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Structural Characterization of Two Oxotungsten(IV) Complexes, $[WOCl(Me_2PCH_2CH_2PMe_2)_2]ClO_4$ and $[WOCl\{Me_2PCH_2P(S)Me_2\}_2]PF_6$

BY F. ALBERT COTTON* AND ROSA LLUSAR

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843, USA

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Abstract. (1) Chlorobis[ethylenebis(dimethylphosphine-*P,P'*)oxotungsten(IV) perchlorate, $[WClO(C_6H_{16}P_2)_2]ClO_4$, $M_r = 635{\cdot}04$, monoclinic, $P2_1/n$, $a = 11{\cdot}823\,(3)$, $b = 14{\cdot}980\,(3)$, $c = 13{\cdot}794\,(3)$ Å, $\beta = 96{\cdot}04\,(2)°$, $V = 2429\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}74$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 53{\cdot}56$ cm^{-1}, $F(000) = 1248$, $T = 284$ K, $R = 0{\cdot}056$ for 1691 observed reflections. (2) Chloro[dimethyl(dimethylphosphinomethyl)thiophosphoric acid-*P,S*]oxotungsten(IV) hexafluorophosphate, $[WClO(C_5H_{14}P_2S)_2]PF_6$, $M_r = 716{\cdot}63$, monoclinic, $P2_1/c$, $a = 12{\cdot}4463\,(9)$, $b = 8{\cdot}6000\,(9)$, $c = 23{\cdot}260\,(2)$ Å, $\beta = 98{\cdot}214\,(6)°$, $V = 2464\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}932$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 54{\cdot}26$ cm^{-1}, $F(000) = 1392$, $T = 284$ K, $R = 0{\cdot}0336$ for 3241 observed reflections. In each case the coordination of W is distorted octahedral with Cl *trans* to O and the two ligands forming roughly coplanar five-membered chelate rings. For (1) and (2) the W=O distances are $1{\cdot}68\,(1)$ and $1{\cdot}711\,(5)$ Å, respectively. In (1) the mean O—W—P angle is $97{\cdot}6\,(15)°$. In (2) the two chelate rings are arranged to give *cis*-S_2 and *cis*-P_2 coordination. The mean O—W—P and O—W—S angles are $91{\cdot}6°$ and $101{\cdot}5°$, respectively. The W—Cl bonds are relatively long, being $2{\cdot}539\,(5)$ and $2{\cdot}554\,(2)$ Å in (1) and (2), respectively.

Introduction. We have unintentionally prepared and structurally characterized two oxotungsten(IV) complexes in the course of a synthetic program directed towards the preparation of sulfur-capped tritungsten cluster compounds. Because of the dearth of structural data on oxotungsten(IV) species, we report this work here, even though the methods of preparation are quite unsatisfactory. No doubt they can be improved, but we have no plans to undertake such work.

Experimental. The two compounds described here were obtained as follows. A suspension of WCl_4 (684 mg, 2·1 mmol) in 20 mL of THF was reduced with sodium amalgam (2·1 mmol). The resulting green solution was filtered under argon over NaHS (112 mg, 2 mmol) and methanol (10 mL) was added in order to dissolve the sulfide. Dmpe (330 μL, 2 mmol) or dmpm (300 μL, 2 mmol) was introduced and the reaction mixture was refluxed for 2 h. After the reaction mixture had cooled to room temperature, a brown precipitate formed which was separated from the brown solution by filtration. This solution was absorbed on a silica gel column. After

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* Author to whom correspondence should be addressed.

