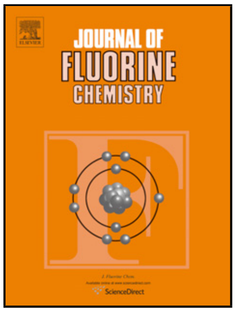

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PII: S0022-1139(17)30149-5
DOI: http://dx.doi.org/doi:10.1016/j.jfluchem.2017.06.015
Reference: FLUOR 9005

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 Chemistryhttp://dx.doi.org/10.1016/j.jfluchem.2017.06.015

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

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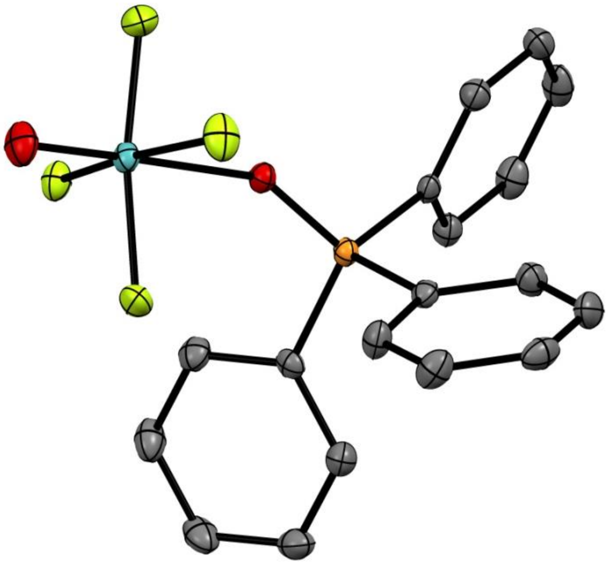
Graphical abstract



Highlights:

- First examples of $MoOF_4$ complexes with neutral ligands
- X-ray structure of $[MoOF_4(Ph_3PO)]$
- Comparisons of $[MoOF_4(L)]$ and $[MoO_2F_2(L)_2]$ complexes
- Comparisons of Mo(VI) and W(VI) oxide fluoride complexes

Abstract

[$MoOF_4$(MeCN)], prepared from reaction of MoF_6 with $(Me_3Si)_2O$ in anhydrous MeCN solution, reacts with the neutral O-donor ligands, thf, Ph_3PO, Me_3PO, dmf and dmso, (L) in a 1:1 molar ratio under rigorously anhydrous conditions to form six-coordinate [$MoOF_4$(L)], which have been characterised by microanalysis, IR, ^{1}H, ^{19}F{^{1}H} and ^{95}Mo NMR spectroscopy. In the presence of moisture the major products are [$MoO_2F_2(L)_2$], which can be made directly by reaction of [$MoOF_4$(L)] with a further equivalent of L and $(Me_3Si)_2O$. [$MoOF_4$(MeCN)] and 2,2'-bipyridyl produce the insoluble [$MoOF_4$(bipy)], which is probably 7-coordinate. Ph_3AsO is quantitatively converted to Ph_3AsF_2 by [$MoOF_4$(MeCN)], and soft ligands, including Me_2S, Me_3P and Me_3As, reduce the oxide fluoride on contact. Unstable [$MoO_2F_2(MeCN)_2$] has also been prepared and the X-ray structure of [$MoO_2F_2(MeCN)_2$]·MeCN is reported. X-ray crystal structures are reported for [$MoOF_4(Ph_3PO)$], [$MoO_2F_2(Ph_3PO)_2$], [$MoO_2F_2(Me_3PO)(H_2O)$] and [$Mo_2O_4F_2(\mu\text{-}F)_2(Me_3PO)_2$]. Comparisons with the corresponding chemistries of WOF_4 and WO_2F_2 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 [WOF_4(L)] derived from tungsten(VI) oxide tetrafluoride, made from [WOF_4(MeCN)] and neutral N- or O-donor ligands (L = thf, py, Ph_3PO, Me_3PO, dmso) in anhydrous MeCN solution [4]. The [WOF_4(MeCN)], which is readily obtained from WF_6 and $(Me_3Si)_2O$ 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 [WOF_4(L)] with further equivalents of L and $(Me_3Si)_2O$ afforded complexes [$WO_2F_2(L)_2$] (L = py, Ph_3PO, Me_3PO, dmso) [4]. Attempts to replace the nitrile in [WOF_4(MeCN)] with soft donor ligands, such as arsines, thioethers or selenoethers, failed, but two seven-coordinate, pentagonal-bipyramidal complexes, [WOF_4(diphosphine)] (diphosphine = $Me_2PCH_2CH_2PMe_2$ or o-$C_6H_4(PMe_2)_2$), were made from [WOF_4(MeCN)] and one equivalent of the diphosphine in anhydrous Et_2O solution. Six-coordinate [$WOF_4(PMe_3)$] 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, $MoOF_4$, is a white powder made by fluorination of MoO_3, or by reaction of molybdenum metal with O_2/F_2 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 MoO_2F_2 involving fluorination of MoO_3 or MoO_2Cl_2 [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 $Mo_3(\mu\text{-}F)_3$ 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 $MoOF_4$, is of [$MoOF_4(Ph_3PO)$], identified *in situ* by its ^{19}F NMR spectrum, but not isolated [10]. There are also adducts of $MoOF_4$ with XeF_2 and KrF_2 [11,12]. In contrast, a number of complexes of the form [$MoO_2F_2L_2$] (L = Ph_3PO, Me_3PO, Ph_2MePO, dmso; L_2 = 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" ($MoO_3{\cdot}nH_2O$) in aqueous HF, or, in some cases, from the corresponding [$MoO_2Cl_2(L)_2$] and Me_3SnF [13-18]. The [$MoO_2F_2(thf)_2$] was made by decomposition of [$MoF_4(NCl)$] in thf [19], and [$MoO_2F_2(dmf)_2$] by dissolution of MoO_2F_2 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 $MoOF_4$ and some structural and spectroscopic data on complexes of MoO_2F_2 for comparison.

