

Structural Characterization of an Oxotungsten(IV) Complex, [WBr(Me₂PCH₂CH₂PMe₂)₂]Br·5H₂O

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Abstract. (1) Bromobis[ethylenebis(dimethylphosphine-*P,P'*)]oxotungsten(IV) bromide pentahydrate, [WBrO(C₆H₁₆P₂)₂]Br·5H₂O, $M_r = 750.03$, orthorhombic, *Pbcm*, $a = 9.595$ (2), $b = 12.278$ (3), $c = 23.488$ (6) Å, $V = 2767$ (2) Å³, $Z = 4$, $D_x = 1.800$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 73.75$ cm⁻¹, $F(000) = 1464$, $T = 294$ K, $R = 0.040$ for 1673 observed reflections. The coordination of W is distorted octahedral with Br *trans* to O and the two phosphine ligands forming five-membered chelate rings. The W=O distance is 1.736 (9) Å. The mean O–W–P angle is 96.9 (4)°.

Introduction. During the course of a synthetic program directed towards the preparation of sulfur-capped tritungsten cluster compounds we inadvertently prepared and structurally characterized [WBr(Me₂PCH₂CH₂PMe₂)₂]Br·5H₂O. This compound was synthesized from two sets of starting materials. Due to the paucity of structural data on oxotungsten complexes, we report this work here.

Experimental. The syntheses of (1) follow. Method *A*. WBr₃(THF)₃ (420 mg, 0.66 mmol) and NaHS (37 mg, 0.66 mmol) were suspended in 15 mL of THF and cooled to 195 K. Methanol (3 mL) was added to dissolve the sulfide. Dmpe (110 µL, 0.66 mmol) was introduced and the mixture was slowly warmed to room temperature and stirred for 16 h. A blue precipitate formed which was separated from the brown solution by filtration under argon. The solution was then absorbed on a silica-gel column. After the column had been washed with a dichloromethane/acetone mixture (1:1), a brown band remained on top of the column which was eluted with an acetone/methanol mixture (1:1). Slow evaporation of the brown solution in air afforded red crystals of (1). Method *B*. A suspension of W₃S₇Br₄ (250 mg, 0.228 mmol) in 20 mL of THF and dmpe (570 µL, 3.42 mmol) was stirred for 72 h. The mixture was filtered under argon leaving a black residue. The residue was suspended in 10 mL of

methanol and stirred for 5 h. This mixture was then filtered under argon and the pale brown filtrate was allowed to evaporate in air affording red crystals of (1).

A small red needle-like crystal was selected from the product and was shown to be of good quality by polarized-light microscopy. The crystal was sealed with epoxy cement to the end of a glass fiber and mounted on the goniometer head of a Syntex P3 diffractometer. The crystal parameters and basic information relating to data collection and structure refinement are summarized in Table 1. Periodically monitored check reflections displayed no significant change in intensity throughout the data collection. The W atom was located by direct methods (*SHELXS86*; Sheldrick, 1986) and the remainder of the molecule was located and refined by alternating difference Fourier maps and least-squares cycles employing the Enraf–Nonius (1979) *Structure Determination Package*. The H atoms were not included in the model. All atoms were refined anisotropically. No disorder or other non-routine problems arose. Atomic scattering factors were those of *SDP*.

Discussion. The positional parameters and equivalent isotropic displacement parameters are given in Table 2.† The structure of the oxotungsten cation is depicted in Fig. 1 where the atom-numbering scheme is also defined. A unit-cell diagram is shown in Fig. 2. Table 3 presents selected important interatomic distances and angles.

