*Inorg. Chem.* **1999,** *38,* 2335−2339 **2335**

# Synthesis and Structural Characterizations of New Mononuclear and Dinuclear Molybdenum(V) Anions Containing Trithiocarbonate Ligands

**C. Simonnet-Jégat, E. Cadusseau, R. Dessapt, and F. Sécheresse***

Institut Lavoisier UMR C173, Université de Versailles, 45 Avenue des Etats-Unis,
78035 Versailles Cedex, France

*Received July 30, 1998*

This paper describes the syntheses and structures of two new Mo(V) compounds obtained via the reductive addition of $CS_2$ on the high-valent tetrathiometalate $MoS_4^{2-}$. The mononuclear compound $(NEt_4)_3[Mo(\eta^2\text{-}CS_3)_4]$, **1**, was selectively produced by reaction of $(NEt_4)_2[MoS_4]$ with excess of $CS_2$ in a mixture of $CH_3OH$ and $NH_3$ in the presence of $H_2S$. Compound **1** crystallizes in the monoclinic system, space group $P2_1/n$, $a = 18.5249(5)$ Å, $b = 11.8058(4)$ Å, $c = 20.2942(5)$ Å, $\beta = 102.951(1)°$, $Z = 4$. In total, 11 176 reflections with $I > 2\sigma(I)$ were employed, and the structure solution was refined to $R = 0.0496$. Compound **1** was revealed to be a mononuclear paramagnetic species containing only $\eta^2$-$CS_3$ ligands. The geometry at the Mo(V) center is described as a regular dodecahedron. Compound **1** represents a unique example of a stable mononuclear Mo(V) complex containing trithiocarbonate ligands. The reaction of $[MoS_4]^{2-}$ with $CS_2$ without $H_2S$ gives $(NBu_4)_2[Mo_2(\eta^2\text{-}CS_3)_4(\mu\text{-}(S_2)_2]$, **2**, obtained as a powder which was recrystallized at 4 °C. Compound **2** crystallizes in the monoclinic system, space group $P2_1/n$, $a = 8.7930(1)$ Å, $b = 22.3059(3)$ Å, $c = 14.5029(2)$ Å, $\beta = 98.445(1)°$, $Z = 4$. In total, 8323 reflections with $I > 2\sigma(I)$ were used, and the structure solution was refined to conventional $R = 0.0425$. Compound **2** is a dinuclear species containing $\eta^2$-$CS_3$ ligands, the two Mo(V) being linked through two disulfido bridging groups. The Mo−Mo distance in **2** is 2.8128(6) Å, a value in very good agreement with those observed for dinuclear Mo(V) species.

## Introduction

Transition metal sulfides are widespread in nature and are reported to be involved in heterogeneous catalysis processes and catalytic activity of enzymes.[1] In recently featured and elegant reports, the preparations and properties of Mo,[2] V,[3] and Re[4] derivatives have been studied. In the tetrachalcogenates of V, Mo, W, and Re the metallic center has the highest formal oxidation state ($d^0$) and is well-known to undergo intricate internal electron transfer upon reaction with external oxidant.[2,4] On this basis we have studied the reaction of $[MoS_4]^{2-}$ with $CS_2$ in nonaqueous medium, $CS_2$ being expected to act here as an electrophilic ligand toward the $S^{2-}$ groups of the chalcogenate.

Many complexes of molybdenum containing trithiocarbonate ligands have been reported,[2] trithiocarbonate and perthiocarbonate ligands being obtained through the electrophilic addition of $CS_2$ to a thiometalate. Trithiocarbonate ligands were also obtained by desulfurization of sulfur-rich compounds or by direct addition of preformed $CS_3^{2-}$ species.[2]

In this paper, we report the synthesis and the structural characterization of a mononuclear and of a dinuclear complex of molybdenum(V) containing trithiocarbonate ligands together with a tentative scheme of reaction.

## Experimental Section

**Syntheses.** All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. $CH_3OH$ and $CH_3CN$ 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). $(NEt_4)_2[MoS_4]$ was prepared according to the reported procedure.[5] Elemental analyses of solids were performed by the Service d'Analyze du CNRS, Gif-sur-Yvette (France). IR spectra (KBr pellets) were recorded on a FTIR Nicolet Magna-550 spectrophotometer. UV−vis spectra were recorded on a Perkin-Elmer λ 19 spectrophotometer. $^{13}C$ NMR spectra were recorded on a Bruker AC300 operating at 75.47 MHz with $Me_4Si$ as internal standard.

