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

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ABSTRACT

[MoOF$_4$(MeCN)], prepared from reaction of MoF$_6$ with (Me$_3$Si)$_2$O in anhydrous MeCN solution, reacts with the neutral O-donor ligands, thf, Ph$_3$PO, Me$_3$PO, 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$_2$F$_2$(L)$_2$], which can be made directly by reaction of [MoOF$_4$(L)] with a further equivalent of L and (Me$_3$Si)$_2$O. [MoOF$_4$(MeCN)] and 2,2′-bipyridyl produce the insoluble [MoOF$_4$(bipy)], which is probably 7-coordinate. Ph$_3$AsO is quantitatively converted to Ph$_3$AsF$_2$ by [MoOF$_4$(MeCN)], and soft ligands, including Me$_2$S, Me$_3$P and Me$_3$As, reduce the oxide fluoride on contact. Unstable [MoO$_2$F$_2$(MeCN)$_2$] has also been prepared and the X-ray structure of [MoO$_2$F$_2$(MeCN)$_2$]·MeCN is reported. X-ray crystal structures are reported for [MoOF$_4$(Ph$_3$PO)], [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)$_2$]. Comparisons with the corresponding chemistries of WOF$_4$ and WO$_2$F$_2$ are described.

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$_3$PO, Me$_3$PO, dmso) in anhydrous MeCN solution [4]. The [WOF$_4$(MeCN)], which is readily obtained from WF$_6$ and (Me$_3$Si)$_2$O 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$_3$Si)$_2$O afforded complexes [WO$_2$F$_2$(L)$_2$] (L = py, Ph$_3$PO, Me$_3$PO, 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$_2$PCH$_2$CH$_2$PMe$_2$ or o-C$_6$H$_4$(PMe$_2$)$_2$), were made from [WOF$_4$(MeCN)] and one equivalent of the diphosphine in anhydrous Et$_2$O 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$_2$F$_2$ involving fluorination of MoO$_3$ or MoO$_2$Cl$_2$ [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$_3$(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 MoOF$_4$, is of [MoOF$_4$(Ph$_3$PO)], 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$_2$F$_2$L$_2$] (L = Ph$_3$PO, Me$_3$PO, Ph$_2$MePO, 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$_3$·nH$_2$O) in aqueous HF, or, in some cases, from the corresponding [MoO$_2$Cl$_2$(L)$_2$] and Me$_3$SnF [13–18]. The [MoO$_2$F$_2$(thf)$_2$] was made by decomposition of

[MoF$_4$(NCl)] in thf [19], and [MoO$_2$F$_2$(dmf)$_2$] by dissolution of MoO$_2$F$_2$ 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$_2$F$_2$ 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$_3$Si)$_2$O (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$_2$Cl$_2$, the solution slowly decomposes, again turning blue, and the ^{19}F{^{1}H} NMR spectrum shows some CH$_2$FCl formed [20]. The ^{19}F{^{1}H} NMR spectrum of [MoOF$_4$(MeCN)] in MeCN shows a singlet at δ = +146.5 with weak six-line pattern satellites due to coupling with ^{95}Mo with ^{1}J$_{MoF}$ = 64 Hz (^{95}Mo, I = 5/2, 15.9%, Q = 0.12 × 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 × 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}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$_2$F$_2$L$_2$] complexes (Table 1) which have δ(^{95}Mo) between around −40 to −170 and ^{1}J$_{MoF}$ > 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$_3$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}H} and ^{31}P{^{1}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}H} NMR spectrum of [MoOF$_4$(Ph$_3$PO)] is a singlet at δ = +139 with weak ^{95}Mo satellites (^{1}J$_{MoF}$ = 65 Hz) and the ^{95}Mo NMR spectrum is a quintet at δ = −270.0 (Fig. 1), which clearly distinguish this complex from [MoO$_2$F$_2$(Ph$_3$PO)$_2$] (δ(^{19}F{^{1}H}) = −51.1, δ (^{95}Mo) = −114 (t), ^{1}J$_{MoF}$ = 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 (Fig. 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 [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{^{1}H} NMR (CD$_2$Cl$_2$, 293 K) +143.1 (s, ^{1}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 [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

