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COMMUNICATION

OXYGEN ABSTRACTION FROM TETRAHYDROFURAN BY MOLYBDENUM-IODIDE COMPLEXES. X-RAY MOLECULAR STRUCTURE OF $[\text{Mo}_2(\mu\text{-O})(\mu\text{-I})(\mu\text{-O}_2\text{CCH}_3)_2(\text{THF})_4][\text{MoOI}_4(\text{THF})]$ (THF = TETRAHYDROFURAN)

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Abstract—The interaction between $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, Me_3SiI and I_2 in THF resulted in oxygen abstraction from the solvent and formation of $[\text{Mo}_2(\mu\text{-O})(\mu\text{-I})(\mu\text{-O}_2\text{CCH}_3)_2(\text{THF})_4]^+[\text{MoOI}_4(\text{THF})]^-$ and $\text{I}-(\text{CH}_2)_4-\text{I}$. The molybdenum complex has been characterized by X-ray diffractometry. *Crystal data*: triclinic, space group $P\bar{1}$, $a = 13.827(3)$ Å; $b = 15.803(7)$ Å; $c = 9.950(3)$ Å; $\alpha = 93.34(4)^\circ$; $\beta = 102.40(2)^\circ$; $\gamma = 90.09(2)^\circ$; $V = 2120(2)$ Å³; $Z = 2$; $d_{\text{calc}} = 2.559$ g cm⁻³; $R = 0.0476$ ($R_w = 0.0613$) for 370 parameters and 3938 data with $F_o^2 > 3\sigma(F_o^2)$. The metal-metal distance in the cation is 2.527(2) Å and indicates a strong interaction. The magnetic behavior is consistent with the assignment of one unpaired electron to the Mo_2^{2+} core of the cation and one to the d^1 Mo(V) center of the anion. The interaction between $\text{Mo}(\text{CO})_6$ and I_2 in THF also results in the formation of 1,4-diiodobutane.

We have recently been investigating the relatively unexplored chemistry of molybdenum-iodide complexes.¹⁻³ Among other things, we spent some time trying to obtain the tetrahydrofuran adduct of molybdenum(III), $\text{MoI}_3(\text{THF})_3$, as this might be expected to be a good starting material for the synthesis of the virtually unknown class of molybdenum(III)-iodide derivatives. We were eventually able to prepare the compound by iodine oxidation of low-valent molybdenum carbonyl derivatives.³ Among other unsuccessful strategies, we also tried to obtain the above mentioned material by iodine oxidation of quadruply bonded molybdenum(II) iodide dimers, $\text{Mo}_2\text{I}_4\text{L}_4$. This led to the discovery of a quite complex reactivity which involves oxygen abstraction from the solvent and formation of a metal complex with a higher average oxidation state. We report here this chemistry and the X-ray

molecular structure of the peculiar molybdenum product.

EXPERIMENTAL

All operations were carried out under an atmosphere of prepurified argon with standard Schlenk-tube techniques. Solvents were dried by conventional methods and distilled under dinitrogen prior to use. Instruments used were as follows: IR, Perkin-Elmer 783; ¹H-NMR, Varian XL-200; GC-MS, HP 5995; magnetic susceptibility, Johnson-Matthey JME. $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ was prepared as described in the literature,⁴ while Me_3SiI was obtained from Aldrich and used as received.

Preparation of $[\text{Mo}_2\text{OI}_3(\text{O}_2\text{CCH}_3)(\text{THF})_4][\text{MoOI}_4(\text{THF})]$

$\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ (1.09 g, 2.54 mmol) was suspended in 15 cm³ of THF and treated with Me_3SiI (1.50 cm³, 10.5 mmol). Most of the insoluble mo-

