suggests an incorrect space-group assignment. The presence of an inversion center would produce chloride–carbonyl disorder, a not uncommon phenomenon.

Crystals of the title compound were the gift of Dr Donald J. Darensbourg, Texas A & M University.

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Structure of Tetrakis(tetraphenylphosphonium) Octakis[chlorocopper(I)]bis[tetrathiotungstate(VI)]*

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Abstract. $[P(C_6H_5)_4]_4[\{WS_4(CuCl)_4\}_2]$, $M_r = 2773 \cdot 8$, triclinic, $P\bar{1}$, $a = 13 \cdot 068$ (1), $b = 14 \cdot 361$ (1), $c = 15 \cdot 556$ (1) Å, $\alpha = 109 \cdot 458$ (6), $\beta = 93 \cdot 626$ (6), $\gamma = 108 \cdot 724$ (4)°, $V = 2559 \cdot 2$ Å^3, $Z = 1$, $D_x = 1 \cdot 799$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71073$ Å, $\mu = 4 \cdot 39$ mm^{-1}, $F(000) = 1360$, $T = 293$ K. $R = 0 \cdot 033$ for 7180 unique observed reflections. In the dimeric anion, each W atom is tetrahedrally coordinated by S $[W-S = 2 \cdot 222 \, (2)-2 \cdot 248 \, (2) \text{Å}]$; six of the Cu atoms have trigonal-planar coordination, with bonds to two μ_3-S^{2-} ligands $[Cu-S = 2 \cdot 253 \, (2)-2 \cdot 267 \, (2) \text{ Å}]$ and one terminal Cl$^-$ ligand $[Cu-Cl = 2 \cdot 130 \, (2)-2 \cdot 151 \, (2) \text{ Å}]$. Distorted tetrahedral coordination of the other two Cu atoms is completed by formation of two asymmetrical μ_2-Cl bridges across an inversion centre $[Cu-Cl = 2 \cdot 272 \, (2), \; 2 \cdot 436 \, (2) \text{ Å}, \; Cu-S = 2 \cdot 293 \, (2), \; 2 \cdot 318 \, (2) \text{ Å}, \; Cu-Cl-Cu = 84 \cdot 9 \, (1)°]$. The range of W···Cu distances, bridged by μ_3-S^{2-} ligands, is $2 \cdot 632 \, (1)-2 \cdot 675 \, (1)$ Å.

Experimental. Compound prepared from [PhP]$_2$[WS$_4$] and CuCl (1:4) in acetone at room temperature, red crystals obtained by slow evaporation of the solvent. Crystal size $0 \cdot 23 \times 0 \cdot 37 \times 0 \cdot 37$ mm, Siemens AED2 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, cell parameters from 2θ values of 32 reflections measured at $\pm\omega$ ($20 < 2\theta < 22°$). Intensity measurements in ω/θ scan mode, scan width =

$1 \cdot 02°$ + α-doublet separation, scan time = 14–56 s, $2\theta_{\max} = 50°$, $h \, -15 \rightarrow 0$, $k \, -17 \rightarrow 17$, $l \, -18 \rightarrow 18$, no significant variation in intensity for three standard reflections, semi-empirical absorption correction (transmission $0 \cdot 282-0 \cdot 424$). 9322 reflections, 9011 unique ($R_{int} = 0 \cdot 019$), 7180 with $F > 4\sigma(F)$ for structure solution (by Patterson and difference syntheses) and refinement (blocked-cascade least squares on F), $w^{-1} = \sigma^2(F) + 0 \cdot 00004F^2$. Anisotropic thermal parameters for all non-H atoms, H atoms constrained [C–H = $0 \cdot 96$ Å on ring-angle external bisectors, U(H) = $1 \cdot 2U_{eq}$(C)], isotropic extinction parameter $x = 5 \cdot 6$ (2) $\times 10^{-7}$ $[F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{1/4}]$, 569 parameters, max. $\Delta/\sigma = 0 \cdot 084$, mean = $0 \cdot 021$, $R = 0 \cdot 033$, $wR = 0 \cdot 035$, slope of normal probability plot = $1 \cdot 48$, max. $\Delta\rho = +0 \cdot 77$ e Å^{-3}, min. = $-0 \cdot 77$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974), *SHELXTL* programs (Sheldrick, 1985).

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1,† selected bond lengths and angles for the anion in Table 2. The atom-numbering scheme for the dimeric anion is shown in Fig. 1.