**$(NEt_4)_3[Mo(\eta^2\text{-}CS_3)_4]$, 1.** $(NEt_4)_2[MoS_4]$ (0.29 g, 0.6 mmol) was dissolved in 25 mL of solution A, and $H_2S$ was bubbled in the solution for few min. After addition of $NEt_4Cl$ (0.3 g, 1.8 mmol) and $CS_2$ (5 mL, 82 mmol), the resulting brown solution was stirred for 3 h at room temperature. A black microcrystalline precipitate identified as **1** was recovered together with traces of $S_8$. After several days at 4 °C black crystals of **1** suitable for X-ray determinations were isolated from the filtrate (yield 50%). Calcd for $C_{28}H_{60}N_3S_{12}Mo$ (**1**): C, 36.60; H, 6.54; N, 4.58; S, 41.83; Mo, 10.46. Found: C, 36.52; H, 6.53; N, 4.60; S, 41.97; Mo, 10.47. IR, $cm^{-1}$: 3000 (sh), 2970 (w), 2933 (w), 1454 (m), 1394 (m), 1300 (w), 1180 (m), 1013 (vs), 900 (s), 785 (m), 515 (w), 478 (w). UV−vis, $CH_3OH$ solution, λ nm (ε, L $mol^{-1}$ $cm^{-1}$): 242

---

(1) Stiefel, E. I.; George, G. N. In *Bioinorganic Chemistry*; Bertini, I., Gray, H. B., Lippard, S. J., Valentine, J. S., Eds.; University Science Books: Mill Valley, CA, 1994.

(2) (a) Coucouvanis, D. *Adv. Inorg. Chem.* **1998**, *45*, 1−73. (b) Coucouvanis, D.; Draganjac, M. E. *J. Am. Chem. Soc.* **1982**, *104*, 6820. (c) Coucouvanis, D.; Draganjac, M. E.; Koo, S. M.; Toupadakis, A.; Hadjikyriacou, A. I. *Inorg. Chem.* **1992**, *31*, 1186.

(3) Sendlinger, S. C.; Nicholson, J. R.; Lobkovsky, E. B.; Huffman, J. C.; Rehder, D.; Christou, G. *Inorg. Chem.* **1993**, *32*, 204.

(4) Murray, H. H.; Wei, L.; Sherman, S. E.; Greaney, M. A.; Eriksen, K. A.; Carstensen, B.; Halbert, T. R.; Stiefel, E. I. *Inorg. Chem.* **1995**, *34*, 841.

(5) McDonald, J. W.; Delbert Friesen, G.; Rosenheim, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205.

(6) (a) Sheldrick, G. M. *SADABS, a program for the Siemens Area Detector ABSorption correction*, Siemens Analytical X-ray Instruments: Madison, WI, 1994. (b) Sheldrick, G. M. *SHELXTL*; Siemens Analytical X-ray Instruments: Madison, WI, 1994.

10.1021/ic980907m CCC: $18.00

**Table 1.** Summary of Crystal Data and Structure Refinements for **1** and **2**

| | **1** | **2** |
|---|---|---|
| empirical formula | $C_{28}H_6N_3S_{12}Mo$ | $C_{18}H_{36}NS_8Mo$ |
| fw | 919.45 | 618.9 |
| crystal system | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/n$ |
| $a$/Å | 18.5249(5) | 8.7930(1) |
| $b$/Å | 11.8058(4) | 22.3059 (3) |
| $c$/Å | 20.2942(5) | 14.5029 (2) |
| $\beta$/deg | 102.951(1) | 98.445(1) |
| $V$/Å$^3$ | 4325.5(2) | 2813.69(6) |
| $Z$ | 4 | 4 |
| $\rho_{calcd}$, g/cm$^3$ | 1.412 | 1.461 |
| $\mu$, cm$^{-1}$ | 9.06 | 10.67 |
| radiation | Mo Kα[a] | Mo Kα[a] |
| $T$/K | 296(2) | 293(2) |
| R1[b] | 0.0496 | 0.0425 |
| wR2[c] | 0.1415 | 0.1044 |

[a] $\lambda = 0.710\,43$ Å. [b] $R1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

**Table 2.** Selected Interatomic Distances (Å) and Angles (deg) for **1**

| | | | |
|---|---|---|---|
| Mo(1)−S(5) | 2.4860(11) | Mo(1)−S(1) | 2.4868(10) |
| Mo(1)−S(7) | 2.4955(10) | Mo(1)−S(10) | 2.5038(12) |
| Mo(1)−S(11) | 2.5348(11) | Mo(1)−S(4) | 2.5400(11) |
| Mo(1)−S(8) | 2.5471(11) | Mo(1)−S(2) | 2.5553(10) |
| S(4)−C(2) | 1.705(4) | S(7)−C(3) | 1.706(4) |
| S(2)−C(1) | 1.714(4) | S(1)−C(1) | 1.711(4) |
| S(8)−C(3) | 1.726(5) | S(10)−C(4) | 1.694(5) |
| S(11)−C(4) | 1.710(6) | S(5)−C(2) | 1.696(4) |
| S(3)−C(1) | 1.672(4) | S(6)−C(2) | 1.677(4) |
| S(9)−C(3) | 1.658(4) | S(12)−C(4) | 1.680(5) |
| S(10)−Mo(1)−S(11) | 66.66(5) | S(5)−Mo(1)−S(4) | 66.57(4) |
| S(7)−Mo(1)−S(8) | 66.96(4) | S(1)−Mo(1)−S(2) | 67.04(3) |
| S(1)−C(1)−S(2) | 108.8(2) | S(5)−C(2)−S(4) | 108.4(2) |
| S(10)−C(4)−S(11) | 108.9(2) | S(7)−C(3)−S(8) | 108.3(2) |