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Table 1. *Crystallographic data for compounds* (1) *and* (2)

	Compound (1)	Compound (2)
Systematic absences	$0k0$, $k \neq 2n$; $h0l$, $h + l \neq 2n$	$0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$
Crystal size, mm	0·15 × 0·15 × 0·10	0·30 × 0·20 × 0·20
Data collection instrument	Rigaku	Enraf–Nonius CAD-4
Orientation reflections, number, range, 2θ(°)	22, 14·0–24·0	25, 9·5–18·0
Scan method	ω–2θ	ω–2θ
Data collection range, 2θ(°)	$4 < 2\theta < 50$	$4 < 2\theta < 45$
No. unique data, total	2600	4640
with $F_o^2 > 3\sigma(F_o^2)$	1691	3241
Number of parameters refined	217	235
Transmission factors, max., min.	1·0, 0·72	0·99, 0·61
R*	0·056	0·0336
wR†	0·070	0·0448
Quality-of-fit indicator‡	1·315	1·278
Largest shift/e.s.d., final cycle	0·04	0·00
Largest peak (e Å^{-3})	1·06	0·887

* $R = \sum \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert / \sum \lvert F_o \rvert$.

† $wR = [\sum w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \sum w \lvert F_o \rvert^2]^{1/2}$; $w = 1/\sigma^2(\lvert F_o \rvert)$.

‡ Quality-of-fit $= [\sum w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$.

Table 2. *Positional parameters and their e.s.d.'s for* (1)

	x	y	z	B_{eq}(Å^2)
W(1)	0·14259 (9)	0·11191 (6)	0·15052 (7)	3·20 (2)
Cl(1)	0·2199 (7)	0·2540 (4)	0·2331 (5)	5·4 (2)
O(1)	0·095 (1)	0·0157 (9)	0·098 (1)	3·9 (4)
P(1)	0·1499 (7)	0·0627 (5)	0·3235 (5)	4·6 (2)
P(2)	0·3437 (6)	0·0630 (5)	0·1794 (5)	4·6 (2)
P(3)	−0·0362 (6)	0·1987 (4)	0·1404 (4)	4·2 (2)
P(4)	0·1557 (7)	0·1975 (5)	−0·0023 (5)	4·8 (2)
C(1)	0·087 (3)	−0·047 (2)	0·336 (2)	6·7 (8)
C(2)	0·091 (3)	0·133 (2)	0·416 (2)	7·2 (9)
C(3)	0·297 (2)	0·049 (3)	0·373 (2)	7·8 (9)
C(4)	0·367 (2)	0·009 (2)	0·302 (2)	6·9 (7)
C(5)	0·459 (2)	0·148 (2)	0·174 (3)	9 (1)
C(6)	0·384 (3)	−0·030 (2)	0·104 (2)	7·8 (9)
C(7)	−0·088 (2)	0·257 (2)	0·244 (2)	5·8 (7)
C(8)	−0·159 (2)	0·138 (2)	0·088 (2)	5·6 (7)
C(9)	−0·033 (3)	0·289 (2)	0·052 (2)	7·2 (8)
C(10)	0·037 (3)	0·276 (2)	−0·028 (2)	9·3 (9)
C(11)	0·142 (4)	0·129 (2)	−0·111 (2)	9 (1)
C(12)	0·281 (3)	0·268 (2)	−0·014 (2)	9 (1)
Cl(2)	0·2749 (6)	0·0037 (5)	0·6740 (5)	5·8 (2)
O(2)	0·351 (2)	−0·013 (2)	0·609 (2)	12·0 (9)
O(3)	0·334 (2)	0·019 (2)	0·766 (1)	8·8 (6)
O(4)	0·225 (2)	0·088 (2)	0·645 (2)	11·9 (8)
O(5)	0·189 (3)	−0·053 (2)	0·678 (3)	16 (1)

