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Notes

Addition of Diphenylacetylene to $MoO_2S_2^{2-}$ in NH_3−CH_3OH Medium

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Introduction

The reaction between electrophiles and tetraoxothiometalates $(MO_{4-n}S_n)^{x-}$ ($n = 1-4$) is a powerful method for preparing sulfur-rich derivatives of transition metals. With Fe^{2+}, Co^{2+}, Ni^{2+}, Pt^{2+},[1] Pd^{2+},[2] Cu^+, and Ag^+,[3] the electrophile−nucleophile interaction is quite simple, consisting of the direct addition of the metal to VS_4^{3-}, MoS_4^{2-}, or WS_4^{2-}. In the resulting clusters, tetrathiometalates act as versatile ligands of the metal centers, leading to a large variety of molecular structures. With protons, the reaction is more complex since the protonation is systematically accompanied with redox processes involving the metal center (Mo, W) and/or the ligand.[4] Recently, we reported on the reaction of CS_2 with MoS_4^{2-}, which led to the concomitant formation of $[Mo(CS_3)_4]^{3-}$ and $[Mo_2(S_2)_2(CS_3)_4]^{2-}$.[5] On the basis of the works of E. I. Stiefel,[6] an internal electron transfer has been postulated to explain the simultaneous formation of the two complexes in the reaction mixture. T. B. Rauchfuss[7] reported on the addition of alkynes to ReS_4^- which through a four-electron reduction led to $[NEt_4]_4\{Re_4S_{12}[S_2C_2(TMS)_2]_2\}$ (TMS: trimethylsilyl), a compound containing rhenium sulfide, disulfido groups, and dithiolene ligands.

To complete our understanding of the reactions between electrophiles and tetraoxothiometalates, we have chosen to react alkynes with MoS_4^{2-} and $MoO_2S_2^{2-}$. On the basis of the results previously obtained with the system MoS_4^{2-}/CS_2, similar reaction conditions have been used with diphenylacetylene (DPA) since a reaction involving an intramolecular redox process was expected. Surprisingly no reaction was observed under these conditions, MoS_4^{2-} was revealed to be a too poor nucleophile to react with DPA. As $MoO_2S_2^{2-}$ reacts with DPA, we focused on this reaction.

Table 1. Crystallographic Data for $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2(C_6H_5)_2)]$

empirical formula	$C_{60}H_{100}N_4O_3S_{13}Mo_4$
FW	1725.98
a, Å	10.7075(2)
b, Å	15.1073(4)
c, Å	23.9746(8)
V, Å^3	3878.2(2)
space group	$P2_12_12_1$
Z	2
λ, Å	0.71073
ρ_{calc}, g cm^{-3}	1.478
μ, cm^{-1}	102.3
temp, K	296(2)
$R_1(F)^a$	0.0849
$wR_2(Fo^2)^b$	0.1473

^{a} $R_1(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $wR_2(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$; with $w^{-1} = \sigma^2F_o^2 + (aP)^2 + bP$, $a = 0.0668$ and $b = 0$.

Experimental Section

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk techniques. CH_3OH was distilled from CaH_2 before use. The NH_3−CH_3OH mixture was prepared by bubbling NH_3 in dried CH_3OH to obtain a concentration of ca. 1.3 mol L^{-1} (solution A). The $(NH_4)_2[MoO_2S_2]$ was prepared according to the reported standard procedure.[8] Elemental analyses of solids were performed by the Service d'Analyses du CNRS, Vernaison (France). IR spectra (KBr pellets) were recorded on an FTIR Nicolet Magna-550 spectrophotometer. ^{13}C NMR spectra were recorded on a Brucker AC300 operating at 75.47 MHz with Me_4Si as internal standard.

