

Table 2. Selected interatomic bond distances (Å) and angles (°) with estimated standard deviations in parentheses

W P(1)	2.500 (4)	W-C(1)	1.96 (1)
W P(2)	2.438 (4)	W-C(2)	1.987 (9)
W P(3)	2.458 (4)	W-C(3)	2.01 (1)
P(1)-C(131)	1.835 (9)	P(2)-C(131)	1.827 (9)
<P-C(phenyl)>	1.827 (6)	<P(3)-C(ethyl)>	1.85 (1)
<C-O>	1.160 (9)		
P(1)-W P(2)	68.5 (2)	P(2)-W-P(3)	166.0 (1)
P(2)-W-C(1)	95.6 (3)	P(3)-W-C(1)	98.3 (3)
C(2)-W-C(3)	170.6 (3)	P(1)-C(131)-P(2)	98.8 (4)
P(1)-C(131)-C(132)	129.6 (7)	P(2)-C(131)-C(132)	131.1 (6)
W-C(2)-O(2)	174.3 (6)	W-C(3)-O(3)	177.1 (7)
W-C(1)-O(1)	175.5 (6)		

the angle P(1)-C(131)-P(2) is considerably reduced from 119.0 (3) to 98.8 (4)°, although the carbon atom retains its planar sp^2 configuration since the angles about it sum to 359.5°. The vinylidene group is bent significantly out of the equatorial plane [the angle between the planes defined by W, P(1), P(2) and P(1), P(2), C(131), C(132) is 20°], which contrasts with the two bridged species, which are essentially planar, and is much greater than the corresponding angle of 10° in the mononuclear iron complex. This may well reflect the increase in steric crowding around the central metal atom brought about by the presence of the triethylphosphine ligand. Steric effects are also apparent on the two apical carbonyl groups which are bent slightly

away from the vdpp chelate leading to a C(2)-W-C(3) angle of 170.6 (3)°.

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Structure of Bis(tetraphenylphosphonium) Tris[chlorocopper(I)]oxotrithiotungstate(VI)*

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Abstract. $[P(C_6H_5)_4]_2[WOS_3(CuCl)_3]$, $M_r = 1271.8$, triclinic, $P\bar{1}$, $a = 9.896$ (1), $b = 11.665$ (1), $c = 23.559$ (2) Å, $\alpha = 78.794$ (7), $\beta = 78.421$ (7), $\gamma = 70.741$ (4)°, $V = 2490.9$ Å³, $Z = 2$, $D_x = 1.695$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 4.00$ mm⁻¹, $F(000) = 1252$, $T = 293$ K, $R = 0.0340$ for 5649 unique reflections with $F > 4\sigma(F)$. The W, three Cu and three S atoms of the anion are arranged on seven vertices of a trigonally distorted cube; the eighth vertex, opposite W, is unoccupied. The W atom

is tetrahedrally coordinated by one terminal O atom and by three S atoms, each of which also bonds to two Cu atoms. The Cu coordination is trigonal planar, by two bridging S and one terminal Cl. Mean bond distances are W-O = 1.711 (4), W-S = 2.268 (5), Cu-S = 2.257 (7), Cu-Cl = 2.155 (5), W...Cu = 2.658 (7) Å.

Introduction. The tetrathiomolybdate(VI) anion $[MoS_4]^{2-}$ and related species have been widely used in transition-metal coordination chemistry, often as bidentate ligands to a later transition metal (Müller, Diemann, Jostes & Bögge, 1981). Particular attention

*IUPAC name: bis(tetraphenylphosphonium) oxo[1,2,3-trichloro-1,2,2,3,3,1-tri- μ -thio-tricuprato(I)-S¹,S²,S³]tungstate(2-).

has been given to Cu–Mo–S clusters, which may be important in understanding the biological antagonism between copper and molybdenum (Sarkar & Mishra, 1984). The structure of the cluster anion [MoOS₃(CuCl)₃]²⁻ has been determined in two different salts (Müller, Schimanski & Schimanski, 1983; Clegg, Garner, Nicholson & Raithby, 1983). We report here the structure of the homologous tungsten-centred anion.