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lybdenum compound, but not all, rapidly dissolved to afford a deep yellow solution. The appearance of the mixture did not change upon brief reflux. Treatment with an additional 0.50 cm³ of Me₃SiI (3.5 mmol) caused the complete disappearance of the yellow solid. A solution of I₂ (0.43 g, 1.68 mmol) in 15 cm³ of THF was then added dropwise at room temperature. The solution first turned green and then a dark grey solid started to precipitate. At the end of the addition there was much precipitate, while the supernatant liquid had a dark red color. The product was filtered off, washed with THF and dried *in vacuo*. Yield: 0.91 g [33% with respect to the molybdenum(II) acetate, 100% with respect to I₂ and the stoichiometry of eq. (2), see Discussion]. IR (nujol mull): 2340 w (br), 1265 w, 1440 vs (br), 1380 s, 1345 s, 1055 m, 1025 m, 945 w, 680 s, 620 m, 595 w, 385 s, and 345 s cm⁻¹. $\chi_g = 2.20 \times 10^{-6}$ c g s; $\mu_{\text{eff}} = 3.14$ BM [diamagnetic correction (molar) = -553.1×10^{-6} c g s]. A GC-MS analysis of the filtered solution showed the presence of I—(CH₂)₄—I (M⁺, *m/e* = 310).

A single crystal for the X-ray analysis was obtained as follows: Mo₂(O₂CCH₃)₄ (0.21 g, 0.50 mmol) in THF (5 cm³) was treated with 0.30 cm³ of Me₃SiI (2.1 mmol). After brief stirring the mixture was filtered and a solution of I₂ (0.08 g, 0.31 mmol) in 10 cm³ of *n*-hexane was carefully layered on top of it. A mixture of well-formed black and yellow crystals was produced upon diffusion. A black crystal was used for the subsequent X-ray analysis. A yellow crystal was selected and its cell constants determined from its X-ray diffraction pattern. These correspond to those reported⁵ for Mo₂(O₂CCH₃)₄. The identity of the black crystals with the grey microcrystalline material obtained in the above described procedure was confirmed by IR analysis.

Reaction between Mo(CO)₆ and I₂ in THF

Mo(CO)₆ (4.62 g, 17.5 mmol) was treated with I₂ (6.69 g, 26.4 mmol) in THF (50 cm³). The mixture was refluxed for 3 days. IR monitoring in the carbonyl stretching region showed the disappearance of the carbonyl starting material (band at 1979 cm⁻¹). The final mixture contained a black insoluble solid, whose nature was not further investigated. After filtration, the solution was reduced in

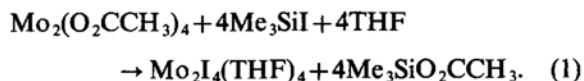
volume by room temperature evaporation at reduced pressure. A dense liquid remained at the end of the treatment. Distillation of this residue under reduced pressure yielded 4.48 g of colorless I—(CH₂)₄—I (b.p. 69–80°C at *ca* 6×10^{-2} mm Hg), identified by IR, ¹H-NMR and MS (55% yield with respect to I₂).

X-ray crystallography for [Mo₂OI₃(O₂CCH₃)₃(THF)₄][MoOI₄(THF)]

A single crystal was glued under argon to the inside of a thin-walled capillary and mounted on the diffractometer. The cell constant determination, data collection and reduction were routine. A semi-empirical absorption correction based on the variation of intensity during azimuthal (ψ) scans for nine standard reflections having an Eulerian angle χ close to 90° was applied.⁶ The structure was solved with the SHELXS-86⁷ direct methods program package and refined by alternating cycles of full-matrix least-squares and difference Fourier maps. An additional absorption correction was applied at the end of isotropic refinement.⁸ The agreement factor *R* was then 0.122. Anisotropic refinement converged at *R* = 0.0476 (*R*_w = 0.0613). The highest peaks in the final difference Fourier map, having a height of > 1 e Å⁻³, were all located at < 1.0 Å distance from the iodine atoms and were attributed to series termination errors and/or deficiencies in the absorption correction. Pertinent crystal data are assembled in Table 1 and selected bond distances and angles are in Table 2.*

RESULTS AND DISCUSSION

We allowed Mo₂(O₂CCH₃)₄ to interact with four equivalents of Me₃SiI in THF as solvent, with the hope that this would afford the reactive intermediate Mo₂I₄(THF)₄ according to eq. (1).



