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# Synthesis and Characterisation of Oxotungsten(VI) Complexes of Phosphines and Phosphine Oxides

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## Abstract

By employing low temperatures it has been found possible to isolate diamagnetic oxotungsten(VI) complexes, $[WOCl_4L]$ (L = $PPh_3$, $PPh_2Et$, $OPPh_3$) and $[WOCl_4L_2]$ (L = $PPh_3$, $PEt_3$, $PPr_3{}^n$, $OPPh_3$), by the reaction of $WOCl_4$ with the ligands. Attempts to isolate analogous phosphine complexes of oxomolybdenum(VI) resulted in reduction to molybdenum(V). The $[WOCl_4L]$ complexes are assigned a six-co-ordinate structure containing the *trans*-O=W–L moiety; the $[WOCl_4L_2]$ are assigned a seven-co-ordinate structure. In addition the seven-co-ordinate $[WOCl_4(aa)]$ (aa = *o*-phenylenebisdiphenylarsine) has been isolated.

## Introduction

In recent years there has been considerable interest in the co-ordination chemistry of high-valent tungsten, and especially of molybdenum, in view of their role in a number of important enzyme systems [1–3].

Although the chemistry associated with oxomolybdenum(VI) complexes has been well investigated the corresponding oxotungsten(VI) system has not been so well explored. A number of simple adducts of general formula $[WOCl_4L]$ (L = MeCN, EtCN, $Et_2O$), $[WOCl_4(py)_2]$, $[WOCl_4(bipy)]$ and $[(WOCl_4)_2dioxan]$ are known [4, 5], and a number of analogous $WSX_4$ and $WSeX_4$ (X = Cl, Br) have also been reported [6]. Some $[MO_2X_2(OPPh_3)_2]$ (M = Mo, W; X = Cl, Br) [4, 7] complexes exhibit distorted octahedral geometry in which the terminal oxygen atoms are *cis* to one another and the halogens mutually *trans*; this illustrates that in such mixed ligand complexes the weaker π-bonding donor ligands, $OPPh_3$, are found to be *trans* to the terminal oxygen atoms where they are not directly competing for the available empty metal π-orbitals [8].

There have been only rare reports of phosphine or arsine complexes of molybdenum or tungsten in the +6 oxidation state; this is not unexpected since the interaction of high-valent metal moieties with soft donor species such as phosphorus or arsenic normally results in reduction of the metal at the expense of ligand oxidation. However, one well characterised complex is $[WOCl_4(diars)]$ (diars = *o*-phenylenebisdimethylarsine). This pale green complex is formed by reacting diars with $WOCl_4$ in dry carbon tetrachloride; a single crystal X-ray structural analysis shows it to have a pentagonal bipyramidal structure [9, 10].

## Results and Discussion

In this study we report the reaction of oxotungsten(VI) tetrachloride, $WOCl_4$, with a range of monodentate and bidentate Group V donor ligands, Table I, under carefully controlled conditions (see Experimental). Only the ligand $PPh_3$, $PPh_2Et$ (and $OPPh_3$) produced both mono and bis ligand adducts, $[WOCl_4L]$ and $[WOCl_4L_2]$, respectively, by employing 1:1 or 1:2 metal:ligand ratios. With $PPr_3{}^n$ and $PEt_3$ only the bis ligand complex $[WOCl_4L_2]$ was formed; $[WOCl_4(aa)]$ (aa = *o*-phenylenebisdiphenylarsine) was also isolated. Other ligands, *e g*, $PBu_3{}^n$, produced only oils or paramagnetic complexes with non-reproducible analyses, probably due to partial reduction of $WOCl_4$. In this study we have observed that the stabilisation of W(VI)–Group V bonds results from factors such as small scale preparations, suitable solvents, low temperatures, and dropwise

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TABLE I. Physical and Spectroscopic Properties of the Tungsten Complexes.