Synthesis of $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2(C_6H_5)_2)]$. The $(NH_4)_2[MoO_2S_2]$ (0.114 g, 0.5 mmol) was dissolved in 20 mL of solution A. After addition of NEt_4Br (0.420 g, 2 mmol) and $(C_6H_5)_2C_2$ (0.356 g, 2 mmol), the resulting yellow−orange solution was stirred for 7 days at room temperature and then filtered. After standing for several days at room temperature, the solution deposited red needles (yield 10%). Anal. Calcd for $C_{30}H_{50}O_{1,5}N_2S_{6,5}Mo_2$: C, 41.76; H, 5.80; N, 3.24; S, 24.13; Mo, 22.20. Found: C, 41.38; H, 5.89; N, 3.35; S, 23.73; Mo, 21.92. IR (cm^{-1}): NEt_4^+ cations, 1483 (s), 1457 (s), 1390 (m), 1175 (m), 1004 (w), 784 (w); monosubstitued aromatic groups, 755 (m), 706 (m); ν(Mo−S), 466 (w), 425 (w), 389 (w), 356 (m); ν(Mo═O), 940 (vs); ν(S−S), 520 (s). ^{13}C NMR (DMSO-d_6): δ 143.41, 143.13, 141.33, 137.79, 129.53, 129.49, 127.44, 127.37, 125.64, 125.46, 51.29 (t), and 6.98. ^1H NMR (DMSO-d_6): aromatic groups of the DPA, δ 7.08−7.15 (m − 10 H); NEt_4^+ cations, δ 3.01 (q − 16 H) (CH_2) and δ 1.04 (tt − 24 H) (CH_3).

Crystallographic Studies. Intensity measurements were carried out on a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector using monochromatized Mo Kα ($\lambda = 0.71073$ Å). Selected crystal data and details of the data collection are given in Table 1.

An absorption correction was applied using the SADABS program[9] based on the Blessing method.[10] The structure was solved by direct methods followed by Fourier difference syntheses, using the SHELXTL package.[9] All atoms except hydrogen, O7, and S7 atoms were anisotropically refined. The final reliability factors converged to $R_1 =$

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(1) Müller, A.; Diemann, E.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934−955.
(2) Potvin, C.; Manoli, J. M.; Sécheresse, F. *Inorg. Chim. Acta* **1990**, *168*, 173−177.
(3) Hou, H. W.; Xin, X. Q.; Shi, S. *Coord. Chem. Rev.* **1996**, *153*, 25−56.
(4) Sécheresse, F.; Cadot, E.; Simonnet-Jégat, C. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: Weinheim, 1999.
(5) Simonnet-Jégat, C.; Cadusseau, E.; Dessapt, R.; Sécheresse, F. *Inorg. Chem.* **1999**, *38*, 2335−2339.
(6) McConnachie, C. A.; Stiefel, E. I. *Inorg. Chem.* **1999**, *38*, 964−972.
(7) Goodman, J. T.; Rauchfuss, T. B. *Inorg. Chem.* **1998**, *37*, 5040−5041.
(8) McDonald, J. W.; Friesen, G. D.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205−210.
(9) (a) Sheldrick, G. M. SADABS, a program for the Siemens Area Detector Absorption correction, **1994**. (b) Sheldrick, G. M. SHELXTL, Siemens Analytical X-ray Instruments, **1994**.
(10) Blessing, R. *Acta Cryst.* **1995**, *A51*, 33.

10.1021/ic001150d CCC: $20.00

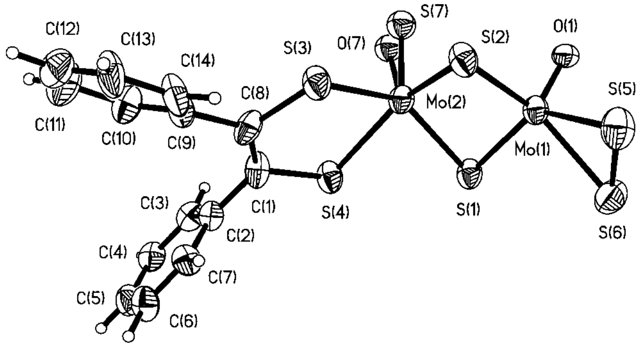

Figure 1. View of the $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2(C_6H_5)_2)]^{2-}$ anion. Displacement ellipsoids are scaled to enclose 30% probability levels; S(7) and O(7), 50% occupancy.