The same strategy has been employed for the preparation of chloride,^{9,10} bromide¹¹ and iodide derivatives¹² of the Mo₂⁴⁺ core containing phosphine ligands, although higher nuclearity clusters were sometimes obtained.⁹ We have evidence that reaction 1 does not proceed to completion when a Me₃SiI/Mo₂(O₂CCH₃)₄ ratio of 4:1 is employed. Some molybdenum acetate remains unreacted in these conditions and even the use of an excess of the silyl reagent over the 4:1 ratio results in the formation of a final product where one acetate group is still present. We believe that the incom-

* A full list of bond distances and angles, positional parameters, anisotropic displacement parameters and *F_o/F_c* data have been deposited with the Editor as supplementary materials. The atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

Table 1. Crystal data for $[\text{Mo}_2(\mu\text{-O})(\mu\text{-I})(\mu\text{-O}_2\text{CCH}_3)_2(\text{THF})_4][\text{MoOI}_4(\text{THF})]$

Formula	$\text{C}_{22}\text{H}_{43}\text{I}_7\text{Mo}_3\text{O}_9$
Formula weight	1627.73
Space group	$P\bar{1}$
Systematic absences	none
a , Å	13.827(3)
b , Å	15.803(7)
c , Å	9.950(3)
α , deg	93.34(4)
β , deg	102.40(2)
γ , deg	90.09(2)
V , Å ³	2120(2)
Z	2
d_{calc} , g cm ⁻³	2.559
Crystal size, mm	0.1 × 0.5 × 0.9
$\mu(\text{MoK}_\alpha)$, cm ⁻¹	59.586
Data collection instrument	CAD-4
Radiation (monochromated in incident beam)	MoK_α ($\lambda_\alpha = 0.71073$ Å)
Orientation reflections, number, range (2θ)	25, 15–25
Temperature, °C	20
Scan method	$\omega-2\theta$
Data col. range, 2θ , deg	4–45
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	4986, 3938
Number of parameters refined	370
Trans. factors, max., min.	1.000, 0.377
R^a	0.0476
R_w^b	0.0613
Quality-of-fit indicator ^c	1.77
Largest shift/esd, final cycle	0.43
Largest peak, e Å ⁻³	1.33

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

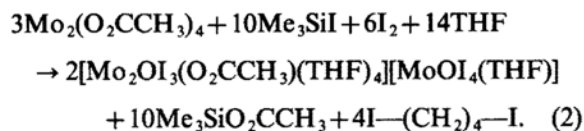
$$^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$^c \text{Quality-of-fit} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

pletteness of reaction 1 is caused by a competitive interaction of Me_3SiI with the solvent (*vide infra*).

Once the interaction between $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and Me_3SiI is completed, a subsequent treatment

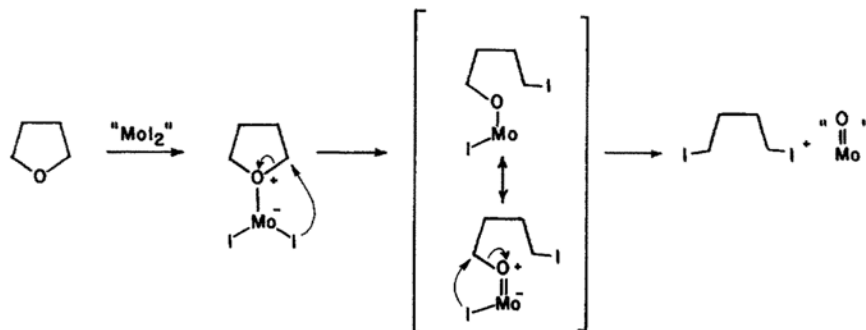
with I_2 causes the formation of a precipitate, identified as $[\text{Mo}_2(\mu\text{-O})(\mu\text{-I})(\mu\text{-O}_2\text{CCH}_3)_2(\text{THF})_4]^+ [\text{MoOI}_4(\text{THF})]^-$ by X-ray analysis. The stoichiometry of the reaction is represented in eq. (2). The formation of 1,4-diiodobutane has been confirmed by GC-MS analysis.



We suggest that the oxophilicity and the Lewis acidity of the molybdenum center make a molybdenum-assisted iodide cleavage of THF possible, as shown in Scheme 1.

