

Mono-oxo Bis(dithiolene) Mo(IV)/W(IV) Complexes as Building Blocks for Sulfide Bridged Bi- and Tri-Nuclear Complexes

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A new electron precise, six-electron, sulfide-bicapped trinuclear cluster complex $[\text{Et}_4\text{N}]_4[\text{Mo}^{\text{IV}}_3(\mu_3\text{-S})_2(\text{mnt})_6]$ (**1**) has been synthesized, where each Mo^{IV} atom is seven coordinated. Identical reaction conditions yielded a dimeric complex, $[\text{PNP}]_2[\text{W}^{\text{V}}_2(\mu_2\text{-S})_2(\text{mnt})_4]$ (**2**) from the starting W^{V} analogue due to oxidation by sulfur formed by the auto-oxidation of H_2S . Two stepwise reversible reductions and no oxidation of **2** as observed by cyclic voltammetry are correlated with the nonbonding nature of the lowest unoccupied molecular orbital and deeply buried highest occupied molecular orbital by theoretical calculations at the density-functional theory level.

Introduction

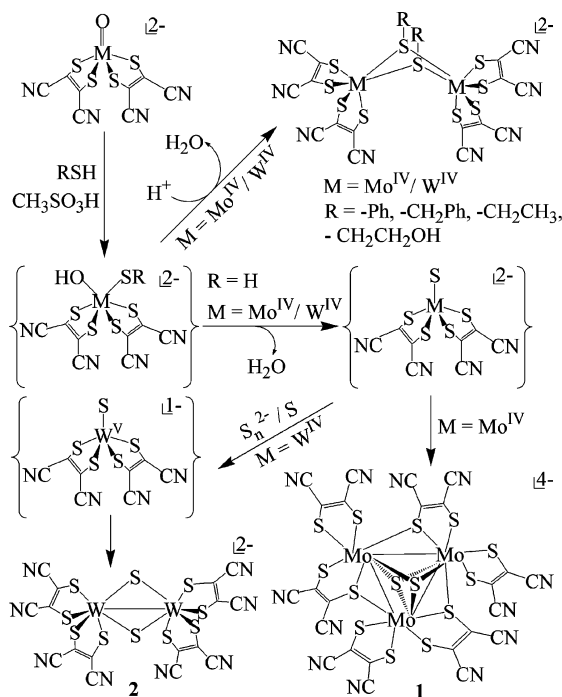
The correlation between the geometrical and electronic structures¹ of trinuclear molybdenum cluster complexes along with their redox chemistry involving core conversion² had been of immense interest in understanding their stability in the light of cuboidal and cubane cluster arrangements. Several trinuclear molybdenum cluster complexes containing electron precise, six^{1a-c} and electron rich, eight^{1e-g} skeletal electrons have been reported. In contrast to the abundance of the Mo_3X_4 -type clusters with ligand combinations (X =

O, S, Cl, etc.)^{3,1a,2g} and a few examples of Mo_3X_5 -type clusters in which the Mo_3 triangle is capped on both sides^{3c,4} there are only two examples of sulfur-bicapped molybdenum trinuclear cluster complexes.⁵ These clusters with, electron rich, eight skeletal electrons contain triphenylphosphine and chloride ligands, where the Mo atom is six coordinated having a formal oxidation state of +3.33.⁵ Here we report the first example of electron precise sulfur-bicapped trinuclear molybdenum cluster with six skeletal electrons where each molybdenum atom is seven coordinated with formal oxidation state of +4. In contrast, the tungsten (IV) analogue of the molybdenum complex under similar reaction yielded a dimer complex instead of the expected trinuclear analogue because of a one electron oxidation of tungsten(IV) by elemental sulfur generated in the reaction mixture. As per the cluster rule, the dimeric W(V) should possess a metal–metal bond. However, cyclic voltammetric study of this complex showed two successive reversible reduction processes suggesting the stability of the species with two

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Scheme 1. Schematic Representation for the Synthesis of Complexes **1**, **2**, and the Thiol Bridged Dimeric Complexes²¹

added electrons in the lowest unoccupied molecular orbital (LUMO) with no tungsten orbital participation.

