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Tetrakis (μ-difluoroacetato)dimolybdenum(II): solution chemistry and mass spectrum ☆

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Abstract

The complex $Mo_2(O_2CCHF_2)_4$ has been prepared and characterized, and its solution chemistry has been studied. In acetone, it exists as the axial adduct; in pyridine, it exists as a mixture of axial and monoequatorial adducts which undergo exchange. It forms axial, mono- and diequatorial adducts with tributylphosphine in acetone; these adducts also exchange. This complex undergoes less carboxylate ring-opening with pyridine or tributylphosphine than does $Mo_2(O_2CCF_3)_4$ under identical conditions. In the mass spectrometer, $Mo_2(O_2CCHF_2)_4$ fragments via early losses of $CHFCO_2$ and F, processes analogous to those undergone by $Mo_2(O_2CCF_3)_4$.

Keywords: Mass spectrometry; Molybdenum complexes; Difluoroacetato complexes; Dinuclear complexes; Solution species

1. Introduction

A significant reaction in the chemistry of dimolybdenum(II) carboxylates is adduct formation. The most widely studied carboxylate is $Mo_2(O_2CCF_3)_4$ [1–12], owing to its good solubility in organic solvents and its amenability to many solution spectroscopic studies – vibrational, electronic and ^{19}F NMR – as well as diffraction studies of solids.

Cotton and Norman [1,2] first reported that $Mo_2(O_2CCF_3)_4$ interacts with many Lewis bases. Pyridine forms an axial adduct (I in Fig. 1) in the solid state; similar structures were inferred for adducts with weaker Lewis bases. From IR measurements, Garner and Senior [3] proposed that 2,2′-bipyridine coordinates to equatorial sites on the Mo_2 core (not as a bridging ligand). They also suggested [4] that $Mo_2(O_2CCF_3)_4$ forms non-axial adducts in pyridine solution, even though the axial adduct crystallizes from such solutions. Two equatorial 2,2′-bipyridine adducts of $Mo_2(O_2CCF_3)_4$ have since [5] been characterized crystallographically. Andersen and co-workers [6] found that small basic tertiary phosphines form isolable equatorial adducts (II in Fig. 1) with $Mo_2(O_2CCF_3)_4$. Several tertiary phosphine adducts have also [7–9] been characterized crystallographically. A ^{19}F NMR study from this laboratory [10] showed that $Mo_2(O_2CCF_3)_4$ also forms a diequatorial adduct in pyridine solution. The adduct is stereochemically non-rigid; the monodentate and

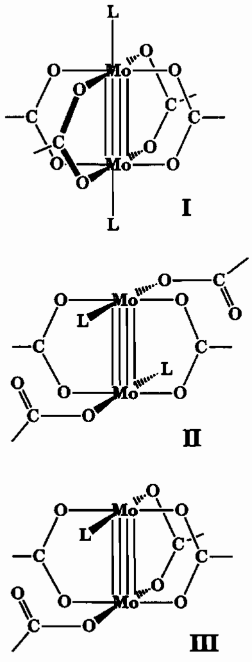

Fig. 1. Structures of dimolybdenum carboxylate adducts: I = axial, II = diequatorial, III = monoequatorial.

☆ Dedicated to Professor F.A. Cotton, with best wishes for many more years of successful chemistry.

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bidentate ligands interconvert via dissociatively controlled ring-opening–closing reactions. We have recently begun [11] an examination of the solution species formed in reactions of $Mo_2(O_2CCF_3)_4$ with diamines.

Less is known about the adduct chemistry of other dimolybdenum carboxylates. Stephenson et al. [13] observed that pyridine solutions of $Mo_2(O_2CMe)_4$ are yellow. This implies [6] that the solution species is an axial adduct, not an equatorial adduct. (Recent studies [14–16] with dmpe and ethylenediamine derivatives indicate that bidentate ligands will displace acetates.) Holste [17,18] prepared the complete series of chloroacetates (mono-, di- and tri-), and has characterized the bis adducts of dichloroacetate with DMSO and pyridine as axial; however he reported no measurements in solutions containing excess pyridine.

