Accepted Manuscript

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PII: S0022-1139(17)30149-5
DOI: http://dx.doi.org/doi:10.1016/j.jfluchem.2017.06.015
Reference: FLUOR 9005

To appear in: FLUOR

Received date: 11-4-2017
Revised date: 27-6-2017
Accepted date: 28-6-2017

Please cite this article as: William Levason, Francesco M. Monzittu, Gillian Reid, Wenjian Zhang, Eric G. Hope, Complexes of molybdenum(VI) oxide tetrafluoride and molybdenum(VI) dioxide difluoride with neutral N- and O-donor ligands, Journal of Fluorine Chemistry http://dx.doi.org/10.1016/j.jfluchem.2017.06.015

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Complexes of molybdenum(VI) oxide tetrafluoride and molybdenum(VI) dioxide difluoride with neutral N- and O-donor ligands

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Graphical abstract

Highlights:
- First examples of MoOF₄ complexes with neutral ligands
- X-ray structure of [MoOF₄(Ph₃PO)]
- Comparisons of [MoOF₄(L)] and [MoO₂F₂(L)₂] complexes
- Comparisons of Mo(VI) and W(VI) oxide fluoride complexes
Abstract

[MoOF₄(MeCN)], prepared from reaction of MoF₆ with (Me₃Si)₂O in anhydrous MeCN solution, reacts with the neutral O-donor ligands, thf, Ph₃PO, Me₃PO, dmf and dmso, (L) in a 1:1 molar ratio under rigorously anhydrous conditions to form six-coordinate [MoOF₄(L)], which have been characterised by microanalysis, IR, ¹H, ¹⁹F{¹H} and ⁹⁵Mo NMR spectroscopy. In the presence of moisture the major products are [MoO₂F₂(L)₂], which can be made directly by reaction of [MoOF₄(L)] with a further equivalent of L and (Me₃Si)₂O. [MoOF₄(MeCN)] and 2,2’-bipyridyl produce the insoluble [MoOF₄(bipy)], which is probably 7-coordinate. Ph₃AsO is quantitatively converted to Ph₃AsF₂ by [MoOF₄(MeCN)], and soft ligands, including Me₂S, Me₃P and Me₃As, reduce the oxide fluoride on contact. Unstable [MoO₂F₂(MeCN)₂] has also been prepared and the X-ray structure of [MoO₂F₂(MeCN)₂]·MeCN is reported. X-ray crystal structures are reported for [MoOF₄(Ph₃PO)], [MoO₂F₂(Ph₃PO)₂], [MoO₂F₂(Ph₃PO)(H₂O)] and [Mo₂O₂F₂(μ-F)₂(Ph₃PO)₂]. Comparisons with the corresponding chemistries of WOF₄ and WO₂F₂ are described.

Keywords: molybdenum; oxide-fluoride; X-ray structures; nitrogen donor ligand; oxygen donor ligand

1. Introduction

Oxide fluorides of the early d-block metals in their group oxidation state are strong Lewis acids and form an extensive range of oxido-fluorido anions, often produced in aqueous HF in the presence of suitable metal cations [1,2]. In contrast, surprisingly few complexes with neutral ligands have been reported [3], which is due at least in part to the strongly polymerised structures and hence unreactive nature of many of the oxide fluorides. We recently reported the synthesis of a series of complexes [WOF₄(L)] derived from tungsten(VI) oxide tetrafluoride, made from [WOF₄(MeCN)] and neutral N- or O-donor ligands (L = thf, py, Ph₃PO, Me₃PO, dmso) in anhydrous MeCN solution [4]. The [WOF₄(MeCN)], which is readily obtained from WF₆ and (Me₃Si)₂O in MeCN, is a convenient synthon and can be stored for weeks in a glove box, although it decomposes rapidly in air and is readily hydrolysed by wet solvents. Treatment of [WOF₄(L)] with further equivalents of L and (Me₃Si)₂O afforded complexes [WO₂F₂(L)₂] (L = py, Ph₃PO, Me₃PO, dmso) [4]. Attempts to replace the nitrile in [WOF₄(MeCN)] with soft donor ligands, such as arsines, thioethers or selenoethers, failed, but two seven-coordinate, pentagonal-bipyramidal complexes, [WOF₄(diphosphine)] (diphoshine = Me₂PCH₂CH₂PMe₂ or o-C₆H₄(PMe₂)₂), were made from [WOF₄(MeCN)] and one
equivalent of the diphosphine in anhydrous Et₂O solution. Six-coordinate [WO₄₂⁻(PMe₃)] was also isolated [4,5].