Related literature. [Ph$_4$P]$_2$[MoS$_4$(CuBr)$_4$], prepared in an analogous manner and obtained as an acetone solvate, contains polymeric anion chains, with monomer units linked by pairs of unsymmetrical bromide bridges (Nicholson, Flood, Garner & Clegg, 1983). In contrast, [Ph$_4$P]$_2$[MoS$_4$(CuCl)$_3$].CH$_3$CN (Clegg, Garner & Nicholson, 1983), the bromo derivative [Ph$_4$P]$_2$-[MoS$_4$(CuBr)$_3$].CH$_3$CN (Nicholson, Boyde, Garner & Clegg, 1987), and the homologous tungsten complex [Ph$_4$P]$_2$[WS$_4$(CuCl)$_3$].CH$_3$CN (Potvin, Manoli, Salis &

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^4$)

$U_{eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}
W	2794 (1)	4865 (1)	1863 (1)	349 (1)
Cu(1)	4071 (1)	6508 (1)	3325 (1)	511 (3)
Cu(2)	1195 (1)	4457 (1)	2793 (1)	551 (3)
Cu(3)	1390 (1)	3269 (1)	440 (1)	491 (3)
Cu(4)	4278 (1)	5179 (1)	781 (1)	488 (3)
Cl(1)	5044 (1)	7847 (1)	4549 (1)	759 (8)
Cl(2)	−177 (1)	4120 (1)	3459 (1)	838 (9)
Cl(3)	71 (1)	2011 (1)	−613 (1)	602 (7)
Cl(4)	5436 (1)	6361 (1)	280 (1)	490 (6)
S(1)	2248 (1)	6070 (1)	2848 (1)	496 (6)
S(2)	1817 (1)	3262 (1)	1867 (1)	481 (6)
S(3)	2435 (1)	4861 (1)	446 (1)	472 (6)
S(4)	4604 (1)	5291 (1)	2301 (1)	429 (6)
P(1)	6803 (1)	2244 (1)	674 (1)	390 (6)
C(111)	7778 (4)	3583 (4)	1069 (3)	383 (22)
C(112)	7506 (5)	4426 (4)	1580 (4)	508 (26)
C(113)	8259 (5)	5447 (4)	1837 (4)	557 (27)
C(114)	9264 (5)	5626 (4)	1587 (4)	559 (27)
C(115)	9540 (4)	4793 (4)	1076 (4)	543 (28)
C(116)	8802 (4)	3760 (4)	808 (4)	494 (26)
C(121)	6076 (4)	1867 (4)	−474 (3)	399 (22)
C(122)	6642 (5)	2139 (4)	−1131 (4)	541 (27)
C(123)	6099 (5)	1810 (5)	−2032 (4)	630 (31)
C(124)	4992 (5)	1236 (5)	−2276 (4)	689 (31)
C(125)	4416 (5)	961 (5)	−1635 (4)	653 (31)
C(126)	4963 (4)	1267 (4)	−742 (4)	508 (26)
C(131)	5858 (4)	2138 (4)	1460 (4)	410 (23)
C(132)	5056 (4)	2592 (4)	1478 (4)	482 (26)
C(133)	4377 (4)	2550 (5)	2133 (4)	561 (29)
C(134)	4474 (4)	2054 (4)	2736 (4)	552 (28)
C(135)	5255 (5)	1603 (5)	2714 (4)	614 (31)
C(136)	5956 (4)	1651 (4)	2076 (4)	519 (27)
C(141)	7526 (4)	1362 (4)	643 (4)	416 (23)
C(142)	8363 (5)	1644 (5)	1376 (4)	633 (30)
C(143)	8874 (5)	939 (5)	1384 (5)	858 (40)
C(144)	8563 (5)	−25 (5)	657 (5)	768 (38)
C(145)	7739 (5)	−300 (5)	−73 (5)	612 (30)
C(146)	7218 (4)	389 (4)	−85 (4)	454 (24)
P(2)	1279 (1)	2324 (1)	4975 (1)	393 (6)
C(211)	1569 (4)	1360 (4)	4047 (3)	414 (22)
C(212)	1266 (4)	1261 (4)	3133 (4)	527 (26)
C(213)	1468 (5)	537 (5)	2411 (4)	645 (29)
C(214)	1988 (5)	−104 (5)	2577 (4)	687 (30)
C(215)	2310 (5)	1 (5)	3470 (4)	653 (31)
C(216)	2103 (4)	735 (4)	4220 (4)	519 (26)
C(221)	−161 (4)	2098 (4)	4721 (4)	471 (25)
C(222)	−545 (5)	2913 (5)	5001 (4)	630 (32)
C(223)	−1668 (6)	2692 (6)	4878 (5)	843 (43)
C(224)	−2396 (5)	1673 (6)	4485 (5)	904 (45)
C(225)	−2009 (5)	860 (6)	4186 (5)	855 (39)
C(226)	−891 (5)	1069 (5)	4304 (4)	653 (31)
C(231)	1559 (4)	2163 (4)	6044 (3)	367 (21)
C(232)	717 (4)	1718 (4)	6452 (4)	464 (24)
C(233)	966 (5)	1616 (4)	7284 (4)	564 (27)
C(234)	2041 (5)	1940 (4)	7709 (4)	551 (28)
C(235)	2886 (4)	2373 (4)	7305 (4)	513 (26)
C(236)	2653 (4)	2494 (4)	6475 (4)	469 (25)
C(241)	2159 (4)	3628 (4)	5095 (3)	438 (23)
C(242)	2863 (4)	3777 (5)	4486 (4)	534 (27)
C(243)	3554 (5)	4796 (5)	4617 (4)	652 (31)
C(244)	3539 (5)	5636 (5)	5330 (4)	731 (33)
C(245)	2841 (6)	5500 (5)	5945 (4)	731 (33)
C(246)	2157 (5)	4500 (4)	5831 (4)	612 (28)