We report here some solution chemistry of $Mo_2(O_2CCHF_2)_4$. We chose this complex for two reasons. First, we can compare its solution chemistry to that of $Mo_2(O_2CCF_3)_4$ as a function of carboxylate basicity (pK_a 0.52 for trifluoroacetic acid, 1.34 for difluoroacetic acid [19]) under strictly comparable conditions. (We have not attempted a study with $Mo_2(O_2CMe)_4$ (pK_a 4.75 for acetic acid [20]) because of its poor solubility.) Furthermore, this complex is amenable to ^{19}F NMR spectroscopy, which has been very useful in studies [6,9–11] on $Mo_2(O_2CCF_3)_4$.

We have also examined the mass spectrum of $Mo_2(O_2CCHF_2)_4$. Cotton and Norman [1] found that $Mo_2(O_2CCF_3)_4$ fragments by loss of CF_2CO_2 and F, while Abbott and co-workers [21] observed that $Mo_2(O_2CMe)_4$ fragments via loss of ketene, acetyl radical or acetoxy radical at various stages. We might therefore expect that complexes containing partially fluorinated acetates should give mass spectra in which fragmentations characteristic of both trifluoroacetate and acetate would be observed. We might also relate the fragmentation patterns to the relative stabilities of the observed fragments or vice versa.

2. Experimental

IR spectra were recorded on a Perkin-Elmer 580 spectrophotometer. Electronic spectra were recorded on a Cary 17 spectrophotometer. NMR spectra (^{19}F, 84.67 MHz; ^{1}H, 90.00 MHz) were recorded on a Varian EM-390 spectrometer; temperatures were calibrated in terms of the chemical shifts [22] of a methanol sample. Mass spectra (EI) were recorded on a VG 7070-EHF double-focussing spectrometer. Elemental analyses were obtained from the UMIST microanalytical laboratory, Manchester, UK.

2.1. Syntheses

Tetrakis (μ-difluoroacetato)dimolybdenum(II) was prepared from $K_4Mo_2Cl_8$ [23] by the procedure outlined previously [24] for the preparation of $Mo_2(glycine)_4Cl_4$. To a stirred solution of difluoroacetic acid (0.40 ml, 6.4 mmol) in water (25 ml) under N_2 was added $K_4Mo_2Cl_8$ (1.0 g, 1.6 mmol). The solution turned yellow within seconds, and a yellow precipitate formed. After the mixture was stirred for 5 min, the product was recovered by filtration, washed with water, and dried in vacuo. Yields routinely exceeded 90%. The product is a yellow powder, stable in air for short periods of time. Solutions are somewhat more air-sensitive but may be handled briefly in air. Both solid and solutions are less air-sensitive than $Mo_2(O_2CCF_3)_4$ under identical conditions. The solid is not very soluble in non-donor solvents and is less soluble than $Mo_2(O_2CCF_3)_4$ in donor solvents. *Anal.* Calc. for $Mo_2(O_2CCHF_2)_4$: C, 16.8; H, 0.7; F, 26.6. Found: C, 16.7; H, 0.6; F, 26.5%. Spectroscopic data: visible spectrum (acetone, room temperature): λ_{max} 432 nm; NMR spectra (d_6-acetone, room temperature): ^{1}H δ 6.74 (t) ppm, ^{2}J (H–F) 54 Hz, ^{19}F δ (versus $CFCl_3$) −122.9 (d) ppm, ^{2}J (F–H) 54 Hz; IR (Nujol and Fluorolube mulls, cm^{-1}) 3011w, 2985w, 2910w, 1567vs, 1550sh, 1446s, 1330vs, 1113vs, 1061vs, 950vs, 810vs, 780sh, 733m, 682w, 610vs, 530s, 520sh, 460sh, 442s, 397m, 370w, 351m, 300w, 272w, 234s. A few IR band assignments are presented in Table 1.