Here we report an investigation of some chemistry in the analogous molybdenum system. Two oxide fluorides of molybdenum(VI) are known. The first, MoOF₄, is a white powder made by fluorination of MoO₃, or by reaction of molybdenum metal with O₂/F₂ mixtures [2]. The solid structure contains polymeric chains with two cis fluoride bridges and hence a distorted octahedral molybdenum centre [6]. In the gas phase it is monomeric with a square-pyramidal geometry [7,8]. There are a variety of reported routes to MoO₂F₂ involving fluorination of MoO₃ or MoO₂Cl₂ [1], although a recent study [9] cast doubt on a number of these. The structure has also proved elusive, but powder X-ray diffraction data suggest it is based upon triangular Mo₃(μ-F)₃ units with axial bridging oxide groups linking the layers, and with disordered terminal Mo-F and Mo=O groups [9]. The only literature report of a neutral organic ligand complex of MoOF₄, is of [MoOF₄(Ph₃PO)], identified in situ by its ¹⁹F NMR spectrum, but not isolated [10]. There are also adducts of MoOF₄ with XeF₂ and KrF₂ [11,12]. In contrast, a number of complexes of the form [MoO₂F₂L₂] (L = Ph₃PO, Me₃PO, Ph₂MePO, dms; L₂ = 2,2’-bipyridyl, 1,10-phenanthroline) have been prepared, mostly by addition of ethanolic solutions of the appropriate ligand to a solution of “molybdic acid” (MoO₃.nH₂O) in aqueous HF, or, in some cases, from the corresponding [MoO₂Cl₂(L)₂] and Me₃SnF [13-18]. The [MoO₂F₂(thf)₂] was made by decomposition of [MoF₄(NCl)] in thf [19], and [MoO₂F₂(dmf)₂] by dissolution of MoO₂F₂ in dmf [9]. The spectroscopic characterisation of these complexes is patchy, but single crystal X-ray structures are available for a few examples [9,14,16,17,19].

Here we report on the synthesis and characterisation of the first series of neutral N- or O-donor complexes of MoOF₄ and some structural and spectroscopic data on complexes of MoO₂F₂ for comparison.

2. Results and Discussion

2.1 Synthons

The route developed to prepare MoOF₄ complexes is based upon [MoOF₄(MeCN)] which is readily obtained by reaction of MoF₆ with (Me₃Si)₂O (HMDSO), in a 1 : 1 molar ratio in anhydrous MeCN. The [MoOF₄(MeCN)] is isolated as a very moisture sensitive white powder, which can be easily scaled to 2-3 g quantities and stored in a sealed container in the freezer for several weeks. The solid slowly darkens, becoming grey and then blue in a glove box at ambient temperatures. It is very moisture sensitive in solution in MeCN, turning blue on hydrolysis, and although it also dissolves easily in anhydrous CH₂Cl₂, the solution slowly decomposes, again turning blue, and the ¹⁹F{¹H} NMR spectrum shows some CH₂FCl formed [20]. The ¹⁹F{¹H} NMR spectrum of [MoOF₄(MeCN)] in MeCN shows a singlet at δ = +146.5 with weak six-line pattern satellites due to coupling with ⁹⁵Mo
with $^{1}J_{\text{MoF}} = 64$ Hz ($^{95}\text{Mo}$, $I = 5/2$, 15.9%, $Q = 0.12 \times 10^{-28}$ m$^{2}$). The other molybdenum isotope with a nuclear spin, $^{97}\text{Mo}$ ($I = 5/2$, 9.5%), has a large $Q = 1.1 \times 10^{-28}$ m$^{2}$ and coupling to it is not observed. The chemical shifts observed in CH$_2$Cl$_2$ solution are only slightly different (Section 3), but due to the slow reaction with the chlorocarbon solvent, MeCN was preferred for most NMR studies in this work. The $^{95}\text{Mo}$ NMR spectrum is a binomial quintet at $\delta(^{95}\text{Mo}) = -287.3$. The value is shifted significantly to lower frequency than those observed for [MoO$_2$F$_2$L$_2$] complexes (Table 1) which have $\delta(^{95}\text{Mo})$ between around $-40$ to $-170$ and $^{1}J_{\text{MoF}} > 100$ Hz. The IR spectrum (Nujol mull) shows $\nu$(CN) = 2324, $\nu$(C–O) + $\delta$(CH$_3$) = 2293 cm$^{-1}$, both shifted to high frequency from free MeCN (2292, 2253 cm$^{-1}$), a very strong, broad feature at 1019 cm$^{-1}$ assigned as $\nu$(MoO) and broad peak at 652 cm$^{-1}$ due to $\nu$(MoF).

### 2.2 MoOF$_4$ complexes

The reaction of [MoOF$_4$(MeCN)] with Ph$_3$PO in a 1:1 molar ratio in rigorously dry MeCN, produces [MoOF$_4$(Ph$_3$PO)] as a white powder. If an excess of Ph$_3$PO is used, also under anhydrous conditions, after several days the $^{19}$F($^1\text{H}$) and $^{31}$P($^1\text{H}$) NMR spectra show that [MoOF$_4$(Ph$_3$PO)] is still the only major product, although a small amount of Ph$_3$PF$_2$ [21] has formed, indicating some slow O/F exchange. If “wet” (i.e. commercial laboratory grade) MeCN is used as solvent for the [MoOF$_4$(MeCN)] + Ph$_3$PO synthesis, [MoO$_2$F$_2$(Ph$_3$PO)$_2$] is isolated upon concentration of the solvent. This is identified by its characteristic NMR and IR spectra (Section 2.3). The supernatant solution shows [HF$_2$]$^+$, [Ph$_3$POH]$^+$ [15, 22] and a number of other unidentified species. The $^{19}$F($^1\text{H}$) NMR spectrum of [MoOF$_4$(Ph$_3$PO)] is a singlet at $\delta = +139$ with weak $^{95}\text{Mo}$ satellites ($^{1}J_{\text{MoF}} = 65$ Hz) and the $^{95}\text{Mo}$ NMR spectrum is a quintet at $\delta = -270.0$ (Figure 1), which clearly distinguish this complex from [MoO$_2$F$_2$(Ph$_3$PO)$_2$] ($\delta(^{19}\text{F}[^{1}\text{H}]) = -51.1, \delta(^{95}\text{Mo}) = -114$ (t), $^{1}J_{\text{MoF}} = 120$ Hz) (Table 1).