| Complex | Colour | %C[a] | %H[a] | %Cl[a] | %P[a] | %W[a] | Electronic Spectra[b] (cm$^{-1}$) | Infrared Spectra (cm$^{-1}$) | | $^{31}$P NMR |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | ν(WO) | ν(WCl) | |
| [$WOCl_4(PPh_3)$] | Orange | 35.8<br>(35.8) | 2.5<br>(2.5) | 23.1<br>(23.5) | 4.9<br>(5.1) | 29.8<br>(30.5) | 26500<br>19800 | 988(s) | 335(m) | +27.87 |
| [$WOCl_4(PPh_2Et)$]·$C_7H_7$ | Orange | 39.1<br>(38.9) | 3.6<br>(3.5) | 21.7<br>(21.9) | 4.5<br>(4.8) | 29.1<br>(28.4) | 25640<br>20000 | 978(s) | 340(m) | +25.67 |
| [$WOCl_4(OPPh_3)$][c] | Yellow | 35.1<br>(34.9) | 2.3<br>(2.4) | 22.5<br>(22.9) | | 30.1<br>(29.7) | 27000<br>19500 | 983(s) | 340(m) | +24.18 |
| [$WOCl_4(PPh_3)_2$] | Yellow–Orange | 50.3<br>(49.9) | 3.2<br>(3.5) | 16.0<br>(16.3) | 7.1<br>(7.2) | 21.2<br>(21.2) | 24800<br>20500 | 960(s) | 350(sh)<br>325(m)<br>294(m) | +51.38 |
| [$WOCl_4(PPr^n_3)_2$]·½$CH_2Cl_2$ | Green | 30.9<br>(31.5) | 6.4<br>(6.1) | 19.8<br>(20.1) | | 25.9<br>(26.1) | 25100<br>19200 | 960(s) | 335(m)<br>318(m) | +48.85 |
| [$WOCl_4(PEt_3)_2$] | Orange | 25.1<br>(25.0) | 4.9<br>(5.2) | 25.1<br>(24.5) | 11.0<br>(10.7) | 31.6<br>(31.8) | 27500<br>20000 | 962(s) | 345(sh)<br>332(m)<br>309(m) | +49.85 |
| [$WOCl_4(OPPh_3)_2$][d] | Yellow | 48.3<br>(48.1) | 3.2<br>(3.3) | | 7.0<br>(6.9) | 21.1<br>(20.5) | 24000<br>19400 | 970(s) | 342(m)<br>320(m)<br>302(sh) | |
| [$WOCl_4(aa)$] | Apple–green | 40.9<br>(41.1) | 2.9<br>(2.8) | 15.5<br>(16.1) | | 22.0<br>(21.0) | 25200<br>20600 | 965(s) | 346(m)<br>332(m)<br>317(w) | |

[a] Found (Calc.). [b] Solid reflectance. [c] ν(P=O), 1163 cm$^{-1}$; [d] ν(P=O), 1152 cm$^{-1}$.

addition of the ligand in dilute solution (see Experimental).

Under the same conditions for the preparation of the oxotungsten(VI) complexes we observed reduction when attempts at oxomolybdenum(VI) complex preparation were made. The relative ease with which $MoOCl_4$ is reduced either by solvents or ligands has previously been noted [11, 12], and thus our ability to isolate $WOCl_4$ derivatives is surprising.

### *The [$WOCl_4L$] Complexes*

These compounds are insoluble in most organic solvents, but very slightly soluble in dry dichloromethane, 1,2-dichloroethane and nitromethane. They are more stable in air than the $WOCl_4$ starting material but, nonetheless, gradually change colour from orange to blue and become sticky on prolonged exposure to air. They appear to be indefinitely stable when sealed in glass ampoules under dry dinitrogen.

The complexes are virtually non-conducting in dry nitromethane and 1,2-dichloroethane solutions. Moreover no bands are observed in mull infrared spectra which are assignable to W–O–W or W–Cl–W linkages, and thus these [$WOCl_4L$] (L = $PPh_3$, $PPh_2Et$, $OPPh_3$) complexes are assigned a monomeric hexaco-ordinate structure. A strong band is observed in the 980 cm$^{-1}$ region assigned to terminal ν(W=O) [13, 14]. Any bridging W–O–W linkages would exhibit absorptions at lower energy; for example, $WOCl_4$ itself exhibits ν(WOW) at 875 cm$^{-1}$ [15]. The only ν(W–Cl) band observable occurs as a single absorption, Table I. The multiplicity of this and the relatively high energy suggests that all the chlorines are in the plane of the molecule and not *trans* to the W=O group; the Cl–W=O moiety usually results in a ν(W–Cl) at significantly lower energy [15].