2. Results and Discussion

2.1 Synthons

The route developed to prepare $MoOF_4$ complexes is based upon [$MoOF_4(MeCN)$] which is readily obtained by reaction of MoF_6 with $(Me_3Si)_2O$ (HMDSO), in a 1 : 1 molar ratio in anhydrous MeCN. The [$MoOF_4(MeCN)$] 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 CH_2Cl_2, the solution slowly decomposes, again turning blue, and the $^{19}F\{^1H\}$ NMR spectrum shows some CH_2FCl formed [20]. The $^{19}F\{^1H\}$ NMR spectrum of [$MoOF_4(MeCN)$] in MeCN shows a singlet at $\delta = +146.5$ with weak six-line pattern satellites due to coupling with ^{95}Mo

with $^1J_{MoF}$ = 64 Hz (^{95}Mo, I = 5/2, 15.9%, Q = 0.12 x 10^{-28} m^2). The other molybdenum isotope with a nuclear spin, ^{97}Mo (I = 5/2, 9.5%), has a large Q = 1.1 x 10^{-28}m^2 and coupling to it is not observed. The chemical shifts observed in CH_2Cl_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}Mo NMR spectrum is a binomial quintet at δ(^{95}Mo) = −287.3. The value is shifted significantly to lower frequency than those observed for [$MoO_2F_2L_2$] complexes (Table 1) which have δ(^{95}Mo) between around −40 to −170 and $^1J_{MoF}$ > 100 Hz. The IR spectrum (Nujol mull) shows ν(CN) = 2324, ν(C–C) + δ(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 ν(MoO) and broad peak at 652 cm^{-1} due to ν(MoF).

2.2 $MoOF_4$ complexes

The reaction of [$MoOF_4$(MeCN)] with Ph_3PO in a 1:1 molar ratio in rigorously dry MeCN, produces [$MoOF_4$(Ph_3PO)] as a white powder. If an excess of Ph_3PO is used, also under anhydrous conditions, after several days the ^{19}F{^{1}H} and ^{31}P{^{1}H} NMR spectra show that [$MoOF_4$(Ph_3PO)] is still the only major product, although a small amount of Ph_3PF_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_3PO synthesis, [$MoO_2F_2(Ph_3PO)_2$] 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_3POH]$^+$ [15, 22] and a number of other unidentified species. The ^{19}F{^{1}H} NMR spectrum of [$MoOF_4$(Ph_3PO)] is a singlet at δ = +139 with weak ^{95}Mo satellites ($^1J_{MoF}$ = 65 Hz) and the ^{95}Mo NMR spectrum is a quintet at δ = −270.0 (Figure 1) , which clearly distinguish this complex from [$MoO_2F_2(Ph_3PO)_2$] (δ(^{19}F{^{1}H}) = −51.1, δ (^{95}Mo) = −114 (t), $^1J_{MoF}$ = 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_3PO)] 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_3PO)] [4], and the bond lengths and angles are very similar between the molybdenum and tungsten analogues, as expected.

The complex [$MoOF_4$(Me_3PO)] was made similarly from [$MoOF_4$(MeCN)] and Me_3PO in anhydrous MeCN. It is also very moisture sensitive in solution, and [Me_3POH]$^+$ [23] and [$MoO_2F_2(Me_3PO)_2$] [15] were identified among the hydrolysis products by multinuclear NMR studies. In contrast, the reaction of [$MoOF_4$(MeCN)] with Ph_3AsO in dry MeCN results in immediate and quantitative formation of Ph_3AsF_2 [24], with no evidence for a molybdenum complex formed.

Evaporation of a solution of [$MoOF_4$(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 (CD_2Cl_2, 293 K) +143.1 (s, $^1J_{Mo\text{-}F}$ = 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 [$MoOF_4$(thf)]. This instability makes [$MoOF_4$(thf)] less suitable as a synthon than the nitrile complex. The complexes [$MoOF_4$(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 [$MoOF_4$(MeCN)]-pyridine system were unsuccessful. In contrast, addition of an MeCN solution of 2,2'-bipyridyl to [$MoOF_4$(MeCN)] in MeCN, results in immediate precipitation of a cream solid, identified by microanalysis as [$MoOF_4$(bipy)]. This complex is completely insoluble in solvents such as MeCN or CH_2Cl_2, 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 [WOF_4(bipy)] [25], [WOF_4(py)$_2$] [26,27] and [WOF_4(diphosphine)] [5], it is seven-coordinate, probably pentagonal bipyramidal with axial O/F. The filtrate from this reaction shows some [MoO_2F_2(bipy)], but attempts to convert a suspension of [$MoOF_4$(bipy)] in MeCN to [MoO_2F_2(bipy)] by stirring with HMDSO failed, with the [$MoOF_4$(bipy)] being recovered, presumably due to its insolubility in the reaction mixture. [$MoOF_4$(bipy)] also appears to be stable in air, which contrasts with the sensitivity to moisture of the [$MoOF_4$(L)] complexes described above.