Dimolybdenum trifluoroacetate was prepared by a modification [11] of the original synthesis [1] in which the trifluoroacetic acid/anhydride–$Mo_2(O_2CMe)_4$ mixture was refluxed for approximately 30 min after all the solid had dissolved. This modification reduces the contamination by incompletely substituted material reported by Santure and Sattelberger [9]. The complexes $Mo_2(O_2CCF_3)_4(PBu_3)_2$, $K_4Mo_2Cl_8$ and $Mo_2(O_2CMe)_4$ were prepared by standard [9,23,27] methods.

Pyridine and toluene (Fisher) were distilled before use (pyridine from KOH pellets). Tributylphosphine

Table 1
IR frequencies for selected Mo_2 carboxylates (cm^{-1})

	ν_{as}(O–C–O)	ν_s(O–C–O)	ν(Mo–O)
$Mo_2(O_2CCH_3)_4$ [a,b]	1510, 1492	1410	369, 348, 338 366, 345, 334
$Mo_2(O_2CCH_2Cl)_4$ [c]	1535	1425	411, 398
$Mo_2(O_2CCHCl_2)_4$ [c]	1552	1405	325
$Mo_2(O_2CCCl_3)_4$ [c]	1560	1372	310
$Mo_2(O_2CCHF_2)_4$ [d]	1567, 1550	1446	397, 370, 351
$Mo_2(O_2CCF_3)_4$ [b,e]	1592, 1572	1459	380, 330

[a] Ref. [25].
[b] Ref. [26].
[c] Ref. [17].
[d] This work.
[e] Ref. [1].

(Alfa) was purified by vacuum distillation. Acetone (Fisher ACS certified), acetone-d_6 (Stohler Isotope Chemical) and α,α,α-trifluorotoluene (Aldrich) were used as received; results in check experiments were independent of the source of acetone.

Samples for NMR spectroscopy were prepared by dissolving weighed amounts of dimolybdenum complex under argon in solvent mixtures that had previously been purged with argon. (Typical Mo_2 concentrations were 0.01–0.02 M.) Samples were then capped. Solvent mixtures contained 10% (volume) α,α,α-trifluorotoluene (TFT) as internal lock and secondary chemical shift reference (^{19}F shifts are reported relative to $CFCl_3$).

2.2. Calculations

Ab initio calculations on the $CXYCO_2$ fragments (X=Y=H; X=H, Y=F; X=Y=F) were carried out using GAUSSIAN 86 [28]. Geometries were optimized using the 3-21G basis set at the single-configurational level with the restricted Hartree–Fock formalism for closed-shell systems and the unrestricted formalism for open-shell systems [29]. Table A1 of the Appendix lists optimized bond lengths and angles. Single-point calculations were made at the MP2/6-31G level in order to evaluate relative energies. For open-shell systems, the largest spin contaminant was projected out when the UMP2/6-31G energy was evaluated (PMP2/6-31G) [30,31]. Absolute energies are listed in Table A2 of the Appendix. Heats of formation of the $CXYCO_2$ fragments were estimated by adding the relative energies of the fragments (with respect to ^{1}CXY and CO_2) to the experimental heats of formation of ^{1}CXY and CO_2; these appear in Table A3 of the Appendix.

3. Results and discussion

3.1. Syntheses

The usual preparations of dimolybdenum(II) carboxylates have been the reaction of $Mo(CO)_6$ with the carboxylic acid [13,21,27] or transcarboxylation [1,17, 32] (reaction of a second carboxylic acid with $Mo_2(O_2CMe)_4$). For water-soluble acids, the synthetic route used here (as for the glycine complex [24]) is an attractive alternative. Both steps in the sequence (preparation of $K_4Mo_2Cl_8$ from $Mo_2(O_2CMe)_4$ and $Mo_2(O_2CCHF_2)_4$ from $K_4Mo_2Cl_8$) are rapid, high-yield reactions. Furthermore, the use of at least four moles of carboxylic acid (or its Na salt with added HCl) per mole of $K_4Mo_2Cl_8$ appears to avert the incomplete substitution noted earlier [9] in the transcarboxylation of $Mo_2(O_2CMe)_4$ with CF_3CO_2H. Test syntheses [33] indicate that several other dimolybdenum carboxylates (for example, all of the chloroacetates reported by Holste [17]) are conveniently prepared similarly.

