Inorg. Chem. **2001,** *40,* 1391−1393

Notes

Synthesis and Characterization of a Tetranuclear Cyclopentadienyl Molybdenum Compound with a μ_4-Sulfido Ligand

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Received September 14, 2000

Introduction

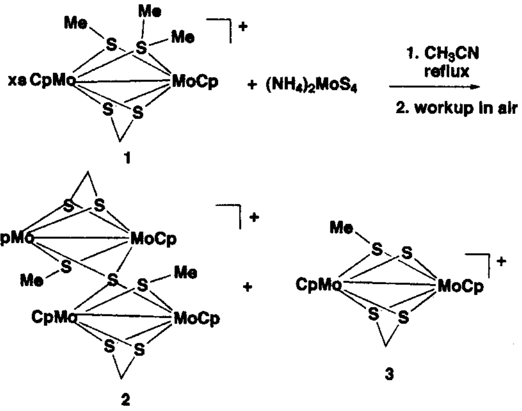
We have recently prepared a cationic dinuclear molybdenum complex with a bridging thioether ligand $[(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]OTf$, **1**, and have shown that the thioether bridge dissociates in refluxing acetonitrile solution.[1] The resulting coordinatively unsaturated (or solvent-stabilized) intermediate shows limited stability under the thermal conditions employed and has not been successfully isolated. Nevertheless, thermal reactions of **1** in the presence of either four- or two-electron donor molecules have been used to synthesize dinuclear complexes with new bridging or terminal ligands, respectively.[1,2]

During the course of this work we began to explore the reactions of **1** with potential bidentate bridging reagents in order to synthesize polynuclear complexes. For example, we wondered whether the reaction of 2 equiv of **1** with $(NH_4)_2MoS_4$ might promote formation of a novel η^1,η^1-thiomolybdate bridge, giving an extended array of molybdenum ions in a sulfur-rich environment. In most cases $[MoS_4]^{2-}$ undergoes bidentate coordination to unsaturated metal centers.[3] However, other coordination modes have been reported, and the tetrathiometalate anions have been used as ligands in the construction of polynuclear metal sulfide complexes.[3−5] There are also previous examples of the reactions of MS_4^{2-} (M = Mo, W) with metal complexes to provide disulfido or polysulfido ligands.[6,7] In the reaction reported here, $[MoS_4]^{2-}$ serves as a sulfide donor to form a new type of tetranuclear product.

Results and Discussion

The reaction of a stoichiometric excess of **1** (1.5−2 equiv) with the tetrathiomolybdate anion was carried out in refluxing acetonitrile under nitrogen, and the resulting products were recrystallized in air. The reaction was found to proceed as shown in Scheme 1 to ultimately form a new tetranuclear complex with the formula $\{[(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)]_2(\mu_4\text{-}S)\}OTf$, **2**, and the known quadruply bridged dinuclear cation **3**.[8] We have confirmed that the reaction of **1** with sodium sulfide in refluxing acetonitrile with a similar workup procedure also leads to the formation of **2**, supporting our suggestion that the tetrathiomolybdate anion plays the role of a sulfide donor in this reaction. The tetranuclear product **2** is not formed when **1** is refluxed in acetonitrile in the absence of an external sulfide source.

Scheme 1



Single crystals of the products were obtained by slow diffusion of hexanes into a dichloromethane solution. An X-ray diffraction study established that the crystal contains both products **2** and **3** as cocrystallized triflate salts. The cation of **2** consists of two $[(CpMo)_2(S_2CH_2)(SMe)]$ units bridged by a single μ_4-sulfido ligand. A perspective drawing of the cation is shown in Figure 1, selected bond distances and angles are given in Table 1, and some crystallographic data of **2**/**3** are listed in Table 2. The μ_4-sulfido ligand shows approximate tetrahedral coordination to the four molybdenum ions. The dihedral angle between the Mo−Mo vectors in the two dinuclear units is 96.5°. For the Mo1−Mo2 dimer in **2**, the average Mo−S1 distance is 2.419 (2) Å, and for the second dimer in **2** the average Mo−S1 distance is 2.442 (3) Å. Both distances are significantly longer than those for μ_2-sulfido ligands, which average about 2.31 Å in the dinuclear molybdenum structures.[9] However, other distances and angles within the dinuclear units of **2**, including the Mo−Mo distances and the Mo−S (thiolate) distances, are similar to the values found in related dinuclear structures. As mentioned above, **2** was cocrystallized with the previously characterized salt $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_3)]$ [OTf], **3**. The structural parameters of the cation of **3** were found to be very similar to those reported previously.[8]