Experimental. The compound was prepared from [PPh₄]₂[WOS₃] and CuCl in 1:3 molar ratio in acetone solution, and obtained as single crystals by cooling the

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

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

	x	y	z	U_{eq}
W	2698.7 (2)	4230.0 (2)	1837.8 (1)	365 (1)
Cu(1)	1526.8 (8)	5852.6 (6)	2588.5 (3)	456 (3)
Cu(2)	1814.1 (8)	2651.9 (6)	2689.1 (3)	445 (3)
Cu(3)	92.1 (8)	4776.1 (7)	1541.3 (3)	462 (3)
Cl(1)	811 (2)	7138 (1)	3211 (1)	620 (7)
Cl(2)	1163 (2)	1347 (1)	3385 (1)	547 (7)
Cl(3)	-1943 (2)	5138 (2)	1244 (1)	603 (7)
S(1)	3008 (2)	3936 (1)	2787 (1)	491 (6)
S(2)	1596 (2)	2874 (1)	1736 (1)	442 (6)
S(3)	1164 (2)	6153 (1)	1648 (1)	458 (6)
O	4298 (4)	4031 (4)	1371 (2)	625 (19)
P(1)	6757 (1)	236 (1)	891 (1)	338 (5)
C(112)	8644 (4)	-1985 (3)	592 (1)	473 (25)
C(113)	9537	-2777	202	539 (28)
C(114)	9688	-2368	-398	532 (29)
C(115)	8945	-1166	-607	552 (29)
C(116)	8052	-373	-217	475 (26)
C(111)	7901	-783	383	361 (22)
C(122)	6742 (3)	2344 (3)	133 (2)	479 (25)
C(123)	6107	3416	-223	532 (28)
C(124)	4618	3795	-232	546 (29)
C(125)	3765	3104	114	524 (27)
C(126)	4401	2033	470	415 (24)
C(121)	5889	1653	480	351 (21)
C(132)	7506 (4)	1719 (3)	1484 (1)	419 (23)
C(133)	8237	1927	1884	521 (28)
C(134)	9214	943	2174	548 (30)
C(135)	9459	-247	2064	604 (31)
C(136)	8727	-455	1665	571 (29)
C(131)	7751	528	1375	360 (22)
C(142)	5149 (5)	-1401 (4)	1165 (1)	666 (34)
C(143)	4169	-1947	1530	807 (41)
C(144)	3513	-1548	2068	712 (34)
C(145)	3837	-602	2241	727 (34)
C(146)	4817	-56	1876	608 (30)
C(141)	5473	-455	1338	382 (22)
P(2)	5636 (2)	7566 (1)	4252 (1)	403 (6)
C(212)	7455 (3)	8981 (3)	3851 (2)	501 (26)
C(213)	7790	10054	3589	600 (31)
C(214)	6688	11118	3439	611 (31)
C(215)	5252	11111	3551	708 (33)
C(216)	4918	10038	3813	553 (28)
C(211)	6019	8974	3963	416 (24)
C(222)	2708 (4)	8254 (4)	4223 (1)	618 (30)
C(223)	1255	8517	4473	708 (35)
C(224)	883	8365	5080	705 (35)
C(225)	1963	7950	5437	741 (37)
C(226)	3415	7686	5187	579 (30)
C(221)	3788	7838	4580	434 (24)
C(232)	7033 (4)	7458 (3)	5167 (2)	513 (27)
C(233)	7862	6856	5613	606 (32)
C(234)	8441	5582	5682	667 (32)
C(235)	8192	4909	5306	740 (34)
C(236)	7364	5511	4861	587 (29)
C(231)	6784	6786	4791	424 (24)
C(242)	6871 (6)	6852 (5)	3165 (2)	902 (45)
C(243)	7101	6141	2722	1278 (65)
C(244)	6406	5247	2795	1137 (59)
C(245)	5480	5064	3312	979 (49)
C(246)	5250	5775	3755	769 (39)
C(241)	5946	6669	3682	531 (28)

