$Et_4N[Mo_2O_2S_2(\mu\text{-}O_2CCF_3)(S_2P(OEt)_2)_2]$, the First Six-Coordinate $[Mo_2O_2(\mu\text{-}S)_2L_2]$ Complex (L = Bidentate Sulfido Ligands)

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Introduction

The chemistry of molybdenum(V) is dominated by dinuclear complexes of which those with the general formula $[Mo_2O_xS_{4-x}L_2]$ ($x = 0-4$) are the most commonly encountered. The synthesis, structure and reactivity of the Mo^V-S_n ($n = 1$, 2) functional groups toward electrophilic molecules have been subjects of numerous reports.[1−6] These Mo(V) dimers have an basic $[Mo_2O_xS_{4-x}]$ unit, which is surrounded by L ligands to complete the five (square pyramidal) or six (octahedral) coordination of each molybdenum atom depending on the identity of the L ligands. In most of the compounds in which L ligands contain such donor atoms as O and/or N, the Mo atoms are octahedrally coordinated. However, in those complexes with L being a sulfido donor ligand, the sixth coordination site trans to the terminal atom is absent and the Mo atoms have square pyramidal coordination geometry. Although in the latter case the Mo atoms might appear to be coordinatively unsaturated, they are considered to have little tendency to form an adduct, which has presumably been attributed to the combined effects of the Mo−Mo bonds, trans repulsive refluence of the terminal atoms, and the folding in the bridge.[7a]

The reactivity of coordinatively unsaturated Mo atoms has been a subject of several studies[7] for understanding the mode of reactions of various molybdoenzymes (e.g., xanthine oxidase[8]) and molybdenum catalysts (e.g., MoS_2[9]). For this purpose the above pentacoordinate molybdenum(V) dimers with bidentate sulfido ligands may serve as valuable probes. However, to our knowledge, there has been only one reported example for a μ-O−μ-S dimolybdenum(V) complex, $[Mo_2O_3S(S_2P(O^iPr)_2)_2]$, which was treated with Py or Pytz to form the adduct $[Mo_2O_2S(S_2P(^iOPr)_2)_2(\mu\text{-}X)]$ (X = Py or Pytz).[7a] Herein, we wish to report the first example for the di-μ-S species, $[Mo_2O_2S_2(S_2P(OEt)_2)_2]$ (**2**),[10] which is supplemented by a trifluoroacetato bridge to form the six-coordinate species $Et_4N[Mo_2O_2S_2(\mu\text{-}O_2CCF_3)(S_2P(OEt)_2)_2]$ (**3**).

Table 1. Crystallographic Data for $Et_4N[Mo_2O_2S_2(O_2CCF_3)(S_2P(OEt)_2)_2]$ (**3**)

formula	$C_{18}H_{40}Mo_2F_3N_1O_8P_2S_6$
fw	901.7
$F(000)$	912
cryst size, mm	0.2 × 0.3 × 0.3
space group	$P\bar{1}$
a, Å	13.270(6)
b, Å	13.291(8)
c, Å	10.559(10)
α, deg	97.86(6)
β, deg	103.70(5)
γ, deg	88.29(5)
V, Å^3	1792(4)
Z	2
Dc̃, g cm^{-3}	1.67
μ, cm^{-1}	11.6
hkl ranges	$h = 0-15$
	$k = -15$ to 15
	$l = 12$ to 12
cor	Lorentz−polarization
	linear decay (0.991−1.196)
	empirical abs (0.643−0.999)
	difabs program (0.300−1.686)
no. of unique reflcns	6320
no. of obsd ($I > 3\sigma(I)$) reflcns	3715
no. of refined params	358
R, R_w[a]	0.075, 0.089
GOF[b]	2.56
$(\Delta/\sigma)_{max}$	0.08
$(\Delta/\rho)_{max}$	1.29

[a] $R = \sum||F_o| - |F_c||/|F_o|$. $R_w = [w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$. [b] GOF $= [w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$.