It is well known that ethers can be cleaved by HI and also by HX (X = Br, Cl) in the presence of Lewis acids such as ZnCl_2 .¹³ Me_3SiI has also been found to be effective in the cleavage reaction of ethers.¹⁴ The room temperature interaction between THF and Me_3SiI in CDCl_3 as solvent was reported to take place rapidly with formation of $\text{Me}_3\text{Si}-\text{O}-(\text{CH}_2)_4-\text{I}$ followed by slow conversion to $\text{I}-(\text{CH}_2)_4-\text{I}$.^{14a} We cannot therefore exclude *a priori* that 1,4-diiodobutane is produced only by interaction of Me_3SiI with THF and that the oxygen atom is then in some way transferred from the silicon to the molybdenum centers. We observe, however, that in our system the molybdenum acetate dimer will compete with THF for the silyl reagent according to eq. (1). The observed fast dissolution of the insoluble $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ upon treatment with Me_3SiI indicates that reaction between these two compounds does occur. The competitive interaction between Me_3SiI and THF may, however, account for the incompleteness of reaction 1.

That the molybdenum center is capable of assisting the cleavage reaction of THF by iodide is proved by the result of the interaction between $\text{Mo}(\text{CO})_6$ and I_2 in THF. The interaction between $\text{Mo}(\text{CO})_6$ and I_2 in a 2:3 ratio in refluxing benzene-toluene



Scheme 1.

Table 2. Selected bond distances (Å) and angles (deg.) for $[\text{Mo}_2(\mu\text{-O})(\mu\text{-I})(\mu\text{-O}_2\text{CCH}_3)_2(\text{THF})_4][\text{MoOI}_4(\text{THF})]$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Mo1	Mo2	2.527(2)	Mo2	I2	2.710(1)	Mo3	I4	2.724(2)
Mo1	I1	2.700(1)	Mo2	I12	2.732(1)	Mo3	I5	2.752(2)
Mo1	I12	2.737(1)	Mo2	O2	2.197(8)	Mo3	I6	2.749(2)
Mo1	O1	2.197(9)	Mo2	O4	2.213(9)	Mo3	O8	1.644(11)
Mo1	O3	2.207(9)	Mo2	O6	2.088(7)	Mo3	O9	2.402(10)
Mo1	O5	2.081(7)	Mo2	O7	1.880(8)			
Mo1	O7	1.859(8)	Mo3	I3	2.761(2)			

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Mo2	Mo1	I1	105.54(5)	O5	Mo1	O7	90.6(3)	O4	Mo2	O7	161.2(3)
Mo2	Mo1	I12	62.38(4)	Mo1	Mo2	I2	104.50(4)	O6	Mo2	O7	91.1(3)
Mo2	Mo1	O1	127.1(2)	Mo1	Mo2	I12	62.58(4)	Mo1	I12	Mo2	55.04(3)
Mo2	Mo1	O3	146.9(3)	Mo1	Mo2	O2	126.2(3)	Mo1	O7	Mo2	85.0(3)
Mo2	Mo1	O5	85.9(2)	Mo1	Mo2	O4	147.0(2)	I3	Mo3	I4	92.63(5)
Mo2	Mo1	O7	47.8(3)	Mo1	Mo2	O6	85.9(2)	I3	Mo3	I5	171.60(6)
I1	Mo1	I12	92.40(4)	Mo1	Mo2	O7	47.1(2)	I3	Mo3	I6	87.45(5)
I1	Mo1	O1	91.7(2)	I2	Mo2	I12	94.23(4)	I3	Mo3	O8	94.3(4)
I1	Mo1	O3	89.2(2)	I2	Mo2	O2	91.7(2)	I3	Mo3	O9	84.4(2)
I1	Mo1	O5	167.9(2)	I2	Mo2	O4	89.6(2)	I4	Mo3	I5	89.09(5)
I1	Mo1	O7	100.2(2)	I2	Mo2	O6	169.4(2)	I4	Mo3	I6	165.69(7)
I12	Mo1	O1	167.9(3)	I2	Mo2	O7	97.6(2)	I4	Mo3	O8	95.3(4)
I12	Mo1	O3	88.0(3)	I12	Mo2	O2	167.6(3)	I4	Mo3	O9	83.1(2)
I12	Mo1	O5	89.2(2)	I12	Mo2	O4	87.0(2)	I5	Mo3	I6	88.85(5)
I12	Mo1	O7	110.0(3)	I12	Mo2	O6	88.5(2)	I5	Mo3	O8	93.7(4)
O1	Mo1	O3	80.7(4)	I12	Mo2	O7	109.5(2)	I5	Mo3	O9	87.7(2)
O1	Mo1	O5	84.4(3)	O2	Mo2	O4	82.1(3)	I6	Mo3	O8	98.9(4)
O1	Mo1	O7	80.4(4)	O2	Mo2	O6	83.8(3)	I6	Mo3	O9	82.7(2)
O3	Mo1	O5	78.8(3)	O2	Mo2	O7	80.4(3)	O8	Mo3	O9	177.9(4)
O3	Mo1	O7	159.1(3)	O4	Mo2	O6	80.3(3)				

