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Novel Mo(V)-Dithiolene Compounds: Characterization of Nonsymmetric Dithiolene Complexes by Electrospray Ionization Mass Spectrometry

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Three new Mo(V) dithiolene compounds have been synthesized by addition of alkynes ($(Me_3Si)_2C_2$ (TMSA), $(Me_3Si)_2C_4$, and $(Ph)_2C_4$ to $MoO_2S_2^{2-}$ in a MeOH/NH$_3$ mixture: $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]^{2-}$ **1**, $[Mo_2(O)(X)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]^{2-}$ **2** (X = O or S), and $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H(C_2H))]^{2-}$ **3**. The structure of **1** as determined by single-crystal X-ray diffraction study (space group *Pbca*, $a = 13.3148(1)$ Å, $b = 15.7467(4)$ Å, $c = 28.4108(7)$ Å, $V = 5956.7(2)$ Å^3) is discussed. **2** and **3** have been identified by ESMS (electrospray mass spectrometry), ^{1}H NMR, ^{13}C NMR, and infrared spectroscopies. This investigation completes our previous study devoted to the addition of DPA (C_2Ph_2) to $MoO_2S_2^{2-}$ which led to $[Mo_2(O)(X)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph_2)]^{2-}$ **4** (X = O or S). A reaction scheme is proposed to explain the formation of the different species present in solution. The reactivity of the remaining nucleophilic site of these complexes (η^2-S$_2$) toward dicarbomethoxyacetylene (DMA) is also discussed.

Introduction

In the past decade, different electrophiles such as proton,[1] transition metals cations,[2] or CS_2[3−5] have been reacted with various tetraoxothiometalates $[MS_nO_{4-n}]^{x-}$ ($n = 1-4$) (M = V, Mo, Re, or W). The related reactions are often complicated by redox processes concerning metal centers and/or ancillary ligands. Because of this redox dependence, the type of the ancillary ligands and the nature of the metal greatly influence the nature of the final products.[6]

Among the wide variety of possible electrophilic reagents, alkynes have proven to prepare interesting new dithiolene ligands,[7] the goal in this case being the study of the formation of carbon−sulfide bond starting from organic substrates and thiometallic complexes. The addition of alkynes on ReS_4^- has been nicely explored by Rauchfuss and co-workers[8] who characterized a rich family of reduced rhenium sulfido complexes containing dithiolene ligands. To understand the influence of the metal, we recently engaged a study of the addition of diphenylacetylene (DPA) ($(C_6H_5)_2C_2$) to $MoO_2S_2^{2-}$.[9] We focused our attention on molybdenum, because dithiolene complexes of molybdenum have attracted attention[10] as they can be used to model the active sites of molybdenum metalloenzymes. A large amount of literature

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is devoted to the formation of molybdenum complexes containing dithiolene ligands obtained by addition of dicarbomethoxyacetylene (DMA)[6] on thio-polymetallic cores, but little is known about mononuclear species such as tetraoxothiomolybdates $[MoS_nO_{4-n}]^{2-}$ ($n = 1-4$).[11]

In this paper, we present the syntheses of three new compounds $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]^{2-}$ **1**, $[Mo_2(O)(X)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]^{2-}$ **2** (X = O or S), and $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H(C_2H))]^{2-}$ **3**, and propose a reaction scheme explaining the formation of these products and also that of $[Mo_2(O)(X)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph_2)]^{2-}$ **4** (X = O or S) previously reported.[9] The reactivity of these complexes with another alkyne, DMA ($C_2(CO_2Me)_2$), is described which permits the preparation of complexes containing two different types of dithiolene ligands.

Solids were characterized using X-ray diffraction and solutions were characterized by electrospray mass spectrometry (ESMS). This latter technique brings substantial promise for inorganic analysis if the compounds studied are soluble and stable in a suitable solvent.

The electrospray "ionization" method merely involves desolvation of ions originally present in solution. Intact ionic species are thus obtained in the gas phase by repeated cycles of solvent evaporation, prompted by a counter-flow of drying gas, and droplet fissioning through excess Coulombic repulsion.

There has been some concern[12,13] that this process might disrupt solution equilibria and bring on significant chemical effects resulting in the detection of new anions and cations. This is undoubtedly true when aqueous solutions are used: it has been shown for inorganic complexes such as isopolyoxomolybdates[12] as well as biological molecules.[14] The use of diluted solutions in organic solvents such as acetonitrile, acetone, or methanol should, however, help reduce the most significant effects of counterion presence and pH. Colton and Traeger[15] and others[16] have thus been able to observe intact heteropolymetalate species. Van Dorsselaer and coworkers[17] have also used ESMS with success for the characterization of new inorganic supramolecular systems.

Here, the combined use of ESMS and X-ray diffraction for $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]$ **1** allowed us to confirm the soundness of our ESMS analyses. ESMS was therefore applied for complexes **2** and **3**, which did not form any crystals.