Although [WOF_4(PMe_3)] and [WOF_4(diphosphine)] (diphosphine = $Me_2PCH_2CH_2PMe_2$ or o-$C_6H_4(PMe_2)_2$) are formed from the reaction of the phosphines with [WOF_4(MeCN)] in Et_2O solution [5], the same ligands immediately produced dark tarry precipitates on contact with [$MoOF_4$(MeCN)] in Et_2O. Similarly, combination of $AsMe_3$, SMe_2 or $SeMe_2$ with [$MoOF_4$(MeCN)] in Et_2O or MeCN solution immediately produced deep red or brown solutions and dark precipitates, indicating reduction of the molybdenum.

2.3 MoO_2F_2 complexes

As described in the Introduction, [$MoO_2F_2(L)_2$] complexes are prepared readily from $MoO_3\cdot nH_2O$ and the appropriate ligand in aqueous HF/EtOH or by Cl/F exchange from the corresponding [$MoO_2Cl_2(L)_2$]. 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 [$MoO_2F_2(L)_2$], rather than devise alternative syntheses for the latter. Spectroscopic and structural data for several [$MoO_2F_2(L)_2$] complexes obtained during this study are also presented.

The reaction of MoF_6 with ≥ 2 equivalents of HMDSO in anhydrous MeCN, or reaction of $[MoOF_4(MeCN)]$ 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 $^{19}F\{^1H\}$ NMR spectra identified some $[SiF_5]^-$ 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 $\delta(^{19}F\{^1H\}) = -33.7$ (s) and $\delta(^{95}Mo) = -162.8$ (t, $^1J_{Mo-F} = 115$ Hz), which were consistent with the formation of $[MoO_2F_2(MeCN)_2]$. 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 $[MoO_2F_2(MeCN)_2]$. 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 $[MoOF_4(MeCN)]$ 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 $[MoO_2F_2(MeCN)_2]\cdot MeCN$. The structure (Figure 3) shows a distorted octahedral molecule with a *cis*-MoO_2 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 MoO_2, are typical of other complexes of MoO_2F_2 [9,14,15]. These results show that $[MoO_2F_2(MeCN)_2]$ is formed in the reactions, but is unstable, losing MeCN (even in MeCN solution) and depositing what is probably largely MoO_2F_2 polymer. Solids isolated by evaporation of the solution are mainly a mixture of MoO_2F_2 polymer [9,28] and $[MoO_2F_2(MeCN)_2]$ (we cannot rule out the presence of other insoluble Mo/O/F species). Extraction of the $[MoO_2F_2(MeCN)_2]$ into MeCN or CH_2Cl_2 results in partial decomposition with generation of more MoO_2F_2. The very broad IR bands below ~1050 cm^{-1} are attributed to the polymer, while the sharper superimposed features correspond to $[MoO_2F_2(MeCN)_2]$. Attempts to prepare $[NbOF_3(MeCN)_2]$ [29] or $[WO_2F_2(MeCN)_2]$ [4] from the parent fluoride and HMDSO in MeCN solution, failed, with only the nitrile-free polymeric oxide/fluoride isolated. The present case of MoO_2F_2 shows that the MeCN adduct can be formed, but that it is unstable with respect to irreversible loss of MeCN.

The reaction of $[MoOF_4(L)]$ with a further equivalent of L (L = Ph_3PO, Me_3PO, dmso) and HMDSO in anhydrous MeCN solution produced $[MoO_2F_2(L)_2]$ (Scheme 1), which were identified by comparison of their key spectroscopic features (Table 1) with literature data. The complexes $[MoO_2F_2(L)_2]$ (L = Ph_3PO, Me_3PO, dmso) were also isolated from reactions of $[MoOF_4(L)]$ with the appropriate ligands in "wet" solvents (i.e. as supplied laboratory grade). Since $[MoO_2F_2(L)_2]$ were originally prepared by combining solutions of L in EtOH and $MoO_3{\cdot}nH_2O$ in aqueous HF, their formation here from hydrolysis is unsurprising.

Crystals of $[MoO_2F_2(Ph_3PO)_2]$ were obtained by slow evaporation from a CH_2Cl_2 solution and the structure is shown in Figure 4 [30].

Although they are not isomorphous, the structure of $[MoO_2F_2(Ph_3PO)_2]$ is very similar to those of $[WO_2F_2(Ph_3PO)_2]$ [4] and $[MoO_2F_2(Ph_2MePO)_2]$ [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 MO_2 group. The bond lengths are unexceptional.

A few crystals each of three complexes containing Me_3PO were isolated from the filtrates from the preparations of $[MoOF_4(Me_3PO)]$. The first shown in Figure 5 was identified by the X-ray structure solution as $[MoO_2F_2(Me_3PO)(H_2O)]$ which has *trans* F–Mo–F and *cis*-MoO_2 groups. The Mo=O distances are surprisingly disparate, $Mo1{-}O2_{\textit{trans}\text{-Me3PO}} = 1.7433(19)$ Å and $Mo1{-}O1_{\textit{trans}\text{-H2O}} = 1.684(2)$ Å, but still clearly double bonds.

The second crystal contained the dimer $[Mo_2O_4F_2(\mu\text{-}F)_2(Me_3PO)_2]$ with the structure shown in (Figure 6), which is related to that of the known anion $[Mo_2O_4F_4(\mu\text{-}F)_2]^{2-}$ [31,32] with the Me_3PO replacing two terminal fluorides.