The sensitivity in solution made growing crystals of these complexes for X-ray analysis challenging. However, after numerous attempts, crystals of [MoOF$_4$(Ph$_3$PO)] were obtained via slow evaporation from a concentrated solution of the complex in MeCN. The structure (Figure 2) shows the presence of a six-coordinate molybdenum centre with the phosphine oxide trans to Mo=O. The molybdenum lies slightly out of the F$_4$ plane towards the oxido-group.

The crystals were isomorphous with those of [WOF$_4$(Ph$_3$PO)] [4], and the bond lengths and angles are very similar between the molybdenum and tungsten analogues, as expected.

The complex [MoOF$_4$(Me$_3$PO)] was made similarly from [MoOF$_4$(MeCN)] and Me$_3$PO in anhydrous MeCN. It is also very moisture sensitive in solution, and [Me$_3$POH]$^+$ [23] and [MoO$_2$F$_2$(Me$_3$PO)$_2$] [15] were identified among the hydrolysis products by multinuclear NMR studies. In contrast, the reaction of [MoOF$_4$(MeCN)] with Ph$_3$AsO in dry MeCN results in immediate and quantitative formation of Ph$_3$AsF$_2$ [24], with no evidence for a molybdenum complex formed.
Evaporation of a solution of [MoOF₄(MeCN)] in anhydrous thf resulted in a cream solid that turned dark blue overnight. The instability prevented a microanalysis being obtained, but the spectroscopic properties of the freshly prepared complex, viz. $^{19}$F{¹H} NMR (CD₂Cl₂, 293 K) +143.1 (s, $J_{Mo-F} = 67$ Hz), $^{95}$Mo NMR −271.6 (quintet), IR (cm$^{-1}$) 1097 (s, thf), 1016 (vs, MoO), 872 (s, thf), 675 (vs, MoF), identified it as [MoOF₄(thf)]. This instability makes [MoOF₄(thf)] less suitable as a synthon than the nitrile complex.

The complexes [MoOF₄(L)] (L = dmf, dmso) (Scheme 1) were obtained similarly to the phosphine oxides and have the expected spectroscopic features (Table 1). Both decompose, turning into blue powders, overnight at ambient temperatures.

Repeated attempts to isolate a pure complex from the [MoOF₄(MeCN)]-pyridine system were unsuccessful. In contrast, addition of an MeCN solution of 2,2’-bipyridyl to [MoOF₄(MeCN)] in MeCN, results in immediate precipitation of a cream solid, identified by microanalysis as [MoOF₄(bipy)]. This complex is completely insoluble in solvents such as MeCN or CH₂Cl₂, precluding solution spectroscopic measurements or the growth of crystals. However, the IR spectrum, which shows ν(MoO) at 959 cm$^{-1}$ and ν(MoF) at 622, 595, 532 and 476 cm$^{-1}$, suggests that like [WOF₄(bipy)] [25], [WOF₄(py)$_2$] [26,27] and [WOF₄(diphosphine)] [5], it is seven-coordinate, probably pentagonal bipyramidal with axial O/F. The filtrate from this reaction shows some [MoO₂F₂(bipy)], but attempts to convert a suspension of [MoOF₄(bipy)] in MeCN to [MoO₂F₂(bipy)] by stirring with HMDSO failed, with the [MoOF₄(bipy)] being recovered, presumably due to its insolubility in the reaction mixture. [MoOF₄(bipy)] also appears to be stable in air, which contrasts with the sensitivity to moisture of the [MoOF₄(L)] complexes described above.

Although [WOF₄(PMe$_3$)] and [WOF₄(diphosphine)] (diphosphine = Me$_2$PCH$_2$CH$_2$PMe$_2$ or o-C$_6$H$_4$(PMe$_2$)$_2$) are formed from the reaction of the phosphines with [WOF₄(MeCN)] in Et$_2$O solution [5], the same ligands immediately produced dark tarry precipitates on contact with [MoOF₄(MeCN)] in Et$_2$O. Similarly, combination of AsMe$_3$, SME$_2$ or SeMe$_2$ with [MoOF₄(MeCN)] in Et$_2$O or MeCN solution immediately produced deep red or brown solutions and dark precipitates, indicating reduction of the molybdenum.

