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Synthesis and Structure of a Mo_3S_4 Cluster Complex with Seven Cluster Electrons

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Introduction

Compounds containing the $(Mo_3S_4)^{4+}$ cluster, and related systems, have been widely studied, and reviews of their synthesis,[1] electrochemistry,[2] and structure[3] have recently appeared. While the earliest members of this class of compounds to be discovered have 6 cluster electrons, various electron counts and structural modifications are now known.[4] Thus the recent review by Young on early transition metal compounds with mixed-valence is also relevant.[5] It is of course of interest to know what effect the electron count has upon the structure of the cluster. This issue remains clouded because the structures of only a few pairs of compounds with the same architecture and ligand set, but with different electron counts are available.[6−9]

The first example of a compound with a 6 electron $(Mo_3S_4)^{4+}$ core was the $(CpMo)_3S_4^+$ cation reported by Dahl et al.[10] On the basis of a simple MO scheme, these authors predicted that it should be possible to reduce this cation to the neutral radical which has 7 cluster electrons. Two years later this prediction was shown to be correct when a German group reported the uncharged $(CpMo)_3S_4$ molecule.[11] While Dahl's group had reported the structure of the 6 electron cluster cation, the structure of the neutral 7 electron cluster was not reported. The Cp* ($=\eta^5$-C_5Me_5) analog of the neutral 7 electron cluster, $(Cp^*Mo)_3S_4$, was reported after another 11 years had passed,[12] but again, no structure was reported.

Here we report a new synthesis of $(Cp^*Mo)_3S_4$ (**1**) as well as its X-ray structure, a rare example of a compound with a 7 electron $(Mo_3S_4)^{3+}$ core. Since this compound is closely related to the $(CpMo)_3S_4^+$ cation, reported and structured by Dahl, we have good experimental evidence of the effect of adding the seventh core electron.

Experimental Section

All experiments were performed under an argon atmosphere by using standard Schlenk techniques. Solvents were distilled from sodium benzophenone ketyl under argon. ^tBuSH was purchased from NACALAI TESQUE and used without further purification. Cp^*MoCl_4 was synthesized by the literature procedure.[13] Synthesis of $Cp^*Mo(S\text{-}^tBu)_3$ will be reported elsewhere.[14a] IR, UV−visible, and EPR spectra were obtained with JASCO A-3, JASCO V-560, and JES-REIX spectrometers, respectively. Elemental analyses were carried out with a LECO CHN-900 microanalyzer.

Synthesis of $(Cp^*Mo)_3S_4$ (1). $Cp^*Mo(S^tBu)_3$ (0.37 g, 0.74 mmol) was stirred with Na/Hg (1.61 mmol) in ether (30 mL) at room temperature for 4 h, during which time the color of the solution turned from black-red to yellow-green. The solvent was removed in vacuo. The resulting green solid was extracted with 50 mL of THF, and the solution was filtered. Removal of the solvent gave a green residue which was recrystallized from toluene. **1** was obtained as green crystals (0.178 g, 87.9%): IR (Nujol, KBr, cm^{-1}) 1030(m, Cp*); UV−vis (λ_{max}, nm, THF) 649. Anal. Calcd for $C_{30}H_{45}S_4Mo_3$: C, 43.85; H, 5.52. Found: C, 44.00; H, 5.70. ^1H NMR (C_6D_6, 90 MHz; δ, ppm): 8.25 (s, broad, Cp*).