Experimental Section

Synthesis of $Na_4Mo_2O_2(O_2CCF_3)_{10}\cdot 4CF_3CO_2H$ (1). A mixture of $Mo(CO)_6$ (0.66 g, 2.5 mmol), $Na_2MoO_2\cdot 2H_2O$ (2.42 g, 10 mmol) and trifluroacetic anhydride (40 mL) was placed in a flask with a refluxing condenser. A few minutes later the mixture began to reflux without external heating and became blue in color. After 1 h the reflux stopped and blue crystals of **1** were formed.

Synthesis of $[Mo_2O_2S_2(S_2P(OEt)_2)_2]$ (2). The preparative procedure was similar to that of compound **3** to be described below, but Et_4NCl was not used. Compound **2** was crystallized as brown−yellow crystals and have properties similar to those of **3**.

Synthesis of $Et_4N[Mo_2O_2S_2(O_2CCF_3)(S_2P(OEt)_2)_2]$ (3). The blue crystals of **1** was dissolved in EtOH solution (50 mL) of P_2S_5 (2.22 g, 10 mmol) to produce a purple-red solution. The solution was mixed with Et_4NCl (0.7 g, 5.1 mmol) and then evaporated in air for 3 days or more to give yellow crystals of **3** (1.5 g, 33% based on $Na_2MoO_4\cdot 2H_2O$). The crystals are stable in air and insoluble in water. They can be dissolved in common organic solvents such as EtOH, CH_3CN, and DMF.

Synthesis of $[Mo_2O_3(S_2P(O^iPr)_2)_4]$ (4). Compound **4** was synthesized similarly using ^{i}PrOH to replace EtOH and isolated as purple-black crystals.

X-ray Crystallography. The crystallographic data for compound **3** are summarized in Table 1. The reflection intensity data were collected on a Rigaku AFC5R diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) at room temperature and a $\omega/2\theta$ scan mode ($3° < 2\theta < 50°$) with scan speed 8° min^{-1}. The accurate cell parameters were determined from a least-squares refinement of the orientation matrix to the setting diffractometer angles of 20 automatically centered reflections. The intensities were corrected

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for absorption using linear decay, empirical scan data, Lorentz–polarization factors, and the DIFABS program.[11a] The structure was solved by direct methods using MULTAN11/82 and refined by full-matrix least-squares methods with all non-hydrogen atoms anisotropic except for F atoms which were refined isotropically. The F atoms are found to be disordered, and the occupancies of the two sites for each F atom were constrained to 0.5. The weighting scheme w was $1/[\sigma(F_o)^2 + (0.02\ F_o)^2 + 1.000]$. All calculations were performed on a VAX 785 computer using the SDP program package with scattering factors taken from ref 11b.

UV–Vis and IR Spectra. The UV–vis spectra and IR spectra of compounds **2** and **3** were recorded on Schimadyzu UV-3000 and Digilab FTS-40 spectrophotometers (KBr pellet), respectively.

Result and Discussion

Synthesis. The starting material, $Na_4Mo_2O_2(O_2CCF_3)_{10}\cdot 4CF_3CO_2H$(**1**), used for the preparation of compounds **2**–**4** was obtained as well-formed blue crystals from the reaction of Na_2MoO_4 with $Mo(CO)_6$ in refluxing trifluoroacetic anhydride. It is noteworthy that similar redox reactions between Na_2MO_4 (M = Mo, W) (or $NaVO_3$) and $M(CO)_6$ (M = Cr, Mo, W) in other carboxylic anhydride such as acetic or propionic anhydride have been known to produce the triangular, trinuclear M(IV) cluster species $[M_3O_2(O_2CCR)_6(H_2O)_3]^{2+}$ (M_3 = Mo_3, MoW_2, W_3; R = Me, Et)[12–14] or the one-dimensional heterooctametallic clusters, $Na_2M'_2[M_3O_4(O_2CEt)_8]_2$ (M′ = Cr, V; M = Mo, W).[15,16] Compound **1** is extremely sensitive to moisture and the preliminary structural determination (the structure is available as Supporting Information)[17] has revealed the above formulation. As shown eq 1, complex **1** can be converted to