Experimental Section

General Methods. All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. CH_3OH and Et_2O were previously distilled from CaH_2 before use. A solution of NH_3 in CH_3OH was obtained by bubbling NH_3 in dried CH_3OH to obtain a concentration of ca. 1.3 mol·L^{-1} (solution A). $(NH_4)_2[MoO_2S_2]$ was prepared according to the reported procedure.[18] Elemental analyses of solids were performed by the Service d'Analyse du CNRS, Vernaison (France). IR spectra (KBr pellets) were recorded on a FTIR Nicolet Magna-550 spectrophotometer. UV−vis spectra were recorded on a Perkin-Elmer lambda 19 spectrophotometer. ^{13}C and ^1H NMR spectra were recorded on a Bruker AC300 operating at 75.47 MHz for ^{13}C with Me_4Si as internal standard.

ESMS measurements were carried out with a HP 5989B single quadrupole mass spectrometer equipped with an electrospray source from Analytica of Branford. The instrument was operated in the negative ion mode. Source parameters were $V_{needle} = 0$ V, $V_{cyl} = 3500$ V, $V_{end} = 3000$ V, $V_{cap} = 3500$ V. Purified air was used as nebulizing and drying gas, with the presence of oxygen helping to prevent corona discharge which is often a problem in negative ion operation. The pressures of nebulizing and drying gas were 5 and 25 psi, respectively, and the nebulizing gas was heated to approximately 100 °C. Mass spectra were obtained by direct infusion with a Harvard Apparatus syringe pump of 10^{-4}, 5×10^{-5}, or 10^{-5} M sample solutions in pure distilled acetonitrile at a flow rate of 5 μL min^{-1}. The cone voltage V_c was varied but most often used at low values of 10 to 40 V relative to the capillary exit voltage. Raising the cone voltage improves the ion transmission through the analyzer. It also increases the kinetic energy, which in turn enhances the formation of daughter ions by collisions with solvent and gas molecules within the region of primary stage pumping between the capillary exit and the sampling cone. The mass spectra shown are the result of approximately 40 scans summed from m/z 50 to 1650. The mass axis was calibrated using the cluster ions observed from a 50 ng/μL solution of SDS (sodium dodecyl sulfate) in acetonitrile.

Synthesis of $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]$ 1. $(NH_4)_2[MoO_2S_2]$ (0.228 g, 1 mmol) was dissolved in 40 mL of solution A. After addition of NEt_4Br (0.840 g, 4 mmol) and TMSA (0.680 g, 4 mmol), the resulting yellow-orange solution was stirred for 2 d at room temperature and then filtered. After standing at room temperature for several days, the solution deposited red-orange crystals (20%). Anal. Calcd for $C_{18}H_{42}O_2N_2S_6Mo_2$: C, 30.77; H, 5.98; N, 3.98; S, 27.35; Mo, 27.34. Found: C, 30.52; H, 6.03; N, 3.91; S, 26.21; Mo, 27.60. IR (cm^{-1}): NEt_4^+ cations, 1483 (s), 1457 (s), 1390 (m), 1175 (m), 1004 (w), 784 (w); ν(C−S), 675 (m); ν(C=C), 1517 (w); ν(Mo−S), 465 (w), 420 (w), 385 (w), 350 (m); ν(Mo=O), 942 (vs), 925 (m); ν(S−S), (520).

^{13}C NMR (DMSO-d_6): NEt_4^+ cations, δ 7.04, 51.33 ppm, δ 127.85 ppm (ethylenic carbons).

^1H NMR (DMSO-d_6): NEt_4^+ cations, δ 3.04 (quadruplet, 8 H) (CH_2), δ 1.06 (triplet, 12 H) (CH_3) ppm; δ 6.80 ppm (ethylenic protons).

Synthesis of $(NPr_4)_2[Mo_2(O)(X)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]$ 2 (X = S, O). $(NH_4)_2[MoO_2S_2]$ (0.456 g, 2 mmol) was dissolved in 40 mL of solution A. After addition of NPr_4Br (1.06 g, 4 mmol) and Ph_2C_4 (0.404 g, 2 mmol), the solution turned slowly from yellow-orange to red. The mixture was stirred at room temperature for a day and filtered to isolate the red-brown precipitate that

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Table 1. Selected Crystal Data and Details for $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]$ **1**

formula	$C_{18}H_{42}N_2O_2S_6Mo_4$
fw	702.78
a, Å	13.3148(1)
b, Å	15.7467(4)
c, Å	28.4108(7)
V, Å^3	5956.7(2)
space group	*Pbca*
Z	8
λ, Å	0.71073
ρ_{calc}, g/cm^3	1.567
μ, cm^{-1}	128.0
temp, K	296(2)
$R_1(F)^a$	0.0589
$wR_2(Fo^2)^b$	0.0843

