(13) (a) Program MULTAN. G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr.*, **127**, 368 (1971); (b) C. K. Prewitt, "SFLS-5. A Fortran IV Full Matrix Least Squares Program", Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1966.

(14) L. E. McCandlisch, G. H. Stout, and L. C. Andrews, *Acta Crystallogr., Sect. A*, **31**, 245 (1975).

(15) N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, **15**, 45 (1974).

(16) D. A. Couch and S. D. Robinson, *Inorg. Chem.*, **13**, 456 (1974).

(17) R. O. Gould, C. L. Jones, W. J. Sime, and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 669 (1977).

(18) J. E. Fergusson, C. T. Page, and W. T. Robinson, *Inorg. Chem.*, **15**, 2270 (1976).

(19) S. Merlino and G. Montagnoli, *Acta Crystallogr., Sect. B*, **24**, 424 (1968).

(20) B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, **14**, 3060 (1975), and references therein.

(21) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **11**, 1088 (1972).

(22) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, 1968.

(23) A. N. Caldwell, L. Manojlovic-Muir, and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 2265 (1977).

(24) B. T. Hine, C. B. Knobler, and H. D. Kaesz, *Inorg. Chem.*, **17**, 1308 (1978).

(25) G. Orpen and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, **34**, 1992 (1978).

(26) J. M. Fernandez, B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, **34**, 1994 (1978).

(27) R. A. Love, H. B. Chin, T. F. Koetzle, S. W. Kirtley, B. R. Whittlesey, and R. Bau, *J. Am. Chem. Soc.*, **98**, 4491 (1976).

(28) M. J. Nolte and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 2406 (1974).

(29) R. A. Marsh, J. Howard, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 778 (1973).

(30) ORTEP II: C. K. Johnson, Report ORNL-3794 revised, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Contribution from the Center for Materials Science, National Bureau of Standards, Washington, D.C. 20234,
and from the Department of Chemistry, University of Maryland, College Park, Maryland 20742

Synthesis and Crystal and Molecular Structure of $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$, a Dimer of Bis((tri-*p*-tolylphosphine)copper)oxotrithiotungsten

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Reaction of tri-*p*-tolylphosphine, cuprous chloride, and $(Ph_3PCH_3)_2WO_2S_2$ produced $[(C_7H_7)_3P]_4Cu_4W_2S_8$ and $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$. The oxotrithiotungsten derivative crystallizes in monoclinic space group $P2_1/n$ with $a = 13.164$ (5) Å, $b = 25.613$ (16) Å, $c = 13.823$ (6) Å, $\beta = 97.25$ (4)°, and $Z = 2$. The X-ray structure ($R = 0.067$) revealed a 12-atom $Cu_4W_2S_6$ cage which may be viewed as consisting of two approximately tetrahedral WOS_3 units bridged on adjacent edges by $[(C_7H_7)_3PCu]$ groups.

Introduction

Evidence that reduction–oxidation reactions catalyzed by metalloenzymes occur at sites in which the metal is coordinated to one or more sulfur atoms[1,2] has stimulated interest in the coordination chemistry of molybdenum and its congeners. It appears that substitution of tungsten for molybdenum in an apoenzyme, when it can be accomplished, as for example in nitrate reductase[3] and sulfite oxidase,[4] produces a protein which is virtually inactive as a catalyst. This may be due to the lower stability of lower oxidation states of tungsten relative to those of molybdenum. Tungsten is also an antagonist to dietary molybdenum.[5] The utility of model tungsten compounds in helping to understand the chemistry of molybdoenzymes has been pointed out,[6,7] and group 6B copper ternary sulfides are of current interest in regard to complex interactions between copper, molybdenum, and sulfur in mammalian metabolism. This paper describes the synthesis and structure of a novel ternary metal–sulfur cluster in which the (tri-*p*-tolylphosphine)copper moiety bridges tetrahedral WOS_3 units. A similar complex in which a substituted phosphine–silver moiety bridges tetrahedral WS_4 units has also been prepared and studied by single-crystal X-ray analysis.[8]

Experimental Section

A mixture of 0.95 g of tri-*p*-tolylphosphine (3.1 mmol), 0.2 g (2 mmol) of cuprous chloride, and 100 mL of dichloromethane was stirred until the cuprous chloride dissolved. Then 1.67 g (2 mmol) of $(Ph_3PCH_3)_2WO_2S_2$ was added and stirring continued for 18 h. After refluxing for 1 h, the reaction mixture was filtered, evaporated to a small volume, and applied to a 13 in. × 1 in. silica gel column. Dichloromethane eluted a broad yellow band. The eluate was evaporated and applied to two 8 in. × 8 in. silica gel preparative thin layer chromatography plates which were then developed with benzene to yield two components. The fast yellow band was eluted with dichloromethane to afford 0.55 g (26%) of $[(C_7H_7)_3P]_4Cu_4W_2S_8$. The slower, orange band was eluted with dichloromethane and the product recrystallized by slow evaporation of a dichloromethane–isopropyl alcohol solution to give 0.05 g (2.2%) of $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$ (**1**) as orange needles, mp 238–239 °C.