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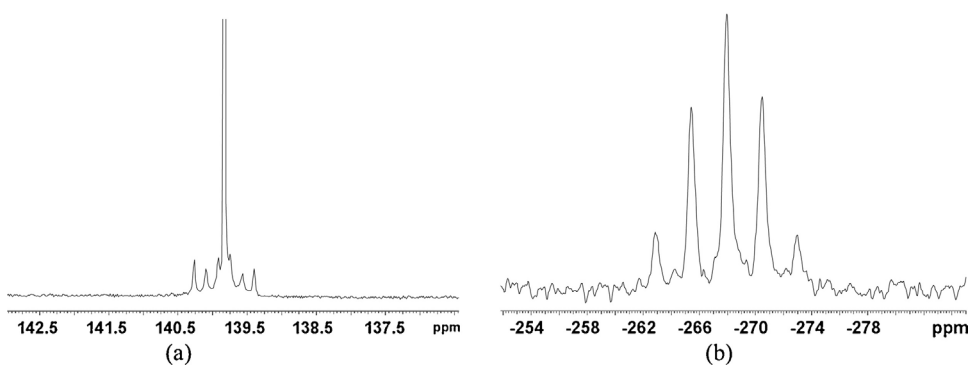
Fig. 1. (a) $^{19}F\{^{1}H\}$ and (b) ^{95}Mo NMR spectra of [MoOF$_4$(Ph$_3$PO)] at 295 K.

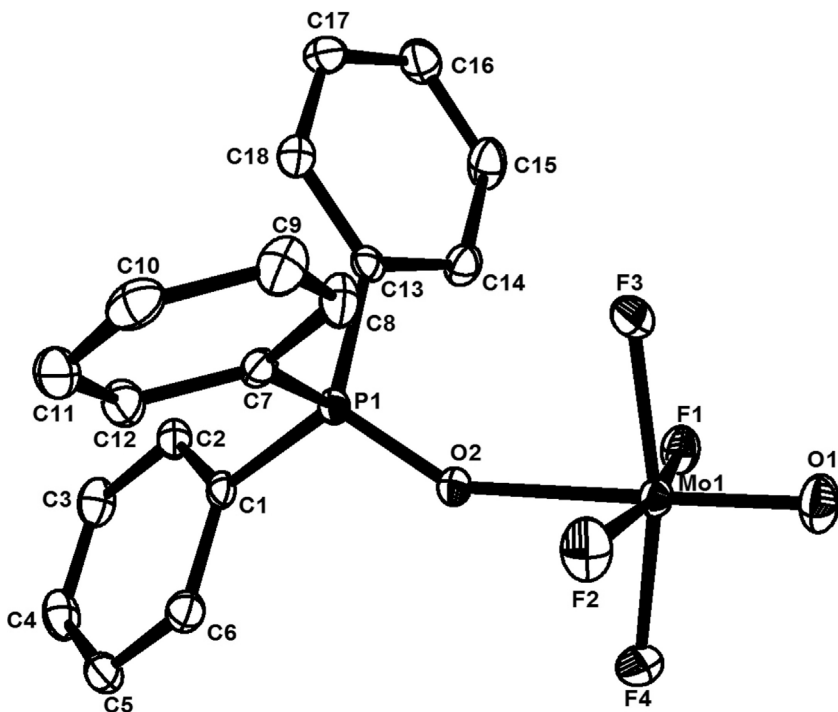**Fig. 2.** View of the structure of [MoOF$_4$(Ph$_3$PO)] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1−F4 = 1.8490(15), Mo1−F3 = 1.8704(14), Mo1−F2 = 1.8540(15), Mo1−F1 = 1.8676(14), 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 = 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).