3.2. Solution chemistry

Dimolybdenum difluoroacetate forms yellow solutions in weak-donor solvents such as acetonitrile and acetone. The visible spectrum is very similar to that reported by Holste [18] for the dichloroacetate, and also resembles other [34] dimolybdenum carboxylate spectra, including solid-state spectra in which the chromophore is known to be the axially symmetric Mo_2 (μ-carboxylate)$_4$ unit. The ^{19}F and ^{1}H NMR spectra in acetone indicate that all the difluoroacetate ligands are equivalent and remain equivalent at least to −40 °C. We therefore conclude that $Mo_2(O_2CCHF_2)_4$ is present as the familiar axial adduct (I in Fig. 1) in acetone (and presumably in other weak-donor solvents).

In pyridine, $Mo_2(O_2CCHF_2)_4$ forms an orange solution. The visible spectrum shows a maximum at 450 nm and a prominent shoulder at 432 nm. This suggests the presence of the axial adduct (432 nm) and another species. This species is not the diequatorial adduct (II in Fig. 1). Such an adduct is the only adduct found in pyridine solutions [10] of $Mo_2(O_2CCF_3)_4$; its absorption maximum occurs [2] at 508 nm. By contrast, pyridine solutions of $Mo_2(O_2CCHF_2)_4$ have little absorption above 500 nm. We propose that the second species is a monoequatorial adduct (III in Fig. 1), with three bridging difluoroacetates, one monodentate difluoroacetate and one equatorial pyridine. Based on the spectra of axial and diequatorial adducts of $Mo_2(O_2CCF_3)_4$, we expect the absorption maximum for the monoequatorial adduct to lie between those of the axial and diequatorial adducts. The absorption maximum of a related [4] complex, $Mo_2(O_2CCF_3)_3Cl_3{}^-$, with three bridging trifluoroacetates and two chlorides as equatorial ligands, occurs at 477 nm. Mountford and Williams [35] have recently reported a phenyldimethylphosphine adduct of $W_2(O_2CBu^t)_4$ which is structurally analogous to III.

The ^{19}F NMR spectra of $Mo_2(O_2CCHF_2)_4$ solutions (0.01–0.02 M) in pyridine/10% TFT support our formulation. At room temperature, only one doublet appears, but the lines are slightly broader than those found in acetone solution. On cooling the sample, the lines broaden further. Below −45 °C, additional lines appear; the spectrum obtained at ~ −55 °C (near the freezing point of the solution) is shown in Fig. 2. We assign the major doublet (−121.5 ppm, ^2J (F–H) = 55 Hz) to the axial adduct and the weaker peaks, three overlapping doublets (−121.0, −121.6 and −122.3 ppm, J ~ 55 Hz, relative intensity 1:2:1), to the monoequatorial adduct, with three bridging difluoroacetates, one monodentate difluoroacetate and one equatorial pyridine. At ~ −55 °C, species I and III are present in ap-

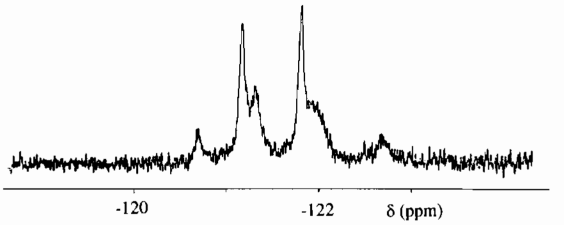

Fig. 2. ^{19}F NMR spectrum of $Mo_2(O_2CCHF_2)_4$ in pyridine/10% TFT at −55 °C.