Crystallography. **1** was crystallized as the toluene solvate. A green crystal of dimensions 0.70 x 0.65 × 0.25 mm was sealed in a glass capillary under argon, and diffraction data were collected using a RIGAKU 5R diffractometer with graphite-monochromatized Mo Kα radiation at the IMS, Okazaki, Japan. The locations of the Mo atoms in the crystal of **1**·toluene were determined from both direct and Patterson methods using SHELX-86. The remainder of the atoms were routinely located and the structure was refined on F^2 using SHELX-93 using 3326 reflections out of 3560 independent reflections collected.[14] A toluene molecule was located in a void near the inversion center at 0, $^1/_2$, 0. It was modeled as a rigid group, including the methyl carbon, and a group occupancy parameter was refined. This led to a value less than one, and peaks as large as 0.7 e/Å^3 remained in the vicinity. A second orientation was added as a second rigid group, and another group occupancy was refined. This process was repeated until a total of five orientations for the toluene molecule had been refined. Each addition of a new orientation for the toluene molecule lowered *R* by 0.1−0.2% and the overall effect of the disordered solvent model was to lower *R* by about 1%. In the final difference map the largest peak was 0.23 e/Å^3 located between two of the Mo atoms while two other peaks of 0.23 e/Å^3 were located near the disordered toluenes. The five orientations for the disordered toluene refined to the following occupancies, 0.22(2), 0.14(1), 0.28(2), 0.09(1), and 0.22(2).

In the final model all Mo, S, and C atoms were refined anisotropically, while the toluene was refined as five partially occupied rigid groups with isotropic thermal parameters. Restraints on temperature factors were applied to pairs of atoms which were closer than 0.6Å to each other using the default SIMU parameters of SHELX-93. This generated 11 restraints, all between thermal parameters of the disordered toluene groups. Hydrogen atoms were included on the methyl groups of the Cp* rings, and were refined as rigid roters with a common group thermal parameter. Hydrogen atoms on the disordered toluene ring carbons were placed at calculated positions, and a group thermal parameter was refined. Attempts to locate the hydrogen atoms of the toluene methyls were not successful, and these were not included in the final model. Crystallographic data for **1**·toluene are summarized in Table 1; fractional atomic coordinates and equivalent isotropic temperature factors for **1** are given in Supporting Information (Table S2).

Molecular Orbital Calculations. All molecular orbital calculations were performed by using the extended Hückel method with a weighted H_{ij} approximation.[16a] The H_{ii} parameters and orbital exponents for Mo were taken from previous work,[16b] and the parameters for H, C, S, and

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Table 1. Crystallographic Data for **1**·toluene

$C_{74}H_{106}Mo_6S_8$	fw = 1827.71
monoclinic	$P2_1/n$ (No. 14)
$a = 11.148(1)$ Å	λ(Mo Kα) = 0.710 69 Å
$b = 17.222(3)$ Å	μ(Mo Kα) = 1.213 mm^{-1}
$c = 20.037(2)$ Å	$D_{calcd} = 1.589$ Mg/m^3
$\beta = 96.75(1)$°	$Z = 4$
R1^a = 0.0275 [$I > 2\sigma(I)$]	wR2^b = 0.0648

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(0.0356P)^2 + 4.41\ P]$ where $P=[\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$.

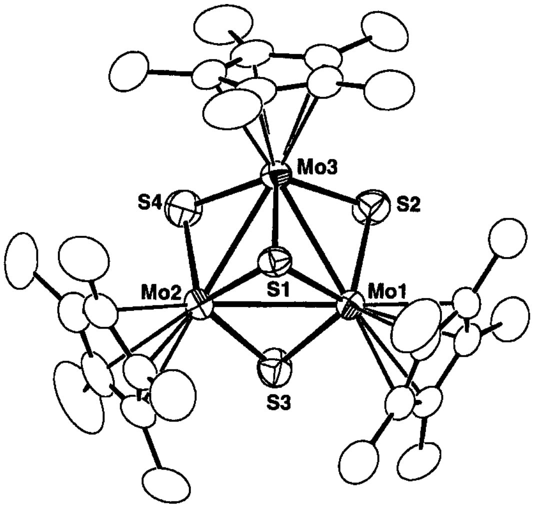

Figure 1. Structure of $(Cp^*Mo)_3S_4$ (**1**) showing 50% thermal ellipsoids.