[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$_2$Cl$_2$, 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$_2$F$_2$(bipy)], but attempts to convert a suspension of [MoOF$_4$(bipy)] in MeCN to [MoO$_2$F$_2$(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.
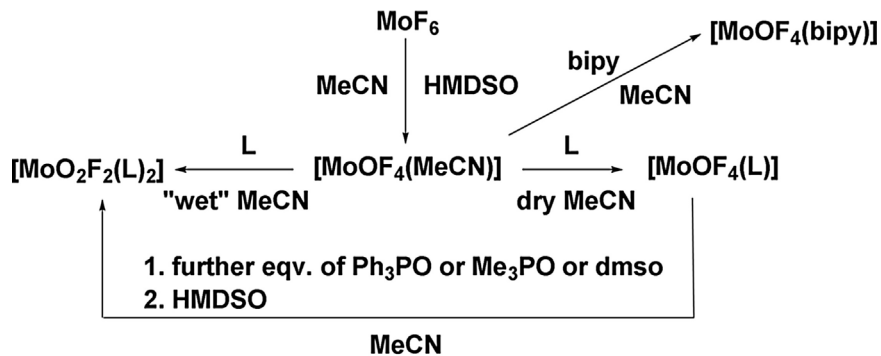
Scheme 1. Synthesis of the complexes.

L = Ph$_3$PO, Me$_3$PO, dmso, dmf

Although [WOF$_4$(PMe$_3$)] and [WOF$_4$(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 [WOF$_4$(MeCN)] in Et$_2$O solution [5], the same ligands immediately produced dark tarry precipitates on contact with [MoOF$_4$(MeCN)] in Et$_2$O. Similarly, combination of AsMe$_3$, SMe$_2$ or SeMe$_2$ with [MoOF$_4$(MeCN)] in Et$_2$O or MeCN solution immediately produced deep red or brown solutions and dark precipitates, indicating the 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 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{^{1}H} 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{^{1}H}) = −33.7 (s) and $\delta(^{95}$Mo) = −162.8 (t, ^{1}J$_{Mo-F}$ = 115 Hz), which were consistent with the formation of [MoO$_2$F$_2$(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$_2$F$_2$(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$_2$F$_2$(MeCN)$_2$]·MeCN. The structure (Fig. 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$_2$F$_2$ [9,14,15]. These results show that [MoO$_2$F$_2$(MeCN)$_2$] is formed in the reactions, but is unstable, losing MeCN (even in MeCN solution) and depositing what is probably largely MoO$_2$F$_2$ polymer. Solids isolated by evaporation of the solution are mainly a mixture of MoO$_2$F$_2$ polymer [9,28] and [MoO$_2$F$_2$(MeCN)$_2$] (we cannot rule out the presence of other insoluble Mo/O/F species). Extraction of the [MoO$_2$F$_2$(MeCN)$_2$] into MeCN or CH$_2$Cl$_2$ results in partial decomposition with generation of more MoO$_2$F$_2$. The very broad IR bands below ~1050 cm^{-1} are attributed to the polymer, while the sharper superimposed features correspond to [MoO$_2$F$_2$(MeCN)$_2$]. Attempts to prepare [NbOF$_3$(MeCN)$_2$] [29] or [WO$_2$F$_2$(MeCN)$_2$] [4] from the parent fluoride and HMDSO in MeCN solution, failed, with only the nitrile-free polymeric oxidefluoride isolated. The present case of MoO$_2$F$_2$ 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$_3$PO, Me$_3$PO, dmso) and HMDSO in anhydrous MeCN solution produced [MoO$_2$F$_2$(L)$_2$] (Scheme 1), which were identified by
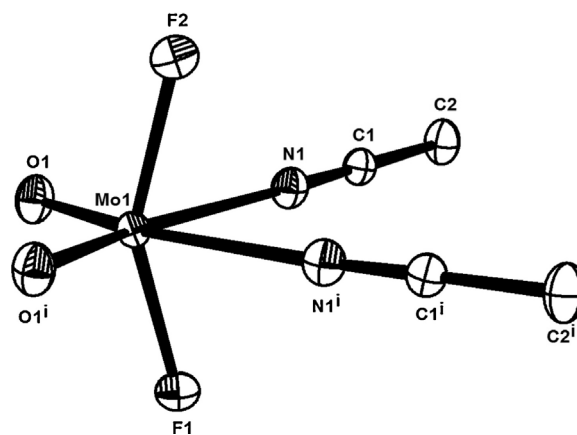