Numbers in parentheses are estimated standard deviations in the least significant digits.

is a good synthetic method for anhydrous MoI_3 .¹⁵ When, however, we carried out the same interaction in boiling THF [hoping to produce the THF adduct, $\text{MoI}_3(\text{THF})_3$], significant amounts of 1,4-diiodobutane were obtained together with an uncharacterized black solid, presumably an oxo-iodide of molybdenum.

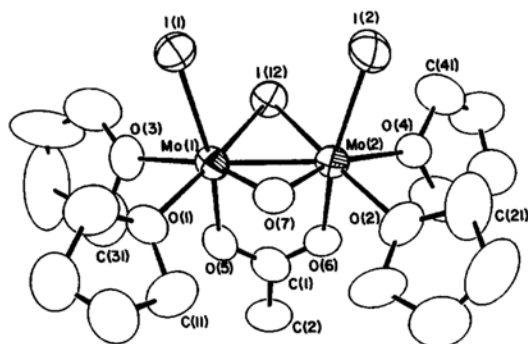


Fig. 1. An ORTEP view of the $[\text{Mo}_2\text{OI}_3(\text{O}_2\text{CCH}_3)(\text{THF})_4]^+$ ion.

Molecular structure

A view of the cation is illustrated in Fig. 1, while the anion is shown in Fig. 2. The assignment of the

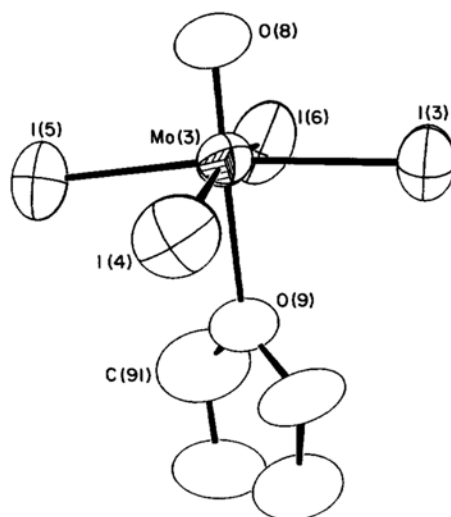


Fig. 2. An ORTEP view of the $[\text{MoOI}_4(\text{THF})]^-$ ion.

charge to the two ions is based on the existence in the literature of another salt of the $[\text{MoOI}_4\text{L}]^-$ anion ($\text{L} = \text{H}_2\text{O}$).¹⁶ Also, this assignment fits well with the observed magnetic properties of the compound (*vide infra*).

The cation is a dinuclear complex with a distorted edge-sharing bioctahedral arrangement of the ligands. A bridging oxygen atom and a bridging iodine atom are the ligands defining the shared edge. An axially coordinated acetate group also bridges the two metal centers. The coordination spheres are completed by one axial iodide ligand and two equatorial THF groups per molybdenum atom. This cation therefore contains three different bridges between the metal atoms. An identical configuration has been found for the rhenium compound $\text{Re}_2\text{OCl}_5(\text{O}_2\text{CC}_2\text{H}_5)(\text{PPh}_3)_2$,¹⁷ the two metal atoms being bridged there by an oxygen atom, a chlorine atom and a propionato group.