Magnetic susceptibility at 300 K was 0.39×10^{-6} cm^3 g^{-1}. Anal. Calcd for $C_{84}H_{84}Cu_4O_2P_4S_6W_2$: C, 48.49; H, 4.10; Cu, 12.32; P, 6.00; S, 9.32; W, 17.85; mol wt 1031. Found: C, 49.14; H, 4.37; Cu, 12.56; P, 5.89; S, 8.21; W, 18.56; mol wt (osmometric in $CHCl_3$) 945. IR (Nujol): strong bands at 940, 930, 446, 428 cm^{-1}. Raman spectrum (4185-Å excitation; 1,2-$C_2H_4Cl_2$ solution): $\Delta\nu$ 456, 467 cm^{-1}. λ_{max} (1,2-$C_2H_4Cl_2$): 400 (sh), 385 (sh) nm. ^1H NMR ($CDCl_3$): −7.6 (m, 4 H), −2.95 ppm (s, 3 H). $\{^1H\}^{31}P$ NMR (CH_2Cl_2): broad singlet at −9.4 ppm.[9]

In a similar experiment in which 1.84 g of tri-*p*-tolylphosphine was used, the yields of $[(C_7H_7)_3P]_4Cu_4W_2S_8$ and $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$ were 0.75 and 0.095 g, respectively; about half of the starting phosphine was recovered.

Experimental details and results of the X-ray crystallographic study are summarized in Tables I–III. A table of observed and calculated structure factors is available as supplementary material.

Results and Discussion

Preparative Chemistry. The reaction of a tertiary phosphine such as diphenylmethylphosphine, copper(I) chloride, and $WO_2S_2^{2-}$ produces the bimetallic net compound $(Ph_2PCH_3)_4Cu_2WS_4$.[10] We found that a like reaction employing tri-*p*-tolylphosphine as both a ligand and reducing agent afforded, in addition to $[(C_7H_7)_3P]_4Cu_4W_2S_8$, a low yield of $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$, **1**, which was isolated by preparative thin-layer chromatography. This material was of interest from the standpoint of the relationship of the M_2MOS_3 core to metalloenzymes and because of the fact that it presented the interesting structural problem of the location of the oxygen atoms in the dimeric structure (vide infra).

Vapor pressure osmometry revealed that the trithiotungstate was a dimer, and the $\{^1H\}^{31}P$ NMR spectrum consisted of only

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[†] From a dissertation to be submitted to the Graduate School, University of Maryland, in partial fulfillment of the requirements for a Ph.D. Degree in Chemistry.

Table I

Experimental Conditions

molecular formula	$[(p\text{-}C_7H_7)_3P]_4Cu_4W_2O_2S_6$
lattice constants	a =13.164 (5) Å b = 25.613 (16) Å c = 13.823 (6) Å β = 97.25 (4)° $Z = 2$
density	d_{calcd} = 1.482 g cm^{-3} d_{obsd} = 1.48 (3) g cm^{-3} (by flotation)
temp	22 (1) °C
radiation	Mo Kα (λ = 0.710 69 Å)
monochromator	graphite
systematic absences	$h0l$; $h + l = 2n + 1$ $0k0$; $k = 2n + 1$
space group	$P2_1/n$
general equiv positions	$x, y, z; -x, -y, -z; {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z; {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$
μ (linear abs coeff)	38.0 cm^{-1}
abs cor method	Gaussian quadrature
max abs cor	1.67
min abs cor	1.15
diffractometer	four-circle diffractometer, bisecting mode
derivation of integrated intens from measurements	integrated step scan
agreement among equiv rflcns	R = 0.051, av dev = 0.98σ
no. of unique rflcns	4483
2θ limits	4.0–40.0°
criterion of $\sigma(I)$	$\sigma(I)^2 = I + 0.00066I^2$
criterion for $\sigma(F)$	$\sigma(F) = [F^2 + \sigma(I)/Lp]^{1/2} - F$

Data Used To Calculate Absorption Corrections

h	k	l	χ	ϕ	dist to cryst center, cm
0	0	1	356.37	343.09	0.0027
0	0	$\bar{1}$	3.63	163.09	0.0027
0	1	1	11.89	319.48	0.0027
0	$\bar{1}$	$\bar{1}$	348.11	139.48	0.0027
1	0	0	54.44	55.27	0.0140
$\bar{1}$	0	0	305.56	235.27	0.0140

Table II. Summary of Solution of Structure

computer and programs	XRAY on Univac 1108[a]
atomic scattering factors	neutral atom scattering factors[b]
anomalous scattering:[c] atom, f', f''	P, 0.090, 0.095 S, 0.110, 0.124 Cu, 0.263, 1.266 W, −1.421, 6.872
solution method	direct methods for heavy atoms; difference Fourier for light atoms
extinction	no correction
weighting procedure	$w = 1/[\sigma(F_o)]^2$
refinement	full-matrix least-squares treating atoms in tolyl moiety as a group; refinement was based on minimization of $\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$; rflcns with $I < 3\sigma(I)$ were excluded
definition of R	$R = \Sigma \lvert \Delta F\rvert / \Sigma \lvert F_o\rvert = 0.067$

[a] J. M. Stewart, XRAY System Report TR 446, Computer Science Center, University of Maryland, College Park, MD, 1976. [b] For hydrogen see R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175–87 (1965). For all other atoms see D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968). [c] "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

a broad singlet. Infrared absorptions at 940 and 930 cm^{-1} are assigned to terminal W═O groups and may be compared with 921 and 908 cm^{-1} in $[Ni(WOS_3)_2]^{2-}$.[11] Bands at 446 and 428 cm^{-1} are due most probably to W–S groups with sulfur bridging copper and tungsten.[12]

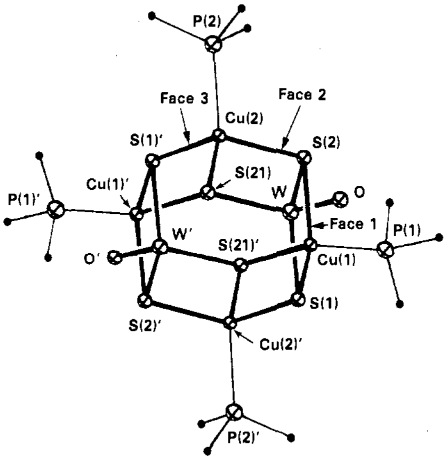


Figure 1. Centrosymmetric 12-membered cage: $Cu_4W_2S_6$.