Fig. 3. View of the structure of [MoO$_2$F$_2$(MeCN)$_2$]·MeCN showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. The disordered MeCN solvate molecule is also omitted. Selected bond lengths (Å) and angles (°): Mo1−O1 = 1.695(3), Mo1−F1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

comparison of their key spectroscopic features (Table 1) with literature data. The complexes [MoO$_2$F$_2$(L)$_2$] (L = Ph$_3$PO, Me$_3$PO, 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$_2$F$_2$(L)$_2$] were originally prepared by combining solutions of L in EtOH and MoO$_3$·nH$_2$O in aqueous HF, their formation here from hydrolysis is unsurprising.

Crystals of [MoO$_2$F$_2$(Ph$_3$PO)$_2$] were obtained by slow evaporation from a CH$_2$Cl$_2$ solution and the structure is shown in Fig. 4 [30].

Although they are not isomorphous, the structure of [MoO$_2$F$_2$(Ph$_3$PO)$_2$] is very similar to those of [WO$_2$F$_2$(Ph$_3$PO)$_2$] [4] and [MoO$_2$F$_2$(Ph$_2$MePO)$_2$] [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$_3$PO were isolated from the filtrates from the preparations of [MoOF$_4$(Me$_3$PO)]. The first shown in Fig. 5 was identified by the X-ray structure solution as [MoO$_2$F$_2$(Me$_3$PO)(H$_2$O)] which has *trans* F−Mo−F and *cis*-MoO$_2$ groups. The Mo=O distances are surprisingly disparate, Mo1−O2$_{trans\text{-}Me3PO}$ = 1.7433(19) Å and Mo1−O1$_{trans\text{-}H2O}$ = 1.684(2) Å, but still clearly double bonds.

The second crystal contained the dimer [Mo$_2$O$_4$F$_2$(μ-F)(Me$_3$PO)$_2$] with the structure shown in (Fig. 6), which is related to that of the known anion [Mo$_2$O$_4$F$_4$(μ-F)$_2$]$^{2-}$ [31,32] with the Me$_3$PO replacing two terminal fluorides.

The third crystal was [Me$_3$POH]$_2$[Mo$_2$O$_4$F$_4$(μ-F)$_2$] (see ESI) which contains the known dimeric Mo(VI) anion. The protonated phosphine oxide, [Me$_3$POH]$^+$ was observed in the ^{31}P{^{1}H} NMR spectra of hydrolysed [MoOF$_4$(Me$_3$PO)] 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}. ^{1}H, ^{19}F{^{1}H}, ^{31}P{^{1}H} 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$_3$PO$_4$ and [MoO$_4$]$^-$ in H$_2$O/D$_2$O at pH 11 respectively. Microanalyses were undertaken by London Metropolitan University. Solvents were dried prior to use: THF and Et$_2$O by distillation from sodium benzophenone ketyl, MeCN and CH$_2$Cl$_2$ from CaH$_2$. MoF$_6$ was obtained from Fluorochem. Ligands were obtained commercially (Sigma Aldrich) and dried over
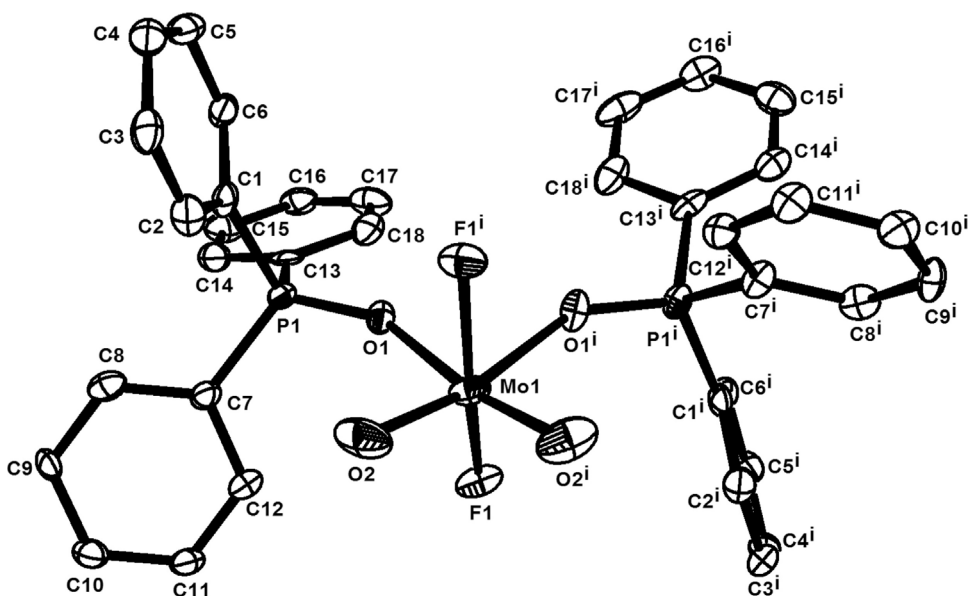
Fig. 4. View of the structure of [MoO$_2$F$_2$(Ph$_3$PO)$_2$] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1−F1 = 1.893(5), Mo1−O2 = 1.689(6,), Mo1−O1 = 2.230(5), F1−Mo1−F1^i = 158.7(2), 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).