$$\mathbf{1}\ \begin{array}{l} \xrightarrow{P_2S_5,EtOH} [Mo_2O_2S_2(S_2P(OEt)_2)_2]\ (\mathbf{2}) \\ \xrightarrow{P_2S_5,EtOH,Et_4NCl} Et_4N[Mo_2O_2S_2(\mu\text{-}O_2CCF_3)(S_2P(OEt)_2)_2]\ (\mathbf{3}) \\ \xrightarrow{P_2S_5,PrOH} [Mo_2O_3(S_2P(O^iPr)_2)_4]\ (\mathbf{4}) \end{array}$$

compounds **2**, **3**, and **4**, respectively, under the different reaction conditions. Compound **1** is dissolved in either EtOH or ^{i}PrOH solution of P_2S_5 to result in a purple red solution. In the latter case the ^{i}PrOH solution is evaporated in air to form purple-black crystals characterized by X-ray crystallography as $[Mo_2O_3(S_2P(O^iPr)_2)_4]$ (**4**) reported previously,[18,19] indicating that the initial purple-red solution was that of $[Mo_2O_3(S_2P(OR)_2)_4]$ (R = Et, ^{i}Pr). However, in the former, the purple-red EtOH solution turns brown yellow in color 2 days later and brown-yellow crystals of compound **2**, $[Mo_2O_2S_2(S_2P(OEt)_2)_2]$, are deposited. This compound has been identified by UV–vis and IR spectra as described below. Compound **2** is belived to result from the conversion of the purple-red complex $[Mo_2O_3(S_2P(OEt)_2)_4]$ that is formed initially as mentioned above. Such skeletal conversion of $[Mo_2O_3]^{4+}$ to $[Mo_2O_2S_2]^{2+}$ has been established previously.[20] Interestingly, in the presence of Et_4NCl, the converting product is crystallized as the yellow trifluoroacetato-bridged species $Et_4N[Mo_2O_2S_2(\mu\text{-}O_2CCF_3)(S_2P(OEt)_2)_2]$ (**3**), indicating that the pentacoordinate compound **2** has a marked tendency to form adducts.

Table 2. Positional Parameters and B_{eq} for $(C_2H_5)_4N[Mo_2O_2S_2(O_2CCF_3)(S_2P(OC_2H_5)_2)_2]$

atom	x	y	z	B_{eq} (Å^2)[a]
Mo(1)	0.66686(6)	0.29831(7)	0.68184(8)	3.57(2)