[a] $R_1(F) = \sum(|Fo| - |Fc|)/\sum|Fo|$. [b] $wR_2(Fo^2) = [\sum[w(Fo^2 - Fc^2)^2]/\sum w(Fo^2)^2]^{1/2}$ (with $w^{-1} = \sigma^2 Fo^2 + (aP)^2 + bP$, $a = 0.0241$, $b = 10.1921$).

formed. The powder was washed with CH_3OH, EtOH, and Et_2O (yield 35%). IR (cm^{-1}): NPr_4^+ cations, 1481 (s), 1458 (sh), 1441 (sh), 1384 (m), 967 (sh), 845 (w); ν(CC triple bond), 2170 (w); monosubstituted aromatic groups, 1595 (m), 1570 (w), 1520 (w), 760 (m), 695 (m); ν(Mo−S), 475 (w), 467 (w), 385 (vw), 345 (m); ν(Mo═O), 945 (vs); ν(S−S), (520).

^{1}H NMR (DMSO-d_6): aromatic groups, δ 7.80−7.86 (m, 2H); δ 7.30−7.42 (m, 8H); NPr_4^+ cations, δ 2.93 (m, 16 H) (CH_2), δ 1.55 (sextuplet, 16 H) (CH_2), and δ 0.89 (t, 24 H) (CH_3).

^{13}C NMR (DMSO-d_6): NPr_4^+ cations, δ 10.53, 14.76, 59.22 ppm; aromatic groups and ethylenic carbons, δ 120−155 ppm; acetylenic groups, δ 89−92 ppm.

Synthesis of $(NPr_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H(C_2H))]$ 3. $(NH_4)_2[MoO_2S_2]$ (0.456 g, 2 mmol) was dissolved in 20 mL of solution A. After addition of NPr_4Br (1.06 g, 4 mmol) and $C_4(SiMe_3)_2$ (0.400 g, 2 mmol), the solution turned slowly from orange to red. The mixture was stirred at room temperature for 6 h and filtered to isolate the orange-brown precipitate that formed (yield 30%). The precipitate was washed with CH_3OH and Et_2O.

IR (cm^{-1}): NPr_4^+ cations, 1479 (s), 1470 (sh), 1457 (sh), 1383 (w), 966 (sh); 840 (m), 756 (m); ν(CC triple bond), 2068 (m), ν(C═C) 1517 (m); ν(Mo−S), 476 (w), 454 (vw), 423 (vw), 341 (m); ν(Mo═O), 949 (vs); ν(S−S), (517).

^{1}H NMR (CD_3CN): δ 7.40 (s, 1H); δ 3.26 (s, 1H); NPr_4^+ cations, δ 2.92 (m, 16 H) (CH_2), δ 1.56 (sextuplet, 16 H) (CH_2), and δ 0.91 (t, 24 H) (CH_3).

^{13}C NMR (CD_3CN): δ 76.44, 85.38, 122.81, 139.41 ppm; NPr_4^+ cations, δ 10.55, 14.76, 59.25 ppm.

X-ray Structure Determination of 1. Intensity measurements for **1** were carried out on a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector using monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature. An absorption correction was applied using the SADABS program[19] based on the Blessing method.[20] The structure was solved by direct methods followed by Fourier difference syntheses using the SHELXTL package.[19] All atoms except hydrogen atoms were anisotropically refined. Selected crystal data and details of the data collection are given in Table 1. Selected interatomic distances and angles are listed in Table 2. Complete crystallographic details are given in the Supporting Information Section. An ellipsoid representation of the structural framework of **1** is given in Figure 1.

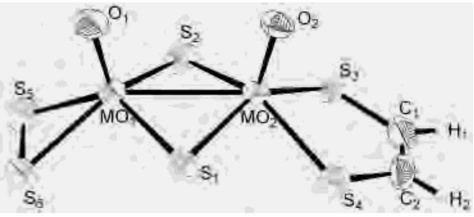

Figure 1. View of the $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2{-}S_2C_2H_2)]^{2-}$ **1** dianion. Displacement ellipsoids are scaled to enclose 30% probability levels (except for hydrogen atoms).

Table 2. Selected Interatomic Distances (Å) for $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]$ **1**

Mo(1)−Mo(2)	2.845(1)		
Mo(1)−O(1)	1.691(5)	Mo(2)−O(2)	1.694(5)
Mo(1)−S(1)	2.312(2)	Mo(2)−S(1)	2.354(2)
Mo(1)−S(2)	2.302(2)	Mo(2)−S(2)	2.345(3)
Mo(1)−S(5)	2.391(3)	Mo(2)−S(3)	2.410(2)
Mo(1)−S(6)	2.405(3)	Mo(2)−S(4)	2.418(2)
S(5)−S(6)	2.063(4)	C(1)−C(2)	1.303(12)