molecular sieves (dmf), CaH$_2$ (dmso), by sublimation *in vacuo* (Me$_3$PO) or by melting *in vacuo* (bipy, Ph$_3$PO) 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$_2$H$_3$F$_4$MoNO (229.0): C, 10.49; H, 1.32; N, 6.12%. Found: C, 10.50; H, 1.35; N, 6.00%. ^{1}H NMR (CD$_2$Cl$_2$, 293 K): 2.30 (s); (CD$_3$CN, 293 K): 2.10

(s). ^{19}F{^{1}H} NMR (CD$_2$Cl$_2$, 293 K): +148.2 (s, ^{1}J$_{Mo-F}$ = 67 Hz); (CD$_3$CN, 293 K): +146.5 (s, ^{1}J$_{Mo-F}$ = 64 Hz). ^{95}Mo NMR (CD$_3$CN, 293 K): −287.3 (quintet ^{1}J$_{MoF}$ = 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. ^{1}H NMR (CD$_2$Cl$_2$, 293 K): 1.92 (s, [H]), 3.86 (s, [H]). ^{19}F{^{1}H} NMR (CD$_2$Cl$_2$, 293 K): +143.1 (s, ^{1}J$_{Mo-F}$ = 67 Hz). ^{95}Mo NMR (CD$_2$Cl$_2$ 293 K): −271.6 (quintet, ^{1}J$_{MoF}$ = 65 Hz). IR (Nujol/cm^{-1}): 1097 (s, thf), 1016 (vs, MoO), 872 (s, thf), 675 (vs, MoF).
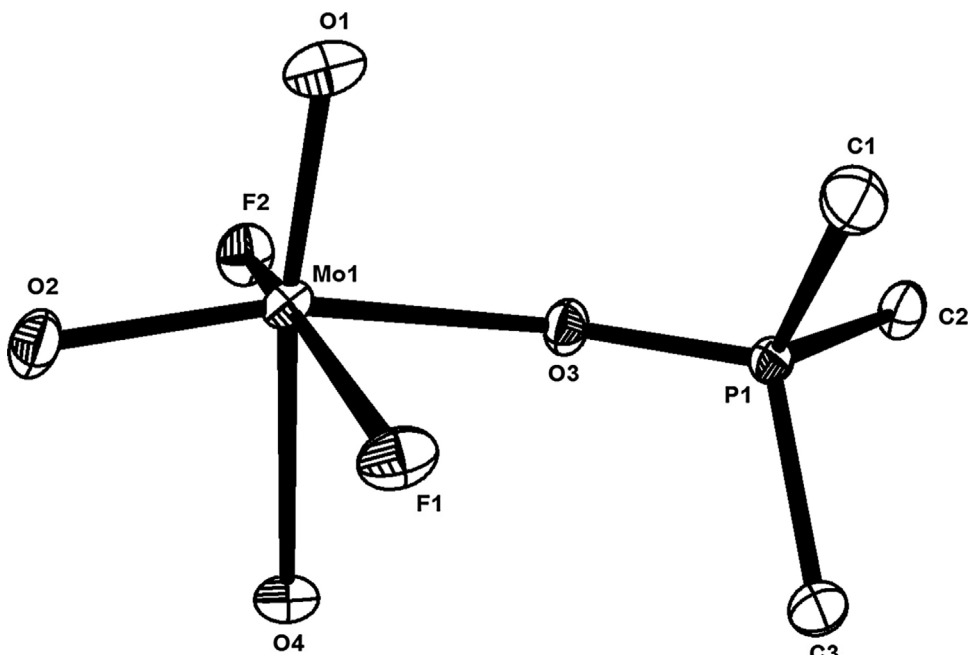