Cl were the standard ones, where 3d orbitals of S and Cl were not included in the calculations. For $Cp_3Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3$, $Mo_3Cl_9(\mu_3\text{-}S)(\mu_2\text{-}S)_3^{5-}$, and $Mo_3Cl_9(\mu_3\text{-}S)(\mu_2\text{-}Cl)_3^{2-}$, all the Mo−Mo distances were fixed at 2.85 Å, and the μ_3-S was placed 1.665 Å above the center of the Mo_3 triangle, with the Mo−(μ_3-S) bond lengths being 2.3338 Å. The Mo−(μ_2-S) and Mo−(μ_2-Cl) bond lengths were set at 2.31 Å, and the Cp(centroid)−Mo distance is 2.04 Å. The Cp(centroid)−Mo vector was bent up by 18° from the Mo_3 plane, and a similar distortion was applied for the terminal Cl_3 group at each Mo in $Mo_3Cl_9(\mu_3\text{-}S)(\mu_2\text{-}S)_3^{5-}$ and $Mo_3Cl_9(\mu_3\text{-}S)(\mu_2\text{-}Cl)_3^{2-}$. The dihedral angle between the Mo_3 plane and the $Mo_2(\mu_2\text{-}S)$ or $Mo_2(\mu_2\text{-}Cl)$ plane was set to be 132°.

Results and Discussion

As a part of our efforts to explore chemistry of half-sandwich molybdenum and tungsten thiolates,[14] we isolated $Cp^*Mo(S^tBu)_3$ from the reaction of Cp^*MoCl_4 with LiS^tBu. In this reaction, the metal center was reduced from Mo(V) to Mo(IV). An attempt to reduce $Cp^*Mo(S^tBu)_3$ even further with sodium amalgam in ether, followed by a standard workup, resulted in formation of green crystals. Although the IR spectrum was not informative, the elemental analysis was consistent with the formula $(Cp^*Mo)_3S_4$ (**1**), which was confirmed by the X-ray analysis. Because of the paramagnetic nature of **1**, the ^{1}H NMR signal of Cp* in C_6D_6 appears at 8.25 ppm as a broad singlet with $\nu_{1/2} = 15.8$ Hz.

An ORTEP drawing of the X-ray derived molecular structure of **1** is shown in Figure 1, and selected bond distances are listed in Table 2. The structure consists of $(Cp^*Mo)_3S_4$ molecules with disordered toluene molecules filling a void. The general geometry of the family of triangular Mo−S clusters is well-known,[3] and since $(Cp^*Mo)_3S_4$ follows this pattern and closely resembles the $(CpMo)_3S_4^+$ cation, little comment is required. The average Mo−ligand and Mo−Mo bond distances in $(Cp^*Mo)_3S_4$ and $(CpMo)_3S_4^+$ are compared in Table 3.

From Table 4 we can see that the all of the distances in the 7 electron cluster, $(Cp^*Mo)_3S_4$ (**1**) are longer than those in the 6 electron cluster $(CpMo)_3S_4{}^+$. In the case of the distance to the Cp centroid, the difference is probably not statistically significant, and for the Mo−(μ_2-S) distance the difference is only 2σ, and thus of marginal significance. In the case of the Mo−(μ_3-S), the increased distance in the 7 electron cluster is small, 0.024Å, but at 4σ, it is firmly established. Finally the increase in the Mo−Mo distance is the largest, 0.049Å and is very firmly established at about 8σ. Thus we can clearly determine that the addition of the 7th cluster electron to the Mo−S core increases the Mo−Mo distances, and the Mo−(μ_3-S) distance, while the effect on the Mo−(μ_2-S) and the Cp distances is less.

The increase in the Mo−Mo distance of 0.049(6)Å is in good agreement with the value given by Cotton[17] of 0.065Å for each increase of 1/6 in the Mo−Mo bond order, however in this case the seventh electron is in an anitbonding orbital and we are observing a decrease in bond order. It is slightly larger than that observed by Cotton in the comparison of the structures of $Mo_3OCl_6(O_2CCH_3)^{3-}$ [18] and $Mo_3OCl_6(O_2CCH_3)_3{}^{2-}$,[19] 0.024Å, although in this case the bridging acetate ligands may diminish the effect of increasing the cluster electron count from 8 to 9. An earlier report of a Mo_3 cluster with 7 electrons has a Mo_3O_4 core and is found in an extended array structure in $LiZn_2Mo_3O_8$.[20] In this case a 6 electron analog is also known, $Zn_2Mo_3O_8$,[21] in which the Mo−Mo distance is 0.054 Å shorter, again in good agreement with that we report here. However for these compounds the effect of the extended array and the differing coordination of the Zn^{2+} and Li^+ ions upon the Mo−Mo bond lengths are unknown.