The third crystal was $[Me_3POH]_2[Mo_2O_4F_4(\mu\text{-}F)_2]$ (see ESI) which contains the known dimeric Mo(VI) anion. The protonated phosphine oxide, $[Me_3POH]^+$ was observed in the $^{31}P\{^1H\}$ NMR spectra of hydrolysed $[MoOF_4(Me_3PO)]$ 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, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$ and ^{95}Mo NMR spectra were recorded using a Bruker AV–II 400 spectrometer and are referenced to the protio resonance of the solvent, external $CFCl_3$, 85% H_3PO_4 and $[MoO_4]^-$ in H_2O/D_2O at pH 11 respectively. Microanalyses were undertaken by London Metropolitan University. Solvents were dried prior to use: THF and Et_2O by distillation from sodium benzophenone ketyl, MeCN and CH_2Cl_2 from CaH_2. MoF_6 was obtained from Fluorochem. Ligands were obtained commercially (Sigma Aldrich) and dried over molecular sieves (dmf), CaH_2 (dmso), by sublimation *in vacuo* (Me_3PO) or by melting *in vacuo* (bipy, Ph_3PO) and all reactions were carried out under dinitrogen in rigorously dry solvents, using Schlenk and glove box techniques.

***CAUTION:** MoF_6 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 [$MoOF_4$(MeCN)]

A mixture of MeCN (50 mL) and HMDSO (1.6 g, 12.0 mmol) were frozen in liquid nitrogen, and then MoF_6 (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 $C_2H_3F_4MoNO$ (229.0): C, 10.49; H, 1.32; N, 6.12%. Found: C, 10.50; H, 1.35; N, 6.00%. ^1H NMR (CD_2Cl_2, 293 K): 2.30 (s); (CD_3CN, 293 K): 2.10 (s). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): +148.2 (s, $^1J_{Mo\text{-}F}$ = 67 Hz); (CD_3CN, 293 K): +146.5 (s, $^1J_{Mo\text{-}F}$ = 64 Hz). ^{95}Mo NMR (CD_3CN, 293 K): −287.3 (quintet $^1J_{MoF}$ = 64 Hz). IR (Nujol/cm^{-1}): 2324 (m, CN), 2293 (ν(C–C) + δ(CH_3)), 1019 (s, MoO), 652 (br, MoF).

3.2 [$MoOF_4$(thf)]

[$MoOF_4$(MeCN)] (0.23 g, 1 mmol) was added to dry thf (10 mL) to produce a clear 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 (CD_2Cl_2, 293 K): 1.92 (s, [H]), 3.86 (s, [H]). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 293 K): +143.1 (s, $^1J_{Mo\text{-}F}$ = 67 Hz). ^{95}Mo NMR (CD_2Cl_2 293 K): −271.6 (quintet, $^1J_{MoF}$ = 65 Hz). IR (Nujol/cm^{-1}): 1097 (s, thf), 1016 (vs, MoO), 872 (s, thf), 675 (vs, MoF).

3.3 [$MoOF_4$(Ph_3PO)]

A solution of Ph_3PO (0.28 g, 1 mmol) in MeCN was added to a solution of [$MoOF_4$(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 $C_{18}H_{15}F_4MoO_2$ (466.2): C, 46.37; H, 3.24%. Found: C, 46.50; H, 3.34%. ^1H NMR (CD_3CN, 293 K): 7.85–7.54 (m). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): +139.1 (s, $^1J_{Mo\text{-}F}$ = 67 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, 293 K): +42.8 (s). ^{95}Mo NMR (CD_3CN, 293 K): −270.0 (quintet, $^1J_{MoF}$ = 65 Hz). IR (Nujol/cm^{-1}): 1085 (s, P=O), 990 (s, MoO), 640 (s, MoF).

3.4 [$MoOF_4$(Me_3PO)]

A solution of Me_3PO (0.097 g, 1 mmol) in CH_3CN was added to a solution of [$MoOF_4$(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 $C_3H_9F_4MoO_2$ (280.0): C, 12.87; H, 3.24%. Found: C, 12.85; H, 3.27%. ^{1}H NMR (CD_3CN, 293 K): 1.88 (d, $^1J_{P-H}$ = 15 Hz). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): +135.9 (s, $^1J_{Mo-F}$ = 62 Hz). $^{31}P\{^1H\}$ NMR (CD_3CN, 293 K): +64.2. ^{95}Mo NMR (CD_3CN, 293 K): −257.0 (quintet, $^1J_{Mo-F}$ = 66 Hz). IR (Nujol/cm^{-1}): 1079 (s, P=O), 970 (s, MoO), 606 (s, MoF).

3.5 [MoOF$_4$(dmf)]

A solution of dmf (0.083 g, 1 mmol) in CH_3CN was added to a solution of [$MoOF_4$(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 %). Anal. – complex significantly decomposed in ~ 12 h, turning blue; this precluded microanalytical measurements. ^{1}H NMR (CD_3CN, 293 K): 8.07 (s), 3.09 (s), 2.97 (s). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): +138.5 (s, $^1J_{Mo-F}$ = 67 Hz). ^{95}Mo NMR (CD_3CN, 293K) −266.3 (quintet, $^1J_{Mo-F}$ = 66 Hz). IR (Nujol/cm^{-1}): 1007 (s, MoO), 643 (s, MoF).

3.6 [MoOF$_4$(dmso)]

A solution of dmso (0.089 g, 1 mmol) in CH_3CN was added to a solution of [$MoOF_4$(MeCN)] (0.21 g, 1 mmol) in CH_3CN 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. ^{1}H NMR (CD_3CN, 293 K): 2.75 (s). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): +139.1 (s, $^1J_{Mo-F}$ = 65 Hz). ^{95}Mo NMR (CD_3CN, 293 K): −251.5 (quintet, $^1J_{Mo-F}$ = 64 Hz). IR (Nujol/cm^{-1}): 1030 (s, SO), 1007 (s, MoO), 653 (s, MoF).