**Table 3.** Selected Interatomic Distances (Å) and Angles (deg) for **2**

| | | | |
|---|---|---|---|
| Mo(1)−S(5) | 2.4337(11) | Mo(1)−S(5)#1 | 2.4349(10) |
| Mo(1)−S(2)#1 | 2.4487(10) | Mo(1)−S(2) | 2.4533(10) |
| Mo(1)−S(7) | 2.4957(11) | Mo(1)−S(6) | 2.4968(11) |
| Mo(1)−S(4) | 2.5003(10) | Mo(1)−S(3) | 2.5049(10) |
| Mo(1)−Mo(1)#1 | 2.8128(6) | S(2)−S(5) | 2.005(2) |
| S(2)−Mo(1)#1 | 2.4489(10) | S(3)−C(2) | 1.723(4) |
| S(4)−C(1) | 1.728(4) | S(5)−Mo(1)#1 | 2.4351(10) |
| S(6)−C(1) | 1.715(5) | S(7)−C(2) | 1.723(4) |
| S(8)−C(1) | 1.646(4) | S(9)−C(2) | 1.642(4) |
| S(5)#1−Mo(1)−S(2)#1 | 48.46(4) | S(5)−Mo(1)−S(2) | 48.43(4) |
| S(6)−Mo(1)−S(4) | 68.28(4) | S(7)−Mo(1)−S(3) | 68.49(4) |
| S(6)−C(1)−S(4) | 109.1(2) | S(3)−C(2)−S(7) | 109.5(2) |

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1, -y, -z$.

**Table 4.** Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ $\times$ $10^3$) for **1**

| | $x$ | $y$ | $z$ | $U$(eq)[a] |
|---|---|---|---|---|
| Mo(1) | 5205(1) | 3153(1) | 2461(1) | 39(1) |
| S(4) | 6416(1) | 3176(1) | 2072(1) | 56(1) |
| S(7) | 4795(1) | 4350(1) | 1432(1) | 50(1) |
| S(2) | 5081(1) | 1727(1) | 1495(1) | 50(1) |
| S(1) | 3981(1) | 2186(1) | 2194(1) | 55(1) |
| S(8) | 4360(1) | 4775(1) | 2634(1) | 59(1) |
| S(10) | 5784(1) | 1438(1) | 3092(1) | 64(1) |
| S(11) | 4973(1) | 3003(1) | 3642(1) | 69(1) |
| S(5) | 6091(1) | 4617(1) | 3036(1) | 59(1) |
| S(3) | 3586(1) | 654(1) | 981(1) | 74(1) |
| S(6) | 7532(1) | 4991(1) | 2632(1) | 71(1) |
| S(9) | 3822(1) | 6370(1) | 1473(1) | 80(1) |
| S(12) | 5468(1) | 917(2) | 4457(1) | 107(1) |
| C(1) | 4179(2) | 1465(3) | 1525(2) | 50(1) |
| C(2) | 6731(2) | 4300(3) | 2583(2) | 50(1) |
| C(4) | 5427(3) | 1734(4) | 3772(2) | 67(1) |
| C(3) | 4296(2) | 5245(3) | 1818(2) | 52(1) |

[a] $U$(eq) is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Table 5.** Selected Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ $\times$ $10^3$) for **2**

| | $x$ | $y$ | $z$ | $U$(eq)[a] |
|---|---|---|---|---|
| Mo(1) | 5982(1) | 378(1) | 593(1) | 38(1) |
| S(2) | 3305(1) | 607(1) | −46(1) | 50(1) |
| S(3) | 8751(1) | 684(1) | 787(1) | 51(1) |
| S(4) | 6947(1) | −115(1) | 2116(1) | 52(1) |
| S(5) | 3561(1) | −32(1) | 935(1) | 50(1) |
| S(6) | 5781(1) | 1057(1) | 1939(1) | 55(1) |
| S(7) | 6309(1) | 1377(1) | −128(1) | 58(1) |
| S(8) | 6664(2) | 563(1) | 3864(1) | 81(1) |
| S(9) | 9482(2) | 1861(1) | −45(1) | 93(1) |
| C(1) | 6463(4) | 508(2) | 2720(3) | 52(1) |
| C(2) | 8275(5) | 1340(2) | 186(3) | 55(1) |

[a] $U$(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

(21 700), 292 (25 000), 312 (25 600), 421 (4600), 483 (5300), 607 (3300).$^{13}$C NMR (DMSO-$d_6$; ppm): $\delta$ 8.13, 52.79 ($Et_4N^+$).

Reaction of $(NBu_4)_2[MoS_4]$ with $H_2S$ and $CS_2$ by using the same protocol described above led to black crystals of the homologue $(NBu_4)_3[Mo(\eta^2\text{-}CS_3)_4]$.

**$(NBu_4)_2[Mo_2\,(\mu\text{-}(S_2)_2(\eta^2\text{-}CS_3)_4]$, 2.** $(NBu_4)_2[MoS_4]$ (0.4 g, 0.6 mmol) was dissolved in 25 mL of solution A, and upon addition of $NBu_4Cl$ (0.5 g, 1.8 mmol) and $CS_2$ (5 mL, 82 mmol) the solution turned immediately from red to red-brown. The mixture was stirred for 3 h and filtered to eliminate the red-brown precipitate that formed. The filtrate was maintained at 4 °C for 7 days to give black crystals of $(NBu_4)_3[Mo(\eta^2\text{-}CS_3)_4]$ (yield in crystals 25%) identified by spectroscopic methods by comparison with **1**.