2.3 MoO$_2$F$_2$ complexes

As described in the Introduction, [MoO$_2$F$_2$(L)$_2$] complexes are prepared readily from MoO$_3$·nH$_2$O and the appropriate ligand in aqueous HF/EtOH or by Cl/F exchange from the corresponding [MoO$_2$Cl$_2$(L)$_2$]. In view of the much greater difficulties of routinely handling MoF$_6$, syntheses based upon this would be much less convenient, and the work described in this section aims to explore the relationship between corresponding [MoOF$_4$(L)] and [MoO$_2$F$_2$(L)$_2$], rather than devise alternative syntheses for the latter. Spectroscopic and structural data for several [MoO$_2$F$_2$(L)$_2$] complexes obtained during this study are also presented.
The reaction of MoF₆ with ≥ 2 equivalents of HMDSO in anhydrous MeCN, or reaction of [MoOF₄(MeCN)] with HMDSO in MeCN was carried out numerous times under a variety of conditions on a preparative scale and also as in situ NMR studies; all gave basically the same results. The products were white solids which turned blue over time in the solid state and more rapidly if left in contact with the MeCN solution. The blue colour also develops slowly from the dry solids in contact with the glass vessels, and ^{19}F{^1}H NMR spectra identified some [SiF₄]⁻ present, indicating the borosilicate glass is slowly attacked (cf. [9]). The MeCN filtrates from the preparations deposited insoluble blue solids over time. The in situ solution NMR data showed a molybdenum species with δ(^{19}F{^1}H) = −33.7 (s) and δ(Mo) = −162.8 (t, J_{Mo-F} = 115 Hz), which were consistent with the formation of [MoO₂F₂(MeCN)]₂. However, all attempts to isolate a pure solid sample were unsuccessful; work-up of the solutions generating white/blue solids that were only partially soluble in MeCN. Microanalyses of these solids showed the C,H,N content to be variable, but typically about 1/3 of the values expected for [MoO₂F₂(MeCN)]₂. The IR spectra of these solids showed weak nitrile bands at 2312, 2285 cm⁻¹ and very broad absorptions at ~ 1020–890 and ~ 670–450 cm⁻¹. Superimposed upon the latter were sharper features at 959, 938 cm⁻¹ (MoO) and 567 cm⁻¹ (MoF). Serendipitously, one attempt to grow crystals of [MoOF₄(MeCN)] by evaporation of an MeCN solution in the dry box, gave a few clear crystals, which were shown by X-ray structure analysis to be [MoO₂F₂(MeCN)]₂⋅MeCN. The structure (Figure 3) shows a distorted octahedral molecule with a cis-MoO₂ unit and with the nitriles trans to Mo=O. The bond lengths are unexceptional, and the wide O–Mo–O angle (104.1(2)°) and the axial F–Mo–F unit bent away from the MoO₂, are typical of other complexes of MoO₂F₂ [9,14,15]. These results show that [MoO₂F₂(MeCN)]₂ is formed in the reactions, but is unstable, losing MeCN (even in MeCN solution) and depositing what is probably largely MoO₂F₂ polymer. Solids isolated by evaporation of the solution are mainly a mixture of MoO₂F₂ polymer [9,28] and [MoO₂F₂(MeCN)]₂ (we cannot rule out the presence of other insoluble Mo/O/F species). Extraction of the [MoO₂F₂(MeCN)]₂ into MeCN or CH₂Cl₂ results in partial decomposition with generation of more MoO₂F₂. The very broad IR bands below ~1050 cm⁻¹ are attributed to the polymer, while the sharper superimposed features correspond to [MoO₂F₂(MeCN)]₂. Attempts to prepare [NbOF₄(MeCN)]₂ [29] or [WO₂F₂(MeCN)]₂ [4] from the parent fluoride and HMDSO in MeCN solution, failed, with only the nitrile-free polymeric oxide/flouride isolated. The present case of MoO₂F₂ shows that the MeCN adduct can be formed, but that it is unstable with respect to irreversible loss of MeCN.

The reaction of [MoOF₄(L)] with a further equivalent of L (L = Ph₃PO, Me₃PO, dmoso) and HMDSO in anhydrous MeCN solution produced [MoO₂F₂(L)]₂ (Scheme 1), which were identified by comparison of their key spectroscopic features (Table 1) with literature data. The complexes [MoO₂F₂(L)]₂ (L = Ph₃PO, Me₃PO, dmoso) were also isolated from reactions of [MoOF₄(L)] with the appropriate ligands in “wet” solvents (i.e. as supplied laboratory grade). Since [MoO₂F₂(L)]₂ were originally prepared by combining
solutions of L in EtOH and MoO₃·nH₂O in aqueous HF, their formation here from hydrolysis is unsurprising.

Crystals of [MoO₂F₂(Ph₃PO)₂] were obtained by slow evaporation from a CH₂Cl₂ solution and the structure is shown in Figure 4 [30].

Although they are not isomorphous, the structure of [MoO₂F₂(Ph₃PO)₂] is very similar to those of [WO₂F₂(Ph₃PO)₂] [4] and [MoO₂F₂(Ph₂MePO)₂] [14], the key features being a cis-O=M=O unit with a wide angle (103.8(4) °) and a near linear F–M–F (158.7(2) °) bent away from the MO₂ group. The bond lengths are unexceptional.

A few crystals each of three complexes containing Me₃PO were isolated from the filtrates from the preparations of [MoOF₄(Me₃PO)]. The first shown in Figure 5 was identified by the X-ray structure solution as [MoO₂F₂(Me₃PO)(H₂O)] which has trans F–Mo–F and cis-MoO₂ groups. The Mo=O distances are surprisingly disparate, Mo1–O₂,trans-Me₃PO = 1.7433(19) Å and Mo1–O₁,trans-H₂O = 1.684(2) Å, but still clearly double bonds.

The second crystal contained the dimer [Mo₂O₄F₄(μ-F)₂(Me₃PO)₂] with the structure shown in (Figure 6), which is related to that of the known anion [Mo₂O₄F₄(μ-F)₂]²⁻ [31,32] with the Me₃PO replacing two terminal fluorides.