Crystallography. The crystal structure of **1** reveals a 12-atom $Cu_4W_2S_6$ cage (Figures 1–3) that contains a center of symmetry. Tri-*p*-tolylphosphine groups are attached to each copper atom, and one oxygen is externally bonded to each tungsten as was inferred from spectroscopic data. The six-membered ring sides of the cage are geometrically analogous to the chair-shaped cyclohexane ring. The dihedral angles between the plane defined by Cu(2)–S(2)–W′–S(21)′ and the planes defined by Cu(1)–S(21)′–S(2) and W′–S(1)′–Cu(2) are 45.2 and 48.1°, respectively. The dihedral angle between the latter two planes is 3.0°. The internal angles in these rings range from 110.9 to 113.9° with a mean of 112.4°. This architecture in transition-metal clusters is highly unusual. The closest approximation to it is $(i\text{-}C_3H_7NAlH)_6$, which contains nearly planar six-membered rings connected by six transverse Al–N bonds.[13]

In contrast to the decidedly nonplanar six-membered rings of the $Cu_4W_2S_6$ cluster, there are three unique four-membered almost planar faces shown in Figure 4: Cu(1)–S(2)–W–S(1) (face 1), S(2)–Cu(2)–S(21)–W (face 2), and Cu(2)–S(1)′–Cu(1)′–S(21) (face 3). The maximum atomic displacement from these four-atom planes is 0.03 Å. The dihedral angle between face 1 and face 2 is 58.9° and that between face 2 and face 3 is 61.2°. The internal angles and dimensions of these faces are shown in Figure 4.

The 12-membered cage appears to have a sizeable cavity (Figure 3). However, since the separation of any given pair of atoms is not much greater than the sum of their van der Waals radii, it appears that, unlike $[Ni(SC_2H_5)_2]_6$,[14] access by small molecules to the cavity would be difficult (see Table IV).

Each copper atom is bonded to an external phosphine ligand and to three sulfur atoms in the cage. The coordination geometry about copper is approximately tetrahedral, but significant deviations from ideal angles occur; the three S–Cu–S angles about Cu(1), for example, are 102.7 (3), 112.2 (3), and 108.2 (3)°. The copper–sulfur distances range from 2.306 (8) Å [Cu(2)–S(2)] to 2.426 (8) Å [Cu(1)–S(21)]. The magnitude and the span of d(Cu–S) values appear to be slightly longer and greater than corresponding values found in other copper–sulfur compounds, shown in Table V. In copper–thiourea complexes[15] and in the copper–sulfur clusters studied by Dance,[16,17] sulfur distances to trigonal copper were about 0.01 Å longer than those to digonal copper. Since sulfur in **1** is three-coordinate, somewhat longer Cu–S bonds are not unexpected.

Randaccio et al.[18] have recently summarized literature on copper–phosphine complexes. The mean Cu–P distance for

Table III. List of Atomic Parameters[a,b]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	0.56263 (9)	0.53320 (4)	0.15618 (8)	5.11 (6)	4.30 (6)	4.40 (6)	−0.17 (6)	0.58 (5)	−0.27 (6)
Cu(1)	0.4040 (2)	0.5758 (1)	0.0286 (2)	4.8 (2)	5.1 (2)	6.3 (2)	0.7 (2)	1.5 (2)	0.4 (2)
Cu(2)	0.4717 (3)	0.4357 (1)	0.1202 (2)	6.1 (2)	5.0 (2)	5.5 (2)	−0.4 (2)	1.5 (2)	0.3 (2)
O(1)	0.606 (1)	0.5584 (8)	0.268 (1)	7.3 (6)					
S(1)	0.5805 (5)	0.5947 (3)	0.0429 (5)	5.4 (4)	4.1 (4)	5.8 (5)	−0.7 (3)	0.8 (4)	0.8 (3)
S(2)	0.3950 (5)	0.5141 (3)	0.1494 (5)	5.2 (4)	5.5 (5)	6.9 (5)	0.5 (4)	2.9 (4)	1.4 (4)
S(21)	0.6477 (5)	0.4594 (3)	0.1331 (5)	4.8 (4)	5.5 (5)	6.0 (5)	−0.1 (4)	−0.1 (3)	0.0 (4)
P(1)	0.2881 (5)	0.6386 (3)	0.0482 (5)	3.8 (4)	5.1 (5)	6.4 (5)	0.7 (4)	0.0 (4)	−0.4 (4)
P(2)	0.4279 (6)	0.3746 (3)	0.2265 (6)	7.5 (6)	4.9 (5)	6.0 (5)	−1.5 (4)	2.5 (4)	0.1 (4)