3.7 [MoOF$_4$(bipy)]

A solution of bipy (0.157 g, 1 mmol) in CH_3CN was added to a solution of [$MoOF_4$(MeCN)] (0.23 g, 1 mmol) in CH_3CN causing, after few minutes, the precipitation of a pale yellow solid. The solid was filtered off and dried *in vacuo* (0.220 g, 65 %). Anal. Required for $C_{10}H_8F_4MoN_2O_2$ (344.1): C, 34.90; H, 2.34; N, 8.14. Found: C, 35.03; H, 2.32; N, 8.24 %. IR (Nujol/cm^{-1}) 959 (s,MoO), 622, 595,532 and 476 (MoF).

3.8 [MoO$_2$F$_2$(MeCN)$_2$]

A mixture of MeCN (15 mL) and HMDSO (0.80 g, 4.5 mmol) were frozen in liquid nitrogen, and then MoF_6 (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_3CN, 293 K): 1.97 (s). $^{19}F\{^{1}H\}$ NMR (CD_3CN, 293 K): −33.7 (s). ^{95}Mo NMR (CD_3CN, 293 K): −162.8 (t, $^{1}J_{Mo\text{-}F}$ = 115Hz). 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 [$MoO_2F_2(Ph_3PO)_2$]

A solution of Ph_3PO (0.28 g, 1 mmol) in laboratory grade (i.e. wet) MeCN (20 mL) was added to a solution of [$MoOF_4$(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 approximately 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 $C_{36}H_{30}F_2MoP_2O_4$ (722.5): C, 59.85; H, 4.19; Found: C, 59.50; H, 4.17%. ^{1}H NMR (CD_2Cl_2, 293 K): 7.68–7.40 (m). $^{19}F\{^{1}H\}$ NMR (CD_3CN, 293 K): −49.0 (s). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_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 [$MoO_2F_2(dmso)_2$]

Dmso (0.08 g, 1 mmol) was added to a solution of [$MoOF_4$(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 $C_4H_{12}F_2MoO_4S_2$ (332.0): C, 14.91; H, 3.75%. Found: C, 14.71; H, 3.81%. ^{1}H NMR (CD_3CN, 293 K): 2.75 (s). $^{19}F\{^{1}H\}$ NMR (CD_3CN, 293 K): −50.8 (s). ^{95}Mo (CD_3CN, 293 K): −92.7 (t, $^{1}J_{Mo\text{-}F}$ = 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 [$MoOF_4$(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 (λ = 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 [$MoO_2F_2(MeCN)_2$]: CCDC 1542410; [$Me_3POH]_2[Mo_2O_4F_4(\mu\text{-}F)_2$]: CCDC 1542411; [$MoO_2F_2(Me_3PO)(H_2O)$]: CCDC 1542412;

[$Mo_2O_4F_2(\mu\text{-}F)_2(Me_3PO)_2$]: CCDC 1542413; [$MoOF_4(Ph_3PO)$]: CCDC 1542414; [$MoO_2F_2(Ph_3PO)_2$]: 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_3PO and Me_3PO) have been prepared and characterised spectroscopically (IR and multinuclear NMR), and the X-ray structure of [$MoOF_4(Ph_3PO)$] determined. All are extremely readily hydrolysed in both the solid state and solution, and the corresponding [$MoO_2F_2(L)_2$] were identified as the major molybdenum containing hydrolysis products. The reaction of the [$MoOF_4$(L)] with L and HMDSO produces the [$MoO_2F_2(L)_2$] 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 [$MoO_2F_2(L)_2$] complexes, along with X-ray structures for [$MoO_2F_2(Ph_3PO)_2$], [$MoO_2F_2(Me_3PO)(H_2O)$] and [$Mo_2O_4F_2(\mu\text{-}F)_2(Me_3PO)_2$]. 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_2F_2 and WO_2F_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.

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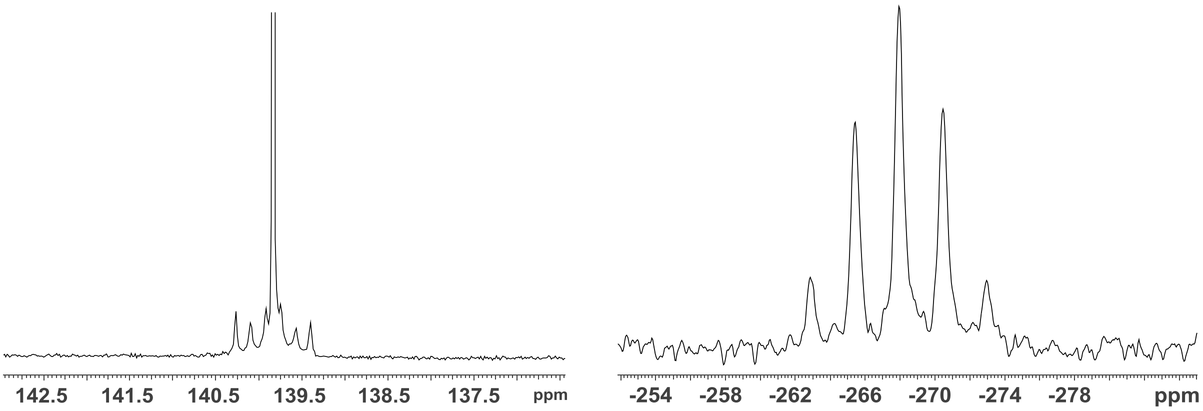


(a)

(b)

Figure 1(a). $^{19}F\{^{1}H\}$ and (b) ^{95}Mo NMR spectra of $[MoOF_4(Ph_3PO)]$ at 295 K.