The third crystal was [Me₃POH]₂[Mo₂O₄F₄(μ-F)₂] (see ESI) which contains the known dimeric Mo(VI) anion. The protonated phosphine oxide, [Me₃POH]⁺ was observed in the ³¹P{¹H} NMR spectra of hydrolysed [MoOF₄(Me₃PO)] solutions.

3. Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm⁻¹. ¹H, ¹⁹F{¹H}, ³¹P{¹H} and ⁹⁵Mo NMR spectra were recorded using a Bruker AV–II 400 spectrometer and are referenced to the proto resonance of the solvent, external CFCCl₃, 85% H₃PO₄ and [MoO₄]⁻ in H₂O/D₂O at pH 11 respectively. Microanalyses were undertaken by London Metropolitan University. Solvents were dried prior to use: THF and Et₂O by distillation from sodium benzophenone ketyl, MeCN and CH₂Cl₂ from CaH₂. MoF₆ was obtained from Fluorochem. Ligands were obtained commercially (Sigma Aldrich) and dried over molecular sieves (dmf), CaH₂ (dmoso), by sublimation in vacuo (Me₃PO) or by melting in vacuo (bipy, Ph₃PO) and all reactions were carried out under dinitrogen in rigorously dry solvents, using Schlenk and glove box techniques.
CAUTION: MoF₆ is highly corrosive and HF is generated by hydrolysis of the complexes, both of which can cause serious skin burns on contact. Appropriate safety precautions should be taken.

3.1 [MoOF₄(MeCN)]

A mixture of MeCN (50 mL) and HMDSO (1.6 g, 12.0 mmol) were frozen in liquid nitrogen, and then MoF₆ (2.5 g, 12.0 mmol) condensed in under vacuum. The mixture was allowed to warm slowly to room temperature turning yellow-brown and then colourless on melting. It was stirred for 5 h, giving a clear, colourless solution. The solvent was removed in vacuo to give a white powder. Yield: 2.5 g, 94%. Anal. Required for C₁₂H₃F₄MoNO (229.0): C, 10.49; H, 1.32; N, 6.12%. Found: C, 10.50; H, 1.35; N, 6.00%.

1H NMR (CD₂Cl₂, 293 K): 2.30 (s); (CD₃CN, 293 K): 2.10 (s).

19F{¹H} NMR (CD₂Cl₂, 293 K): +148.2 (s, ¹JMo-F = 67 Hz); (CD₃CN, 293 K): +146.5 (s, ¹JMo-F = 64 Hz).

195Mo NMR (CD₃CN, 293 K): -287.3 (quintet ¹JMoF = 65 Hz). IR (Nujol/cm⁻¹): 2324 (m, CN), 2293 (ν(C–C) + δ(CH₃)), 1019 (s, MoO), 652 (br, MoF).

3.2 [MoOF₄(thf)]

[MoOF₄(MeCN)] (0.23 g, 1 mmol) was added to dry thf (10 mL) to produce a cream solution. After 1 h. the solvent was removed in vacuo to leave a sticky cream solid which darkened becoming dark blue overnight. The complex is very moisture sensitive turning deep blue on exposure to air, and slowly gives a blue precipitate in chlorocarbon solvents. ¹H NMR (CD₂Cl₂, 293 K): 1.92 (s, [H]), 3.86 (s, [H]).

19F{¹H} NMR (CD₂Cl₂, 293 K): +143.1 (s, ¹JMo-F = 67 Hz).

195Mo NMR (CD₂Cl₂, 293 K): -271.6 (quintet, ¹JMoF = 65 Hz). IR (Nujol/cm⁻¹): 1097 (s, thf), 1016 (vs, MoO), 872 (s, thf), 675 (vs, MoF).

3.3 [MoOF₄(Ph₃PO)]

A solution of Ph₃PO (0.28 g, 1 mmol) in MeCN was added to a solution of [MoOF₄(MeCN)] (0.23 g, 1 mmol) in MeCN giving a clear slightly yellow solution. The reaction mixture was left stirring for 1 h. The solvent was then reduced approximatively to 5 mL when a white solid precipitated out of solution. The solid was filtered and dried in vacuo. Yield: 0.24 g, 52%. Anal. Required for C₁₈H₁₅F₄MoO₂ (466.2): C, 46.37; H, 3.24%. Found: C, 46.50; H, 3.34%. ¹H NMR (CD₂CN, 293 K): 7.85–7.54 (m). ¹9F{¹H} NMR (CD₂CN, 293 K): +139.1 (s, ¹JMo-F = 67 Hz). ³¹P{¹H} NMR (CD₂CN, 293 K): +42.8 (s). ¹⁹⁵Mo NMR (CD₂CN, 293 K): -270.0 (quintet, ¹JMoF = 65 Hz). IR (Nujol/cm⁻¹): 1085 (s, P=O), 990 (s, MoO), 640 (s, MoF).

3.4 [MoOF₄(Me₃PO)]

A solution of Me₃PO (0.097 g, 1 mmol) in CH₃CN was added to a solution of [MoOF₄(MeCN)] (0.23 g, 1 mmol) in MeCN giving a clear, slightly yellow solution. The reaction mixture was left stirring for 1 h. The solvent was then reduced approximatively to 2 mL, when a white solid precipitated out of solution.
The solid was filtered and dried in vacuo. Yield: 0.087 g, 31%. Anal. Required for C₉H₆F₄MoO₂ (280.0): C, 12.87; H, 3.24%. Found: C, 12.85; H, 3.27 %.