Table 2. Selected Bond Lengths (Å) for $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2(C_6H_5)_2)]$

Mo(1)−Mo(2)	2.843(2)	Mo(2)−S(1)	2.334(4)
Mo(1)−O(1)	1.678(10)	Mo(2)−S(2)	2.348(4)
Mo(1)−S(1)	2.310(4)	Mo(2)−S(3)	2.382(5)
Mo(1)−S(2)	2.296(5)	Mo(2)−S(4)	2.414(5)
Mo(1)−S(5)	2.397(5)	Mo(2)−S(7)	2.080(13)
Mo(1)−S(6)	2.384(5)		

0.0849 and $wR_2 = 0.1473$. Selected interatomic distances and angles are listed in Table 2.

Results and Discussion

The structure consists of isolated $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2(C_6H_5)_2)]^{2-}$ anions and tetraethylammonium cations. The geometry of the anion is given in Figure 1. The dianion is formed by two pentacoordinated molybdenum atoms; the Mo(1)−Mo(2) distance is quite short (2.843(2) Å).

This distance is in the range of that observed for a metal−metal bond in compounds which present the similar $\{Mo_2(O)_2(\mu\text{-}S)_2\}$ central core formed of two Mo^V ions, as in the recently published $[NEt_4]_2[Mo_2(O)_2(\mu\text{-}S)_2(CS_4)(CS_3)]$[11] complex (Mo−Mo: 2.835(2) Å). The two metal centers are doubly bridged by two sulfido groups. The Mo−S distances in the equatorial plane are different for Mo(1), 2.296(5)−2.310(4) and 2.384(5)−2.397(5) Å, and for Mo(2), 2.334(4)−2.348(4) and 2.382(5)−2.414(5) Å. The Mo−S bonds of the sulfido bridging atoms are always shorter than the Mo−S bonds of the organic ligands. Such features were already mentioned by Coucouvanis et al.[11] The coordination sphere of Mo(1) is completed by a disulfido group S_2^{2-} and a terminal oxygen atom. The S(5)−S(6) distance (2.061(8) Å) is usual for terminal disulfido groups and is longer than bridging disulfido groups, as in $(NBu_4)_2[Mo_2(\eta^2\text{-}CS_3)_4(\mu\text{-}(S_2))_2]$[5] (2.005(2) Å). Mo(2) is coordinated to two bridging sulfides and a dithiolene ligand $[S_2C_2(C_6H_5)_2]^{2-}$ located in the equatorial plane. A sulfur−oxygen disorder is observed in the terminal fifth position of Mo(2). The terminal Mo−O distances are 1.70(3) Å for Mo(2)−O(7) and 1.68(1) Å for Mo(1)−O(1); the terminal Mo−S distance is 2.08(1) Å. These values are in the range expected for terminal bonds in such types of compounds: in $[Mo_2(S)_2(\mu\text{-}S)_2(CS_4)_2]^{2-}$, the Mo−S distances are 2.10(5) Å[11], and in $[Mo_2(O)_2(\mu\text{-}S)_2(CS_4)(CS_3)]^{2-}$, the Mo−O distances are 1.672(13)−1.684(9) Å.[11] Numerous Mo^V complexes containing the $\{Mo_2(O)_2(\mu\text{-}S)_2\}$ core were reported by Shibahara,[12] but never with a dithiolene ligand and a terminal disulfido group.