The room and frozen (–150 °C) temperature electron spin resonance spectra in dichloromethane solution display a very weak signal (a broad weak isotropic singlet, $g_{iso}$ = 1.77, with no hyperfine or superhyperfine coupling), probably due to a small amount of impurity arising from reduction to a lower oxidation state, probably tungsten(V). That this impurity is present in only small amounts is somewhat confirmed by the essentially diamagnetic properties of the complexes ($\mu_{eff} \simeq 0.20\ \mu_B$).

The $^{31}$P NMR spectra of the [$WOCl_4L$] complexes show only one somewhat ill-defined phosphorus environment, but the low solubility precluded detailed observation of $J(^{183}W–P)$ coupling. The presence of only one peak suggests the existence of only one isomer. Taking into account the magnetic, infrared and NMR spectroscopic results we assign structure **I** to the complexes rather than structure **II**.

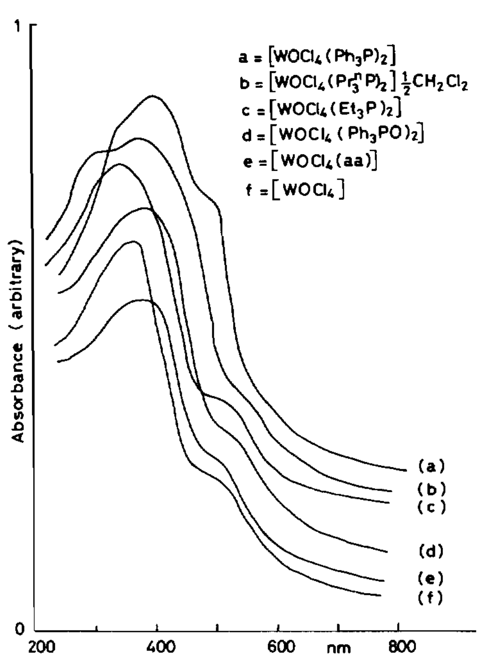
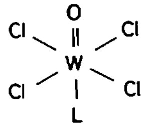
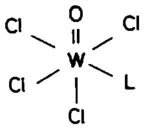


Fig. 1. Solid reflectance spectra of $[WOCl_4L_2]$ complexes.



I



II

The electronic reflectance spectral maxima for the complexes are listed in Table I and illustrated in Fig.1. The observed bands are similar to those reported for oxotungsten(VI) complexes such as $[WOCl_4(CH_3CN)]$, $[WOCl_4(EtCN)]$ and $[(WOCl_4)_2(dioxan)]$ [4, 7].

### *The $[WOCl_4L_2]$ Complexes*

The physical properties of these complexes, $[WOCl_4L_2]$ (L = $PPh_3$, $PEt_3$, $PPr_3^n$, $OPPh_3$) are similar to those of the mono-adducts, *viz* they appear to be indefinitely stable when stored in sealed ampoules under a dry inert atmosphere, but become sticky when stored in moist air; they are only poorly soluble in organic solvents. The presence of solvent in the $[WOCl_4(PPr_3^n)_2]\cdot \frac{1}{2}CH_2Cl_2$ is confirmed by infrared absorptions at 2940, 1260, 726 $cm^{-1}$. The complexes are essentially non-conducting in nitromethane solution.

The $[WOCl_4L_2]$ complexes are diamagnetic and exhibit no ESR signal at room temperature, consistent with the presence of tungsten(VI) species.

