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Phosphine and diphosphine complexes of tungsten(VI) oxide tetrafluoride

James W. Emsley[a], William Levason[a,*], Gillian Reid[a], Wenjian Zhang[a], Giuseppina De Luca[b]

[a] Chemistry, University of Southampton, Southampton SO17 1BJ, UK
[b] Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, via P. Bucci, 87036 Arcavacata di Rende, CS, Italy

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ABSTRACT

The reaction of $[WOF_4(MeCN)]$ with the diphosphines, $Me_2PCH_2CH_2PMe_2$ or o-$C_6H_4(PMe_2)_2$, in anhydrous Et_2O produced high yields of $[WOF_4(diphosphine)]$, the X-ray crystal structures of which reveal seven-coordinate pentagonal bipyramidal molecules with axial O/F. In contrast, the reaction of $[WOF_4(MeCN)]$ and PMe_3 forms the six-coordinate $[WOF_4(PMe_3)]$. These unusual W(VI) complexes have been characterised by microanalysis, IR, ^1H, $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. The second-order $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of the $[WOF_4(diphosphine)]$ have been analysed. Similar complexes do not form with the other o-phenylene-linked bidentate ligands, o-$C_6H_4(PPh_2)_2$, o-$C_6H_4(AsMe_2)_2$ or o-$C_6H_4(SMe)_2$.

1. Introduction

Soft-donor neutral ligand complexes of early d-block metal oxide fluorides are very rare, even more so than the corresponding binary fluoride complexes [1]. Very unstable $[VOF_3(RSCH_2CH_2SR)]$ (R = Me, Et, ^{i}Pr) have been isolated, but decompose in a few hours, whilst phosphines, arsines and selenoethers reduce VO_2F or VOF_3 to lower oxidation states [2,3]. Complexes of $NbOF_3$ with hard N- or O-donors can be prepared from NbF_5, $(Me_3Si)_2O$ and the ligand in anhydrous MeCN, but attempts to isolate phosphine, arsine or thioether complexes failed, with only (polymeric) $NbOF_3$ being formed [4]. In contrast, complexes of NbF_5 with soft (P, As, S or Se) donors have been fully characterised [5–7]. We recently reported a general route to complexes of WOF_4 with nitrogen- or oxygen-donor ligands, including $[WOF_4(L)]$ (L = py, Me_3PO, Ph_3PO, Me_2SO) using substitution of the MeCN in $[WOF_4(MeCN)]$ [8] with the neutral ligand in MeCN or CH_2Cl_2 solution. $[WOF_4(MeCN)]$ is a convenient synthon, easily prepared from WF_6 and $(Me_3Si)_2O$ in a 1:1 molar ratio in anhydrous MeCN solution. Reaction of $[WOF_4(L)]$ with more ligand, together with a second equivalent of $(Me_3Si)_2O$, produced the distorted octahedral $[WO_2F_2(L)_2]$ [8]; the complexes $[WO_2F_2(L–L)]$ (L–L = $Ph_2P(O)CH_2P(O)Ph_2$ or 1,10-phenanthroline) were also obtained. Attempts to prepare analogues with soft-donor ligands such as thioethers, selenoethers or arsines were unsuccessful, with these soft-donor ligands failing to displace the MeCN ligands.

Here we report examples of phosphine complexes of the mono-oxido tetrafluorido tungsten, WOF_4, the successful syntheses being very dependent upon the particular phosphine, the solvent and the reaction conditions. Two examples of type $[WF_6(PR_3)]$ (R_3 = Me_3, Me_2Ph) have been characterised as yellow and red crystals respectively, both seven-coordinate, the former a capped trigonal prism and the latter a capped octahedron [9]. Phosphine complexes of $WOCl_4$ have been described [10], but lack X-ray crystallographic authentication, although the structure of the green, pentagonal bipyramidal $[WOCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$, which has axial O/Cl donors, has been reported [11,12].

2. Results and discussion

2.1. Synthesis and structures of $[WOF_4(diphosphine)]$

Reaction of $[WOF_4(MeCN)]$ with one equivalent of the diphosphines $Me_2PCH_2CH_2PMe_2$ or o-$C_6H_4(PMe_2)_2$ in anhydrous Et_2O solution produced high yields of the complexes $[WOF_4(diphosphine)]$ as white, highly moisture sensitive powders. Attempts to obtain these complexes using MeCN or CH_2Cl_2 as solvents were unsuccessful. The success of Et_2O as solvent, despite the fact that

* Corresponding author.
E-mail address: wxl@soton.ac.uk (W. Levason).