Results

Structural Description of $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]$ 1. The structure consists of an isolated dianion $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]^{2-}$ associated with two NEt_4^+ cations. As shown in Figure 1, the dianion is formed by two pentacoordinated molybdenum (V) atoms. The Mo(1)−Mo(2) distance is quite short (2.845(1) Å) and consistent with a metal−metal bond. The two metal centers are doubly bridged by two sulfido groups, the Mo−S distances are quite different for the two molybdenum atoms: short for Mo(1) (Mo(1)−S(1), 2.312(2) Å; Mo(1)−S(2), 2.303(2) Å), and long for Mo(2) (Mo(2)−S(1), 2.354(2) Å; Mo(2)−S(2), 2.345(3) Å). Such a difference has already been noticed for $[Mo_2(O)(X)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph_2)]^{2-}$ **4** (X = S, O).[9] This apparent distortion of the syn-$[Mo_2(O)_2(\mu\text{-}S)_2]^{2+}$ core is probably due to the presence of two types of terminal ligands attached to the metal centers. Each metal atom is coordinated by a terminal oxygen atom through quite short distances Mo−O, 1.691(5)−1.694(5) Å. The coordination sphere of Mo(1) is completed by a disulfido group (S(5)−S(6), 2.063(4) Å) while Mo(2) is bonded to a dithiolene ligand. The structure of **1** is quite similar to that of $[Mo_2(O)(X)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph_2)]^{2-}$ **4** (X = S, O)[9] except the nature of the dithiolene ligand and the lack of sulfur-oxygen disorder for the apical chalcogenide ligand linked to Mo(2).

ESMS Spectra. The ESMS spectra of $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]$ **1**, $(NPr_4)_2[Mo_2(O)(X)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]$ **2**, and $(NEt_4)_2[Mo_2(O)(X)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph_2)]$ **4** (X = S, O) have been obtained from 10^{-4} mol·L^{-1} solutions of CH_3CN; for $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H(C_2H))]$ **3** the concentration used was 5×10^{-5} mol·L^{-1}. All the results are presented in Figure 2 and Table 3. The formulas for the anions observed were confirmed by the experimental values of *m*/*z* (most abundant isotopic mass) as well as the isotopic profile. For compounds **1**, **2**, and **4**, the presence in solution of two types of complexes was revealed: a complex containing two oxygen atoms in the M═O terminal position, and a complex containing one oxygen atom and one sulfur atom in the same terminal position. In

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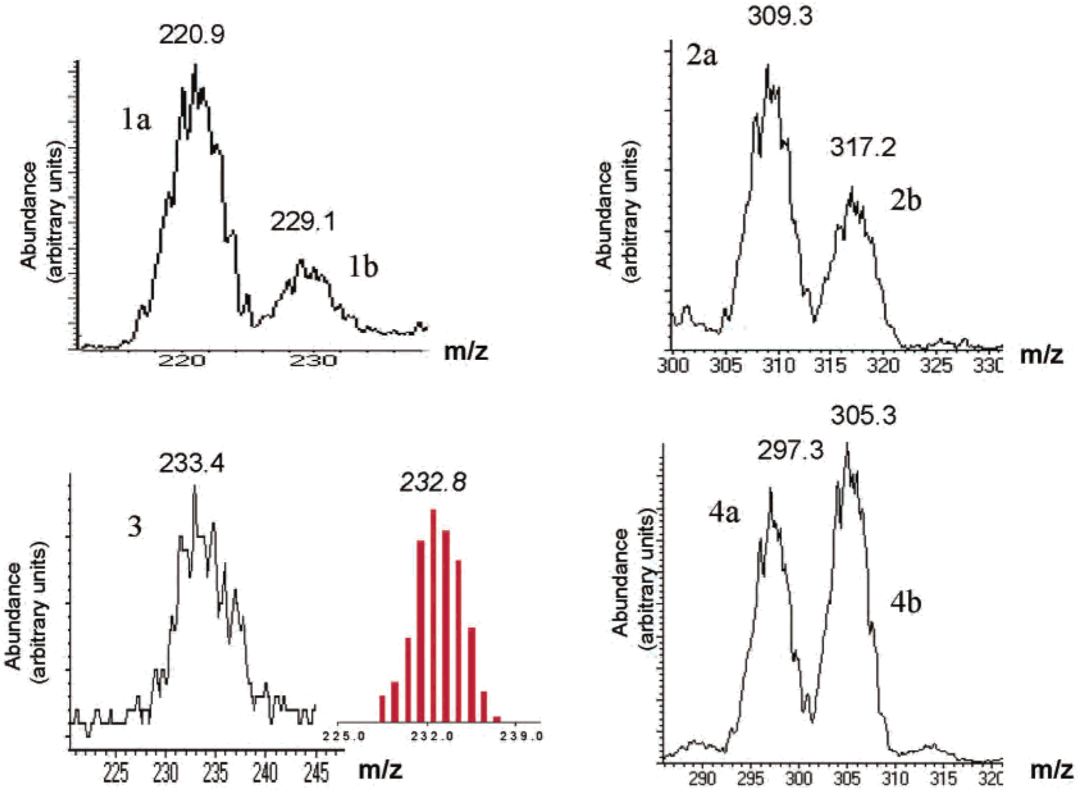

Figure 2. ESMS spectra of: **1a** $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]^{2-}$ and **1b** $[Mo_2(O)(S)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]^{2-}$; **2a** $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]^{2-}$ and **2b** $[Mo_2(O)(S)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]^{2-}$; **3a** $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H(C_2H))]^{2-}$; **4a** $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph_2)]^{2-}$ and **4b** $[Mo_2(O)(S)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph_2)]^{2-}$.