The red-brown powder was recrystallized at room temperature from a mixture of $CH_3CN$ and $CS_2$. The red well-shaped crystals obtained within 10 days at room temperature were suitable for X-ray determinations. Anal. Calcd for $C_{36}N_2H_{72}\,S_{16}Mo_2$ (**2**): C, 34.95; H, 5.82; N, 2.26; S, 41.42; Mo, 15.53. Found: C, 35.14; H, 5.89; N, 2.27; S, 41.11; Mo, 15.57. IR, cm$^{-1}$: 2956 (s), 2928 (sh), 2870 (m), 1478 (sh), 1467 (m), 1378 (m), 1358 (vw), 1317 (vw), 1237 (vw), 1168 (w), 1148 (sh), 1105 (w), 1040 (vs), 1024 (sh), 951 (vw), 925 (vw), 875 (s), 798 (w), 734 (m), 577 (m), 536 (vw), 515 (vw), 473 (w), 373 (w), 351 (vw), 322 (vw), 314 (vw). UV−vis, $CH_3CN$ solution, $\lambda$ nm ($\epsilon$, L mol$^{-1}$ cm$^{-1}$): 234 (67 700), 270 (45 200), 318 (75 200), 415 (14 300), 470 (sh), 607 (1000). $^{13}$C NMR (DMSO-$d_6$; ppm): $\delta$ 243.59, 243.64 ($CS_3^{2-}$); $\delta$ 13.51, 19.22, 23.10, 57.59 ($Bu_4N^+$).

Reaction of $(NEt_4)_2[MoS_4]$ with $CS_2$ in the same conditions led to a red powder identified by IR spectroscopy as the dinuclear $(NEt_4)_2$-$[Mo_2\,(\mu\text{-}(S_2)_2(\eta^2\text{-}CS_3)_4]$ compound, and in the filtrate the mononuclear compound $(NEt_4)_3[Mo(\eta^2\text{-}CS_3)_4]$ was identified by spectroscopic methods.

**Crystal Structure Analyses.** Two crystals of dimensions 0.86 × 0.22 × 0.06 mm for **1** and 0.30 × 0.04 × 0.08 mm for **2** were selected for indexing and intensity data collection. Intensity measurements were carried out on a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector. The crystal-to-detector distance was 45 mm, and data were collected up to $2\theta = 65°$. Selected crystal data and details of the data collection for compounds **1** and **2** are given in Table 1.

An empirical absorption correction was applied using the SADABS program[6] based on the Blessing method.[7] The structures were solved by direct methods followed by Fourier difference syntheses using the SHELXTL package.[6] All atoms except hydrogen atoms were anisotropically refined. Hydrogen atoms were refined with geometrical constraints for compound **2**. The final reliability factors converged to $R_1 = 0.0496$ and w$R_2 = 0.1415$ for compound **1** and to $R_1 = 0.0425$

---

(7) Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.

**Table 6.** Comparison of the Structural Parameters of Some Molybdenum Clusters Containing Thio-Ligands

| compounds | S−S (Å) | Mo−Mo (Å) | Mo−S (bridge) (Å) | Mo−S (ligand) (Å) | C−S (terminals) (Å) | S−Mo−S (bridge) (deg) | ref[a] |
|---|---|---|---|---|---|---|---|
| $[Mo_2(\eta^2\text{-}CS_3)_4(\mu\text{-}(S_2))_2]^{2-}$ | 2.005(2) | 2.8128(6) | 2.4337(11)−2.4533(10) | 2.4957(11)−2.5049(10) | 1.642(4)−1.646(4) | 48.43(4)<br>48.46(4) | **2** |
| $[Mo_2(S_2)_4(\mu\text{-}(S_2))_2]^{2-}$ | 2.038(5) | 2.828(2) | | | | | 13 |
| $[Mo_2(S_2CNEt_2)_4(\mu\text{-}(S_2))_2]^{2+}$ | 1.999(2) | 2.808(1) | 2.426(2)−2.443(2) | 2.491(2)−2.506(1) | | 48.4(1) | 12 |
| $[X_4Mo(\mu\text{-}(S_2))_2MoX_4]^{2-}$ (X = Cl, Br) | | 2.86 | | | | | 14 |
| $[Mo(\eta^2\text{-}CS_3)_4]^{3-}$ | | | | | 1.658(4)−1.680(5) | | **1** |

[a] Boldface characters refer to compound numbers; lightface characters refer to reference numbers.

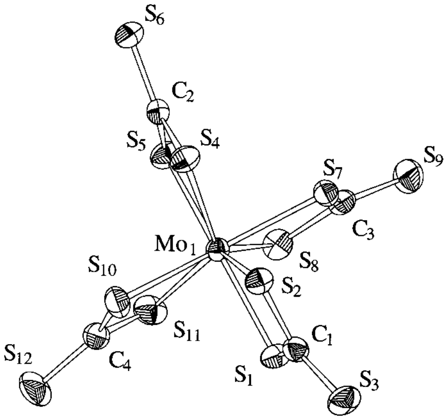


**Figure 1.** Molecular structure of $[Mo(\eta^2\text{-}CS_3)_4]^{3-}$, **1**, with thermal ellipsoids shown at 30% probability level.