There are very few oxotungsten(IV) complexes known. The first report describing preparation in moderate yields of WOCl₂(PR₃)₃, PR₃ = PMePh₂, PMe₂Ph and PEt₂Ph, appeared in 1972 (Butcher, Chatt, Leigh & Richards, 1972). In 1983 more efficient preparative methods for the PMe₃, PMe₂Ph and PMePh₂ derivatives were reported. These compounds

† Lists of structure factors and anisotropic thermal parameters, and fuller lists of bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51755 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Crystallographic data for* $[\text{WOBr}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]\text{Br}\cdot 5\text{H}_2\text{O}$

Systematic absences	$0kl: k = 2n + 1$ $h0l: l = 2n + 1$
Crystal size (mm)	$0.55 \times 0.45 \times 0.35$
Data collection instrument	Syntex P3
Orientation reflections: number; range, 2θ (°)	$25; 20 < 2\theta < 30$
Scan method	ω - 2θ
Data collection range (°)	$4 \leq 2\theta \leq 50$
h, k, l , ranges	$0 < h < 12$ $0 < k < 15$ $0 < l < 28$
No. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	2068, 1673
No. of parameters refined	119
Transmission factors: max., min.	1.000, 0.896
R^*	0.0399
wR^\dagger	0.0600
Quality-of-fit indicator‡	1.283
Largest shift/e.s.d. final cycle	0.01
Largest peak ($e \text{ \AA}^{-3}$)	2.27§ -0.88

$$* R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^\dagger wR = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$^\ddagger \text{Quality-of-fit} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{(N_{\text{obs}} - N_{\text{parameters}})} \right]^{1/2}$$

§ The second highest positive peak is $1.39 e \text{ \AA}^{-3}$. Both peaks are within 0.9 \AA of the W atom. All other peaks are random and below $0.8 e \text{ \AA}^{-3}$.

were characterized spectroscopically and utilized in some exchange reactions to give $\text{WOX}_2(\text{Me}_3)_3$ with $X = \text{NCO}$ and NCS and with $X_2 = \text{Me}_2\text{NCS}_2$ (Carmona, Sanchez, Poveda, Jones & Hefner, 1983). The preparation of three diphosphine compounds of the type $[\text{WOC}(\text{L-L})_2]\text{BPh}_4$, where $\text{L-L} = \text{dppe}$, $o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$ and $\text{cis-Ph}_2\text{PCH}=\text{CHPPh}_2$, were also reported (Levason, McAuliffe & McCullough, 1977). The first crystallographically characterized oxotungsten(IV) compound, $\text{WOC}(\text{PMePh}_2)_2(\text{CH}_2=\text{CH}_2)$, (2), was reported in 1986 (Su, Cooper, Geib, Rheingold & Mayer, 1986). More recently, Cotton & Llusar (1988) reported a structural study of $[\text{WOC}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]\text{ClO}_4$, (3) and $[\text{WOC}\{\text{Me}_2\text{PCH}_2\text{P}(\text{S})\text{Me}_2\}_2]\text{PF}_6$, (4). The compound we report here is closely related to (3) and shares several key characteristics with (2). The W=O bond lengths are the same to within $\pm 3\sigma$, viz W=O 1.736 (9), 1.714 (6), 1.68 (1) and 1.711 (5) Å for (1), (2), (3) and (4), respectively. The W=O unit appears to demand a large solid angle in the coordination sphere as all O-W-P angles are greater than 90° . We also note that (1) crystallizes with five interstitial water molecules which results in a layered structure with extensive hydrogen bonding (see Fig. 2).

Table 2. *Positional and equivalent isotropic displacement parameters and their estimated standard deviations for* $[\text{WOBr}(\text{dmpe})_2]\text{Br}\cdot 5\text{H}_2\text{O}$

The equivalent isotropic displacement parameter is: $\frac{1}{3}[a^2 B_{11} + b^2 B_{22} + c^2 B_{33} + 2ab(\cos\gamma)B_{12} + 2ac(\cos\beta)B_{13} + 2bc(\cos\alpha)B_{23}]$.