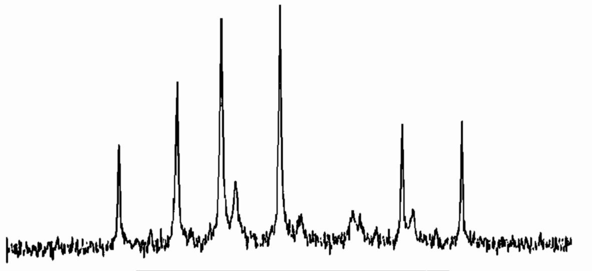

Fig. 3. ^{19}F NMR spectrum of $Mo_2(O_2CCHF_2)_4/PBu_3$ in acetone/10% TFT at −60 °C.

proximately a 3:2 ratio. The (reversible) temperature dependence of the ^{19}F NMR spectrum indicates that these species exchange. In 1:1 (volume) pyridine/acetone (10% TFT), the small peaks almost disappear; at least 90% of the complex in solution is present as the axial adduct. By contrast, we find that $Mo_2(O_2CCF_3)_4$ forms only the diequatorial adduct in 1:1 pyridine/acetone; this is similar to our earlier result [10] in 1:1 pyridine/toluene.

Santure and Sattelberger [9] reported that the ^{19}F NMR spectrum of $Mo_2(O_2CCF_3)_4(PBu_3)_2$ in $CDCl_3$ at low temperature consists of two lines of equal area, corresponding to diequatorial adduct II. We confirm this observation in $CDCl_3$. However, in acetone at −60 °C, we observe some 16 lines – eight lines in the bidentate region and eight in the monodentate region of the spectrum. The integrated areas of the two sets remain 1:1 (within 2%). This solution clearly contains a number of species (which exchange at NMR-accessible rates). These may include isomers of the diequatorial adduct [6] and disproportionation products containing more or fewer than two phosphine ligands. The same spectrum results from adding two equivalents of tributylphosphine to an acetone solution of $Mo_2(O_2CCF_3)_4$.

In acetone, $Mo_2(O_2CCHF_2)_4$ reacts with two equivalents of tributylphosphine to give an orange solution. The ^{19}F NMR spectrum at −60 °C (Fig. 3) clearly indicates that two major species are present: axial adduct I (sharp doublet at −123.1 ppm) and diequatorial adduct II (two sharp doublets of equal area at −122.1 and −125.1 ppm). We assign the three weaker doublets (−122.6, −123.9 and −124.6 ppm, areas 2:1:1) to monoequatorial adduct III; the relative abundances of these species are roughly 2:2:1 (I:II:III). On increasing the phosphine:Mo_2 ratio to 5:1, the axial adduct almost disappears, while the di- and monoequatorial adducts become about equally abundant. At a 10:1 phosphine:Mo_2 ratio, the diequatorial/monoequatorial ratio is about 3/1. These solutions show reversible temperature-dependent spectral changes similar to the pyridine solutions, implying that the PBu_3 adducts also exchange.

These observations clearly show that $Mo_2(O_2CCHF_2)_4$ is considerably less prone to form equatorial adducts with monodentate bases than is $Mo_2(O_2CCF_3)_4$. The difference is particularly striking in the reactions with pyridine. The only species observed in solutions of $Mo_2(O_2CCF_3)_4$ in pyridine or 1:1 pyridine/acetone is the diequatorial adduct, whereas the axial adduct is the major species in solutions of $Mo_2(O_2CCHF_2)_4$. Similarly, $Mo_2(O_2CCHF_2)_4$ undergoes less ring-opening with tributylphosphine than does $Mo_2(O_2CCF_3)_4$. At a 2:1 P:Mo_2 ratio, 75% of the difluoroacetate ligands remain bidentate, whereas only 50% of the trifluoroacetate ligands are bidentate.