The mull infrared spectra exhibit a strong absorption in the 970–960 $cm^{-1}$ range, assignable to terminal $\nu$(W=O); no bands due to bridging W–O–W moieties are observed. It is noticeable that $\nu$(W=O) occurs at lower energy in the $[WOCl_4L_2]$ than in the $[WOCl_4L]$ complexes, indicating that the former seven-coordinate compounds have a somewhat weaker W=O bond than the six-co-ordinate species. However, whereas $\nu$(P=O) appears at 1163 $cm^{-1}$ in $[WOCl_4(OPPh_3)]$ it appears at 1152 $cm^{-1}$ in $[WOCl_4(OPPh_3)_2]$ (free $OPPh_3$ exhibits $\nu$(P=O) at 1193 $cm^{-1}$). The appearance of only one $\nu$(P=O) absorption in the latter complex suggests that both ligands have similar environments. For the $[WOCl_4L_2]$ (L = $PPh_3$, $PEt_3$, $PPr_3^n$) only one $^{31}P$ NMR signal is observed, Table I, again suggesting equivalent positions of both phosphines in the complex.

The $[WOCl_4(aa)]$ complex, Table I, has similar properties to the $[WOCl_4L_2]$ complexes, and is also assigned a monomeric seven-co-ordinate structure.

## Experimental

Physical measurements were obtained as previously described [16]; in addition, $^{31}P$ NMR spectra were obtained in dichloromethane on a Jeol FX-60 F.T. spectrometer, with 85% $H_3PO_4$ as an external reference.

### *Preparative Methods*

Oxotungsten(VI) tetrachloride, $WOCl_4$, was prepared by literature methods [4, 17].

All of the oxotunsgen(VI) complexes were made at *low temperature* by almost the same method. Special precautions were taken to avoid hydrolysis of highly sensitive materials such as $WOCl_4$; we observed that even trace quantities of moisture caused the reactions to give impure products. In all reactions the dropwise addition of well-diluted ligands was important and necessary. Also, addition of n-pentane (*ca* 20 $cm^3$) to the reaction mixture of a few hours prior to filtering improved the yield of complex. Typical preparations are given below.

### *Oxotetrachlorobis(triphenylphosphine)tungsten(VI), $[WOCl_4(PPh_3)_2]$*

Oxotungsten(VI) tetrachloride, $WOCl_4$, (1.09 g, 3.2 mmol) was suspended in freshly distilled, deoxygenated toluene (30 $cm^3$). To this was added dropwise with vigorous stirring pre-dried triphenylphosphine (1.67 g, 6.4 mmol) (drying achieved by warming to 40 °C and pumping on 5 × 10 $cm^{-2}$ Torr for several hours) in dry dichloromethane (25 $cm^3$) at *ca.* –25 °C. When the addition was complete the solution was stirred at –25 °C for 1 day. After this period of time a small amount of yellowish–orange precipitate was observed. The solution was concentrated under gentle evaporation to half its volume and dry n-pentane (20 $cm^3$) was added and vigorously stirred for an additional 2 h. This produced an orange-crystalline solid product which was left for several days in the refrigerator and the resulting solid was collected by *in vacuo* filtration using a Schlenk apparatus, rinsed with very cold toluene/dichloromethane (8 $cm^3$)and twice with cold n-pentane (2 X 10 $cm^3$). The product was then dried *in vacuo*. Yield ~75%.

A similar reaction was carried out under the same conditions using oxomolybdenum(VI) tetrachloride in place of $WOCl_4$. The product was investigated and showed characteristics of oxomolybdenum(V) complexes.

### *Oxotetrachlorotriphenylphosphinetungsten(VI), [$WOCl_4(PPh_3)$]*

$WOCl_4$ (0.92 g, 2.7 mmol) was suspended in dry toluene (20 $cm^3$). To this was added previously dried triphenylphosphine (0.70 g, 2.7 mmol) in dichloromethane (25 $cm^3$) dropwise, very slowly, with moderate stirring at low temperature, *ca.* −40 °C. After the addition of the ligand stirring was continued for several days to ensure complete reaction. After this period a small amount of orange coloured crystalline product was observed. The reaction mixture was concentrated under gentle evaporation *in vacuo* to half its volume and was then stored in the refrigerator for 3–4 days. The resulting orange crystalline solid was collected with vacuum filtration, rinsed with very cold n-pentane (2 X 10 $cm^3$) and dried *in vacuo*. Yield *ca.* 60%.

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