Fig. 5. View of the structure of [MoO$_2$F$_2$(Me$_3$PO)(H$_2$O)] showing atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1−F2 = 1.9042(15), Mo1−F1 = 1.9067(15), Mo1−O4 = 2.2881(19), Mo1−O3 = 2.1475(19), 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).
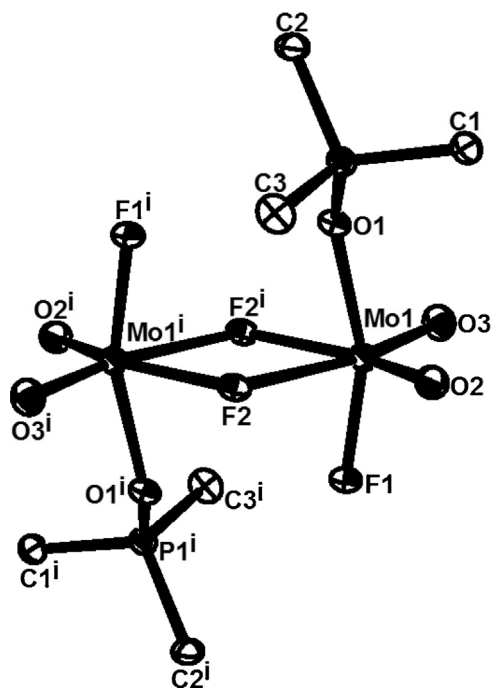
Fig. 6. View of the structure of $[Mo_2O_4F_2(\mu\text{-}F)_2(Me_3PO)_2]$ showing atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°): $Mo1-F1 = 1.898(4)$, $Mo1-F2 = 2.210(4)$, $Mo1-F2^i = 2.105(4)$, $Mo1-O1 = 2.028(4)$, $Mo1-O2 = 1.696(5)$, $Mo1-O3 = 1.685(5)$, $Mo1-F2-Mo1^i = 111.49(16)$, $F1-Mo1-F2 = 83.99(15)$, $F1-Mo1-F2^i = 83.36(15)$, $F2-Mo1-F2^i = 68.51(16)$, $O1-Mo1-F2 = 81.55(16)$, $O1-Mo1-F2^i = 79.53(16)$, $O2-Mo1-F1 = 98.4(2)$, $O2-Mo1-F2 = 88.55(19)$, $O2-Mo1-O1 = 93.9(2)$, $O3-Mo1-F1 = 98.2(2)$, $O3-Mo1-F2 = 98.4(2)$, $O3-Mo1-O1 = 93.0(2)$, $O3-Mo1-O2 = 104.2(2)$.