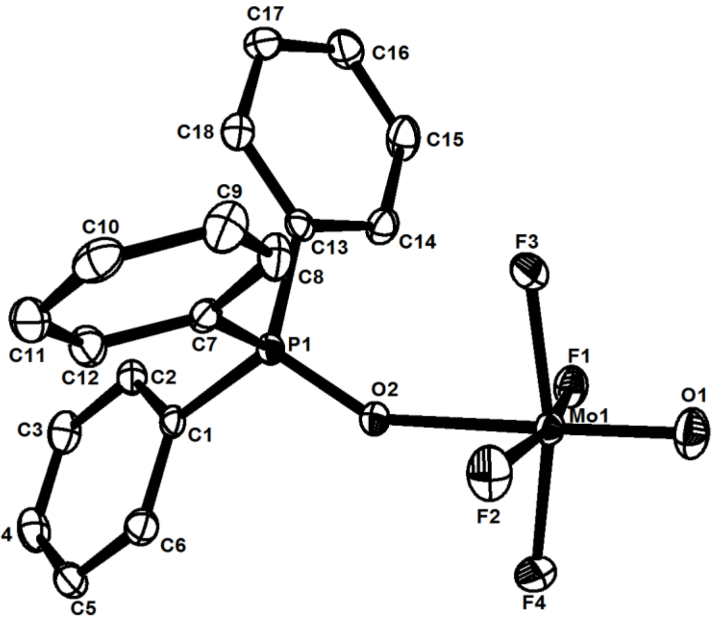


Figure 2. View of the structure of $[MoOF_4(Ph_3PO)]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1−F4 = 1.8490(15), Mo1−F3 = 1.8704(14), Mo1−F2 = 1.8540(15), Mo1−F1 = 1.8676(14), Mo1−O1 = 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 = 88.11(7), O1−Mo1−F1 = 95.91(8), O1−Mo1−F4 = 97.97(8), O1−Mo1−F3 = 95.47(8), O1−Mo1−F2 = 96.77(8), F3−Mo1−O2 = 83.46(6), F2−Mo1−O2 = 83.02(6), F1−Mo1−O2 = 84.31(6), F4−Mo1−O2 = 83.11(6).

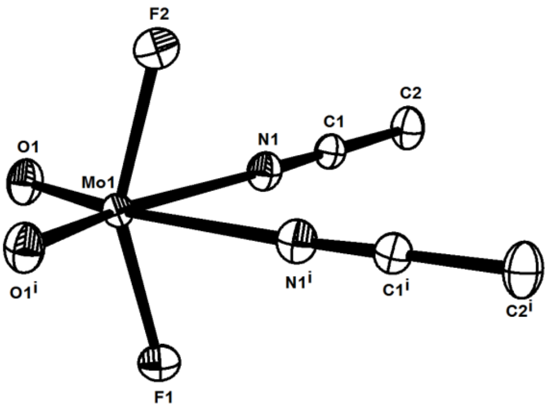


Figure 3. View of the structure of $[MoO_2F_2(MeCN)_2]\cdot MeCN$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. The disordered MeCN solvate molecule is also omitted. Selected bond lengths (Å) and angles (°): Mo1−O1 = 1.695(3), Mo1−F1 = 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).

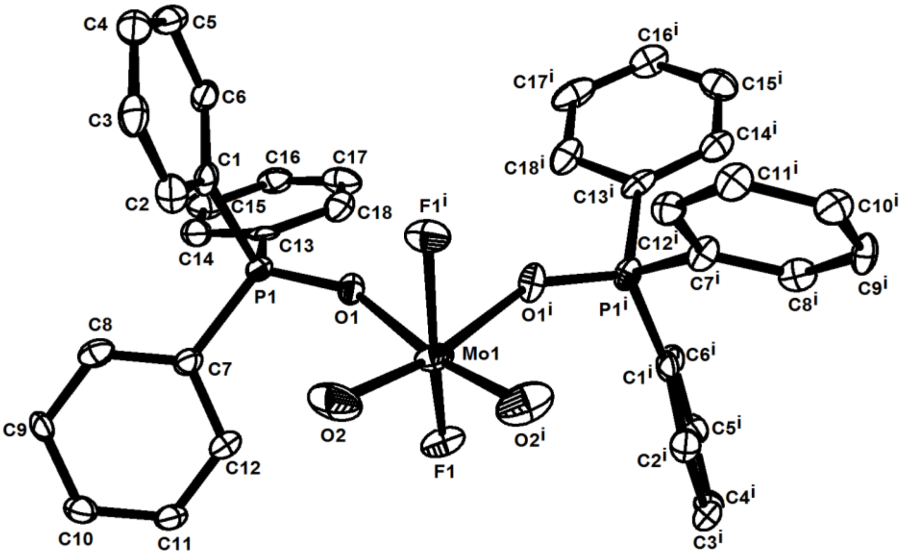


Figure 4 View of the structure of $[MoO_2F_2(Ph_3PO)_2]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1−F1 = 1.893(5), Mo1−O2 = 1.689(6,), Mo1−O1 = 2.230(5), F1−Mo1−F1^{i} = 158.7(2), 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).