Table 2. *Selected bond lengths* (Å) *and angles* (°) *for the anion*

W···Cu(1)	2·634 (1)	W···Cu(2)	2·639 (1)
W···Cu(3)	2·632 (1)	W···Cu(4)	2·675 (1)
W−S(1)	2·239 (2)	W−S(2)	2·248 (2)
W−S(3)	2·222 (2)	W−S(4)	2·241 (1)
Cu(1)−S(1)	2·264 (2)	Cu(1)−S(4)	2·267 (2)
Cu(2)−S(1)	2·253 (2)	Cu(2)−S(2)	2·253 (2)
Cu(3)−S(2)	2·258 (2)	Cu(3)−S(3)	2·253 (2)
Cu(4)−S(3)	2·293 (2)	Cu(4)−S(4)	2·318 (2)
Cu(1)−Cl(1)	2·151 (2)	Cu(2)−Cl(2)	2·130 (2)
Cu(3)−Cl(3)	2·143 (1)	Cu(4)−Cl(4)	2·272 (2)
Cu(4)−Cl(4')	2·436 (2)		
S(1)−W−S(2)	108·4 (1)	S(1)−W−S(3)	108·4 (1)
S(2)−W−S(3)	108·9 (1)	S(1)−W−S(4)	109·3 (1)
S(2)−W−S(4)	111·5 (1)	S(3)−W−S(4)	110·2 (1)
S(1)−Cu(1)−S(4)	107·5 (1)	S(1)−Cu(2)−S(2)	107·7 (1)
S(2)−Cu(3)−S(3)	107·5 (1)	S(3)−Cu(4)−S(4)	105·1 (1)
Cl(1)−Cu(1)−S(1)	123·7 (1)	Cl(1)−Cu(1)−S(4)	128·7 (1)
Cl(2)−Cu(2)−S(1)	126·0 (1)	Cl(2)−Cu(2)−S(2)	126·3 (1)
Cl(3)−Cu(3)−S(2)	123·0 (1)	Cl(3)−Cu(3)−S(3)	129·1 (1)
Cl(4)−Cu(4)−S(3)	117·1 (1)	Cl(4)−Cu(4)−S(4)	121·3 (1)
Cl(4')−Cu(4)−S(3)	106·2 (1)	Cl(4')−Cu(4)−S(4)	110·8 (1)
Cl(4)−Cu(4)−Cl(4')	95·1 (1)	Cu(4)−Cl(4)−Cu(4')	84·9 (1)
W−S(1)−Cu(1)	71·6 (1)	W−S(1)−Cu(2)	71·9 (1)
Cu(1)−S(1)−Cu(2)	114·0 (1)	W−S(2)−Cu(2)	71·8 (1)
W−S(2)−Cu(3)	71·5 (1)	Cu(2)−S(2)−Cu(3)	103·8 (1)
W−S(3)−Cu(3)	72·0 (1)	W−S(3)−Cu(4)	72·7 (1)
Cu(3)−S(3)−Cu(4)	111·9 (1)	W−S(4)−Cu(1)	71·5 (1)
W−S(4)−Cu(4)	71·8 (1)	Cu(1)−S(4)−Cu(4)	114·1 (1)

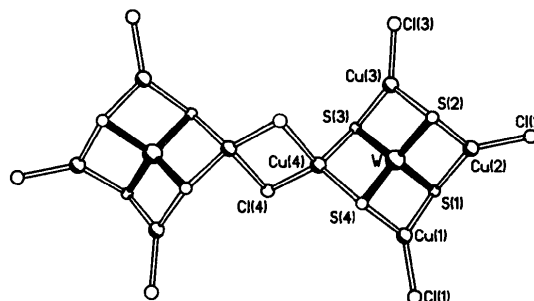The prime denotes an atom generated by the centre of symmetry; symmetry operation $1 - x, 1 - y, -z$.

Fig. 1. The structure of the dimeric anion, showing the labelling scheme.

Secheresse, 1984) form an isostructural series, the monomeric anions having only terminal halide ligands.

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