0.4553(2)	0.1738(2)	2.99(13)	2.89(12)	2.79(12)	−0.33(10)	1.50(11)	−0.26(10)
S3	0.0231(3)	0.2873(2)	−0.0196(3)	3.01(13)	2.44(11)	3.24(13)	0.64(10)	1.24(11)	−0.09(10)
O	0.1870(8)	0.3230(7)	0.2593(7)	4.25(47)	4.20(42)	3.04(37)	0.48(37)	0.62(36)	1.74(32)
P1	0.1323(3)	0.7098(2)	0.3481(3)	2.70(13)	2.03(11)	2.72(12)	0.15(10)	0.90(11)	−0.11(9)
P2	−0.2982(3)	0.2312(2)	−0.0137(3)	2.11(12)	2.78(13)	3.53(14)	−0.00(10)	1.23(11)	0.18(11)

	x	y	z	B		x	y	z	B
C1	0.1543(11)	0.8575(9)	0.3545(10)	2.9(2)	C19	−0.4054(13)	0.2858(11)	0.0239(12)	4.3(3)
C2	0.1276(13)	0.9236(11)	0.4289(11)	4.1(3)	C20	−0.5243(16)	0.2323(13)	−0.0181(14)	5.8(4)
C3	0.1407(14)	1.0361(12)	0.4226(12)	4.7(3)	C21	−0.6055(21)	0.2727(17)	0.0131(18)	8.7(6)
C4	0.1773(14)	1.0799(11)	0.3468(12)	4.5(3)	C22	−0.5784(29)	0.3917(24)	0.0659(24)	13.2(9)
C5	0.2036(14)	1.0132(12)	0.2747(12)	4.8(3)	C23	−0.4549(37)	0.3918(30)	0.1548(31)	18.8(14)
C6	0.1903(12)	0.9005(10)	0.2775(11)	3.8(3)	C24	−0.3695(27)	0.3856(23)	0.0868(23)	12.4(8)
C7	0.0241(11)	0.6886(9)	0.4028(10)	3.0(2)	C25	−0.3971(12)	0.1568(10)	−0.1549(10)	3.6(2)
C8	−0.1006(14)	0.6790(11)	0.3223(12)	4.6(3)	C26	−0.4207(15)	0.0446(13)	−0.1695(13)	5.5(4)
C9	−0.1893(18)	0.6744(15)	0.3680(16)	7.0(4)	C27	−0.4981(18)	−0.0094(15)	−0.2815(16)	7.0(4)
C10	−0.1551(17)	0.6794(14)	0.4813(15)	6.5(4)	C28	−0.5456(18)	0.0492(15)	−0.3702(16)	7.2(5)
C11	−0.0336(17)	0.6858(14)	0.5565(15)	6.5(4)	C29	−0.5321(16)	0.1642(13)	−0.3633(14)	6.0(4)
C12	0.0568(14)	0.6887(12)	0.5220(13)	4.9(3)	C30	−0.4519(15)	0.2167(12)	−0.2480(13)	5.2(3)
C13	0.2767(12)	0.6758(10)	0.4605(10)	3.4(2)	C31	−0.2432(13)	0.1257(11)	0.0811(11)	4.1(3)
C14	0.3808(15)	0.7502(12)	0.5121(13)	5.3(3)	C32	−0.1575(17)	0.0705(14)	0.0643(14)	6.3(4)
C15	0.4952(17)	0.7165(14)	0.5905(15)	6.5(4)	C33	−0.1202(19)	−0.0261(16)	0.1323(16)	7.7(5)
C16	0.5024(19)	0.6070(16)	0.6201(17)	7.8(5)	C34	−0.1675(20)	−0.0430(16)	0.2060(17)	8.0(5)
C17	0.3992(19)	0.5334(15)	0.5564(16)	7.3(5)	C35	−0.2432(22)	0.0138(18)	0.2295(19)	9.5(6)
C18	0.2822(15)	0.5651(12)	0.4765(13)	5.4(3)	C36	−0.2900(17)	0.1011(14)	0.1573(15)	6.5(4)

[a]The anisotropic temperature factor used is defined as $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

TABLE III. Interatomic Distances (Å) in $\{Cu_4W_2S_6\}(PPh_3)_4O_2$, with Standard Deviations.[a]