Table 3. Summary of the *m/z* Obtained from ESMS Spectra (most abundant isotopic mass) for **1**, **2**, **3**, and **4**

	complexes	*m/z* experimental	*m/z* theoretical
1	**1a**$[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]^{2-}$	220.9	220.9
	1b$[Mo_2(O)(S)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]^{2-}$	229.1	228.9
2	**2a**$[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]^{2-}$	309.3	308.9
	2b$[Mo_2(O)(S)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]^{2-}$	317.2	316.9
3	**3a**$[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H(C_2H)]^{2-}$	233.4	232.8
	3b$[Mo_2(O)(S)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H(C_2H)]^{2-}$		240.8
4	**4a**$[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph_2)]^{2-}$	297.3	296.9
	4b$[Mo_2(O)(S)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph_2)]^{2-}$	305.3	304.9

each case, however, the relative intensities of the two peaks differ (Figure 2).

It should be noted that relative peak intensities in electrospray mass spectra may not always be directly related to relative concentrations in solution. In fact, electrospray response has been shown to be greatly dependent on the structure of the compounds analyzed.[14] Here, however, we may reasonably assume that the response should be similar as in each case the two compounds are structurally very close. Thus *qualitative* information may be derived from relative peak intensities. In the spectrum of complex **4**, the two dianions $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph_2)]^{2-}$ **4a** (*m/z* 297.3) and $[Mo_2(O)(S)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph_2)]^{2-}$ **4b** (*m/z* 305.3) were observed in quite similar proportions. This was consistent with the X-ray diffraction result which showed a sulfur/oxygen disorder in the terminal Mo-X positions.[9]

Conversely, the mass spectrum of compound **1** showed the presence of one major oxo-dianion $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]^{2-}$ **1a** (*m/z* 220.9) and a small peak at *m/z* 229.1 corresponding to $[Mo_2(O)(S)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]^{2-}$ **1b**, in agreement with the X-ray data which did not reveal any sulfur/oxygen disorder. The abundance of **1b** in the solid state was probably not large enough to be revealed by X-ray methods. As supporting evidence to the minor presence of **1b**, ^{13}C NMR spectra exhibit a little peak at δ 131.53 ppm and a little resonance is observed on the ^1H NMR spectra at δ 6.82 ppm, attributed to the ethylenic carbons and the ethylenic protons, respectively, as expected for **1b**.

Therefore, electrospray mass spectrometry proved in these two cases to be a reliable and accurate method of characterization which was applied with confidence to compounds **2** and **3**, for which no crystals were available. For compound $[Mo_2(O)(X)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]^{2-}$ (X = O or S) **2**, two peaks are also observed at *m/z* 309.3 for $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]^{2-}$ **2a**, and at *m/z* 317.2 for $[Mo_2(O)(S)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]^{2-}$ **2b**. In contrast, only one peak is obtained for **3** at *m/z* 233.5 corresponding to the oxo-dianion $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H(C_2H))]^{2-}$ (see Figure 2 and Table 3).

Discussion. Three new complexes **1**, **2**, and **3** (see Figure 3) containing dithiolene ligands have been obtained by addition of alkynes to $MoO_2S_2^{2-}$ in a MeOH/NH$_3$ mixture. This study confirmed the preliminary result obtained with compound **4**.[9]

In **1** and **3**, the parent SiMe$_3$ groups have been replaced by protons, this substitution resulting from the basic hydrolysis of the C−Si bond in the CH_3OH/NH_3 mixture used. In **3** and **4**, one alkyne group remains unreacted, meaning it is not electrophilic enough to form another dithiolene ligand.