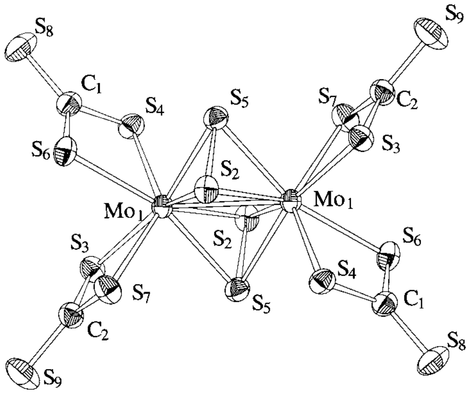


**Figure 2.** Molecular structure of $[Mo_2\ (\mu\text{-}(S_2)_2(\eta^2\text{-}CS_3)_4]^{2-}$, **2**, with thermal ellipsoids shown at 30% probability level.

and $wR_2 = 0.1044$ for compound **2**. The weighting scheme is defined as follows: $w^{-1} = \sigma^2(F_o^2) + (0.0906p)^2 + 2.1768p$ for compound **1** and $w^{-1} = \sigma^2(F_o^2) + (0.0839p)^2 + 2.1601p$, with $p = [\max((F_o^2,0) + 2F_c^2)/3]$.

Selected interatomic distances and angles are listed in Table 2 for **1** and in Table 3 for **2**. Selected atomic coordinates for **1** are listed in Table 4 and for **2** in Table 5.

## Results and Discussion

**Structure of $(NEt_4)_3[Mo(\eta^2\text{-}CS_3)_4]$, 1.** The crystal structure of **1** consists of a discrete mononuclear $[Mo(\eta^2\text{-}CS_3)_4]^{3-}$ anion and $[NEt_4]^+$ cations (see Figure 1).

One of the three cations was found disordered. The occupancy factors of the carbon atoms of the ethyl groups attached to N(3) was refined to the values given in Table S4.

The molybdenum atom is chelated by four trithiocarbonate ligands in a regular dodecahedron geometry. The two $CS_3^{2-}$ ligands containing the S(1), S(2), and S(4), S(5) atoms are in the same plane (mean plane deviation 0.045 Å) and perpendicular (89.3°) to the plane defined by the S(10), S(11), and S(7), S(8) atoms (mean deviation 0.04 Å) of the two other $CS_3^{2-}$ groups. This angle between the two planes is close to the ideal value expected for a regular dodecahedron.[8] Similar ideal geometries were already reported in the literature for $[Mo(S_2CNMe_2)_4]^+$,[9] $[Ta(S_2CNMe_2)_4]^+$,[10] and $[Re(S_2CN(CH_3)_2)_4][Cl]$.[4]

Two different types of Mo−S distances are observed. The average value $Mo-S_A = 2.493$ Å ($S_A$ = S(1), S(5), S(7), S(10)) is 0.05 Å shorter than the average value $Mo-S_B = 2.544$ Å ($S_B$ = S(2), S(4), S(8), S(11)). This difference agrees with the observations of Hoard and Silverton[8] who reported that the overall dodecahedral geometry could be described through the overlapping of an elongated tetrahedron and a collapsed tetrahedron.[4,8]

The terminal C−S distances (1.658(4)−1.680(5) Å) are shorter than the C−S bonds directly attached to the molydenum atom (1.694(5)−1.726(5) Å) (see Table 2) which reflects that they have retained some double-bond character. These values are comparable to the related distances observed in $[Mo_2(S)_2(\mu\text{-}S)_2(\eta^2\text{-}CS_3)_2]^{2-}$ [2] (C=S, 1.622(6)−1.627(6) Å and C−S, 1.725(5)−1.739(7) Å). The angles at the $CS_3^{2-}$ ligands in **1** are similar to the data available in the literature.[2] Although many molybenum(V) architectures are reported, compound **1** is the only structurally characterized mononuclear compound with $CS_3$ ligands.

**$(NBu_4)_2[Mo(\eta^2\text{-}CS_3)_4(\mu\text{-}(S_2)_2]$, 2.** The crystal structure of **2** consists of a discrete dinuclear anion and $NBu_4^+$ cations. The two molybdenum atoms are eight-coordinate by two trithiocarbonate ligands and two disulfide bridges as represented in Figure 2.

The central $\{Mo_2(\mu\text{-}(S_2)_2\}^{6+}$ core has been already observed in several compounds of molybdenum(V)[11] but never with $CS_3^{2-}$ ligands. The closest Mo-related compound we have found in the literature is $[Mo_2(S_2CNEt_2)_4(\mu\text{-}(S_2)_2]^{2+}$ [12] which contains four $[S_2CNEt_2]$ ligands bonded to the central $\{Mo_2(S_2)_2\}^{6+}$ core in a similar way.

The Mo−Mo distance of 2.8128(6) Å is quite short and agrees with the presence of a metal−metal bond as usually observed for Mo(V, d$^1$) compounds that present the similar $\{Mo_2(\mu\text{-}(S_2)_2\}$ central core. Some information about the dimensions in **2** is given in Table 6 for comparison with selected examples of the literature.