Experimental Section

Materials and Methods. All reactions and manipulations were performed under a pure argon atmosphere using a modified Schlenk technique. CH_3SO_3H was obtained from S. D. Fine Chemicals Ltd., India. Solvents were distilled and dried by standard procedures before being used. X-ray data were collected on a Bruker-AXS Smart APEX CCD diffractometer. Infrared spectra were recorded on a Bruker Vertex 70, FT-IR spectrophotometer as pressed KBr disks. Elemental analyses for carbon, hydrogen, nitrogen, and sulfur were carried out with a Perkin-Elmer 2400 microanalyser. Electronic spectra were recorded using a USB 2000 (Ocean Optics Inc.) UV-vis spectrophotometer equipped with fiber optics. Cyclic voltammetric measurements were made with BASi Epsilon-EC Bioanalytical Systems Inc. Cyclic voltammograms of a 10^{-3} M solution of the compounds (**1** and **2**) were recorded (scan rate = 100 mV/sec) using a glassy carbon electrode as a working electrode, 0.2 M $[Bu_4N][ClO_4]$ as supporting electrolyte, Ag/AgCl electrode as reference electrode, and platinum wire as auxiliary electrode. Sample solutions were prepared in acetonitrile (**1**) and in dimethylformamide (**2**). Differential pulse polarography was performed with scan rate = 20 mV/sec, pulse width = 50 ms, pulse period = 200 ms, pulse amplitude = 50 mV. All electrochemical experiments were done under an argon atmosphere at 298 K. Potentials are referenced against internal ferrocene (Fc) and are reported relative to the Ag/AgCl electrode ($E_{1/2}(Fc+/Fc) = 0.459$ V vs Ag/AgCl electrode).

Synthesis. $[Et_4N]_4[Mo^{IV}_3(\mu_3-S)_2(mnt)_6] \cdot CH_3CN$ (**1**). One milliliter of methanesulfonic acid was dropwise added to a H_2S saturated solution of 4 mmol (2.62 g) of $[Et_4N]_2[Mo^{IV}O(mnt)_2]$ in dichloromethane in cold. The solution turns green to dirty green via reddish brown. Petroleum ether was added to separate out an oily mass which was dissolved in acetonitrile. Block shaped diffraction quality crystals were obtained upon addition of isopropanol into it

and keeping it overnight at 4 °C. Yield: 0.70 g (30%). Required for $Mo_3S_{14}C_{58}H_{83}N_{17}$: C, 39.69; H, 4.77; N, 13.57; S, 25.58%; found C, 39.75; H, 4.84; N, 13.64; S 25.65%. Absorption spectrum (acetonitrile) λ_{max} (ϵ_M): 500 (sh, 6400), 630 (5240) nm. IR (KBr pellet): ν 2207 (CN).

$[PNP]_2[Mo^{IV}_2(\mu_2-S)_2(mnt)_4]$ (**2**). One milliliter of methanesulfonic acid was dropwise added to a H_2S saturated solution of 4 mmol (2.96 g) of $[Et_4N]_2[W^{IV}O(mnt)_2]$ along with 8 mmol (4.60 g) of $[PNP][Br]$ in dichloromethane in cold. The solution turns light purple to dirty purple via brown. Petroleum ether was added to separate out an oily mass which was dissolved in acetonitrile followed by addition of isopropanol. Needle shaped diffraction quality crystals separated out upon keeping this solution overnight at 4 °C. Yield: 0.85 g (30%). Required for $W_2P_4S_{10}C_{88}H_{60}N_{10}$: C, 51.11; H, 2.92; N, 6.77; S, 15.50%; found C, 51.20; H, 3.01; N, 6.82; S 15.58%. Absorption spectrum (DMF) λ_{max} (ϵ_M): 498 (1170), 550 (sh, 9100) nm. IR (KBr pellet): ν 2207 (CN).