While a variety of electron counts are now known for triangular metal clusters, the 7 electron count remains rare. Molecular orbital calculations of several types have been carried out on Mo_3 clusters over the past three decades.[4,6,10,22−24] From these results Cotton has concluded that the energy levels and hence the electron count depends on the detailed nature of the atoms in the M_3X_4 core.[25] In particular he has used MO studies to rationalize the observation that replacement of the μ_2 oxides in a $Mo_3O_4{}^{4+}$ core with μ_2 chloro ligands favors an 8 or 9 electron count, instead of the 6 usually found for the former. Since the 7 electron count found in the title compound is unusual and since it is found in the company of terminal Cp* ligands, which have rather different electronic properties, we sought to probe the electronic structure of this compound via extended Hückel MO calculations. In order to compare our results with the conclusions drawn by Cotton,[24,25] we have also carried out ETH calculations on the model anions $(Mo_3S_4Cl_9)^{5-}$ and $(Mo_3SCl_{12})^{2-}$. In the case of the two latter anions, we have used the same geometry as for $Cp^*{}_3Mo_3S_4$, although in fact, there may be significant differences in the Mo−Mo distances in these compounds. The energy levels we obtain for these three species for the orbitals of interest are presented in Figure 2. Hoffmann has previously reported an ETH calculation for the $(Mo_3SCl_{12})^{2-}$ species.[4] He obtains the same energy level

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Table 2. Selected Bond Distances (Å) and Angles (°) for **1**

Mo(1)−Mo(3)	2.8543(7)	Mo(1)−Mo(2)	2.8651(7)	Mo(2)−Mo(3)	2.8637(7)
Mo(1)−S(3)	2.296(2)	Mo(1)−S(2)	2.314(2)	Mo(1)−S(1)	2.341(2)
Mo(2)−S(4)	2.310(2)	Mo(2)−S(3)	2.312(2)	Mo(2)−S(1)	2.337(2)
Mo(3)−S(4)	2.309(2)	Mo(3)−S(2)	2.310(2)	Mo(3)−S(1)	2.337(1)
Mo(1)−C(14)	2.363(5)	Mo(1)−C(12)	2.368(5)	Mo(1)−C(13)	2.372(5)
Mo(1)−C(11)	2.379(5)	Mo(1)−C(10)	2.382(5)	Mo(2)−C(20)	2.359(3)
Mo(2)−C(24)	2.362(3)	Mo(2)−C(21)	2.367(3)	Mo(2)−C(23)	2.369(3)
Mo(2)−C(22)	2.372(3)	Mo(3)−C(30)	2.358(3)	Mo(3)−C(31)	2.361(3)
Mo(3)−C(34)	2.374(2)	Mo(3)−C(32)	2.379(2)	Mo(3)−C(33)	2.388(3)

Mo(3)−Mo(1)−Mo(2)	60.09(2)	Mo(3)−Mo(2)−Mo(1)	59.77(2)
Mo(1)−Mo(3)−Mo(2)	60.14(2)	S(3)−Mo(1)−S(2)	101.44(6)
S(3)−Mo(1)−S(1)	102.65(6)	S(2)−Mo(1)−S(1)	102.49(5)
S(4)−Mo(2)−S(3)	98.61(6)	S(4)−Mo(2)−S(1)	102.75(5)
S(3)−Mo(2)−S(1)	102.28(5)	S(4)−Mo(3)−S(2)	100.49(6)
S(4)−Mo(3)−S(1)	102.78(6)	S(2)−Mo(3)−S(1)	102.70(5)
Mo(2)−S(1)−Mo(3)	75.57(4)	Mo(2)−S(1)−Mo(1)	75.54(4)
Mo(3)−S(1)−Mo(1)	75.20(4)	Mo(3)−S(2)−Mo(1)	76.24(5)
Mo(1)−S(3)−Mo(2)	76.89(5)	Mo(3)−S(4)−Mo(2)	76.63(5)