The geometry of **2** is strictly comparable to that of the dinuclear vanadium(IV) compound prepared by Christou and

---

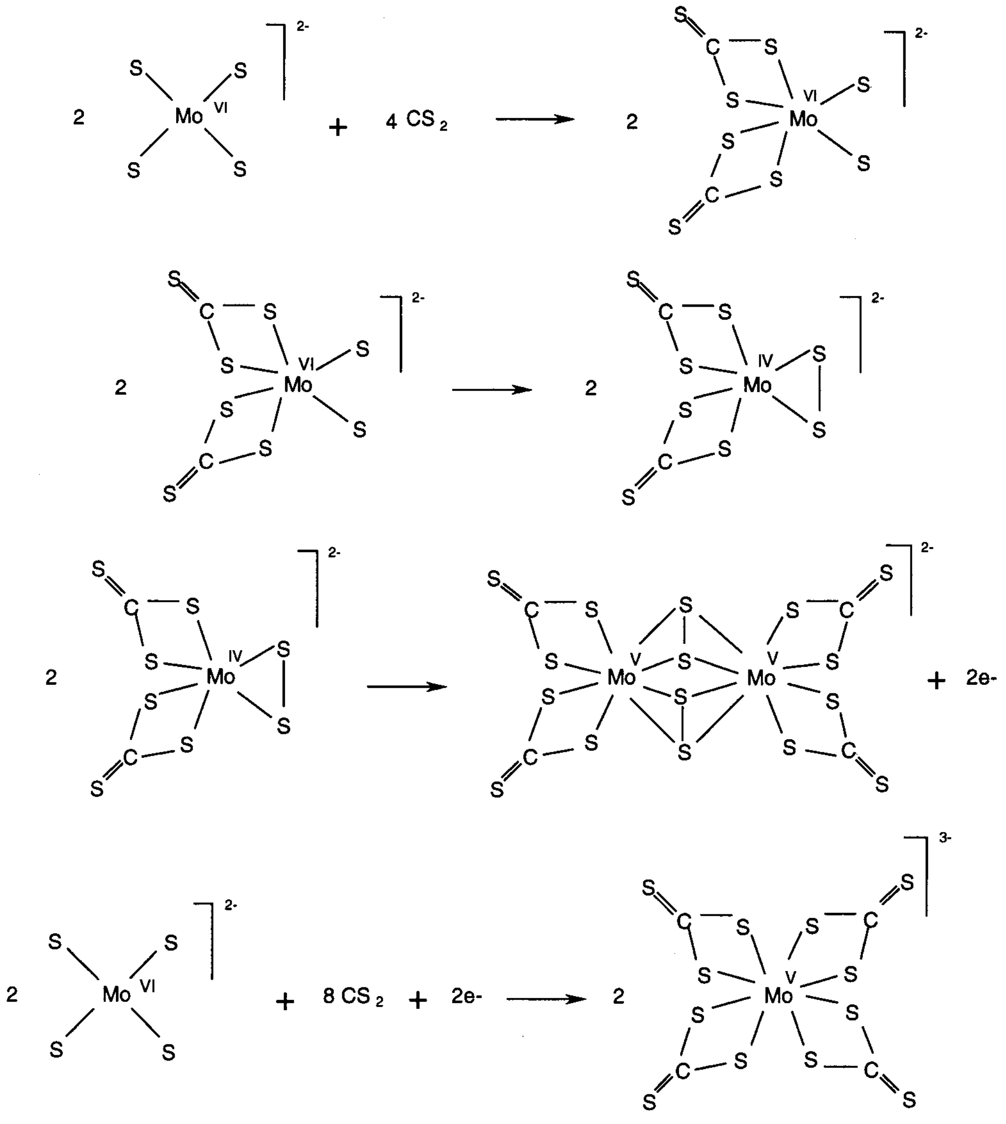
(8) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235.

(9) Garner, C. D.; Howlader, N. C.; Mabbs, F. E.; McPhail, A. T.; Miller, R. W.; Onan, K. D. *J. Chem. Soc., Dalton Trans.* **1978**, 1582.

(10) Lewis, D. F.; Fay, R. C. *Inorg. Chem.* **1976**, *15*, 2219.

(11) Shibahara, T. *Coord. Chem. Rev.* **1993**, *123*, 73.

(12) (a) Kocaba, T. O.; Young, C. G.; Tiekink, E. R. T. *Inorg. Chim. Acta* **1990**, *174*, 143. (b) Young, C. G.; Kobaca, T. O.; Yan, X. F.; Tiekink, E. R. T.; Wei, L.; Murray, H. H., III; Coyle, C. L.; Stiefel, E. I. *Inorg. Chem.* **1994**, *33*, 6252.