Mo(2)	0.81300(7)	0.29194(7)	0.53224(9)	3.79(2)
S(1)	0.6766(2)	0.1773(2)	0.5030(3)	4.40(6)
S(2)	0.8195(3)	0.3926(2)	0.7334(3)	5.16(7)
S(3)	0.5333(2)	0.1800(2)	0.7189(3)	4.97(7)
S(4)	0.6555(2)	0.3643(3)	0.9158(3)	5.21(7)
S(5)	0.8778(2)	0.1627(2)	0.3717(3)	4.75(6)
S(6)	0.9996(2)	0.3458(2)	0.5701(3)	5.64(7)
P(1)	0.5416(2)	0.2647(2)	0.8911(3)	4.70(7)
P(2)	1.0082(2)	0.2439(2)	0.4161(3)	4.77(6)
O(1)	0.5801(5)	0.3799(5)	0.6106(7)	4.4(2)
O(2)	0.7607(5)	0.3698(6)	0.4223(7)	4.9(2)
O(3)	0.8954(5)	0.1764(5)	0.6765(7)	4.0(2)
O(4)	0.7773(5)	0.1828(5)	0.7974(7)	4.1(2)
O(11)	0.4355(6)	0.3148(6)	0.9033(7)	5.4(2)
O(12)	0.5536(6)	0.2010(7)	1.0091(8)	6.3(2)
O(13)	1.0284(6)	0.2924(6)	0.2961(8)	6.2(2)
O(14)	1.1088(1)	0.1781(6)	0.4427(8)	6.1(2)
C(1)	0.8603(7)	0.1534(7)	0.767(1)	3.4(2)
C(2)	0.9207(9)	0.0807(9)	0.849(1)	5.0(3)
C(11)	0.392(1)	0.392(1)	0.819(1)	8.4(4)
C(12)	0.656(1)	0.153(1)	1.056(2)	9.3(4)
C(13)	0.955(1)	0.368(1)	0.240(2)	10.6(4)
C(14)	1.118(1)	0.101(1)	0.534(2)	7.6(4)
C(15)	0.283(1)	0.408(1)	0.816(2)	7.2(4)
C(16)	0.642(2)	0.060(1)	1.108(2)	9.8(5)
C(17)	0.968(2)	0.389(2)	0.115(2)	10.7(6)
C(18)	1.224(2)	0.106(2)	0.618(2)	12.5(6)
F(1)	0.907(1)	−0.014(1)	0.788(1)	7.0(3)
F(2)	1.018(1)	0.099(1)	0.886(2)	8.7(4)
F(3)	0.886(1)	0.069(1)	0.959(2)	7.9(4)
F(4)	0.958(1)	0.121(1)	0.971(2)	8.1(4)
F(5)	0.870(1)	0.000(1)	0.851(2)	8.2(4)
F(6)	1.012(1)	0.052(1)	0.818(1)	6.5(3)
N(1)	0.3480(6)	0.2690(6)	0.2676(8)	3.7(2)
C(21)	0.326(1)	0.240(1)	0.115(2)	8.7(5)
C(22)	0.215(1)	0.208(2)	0.051(2)	9.8(5)
C(23)	0.323(1)	0.179(1)	0.335(2)	8.9(4)
C(24)	0.372(2)	0.080(1)	0.301(2)	9.7(5)
C(25)	0.284(1)	0.358(1)	0.301(1)	7.6(4)
C(26)	0.303(1)	0.398(1)	0.447(1)	6.9(4)
C(27)	0.464(1)	0.288(1)	0.311(2)	7.6(4)
C(28)	0.503(1)	0.383(1)	0.273(2)	6.8(4)