1H NMR (CD₃CN, 293 K): 1.88 (d, Jₚ₋H = 15 Hz).

19F{¹H} NMR (CD₂CN, 293 K): +135.9 (s, JMo₋F = 62 Hz).

31P{¹H} NMR (CD₂CN, 293 K): +64.2.

95Mo NMR (CD₂CN, 293 K): −257.0 (quintet, JMo₋F = 66 Hz).

IR (Nujol/cm⁻¹): 1079 (s, P=O), 970 (s, MoO), 606 (s, MoF).

3.5 [MoOF₄(dmf)]

A solution of dmf (0.083 g, 1 mmol) in CH₃CN was added to a solution of [MoOF₄(MeCN)] (0.23 g, 1 mmol) in MeCN giving a clear solution. The reaction mixture was left stirring for 1 h. The solvent was then removed in vacuo giving a slightly yellow oil. Hexane (2 mL) was added causing the formation of a white solid which was filtered off and dried in vacuo (0.075 g, 29 %).

1H NMR (CD₃CN, 293 K): 8.07 (s), 3.09 (s), 2.97 (s).

19F{¹H} NMR (CD₃CN, 293 K): +138.5 (s, JMo₋F = 67 Hz).

95Mo NMR (CD₂CN, 293K) −251.5 (quintet, JMo₋F = 64 Hz). IR (Nujol/cm⁻¹): 1030 (s, SO), 1007 (s, MoO), 653 (s, MoF).

3.6 [MoOF₄(dmso)]

A solution of dmso (0.089 g, 1 mmol) in CH₃CN was added to a solution of [MoOF₄(MeCN)] (0.21 g, 1 mmol) in CH₃CN giving a clear, slightly yellow solution. The reaction mixture was left stirring for 1 h. The solvent was then removed in vacuo giving a slightly yellow waxy solid. Anal. – complex significantly decomposed in ~ 24 h, turning blue; this precluded microanalytical measurements. ¹H NMR (CD₂CN, 293 K): 2.75 (s).

19F{¹H} NMR (CD₂CN, 293 K): +139.1 (s, JMo₋F = 65 Hz).

95Mo NMR (CD₂CN, 293 K): −266.3 (quintet, JMo₋F = 66 Hz). IR (Nujol/cm⁻¹): 1007 (s, MoO), 643 (s, MoF).

3.7 [MoOF₄(bipy)]

A solution of bipy (0.157 g, 1 mmol) in CH₃CN was added to a solution of [MoOF₄(MeCN)] (0.23 g, 1 mmol) in CH₃CN causing, after few minutes, the precipitation of a pale yellow solid. The solid was filtered off and dried in vacuo (0.220 g, 65 %).

IR (Nujol/cm⁻¹) 959 (s,MoO), 622, 595,532 and 476 (MoF).

3.8 [MoO₂F₂(MeCN)₂]

A mixture of MeCN (15 mL) and HMDSO (0.80 g, 4.5 mmol) were frozen in liquid nitrogen, and then MoF₆ (0.42 g, 2 mmol) condensed in under vacuum. The mixture was allowed to warm slowly to room temperature and stirred for 5 h, giving a colourless solution with some white solid. The solvent was removed in vacuo to give a very pale blue-white powder. The product was only partially soluble in dry
MeCN in which it gave a bluish solution which darkened over time. Solution data on the soluble component (see text): \(^1\)H NMR (CD\(_2\)CN, 293 K): 1.97 (s). \(^{19}\)F\(^{\text{[1]}\text{H}}\) NMR (CD\(_2\)CN, 293 K): −33.7 (s). \(^{95}\)Mo NMR (CD\(_2\)CN, 293 K): −162.8 (t, \(^{1}J_{\text{Mo,F}} = 115\) Hz). IR (Nujol/cm\(^{-1}\)): 2312 (m, CN), 2285 (m, ν(C–C) + δ(CH\(_3\))), 959(m), 938 (m) MoO), 567 (br, MoF). There are also very broad absorptions at ~1020–890 and ~670–450 cm\(^{-1}\).

3.9 \([\text{MoO}_2F_2(\text{Ph}_3\text{PO})_2]\)

A solution of Ph\(_3\)PO (0.28 g, 1 mmol) in laboratory grade (i.e. wet) MeCN (20 mL) was added to a solution of \([\text{MoOF}_3(\text{MeCN})]\) (0.23 g, 1 mmol) in MeCN (10 mL) giving a clear slightly yellow solution. The reaction mixture was left stirring for 1 h. The solvent was then reduced to 5 mL, when a cream solid precipitated out of solution. The solid was filtered and dried in vacuo. Yield: 0.24 g, 35% (based upon OPPh\(_3\)). Anal. Required for C\(_{56}\)H\(_{30}\)F\(_2\)MoP\(_2\)O\(_4\): C, 59.85; H, 4.19; Found: C, 59.50; H, 4.17%. \(^1\)H NMR (CD\(_2\)Cl\(_2\), 293 K): 7.68–7.40 (m). \(^{19}\)F\(^{\text{[1]}\text{H}}\) NMR (CD\(_2\)CN, 293 K): −49.0 (s). \(^{31}\)P\(^{\text{[1]}\text{H}}\) NMR (CD\(_2\)Cl\(_2\), 293 K): +40.2 (s). IR (Nujol/cm\(^{-1}\)): 1143(s), 1085(s) (P=O), 949(m), 916 (m) (MoO), 587 (s, MoF).