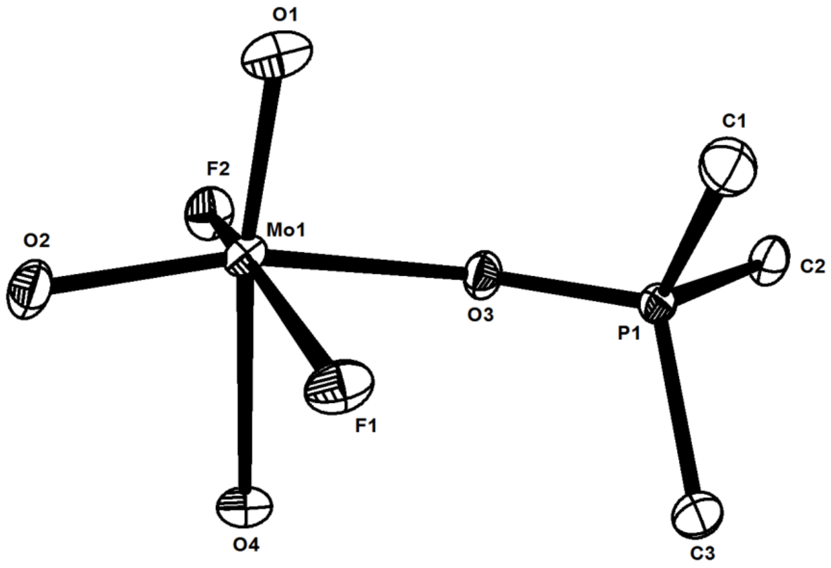


Figure 5 View of the structure of [$MoO_2F_2(Me_3PO)(H_2O)$] showing atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1−F2 = 1.9042(15), Mo1−F1=1.9067(15), Mo1−O4 = 2.2881(19), Mo1−O3 = 2.1475(19), Mo1−O2 = 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) .

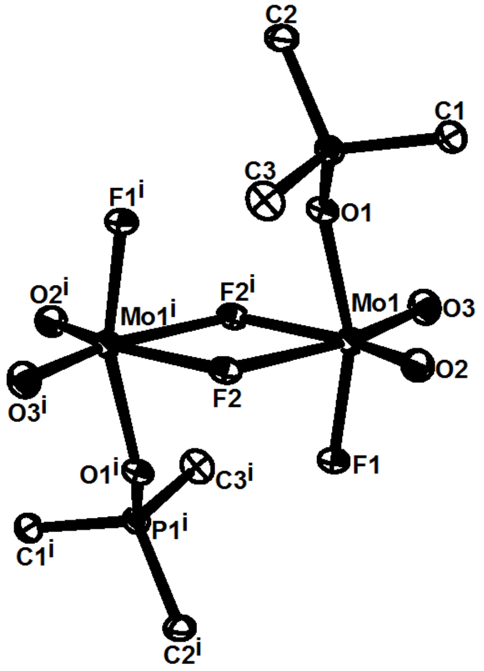
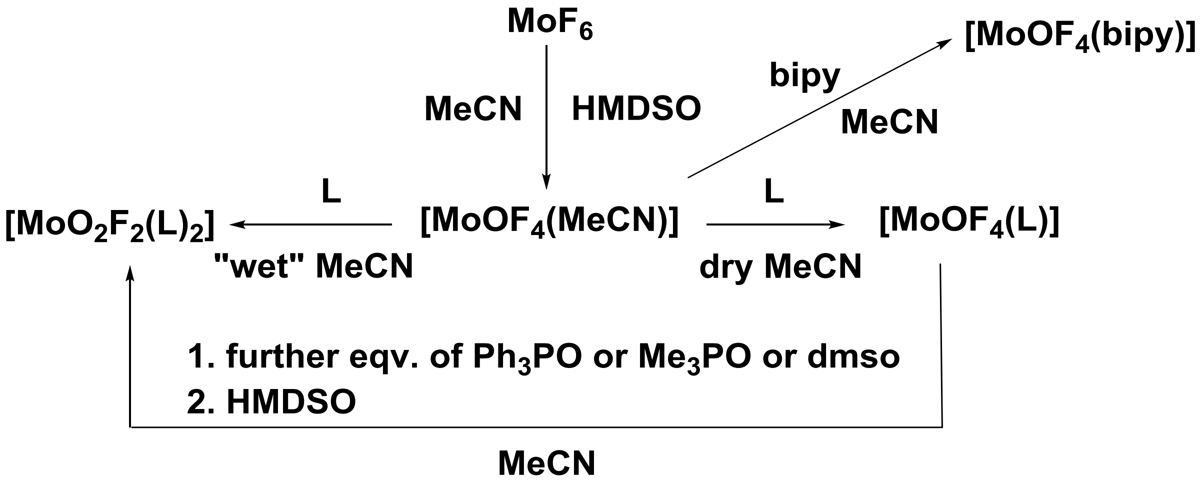


Figure 6 View of the structure of [$Mo_2O_4F_2(\mu\text{-}F)_2(Me_3PO)_2$] showing atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1−F1 = 1.898(4), Mo1−F2 = 2.210(4), Mo1−$F2^i$ = 2.105(4), Mo1−O1= 2.028(4), Mo1−O2 = 1.696(5), Mo1−O3 =1.685(5), Mo1− F2−$Mo1^i$ = 111.49(16), F1−Mo1−F2 = 83.99(15), F1−Mo1−$F2^i$ = 83.36(15), F2−Mo1−$F2^i$ = 68.51(16), O1−Mo1−F2 = 81.55(16),

O1−Mo1−F2^i = 79.53(16), O2−Mo1−F1 = 98.4(2), O2−Mo1−F2 = 88.55(19), O2−Mo1−O1 = 93.9(2), O3−Mo1−F1 = 98.2(2), O3−Mo1−F2 = 98.4(2), O3−Mo1−O1 = 93.0(2), O3−Mo1−O2 =104.2(2).