These differences are in one sense very explicable: a more basic carboxylate ligand should bind more strongly to the Mo_2 core and would therefore be less subject to displacement. This trend in reactivity correlates with some of the vibrational frequencies of the complexes (Table 1). The metal–oxygen stretching frequencies increase on going from $Mo_2(O_2CCF_3)_4$ to $Mo_2(O_2CCHF_2)_4$. This increase correlates with carboxylate basicity – a more basic carboxylate bonds more strongly to the Mo_2 core – in agreement with the reactivities observed here. Holste [17] has noted the same trend within the chloroacetate series. Interestingly, the data from the chloroacetate and fluoroacetate series do not simply interrelate, and the acetate does not fit smoothly into either series. The bands assigned as Mo–O stretching may include other ligand-based motions as well; the effective mass of the ligand may also affect the frequencies.

There are also noteworthy correlations between ligand basicity and C–O stretching motions; ν_{as}(O–C–O) increases with decreasing basicity from acetate through both the chloroacetate and fluoroacetate series. These two series also fail to interrelate. Furthermore, the trends in ν_s(O–C–O) are opposite in the two series.

3.3. Mass spectrum

There are some reports of the mass spectra of simple dimolybdenum(II) carboxylates [1,21]. Although the aliphatic carboxylates are structurally quite similar [1,36–38], they undergo different fragmentation processes. The molecular ions of $Mo_2(O_2CH)_4$, $Mo_2(O_2CCH_3)_4$ and $Mo_2(O_2CCF_3)_4$ undergo six independent fragmentations (reactions (1)–(6)), with reactions (1), (4) and (6) being the primary modes of fragmentation, based on the intensities of the

$$Mo_2(O_2CH)_4{}^+ \longrightarrow Mo_2(O_2CH)_3H^+ + CO_2 \quad (1)$$

$$Mo_2(O_2CCH_3)_4{}^+ \longrightarrow Mo_2(O_2CCH_3)_3OH^+ + CH_2CO \quad (2)$$

$$Mo_2(O_2CCH_3)_4{}^+ \longrightarrow Mo_2(O_2CCH_3)_3O^+ + CH_3CO \quad (3)$$

$$Mo_2(O_2CCH_3)_4{}^+ \longrightarrow Mo_2(O_2CCH_3)_3{}^+ + CH_3CO_2 \quad (4)$$

$$Mo_2(O_2CCF_3)_4{}^+ \longrightarrow Mo_2(O_2CCF_3)_3(O_2CCF_2)^+ + F \quad (5)$$

$$Mo_2(O_2CCF_3)_4{}^+ \longrightarrow Mo_2(O_2CCF_3)_3F^+ + CF_2CO_2 \quad (6)$$

fragment ions in the mass spectra of these compounds. How will the spectrum of a partially fluorinated complex compare with those of the acetate and trifluoroacetate?