atom	x	y	z	U	atom	x	y	z	U
C(111)	0.269 (2)	0.692 (1)	−0.038 (2)	5 (1)	C(225)	0.133 (5)	0.422 (3)	0.251 (5)	20 (2)
C(112)	0.273 (2)	0.680 (1)	−0.136 (2)	7 (1)	C(226)	0.235 (4)	0.421 (3)	0.234 (4)	16 (2)
C(113)	0.258 (3)	0.719 (1)	−0.207 (3)	9 (1)	C(231)	0.458 (2)	0.306 (1)	0.203 (2)	7 (1)
C(114)	0.239 (3)	0.770 (1)	−0.180 (3)	10 (1)	C(232)	0.483 (2)	0.271 (1)	0.280 (2)	7 (1)
C(1141)	0.223 (3)	0.813 (2)	−0.257 (3)	13 (2)	C(233)	0.503 (3)	0.219 (1)	0.259 (2)	9 (1)
C(115)	0.236 (3)	0.783 (1)	−0.082 (3)	9 (1)	C(234)	0.498 (2)	0.202 (1)	0.163 (2)	8 (1)
C(116)	0.251 (2)	0.744 (1)	−0.011 (2)	7 (1)	C(2341)	0.519 (3)	0.145 (2)	0.141 (3)	11 (1)
C(121)	0.320 (2)	0.670 (1)	0.168 (2)	5 (1)	C(235)	0.472 (2)	0.237 (1)	0.086 (2)	7 (1)
C(122)	0.423 (2)	0.680 (1)	0.199 (2)	8 (1)	C(236)	0.453 (3)	0.290 (1)	0.107 (2)	8 (1)
C(123)	0.452 (3)	0.701 (1)	0.292 (3)	10 (1)	H(112)	0.29 (2)	0.64 (1)	−0.16 (2)	10 (10)
C(124)	0.377 (3)	0.712 (1)	0.353 (3)	9 (1)	H(113)	0.27 (2)	0.71 (1)	−0.28 (2)	10 (10)
C(1241)	0.408 (3)	0.735 (2)	0.454 (3)	13 (2)	H(115)	0.22 (2)	0.82 (1)	−0.07 (2)	10 (10)
C(125)	0.274 (3)	0.701 (1)	0.322 (3)	10 (1)	H(116)	0.24 (2)	0.75 (1)	0.06 (2)	10 (10)
C(126)	0.246 (3)	0.680 (1)	0.229 (3)	9 (1)	H(122)	0.48 (2)	0.67 (1)	0.15 (2)	10 (10)
C(131)	0.159 (2)	0.614 (1)	0.053 (2)	6 (1)	H(123)	0.53 (2)	0.71 (1)	0.32 (2)	10 (10)
C(132)	0.147 (3)	0.570 (2)	0.112 (3)	10 (1)	H(125)	0.22 (2)	0.71 (1)	0.36 (2)	10 (10)
C(133)	0.049 (4)	0.550 (2)	0.118 (3)	14 (2)	H(126)	0.17 (2)	0.67 (1)	0.20 (2)	10 (10)
C(134)	−0.037 (3)	0.574 (2)	0.065 (3)	11 (1)	H(132)	0.21 (2)	0.55 (1)	0.14 (2)	10 (10)
C(1341)	−0.143 (4)	0.551 (2)	0.071 (3)	14 (2)	H(133)	0.04 (2)	0.52 (1)	0.16 (2)	10 (10)
C(135)	−0.025 (3)	0.617 (2)	0.007 (3)	13 (1)	H(135)	−0.09 (2)	0.64 (1)	−0.02 (2)	10 (10)
C(136)	0.073 (3)	0.638 (2)	0.001 (3)	10 (1)	H(136)	0.08 (2)	0.67 (1)	−0.04 (2)	10 (10)
C(211)	0.496 (2)	0.389 (1)	0.347 (2)	7 (1)	H(212)	0.64 (2)	0.38 (1)	0.30 (2)	10 (10)
C(212)	0.603 (3)	0.392 (1)	0.355 (3)	10 (1)	H(213)	0.74 (2)	0.41 (1)	0.45 (2)	10 (10)
C(213)	0.658 (3)	0.408 (1)	0.443 (3)	9 (1)	H(215)	0.47 (2)	0.43 (1)	0.57 (2)	10 (10)
C(214)	0.607 (3)	0.422 (1)	0.522 (2)	9 (1)	H(216)	0.37 (2)	0.40 (1)	0.42 (2)	10 (10)
C(2141)	0.668 (4)	0.440 (2)	0.617 (4)	17 (2)	H(222)	0.29 (2)	0.30 (1)	0.29 (2)	10 (10)
C(215)	0.500 (3)	0.419 (2)	0.514 (3)	11 (1)	H(223)	0.11 (2)	0.30 (1)	0.32 (2)	10 (10)
C(216)	0.445 (3)	0.403 (2)	0.426 (3)	11 (1)	H(225)	0.09 (2)	0.45 (1)	0.23 (2)	10 (10)
C(221)	0.290 (2)	0.374 (1)	0.242 (2)	5 (1)	H(226)	0.27 (2)	0.45 (1)	0.20 (2)	10 (10)
C(222)	0.243 (4)	0.328 (2)	0.269 (4)	15 (2)	H(232)	0.49 (2)	0.28 (1)	0.35 (2)	10 (10)
C(223)	0.140 (4)	0.329 (2)	0.287 (3)	14 (2)	H(233)	0.52 (2)	0.19 (1)	0.31 (2)	10 (10)
C(224)	0.085 (3)	0.376 (2)	0.278 (3)	12 (1)	H(235)	0.46 (2)	0.23 (1)	0.02 (2)	10 (10)
C(2241)	−0.026 (4)	0.377 (2)	0.297 (3)	13 (2)	H(236)	0.43 (2)	0.32 (1)	0.05 (2)	10 (10)

[a] The carbon atoms in the phenyl moiety of the tolyl groups are specified by three integers. The first indicates the P atom to which to tolyl group is bonded, the second specifies which of the three tolyl groups is bonded to a given P, and the third specifies the C atom within a given tolyl group. Each H atom is labeled the same as the C atom to which it is bonded. The methyl moiety of the tolyl group is specified by four integers with the first three integers the same as those of the C to which the methyl is bonded. Each tolyl group was refined by group refinement. To obtain an estimate of the errors on the individual atoms in these groups, we refined the structure one cycle by using block-diagonal least-squares analysis with dampened shifts (0.000 01). [b] The temperature factor has the form exp(−T) where $T = 8\pi^2 U((\sin\theta)/\lambda)^2$ for isotropic atoms and $T = 2\pi^2 \Sigma_{i,j}(H_iH_jU_{i,j}L_iL_j)$ for anisotropic atoms. The L_i are the reciprocal axial lengths and the H_i are the Miller indices. Printed temperature factors are $U \times 10^2$ and $U_{ij} \times 10^2$. The esd of the last significant digit is given in parentheses.