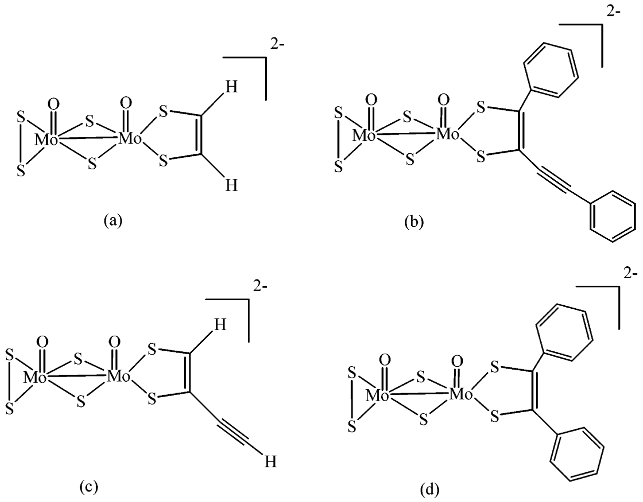

Figure 3. Representation of the dianions: (a) $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]^{2-}$ **1a**, (b) $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]^{2-}$ **2a**, (c) $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H(C_2H))]^{2-}$ **3a**, (d) $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph_2)]^{2-}$ **4a**.

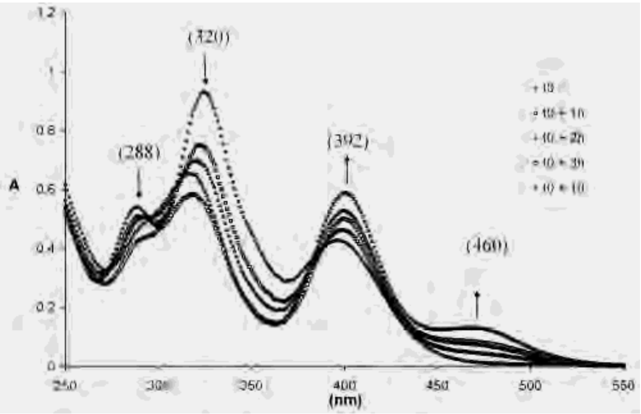

Figure 4. UV−Visible spectra of $MoO_2S_2^{2-}$ ($c = 10^{-3}$ M) in a CH_3OH/NH_3 solution. (a) $MoO_2S_2^{2-}$, λ nm, (ϵ L·mol^{-1}·cm^{-1}): 288 (3000), 319 (6000), 394 (3000). (b) $MoOS_3^{2-}$, λ nm, (ϵ L·mol^{-1}·cm^{-1}): 270(−), 319 (6600), 392 (8700), 460 (2300). (c) MoO_3S^{2-}, λ nm, (ϵ L·mol^{-1}·cm^{-1}): 288 (−), 392 (−).

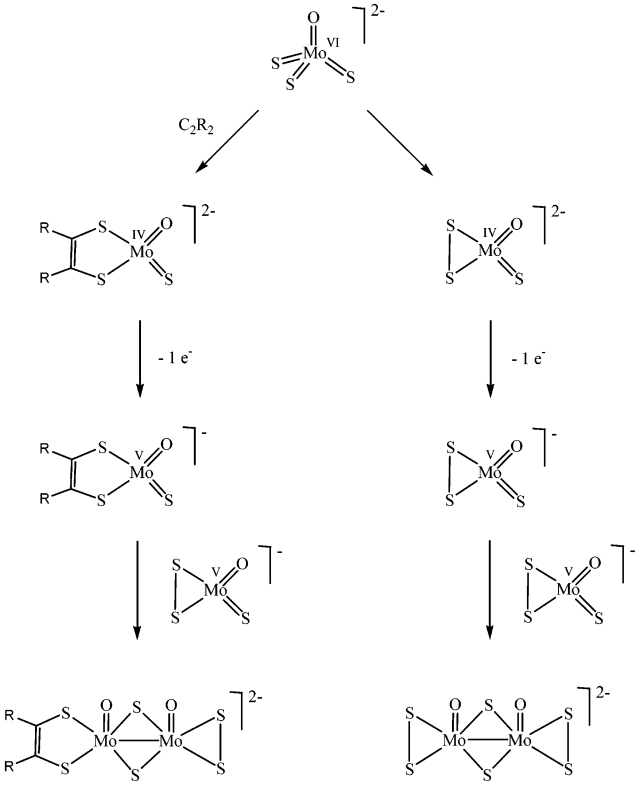

Figure 5. Reaction scheme illustrating the formation of the dianions $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)_2]^{2-}$ or $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2R_2)]^{2-}$.

The reaction of $MoO_2S_2^{2-}$ with diynes has been initially studied to increase the nuclearity of the thiometalate by formation of bis(dithiolene) complexes. After the formation of the first dithiolene ligand, the second alkyne group of the diynes does not seem electrophilic enough to react with a second molecule of $MoO_2S_2^{2-}$, preventing the formation of a bis(dithiolene) ligand.

