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Tetraphenylphosphonium (Hydrogensulfido-*S*)trisulfidotungstate(VI)

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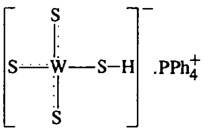
Abstract

The cations and anions of the title compound, $[(C_6H_5)_4P][W(HS)S_3]$, are separated by normal van der Waals distances. The ions each lie on $\bar{4}$ sites such that the H atom of the anion is disordered over four sites with 0.25 occupancies. The W—S distances in the anion are 2.171 (2) Å, with S—W—S angles of 108.1 (1) and 112.4 (2)°. In the cation, identical P—C distances of 1.793 (6) Å are observed, with C—P—C angles of 106.3 (4) and 111.1 (2)°.

Comment

The recently reported synthesis of $[(C_6H_5)_4P][W(C_2H_5S)S_3]$ (Boorman, Wang & Parvez, 1995) allowed exploration of the use of this complex, and other alkylated analogs, as a synthon for heterometallic sulfido–thiolato clusters. In this context, $[(C_6H_5)_4P][W(C_2H_5S)S_3]$ was reacted with CuCl using MeCN as solvent and from this solution, red crystals were isolated. Based on a parallel study of this reaction using ^{1}H NMR, it was believed that the crystals were likely to be a W–S–Cu cluster and hence, an X-ray structure determination was undertaken. The product is shown here to be $[(C_6H_5)_4P][W(HS)S_3]$, (1), for which no single-crystal structure determination had been reported previously. A structure based on X-ray powder data has been published (Königer-Ahlhorn, Schulze & Müller, 1977).



(1)

The observed W—S distance [2.171 (2) Å] is the average of one W—S and three W=S bonds due to disorder of the H atom over four sites. It is comparable with the distances previously reported (Boorman, Wang & Parvez, 1995) for $[(C_6H_5)_4P][W(C_2H_5S)S_3]$; W=S(ave.) 2.154 (3), W—S 2.323 (3) and W—S(ave.) 2.196 (3) Å. Previously reported structures of tungsten containing terminal SH groups involve the anions

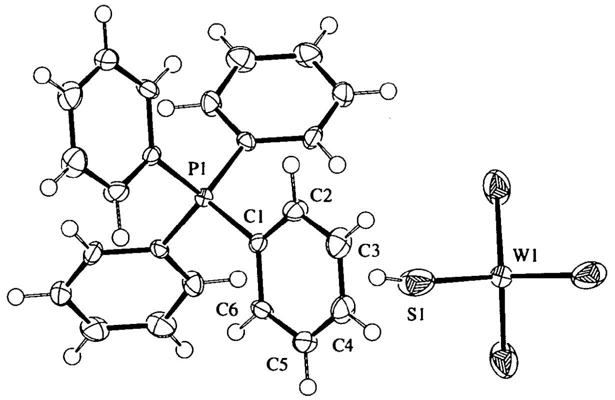


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound. Displacement ellipsoids are plotted at 50% probability level and H atoms have been assigned arbitrary radii; the disordered H atom of the anion has been plotted on one site only.

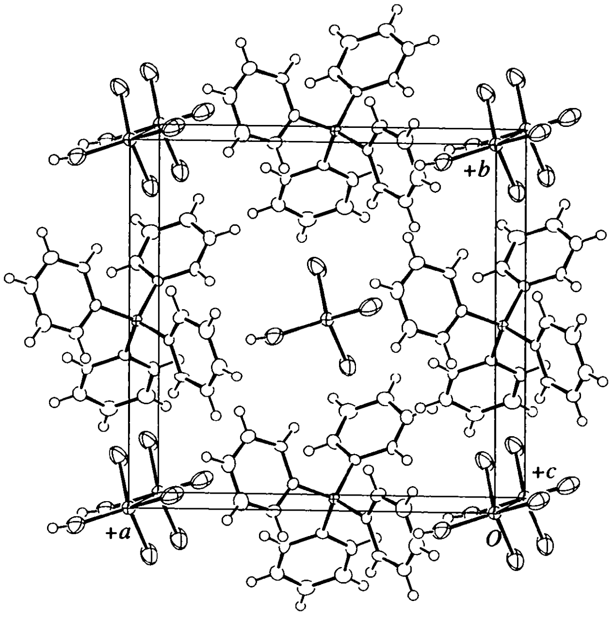


Fig. 2. Unit-cell packing of the title compound.