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

Table 3. *Positional parameters and their e.s.d.'s for* (2)

	x	y	z	B_{eq}(Å^2)
W(1)	−0·05046 (2)	0·22232 (4)	0·34314 (1)	2·367 (5)
Cl(1)	−0·1000 (2)	0·1042 (3)	0·43660 (8)	3·97 (4)
S(1)	−0·2057 (2)	0·4042 (3)	0·34207 (9)	3·45 (4)
S(2)	0·0534 (2)	0·4249 (3)	0·40134 (9)	3·65 (5)
P(1)	−0·1868 (2)	0·0300 (3)	0·30356 (8)	2·88 (4)
P(2)	0·1812 (2)	0·3225 (3)	0·45087 (9)	3·41 (4)
P(3)	0·1068 (2)	0·0520 (3)	0·37075 (8)	3·07 (4)
P(4)	−0·3393 (2)	0·2728 (3)	0·3447 (1)	3·75 (5)
O(1)	−0·0160 (4)	0·2540 (7)	0·2755 (2)	3·6 (1)
C(1)	−0·3796 (9)	0·273 (1)	0·4163 (4)	6·0 (3)
C(2)	−0·3198 (8)	0·069 (1)	0·3269 (5)	5·8 (2)
C(3)	−0·1728 (8)	−0·179 (1)	0·3185 (4)	4·6 (2)
C(4)	−0·2125 (7)	0·040 (1)	0·2245 (3)	4·9 (2)
C(5)	0·2036 (7)	0·065 (1)	0·3188 (4)	5·3 (2)
C(6)	0·0955 (9)	−0·157 (1)	0·3854 (5)	5·7 (2)
C(7)	0·3071 (8)	0·403 (2)	0·4364 (5)	7·3 (3)
C(8)	0·1721 (9)	0·354 (2)	0·5255 (4)	6·4 (3)
C(9)	−0·454 (1)	0·352 (2)	0·2953 (6)	8·5 (4)
C(10)	0·1828 (7)	0·111 (1)	0·4418 (4)	4·3 (2)
P(6)	−0·4838 (2)	0·2895 (3)	0·0976 (1)	4·70 (6)
F(1)	−0·5805 (6)	0·369 (1)	0·0600 (4)	11·2 (2)
F(2)	−0·4664 (5)	0·4453 (9)	0·1329 (4)	10·9 (2)
F(3)	−0·3877 (7)	0·213 (1)	0·1339 (4)	14·9 (3)
F(4)	−0·5059 (6)	0·1361 (9)	0·0630 (4)	11·2 (2)
F(5)	−0·3972 (7)	0·330 (2)	0·0612 (4)	15·0 (3)
F(6)	−0·5689 (7)	0·243 (1)	0·1365 (5)	14·0 (3)

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

the column had been washed with an acetone/hexane mixture (4:1), a dark purple band remained on the top of the column; this was eluted with methanol. In the case of compound (1), addition of $NaClO_4$ to the above purple solution followed by slow evaporation in air afforded black crystals together with a small amount of orange crystals. The orange crystals have been characterized by X-ray crystallography to be $[WClO\{(CH_3)_2P(CH_2)_2P(CH_3)_2\}_2]ClO_4$. The major product (the black crystals) is still under investigation. Preliminary crystallographic studies have shown the presence of a trinuclear W_3 unit bicapped by sulfur atoms.

In the case of compound (2), the purple solution was treated with NH_4PF_6 and then allowed to evaporate slowly in air to give a blue powder together with a small amount of orange crystals which have been characterized as $[WClO\{(CH_3)_2P(CH_2)PS(CH_3)_2\}_2]PF_6$.

The two compounds crystallized as orange prisms having well developed faces. In each case the crystal was sealed with epoxy cement to the end of a glass fiber. The crystal parameters and basic information relating to data collection and structure refinement are summarized in Table 1. Data of a unique quadrant ($+h$, $+k$, $\pm l$) were collected in the ranges 4–50° and 4–45° (in 2θ) for compounds (1) and (2) respectively on an automated four-circle diffractometer.

Periodically monitored check reflections displayed no significant change in intensity throughout the experiment for compound (2). In the case of compound (1), the intensities of three check reflections decreased by an average of 10% during 30·7 h of X-ray exposure time. In each case some of the atoms were located by direct methods (*SHELX*86; 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. Anisotropic thermal parameters were utilized for all the remaining atoms. Atomic scattering factors were those of *SHELX*.