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 $C_{18}H_{15}F_4MoO_2$ (466.2): C, 46.37; H, 3.24. Found: C, 46.50; H, 3.34%. ¹H NMR (CD₃CN, 293 K): 7.85 − 7.54 (m). ¹⁹F{¹H} NMR (CD₃CN, 293 K): +139.1 (s, $^1J_{\text{Mo-F}}$ = 67 Hz). ³¹P{¹H} NMR (CD₃CN, 293 K): +42.8 (s). ⁹⁵Mo NMR (CD₃CN, 293 K): −270.0 (quintet, $^1J_{\text{MoF}}$ = 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 $C_3H_9F_4MoO_2$ (280.0): C, 12.87; H, 3.24. Found: C, 12.85; H, 3.27%. ¹H NMR (CD₃CN, 293 K): 1.88 (d, $^1J_{\text{P-H}}$ = 15 Hz). ¹⁹F{¹H} NMR (CD₃CN, 293 K): +135.9 (s, $^1J_{\text{Mo-F}}$ = 62 Hz). ³¹P{¹H} NMR (CD₃CN, 293 K): +64.2. ⁹⁵Mo NMR (CD₃CN, 293 K): −257.0 (quintet, $^1J_{\text{Mo-F}}$ = 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%). Anal. − complex significantly decomposed 12 h, turning blue; this precluded microanalytical measurements. ¹H NMR (CD₃CN, 293 K): 8.07 (s), 3.09 (s), 2.97 (s). ¹⁹F{¹H} NMR (CD₃CN, 293 K): +138.5 (s, $^1J_{\text{Mo-F}}$ = 67 Hz). ⁹⁵Mo NMR (CD₃CN, 293 K) −266.3 (quintet, $^1J_{\text{Mo-F}}$ = 66 Hz). IR (Nujol/cm⁻¹): 1007 (s, MoO), 643 (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 (CD₃CN, 293 K): 2.75 (s). ¹⁹F{¹H} NMR (CD₃CN, 293 K): +139.1 (s, $^1J_{\text{Mo-F}}$ = 65 Hz). ⁹⁵Mo NMR (CD₃CN, 293 K): −251.5 (quintet, $^1J_{\text{Mo-F}}$ = 64 Hz). IR (Nujol/cm⁻¹): 1030 (s, SO), 1007 (s, MoO), 653 (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%). 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. [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)*: ¹H NMR (CD₃CN, 293 K): 1.97 (s). ¹⁹F{¹H} NMR (CD₃CN, 293 K): −33.7 (s). ⁹⁵Mo NMR (CD₃CN, 293 K): −162.8 (t, $^1J_{\text{Mo-F}}$ = 115 Hz). IR (Nujol/cm⁻¹): 2312 (m, CN), 2285 (m, ν(C−C) + δ(CH₃)), 959(m), 938 (m) MoO), 567 (br, MoF). There are also very broad absorptions at ~1020 − 890 and ~670 − 450 cm⁻¹.

3.9. [MoO₂F₂(Ph₃PO)₂]

A solution of Ph₃PO (0.28 g, 1 mmol) in laboratory grade (i.e. wet) MeCN (20 mL) was added to a solution of [MoOF₄(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 OPPh₃). 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%. ¹H NMR (CD₂Cl₂, 293 K): 7.68 − 7.40 (m). ¹⁹F{¹H} NMR (CD₃CN, 293 K): −49.0 (s). ³¹P{¹H} NMR (CD₂Cl₂, 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. [MoO₂F₂(dmso)₂]

Dmso (0.08 g, 1 mmol) was added to a solution of [MoOF₄(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%. ^1H NMR (CD_3CN, 293 K): 2.75 (s). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): −50.8 (s). ^{95}Mo (CD_3CN, 293 K): −92.7 (t, $^1J_{Mo-F}$ = 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 $[MoOF_4(MeCN)]$, 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 mo-lybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (70 μm 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

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$_\alpha$)/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 > 2σ(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

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)	$P\text{-}1$ (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 > 2σ(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

[a] Common items: T = 293 K; wavelength (Mo-K$_\alpha$) = 0.71073 Å; θ(max) = 27.5°.
[b] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; w$R_2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma wFo^4]^{1/2}$.

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

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2017.06.015.

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