The originality of **1**, **2**, **3**, and **4** is the presence of two different ligands in the coordination sphere of the metals, a terminal disulfido ligand, and a dithiolene ligand, respectively. For these complexes, the reactions yields are not very high because in addition to the expected main products, the formation of orange crystals of the dianion $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)_2]^{2-}$ (identified by X-ray diffraction study) was systematically observed in the filtrate. The dianion $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)_2]^{2-}$ has already been prepared by several methods.[21] In all complexes, the S/Mo ratio is around three, inconsistent with the chemical composition of the starting material $MoO_2S_2^{2-}$. A study by UV−Visible spectroscopy of a solution of the starting material $MoO_2S_2^{2-}$ along 24 h confirmed this point (see Figure 4). The two absorption bands at 288 and 320 nm decrease while that at 392 nm increases and a new band appears at 460 nm, characteristic of $MoOS_3^{2-}$. $MoO_2S_2^{2-}$ and $MoOS_3^{2-}$ both have absorptions at about 392 nm, but the associated molar extinction coefficients are different, 3000 and 8700 L·mol^{-1} cm^{-1}, respectively, in MeOH/NH_3, justifying the observed increase of absorption at 392 nm. All these results are consistent with the conversion of $MoO_2S_2^{2-}$ initially present in solution into equimolar quantities of $MoOS_3^{2-}$ and MoO_3S^{2-}:

$$2\,MoO_2S_2^{\,2-} \rightarrow MoO_3S^{2-} + MoOS_3^{\,2-}$$

This conversion, due to the poor stability of $MoO_2S_2^{2-}$ in MeOH/CH_3OH solution, has been previously observed by Müller and co-workers in water.[22] A direct evidence of the formation of MoO_3S^{2-} is not possible because it was never isolated as a solid, and so far its UV−visible spectrum in a CH_3OH/NH_3 solution remains unknown. Nevertheless, the UV−visible spectrum of MoO_3S^{2-} in water exhibits two absorptions located at 288 and 392 nm, but no values of molecular extinction coefficients are available.[22] The decrease of the band at about 320 nm indicates the concentration of $MoO_2S_2^{2-}$ is decreased (ϵ: 6000 L·mol^{-1} cm^{-1} in MeOH/

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[21] (a) Müller, A.; Rittner, W.; Neumann, A.; Sharma, R. C. *Z. Anorg. Allg. Chem.* **1981**, *472*, 69. (b) Rittner, W.; Müller, A.; Neumann, A.; Bäther, W.; Sharma, R. C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 530. (a) Müller, A.; Krickemeyer, E.; Reinsch, U. *Z. Anorg. Allg. Chem.* **1980**, *470*, 35.

[22] Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934.

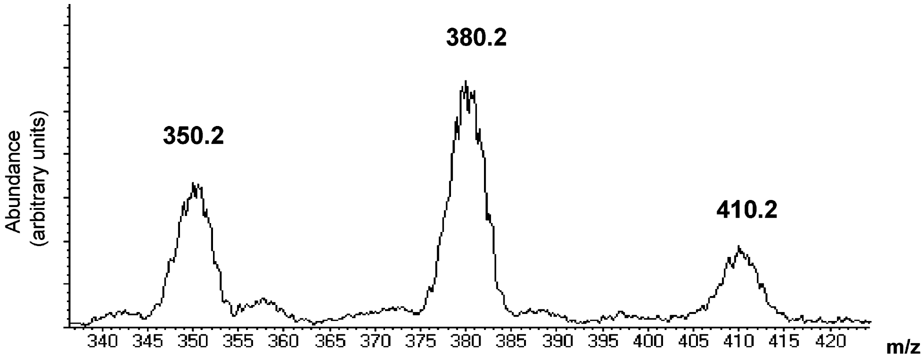

Figure 6. ESMS spectrum obtained after addition of DMA to $(NPr_4)_2[Mo_2(X)(O)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]$ (X = S, O) in CH_3CN solution (10^{-5} mol·L^{-1}) (*m/z* 350.2, $[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2Me)_2)_2]^{2-}$; *m/z* 380.2, $[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2Me)_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]^{2-}$; and *m/z* 410.2, $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2C_2Ph(C_2Ph))_2]^{2-}$).

Table 4. Summary of the *m/z* of the Different Species Obtained after Addition of DMA to $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2R_2)]^{2-}$

starting materials	complexes observed on the ESMS spectra	*m/z* experimental	*m/z* theoritical
1 $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]^{2-}$	$[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2Me)_2)(\eta^2\text{-}S_2C_2H_2)]^{2-}$	292.1	291.9
	$[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2Me)_2)_2]^{2-}$	350.4	349.9
	$[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2C_2H_2)_2]^{2-}$	234.1	234.2
4 $[Mo_2(O)(X)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph_2)]^{2-}$	$[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2Me)_2)(\eta^2\text{-}S_2C_2Ph_2)]^{2-}$	368.2	367.9
	$[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2Me)_2)_2]^{2-}$	348.8	349.9
	$[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2C_2Ph_2)_2]^{2-}$	386.0	385.9
2 $[Mo_2(O)(X)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]^{2-}$	$[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2Me)_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]^{2-}$	380.2	379.9
	$[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2Me)_2)_2]^{2-}$	350.2	349.9
	$[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2C_2Ph(C_2Ph))_2]^{2-}$	410.2	409.9
3 $Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H(C_2H))]^{2-}$	$[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2Me)_2)(\eta^2\text{-}S_2C_2H(C_2H))]^{2-}$	258.0	258.2
	$[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2C_2H(C_2H))_2]^{2-}$	304.3	304.2
	$[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2Me)_2)_2]^{2-}$	350.9	349.9