The mass spectrum of $Mo_2(O_2CCHF_2)_4$ (Table 2) exhibits a distinct molecular ion cluster whose most intense peak appears at *m/e* 572. This cluster shows the isotopic pattern for the Mo_2 core. Like the molecular ion of $Mo_2(O_2CCF_3)_4$ [1], this ion undergoes two primary fragmentations. The major fragmentation is the loss of $CHFCO_2$ to give the fragment at *m/e* 496, analogous to the loss of CF_2CO_2 from $Mo_2(O_2CCF_3)_4$ (Eq. (6)). We do not observe loss of CF_2CO_2 itself during fragmentation of $Mo_2(O_2CCHF_2)_4$. According to our ab initio calculations, the heat of formation of CF_2CO_2 is some 50 kcal mol^{-1} more negative (Table A3 of the Appendix) than that of $CHFCO_2$. If the observed spectrum reflects thermodynamically controlled fragmentation, we infer that the dimolybdenum hydride ion ($Mo_2(O_2CCHF_2)_3H^+$) that would result from loss of CF_2CO_2 has a heat of formation at least 50 kcal mol^{-1} more positive than that of the observed dimolybdenum fluoride ion (*m/e* 496), so that loss of CF_2CO_2 is not observed. The minor fragmentation is the loss of F to give the *m/e* 553 ion (analogous to Eq. (5)). The *m/e* 496 ion further loses $CHFCO_2$ to give the *m/e* 420 ion. The *m/e* 477 ion could arise in three ways: loss of CHF_2CO_2 from the molecular ion (analogous to Eq. (4)), loss of $CHFCO_2$ from the *m/e* 553 ion, or loss of F from the *m/e* 496 ion. A series of linked B/E scans [39] indicate that the second of these pathways is the major source (small contribution from the third) of the *m/e* 477 ion, which loses another $CHFCO_2$ to give the *m/e* 401 ion. Linked scans also indicate that both *m/e* 553 and *m/e* 477 lose CFCO during fragmentation, but the daughter ions lie beneath the isotopic clusters for the *m/e* 496 and 420 ions and cannot be unequivocally assigned in the low-resolution spectrum.

Table 2
Mass spectrum of $Mo_2(O_2CCHF_2)_4$

m/e	Base (%)	Assignment	
572	40	$Mo_2O_8C_8H_4F_8{}^+$	(M^+)
553	11	$Mo_2O_8C_8H_4F_7{}^+$	$(M-F)^+$
496	27	$Mo_2O_6C_6H_3F_7{}^+$	$(M-CHFCO_2)^+$
477	12	$Mo_2O_6C_6H_3F_6{}^+$	$(553-CHFCO_2)^+$
420	36	$Mo_2O_4C_4H_4F_8{}^+$	$(496-CHFCO_2)^+$
401	9	$Mo_2O_4C_4H_4F_7{}^+$	$(477-CHFCO_2)^+$
360	3	$Mo_2O_4C_4HF_5{}^+$	
342	18	$Mo_2O_3C_2H_2F_4{}^+$	$(401-CFCO)^+$
323	2	$Mo_2O_3C_2H_2F_3{}^+$	
295	6	$Mo_2O_3CH_2F_3{}^+$	
276	7	$Mo_2O_3CH_2F_2{}^+$	
259	6	$Mo_2OCHF_2{}^+$	
244	2	$Mo_2C_2HF^+$	
193	2	$MoF_5{}^+$	
174	10	$MoF_4{}^+$	
171	10	$MoOF_3{}^+$	
149	9	MoO_2F^+	
146	8	$MoO_3{}^+$	
133	14	$MoOF^+$	
130	16	$MoO_2{}^+$	
114	16	MoO^+	
98	14	Mo^+	
51	100	$CHF_2{}^+$	

Additional B/E scans indicate that the *m/e* 420 ion loses a third $CHFCO_2$ fragment to generate an *m/e* 344 ion. This also resembles [1] the loss of three CF_2CO_2 groups by $Mo_2(O_2CCF_3)_4$. However, this ion cannot be unambiguously assigned, as it lies beneath the cluster of the *m/e* 342 ion. The *m/e* 342 ion arises from the *m/e* 401 ion by loss of CFCO (a fragmentation noted above for the *m/e* 553 and 477 ions). The *m/e* 360 ion could result from loss of CHFCO from the *m/e* 420 ion (analogous to Eq. (2), the loss of ketene [21] from $Mo_2(O_2CCH_3)_4$), but B/E scans suggest that this may occur by successive losses of CFCO and H. The *m/e* 323 ion may arise by loss of F from the *m/e* 342 ion. Below this point, fragmentation is much less systematic. A number of low-intensity peaks (less than 5% relative abundance) appear in the *m/e* 200–300 region, and several mononuclear fragments appear below *m/e* 200. We also observe a significant low-mass ion (the base peak) derived from the difluoroacetate ligand at *m/e* 51 $(CHF_2)^+$.

