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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71747 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1062]

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μ-(*O,O'*-Diethyl dithiophosphato-2κ*S*:3κ*S'*)-oxo-1κ*O*-tri-μ$_3$-sulfido-1:2:3κ^3*S*;1:2:4κ^3*S*;-1:3:4κ^3*S*-tris(triphenylphosphine)-2κ*P*;3κ*P*;4κ*P*-tricoppertungsten

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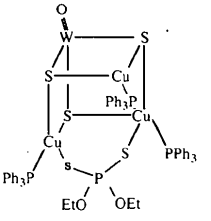
Abstract

The structure of the title comopound, [WCu$_3$(O)S$_3$(C$_4$H$_{10}$O$_2$PS$_2$)(C$_{18}$H$_{15}$P)$_3$], contains an incomplete cubane-like cluster core, [WCu$_3$S$_3$-{S$_2$P(OCH$_2$CH$_3$)$_2$}]$^{2+}$, in which the two S atoms of the diethyl dithiophosphato ligand coordinate to two Cu atoms with bond lengths of 2.472 (3) Å [Cu(1)—S(4)] and 2.337 (3) Å [Cu(3)—S(5)].

Comment

Several different structural types of *M*—Cu—S complexes (*M* = Mo, W) have been found during recent years. For example, clusters containing the cores [M_3CuS$_4$]$^{5+}$ (Lu, Zhu, Wu, Wu & Lu, 1989; Zhan, Zheng Wu & Lu, 1989), [M_2Cu$_2$S$_4$]$^{4+}$ (Zhu, Zheng & Wu, 1990) and MCu$_3$S$_3X$ (X = Cl, Br) (Müller, Bögge & Schimanski, 1983) have been prepared. The structure of the title compound (I) is similar to that of [WCu$_3$(O)S$_3$Cl(Ph$_3$P)$_3$], except that the chloride anion is replaced by a bidentate diethyl dithiophosphato ligand.



(I)

Mean bond lengths of W—Cu 2.775 (2), Cu—(μ$_3$-S) 2.347 (3), W—(μ-S) 2.250 (2) and W=O 1.715 (6) Å are found. The W atom is tetrahedrally coordinated by three S atoms and one O atom; the Ph$_3$P ligands complete the tetrahedral geometry at each Cu atom. The Cu(2)···S(4) distance (2.640 Å) is too long to be considered as a bond.

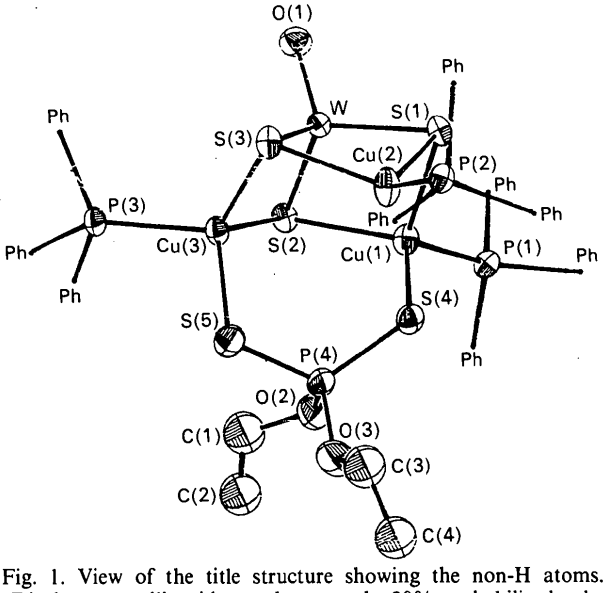


Fig. 1. View of the title structure showing the non-H atoms. Displacement ellipsoids are shown at the 30% probability level.