	x	y	z	$B_{\text{eq}}(\text{Å}^2)$
W	0.22446 (6)	0.00611 (4)	0.250	2.34 (1)
Br(-)	0.0273 (2)	0.250	0.500	6.34 (5)
Br(1)	0.3882 (2)	-0.1705 (1)	0.250	4.29 (4)
P(1)	0.3788 (3)	0.0557 (2)	0.3310 (1)	3.15 (6)
P(2)	0.1009 (3)	-0.0858 (2)	0.3304 (1)	3.43 (6)
O	0.124 (1)	0.1238 (8)	0.250	3.0 (2)
C(11)	0.349 (1)	0.1961 (9)	0.3544 (6)	5.0 (3)
C(12)	0.572 (1)	0.046 (1)	0.3276 (6)	5.0 (3)
C(13)	0.338 (2)	-0.031 (1)	0.3925 (5)	5.8 (3)
C(21)	0.100 (1)	-0.2337 (9)	0.3357 (6)	4.5 (3)
C(22)	-0.089 (1)	-0.052 (1)	0.3363 (7)	6.5 (4)
C(23)	0.172 (2)	-0.040 (1)	0.3980 (6)	6.4 (4)
O1	0.269 (1)	0.6214 (9)	0.4534 (5)	7.6 (3)
O2	0.310 (1)	0.3977 (8)	9.4653 (5)	6.8 (3)
O3	0.520 (1)	0.250	0.500	7.2 (4)

Table 3. *Selected bond distances (Å) and angles (°) for* $[\text{WOBr}(\text{dmpe})_2]\text{Br}\cdot 5\text{H}_2\text{O}$

Numbers in parentheses are estimated standard deviations in the least significant digits.

W-Br(1)	2.678 (2)	W-P(1)	2.487 (3)
W-O	1.736 (9)	W-P(2)	2.500 (3)
Br(1)-W-P(1)	81.31 (7)	P(2)-W-P(2)'	98.2 (1)
Br(1)-W-P(2)	84.98 (7)	P(1)-W-P(1)'	99.9 (1)
Br(1)-W-O	177.8 (3)	P(1)-W-O	97.3 (2)
P(1)-W-P(2)	79.3 (1)	P(2)-W-O	96.5 (2)
P(1)-W-P(2)'	166.2 (1)		

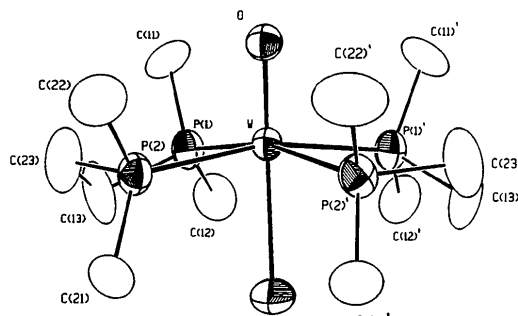
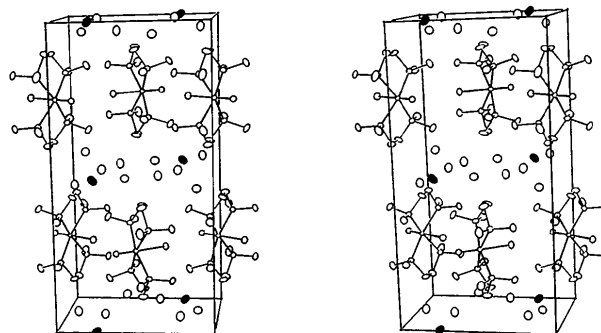


Fig. 1. A view of the cation in compound (1). Atoms are represented by displacement ellipsoids at the 50% level.

Fig. 2. Unit-cell diagram for (1). Solid ellipsoids represent bromide ions. Axes orientation: b across, c down, a toward viewer.

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Protonated Phosphorus Ylides: Tetrachlorometalates(II) $2[C_6H_5C(O)CH_2P(C_6H_5)_3]^+.[MCl_4]^{2-}$, $M = Co$ or Ni