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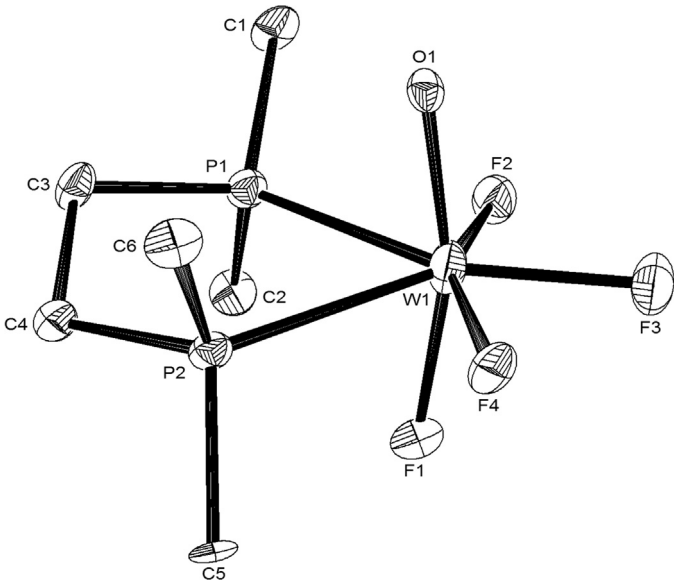

Fig. 1. The structure of $[WOF_4(Me_2PCH_2CH_2PMe_2)]$ showing atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. There was disorder in the axial F/O and only the major component is shown. Selected bond lengths (Å) and angles (°): W1–O1 = 1.757(12), W1–F1 = 1.923(9), W1–F3 = 1.924(3),W1–F2 = 1.960(4), W1–F4 = 1.959(4), W1–P1 = 2.5584(18), W1–P2 = 2.5714(17), O1–W1–F1 = 163.6(5), O1–W1–F3 = 100.4(5), F1–W1–F3 = 95.9(3), O1–W1–F4 = 90.7(5), F1–W1–F4 = 91.8(3), F3–W1–F4 = 76.30(16), O1–W1–F2 = 97.5(5), F1–W1–F2 = 87.3(3), F3–W1–F2 = 77.72(16), O1–W1–P1 = 83.1(5), F1–W1–P1 = 84.5(3), F2–W1–P1 = 67.06(11), O1–W1–P2 = 86.5(5), F1–W1–P2 = 79.6(3), F4–W1–P2 = 66.99(10), P1–W1–P2 = 72.15(6).

the hard oxygen donor ether might be expected to be a better donor to a very hard Lewis acid than a soft phosphine, lies in the fact that the complexes precipitate from the reaction mixture immediately on formation. (We did not observe any evidence for diethyl ether adducts in the NMR spectra of the isolated phosphine complexes). CH_2Cl_2 fails as a solvent since the Lewis acidic tungsten centre promotes protonation/quaternisation of the phosphine by the solvent [1,5,6]. In the case of MeCN the phosphine complexes are soluble in this solvent and it is likely that a mixture of phosphine and nitrile complexes and "free" phosphine are present, and the latter can reduce the tungsten. In many high valent metal systems [1] there is some competition between complexation of the phosphine (fast) and redox chemistry (slower). Coordinated phosphine does not produce metal reduction, hence the Et_2O solvent system, from which the complex with bound phosphine precipitates is successful.

The isolated solid complexes appear stable under a dry dinitrogen atmosphere for several weeks. Colourless crystals of $[WOF_4(Me_2PCH_2CH_2PMe_2)]$ were grown by evaporation of a solution in anhydrous CH_2Cl_2. The refinement revealed disorder of the axial O/F atoms which was satisfactorily modelled as two components in the ratio 68:32 (Section 3.4) (Fig. 1).

Several batches of crystals were grown from CH_2Cl_2 solutions of $[WOF_4\{o\text{-}C_6H_4(PMe_2)_2\}]$ and all showed a similar pentagonal bipyramidal geometry to $[WOF_4(Me_2PCH_2CH_2PMe_2)]$, but also O/F disorder of the two axial ligands. Attempts to model the disorder were not successful in this case and the highest quality data set led to the structure in Fig. 2. The bond lengths in the pentagonal plane are not significantly different to those in $[WOF_4(Me_2PCH_2CH_2PMe_2)]$, although because of the disorder present, comparisons of the metrical parameters should be made with due care.