There are several reasons for the deviation of the geometry from the ideal edge-sharing bioctahedral one. The first one is the different bond lengths to the two bridging atoms in the shared edge (average values are given): $\text{Mo}-(\mu\text{-O})$, 1.87 Å; $\text{Mo}-(\mu\text{-I})$, 2.734 Å. Another is the close contact between the two axial iodide ligands ($\text{I}\cdots\text{I}$: 3.931 Å), which is less than the sum of the van der Waals radii (4.30 Å).¹⁸ These two atoms thus push each other away from the ideal axial positions (the average $\text{I}-\text{Mo}-\text{O}$ angle involving the acetate oxygen atom is 168.6°). The equatorial donor atoms show only slight deviations from the respective least-squares planes. Each molybdenum atom, on the other hand, is displaced away from its own local equatorial plane by 0.140(1) Å towards the axial iodine atom. The two planes form a dihedral angle of 21.2(4)°.

The metal-metal separation of 2.527(2) Å indicates a strong bonding interaction. A Mo_2^{2+} core is present in the cation, with five electrons available for metal-metal bonding. These may be distributed among the orbitals of the dimetal core either in the $\sigma^2\pi^2\delta^1$ or in the $\sigma^2\pi^2\delta^*1$ order.¹⁹ In either case a paramagnetism for the ion is expected corresponding to one unpaired electron. A distance of 2.789(1) has been reported for the d^3-d^3 compound $\text{Mo}_2\text{Cl}_6(\text{dppm})_2$ [$\text{dppm} = \text{bis}(\text{diphenylphosphino})\text{methane}$], which is believed to have a $\sigma^2\pi^2\delta^*2$ configuration. No edge-sharing bioctahedral compound of Mo(IV) with a metal-metal bonding interaction seems to have been reported. The edge-sharing bioctahedral $[\text{Mo}_2\text{Cl}_{10}]^{2-}$ complex has a metal-metal separation of 3.80 Å, which indicates no bonding interaction.²⁰ The compound $\text{Mo}_2\text{S}_2(\text{SCNPr}_2)_2(\text{S}_2\text{CNPr}_2)_2$, however, has been described as containing a double bond between Mo(IV) centers,²¹ with a metal-metal distance of

2.705(2) Å. The shorter distance in our compound might then be due to the occupation of the δ orbital by the fifth electron, but it is also possible that the two metals are forced closer to each other by the presence of the small oxo bridge.

The average separation between molybdenum and terminal iodine atoms is a little shorter (2.705 Å) than those involving the bridging iodine atom. These Mo—I bond lengths are shorter than those commonly found for other molybdenum-iodide complexes,^{1-3,22} in agreement with the higher oxidation state and the positive charge of the ion. The Mo—($\mu\text{-O}$) distances are slightly shorter than those typical of Mo—($\mu\text{-O}$)—Mo moieties in trinuclear clusters of molybdenum(IV) (the latter being in the 1.91–1.94 Å range)²³ and may indicate some double bond character. The Mo—O distances involving the acetate group (average 2.084 Å) compare with those found in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ (2.10–2.21 Å),⁵ while those involving the THF ligands (2.19–2.21 Å) are in the same range found in $\text{MoI}_3(\text{THF})_3$.³

The anion (see Fig. 2) is a distorted octahedral complex of Mo(V). The structural parameters compare well with those of the very similar anion $[\text{MoOI}_4(\text{H}_2\text{O})]^-$.¹⁶ The Mo—I distances are longer than those found in the cation (*vide supra*) in spite of the higher oxidation state in the anion. This may be due to the different charge of the two ions. The Mo—O(THF) bond length is also substantially longer in the anion, mainly because of the well-known strong *trans* influence of the oxo group. The molybdenum atom is displaced away from the least-squares plane of the four iodine atoms by 0.265(1) Å, towards the oxo ligand.

A d^1 electronic configuration for the Mo(V) center is present in the anion. The salt $[\text{Mo}_2\text{OI}_3(\text{O}_2\text{CCH}_3)(\text{THF})_4][\text{MoOI}_4(\text{THF})]$ is therefore expected to have two unpaired electrons, one in the cation and one in the anion. A magnetic susceptibility measurement agrees with this view, as an effective magnetic moment of 3.14 BM is found at room temperature.

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