Discussion. The positional parameters and equivalent isotropic thermal parameters are given in Tables 2 and 3. The structures of the oxotungsten cations are depicted in Figs. 1 and 2 where the atom-numbering schemes are also defined. Tables 4 and 5 present interatomic distances and angles.*

Little has been known heretofore of oxotungsten(IV) complexes. The earliest report appeared in 1972 and described the preparation in moderate yields of $WOCl_2(PR_3)_3$ compounds with $PR_3 = PMePh_2$, PMe_2Ph and PEt_2Ph (Butcher, Chatt, Leigh & Richards, 1972). About a decade later, more efficient preparative methods for the PMe_2Ph and $PMePh_2$ compounds as well as $WOCl_2(PMe_3)_3$ were reported, the compounds were characterized spectroscopically, and some exchange reactions to give $WOX_2(PMe_3)_3$ with $X =$ NCO and NCS and $WOX_2(PMe_3)$ with $X = Me_2NCS_2$ were described (Carmona, Sanchez, Poveda, Jones & Hefner, 1983). In 1977 the preparation of three diphosphine compounds of the type $[WOCl(L\text{-}L)_2]BPh_4$, where $L\text{-}L$ = 1,2-bis(diphenylphosphino)ethane, *o*-

Table 4. *Bond lengths* (Å) *and angles* (°) *for* (1)

W(1)–Cl(1)	2·539 (5)	P(3)–C(7)	1·83 (2)
W(1)–O(1)	1·68 (1)	P(3)–C(8)	1·80 (2)
W(1)–P(1)	2·489 (6)	P(3)–C(9)	1·83 (2)
W(1)–P(2)	2·479 (7)	P(4)–C(10)	1·84 (3)
W(1)–P(3)	2·473 (6)	P(4)–C(11)	1·81 (2)
W(1)–P(4)	2·486 (5)	P(4)–C(12)	1·84 (3)
P(1)–C(1)	1·82 (3)	C(3)–C(4)	1·46 (4)
P(1)–C(2)	1·85 (2)	C(9)–C(10)	1·47 (3)
P(1)–C(3)	1·81 (3)	Cl(2)–O(2)	1·36 (2)
P(2)–C(4)	1·87 (2)	Cl(2)–O(3)	1·40 (2)
P(2)–C(5)	1·87 (3)	Cl(2)–O(4)	1·43 (2)
P(2)–C(6)	1·83 (2)	Cl(2)–O(5)	1·33 (3)
Cl(1)–W(1)–O(1)	178·1 (5)	C(4)–P(2)–C(6)	100· (1)
Cl(1)–W(1)–P(1)	81·0 (2)	C(5)–P(2)–C(6)	105· (2)
Cl(1)–W(1)–P(2)	83·2 (2)	W(1)–P(3)–C(7)	124·0 (8)
Cl(1)–W(1)–P(3)	81·4 (2)	W(1)–P(3)–C(8)	114·1 (9)
Cl(1)–W(1)–P(4)	84·1 (2)	W(1)–P(3)–C(9)	111 (1)
O(1)–W(1)–P(1)	97·9 (5)	C(7)–P(3)–C(8)	103· (1)
O(1)–W(1)–P(2)	95·1 (5)	C(7)–P(3)–C(9)	101· (1)
O(1)–W(1)–P(3)	100·4 (5)	C(8)–P(3)–C(9)	100· (1)
O(1)–W(1)–P(4)	97·0 (4)	W(1)–P(4)–C(10)	112·4 (9)
P(1)–W(1)–P(2)	79·8 (2)	W(1)–P(4)–C(11)	114· (1)
P(1)–W(1)–P(3)	98·8 (2)	W(1)–P(4)–C(12)	120· (1)
P(1)–W(1)–P(4)	165·0 (2)	C(10)–P(4)–C(11)	102· (2)
P(2)–W(1)–P(3)	164·5 (2)	C(10)–P(4)–C(12)	102· (2)
P(2)–W(1)–P(4)	98·3 (2)	C(11)–P(4)–C(12)	105· (2)
P(3)–W(1)–P(4)	79·1 (2)	P(1)–C(3)–C(4)	113· (2)
W(1)–P(1)–C(1)	112·8 (9)	P(2)–C(4)–C(3)	113· (2)
W(1)–P(1)–C(2)	121·0 (8)	P(3)–C(9)–C(10)	117· (2)
W(1)–P(1)–C(3)	109· (1)	P(4)–C(10)–C(9)	115· (2)
C(1)–P(1)–C(2)	105· (1)	O(2)–Cl(2)–O(3)	109· (1)
C(1)–P(1)–C(3)	104· (1)	O(2)–Cl(2)–O(4)	105· (2)
C(2)–P(1)–C(3)	103· (1)	O(2)–Cl(2)–O(5)	118· (2)
W(1)–P(2)–C(4)	109 (1)	O(3)–Cl(2)–O(4)	105· (1)
W(1)–P(2)–C(5)	119 (1)	O(3)–Cl(2)–O(5)	112· (2)
W(1)–P(2)–C(6)	116 (1)	O(4)–Cl(2)–O(5)	106· (2)
C(4)–P(2)–C(5)	107· (1)		