The structure of the pentagonal bipyramidal $[WOF_4(py)_2]$ was reported to show axial fluorides with an OF_2N_2 donor set in the pentagonal plane [13], but a subsequent NMR study showed the structure to contain axial O/F donors, and concluded that the crystal structure had contained unrecognised disorder of the axial O/F groups [14] and thus the bond length data are unreliable. The $[WOF_4(2,2'\text{-bipy})]$ and $[WOF_4(napy)]$ (napy = 1,8-naphthyridine, 2,7-Me_2-1,8-naphthyridine) [15,16], which are probably of similar structure to $[WOF_4(Me_2PCH_2CH_2PMe_2)]$, were insoluble in most solvents precluding the growth of crystals. The structure of the pentagonal bipyramidal $[WOCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$ is of low precision, but has axial O/Cl donors with d(W = O) = 1.89(4) Å [11]. In the $[WOF_4(diphosphine)]$ species the axial O–W–F units are bent towards the diphosphine, O1–W1–F1 ~164°. Both the d(W = O) and the d(W–F) are longer in $[WOF_4(Me_2PCH_2CH_2PMe_2)]$ than in the six-coordinate $[WOF_4(OPPh_3)]$ and $[WOF_4(F\text{-py})]$ [8,13], which can largely be attributed to the higher coordination number.

Attempts to isolate analogous complexes with the softer and weaker σ-donor diphosphine *o*-$C_6H_4(PPh_2)_2$, the diarsine, *o*-

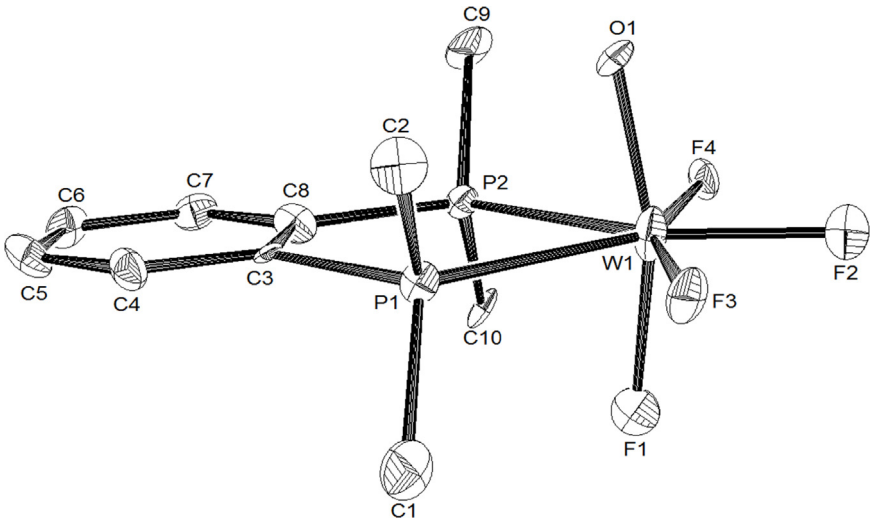

Fig. 2. The structure of $[WOF_4\{o\text{-}C_6H_4(PMe_2)_2\}]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Note that F1/O1 are disordered. Selected bond lengths (Å) and angles (°): W1–O1 = 1.792(7), W1–F1 = 1.843(6), W1–F3 = 1.959(6), W1–F2 = 1.891(7), W1–F4 = 1.957(6), W1–P1 = 2.554(3), W1–P2 = 2.554(3), O1–W1–F1 = 164.3(3), O1–W1–F2 = 99.5(3), F1–W1–F2 = 96.2(3), O1–W1–F4 = 92.2(3), F1–W1–F4 = 92.6(3), F2–W1 F4 = 76.8(3), O1–W1–F3 = 91.8(3), F1–W1–F3 = 90.3(3), F2–W1–F3 = 77.5(3), O1–W1–P2 = 84.9(2), F1–W1–P2 = 83.4(2), F4–W1–P2 = 66.32(19), O–1W1–P1 = 82.1(2), F1–W1–P1 = 84.5(2), F3–W1–P1 = 66.98(19), P2–W1–P1 = 72.49(9).