[a] $B_{eq} = {}^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Crystal Structure. Complex **3**, $Et_4N[Mo_2O_2S_2(\mu\text{-}O_2CCF_3)(S_2P(OEt)_2)_2]$, has been characterized by X-ray crystallography. The atomic coordinates and selected bond lengths and angles are given in Tables 2 and 3. The structure of the anion, shown in Figure 1, has no imposed crystallographic symmetry. The structure contains two bridging S atoms and two terminal O atoms to constitute an basic $Mo_2O_2(\mu\text{-}S)_2$ unit which is

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(17) Blue crystals of **1** were crystallized in monoclinic system (space group $P2_1/n$) with $a = 14.2472(56)$ Å, $b = 16.7926(107)$ Å, $c = 15.3200(50)$ Å, $\beta = 112.4024(40)°$, $V = 3388(5)$ Å^3, and $Z = 2$. Only 1683 observable reflections ($I \geqslant 3(\sigma)I$) were obtained due to the instability of the crystals toward X-ray, leading to the poor R index of 0.17. The preliminary molecular structure is available as Supporting Information.

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Mo_2O_2S_2(O_2CCF_3)(dtp)_2]^-$

Mo(1)−Mo(2)	2.7691(8)	Mo(2)−S(1)	2.338(3)
Mo(1)−S(1)	2.333(2)	Mo(2)−S(2)	2.336(2)
Mo(1)−S(2)	2.326(2)	Mo(2)−S(5)	2.524(2)
Mo(1)−S(3)	2.536(3)	Mo(2)−S(6)	2.523(2)
Mo(1)−S(4)	2.544(3)	Mo(2)−O(2)	1.674(5)
Mo(1)−O(1)	1.675(4)	Mo(2)−O(3)	2.372(4)
Mo(1)−O(4)	2.350(4)		
Mo(2)−Mo(1)−S(1)	53.72(5)	S(2)−Mo(1)−S(4)	84.83(7)
Mo(2)−Mo(1)−S(2)	53.71(5)	S(2)−Mo(1)−O(2)	101.9(2)
Mo(2)−Mo(1)−S(3)	137.62(5)	S(2)−Mo(1)−O(4)	81.6(1)
Mo(2)−Mo(1)−S(4)	137.47(6)	S(3)−Mo(1)−S(4)	77.91(7)
Mo(2)−Mo(1)−O(1)	101.6(2)	S(3)−Mo(1)−O(2)	95.3(2)
Mo(2)−Mo(1)−O(4)	84.5(1)	S(3)−Mo(1)−O(4)	80.1(1)
Mo(1)−Mo(2)−S(1)	53.55(5)	S(4)−Mo(1)−O(2)	95.4(2)
Mo(1)−Mo(2)−S(2)	53.40(5)	S(4)−Mo(1)−O(4)	79.9(1)
Mo(1)−Mo(2)−S(5)	136.85(5)	O(2)−Mo(1)−O(4)	173.9(2)
Mo(1)−Mo(2)−S(6)	136.28(6)	S(1)−Mo(2)−S(2)	106.06(7)
Mo(1)−Mo(2)−O(2)	101.8(2)	S(1)−Mo(2)−S(5)	84.67(6)
Mo(1)−Mo(2)−O(3)	82.6(2)	S(1)−Mo(2)−S(6)	155.89(7)
Mo(1)−S(1)−Mo(2)	72.74(6)	S(1)−Mo(2)−O(1)	100.8(2)
Mo(1)−S(2)−Mo(2)	72.88(7)	S(1)−Mo(2)−O(3)	80.6(1)
Mo(1)−S(3)−P(1)	87.34(9)	S(2)−Mo(2)−S(5)	156.03(8)
Mo(1)−S(4)−P(1)	87.1(1)	S(2)−Mo(2)−S(6)	84.31(8)
Mo(2)−S(5)−P(2)	87.0(1)	S(2)−Mo(2)−O(1)	103.0(2)
Mo(2)−S(6)−P(2)	87.03(9)	S(2)−Mo(2)−O(3)	80.7(1)
S(1)−Mo(1)−S(2)	106.52(7)	S(5)−Mo(2)−S(6)	78.35(7)
S(1)−Mo(1)−S(3)	85.00(7)	S(5)−Mo(2)−O(1)	95.7(2)
S(1)−Mo(1)−S(4)	156.88(7)	S(5)−Mo(2)−O(3)	80.1(1)
S(1)−Mo(1)−O(1)	101.6(2)	S(6)−Mo(2)−O(2)	97.8(2)
S(1)−Mo(1)−O(4)	82.0(1)	S(6)−Mo(2)−O(3)	79.7(1)
S(2)−Mo(1)−S(3)	156.70(8)	O(2)−Mo(2)−O(3)	175.4(2)

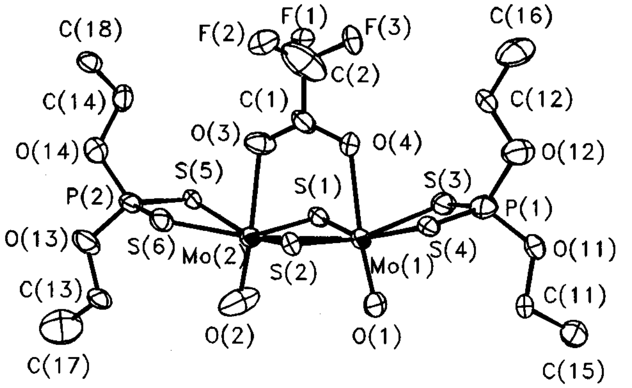

Figure 1. Ortep drawing of the anion $[Mo_2O_2S_2(O_2CCF_3)(S_2P(OEt)_2)_2]^-$ of **3** with 50% probability thermal ellipsoids.