**reaction equation**

$$4\,[MoS_4]^{2-} + 12\,CS_2 \rightarrow [Mo_2(\eta^2\text{-}CS_3)_4(\mu\text{-}(S_2))_2]^{2-} + 2\,[Mo(\eta^2\text{-}CS_3)_4]^{3-}$$

**Figure 3.** Tentative reaction scheme explaining the concomitant formations of **1** and **2**.

**Table 7.** $^{13}$C NMR and Electronic Spectral Data for Some Molybdenum Compounds Containing ($\eta^2$-$CS_3$) or ($\eta^2$-$CS_4$) Ligands

| | $^{13}$C NMR (ppm) | electronic data nm ($\epsilon$: L mol$^{-1}$ cm$^{-1}$) | ref[f] |
|---|---|---|---|
| $(NEt_4)_3[Mo(\eta^2\text{-}CS_3)_4]$ | | 242 (21 700); 292 (25 000); 312 (25 600); 421 (4600); 483 (5300); 607 (3300)[a] | **1** |
| $(NBu_4)_2[Mo(\mu\text{-}(S_2)_2(\eta^2\text{-}CS_3)_4]$ | 243.49, 243.64[d] | 234 (67 700); 270 (45 200); 318 (75 200); 415 (14 300); 470 (sh); 607 (1000)[b] | **2** |
| $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}CS_3)(\eta^2\text{-}S_2)]$ | 255[e] | 460; 380 (sh); 330 (sh)[c] | 2c |
| $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}CS_3)_2]$ | 252.97[e] | 450[c] | 2c |
| $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}CS_3)(\eta^2\text{-}CS_4)]$ | 244.5, 251.3[d] | 460, 374 (sh)[c] | 2c |
| $(Ph_4P)_2[Mo_2(S)_2(\mu\text{-}S)_2(\eta^2\text{-}CS_4)_2]$ | 235.2, 237.2[e] | 610 (sh); 470 (sh); 365 (sh); 314 (sh)[c] | 2c |
| $(Ph_4P)_2[Mo_2(S)_2(\mu\text{-}S)_2(\eta^2\text{-}CS_3)_2]$ | 252.8[d] | 444 (sh); 344[c] | 2c |
| $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}CS_3)(\eta^2\text{-}S_4)]$ | 252 | 310 (sh); 258 (sh)[c] | 2c |
| $(Ph_4P)_2[\textit{trans}\text{-}Mo(S)(\eta^2\text{-}CS_4)_2]$ | 245.6, 246.0[e] | 430; 334[c] | 2c |
| $(NEt_4)(Ph_4P)[\textit{cis}\text{-}Mo(S)(\eta^2\text{-}CS_4)_2]$ | 245.6, 246.0[e] | 430 (sh); 393; 335[c] | 2c |

[a] Obtained in $CH_3OH$. [b] Obtained in $CH_3CN$. [c] Obtained in DMF. [d] Obtained in DMSO-$d_6$. [e] Obtained in $CD_3CN$. [f] Boldface characters refer to compound numbers; lightface characters refer to reference numbers.

co-workers,[3] $[V_2(\eta^2\text{-}CS_3)_4(\mu\text{-}(S_2)_2]^{4-}$, although the precursors and the protocols of synthesis employed to isolate the two related compounds were completely different.

**Infrared Spectra.** The frequencies of the C=S vibrations of the coordinated $CS_4^{2-}$ and $CS_3^{2-}$ ligands are located in the range 980−1058 cm$^{-1}$.[2] In the low-frequency region of the spectrum of **1** the two absorptions at 515 and 478 cm$^{-1}$ have been attributed to Mo−S vibrations.[15] After checking the

---

(13) Müller, A.; Nolte, W. O.; Krebs, B. *Inorg. Chem.* **1980**, *19*, 2835.

characteristic features of the $NEt_4^+$ cations, the two remaining absorptions at 1013 and 900 $cm^{-1}$, respectively, have been attributed to the $CS_3^{2-}$ group. In uncoordinated $CS_3^{2-}$ the ideal symmetry is $D_3h$, and a single absorption is observed at 905 $cm^{-1}$.[16] In **1**, the local symmetry of $CS_3^{2-}$ is lowered to $C_{2v}$, which is probably the origin of the splitting of this band in the two components located at 1013 and 900 $cm^{-1}$, respectively.

For compound **2** the absorptions of $CS_3^{2-}$ ligands are observed at 1040 and 1024 $cm^{-1}$, the Mo−S vibrations at 473, 536, and 515 $cm^{-1}$, and the $\nu_{S-S}$ vibrations of the bridge at 577 $cm^{-1}$. Such a high value for the $\nu_{S-S}$ vibration has been observed for molydenum complexes containing disulfur bridging ligands[17] in contrast to terminal disulfur ligands which are observed at low frequencies.

**$^{13}$C NMR Spectra.** Because of the paramagnetism of compound **1** no signal is observed for the carbon atoms of the $CS_3^{2-}$ groups. For compound **2** two signals are observed at 243.64 (243.21 at 60 °C) and 243.59 (243.33 at 60 °C) ppm, respectively. $^{13}$C chemical shifts in the same range were reported by Coucouvanis and co-workers [2c] for $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}CS_3)(\eta^2\text{-}S_2)]$ at 255 ppm, $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}CS_3)_2]$ at 252.97 ppm, and $(NEt_4)_2[Mo_2(O)_2(\mu\text{-}S)_2(\eta^2\text{-}CS_3)(\eta^2\text{-}CS_4)]$ at 252.97 ppm as shown in Table 7.