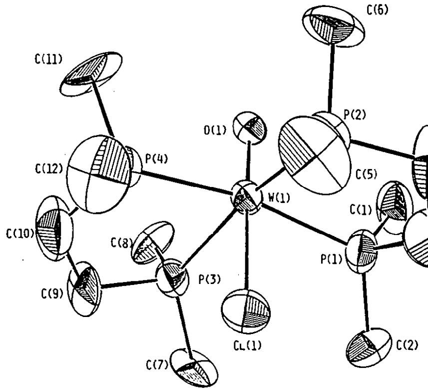

Fig. 1. A view of the cation in compound (1). Atoms are represented by thermal displacement ellipsoids at the 40% level.

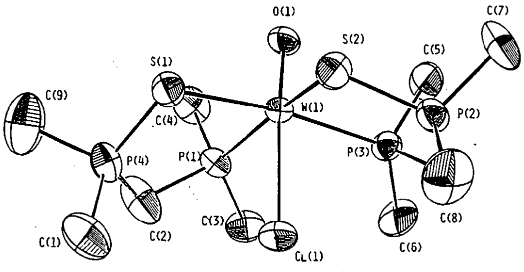

Fig. 2. A view of the cation in compound (2). Atoms are represented by thermal displacement ellipsoids at the 40% level.

Table 5. *Bond lengths* (Å) *and angles* (°) *for* (2)