NH_3) while $MoOS_3^{2-}$ (ε: 6600 L·mol^{-1} cm^{-1} in MeOH/NH_3) is simultaneously formed together with another compound which does not absorb in this region, which is the case for MoO_3S^{2-}. Therefore the formation of MoO_3S^{2-} is naturally suspected, and its presence contributes to explaining the low yields of the reactions.

The reaction scheme given in Figure 5 is a tentative justification of the simultaneous formations of $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2R_2)]^{2-}$ (**1**, **2**, **3**, and **4**) and $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)_2]^{2-}$. The first step is either the reducing addition of alkyne to $MoOS_3^{2-}$ to form a mononuclear molybdenum (IV) species with a dithiolene ligand or the formation via an internal molecular redox process of a mononuclear entity of molybdenum (IV) containing a disulfido ligand. These two species could be oxidized into mononuclear species of molybdenum (V) by an external oxidant (not identified), (see Figure 5).

Then, two pathways could be involved (see Figure 5) in the formation of those species: (i) the reaction of $[Mo(O)(S)(\eta^2\text{-}S_2)]^-$ with $[Mo(O)(S)(\eta^2\text{-}S_2C_2R_2)]^-$ to produce the species of general formula $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2R_2)]^{2-}$, and (ii) the formation of $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)_2]^{2-}$ by the condensation of two $[Mo(O)(S)(\eta^2\text{-}S_2)]^-$.

Study of the Reactivity of the Mixed Species: $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2R_2)]^{2-}$. We were interested in the possibility of grafting different alkynes on a thiometallic core. Stiefel and co-workers showed that the disulfido groups in $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)_2]^{2-}$ reacted easily with a strong electrophilic alkyne such as DMA (dicarbomethoxyacetylene) to form the $[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2Me)_2)_2]^{2-}$ complex.[23] In this example, DMA is not added on the S−S bond of the disulfido group but is inserted into the Mo−S bond to form a vinyl disulfido ligand. Vinyl disulfido ligands are well-known to give dithiolene ligand in the presence of an excess of sulfur or on heating.[6] The mixed species **1**, **2**, **3**, and **4** contain a remaining nucleophilic terminal disulfido ligand. The addition of DMA toward these species has been checked and these reactions were followed by ESMS. In Figure 6, an example spectrum obtained after addition of DMA to $(NPr_4)_2[Mo_2(O)(X)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]$ (X = S, O) **2** is depicted. The main peak, (*m/z* 380.2), is related to the mixed species $[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2Me)_2)(\eta^2\text{-}S_2C_2Ph(C_2Ph))]^{2-}$, resulting from the addition of DMA to the terminal disulfido ligand.

Surprisingly, two other peaks are observed (*m/z* 350.2 and *m/z* 410.2) attributed respectively to the symmetric species $[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2Me)_2)_2]^{2-}$ and $[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2Ph(C_2Ph))_2]^{2-}$. The mechanisms involved in the formation of these unexpected rearranged species remain unsolved. In Table 4, a summary of the results obtained during the addition of DMA to complexes **1**, **2**, and **3** is presented illustrating the same behavior: besides the main peak, due to the asymmetric species, two peaks corresponding to the symmetric species are also observed.

Summary

A novel series of complexes of molybdenum (V) containing different ligands has been obtained by addition of alkynes

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(23) Halbert, T. R.; Pan, W.-H; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476.

to tetraoxothiometalates. This strategy of synthesis is a good way to provide complexes containing dithiolene ligands. To get mononuclear complexes of molybdenum with dithiolene ligand, which are good candidates to simulate enzyme active sites, Holm et al. chose also this strategy:[11] addition of DPA to $MoO_2S_2^{2-}$ in the presence of a chelating ligand to avoid the condensation and the formation of dinuclear complexes.

These complexes present a remaining active nucleophilic site which can been used to prepare dinuclear complexes of molybdenum (V) containing two different ligands: a dithiolene ligand and a vinyl-disulfido ligand.

ESMS has been shown to be an excellent method to characterize this type of complex. Application of this method[24] to inorganic species is quite recent. From those reactions it is not always easy to obtain crystals because mixtures quite systematically take place. Thus, ESMS provides an excellent way to identify the different species present in solutions. To broaden our understanding and use of electrospray mass spectrometry, research on fragmentation processes has been undertaken.

Supporting Information Available: X-ray crystallographic file in CIF format for the structure determination of $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2H_2)]$. This material is available free of charge via the Internet at htpp://pubs.acs.org.

IC0342907

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