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Abstract. (Benzoylmethyl)triphenylphosphonium tetrachlorocobaltate(II), $2C_{26}H_{22}OP^+CoCl_4^{2-}$, $M_r = 963.54$, triclinic, $P\bar{1}$, $a = 10.660$ (6), $b = 15.631$ (8), $c = 15.760$ (8) Å, $\alpha = 110.03$ (4), $\beta = 96.53$ (5), $\gamma = 106.03$ (4)°, $V = 2307$ (2) Å³, $Z = 2$, $D_x = 1.39$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 7.11$ cm⁻¹, $F(000) = 994$, $T = 296$ K, $R_F = 6.36\%$ for 4005 observed reflections and 455 least-squares parameters. (Benzoylmethyl)triphenylphosphonium tetrachloronickelate(II), $2C_{26}H_{22}OP^+NiCl_4^{2-}$, $M_r = 963.30$, triclinic, $P\bar{1}$, $a = 10.652$ (3), $b = 15.626$ (5), $c = 15.749$ (7) Å, $\alpha = 109.92$ (3), $\beta = 96.48$ (3), $\gamma = 106.08$ (2)°, $V = 2305$ (1) Å³, $Z = 2$, $D_x = 1.39$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 6.44$ cm⁻¹, $F(000) = 920$, $T = 296$ K, $R_F = 4.38\%$ for 4231 observed reflections and 454 least-squares parameters. The structures are isomorphous and contain previously reported tetrachlorometalate(II) anions. The cation reflects the effects of protonation. Lengthening of the P–C(methylene) bond, as well as the shortening of the carbonyl C=O bond is observed, relative to the dimensions of the free ylide. The M^{II} environments are tetrahedral, surrounded by two protonated ylide cations.

Introduction. The title structures should offer indirect confirmation of the proposed structures of a series of similar phosphonium salts of a variety of chloro, bromo and mixed bromochloro metalates previously reported by Burmeister, Silver, Weleski, Schweizer & Kopay (1973).

Experimental. The metalates were prepared by the addition of benzoylmethylenetriphenylphosphorane to

the anhydrous metal(II) chloride in refluxing acetonitrile. Cobaltate crystals were obtained by the slow evaporation of an acetone solution. Blue-green, $0.42 \times 0.22 \times 0.22$ mm, mounted on a glass fiber. $2\theta_{max} = 46^\circ$, range of $h = \pm 12$, $k = \pm 18$, $l = +18$, 6666 reflections collected, 6398 independent reflections, three standards every 197 reflections, variation $< 1\%$, $R_{int} = 6.88\%$, 2393 unobserved reflections, 4005 observed reflections with $F_o > 5\sigma(F_o)$, direct-methods (*SOLV*) solution, empirical absorption correction (*XEMP*), max. and min. values 0.923 and 0.521, refinement on F for 455 least-squares parameters. $R_F = 6.36\%$, $wR_F = 6.45\%$, $S = 1.490$, $g = 0.001$, $w^{-1} = \sigma^2(F_o) + g(F_o)^2$, $\Delta/\sigma = 0.036$, $(\Delta/\rho)_{max} = 0.577$, $(\Delta/\rho)_{min} = -1.00$ e Å⁻³. Nickelate crystals were obtained by the slow evaporation of an acetone solution. Blue, $0.24 \times 0.35 \times 0.42$ mm, mounted on a glass fiber. $2\theta_{max} = 45^\circ$, range of $h = \pm 12$, $k = \pm 17$, $l = +17$, 6292 reflections collected, 6027 independent reflections, three standards every 197 reflections, variation $< 1\%$, $R_{int} = 1.65\%$, 1796 unobserved reflections, 4231 observed reflections with $F_o > 5\sigma(F_o)$, direct-methods (*SOLV*) solution, no absorption correction, refinement on F for 454 least-squares parameters. $R_F = 4.38\%$, $wR_F = 4.71\%$, $S = 1.196$, $g = 0.001$, $w^{-1} = \sigma^2(F_o) + g(F_o)^2$, $\Delta/\sigma = 0.101$, $(\Delta/\rho)_{max} = 0.330$, $(\Delta/\rho)_{min} = -0.224$ e Å⁻³.

Nicolet *R3m/μ* diffractometer, graphite monochromator, unit cell from least-squares fit of angular settings of 25 reflections ($21 < 2\theta < 26^\circ$). Phenyl rings constrained to fit rigid hexagons [$d(C-C) = 1.395$ Å], all non-H atoms anisotropic, H atoms calculated and fixed in idealized positions [$d(C-H) = 0.96$ Å, $U = 1.2U$ of attached C]. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). *SHELXTL* program system (Sheldrick, 1984).

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