solution to 258 K. Crystal size $0.35 \times 0.35 \times 0.12$ mm, Siemens AED2 diffractometer with graphite-monochromated Mo $K\alpha$ radiation, cell parameters from 2θ values (20 – 23°) of 32 reflections measured on both sides of the direct beam. Intensity-data collection in ω/θ scan mode, scan width = 0.51° below α_1 to 0.51° above α_2 , scan time 14–56 s, $2\theta_{max} = 45^\circ$, h – 10 – 0 , k – 12 – 12 , l – 25 – 25 , no significant variation for three standard reflections, semi-empirical absorption correction, transmission 0.306–0.550. 6837 reflections measured, 6517 unique ($R_{int} = 0.014$ for $0kl$ reflections), 5649 with $F > 4\sigma(F)$ for structure solution by Patterson and difference syntheses and blocked-cascade refinement on F with $w^{-1} = \sigma^2(F) + 0.00026F^2$, anisotropic thermal parameters and constraints on phenyl groups [$C-C = 1.395$, $C-H = 0.96$ Å, $C-C-C = C-C-H = 120^\circ$, $U(H) = 1.2U_{eq}(C)$]. 455 parameters, isotropic extinction parameter $x = 3.8 (6) \times 10^{-7}$ [$F'_c = F'_c / (1 + xF'_c / \sin 2\theta)^{1/4}$], $R = 0.0340$, $wR = 0.0405$, mean $\Delta/\sigma = 0.008$, max. = 0.026 , max. $\Delta\rho = 0.92$, min. = $-1.27 e \text{ \AA}^{-3}$, slope of normal probability plot = 1.48. Scattering factors from *International Tables for X-ray Crystallography* (1974); *SHELXTL* programs (Sheldrick, 1985).

Table 2. Selected bond lengths (Å) and angles ($^\circ$)

W–Cu(1)	2.662 (1)	W–Cu(2)	2.665 (1)
W–Cu(3)	2.648 (1)	W–S(1)	2.262 (2)
W–S(2)	2.268 (2)	W–S(3)	2.275 (2)
W–O	1.711 (4)	Cu(1)–Cl(1)	2.154 (2)
Cu(1)–S(1)	2.252 (2)	Cu(1)–S(3)	2.258 (2)
Cu(2)–Cl(2)	2.161 (2)	Cu(2)–S(1)	2.259 (2)
Cu(2)–S(2)	2.255 (2)	Cu(3)–Cl(3)	2.149 (2)
Cu(3)–S(2)	2.247 (2)	Cu(3)–S(3)	2.271 (2)
S(1)–W–S(2)	107.5 (1)	S(1)–W–S(3)	107.4 (1)
S(2)–W–S(3)	108.0 (1)	S(1)–W–O	112.5 (2)
S(2)–W–O	110.0 (2)	S(3)–W–O	111.3 (1)
Cl(1)–Cu(1)–S(1)	122.3 (1)	Cl(1)–Cu(1)–S(3)	129.1 (1)
S(1)–Cu(1)–S(3)	108.4 (1)	Cl(2)–Cu(2)–S(1)	125.1 (1)
Cl(2)–Cu(2)–S(2)	126.7 (1)	S(1)–Cu(2)–S(2)	108.0 (1)
Cl(3)–Cu(3)–S(2)	123.0 (1)	Cl(3)–Cu(3)–S(3)	128.0 (1)
S(2)–Cu(3)–S(3)	108.9 (1)	W–S(1)–Cu(1)	72.3 (1)
W–S(1)–Cu(2)	72.2 (1)	Cu(1)–S(1)–Cu(2)	106.5 (1)
W–S(2)–Cu(2)	72.2 (1)	W–S(2)–Cu(3)	71.8 (1)
Cu(2)–S(2)–Cu(3)	105.3 (1)	W–S(3)–Cu(1)	71.9 (1)
W–S(3)–Cu(3)	71.3 (1)	Cu(1)–S(3)–Cu(3)	108.3 (1)

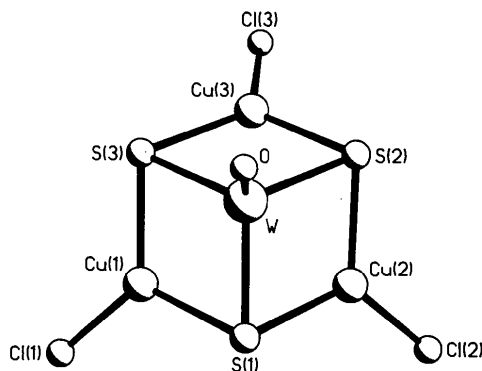


Fig. 1. The [WOS₃(CuCl)₃]²⁻ anion, with the atom-numbering scheme.