A. W–S, W–O, Cu–S and Cu–P Distances			
W–S1	2.246(3)	Cu1–S3a	2.403(3)
W–S2	2.252(4)	Cu1–P1	2.273(3)
W–S3	2.256(3)		
W–O	1.696(8)	Cu2–S1a	2.448(3)
		Cu2–S2	2.312(3)
Cu1–S1	2.358(4)	Cu2–S3	2.363(4)
Cu1–S2	2.328(4)	Cu2–P2	2.266(4)
B. W···Cu Distances			
W···Cu1	2.789(1)	W···Cu2	2.771(2)
C. S···S and S···O Distances			
S1···S2	3.646(5)	S1···O	3.196(9)
S1···S3	3.765(4)	S2···O	3.232(11)
S2···S3	3.660(5)	S3···O	3.249(8)
D. P–C and C–C Mean Values			
P–C	1.820	C–C	1.421

[a]The index a refers to the transformation $\bar{x}, \bar{y}, \bar{z}$.

membered SCu_2S_2W rings, which are connected by nearly parallel Cu–S and W–S bonds, respectively. In the compound the metal atoms form a six-membered ring having W–Cu and Cu–Cu distances of 2.771(2)–2.789(1) Å and 2.867(2) Å (Fig. 2). The tungsten atom is tetrahedrally coordinated (107.53(33)–113.52(12)°). The coordination polyhedra of Cu are distorted tetrahedra (102.16(13)– 121.08(13)°), where the terminal positions are occupied by the triphenylphosphine ligands.

As expected, the bridging W–S bonds (2.246(3)–2.256(3) Å) are longer than the W–S bonds in the isolated WOS_3^{2-} ion (2.193(6)–2.206(6) Å) [8]. The Cu–S bond lengths within the asymmetric unit (2.312(3)–2.363(4) Å) compare well with the value observed for $CuNH_4MoS_4$ (2.31(3) Å) [9], whereas the Cu–S bonds connecting the two symmetrically related parts of the molecule are longer (2.403(3)–2.448(3) Å).

As mentioned above, two compounds $\{Cu_4W_2S_6\}(PPh_3)_4O_2$ and $\{Cu_3WS_3Cl\}(PPh_3)_3O$ are formed

TABLE IV. Bond Angles (deg) in $\{Cu_4W_2S_6\}(PPh_3)_4O_2$ with Standard Deviations.[a]

A. Angles within the $\{Cu_4W_2S_6\}P_4O_2$ *Unit*			
S1–W–S2	108.30(12)	S1a–Cu2–S2	108.49(13)
S1–W–S3	113.52(12)	S1a–Cu2–S3	105.51(12)
S1–W–O	107.53(33)	S1a–Cu2–P2	105.98(13)
S2–W–S3	108.54(12)	S2–Cu2–S3	103.01(13)
S2–W–O	109.07(33)	S2–Cu2–P2	112.17(13)
S3–W–O	109.79(33)	S3–Cu2–P2	121.08(13)
S1–Cu1–S2	102.16(13)	W–S1–Cu1	74.51(10)
S1–Cu1–S3a	107.11(13)	W–S1–Cu2a	114.69(14)
S1–Cu1–P1	116.72(13)	Cu1–S1–Cu2a	73.20(11)
S2–Cu1–S3a	113.74(13)		
S2–Cu1–P1	107.02(13)	W–S2–Cu1	75.00(11)
S3a–Cu1–P1	110.07(13)	W–S2–Cu2	74.75(11)
		Cu1–S2–Cu2	115.26(14)
		W–S3–Cu1a	110.01(14)
		W–S3–Cu2	73.70(10)
		Cu1a–S3–Cu2	73.94(11)
B. Mean Values for the $CuPPh_3$ *Units*			
Cu–P–C	114.7	P–C–C	119.0
C–P–C	103.8	C–C–C	118.6

[a]The index a refers to the transformation $\bar{x}, \bar{y}, \bar{z}$.

in the course of the same reaction, showing that they have comparable formation tendencies.

That is, completely different cage systems can be formed even though in both structures WOS_3^{2-} acts as terdentate ligand and the coordination polyhedra of the Cu atoms are distorted tetrahedra. The corresponding compounds of Ag^+ with $MoOS_3^{2-}$ and WOS_3^{2-} probably have a similar structure as $\{Cu_4W_2S_6\}(PPh_3)_4O_2$ [10].

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