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$[W_2O(S_2)_2(\mu\text{-}S)(SH)_3]^-$ (Sécheresse, Lefebvre, Daran & Jeannin, 1981) and $[W_2(S_2)_4(S)_2(SH)]^-$ (Sécheresse, Manoli & Potvin, 1986). In both instances, the presence of the H atoms was implied by extended W—S distances and spectroscopic data.

Experimental

All of the following operations were carried out under an atmosphere of dry nitrogen. To a THF (40 ml) solution of $[(C_6H_5)_4P][W(C_2H_5S)S_3]$ (0.300 g, 0.438 mmol) was added CuCl (0.044 g, 0.442 mmol) as a white slurry in THF (5 ml) at 273 K. An immediate color change from milky brown to dark red was observed as the CuCl dissolved and reacted. After 2 h, the solution was filtered to give a red filtrate and a red precipitate. The filtrate was pumped to dryness and the residue washed with ether. After redissolving in THF, ether was added and the solution stored at 273 K until red crystals of X-ray quality were formed (yield 0.045 g, 15%).

Crystal data

$(C_{24}H_{20}P)[W(HS)S_3]$
$M_r = 652.49$
Tetragonal
$I\bar{4}$
$a = 12.995$ (1) Å
$c = 7.143$ (1) Å
$V = 1206.3$ (2) Å^3
$Z = 2$
$D_x = 1.796$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 5.3$ mm^{-1}
$T = 170$ K
Needle
0.45 × 0.20 × 0.15 mm
Dark orange

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.41$, $T_{max} = 0.45$
639 measured reflections
587 independent reflections

575 reflections with $[I > 3\sigma(I)]$
$R_{int} = 0.043$
$\theta_{max} = 25°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 8$
3 standard reflections every 200 reflections intensity decay: 1.3%

Refinement

Refinement on F
$R = 0.024$
$wR = 0.023$
$S = 1.40$
575 reflections
68 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o) + 0.013(F_o^2)]$

$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
W1	0	0	1	0.02728 (9)
S1	0.1323 (2)	−0.0422 (2)	0.8310 (4)	0.0587 (8)
P1	1/2	0	3/4	0.0168 (5)
C1	0.3990 (5)	−0.0448 (5)	0.600 (1)	0.018 (2)
C2	0.3570 (5)	0.0241 (5)	0.472 (2)	0.026 (2)
C3	0.2774 (6)	−0.0058 (6)	0.356 (1)	0.034 (2)
C4	0.2424 (6)	−0.1073 (6)	0.361 (1)	0.033 (2)
C5	0.2858 (5)	−0.1769 (5)	0.486 (3)	0.033 (2)
C6	0.3643 (5)	−0.1466 (5)	0.606 (1)	0.023 (2)

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

W1—S1	2.171 (2)	P1—C1	1.793 (6)
S1—W1—S1^{i}	112.4 (2)	C1^{iv}—P1—C1	106.3 (4)
S1—W1—S1^{ii}	108.0 (1)	P1—C1—C2	118.2 (5)
C1^{iii}—P1—C1	111.1 (2)	P1—C1—C6	121.6 (5)

Symmetry codes: (i) $-x, -y, z$; (ii) $-y, x, 2-z$; (iii) $\frac{1}{2}+y, \frac{1}{2}-x, \frac{3}{2}-z$; (iv) $1-x, -y, z$.

Based on the systematic absences of *hkl* ($h+k+l = 2n + 1$), packing considerations, a statistical analysis of intensity distribution and the successful solution and refinement of the structure, the space group was determined to be $I\bar{4}$ (No. 82). H atoms of the cation were included at geometrically idealized positions with C—H distances of 0.95 Å. A low peak in a difference map was assigned a 25% occupancy to represent the disordered H atom of the anion, which was allowed to refine in a couple of cycles of refinement, but was fixed in the final rounds of calculations.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1296). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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