Other examples of tetranuclear complexes with μ_4-S ligands have been reported. For example, complexes with the formula

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(1) Gabay, J.; Dietz, S.; Bernatis, P.; Rakowski DuBois, M. *Organometallics* **1993**, *12*, 3630−3635.

(2) Tucker, D. S.; Dietz, S.; Parker, K. G.; Carperos, V.; Gabay, J.; Noll, B.; Rakowski DuBois, M. *Organometallics* **1995**, *14*, 4325−4333.

(3) Coucouvanis, D. *Adv. Inorg. Chem.* **1998**, *45*, 1−74.

(4) (a) Secheresse, F.; Salis, M.; Potvin, C.; Manoli, J. M. *Inorg. Chim. Acta* **1986**, *114*, L19. (b) Cleggg, W.; Garner, C. D.; Nicholson, J. R. *Acta Crystallogr., Sect. C.* **1983**, *39*, 552.

(5) Massa, M. A.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1991**, *30*, 4667−4669.

(6) Mizobe, Y.; Hosomizu, M.; Kubota, Y.; Hidai, M. *J. Organomet. Chem.* **1996**, *507*, 179.

(7) Umakoshi, K.; Sasaki, Y. *Inorg. Chem.* **1997**, *36*, 4296−4297.

(8) Casewit, C. J.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 119−129.

(9) (a) Miller, W. K.; Haltiwanger, R. C.; Van Derveer, M. C.; Rakowski DuBois, M. *Inorg. Chem.* **1983**, *22*, 2973−2979. (b) Kaul, B. B.; Noll, B. C.; Renshaw, S.; Rakowski DuBois, M. *Organometallics* **1997**, *16*, 1604−1611.

10.1021/ic001043j CCC: $20.00

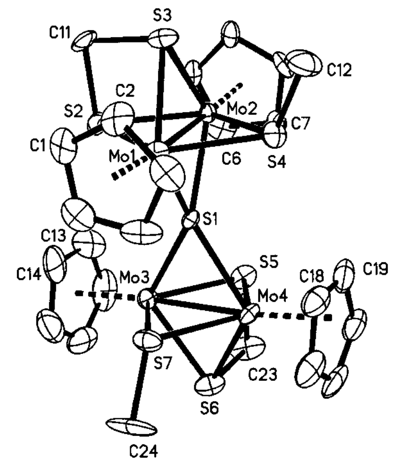

Figure 1. Perspective drawing (at 50% probability level) and numbering scheme for the cation $\{[(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)]_2(\mu_4\text{-}S)\}^+$, **2**.

Table 1. Selected Bond Distances and Bond Angles for $\{[C_5H_5Mo)_2(S_2CH_2)(\mu\text{-}SCH_3)]_2(\mu_4\text{-}S)\}$OTf, **2**

Bond Distances (Å)			
Mo(1)−S(1)	2.426 (2)	Mo(2)−S(1)	2.413 (2)
Mo(3)−S(1)	2.436 (2)	Mo(4)−S(1)	2.447 (3)
Mo(1)−Mo(2)	2.6355 (15)	Mo(3)−Mo(4)	2.6233 (15)
Mo(1)−S(4)	2.454 (3)	Mo(2)−S(4)	2.444 (3)
Mo(3)−S(7)	2.442 (3)	Mo(4)−S(7)	2.423 (3)
Bond Angles (deg)			
Mo(1)−S(1)−Mo(2)	65.99 (7)	Mo(3)−S(1)−Mo(4)	65.00 (6)
Mo(1)−S(1)−Mo(3)	130.15 (11)	Mo(2)−S(1)−Mo(4)	134.63 (11)