Discussion. Atomic coordinates and geometrical parameters of the anion are given in Tables 1 and 2.* The structure of the anion is shown in Fig. 1. The compound is isomorphous, and presumably isostructural, with $[\text{PPh}_4]_2[\text{MoOS}_3(\text{CuCl})_3]$ (Müller, Schimanski & Schimanski, 1983; coordinates have not been published for this structure). The same Mo-centred anion occurs in the double salt $[\text{PPh}_4]_3[\text{MoOS}_3(\text{CuCl})_3][\text{CuCl}_2]$ (Clegg, Garner, Nicholson & Raithby, 1983) and differs from the W-centred anion only in having slightly shorter bonds to Mo than to W. The MOS_3Cu_3 core ($M = \text{Mo}, \text{W}$) is also observed in $[\text{MOS}_3(\text{CuPPh}_3)_3\text{Cl}]$, in which the eighth vertex of the $\text{MS}_3\text{Cu}_3\text{Cl}$ cube, opposite M , is occupied by Cl (Müller, Bögge & Schimanski, 1983); this eighth vertex is vacant in the $[\text{MOS}_3(\text{CuCl})_3]^{2-}$ anions. A cube cluster occurs as the $\text{ReS}_3\text{Cu}_3\text{Cl}$ core of $[\text{ReS}_4(\text{CuCl})_3\text{Cl}]^{2-}$ (Scattergood, Garner & Clegg, 1987), again with Cl in the eighth vertex position. By contrast, all four S atoms are involved in bonding to Mo and Cu in $[\text{MoS}_4(\text{CuCl})_3]^{2-}$, giving a T-shaped MoCu_3 arrangement instead of a pyramidal one (Clegg, Garner & Nicholson, 1983). In $[\text{MS}_4(\text{CuCl})_4]^{2-}$ ($M = \text{Mo}$ or W), a square of Cu atoms surrounds the central M atom, with all S atoms involved in bonding to Mo and Cu; Cl bridges link the anions together into polymeric chains ($M = \text{Mo}$; Nicholson, Flood, Garner & Clegg, 1983) or dimers ($M = \text{W}$; Clegg, Scattergood & Garner, 1987).

*Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44332 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Thus we find that a pseudo-cubane core is adopted in complexes of this type for a central MOS_3 unit, where S bonds to the remaining metal atoms and O does not, and for a central MS_4 unit when an additional atom can occupy the eighth vertex position to complete the distorted cube. Without the additional atom, a central MS_4 unit forms complexes in which all the S atoms bond to the other metal atoms.

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trans-Dichlorobis(ethylenediamine)rhodium(III) Nitrate and Hydrogen Oxalate Salts

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Abstract. (1) $[\text{RhCl}_2(\text{C}_2\text{H}_8\text{N}_2)_2]\text{NO}_3$, $M_r = 356.0$, monoclinic, $P2_1/n$, $a = 6.441$ (2), $b = 9.275$ (3), $c = 10.005$ (3) Å, $\beta = 102.45$ (2)°, $V = 583.6$ (5) Å³, $Z = 2$, $D_x = 2.026$ (3) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 19.0$ cm⁻¹, $F(000) = 356$, $T = 295$ (1) K, final $R = 0.016$ for 1401 observed reflections (θ – 2θ scan) with $F_o^2 > 2\sigma(F_o^2)$. (2) $[\text{RhCl}_2(\text{C}_2\text{H}_8\text{N}_2)_2][\text{C}_2\text{HO}_4] \cdot 2\text{H}_2\text{O}$, $M_r = 419.1$, monoclinic, $P2_1/m$, $a = 6.434$ (2), $b = 15.391$ (4), $c = 7.432$ (2) Å, $\beta = 93.72$ (2)°, $V =$

734.4 (6) Å³, $Z = 2$, $D_x = 1.895$ (3) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 15.4$ cm⁻¹, $F(000) = 424$, $T = 295$ (1) K, final $R = 0.023$ for 1226 observed reflections (θ – 2θ scan) with $F_o^2 > 2\sigma(F_o^2)$. Both compounds contain centrosymmetric dichloro octahedral rhodium(III) complexes with two chelated ethylenediamine ligands in *gauche* conformation in a square plane. The Rh–Cl distances are (1) 2.3325 (3) and (2) 2.3291 (4) Å, and the Rh–N distances are (1)