Experimental

Crystal data

$[WCu_3OS_3(C_4H_{10}O_2PS_2)(C_{18}H_{15}P)_3]$	D_x = 1.61 Mg m^{-3}
M_r = 1458.75	Mo $K\alpha$ radiation
Triclinic	λ = 0.71069 Å
$P\bar{1}$	Cell parameters from 20 reflections
a = 13.808 (6) Å	θ = 6-27.5°
b = 19.764 (6) Å	μ = 3.306 mm^{-1}
c = 11.696 (4) Å	T = 296 K
α = 99.27 (3)°	Cubic
β = 107.08 (3)°	Crystal size not measured
γ = 88.12 (3)°	Orange
V = 3011 (2) Å^3	Crystal source: crystallized from $CH_2Cl_2/(C_2H_5)_2O$
Z = 2	

Data collection

Rigaku AFC-5R diffractometer	R_{int} = 0.027
ω-2θ scans	θ_{max} = 25°
Absorption correction: empirical	h = 0 → 16
T_{min} = 0.96, T_{max} = 1.04	k = −24 → 24
11 084 measured reflections	l = −14 → 14
10 598 independent reflections	3 standard reflections monitored every 250 reflections
8310 observed reflections [$I > 3\sigma(I)$]	intensity variation: none

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.37
R = 0.045	$\Delta\rho_{max}$ = 1.08 e Å^{-3}
wR = 0.063	$\Delta\rho_{min}$ = −0.81 e Å^{-3}
S = 1.58	Atomic scattering factors from Cromer & Waber (1974)
8310 reflections	
377 parameters	
$w = 1/\sigma^2(F_o)$	