Table 2. Details of Data Collection and Structure Refinement for Cocrystallized Salt **2/3**

empirical formula	$C_{38}H_{37}F_6Mo_6O_6S_{13}$
fw	1701.14
space group	$P2_1$
a, Å	12.001(2)
b, Å	14.964(3)
c, Å	15.128(3)
β, deg	102.50(3)
V, Å^3	2652.3(9)
Z	2
temp, K	153
λ (Mo Kα), Å	0.710 73
D_{calcd}, g cm^{-3}	2.130
μ, mm^{-1}	1.951
R1[a]	0.0528
wR2[b]	0.1257

[a] $R = R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

$[(\mu\text{-}SR)Fe_2(CO)_6]_2(\mu_4S)$[10] contain a tetrahedral arrangement of metal ions, while the metals in $[Fe_3Mn(CO)_{12}(\mu_4\text{-}S)]^-$ [11] adopt a butterfly arrangement. However, to our knowledge, **2** is the first example of carbonyl-free cyclopentadienylmetal dimers arranged around a μ_4-sulfido ligand. A related tetranuclear molybdenum complex, $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)_2]_2^{2+}$, **4**, has been reported previously in which two quadrupally bridged dimers are linked through an S−S bond between the sulfido ligands.[12] Significant electronic differences between **2** and **4** are noted below.

Although the oxidation level of **2** is formally described by a mixed-valence $[Mo(III)]_3Mo(IV)$ formulation, the initial product formed in the reaction appears to be the neutral diamagnetic $[Mo(III)]_4$ analogue. In the NMR spectrum of the crude product prior to exposure to air, a sharp singlet near 5.8 ppm is tentatively assigned as the Cp resonance of this product. After air exposure the resonance broadens and shifts, consistent with the paramagnetic nature of **2**. Resonances for **3** are also observed in the spectrum.

The cyclic voltammogram of **2** in acetonitrile solution shows a reversible electron-transfer process near −0.18 V vs Fc. This suggests that the initially formed diamagnetic product is likely to be oxidized to the observed cationic complex **2** under the aerobic workup conditions. Two additional reversible reduction waves are observed in the CV of **2** at − 0.71 and −1.00 V vs Fc, and a quasi-reversible oxidation occurs at +0.43 V. The CV also includes waves for the cation **3**.[8] The multiple redox waves of **2** suggest that there is electronic communication between the dinuclear units in this structure. In contrast, the tetranuclear complex **4** shows only two electron-transfer processes at potentials identical to those of its dinuclear component.

In summary, we have characterized a new tetranuclear complex in which the metal ions in two $Cp_2Mo_2(\mu\text{-}SR)_3$ units are coordinated to a single μ_4-sulfido ligand. The source of the sulfido bridge is the tetrathiomolybdate ion. The stability of the tetranuclear product is a striking demonstration of the high affinity of Mo(III) and Mo(IV) ions for bridging sulfido ligands.

Experimental Section

General Procedures. Reactions were carried out under nitrogen using standard Schlenk procedures. $[(CpMo)_2(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]$-OTf, **1**,[1] and $(NH_4)_2MoS_4$[13] were prepared according to published procedures. Acetonitrile was dried prior to use by distillation from calcium hydride. ^1H NMR spectra were recorded at 300 or 500 MHz on Varian VXR-300 or Varian Inova 500 MHz instruments, respectively. Mass spectra were obtained on a VG Autospec with EI/CI sources and liquid secondary ion MS capabilities or on a VG Analytical 7070 EQ-HF instrument. Cyclic voltammetry experiments were carried out with a Cypress Systems electrolysis system using a glassy carbon working electrode and acetonitrile solutions containing 0.1 M Bu_4NBF_4. Ferrocene was used as an internal standard, and all potentials are referenced to the ferrocene/ferrocenium couple. Elemental analyses were performed by Desert Analytical Laboratory, Tucson, AZ.