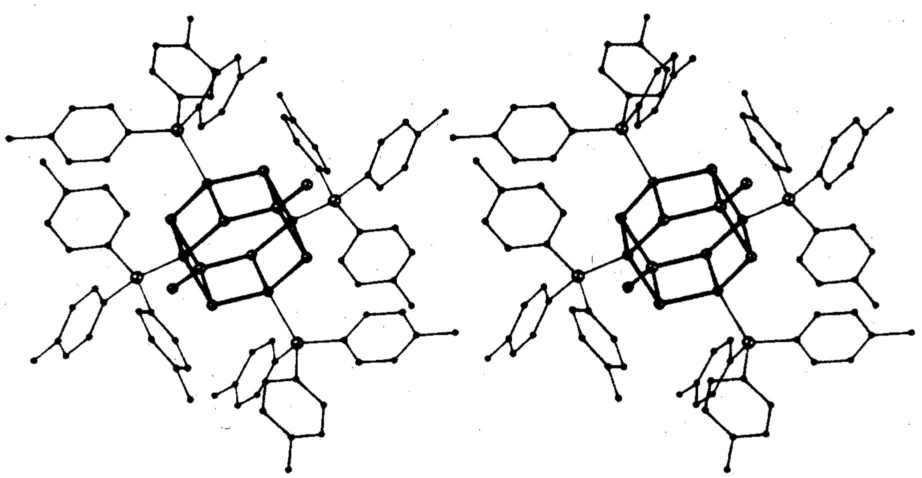


Figure 2. Stereoscopic view of $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$.

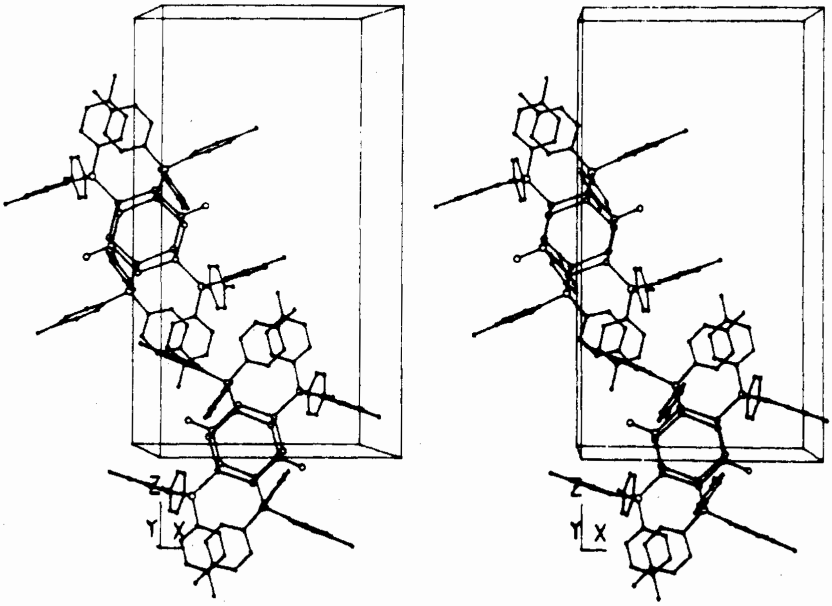


Figure 3. Packing of $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$.

Table IV

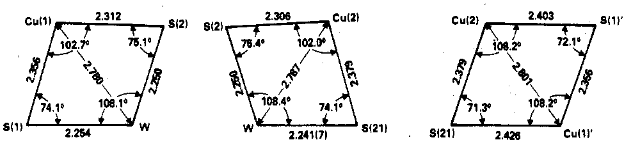
	Bond Distances (Å)		
Cu(1)-S(1)	2.356 (8)	Cu(2)-S(1)′	2.403 (8)
Cu(1)-S(2)	2.312 (8)	Cu(2)-S(2)	2.306 (8)
Cu(1)-S(21)′	2.426 (8)	Cu(2)-S(21)	2.379 (8)
Cu(1)-P(1)	2.258 (8)	Cu(2)-P(2)	2.271 (9)
Cu(1)-W	2.780 (3)	Cu(2)-W	2.787 (4)
W-O	1.70 (2)	P(1)-C(111)	1.81 (3)
W-S(1)	2.254 (7)	P(1)-C(121)	1.83 (3)
W-S(2)	2.250 (7)	P(1)-C(131)	1.82 (3)
W-S(21)	2.241 (7)	P(2)-C(211)	1.82 (3)
W-Cu(1)	2.780 (3)	P(2)-C(221)	1.86 (3)
W-Cu(2)	2.787 (4)	P(2)-C(231)	1.83 (3)
	Bond Angles (deg)		
S(2)-Cu(1)-S(1)	102.7 (3)	Cu(1)-S(2)-W	75.1 (2)
S(2)-Cu(1)-S(21)′	112.2 (3)	Cu(2)-S(2)-W	75.4 (2)
P(1)-Cu(1)-S(21)′	105.0 (3)	Cu(1)-S(2)-Cu(2)	111.9 (3)
S(2)-Cu(1)-P(1)	107.7 (3)	Cu(2)-S(21)-Cu(1)′	71.3 (2)
S(1)-Cu(1)-S(21)′	108.2 (3)	Cu(2)-S(21)-W	74.1 (2)
S(1)-Cu(1)-P(1)	121.2 (3)	Cu(1)′-S(21)-W	110.9 (3)
S(2)-Cu(2)-S(1)′	111.5 (3)	C(111)-P(1)-C(131)	104 (1)
S(2)-Cu(2)-S(21)	102.0 (3)	C(111)-P(1)-C(121)	105 (1)
S(1)′-Cu(2)-S(21)	108.2 (3)	C(121)-P(1)-Cu(1)	109.6 (9)
S(2)-Cu(2)-P(2)	109.6 (3)	C(131)-P(1)-Cu(1)	114.1 (9)
S(1)′-Cu(2)-P(2)	108.6 (3)	C(111)-P(1)-Cu(1)	120 (1)
S(21)-Cu(2)-P(2)	116.8 (3)	C(121)-P(1)-C(131)	103 (1)
S(1)-W-O(1)	108.1 (7)	C(211)-P(2)-C(231)	105 (1)
S(21)-W-O(1)	109.3 (7)	C(211)-P(2)-C(221)	106 (1)
S(1)-W-S(2)	108.1 (3)	C(221)-P(2)-Cu(2)	114.4 (9)
S(2)-W-S(21)	108.4 (3)	C(231)-P(2)-Cu(2)	118 (1)
S(2)-W-O(1)	109.7 (7)	Cu(2)-P(2)-C(211)	108 (1)
S(1)-W-S(21)	113.2 (3)	Cu(2)-P(2)-C(231)	105 (1)
Cu(1)-S(1)-W	74.1 (2)		
Cu(1)-S(1)-Cu(2)′	72.1 (2)		
Cu(2)′-S(1)-W	112.5 (3)		