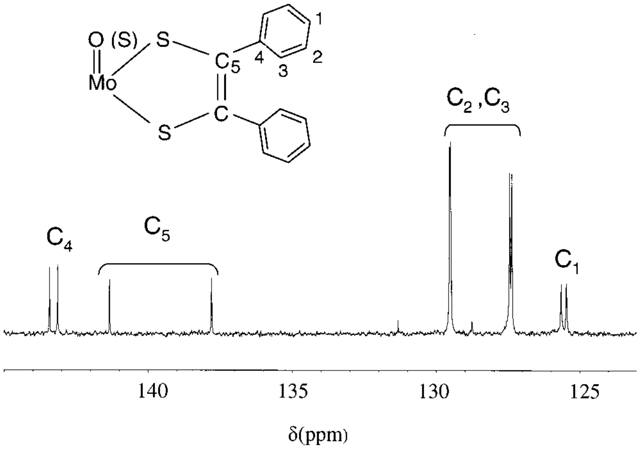

Figure 2. ^{13}C NMR spectra showing the splittings for the carbon atoms of the dithiolene ligands related to the S/O disorder in the coordination sphere of Mo(2).

The ^{13}C NMR spectrum contains eight lines in the range 143.41−125.46 ppm attributed to the carbon atoms of the aromatic groups, and two single lines at 141.33 and 137.79 ppm attributed to alkene carbon atoms. As the $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2(C_6H_5)_2)]^{2-}$ anion has C_s symmetry, only four lines corresponding to the twelve carbon atoms of the two equivalent aromatic groups, and one line corresponding to the two alkene carbon atoms are expected. Because of the sulfur−oxygen disorder in the terminal Mo = X (X = O, S) core, the two molecules $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2(C_6H_5)_2)]^{2-}$ and $[Mo_2(O)(S)(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2(C_6H_5)_2)]^{2-}$ are present in solution, which can explain the 2 × 5 lines observed in the range 143.41−125.46 ppm.

An attribution of the different features of the ^{13}C spectra is given in Figure 2. It is interesting to note that the presence of a sulfur or oxygen ligand in the coordination sphere of the Mo atoms introduces a gap of 3.53 ppm between the two chemical shifts of the carbon atoms of the C=C bonds. This effect is less sensitive for the carbon atoms of the aromatic groups.

The most related compound described in the literature is $[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2CH_3)_2)_2]^{2-}$ isolated by Stiefel and coworkers.[13] In Stiefel's compound, the two alkynes have been inserted in the Mo−S bonds of the terminal disulfides (rather than into the S−S bonds) to form five-membered metalla-2,3-dithiacyclopent-4-ene rings. This product was isolated through the reaction of $[Mo_2(O)_2(\mu\text{-}S)_2(S_2)_2]^{2-}$ with dimethyl-acetylene-dicarboxylate (DMA) in CH_3CN. Here, the title compound, obtained from a methanol ammonia solution of $MoO_2S_2^{2-}$ with an excess of diphenylacetylene, involves a dithiolene ligand but not a vinyl disulfide ligand. The isomerization of vinyl disulfide into a dithiolene is reported to be thermally or S catalyzed.[14] By using $[Mo_2(O)_2(\mu\text{-}S)_2(S_2)(S_4)]^{2-}$ as starting material instead of $[Mo_2(O)_2(\mu\text{-}S)_2(S_2)_2]^{2-}$, $[Mo_2(O)_2(\mu\text{-}S)_2(S_2C_2(CO_2CH_3)_2)_2]^{2-}$ involving two dithiolene ligands is obtained.[14] In this example, it is assumed that sufficient amounts of dissociated sulfur are present in solution to catalyze the so-called vinyl disulfide isomerization. During the formation of $[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2(C_6H_5)_2)]^{2-}$, this type of isomerization can also be postulated as represented in Figure 3. By reacting $[Mo_2(O)_2(\mu\text{-}S)_2(S_2)_2]^{2-}$ with diphenylacetylene no reaction was observed, which confirmed that DMA is much more electrophilic than

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(11) Coucouvanis, D.; Draganjac, M. E.; Koo, S. M.; Toupadakis, A.; Hadjikyriacou, A. I. *Inorg. Chem.* **1992**, *31*, 1186−1196.