3.10 \([\text{MoO}_2F_2(\text{dmso})_2]\)

Dmso (0.08 g, 1 mmol) was added to a solution of \([\text{MoOF}_3(\text{MeCN})]\) (0.23 g, 1 mmol) in laboratory grade MeCN (20 mL) to produce a clear solution. After 2 h the solution was concentrated in vacuo to ~3 mL, resulting in precipitation of a white powder, which was filtered off and dried in vacuo. Anal. Required for C\(_{68}\)H\(_{32}\)F\(_2\)MoO\(_4\)S\(_2\) (332.0): C, 14.91; H, 3.75%. Found: C, 14.71; H, 3.81%. \(^1\)H NMR (CD\(_2\)CN, 293 K): 2.75 (s). \(^{19}\)F\(^{\text{[1]}\text{H}}\) NMR (CD\(_2\)CN, 293 K): −50.8 (s). \(^{95}\)Mo (CD\(_2\)CN, 293 K): −92.7 (t, \(^{1}J_{\text{Mo,F}} = 112\) Hz). IR (Nujol/cm\(^{-1}\)): 1002(s), 994 sh (S=O) 928(m), 897(m) (MoO), 583(m), 554 (w,br, MoF). The complex was also made from \([\text{MoOF}_3(\text{MeCN})]\), dmso, and HMDSO in a 1:2:2 molar ratio, and was spectroscopically identical.

3.11 X-ray experimental

Crystals of the complexes were grown from MeCN solutions of the complexes as described above. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (\(\lambda = 0.71073\) Å) rotating anode generator with VHF Varimax optics (70 micron focus) with the crystal held at 100 K. Structure solution and refinement were performed using SHELX(S/L)97, SHELX-2013 or SHELX-2014/7 [33]. H atoms bonded to C were placed in calculated positions using the default C–H distance, and refined using the riding model. Details of the crystallographic parameters are given in Table 2. CCDC reference numbers in cif format are \([\text{MoO}_2F_2(\text{MeCN})_2]\): CCDC 1542410; \([\text{Me}_3\text{POH}]_2[\text{Mo}_2\text{O}_4\text{F}_4(\mu-\text{F})_2]\): CCDC 1542411; \([\text{MoO}_2F_2(\text{Me}_3\text{PO})(\text{H}_2\text{O})]\): CCDC 1542412;
[Mo$_2$O$_4$F$_2$(μ-F)$_2$(Me$_3$PO)$_2$]: CCDC 1542413; [MoOF$_4$(Ph$_3$PO)]: CCDC 1542414; [MoO$_2$F$_2$(Ph$_3$PO)$_2$]: CCDC 1542415.

4. Conclusions

The first series of neutral ligand (N- or O-donor) complexes of MoOF$_4$, specifically [MoOF$_4$(L)] (L = MeCN, thf, dmf, dmso, Ph$_3$PO and Me$_3$PO) have been prepared and characterised spectroscopically (IR and multinuclear NMR), and the X-ray structure of [MoOF$_4$(Ph$_3$PO)] determined. All are extremely readily hydrolysed in both the solid state and solution, and the corresponding [MoO$_2$F$_2$(L)$_2$] were identified as the major molybdenum containing hydrolysis products. The reaction of the [MoOF$_4$(L)] with L and HMDSO produces the [MoO$_2$F$_2$(L)$_2$] analogues, although the latter are more easily made in other ways. In contrast, the [MoOF$_4$(bipy)] is insoluble in common solvents and appears stable in air as a solid and does not react with HMDSO in MeCN, presumably due to its insolubility. Full spectroscopic data are reported for the [MoO$_2$F$_2$(L)$_2$] complexes, along with X-ray structures for [MoO$_2$F$_2$(Ph$_3$PO)$_2$], [MoO$_2$F$_2$(Me$_3$PO)(H$_2$O)] and [Mo$_2$O$_4$F$_2$(μ-F)$_2$(Me$_3$PO)$_2$]. In general there is a close similarity between the corresponding complexes of MoOF$_4$ and WOF$_4$ as might be expected, but the former are very significantly less stable both as solids and in solution. In contrast, corresponding MoO$_2$F$_2$ and WO$_2$F$_2$ complexes are both robust, presumably due to the increased stabilisation of the metal centre by the second π-donor oxide ligand. The instantaneous reduction of [MoOF$_4$(MeCN)] by soft donor ligands, contrasting with the isolation of WOF$_4$-phosphine complexes [5], is a reflection of the significantly greater oxidising power of analogous 4d versus 5d metal centres.

Acknowledgements

We thank EPSRC for support (EP/K039466, EP/M023664, and EP/N035437/1), FMM thanks the EPSRC and GE Healthcare for a Case studentship.
References


[30] The unit cell of [MoO$_2$F$_2$(Ph$_3$PO)$_2$], described as monoclinic, was reported in Ref 18 and the CCDC (CCDC code FXPOMO), but no space group or structural information were provided. It is not the same cell or space group as reported here.


Figure 1(a). \(^{19}\text{F}\) \(^{1}\text{H}\) and (b) \(^{95}\text{Mo}\) NMR spectra of \([\text{MoOF}_4(\text{Ph}_3\text{PO})]\) at 295 K.