compounds with one phosphine per copper is 2.194 Å with the values ranging from 2.135 Å in $(Ph_3P)Cu(C_5H_5)$ to 2.240 Å in $(Ph_3P)_6Cu_6H_6$. These authors have pointed out that while the number of phosphine ligands bonded to copper is an important determinant of d(Cu–P), other secondary effects may also be operative. In **1**, we find $d(\text{Cu–P})_{av}$ to be 2.264 Å. This value is slightly longer than expected on the basis of the values reported for other systems. It appears that this lengthening is not traceable to an effect of the copper coordination number. It may instead be attributed to the influence

Table V. Copper–Sulfur Distances

compd	d(Cu–S), Å	ref
CuSCN	2.344–2.367	*d*
$Cu_5(\mu_2\text{-SBu})_6^-$	2.17–2.27	*e*
$Cu_5(SPh)_7^{2-}$	2.16–2.33	*f*
$Cu_4(\mu_2\text{-SPh})_6^{2-}$	2.29 (av)	*g*
$[Cu^{II}_6Cu^I_8(pen)_{12}Cl]^{5-}$ [a]	2.21–2.34	*h*
$Cu_8(MNT)_6^{4-}$ [b]	2.237–2.266	*i*
$[SC(NH_2)_2]_3CuCl$	2.27–2.43	*j*
$Cu_4(SC(NH_2)_2)_{10}(SiF_6)_2\cdot H_2O$	2.27–2.46	*k*
$[(C_2H_5)_2NCS_2Cu]_4$	2.246–2.290	*l*
$[(C_3H_7)_2NCOSCu]_6$	2.23	*m*
$Cu_2(C_8H_{20}N_2S_2)_2]^{2+}$	2.288–2.326	*n*
$((C_2H_5)_2NCS_2)_2Cu_2Cl_2$	2.261–2.286	*o*
$((C_2H_5)_2NCS_2)_2Cu_3Cl_3$	2.268–2.299	*o*
$Cu(MNT)_2^-$ [b]	2.158–2.177	*p*
$[Cu_8(S_2CC(CO_2C_2H_5)_2)_6]^{4-}$	2.247 (av)	*q*
$[(C_2H_5)_2NCS_2]_2Cu$	2.297–2.339	*r*
$CuBr_2S_2CN(n\text{-}C_4H_9)_2$	2.193	*s*
$Cu_{10}(Bu(DED)H)_6(BuDED)_2$ [c]	2.269 (av)	*t*
$[(C_4H_{10}S_2)_2Cu](BF_4)_2$	2.317	*u*
$(Me_4P_2S_2)_2Cu_2Cl_2$	2.311–2.486	*v*
$(Me_4P_2S_2)CuCl_2$	2.327 (av)	*w*

[a] pen = D-penicillaminato (see ref 2). [b] MNT = maleonitriledithiolato. [c] DED = $S_2CC(CO_2\text{-}t\text{-}C_4H_9)_2$. [d] M. Kakesova, M. Dunaj-Jurco, M. Serator, J. Gazo, and J. Garaj, *Inorg. Chim. Acta*, 17, 161 (1976). [e] I. G. Dance, *J. Chem. Soc., Chem. Commun.*, 68 (1976). [f] I. G. Dance, *ibid.*, 103 (1976). [g] I. G. Dance and J. C. Calabrese, *Inorg. Chim. Acta*, 19, L41 (1976). [h] P. J. M. W. L. Birker and H. C. Freeman, *J. Am. Chem. Soc.*, 99, 6890 (1977). [i] L. E. McCandish, E. C. Bissell, D. Coucouvanis, J. P. Fackler, and K. Knox, *ibid.*, 90, 7357 (1968). [j] Y. Okaya and C. B. Knobler, *Acta Crystallogr.*, 17, 928 (1964). [k] A. G. Gash, E. H. Griffith, W. A. Spofford III, and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 256 (1973). [l] R. Hesse, *Ark. Kemi*, **20**, 481 (1963). [m] R. Heesse and U. Aava, *Acta Chem. Scand.*, **24**, 1355 (1970). [n] T. Ottersen, L. G. Warner, and K. Seff, *Inorg. Chem.*, 13, 1904 (1974). [o] A. Hendrickson, R. L. Martin, and D. Taylor, *Chem. Commun.*, 843 (1975). [p] J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 3, 1507 (1964). [q] F. J. Hollander and D. Coucouvanis, *J. Am. Chem. Soc.*, 99, 6268 (1977). [r] M. Bonamico, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, 19, 886 (1965). [s] P. T. Beurskens, J. A. Cras, and J. J. Steggerda, *Inorg. Chem.*, 7, 810 (1968). [t] D. Coucouvanis, D. Swenson, N. C. Baenziger, R. Pedelty, and M. L. Caffery, *J. Am. Chem. Soc.*, 99, 8097 (1977). [u] E. N. Baker and G. E. Norris, *J. Chem. Soc., Dalton Trans.*, 877 (1977). [v] F. A. Cotton, B. A. Frenz, D. L. Hunter, and Z. C. Mester, *Inorg. Chim. Acta*, **11**, 111 (1974). [w] F. A. Cotton, B. A. Frenz, D. L. Hunter, and Z. C. Mester, *ibid.*, 11, 119 (1974).