(12) Shibahara, T. *Coord. Chem. Rev.* **1993**, *123*, 73−147.

(13) Halbert, T. R.; Pan, W. H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476−5477.

(14) Coucouvanis, D. *Adv. Inorg. Chem.* **1997**, *45*, 1−73.

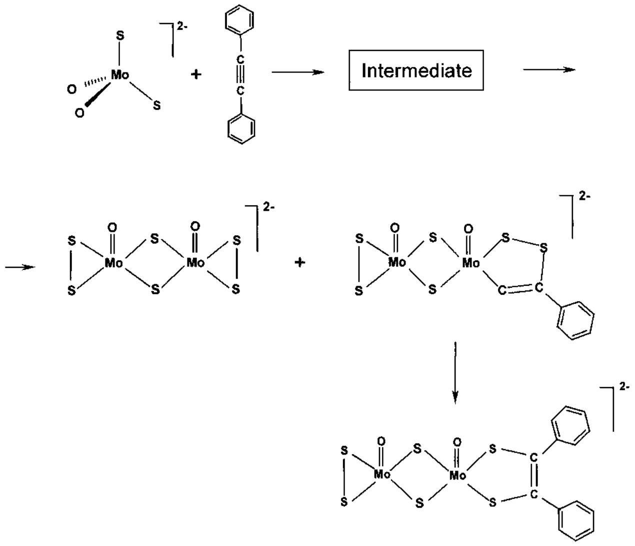

Figure 3. Reaction scheme illustrating the reaction of DPA with $MoO_2S_2^{2-}$.

DPA. Coucouvanis[14] showed that both disulfido and terminal Mo=S groups in thiometalates are nucleophilic to undergo a DMA attack; with $[Mo_2(S)_2(\mu\text{-}S)_2(S_2)_2]^{2-}$ the reaction proceeded until all sulfido groups, except bridging ligands, were converted into dithiolene ligands to yield $[Mo_2(\mu\text{-}S)_2(S_2C_2(CO_2CH_3)_2)_4]^{2-}$.[14] All of these observations suggest that DPA, in contrast to DMA, is not electrophilic enough to react with terminal disulfide groups. With $MoO_2S_2^{2-}$, the reaction with alkynes can exclusively occur through the Mo−S groups. The formation of $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2(C_6H_5)_2)]$ necessitates the reduction of Mo^{VI} into Mo^{V} and the formation of disulfido and dithiolene ligands. Since a terminal disulfido group is present in the final compound, but not in the starting oxothiometalate, it can be assumed that an intermediate probably exists in solution which could contain both terminal disulfido and terminal sulfido groups. The terminal disulfido ligand present in $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2(C_6H_5)_2)]$ did not react with DPA even if a large excess of alkyne was used or if the solution was heated at 50 °C. Besides $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2(C_6H_5)_2)]$, the formation of red crystals of $[Mo_2(O)_2(\mu\text{-}S)_2(S_2)_2]^{2-}$ was systematically observed (characterized by an X-ray diffraction study). The presence in solution of two sulfur-rich dinuclear compounds explains the low yield of the reaction. $[Mo_2(O)_2(\mu\text{-}S)_2(S_2)_2]^{2-}$ is not the postulated intermediate since it did not react with DPA in this medium.

The synthesis of $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2(C_6H_5)_2)]$ and, in particular, the presence of both terminal disulfido and dithiolene ligand represents an interesting problem from a mechanistic point of view.

Supporting Information Available: X-ray crystallographic file in CIF format for the structure determination of $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}S_2)(\eta^2\text{-}S_2C_2(C_6H_5)_2)]$. This material is available free of charge via the Internet at htpp://pubs.acs.org.

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