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

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
W	−0.19315 (2)	0.18398 (2)	0.20611 (3)	2.57 (1)
Cu(1)	−0.29787 (7)	0.21002 (5)	−0.02422 (8)	3.40 (4)
Cu(2)	−0.23510 (8)	0.32250 (5)	0.2152 (1)	4.21 (4)
Cu(3)	−0.02204 (7)	0.22964 (5)	0.16106 (9)	3.13 (4)
S(1)	−0.3495 (1)	0.2277 (1)	0.1547 (2)	3.30 (7)
S(2)	−0.1471 (1)	0.1513 (1)	0.0360 (2)	3.07 (7)
S(3)	−0.0893 (1)	0.2704 (1)	0.3201 (2)	3.36 (7)
S(4)	−0.2534 (2)	0.3315 (1)	−0.0129 (2)	3.84 (8)
S(5)	0.0048 (2)	0.3276 (1)	0.0853 (3)	5.2 (1)
P(1)	−0.4272 (2)	0.1649 (1)	−0.1825 (2)	3.01 (7)
P(2)	−0.2791 (2)	0.4211 (1)	0.3068 (2)	3.17 (7)
P(3)	0.1310 (1)	0.1756 (1)	0.2053 (2)	3.15 (7)
P(4)	−0.1203 (2)	0.3330 (1)	−0.0482 (2)	4.2 (1)
O(1)	−0.1910 (5)	0.1163 (3)	0.2819 (6)	4.5 (3)
O(2)	−0.1274 (5)	0.2752 (4)	−0.1610 (6)	5.8 (3)
O(3)	−0.1113 (7)	0.3979 (5)	−0.108 (1)	8.4 (5)
C(1)	−0.039 (2)	0.239 (1)	−0.187 (2)	13.3 (6)
C(2)	−0.031 (2)	0.235 (1)	−0.292 (3)	18 (1)
C(3)	−0.131 (2)	0.458 (1)	−0.072 (2)	13.1 (6)
C(4)	−0.150 (1)	0.5082 (9)	−0.155 (1)	9.4 (4)
C(111)	−0.4658 (6)	0.0815 (4)	−0.1632 (7)	3.0 (1)
C(112)	−0.5666 (6)	0.0593 (4)	−0.1919 (7)	3.4 (1)
C(113)	−0.5884 (7)	−0.0067 (5)	−0.1768 (8)	4.2 (2)
C(114)	−0.5017 (7)	−0.0503 (5)	−0.1375 (8)	4.0 (2)
C(115)	−0.4113 (7)	−0.0292 (5)	−0.1078 (8)	4.0 (2)
C(116)	−0.3886 (6)	0.0357 (4)	−0.1209 (7)	3.3 (1)
C(121)	−0.5423 (7)	0.2164 (5)	−0.2061 (8)	4.0 (2)
C(122)	−0.5770 (8)	0.2395 (5)	−0.108 (1)	5.2 (2)
C(123)	−0.664 (1)	0.2797 (7)	−0.120 (1)	6.7 (3)
C(124)	−0.712 (1)	0.2961 (7)	−0.231 (1)	7.4 (3)
C(125)	−0.682 (1)	0.2758 (9)	−0.326 (1)	9.5 (4)
C(126)	−0.592 (1)	0.2357 (7)	−0.317 (1)	7.4 (3)
C(131)	−0.4068 (6)	0.1472 (4)	−0.3311 (7)	3.4 (1)
C(132)	−0.4717 (7)	0.1051 (5)	−0.4292 (8)	4.4 (2)
C(133)	−0.4517 (7)	0.0933 (5)	−0.5411 (9)	5.0 (2)
C(134)	−0.3717 (7)	0.1227 (5)	−0.5554 (9)	4.9 (2)
C(135)	−0.3032 (9)	0.1621 (6)	−0.459 (1)	6.2 (2)
C(136)	−0.3217 (7)	0.1742 (5)	−0.3473 (9)	4.9 (2)
C(211)	−0.3089 (6)	0.4107 (4)	0.4449 (7)	3.4 (1)
C(212)	−0.3667 (6)	0.4581 (5)	0.4973 (8)	3.8 (2)
C(213)	−0.3919 (7)	0.4470 (5)	0.5994 (8)	4.6 (2)
C(214)	−0.3589 (9)	0.3899 (6)	0.650 (1)	6.4 (3)
C(215)	−0.301 (1)	0.3439 (8)	0.600 (1)	8.2 (3)
C(216)	−0.2759 (8)	0.3537 (6)	0.498 (1)	5.5 (2)
C(221)	−0.3938 (6)	0.4607 (4)	0.2230 (7)	3.5 (1)
C(222)	−0.3998 (7)	0.5311 (5)	0.2182 (8)	4.3 (2)
C(223)	−0.4919 (8)	0.5576 (5)	0.1537 (9)	5.0 (2)
C(224)	−0.5719 (7)	0.5176 (5)	0.0996 (9)	4.9 (2)
C(225)	−0.5679 (8)	0.4483 (6)	0.103 (1)	5.3 (2)
C(226)	−0.4774 (7)	0.4187 (5)	0.1643 (8)	4.3 (2)
C(231)	−0.1838 (6)	0.4895 (5)	0.3527 (8)	3.9 (2)
C(232)	−0.140 (1)	0.5030 (6)	0.266 (1)	6.5 (3)
C(233)	−0.067 (1)	0.5572 (7)	0.294 (1)	7.4 (3)
C(234)	−0.039 (1)	0.5929 (7)	0.409 (1)	6.9 (3)
C(235)	−0.078 (1)	0.5792 (7)	0.493 (1)	6.8 (3)
C(236)	−0.1512 (8)	0.5269 (6)	0.467 (1)	5.3 (2)
C(311)	0.2438 (6)	0.2315 (5)	0.2692 (7)	3.8 (2)
C(312)	0.3403 (9)	0.2087 (6)	0.276 (1)	6.3 (2)
C(313)	0.425 (1)	0.2521 (7)	0.327 (1)	7.3 (3)
C(314)	0.412 (1)	0.3179 (8)	0.368 (1)	7.9 (3)
C(315)	0.315 (1)	0.3420 (9)	0.360 (1)	9.5 (4)
C(316)	0.231 (1)	0.2972 (7)	0.311 (1)	6.6 (3)
C(321)	0.1488 (6)	0.1287 (4)	0.0649 (7)	3.3 (1)
C(322)	0.1099 (7)	0.0628 (5)	0.0205 (9)	4.8 (2)
C(323)	0.1109 (8)	0.0303 (6)	−0.094 (1)	5.9 (2)
C(324)	0.1509 (8)	0.0625 (5)	−0.164 (1)	5.1 (2)
C(325)	0.1911 (8)	0.1281 (5)	−0.1207 (9)	5.0 (2)
C(326)	0.1892 (7)	0.1609 (5)	−0.0059 (8)	4.2 (2)
C(331)	0.1500 (6)	0.1122 (4)	0.3072 (7)	3.7 (2)
C(332)	0.0913 (9)	0.1159 (6)	0.384 (1)	6.5 (3)
C(333)	0.101 (1)	0.0683 (8)	0.466 (1)	9.0 (4)
C(334)	0.173 (1)	0.0201 (8)	0.469 (1)	8.1 (3)
C(335)	0.233 (1)	0.0157 (7)	0.394 (1)	7.4 (3)
C(336)	0.220 (1)	0.0619 (6)	0.311 (1)	6.6 (3)