The presence of two signals is unexpected and is probably related to small geometrical changes in solution since no decomposition was observed during the scan of the spectra. In particular, no signal which could be attributed to released $CS_2$ (193 ppm[2c]) was observed and no changes in UV−vis spectra were detected for 48 h.

**UV−Vis Spectra.** The data concerning **1** and **2** and some other related compounds are given in Table 7. The profiles of the spectra of **1** and **2** are very similar, showing common absorptions about 600, 475, 420, 315, 280, and 240. These features can be attributed to charge transfer of $CS_3^{2-}$ ligands to Mo(V) by reference to **1** which only contains $CS_3^{2-}$ groups.

**Syntheses.** The reaction of $CS_2$ with $MoS_4^{2-}$ results in the formation of only **1** $[Mo(\eta^2\text{-}CS_3)_4]^{3-}$ when the reaction is carried out *in the presence of $H_2S$* while both compounds **1** and **2** $[Mo_2(\eta^2\text{-}CS_3)_4(\mu\text{-}(S_2)_2]^{2-}$ are obtained *without any addition of $H_2S$*. The formation of these two compounds is complex for involving the electrophilic addition of $CS_2$ to the M═S bonds of the thiometalate together with the reduction of Mo(VI) into Mo(V) and in addition a dimerization for **2**.

A common feature of **1** and **2** is they contain terminal $CS_3^{2-}$ ligands. The formation of these $CS_3^{2-}$ chelating ligands can be explained by the [2+2] cycloaddition of $CS_2$ on the Mo═S bond as postulated early on for $[V_2(S_2)_2(CS_3)_4]^{4-}$.[3]

In the absence of $H_2S$ the synthetic route involves the concomitant formations of compounds **1** and **2**. In all the various attempts we performed, **2** precipitated *first* from the reaction mixture as it was less soluble than **1** and was *systematically* followed by the formation of **1** in the resulting filtrate. The reaction scheme given in Figure 3 is a tentative justification of the simultaneous formations of **1** and **2** coupled with the related oxidation states.

The first step which can simultaneously occur with the second one, the cycloaddition of $CS_2$ to $S^{2-}$ ligands, leads to the formation of trithiocarbonate ligands.

The second step consists of the generally postulated intramolecular redox process, molybenum(VI) is reduced to molybdenum (IV) while two $S^{2-}$ ligands are oxidized to $S_2^{2-}$ ligands. The formation of $MoS_9^{2-}$ from $MoS_4^{2-}$ [18] in the presence of an external oxidant, sulfur or dibenzyl trisulfide, has been understood through this redox process which has been also illustrated by the formation of $Mo_2S_8^{2-}$ from $MoS_4^{2-}$ [19] and recently extended to Re.[4] Here this second step is probably induced by $CS_2$ used in large excess.

The third step consists of the formation of **2** by dimerization of $[Mo(S_2)(CS_3)_2]^{2-}$ accompanied by the oxidation of Mo(IV) into Mo(V).

In the last step $MoS_4^{2-}$ acts as an oxidant and adds four molecules of $CS_2$ to form the expected mononuclear compound **1**.

In the presence of $H_2S$ only **1** was obtained with the concomitant formation of sulfur. This observation agrees with the proposed mechanism, where the formation of **2** is avoided, the sulfides being more reducing than the $[Mo(S_2)(CS_3)_2]^{2-}$ intermediate.

The highest yield obtained for **2** (50% referred to Mo) is in good agreement with the stoichiometry of the proposed overall reaction.

**Supporting Information Available:** Complete crystal data and structure refinement for **1** (Table S1), complete interatomic distances (Å) and angles (deg) for **1** (Table S2), anisotropic displacement parameters (Å$^2$ × $10^3$) for **1** (Table S3), complete atomic coordinates (×$10^4$), and equivalent isotropic displacement parameters (Å$^2$ × $10^3$) with estimated standard deviations in parentheses and occupancy factors for **1** (Table S4). Complete crystal data and structure refinement for **2** (Table S5), complete interatomic distances (Å) and angles (deg) for **2** (Table S6), anisotropic displacement parameters (Å$^2$ × $10^3$) for **2** (Table S7), hydrogen coordinates (×$10^4$) and isotropic displacement parameters (Å$^2$ × $10^3$) for **2** (Table S8), complete atomic coordinates (×$10^4$), and equivalent isotropic displacement parameters (Å$^2$ × $10^3$) with estimated standard deviations in parentheses for **1** (Table S9) This material is available free of charge via the Internet at http://pubs.acs.org.

IC980907M

---

(14) Fenske, D.; Czeska, B.; Schumacher, C.; Schmidt, R. E.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1985**, *520*, 7.

(15) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination compounds*, 4th ed.; Wiley-Interscience New York, 1986.

(16) Bueno, W. A.; Lautie, A.; Sourisseau, C.; Zins, D.; Robineau, M. *J. Chem. Soc., Perkin II Trans.* **1978**, 1011.

(17) Müller, A.; Jaegermann, W.; Enemark, J. H. *Coord. Chem. Rev.* **1982**, *46*, 245.

(18) Simhon, E. D.; Baezinger, N. C.; Kanatzidis, M.; Dragangac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1981**, *13*, 1218.

(19) Pan, W. H.; Harmer, M. A.; Halbert, T. R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 459.