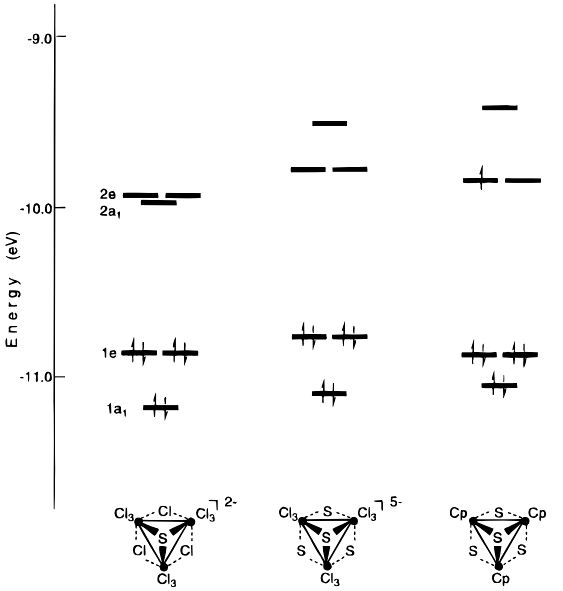

Figure 2. Low-lying Mo d type molecular orbitals for $Mo_3Cl_9(\mu_3\text{-}S)(\mu_2\text{-}Cl)_3{}^{2-}$, $Mo_3Cl_9(\mu_3\text{-}S)(\mu_2\text{-}S)_3{}^{5-}$, and $Cp_3Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3$.

Table 3. Average Bond Distances of $(CpMo)_3S_4{}^+$ and $(Cp^*Mo)_3S_4$ (in Å)

bond	$(CpMo)_3S_4{}^+$	$(Cp^*Mo)_3S_4$
Mo−Cp	2.030	2.046
Mo−(μ_2-S)	2.294(6)	2.309(6)
Mo−(μ_3-S)	2.314(6)	2.338(2)
Mo−Mo	2.812(2)	2.861(6)

Table 4. Overlap Populations in $(CpMo)_3S_4$

orbital	Mo−Mo	Mo−(μ_3-S)	Mo−(μ_2-S)
tot.	0.1543	0.5350	0.6429
$1a_1$	0.0833	−0.0349	−0.0166
1e	0.0443	−0.0056	−0.0305
2e	−0.0204	−0.0048	−0.0119

ordering as we report here, but the gap he reports between the $2a_1$ level and the 2e level is considerably greater than we have found. This is probably because Hoffmann used a shorter Mo−Mo distance in his calculation. Upon replacing the three bridging Cl ligands in $(Mo_3SCl_{12})^{2-}$ with S^{2-} ligands to make $(Mo_3S_4Cl_9)^{5-}$, we find that all orbitals increase in energy and in agreement with Cotton's[24,25] conclusion we find the $2a_1$ orbital is raised above the 2e level. Upon replacing the terminal Cl ligands of $(Mo_3S_4Cl_9)^{2-}$ with Cp ligands to form $Cp_3Mo_3S_4$, we see that the $2a_1$ level is raised further, but more importantly the 2e level is slightly stabilized. Thus the seventh cluster electron enters this doubly degenerate 2e level.

The overlap populations presented in Table 4 show that all of the cluster electrons are slightly anitbonding with respect to the cluster sulfur atoms. Nearly all of the metal−metal bonding character is found in the $1a_1$ orbital and 1e orbitals. The unpaired electron in the 2e orbital is antibonding with respect to both the metal−metal bond and the bonds to the sulfur atoms. This is in agreement with the experimental results which show an increase in the Mo−Mo bond length upon addition of the seventh cluster electron, and a smaller and less certain increase in the bond lengths to the sulfurs.