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

W—S(1)	2.247 (2)	S(4)—P(4)	2.001 (3)
W—S(2)	2.255 (2)	S(5)—P(4)	1.973 (4)
W—S(3)	2.249 (2)	P(4)—O(2)	1.582 (8)
W—O(1)	1.715 (6)	P(4)—O(3)	1.580 (7)
W—Cu(1)	2.779 (2)	O(2)—C(1)	1.48 (2)
W—Cu(2)	2.771 (1)	O(3)—C(3)	1.24 (2)
W—Cu(3)	2.775 (2)	C(1)—C(2)	1.26 (3)
Cu(1)—S(1)	2.373 (2)	C(3)—C(4)	1.46 (2)
Cu(1)—S(2)	2.329 (2)	P(1)—C(111)	1.817 (8)
Cu(1)—S(4)	2.472 (3)	P(1)—C(121)	1.834 (9)
Cu(1)—P(1)	2.246 (2)	P(1)—C(131)	1.819 (8)
Cu(2)—S(1)	2.371 (3)	P(2)—C(211)	1.823 (8)
Cu(2)—S(3)	2.332 (3)	P(2)—C(221)	1.826 (8)
Cu(2)—P(2)	2.225 (2)	P(2)—C(231)	1.820 (9)
Cu(3)—S(2)	2.341 (3)	P(3)—C(311)	1.835 (9)
Cu(3)—S(3)	2.336 (2)	P(3)—C(321)	1.830 (8)
Cu(3)—S(5)	2.337 (3)	P(3)—C(331)	1.827 (9)
Cu(3)—P(3)	2.293 (2)		
Cu(2)—W—Cu(1)	70.38 (5)	C(331)—P(3)—Cu(3)	117.6 (3)
Cu(2)—W—Cu(3)	80.31 (4)	Cu(2)—S(3)—Cu(3)	100.0 (1)
Cu(3)—W—Cu(1)	85.95 (5)	W—S(1)—Cu(2)	73.7 (7)
S(1)—W—S(2)	108.48 (8)	W—S(1)—Cu(1)	73.89 (7)