surrounded by the two phosphorodithioate ligands, $S_2P(OEt)_2$, to form the known compound $[Mo_2O_2S_2(S_2P(OEt)_2)_2]$.[10a] Many similar complexes with bidentate sulfido ligands such as *S*,*S*-dmad,[3d] CS_n (n = 3, 4),[3f] Rxan,[21] R_2dtc,[10,22] Et_2dtp,[10] S_x^{2-} (X = 2, 4),[23] imnt,[22d,24] dithiothreito,[25] and S_3O_2[23d,e] have been synthesized and structurally characterized. However, in all of these complexes, the Mo atoms have square-pyramidal coordination environments. This may be attributed to the cis-repulsion of the S donor atoms in these sulfide-containing ligands based on the fact that most of such species with O and/or N donor ligands such as DMF,[3c,26] NCS^-,[27] ox^{2-},[28] EDTA,[29] cys,[29a,b,20,30] and hist[30,31] are six-coordinate. The structure shown in Figure 1 is of interest in that there is a trifluoroacetato bridge between the two Mo atoms to complete their octahedral coordination in spite of the existence of the repulsive influence of the equatorial S donor atoms from $S_2P(OEt)_2$. It is worth noting that similar carboxylato bridges have also been found in $[\{Mo_2O_3S(ox)_2\}_2(ox)]^{6-}$,[32] $[\{Mo_2O_3S(mal)_2\}_2(mal)]^{6-}$,[33] $[Mo_2O_4(\mu\text{-}O_2CMe)(SCN)_4]^{3-}$,[34] and $[Mo_2O_4(\mu\text{-}O_2CH)(O_2CH_4]^{3-}$.[35] Owing to the trans influence of the $Mo{-}O_t$ double bonds, the $Mo{-}O_1(O_2CCF_3)$ bonds [2.372(4) and 2.350(4) Å, respectively] are rather long for a Mo−O(carboxylate) bond (ca. 2.10 Å). Significantly, the distances are 0.06−0.2 Å longer than the corresponding distances in $[\{Mo_2O_2S_2(S_2)(DMF)_3]^{2+}$ [2.224(5) Å],[3c] $[Mo_2O_2S_2(ox)_2(H_2O)_2]^{2-}$ [2.160(6) Å],[28] and $[Mo_2O_4(\mu\text{-}O_2CH)(O_2CH)_4]^{3-}$ [2.302(2) Å],[35] which is presumably attributed to the further cis influence of the S atoms from $S_2P(OEt)_2$ and/or the steric effect of the CF_3CO_2 and $S_2P(OEt)_2$ groups of great size. A similar case has also been found in ref 7a (Mo−N(Py), 2.948(19) Å; Mo−N(Pytz), 2.587(16) Å; vs 2.23 Å for a Mo−N bond) and ascribed to the trans and steric influence. The Mo−Mo bond length [2.7691(8) Å] is about 0.03 Å longer than that in $[Mo_2O_2S_2(S_2P(OEt)_2)_2]$ [2.739(4) Å],[10a] indicating that the Mo−Mo bonding is slightly weakened by the $CF_3CO_2^-$ bridge, in contrast to the case in ref 7a where the Mo−Mo bonds are shortened by the Py or Pytz bridges by 0.036 or 0.019 Å. Nevertheless, the Mo−Mo bond in the present case is still remarkably shorter than in those $[Mo_2O_2S_2L_2]$ species with other bidentate sulfido ligands [Mo−Mo, 2.811(1)−2.901(1) Å],[2,3,21−25] in contrast to the longer $Mo{-}S_1(S_2P(OEt)_2)$ distances [average 2.532(4) Å] than in the latter compounds (2.378(3)−2.463(2) Å).[2,3,21−25] The mean $Mo{-}S_1$ bond is also longer than those in $[Mo_2S_4(S_2P(OEt)_2)_2]$ [2.477(2) Å],[10b] $[Mo_2O_3S(S_2P(OEt)_2)_2]$ [2.489(4) Å],[7a] $[Mo_2O_3S(S_2P(OEt)_2)_2(\mu\text{-}Py)]$[2.511(4) Å],[7a] and $[Mo_2O_3S(S_2P(OEt)_2)_2(\mu\text{-}Pytz)]$ [2.518(7) Å].[7a] The mean $Mo{-}S_b$ [2.333(3) Å] and $Mo{-}O_t$ [1.675(5) Å] are slightly longer than those in $[Mo_2O_2S_2(S_2P(OEt)_2)_2]$ [$Mo{-}S_b$, 2.29(2) Å, $Mo{-}O_t$, 1.657(6) Å][10a] but within the range in other $[Mo_2O_2S_2L_2]$ complexes (L = bidentate sulfido ligands)

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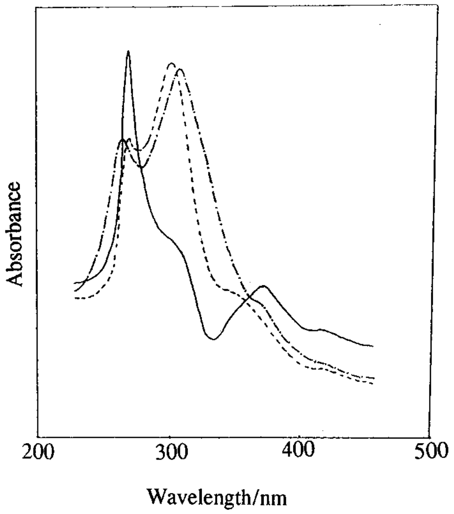

Figure 2. UV−vis spectra of compounds **2**, **3**, and **5** in DMF: (—) **3**; (- -) **2**; (− • −) **5**.