Since the ETH calculations for the title molecule place the odd electron into an orbital of e symmetry, the probability of a Jahn−Teller distortions arises. This question has been addressed before for similar compounds with 9 cluster electrons.[4,19] At first glance, the title compound seems to be very symmetrical. One of the μ_2 Mo-S distances, Mo(1)−S(3), 2.296(3) Å, is shorter, and significantly so, than all of the others, but we see no pattern involving this distance which appears to be due to a Jahn−Teller type of distortion, and so we believe it to be a random distortion. The capping μ_3 sulfur is pushed slightly away from Mo(1), but this displacement of only 0.004(1)Å is very tiny and is again not consistent with a distortion in the rest of the molecule. However, while the molecule at first glance appears to be very symmetrical, upon closer examination, a very subtle distortion can be seen. The Mo−Mo distances are not equal. The Mo(1)−Mo(3) distance, 2.854(1) Å is 10σ shorter than the other two Mo−Mo distances of 2.865(1) and 2.864(1) Å, which are clearly indistinguishable. In addition the dihedral angle made by the Mo(1)−S(2)−Mo(3) plane, which contains the short Mo−Mo edge, with the plane of the three Mo atoms is 45.8°. This is 2−3° smaller than the dihedral angles made by the trimetal plane with the two Mo−S−Mo planes which do not contain the short edge, Mo(1)−S(3)−Mo(2), 48.1°, and Mo(2)−S(4)−Mo(3), 49.3°. In addition there is also a difference between the dihedral angles between the Cp* planes on the Mo atoms which span the short edge and those which do not. Thus the unique dihedral angle between Cp*(1) (Cp*(1) is bound to Mo(1), etc.) and Cp*(3) is 66.2°, while that between Cp*(1) and Cp*(2) is 70.7° and that between Cp*(2) and Cp*(3) is 71.0°. On the other hand the dihedral angles between the Cp* planes and the trimetal plane do not show any variation the angles being 72.3°, 71.5° and 71.6° for Cp*(1−3) respectively. Thus there is a consistent pattern of distortion on the Mo(1)−S(2)−Mo(3) face which has moved S(2), Cp*(1) and Cp*(2) toward each other, while compressing the Mo(1)−Mo(3) edge and lowering the symmetry from C_{3v}

to C_{2v}. The distortion is very slight and the angular distortions are subtle. As Cotton has pointed out in the case of a 9 electron system where a slight distortion was also identified, the distortion is small because it involves only one electron spread out over the seven atom core. Also since the molecule occupies a general crystallographic position, it is not possible to be sure that the small change in geometry is not coming from packing effects. Hoffmann[4] also investigated a Jahn–Teller distortion in a 9 electron cluster and found, by EHT calculations, two minima leading to stabilization of the cluster, one which lengthens one Mo–Mo bond and one which shortens it. The case investigated by those workers involved a lengthening while that presented here seems to be the opposite case.

ESR measurements on the title compound dissolved in toluene were carried out. At ambient temperature, no signal was observed, however at liquid nitrogen temperature, a broad asymmetric signal was found (Supporting Information). The shape of the signal indicates there is a $g_{\parallel}$ and $g_{\perp}$ component, and there is a poorly resolved Mo hyperfine component. The spectra are similar to that reported for 9 electron systems $Mo_3(\mu_3\text{-}O)(\mu_2\text{-}Cl)_3(\mu_2\text{-}OCCH_3)_3Cl(PMe_3)_2$[19] and $Mo_3O_4(H_2O)_9{}^+$.[26]

Conclusion

Comparison of the structures of the 6 cluster electron cation $(CpMo)_3S_4{}^+$ and the uncharged 7 electron molecule $(Cp^*Mo)_3S_4$ clearly demonstrates that the cluster expands upon addition of the seventh electron. ETH MO calculations suggest that this expansion is due to the population of an orbital of e symmetry which is anitbonding with respect to the cluster atoms. There is evidence for a subtle distortion of the cluster due to the Jahn–Teller effect.

Acknowledgment. We are grateful to Professor O. Yamauchi at Nagoya University for open access to the EPR spectrometer, and we also thank Associate Professor A. Odani for aid with the EPR measurement.

Supporting Information Available: Tables S1–S5 and Figures S1–S3 giving crystal data, atomic coordinates with equivalent isotropic displacement parameters, complete bond lengths and angles, anisotropic displacement parameters, H-atom coordinates and isotropic displacement parameters, atom numbering schemes, and an ESR spectrum for **1** (11 pages). Ordering information in given on any current masthead page.

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