Face 1 Face 2 Face 3

Figure 4. Bond angles and distances for the three unique 4-membered sides of the 12-membered cage in $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$.

Table VI. Tungsten–Sulfur Distances

compd	*d*(W–S), Å	ref
$WSCl_4$–$WOSCl_2[(1,2(MeO)_2C_2H_4]$	2.10	*a*
$W(MNT)_3{}^{2-}$	2.383, 2.368	*b*
$(NH_4)_2WS_4$	2.165	*c*
$WSCl_4$	2.098	*d*
K_3WOS_3Cl	2.198 (av)	*e*
(thiazolidine-2-thione)$W(CO)_5$	2.56	*f*
(thiomorpholine-3-thione)$W(CO)_5$	2.556	*g, h*
$(C_5H_5)_2W(S_2C_6H_4)$	2.421	*i*
$(C_5H_5)_2W(\mu\text{-}SPh)_2Cr(CO)_4$	2.487 (av)	*j*
$(C_5H_5)_2W(\mu\text{-}SPh)_2Mo(CO)_4$	2.526, 2.483	*j*
$(C_5H_5)_2W(\mu\text{-}SPh)_2W(CO)_4$	2.49, 2.58	*j*
$(t\text{-}BuSC_2H_4S\text{-}t\text{-}Bu)W(CO)_4$	2.565, 2.559	*k*
$(t\text{-}BuS\text{-}C_3H_6S\text{-}t\text{-}Bu)W(CO)_4$	2.582, 2.574	*k*
$(C_5H_5)_2WS_4$	2.419	*l*
$(C_4H_{10}S_2)W(CO)_3Cl[Sn(CH_3)Cl_2]$	2.537, 2.580	*m*

[a] D. Britnell, M. G. B. Drew, G. W. A. Fowles, and D. A. Rice, *J. Chem. Soc., Chem. Commun.*, 462 (1972). [b] G. F. Brown and E. I. Stiefel, *Inorg. Chem.*, **12**, 2140 (1973). [c] K. Sasvari, *Acta Crystallogr.*, **16**, 719 (1963). [d] M. G. B. Drew and R. Mandyczewski, *J. Chem. Soc. A*, 2815 (1970). [e] A. Muller, N. Weinstock, B. Krebs, B. Buss, and A. Ferwanah, *Z. Naturforsch. B*, **26**, 268 (1972). [f] M. Cannas, G. Carta, G. Marongiu, and E. Trogu, *Acta Crystallogr., Sect. B*, **30**, 2252 (1974). [g] M. Cannas, G. Carta, A. Cristini, and G. Marongiu, *ibid.*, **31**, 2909 (1975). [h] M. Cannas, G. Carta, D. DeFilippo, G. Marongiu, and E. F. Torgu, *Inorg. Chim. Acta*, **10**, 145 (1974). [i] T. Debaerdemaeker and A. Kutoglu, *Acta Crystallogr., Sect. B*, **29**, 2664 (1973). [j] K. Prout and G. V. Rees, *ibid.*, **30**, 2717 (1974). [k] G. Reisner, I. Bernal, and G. R. Dobson, *J. Organomet. Chem.*, **157**, 23 (1978). [l] B. R. Davis and I. Bernal, *J. Cryst. Mol. Struct.*, **2**, 637 (1973). [m] M. Elder and D. Hall, *Inorg. Chem.*, 8, 1273 (1969).

of the three sulfur atoms which are also bonded to copper. The σ-donor properties of the chalcogen atoms and back-bonding involving W–S orbitals may weaken the bonds between copper and the external phosphorus.

The coordination geometry about tungsten is also roughly tetrahedral; the S(2)–W–S(1), S(2)–W–S(21), and S(1)–W–S(21) angles are 108.1 (3), 108.4 (3), and 113.2 (3)°, respectively. The average tungsten–sulfur separation is 2.248 Å. Comparison with the limited data (Table VI) for *d*(W–S) values indicates that this distance is too long by about 0.1 Å for a tungsten–sulfur double bond and about 0.13 Å shorter than the 2.383 and 2.368 Å values found in tris(maleonitriledithiolato)tungsten(2–).[19] The W–O separation, 1.70 Å, is clearly consistent with a formal tungsten–oxygen double bond; cf. Table VII for related data. This is consistent with the infrared spectrum, which exhibits high-frequency W–O stretching bands.