We therefore conclude that the mass spectrum of $Mo_2(O_2CCHF_2)_4$ initially resembles that of $Mo_2(O_2CCF_3)_4$. We do not observe two of the fragmentations (loss of acyl or carboxyl radicals) noted for $Mo_2(O_2CCH_3)_4$ [20]; the third (loss of a ketene) may not be concerted in this fragmentation. We also do not observe loss of CO_2, which occurs in $Mo_2(O_2CH)_4$ [21].

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Appendix

Table A1
Optimized geometries of $CXYCO_2$ [a]

	Bond length (Å)		Bond angles (°)	
CH_2CO_2	C–O	1.285	OCO	119.94
	C–C	1.511	CCO	120.03
	C–H	1.068	CCH	118.78
			HCH	112.43
$CHFCO_2$	C–O (*cis*-F)	1.426	OCO	121.39
	(*cis*-H)	1.255	CCO (*cis*-F)	115.96
	C–C	1.371	CCO (*cis*-H)	122.65
	C–H	1.065	CCH	122.10
	C–F	1.336	CCF	121.65
			HCF	116.25
CF_2CO_2	C–O	1.275	OCO	122.70
	C–C	1.501	CCO	118.65
	C–F	1.331	CCF	121.75
			FCF	116.49

[a] CH_2CO_2 and CF_2CO_2 were constrained to C_{2v} symmetry; $CHFCO_2$ was constrained to C_s symmetry.

Table A2
Absolute energies (Hartrees) for various species

Species	Elec sym	Mol sym	3-21G	6-31G	(U)MP2/6-31G	PMP2/6-31G [a]
CH_2	$^1A_1$	C_{2v}	−38.65185	−38.85336	−38.91821	
CHF	$^1A'$	C_s	−137.00206	−137.70458	−137.89772	
CF_2	$^1A_1$	C_{2v}	−235.37481	−236.57235	−236.89438	
CO_2	$^1\Sigma_g$	$D_{\infty h}$	−186.56126	−187.51483	−187.86342	
CH_2CO_2 [b]	$^1B_2$	C_{2v}	−225.26448	−226.42889	−226.76762	−226.85240
$CHFCO_2$ [c]	$^1A'$	C_s	−323.58578	−325.25008	−325.71379	−325.76412
CF_2CO_2 [b]	$^1B_2$	C_{2v}	−421.88308	−424.04690	−424.62877	−424.71653

[a] Refs. [30,31].

[b] Open-shell solution is strongly spin contaminated and corresponds to alpha spin density on both oxygens and beta spin density on both carbons.

[c] Open-shell solution is strongly spin contaminated and corresponds to alpha spin density on one oxygen and adjacent carbon and beta spin density on the remaining oxygen and carbon.

Table A3
Relative energy (kcal mol^{-1}) of $CXYCO_2$ with respect to CXY and CO_2 at various levels and estimated ΔH_f (kcal mol^{-1}) of $CXYCO_2$

Species	3-21G	6-31G	(P)MP2/6-31G [a]	Estimated ΔH_f [b]
CH_2CO_2	−32.2	−38.1	−44.4	−35.9
$CHFCO_2$	−14.1	−19.2	−1.9	−70.0
CF_2CO_2	33.3	25.3	25.9	−117.2

[a] Refs. [30,31]. For closed-shell systems the MP2/6-31G energy was used, while for open-shell systems the PMP2/6-31G energy was used to determine relative energies.

[b] The estimated heat of formation of $CXYCO_2$ is determined by adding the relative energy of $CXYCO_2$, with respect to CXY plus CO_2, to the experimental heats of formation of CXY and CO_2. $\Delta H_f(CO_2) = -94.1$ [40]. $\Delta H_f(CH_2) = 102.6$, triplet CH_2 [41], singlet–triplet splitting [42]; $\Delta H_f(CHF) = 26$, $\Delta H_f(CF_2) = -49.0$ [43].

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