Figure 2. View of the structure of \([\text{MoOF}_4(\text{Ph}_3\text{PO})]\) showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1–F4 = 1.8490(15), Mo1–F3 = 1.8704(14), Mo1–F2 = 1.8540(15), Mo1–F1 = 1.8676(14), Mo1–O1 = 1.6643(18), Mo1–O2 = 2.1533(16), P1–O2 = 1.5171(17), F4–Mo1–F2 = 90.68(7), F4–Mo1–F1 = 87.58(7), F2–Mo1–F3 = 90.66(7), F1–Mo1–F3 = 90.47(8), O1–Mo1–F1 = 88.11(7), O1–Mo1–F2 = 84.31(6), F4–Mo1–O2 = 83.11(6).
Figure 3. View of the structure of $[\text{MoO}_2\text{F}_2\text{(MeCN)}_2]\text{MeCN}$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. The disordered MeCN solvate molecule is also omitted. Selected bond lengths (Å) and angles (°): Mo1−O1 = 1.695(3), Mo1−F1 = 1.898(4), Mo1−F2 = 1.901(4), Mo1−N1 = 2.350(4), O1−Mo1−O1$^i$ = 104.1(2), O1−Mo1−F1 = 98.44(13), O1−Mo1−F2 = 98.47(13), F1−Mo1−F2 = 152.34(16), O1−Mo1−N1 = 89.51(14), F1−Mo1−N1 = 79.85(12), F2−Mo1−N1 = 78.57(12), O1−Mo1−N1 = 89.51(13), N1−Mo1−N1$^i$ = 76.86(17).

Figure 4. View of the structure of $[\text{MoO}_2\text{F}_2\text{(Ph}_3\text{PO})_2]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1−F1 = 1.893(5), Mo1−O2 = 1.689(6), Mo1−O1 = 2.230(5), F1−Mo1−F1$^i$ = 158.7(2), F1−Mo1−O2 = 95.5(2), F1−Mo1−O2$^i$ = 97.6(2), O2−Mo1−O2$^i$ = 103.8(4), O1−Mo1−F1 = 80.72(17), O1−Mo1−F1$^i$ = 82.48(19), O1−Mo1−O2 = 90.4(2), O1−Mo1−O1$^i$ = 75.5(2).
Figure 5 View of the structure of [MoO$_2$F$_2$(Me$_3$PO)(H$_2$O)] showing atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1–F2 = 1.9042(15), Mo1–F1 = 1.9067(15), Mo1–O4 = 2.2881(19), Mo1–O3 = 2.1475(19), Mo1–O2 = 1.7433(19), Mo1–O1 = 1.684(2), F2–Mo1–F1 = 155.92(7), F2–Mo1–O4 = 79.66(7), F2–Mo1–O3 = 80.40(7), F1–Mo1–O4 = 79.47(7), F1–Mo1–O3 = 83.80(7), O3–Mo1–O4 = 78.54(7), O2–Mo1–F2 = 94.57(8), O2–Mo1–F1 = 95.97(8), O2–Mo1–O4 = 86.36(9), O1–Mo1–F2 = 100.42(8), O1–Mo1–F1 = 98.48(8), O1–Mo1–O3 = 93.15(9), O1–Mo1–O2 = 102.0(1).

Figure 6 View of the structure of [Mo$_2$O$_4$F$_2$(μ-F)$_2$(Me$_3$PO)$_2$] showing atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1–F1 = 1.898(4), Mo1–F2 = 2.210(4), Mo1–F2’ = 2.105(4), Mo1–O1 = 2.028(4), Mo1–O2 = 1.696(5), Mo1–O3 = 1.685(5), Mo1–F2–Mo1’ = 111.49(16), F1–Mo1–F2 = 83.99(15), F1–Mo1–F2’ = 83.36(15), F2–Mo1–F2’ = 68.51(16), O1–Mo1–F2 = 81.55(16).
$O_1\text{--Mo1--F}_2' = 79.53(16)$, $O_2\text{--Mo1--F}_1 = 98.4(2)$, $O_2\text{--Mo1--F}_2 = 88.55(19)$, $O_2\text{--Mo1--O}_1 = 93.9(2)$, $O_3\text{--Mo1--F}_1 = 98.2(2)$, $O_3\text{--Mo1--F}_2 = 98.4(2)$, $O_3\text{--Mo1--O}_1 = 93.0(2)$, $O_3\text{--Mo1--O}_2 = 104.2(2)$.

Scheme 1

$L = \text{Ph}_3\text{PO, Me}_3\text{PO, dmso, dmf}$

Scheme 1
Table 1 Selected spectroscopic data

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<th>complex</th>
<th>$\delta(^{19}F{^1H})^a$ ($^{1}J_{Mo\text{F}}$/Hz)</th>
<th>$\delta(^{95}Mo)^a$ ($^{1}J_{Mo\text{F}}$/Hz)</th>
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a. in CD$_3$CN, 293 K.  b. Nujol mull.  c. CD$_2$Cl$_2$ solution, 295 K.  d. data from Ref. 14.  e. data from Refs. 13 and 17.
### Table 2 X-ray crystallographic data

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$^a$Common items: T = 293 K; wavelength (Mo-K$_\alpha$) = 0.71073 Å; $\theta$(max) = 27.5°; $b$ R$_1 = \Sigma||Fo||Fc||/\Sigma||Fo||$; wR$_2$=[Σw(Fo$^2$-Fc$^2$)$^2$/ΣwFo$^4$]$^{1/2}$
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