W(1)–Cl(1)	2·554 (2)	P(2)–C(10)	1·835 (9)
W(1)–S(1)	2·483 (2)	P(3)–C(5)	1·83 (1)
W(1)–S(2)	2·457 (2)	P(3)–C(6)	1·84 (1)
W(1)–P(1)	2·452 (2)	P(3)–C(10)	1·853 (8)
W(1)–P(3)	2·456 (2)	P(4)–C(1)	1·81 (1)
W(1)–O(1)	1·711 (5)	P(4)–C(2)	1·83 (1)
S(1)–P(4)	2·019 (3)	P(4)–C(9)	1·83 (1)
S(2)–P(2)	2·027 (3)	P(6)–F(1)	1·540 (8)
P(1)–C(2)	1·85 (1)	P(6)–F(2)	1·571 (9)
P(1)–C(3)	1·834 (9)	P(6)–F(3)	1·514 (9)
P(1)–C(4)	1·822 (8)	P(6)–F(4)	1·550 (9)
P(2)–C(7)	1·79 (1)	P(6)–F(5)	1·50 (1)
P(2)–C(8)	1·78 (1)	P(6)–F(6)	1·54 (1)
Cl(1)–W(1)–S(1)	88·67 (7)	W(1)–P(3)–C(5)	111·5 (3)
Cl(1)–W(1)–S(2)	89·14 (7)	W(1)–P(3)–C(6)	123·5 (3)
Cl(1)–W(1)–P(1)	79·23 (6)	W(1)–P(3)–C(10)	110·9 (3)
Cl(1)–W(1)–P(3)	79·67 (7)	C(5)–P(3)–C(6)	105·0 (5)
Cl(1)–W(1)–O(1)	165·7 (2)	C(5)–P(3)–C(10)	105·8 (4)
S(1)–W(1)–S(2)	84·63 (7)	C(6)–P(3)–C(10)	98·2 (4)
S(1)–W(1)–P(1)	85·72 (7)	S(1)–P(4)–C(1)	111·4 (4)
S(1)–W(1)–P(3)	165·54 (7)	S(1)–P(4)–C(2)	113·2 (3)
S(1)–W(1)–O(1)	100·8 (2)	S(1)–P(4)–C(9)	110·2 (5)
S(2)–W(1)–P(1)	165·04 (7)	C(1)–P(4)–C(2)	105·9 (5)
S(2)–W(1)–P(3)	86·66 (7)	C(1)–P(4)–C(9)	106·4 (6)
S(2)–W(1)–O(1)	102·3 (2)	C(2)–P(4)–C(9)	109·4 (6)
P(1)–W(1)–P(3)	100·30 (7)	P(1)–C(2)–P(4)	113·2 (5)
P(1)–W(1)–O(1)	90·8 (2)	P(2)–C(10)–P(3)	111·1 (4)
P(3)–W(1)–O(1)	92·3 (2)	F(1)–P(6)–F(2)	87·6 (4)
W(1)–S(1)–P(4)	106·9 (1)	F(1)–P(6)–F(3)	179·1 (6)
W(1)–S(2)–P(2)	108·3 (1)	F(1)–P(6)–F(4)	90·9 (4)
W(1)–P(1)–C(2)	111·6 (3)	F(1)–P(6)–F(5)	98·1 (5)
W(1)–P(1)–C(3)	123·2 (3)	F(1)–P(6)–F(6)	84·3 (5)
W(1)–P(1)–C(4)	111·0 (3)	F(2)–P(6)–F(3)	92·4 (5)
C(2)–P(1)–C(3)	100·8 (5)	F(2)–P(6)–F(4)	177·7 (4)
C(2)–P(1)–C(4)	104·6 (4)	F(2)–P(6)–F(5)	92·2 (6)
C(3)–P(1)–C(4)	103·7 (5)	F(2)–P(6)–F(6)	88·1 (5)
S(2)–P(2)–C(7)	111·2 (4)	F(3)–P(6)–F(4)	89·2 (5)
S(2)–P(2)–C(8)	109·5 (4)	F(3)–P(6)–F(5)	81·0 (6)
S(2)–P(2)–C(10)	112·8 (3)	F(3)–P(6)–F(6)	96·6 (5)
C(7)–P(2)–C(8)	107·7 (5)	F(4)–P(6)–F(5)	89·7 (6)
C(7)–P(2)–C(10)	109·8 (5)	F(4)–P(6)–F(6)	90·0 (5)
C(8)–P(2)–C(10)	105·6 (5)	F(5)–P(6)–F(6)	177·6 (5)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44759 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$C_6H_4(PPh_2)_2$ and *cis*-$Ph_2PCH{=}CHPPh_2$, was reported (Levason, McAuliffe & McCullough, 1977). Only in 1986 was the first crystallographic structural study of an oxotungsten(IV) compound, namely $WOCl_2(PMePh_2)_2(CH_2{=}CH_2)$, (3), reported (Su, Cooper, Geib, Rheingold & Mayer, 1986).