Synthesis of $\{[(CpMo)_2(S_2CH_2)(SCH_3)]_2\mu_4\text{-}S\}$OTf, 2. $[(CpMo)_2(S_2CH_2)(\mu\text{-}SCH_3)(\mu\text{-}S(CH_3)_2)]$OTf, **1**, (0.100 g, 0.152 mmol) and $(NH_4)_2MoS_4$ (0.0284 g, 0.109 mmol) were dissolved in acetonitrile, and the solution was refluxed under nitrogen for 1−2 days. The resulting orange-brown solution was filtered and evaporated to dryness. The crude product was recrystallized from dichloromethane/ether in air to give a mixture of **2** and $[(CpMo)_2(S_2CH_2)(\mu\text{-}S)\ (\mu\text{-}SCH_3)]$OTf, **3.** Ratios were often approximately 1:1, although this varied in different reactions. Yield: 67%. Attempts to isolate **2** in the absence of **3** by recrystallization or by column chromatography were not successful. At least some **3** was usually detected in cyclic voltammograms of **2**. ^1H NMR ($CDCl_3$) prior to exposure to air: δ 5.78 (s, Cp); 1.45 (s, Me). These broaden and/or shift after exposure to air. Resonances for **3** are also observed: δ 6.92 (s, 10 Cp); 4.28 (s, 2 H, S_2CH_2); 1.70 (s, 3 H, Me). Mass spectrum (FAB+): m/z 926 (P^+ of the cation of **2**); 480 (P^+ of the cation of **3**). Anal. Calcd. for a 1:1 mixture of **2** and **3** (confirmed by CV): $C_{38}H_{45}F_6Mo_6O_6S_{13}$: C, 26.78; H, 2.66. Found: C, 26.93; H, 2.80.

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[10] (a) Coleman, J. M.; Wojcicki, A.; Pollic, P. J.; Dahl, L. F. *Inorg. Chem.* **1967**, *6*, 1236. (b) Song, L. C.; Kadiata, M.; Wang, J. T.; Wang, R. J.; Wang, H. G. *J. Organomet. Chem.* **1988**, *340*, 239. (c) Song, L. C.; Hu, Q. M.; Shang, L. Y.; Wang, H.; Zhou, Z. Y.; Liu, L. *J. Organomet. Chem.* **1991**, *412*, C19.

[11] Schauer, C. K.; Harris, S.; Sabat, M.; Voss, E. J.; Shriver, D. F. *Inorg. Chem.* **1995**, *34*, 5017−5028.

[12] Birnbaum, J.; Godziela, G.; Maciejewski, M.; Tonker, T. L.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1990**, *9*, 394−401.

[13] Hein, F.; Herzog, S. In *Preparative Inorganic Chemistry*; Brauer, G., Ed.; Academic Press: New York, 1965; Vol. 2, p 1416.

X-ray Diffraction Study of 2/3. Crystals were examined under light hydrocarbon oil. The specimen crystal was affixed with a small amount of epoxy to a thin glass fiber attached to a brass pin. This assembly was transferred to the goniometer of a Siemens R3 diffractometer. Cell dimensions were determined using 12 reflections measured from a 10 min ϕ-rotation photo. Additional high-angle reflections were harvested and centered to improve the cell metrics. Data collection was to 55° 2θ using 1° ω scans. All data were corrected for Lorentz and polarization effects, as well as for absorption.

Structure solution in the noncentrosymmetric space group $P2_1$ revealed the heavy atom positions. Additional atoms were located during subsequent cycles of least-squares refinement followed by difference Fourier synthesis. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. Non-hydrogen atoms, except those involved in disordered groups, were refined with anisotropic parameters for thermal motion. The asymmetric unit consists of one dinuclear cation, **3**, one tetranuclear cation, **2**, and two triflate anions. The methyl sulfur and methylene sulfur groups are disordered in two of their three locations within the asymmetric unit.

Acknowledgment. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy. Preliminary investigations were supported by the National Science Foundation.

Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of $\{[(CpMo)_2(S_2CH_2)(SCH_3)]_2\mu_4\text{-}S\}OTf$, **2.** This material is available free of charge via the Internet at http://pubs.acs.org.

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