[Mo−S$_b$, 2.269(5)−2.33(1) Å; Mo−O$_t$, 1.664(7)−1.700(2) Å].[2,3,21−25] The two Mo atoms deviate from the least-square planes defined by S(1)S(2)S(3)S(4) and S(1)S(2)S(5)S(6) atoms toward the terminal O atoms by 0.378(1) and 0.406(1) Å, respectively, within the range in six-coordinate Mo dimers (0.30−0.42 Å) but considerably smaller than in [Mo$_2$O$_3$S(dtp)$_2$-(μ-Y)] (Y = Py, 0.56(1) Å; Y = Pytz, 0.48(1) Å)[7a] and five-coordinate dimolybdenum compounds (ca. 0.70 Å), indicating that the effect of the bridging trifluoroacetato ligand in the present case on the geometry of the molybdenum atoms in the parent compound is significantly greater than that of the Py or Pytz bridge[7a] due to the stronger Mo−O(O$_2$CCF$_3$) interaction.

UV−Vis and IR Spectra. The UV−vis spectra of compounds **2** and **3**, together with that of [Mo$_2$O$_2$S$_2$(S$_2$CN(C$_4$H$_8$))$_2$] (**5**),[22f] shown in Figure 2, have been recorded in DMF with the following data, λ_{max} (ϵ, L cm^{-1} mol^{-1}): for **2**, 420 sh, 348 sh, 296 and 264 nm; for **3**, 420 sh (2100), 368 (3600), 300 sh (3800), 264 nm (7700); for **5**, 420 sh, 370 sh, 307, 262. The spectra of **2** and **5** are virtually identical with each other. However, the spectrum of **3** differs remarkably from those of **2** and **5** in shape and relative absorption intensity due to the refluence of the CF$_3$CO$_2^-$ bridge although the maximum absorption positions of the spectra are near to one another, indicating that there is still the considerable bonding interaction between the Mo atoms and the CF$_3$CO$_2$ group in DMF solution of compound **3**. This is unlike the case in the literature,[7a] where the UV−vis spectra of [Mo$_2$O$_3$S(S$_2$P(O^{i}Pr)$_2$)$_2$(μ-X)] (X = Py, Pytz) and [Mo$_2$O$_3$S(S$_2$P(O^{i}Pr)$_2$)$_2$] are almost the same. The IR spectrum of **3** shows a strong band at 1644 cm^{-1} which is absent in **2** and **5** and thus assigned to ν(C═O) of the CF$_3$CO$_2^-$ bridge. The ν(Mo═O$_t$) ν(Mo—S$_b$), and ν(Mo—S$_1$) stretching vibrations of **3** are found at 955 (vs), 928 (m) [ν(Mo═O$_t$)], 432 m [ν(Mo—S$_b$)], and 300 ms [ν(Mo—S$_1$)], respectively, similar to those reported data for [Mo$_2$O$_2$S$_2$]$^{2+}$-type species.[29a,36] It is noteworthy that they appear at lower frequencies than those of **2** (966 vs, 940 m, 450 m, 320 ms) and **5** (970 vs, 958 m, 477 s, 352 s) due to the slightly longer Mo−O$_t$, Mo−S$_b$, and Mo−S$_1$ bonds in compound **3**.

Compounds **2** and **3** are both diamagnetic and ESR-inactive, as expected for the Mo(V) and the direct Mo−Mo bond.

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Supporting Information Available: Tables of bond lengths, bond angles and thermal parameters (**U**$_{ij}$) of compound **3** and a figure showing the preliminary molecular structure of compound **1** (4 pages). Ordering information is given on any current masthead page.

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