Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1368). Services for accessing these data are described at the back of the journal.

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Tetraphenylphosphonium Hexatungstate(VI) Acetonitrile Solvate

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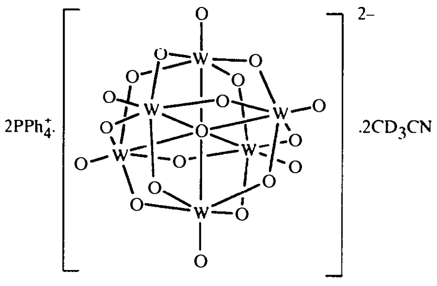
Abstract

Crystals of the title compound, $(C_{24}H_{20}P)_2[W_6O_{19}]$.-$2CD_3CN$, are composed of $[W_6O_{19}]^{2-}$ anions lying on inversion centres, and Ph_4P^+ cations and acetonitrile molecules of solvation in general positions. In the anion, each W atom is bonded to a central O atom, which lies on an inversion centre, a terminal O and four bridging O atoms, with average W—O distances of 2.323 (4), 1.714 (13) and 1.917 (15) Å, respectively.

Comment

It is known that alkylation of the tetrathiotungstate ion with alkyl bromides leads initially to unstable alkylated intermediates and eventually to polytungsten sulfide clusters as condensation products (Dhar & Chandrasekaran, 1989; Boorman *et al.*, 1995). While investigating analogous reactions of the dioxodithiotungstate ion with *tert*-butyl bromide, an NMR-scale reaction was performed in CD_3CN and red crystals were obtained. The crystals were believed to be the alkylated dioxodithiotungstate ion but were shown to be tetraphenylphosphonium hexatungstate acetonitrile solvate, (I), by X-ray diffraction. This finding was unexpected since the W atoms are coordinated exclusively to O atoms in the hexatungstate product, indicating displacement of the S atoms in the starting material.



(I)

The crystal structure is composed of $[W_6O_{19}]^{2-}$ anions (Fig. 1), $C_{24}H_{20}P^+$ cations and acetonitrile (CD_3CN) of solvation, all separated by normal van der Waals distances. The anion has a cage structure in which each W atom is octahedrally bonded to a central O atom, lying on an inversion centre, a terminal O and four bridging O atoms, with mean W—O distances of 2.323 (4), 1.714 (13) and 1.917 (15) Å, respectively. The central O atom exhibits octahedral geometry, with W—O—W angles in the narrow range 89.89 (2)–90.11 (2)°. Similar cage structures for the anion have been reported (Fuchs *et al.*, 1978; Fedin *et al.*, 1992; Hou *et al.*, 1995; Lehtonen & Sillanpää, 1995). The PPh_4 cation

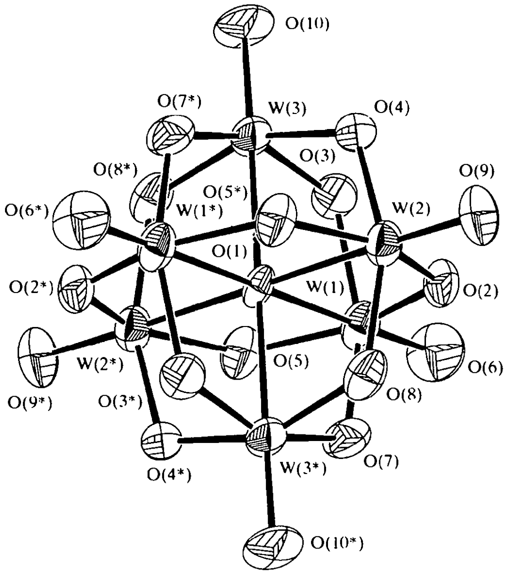


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title anion. Displacement ellipsoids are plotted at 50% probability. The symmetry operation for the starred (*) atoms is 2 − *x*, −*y*, −*z*.

also displays normal bond lengths and angles, with mean P—C and C—C distances of 1.80 (2) and 1.38 (2) Å, respectively.

Experimental

All the following operations were carried out under an atmosphere of dry nitrogen. To an NMR tube containing $[PPh_4]_2[WO_2S_2]$ (0.005 g, 0.0052 mmol), 0.8 ml of CD_3CN was added to give a green solution. ^{t}BuBr (10 μl, 0.0867 mmol) was added by syringe and the reaction maintained at room temperature. After 5 h, an orange colour was observed and after 18 h, a red precipitate and red crystals of the title compound had formed in the NMR tube.

Crystal data

$(C_{24}H_{20}P)_2[W_6O_{19}].2C_2D_3N$
M_r = 2174.04
Monoclinic
$P2_1/n$
a = 13.102 (3) Å
b = 11.570 (2) Å
c = 19.345 (3) Å
β = 101.126 (12)°
V = 2877.3 (9) Å^3
Z = 2
D_x = 2.509 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 10.0–15.0°
μ = 12.07 mm^{-1}
T = 170 K
Prism
0.30 × 0.22 × 0.18 mm
Orange

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (3 reflections) (North *et al.*, 1968)
$T_{\min}$ = 0.055, $T_{\max}$ = 0.114
5095 measured reflections
5095 independent reflections

2765 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 25.0°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 13$
$l = -23 \rightarrow 22$
3 standard reflections every 200 reflections intensity decay: 1.05%

Refinement

Refinement on F
R = 0.035
wR = 0.022
S = 1.31
5095 reflections
368 parameters
H atoms geometrically idealized with C—H 0.95 Å
$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\max}$ = 0.024
$\Delta\rho_{\max}$ = 0.87 e Å^{-3}
$\Delta\rho_{\min}$ = −0.93 e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: 8.0 (5) × 10^{-8}
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

W(1)—O(1)	2.3198 (6)	W(2)—O(5^{i})	1.919 (7)
W(1)—O(2)	1.928 (9)	W(2)—O(8)	1.939 (9)
W(1)—O(3)	1.925 (9)	W(2)—O(9)	1.727 (9)
W(1)—O(5)	1.901 (9)	W(3)—O(1)	2.3189 (6)
W(1)—O(6)	1.697 (8)	W(3)—O(3)	1.896 (8)
W(1)—O(7)	1.901 (9)	W(3)—O(4)	1.944 (9)
W(2)—O(1)	2.3292 (6)	W(3)—O(7^{i})	1.930 (8)
W(2)—O(2)	1.907 (7)	W(3)—O(8^{i})	1.903 (9)
W(2)—O(4)	1.910 (9)	W(3)—O(10)	1.718 (10)

Symmetry code: (i) $2 - x, -y, -z$.

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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[Pd(H*L*)Cl$_2$] and [Pd*L*$_2$], where H*L* is 2-(3-Pyrazolyl)pyridine

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Abstract

The complexes *cis*-[Pd(H*L*)Cl$_2$] {dichloro[2-(3-pyrazolyl-N^2)pyridine-*N*]palladium(II), $[PdCl_2(C_8H_7N_3)]$} and *trans*-[Pd*L*$_2$] {bis[2-(3-pyrazolyl-N^2)pyridinato-