Figure 4 shows the very acute angles about the sulfur atoms bridging copper and tungsten in the four-membered rings: the average Cu–S–W angle is 74.7°. These acute bridging angles are, as noted earlier,[10] suggestive of tungsten–copper bonding. Likewise, angles Cu(2)–S(1)–Cu(1) and Cu(2)–S(21)–Cu(1) are even more acute, with an average value of 71.7°. The Cu⋯W separations, d_{av} = 2.784 Å, and *d*(Cu(1)⋯Cu(2)) = 2.801 Å may be compared with the metal–metal bond lengths *d*(Cu⋯W) = 2.65 Å and *d*(Cu⋯Cu) = 2.56 Å calculated by using sums of atomic radii. Calculating metal–metal bond lengths from atomic radii is fraught with possibilities for error, and the situation is worse when bridging atoms are involved. The rigidity imposed by the 12-atom cage structure is probably not relevant since one is concerned with the possible significance of interatomic spacings regardless of how they came into being. Although no definitive statement can be made about the existence of a bond between copper and tungsten, the observed distance is consistent with a weak, attractive interaction between these two atoms.

Table VII. Tungsten–Oxygen Distances

compd	*d*(W–O), Å	ref
$(C_5H_5)W(O)(C_6H_5)(Ph_2C_2)$	1.69	*a*
$[(1,2\text{-}Me_2As)_2C_6H_4]WOCl_4$	1.89	*b*
$WOCl_4$	1.80	*c*
$WO_4{}^{2-}$	1.79	*d*
$WSCl_4$–$WOCl_2[1,2\text{-}(MeO)_2C_2H_4]$	1.72–2.27	*e*
$W(O)(O_2)F_4{}^{2+}$	1.75 (2), 1.92, 2.03	*f*
$(Ph_3PO)_2WO_2Cl_2$	1.704 (av)	*g*
$(PhN)_2O\cdot WOCl_4$	1.67, 2.28	*h*
Cu_3WO_6	1.79, 2.09	*i*
$[(C_5H_7O_2)WO_2Cl_2]^-$	1.722–2.171	*j*

[a] N. G. Bokiy, Y. V. Gatilov, Y. T. Struchkov, and N. A. Ustynyuk, *J. Organomet. Chem.*, 54, 213 (1973). [b] M. G. B. Drew and R. Mandyczewski, *J. Chem. Soc., Chem. Commun.*, 292 (1970). [c] H. Hess and H. Hartung, *Z. Anorg. Allg. Chem.*, **344**, 157 (1966). [d] F. X. N. M. Kools, A. S. Koster, and G. D. Rieck, *Acta Crystallogr., Sect. B*, **26**, 1974 (1970). [e] D. Britnell, M. G. B. Drew, G. W. A. Fowles, and D. A. Rice, *J. Chem. Soc., Chem. Commun.*, 462 (1972). [f] Z. Ruzic-Toros, B. Kojic-Prodic, F. Gabela, and M. Sljukic, *Acta Crystallogr., Sect. B*, **33**, 692 (1977). [g] J. F. DeWet, M. R. Caira, and B. J. Gellatly, *ibid.*, **34**, 762 (1978). [h] I. W. Bassi and R. Scordamaglia, *J. Organomet. Chem.*, 99, 127 (1975). [i] E. Gebert and L. Kihlborg, *Acta Chem. Scand.*, **23**, 221 (1969). [j] M. G. B. Drew, G. W. A. Fowles, D. A. Rice, and K. J. Shanton, *J. Chem. Soc., Chem. Commun.*, 614 (1974).

Dimeric $[(C_7H_7)_3P]_4Cu_4W_2S_8$, whose molecular weight in chloroform solution was 1018 (vapor pressure osmometry; calculated 1046), presumably has a structure similar to **1** with sulfurs replacing the external oxygens.

Registry No. **1**, 70576-05-5; $[(C_7H_7)_3P]_4Cu_4W_2S_8$, 70576-06-6; $(Ph_3PCH_3)_2WO_2S_2$, 60033-53-6.

Supplementary Material Available: Listing of structure factors for $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$ (19 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. C. Bray, *Enzymes, 3rd Ed.*, **12**, 299 (1975).
(2) E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977).
(3) E. A. Notton and E. J. Hewitt, *J. Less-Common Met.*, **36**, 437 (1974).
(4) J. L. Johnson, H. J. Cohen, and K. V. Rajagopalan, *J. Biol. Chem.*, **249**, 5046 (1974).
(5) E. J. Underwood, "Trace Elements in Human and Animal Nutrition", 4th ed., Academic Press, New York, 1977, p 122.
(6) R. A. D. Wentworth, *Coord. Chem. Rev.*, **18**, 1 (1976).
(7) J. Chatt, A. J. Pearman, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1852 (1977).
(8) J. Stalick, C. Hubbard, A. Mighell, and A. Siedle, *J. Am. Chem. Soc.*, **101**, 2903 (1979).
(9) Negative shifts are downfield of internal $(CH_3)_4Si$ and external H_3PO_4 references.
(10) J. C. Huffman, R. Roth, and A. R. Siedle, *J. Am. Chem. Soc.*, **98**, 4340 (1976).
(11) A. Müller and H. H. Heinsen, *Chem. Ber.*, **105**, 1730 (1972).
(12) A. Müller, H. H. Heinsen, and G. Vandrish, *Inorg. Chem.*, **13**, 1001 (1974).
(13) M. Cesari, G. Perego, G. Del Piero, S. Cucinella, and E. Cernia, *J. Organomet. Chem.*, **78**, 203 (1974).
(14) P. Woodward, L. F. Dahl, E. W. Abel, and B. C. Crosse, *J. Am. Chem. Soc.*, **87**, 5251 (1965).
(15) E. H. Griffith, G. W. Hunt, and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 432 (1976).
(16) I. G. Dance, *J. Chem. Soc., Chem. Commun.*, 103 (1976).
(17) I. G. Dance, *J. Chem. Soc., Chem. Commun.*, 68 (1976).
(18) A. Camus, N. Marsich, G. Nardin, and L. Randaccio, *J. Chem. Soc., Dalton Trans.*, 2560 (1975).
(19) G. F. Brown and E. I. Stiefel, *Inorg. Chem.*, **12**, 2140 (1973).