The structures of the two compounds are fundamentally similar and also share several key characteristics with the structure of (3) (Su, Cooper, Geib, Rheingold & Mayer, 1986). The W=O bond lengths are the same to within $\pm 3\sigma$, *viz* 1·68 (1), 1·711 (5) and 1·714 (6) Å for (1), (2) and (3) respectively. Also, in each case the *trans* influence of the W=O bond is seen in the relatively long W—Cl bonds *trans* to it, namely, 2·539 (5), 2·554 (2) and 2·495 (3) Å for (1), (2) and (3). In (3) one has an internal comparison of W—Cl bond lengths since there is a *cis* W—Cl bond that has a length of only 2·444 (3) Å. In all three cases, the W=O unit tends to demand a larger solid angle in the coordination sphere and the O—W—P or O—W—S angles are larger than 90°.

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Structure of $Sr_8PtSi_2O_{14}$

By Lars Stenberg

Inorganic Chemistry 2, *Chemical Centre, PO Box* 124, 221 00 *Lund, Sweden*

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Abstract. $Sr_8(PtO_6)(SiO_4)_2$, $M_r = 1176{\cdot}21$, monoclinic, $C2$, $a = 18{\cdot}830$ (2), $b = 5{\cdot}744$ (1), $c = 7{\cdot}172$ (1) Å, $\beta = 110{\cdot}72$ (1)°, $V = 725{\cdot}547$ Å^3, $Z = 2$, $D_x = 5{\cdot}383$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7093 Å, $\mu = 383{\cdot}38$ cm^{-1}, $F(000) = 1044$, $T = 292$ K, $R = 0{\cdot}026$ for 1495 independent reflexions. This is a new structure type, with isolated SiO_4 tetrahedra and PtO_6 octahedra. Three of the four nonequivalent Sr atoms are coordinated by O in distorted trigonal prisms. The fourth is located in a square antiprism, which has one small and one large square face, *i.e.* half a cuboctahedron. Two such small faces are shared, which gives a short Sr—Sr distance of 3·28 Å.

Introduction. A great deal of interest has been spent on the structure and chemistry of platinum oxides over the years. The main interest has been focused on properties like catalysis, inertness or metallic conduction in the 'bronzes'. The chemistry of platinum is not trivial, depending on the inertness of the metal itself and the ease with which PtO_2 decomposes. Sometimes highly sophisticated methods have to be used (Gallagher, Johnson, Vogel, Wertheim & Schnettler, 1977; Muller & Roy, 1969) and sometimes again good crystals grow by mistake (Boivin, Conflant & Thomas, 1976; Czaya, 1970). In the present case, during synthesis of a strontium silicate, light brown crystals of $Sr_8PtSi_2O_{14}$ were found growing on the wall of the platinum crucible used. To the best of our knowledge, this compound is the first platinum silicate reported.

Experimental. An irregular crystal of approximate size 0·07 × 0·06 × 0·05 mm was studied with a CAD-4 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. The data set was collected in a hemisphere for $6 \le 2\theta \le 60°$ with $-27 \le h \le 27$, $-10 \le k \le 10$ and $0 \le l \le 8$. Three standard reflexions measured every 2 h showed no systematic variations. Unit-cell dimensions were determined from least-squares refinements of 44 2θ values from powder data. The data set was corrected for polarization and the Lorentz effect and for absorption. Systematic absences of reflexions for hkl when $h + k \ne 2n$, $h0l$ when $h \ne 2n$ and $0k0$ when $k \ne 2n$ suggested space groups $C2/m$, Cm or $C2$. After averaging of equivalent reflexions 2090 unique data remained. 1495 reflexions with $I > 2\sigma(I)$ were used in the structure determination. The structure was solved by the heavy-atom method, which gave the Pt and Sr

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