S(1)—W—S(3)	106.38 (8)	W—S(2)—Cu(1)	74.63 (7)
S(3)—W—S(2)	107.97 (8)	W—S(2)—Cu(3)	74.25 (7)
O(1)—W—S(1)	110.4 (2)	W—S(3)—Cu(2)	74.42 (7)
O(1)—W—S(2)	111.1 (2)	W—S(3)—Cu(3)	74.46 (7)
O(1)—W—S(3)	112.3 (2)	P(4)—S(4)—Cu(1)	107.1 (1)
S(1)—Cu(1)—S(4)	95.28 (9)	P(4)—S(5)—Cu(3)	103.4 (1)
S(2)—Cu(1)—S(1)	101.94 (8)	O(2)—P(4)—S(5)	112.5 (3)
S(2)—Cu(1)—S(4)	107.51 (8)	O(2)—P(4)—S(4)	106.4 (3)
S(3)—Cu(2)—S(1)	99.89 (9)	O(3)—P(4)—O(2)	99.1 (5)
S(3)—Cu(3)—S(2)	102.32 (8)	O(3)—P(4)—S(5)	108.3 (4)
S(3)—Cu(3)—S(5)	104.8 (1)	O(3)—P(4)—S(4)	110.6 (3)
S(5)—Cu(3)—S(2)	117.5 (1)	S(5)—P(4)—S(4)	118.3 (2)
P(1)—Cu(1)—S(1)	109.70 (9)	C(1)—O(2)—P(4)	124 (1)
P(1)—Cu(1)—S(2)	121.42 (9)	C(3)—O(3)—P(4)	127 (1)
P(1)—Cu(1)—S(4)	116.8 (1)	C(2)—C(1)—O(2)	118 (2)
P(2)—Cu(2)—S(1)	119.5 (1)	O(3)—C(3)—C(4)	120 (2)
P(2)—Cu(2)—S(3)	117.42 (9)	C(111)—P(1)—Cu(1)	111.3 (3)
P(3)—Cu(3)—S(3)	118.21 (9)	C(131)—P(1)—Cu(1)	118.1 (3)
P(3)—Cu(3)—S(5)	105.6 (1)	C(121)—P(1)—Cu(1)	114.1 (3)
P(3)—Cu(3)—S(2)	109.03 (9)	C(231)—P(2)—Cu(2)	115.5 (3)
Cu(1)—S(2)—Cu(3)	108.32 (9)	C(211)—P(2)—Cu(2)	111.7 (3)
Cu(2)—S(1)—Cu(1)	84.79 (8)	C(221)—P(2)—Cu(2)	116.6 (3)
C(321)—P(3)—Cu(3)	109.0 (3)	C(311)—P(3)—Cu(3)	116.2 (3)

Data collection used *CONTROL* software (Molecular Structure Corporation, 1988). The scan speed varied between 2.4 and 8° min^{-1} (in ω) on the basis of *SEARCH* intensity. The scan width was (1.207 + 0.350tanθ)° with maximum (sinθ)/λ = 0.5946 $Å^{-1}$. The structure was solved by conventional heavy-atom methods. The W atom was located from a three-dimensional Patterson synthesis and the remaining non-H atoms were located using the *DIRDIF* program (Beurskens, 1984). H atoms were placed in geometrically calculated positions (C—H 0.95 Å) but were not included in the refinement. The structure was refined by full-matrix least-squares techniques with anistropic displacement parameters for the W, Cu, S, P and O atoms and isotropic displacement parameters for all C atoms. All calculations were performed on a VAX 785 computer using the *TEXSAN* (Molecular Structure Corporation, 1985) program package. The view of the molecule (Fig. 1) was produced using *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71595 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1053]

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Azido(η^5-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II)

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Abstract

The molecule $[RuN_3(C_5H_5)\{P(C_6H_5)_3\}_2]$ has a typical three-legged-piano-stool geometry; Ru—Cp^0 (where Cp^0 is the centre of the ring) is 1.843 (3) Å, the three legs are 2.3293 (5) and 2.3304 (5) (Ru—P) and 2.135 (3) Å (Ru—N) in length while the angles are P—Ru—P 105.22 (2), P—Ru—N 85.39 (6) and 86.65 (5)°. The azide group is almost linear [N—N—N 175.2 (3)°] and is coordinated to Ru with an Ru—N—N angle of 124.5 (2)°; there is a small difference between the N—N distances [1.186 (3) and 1.164 (3) Å], the longer being adjacent to the Ru atom.

Comment

The complex $CpRu(Cl)(PPh_3)_2$ (Bruce, Cifuentes, Snow & Tiekink, 1989) has been used as the starting material for the synthesis of several complexes because of its substitutionally labile chloride and