L = Ph_3PO, Me_3PO, dmso, dmf

Scheme 1

Table 1 Selected spectroscopic data

complex	δ(^{19}F{^{1}H}) [a] ($^{1}J_{MoF}$ /Hz)	δ(^{95}Mo) [a] ($^{1}J_{MoF}$ /Hz)	ν (Mo=O) cm^{-1} [b]	ν (Mo–F) cm^{-1} [b]
[MoOF$_4$(MeCN)]	+146.5 (s, 64)	−287.3 (q)	1019	652
[MoOF$_4$(thf)]	+143.1 (s, 67)[c]	−271.6 (q) [c]	1016	675
[MoOF$_4$(Ph$_3$PO)]	+139.1 (s, 65)	−270.0 (q)	990	640
[MoOF$_4$(Me$_3$PO)]	+135.9 (s, 62)	−257.0 (q)	990	639
[MoOF$_4$(dmso)]	+ 139.1 (s, 65)	−251.5 (q)	1007	653
[MoOF$_4$(dmf)]	+138.5 (s, 67)	−266.3 (q)	1007	643
[MoOF$_4$(bipy)]	Insol.	Insol.	959	622, 595, 532, 476
[MoO$_2$F$_2$(MeCN)$_2$]	−33.7 (s)	−162.8 (t, 115)	959, 930	567
[MoO$_2$F$_2$(Ph$_3$PO)$_2$]	−51.8 (s).	−114 (t, 120)[c]	949, 916	587
[MoO$_2$F$_2$(Me$_3$PO)$_2$]	−57.2 (s)[c]	−95 (t, 115)[c]	955, 906 [d]	566 [d]
[MoO$_2$F$_2$(dmso)$_2$]	−50.8 (s)	−92.7 (t, 112)	928, 897	583, 554
[MoO$_2$F$_2$(bipy)]	−52.8 (s)	−58.1 (t, 109)	947, 918[e]	585, 554[e]

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 [a]

Compound	$[MoO_2F_2(Me_3PO)(H_2O)]$	$[Mo_2O_4F_4(Me_3PO)_2]$	$[MoO_2F_2(Ph_3PO)_2]$
Formula	$C_3H_{11}F_2MoO_4P$	$C_6H_{18}F_4Mo_2O_6P_2$	$C_{36}H_{30}F_2MoO_4P_2$
M	276.03	516.02	722.48
Crystal system	monoclinic	monoclinic	orthorhombic
Space group (no.)	$P2_1/c$ (14)	$P2_1/n$ (14)	Fdd2 (43)
a /Å	7.3572(2)	8.3279(5)	18.4570(10)
b /Å	7.1853(3)	10.4904(5)	33.049(3)
c /Å	16.8798(8)	9.1604(5)	9.9908(10)
α /°	90	90	90
β /°	91.036(3)	96.681(5)	90
γ /°	90	90	90
U /$Å^3$	892.18(6)	794.84(8)	6094.3(9)
Z	4	2	8
μ(Mo-K_α) /mm^{-1}	1.652	1.837	0.589
F(000)	544	504	2944
Total number reflns	7463	5870	6531
R_{int}	0.023	0.049	0.071
Unique reflns	1748	1564	2892
No. of params, restraints	111, 0	94, 0	204, 1
R_1, wR_2 [$I > 2\sigma(I)$] [b]	0.024, 0.054	0.043, 0.135	0.055, 0.109
R_1, wR_2 (all data)	0.032, 0.058	0.046, 0.136	0.082, 0.136

[a] Common items: T = 293 K; wavelength (Mo-K_α) = 0.71073 Å; θ(max) = 27.5°; [b] $R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; $wR_2=[\Sigma w(Fo^2-Fc^2)^2/\Sigma wFo^4]^{1/2}$

Table 2 cont.

Compound	$[MoO_2F_2(MeCN)_2]\cdot MeCN$	$[MoOF_4(Ph_3PO)_2]$	$[Me_3POH]_2[Mo_2O_4F_4(\mu\text{-}F)_2]$
Formula	$C_6H_9F_2MoN_3O_2$	$C_{18}H_{15}F_4MoO_2P$	$C_3H_{10}F_3MoO_3P$
M	289.10	466.21	278.02
Crystal system	orthorhombic	monoclinic	triclinic
Space group (no.)	Pnma (62)	$P2_1/c$ (14)	P-1 (2)
a /Å	9.1511(10)	10.2899(3)	7.3172(6)
b /Å	12.5300(10)	8.4748(2)	7.3172(6)
c /Å	9.0718(10)	20.5446(6)	8.2791(7)
α /°	90	90	77.370(7)
β /°	90	94.754(3)	67.015(8)
γ /°	90	90	86.101(7)
U /Å^3	1040.20(18)	1785.42(9)	427.45(7)
Z	4	4	2
μ(Mo-K$_\alpha$) /mm^{-1}	1.270	0.873	1.732
F(000)	568	928	272
Total no. reflns	8057	14889	6271
R_{int}	0.026	0.031	0.024
Unique reflns	1072	3517	1675
No. of params, restraints	81, 2	235, 0	104, 0
R_1, wR_2 [$I > 2\sigma(I)$] [b]	0.0350, 0.0966	0.027, 0.061	0.024, 0.066
R_1, wR_2 (all data)	0.0367, 0.0978	0.034, 0.064	0.025, 0.066