X-ray Crystallography. Suitable diffraction quality single crystals of **1** and **2** were obtained from the crystallization procedures described in each synthesis. The crystals used in the analyses were glued to glass fibers and mounted on a BRUKER SMART APEX diffractometer. The instrument was equipped with CCD area detector, and data were collected using graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å) at low temperature (100 K). Cell constants were obtained from the least-squares refinement of three-dimensional centroids through the use of CCD recording of narrow ω rotation frames, completing almost all-reciprocal space in the stated θ range. All data were collected with SMART 5.628(BRUKER, 2003), and were integrated with the BRUKER SAINT⁶ program. The structure was solved using SIR97⁷ and refined using SHELXL-97.⁸ Crystal structures were viewed using an Oak Ridge thermal ellipsoid plot (ORTEP)⁹ and Diamond 3.1.e. The empirical absorption correction was applied using SADABS, as described by Blessing.¹⁰ The space group of the compounds was determined based on the lack of systematic absence and intensity statistics. Full-matrix least-squares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Asymmetric units contain one ($[Et_4N]_4[1]$) \cdot CH_3CN and half-of ($[PNP]_2[2]$) formula weights.

Computational Details. All calculations were performed using the Gaussian 03 (Revision B.04) package¹¹ on an IBM PC platform.

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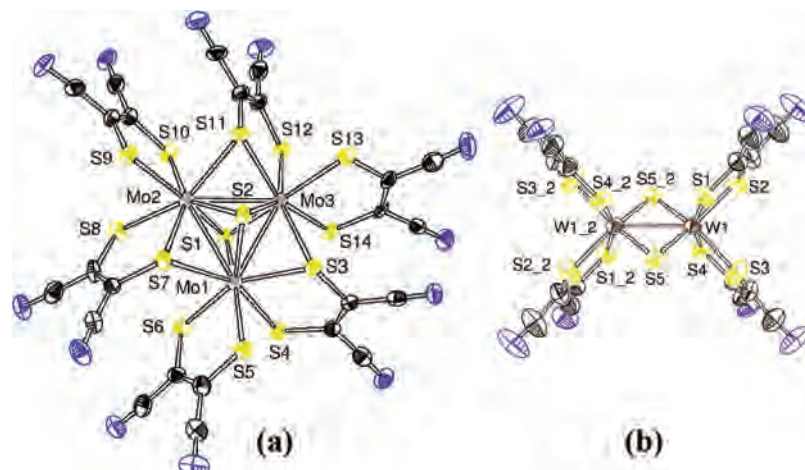


Figure 1. Structure (ORTEP view) of anions of **1** (a) and **2** (b) showing 50% probability thermal ellipsoids with atom labeling scheme. Color code: pink, Mo; plum, W; yellow, S; blue, N; black, C.

Table 1. Crystallographic Data^a for Complexes **1** and **2**

complexes	1	2
formula	Mo ₃ S ₁₄ C ₅₈ H ₈₃ N ₁₇	W ₂ P ₄ S ₁₀ C ₈₈ H ₆₀ N ₁₀
formula weight	1755.07	2068.02
crystal system	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>T</i> , K	100	100
<i>Z</i>	2	2
<i>a</i> , Å	12.493(5)	9.596(5)
<i>b</i> , Å	13.593(5)	14.382(5)
<i>c</i> , Å	23.749(5)	16.810(5)
α , deg	101.393(5)	96.992(5)
β , deg	95.131(5)	101.490(5)
γ , deg	98.312(5)	101.887(5)
<i>V</i> , Å ³	3883(2)	2192.4(15)
<i>d</i> _{calcd} , g/cm ³	1.501	1.568
μ , mm ⁻¹	0.901	2.983
θ range, deg	2.07–28.29°	2.23–28.30°
GOF (<i>F</i> ²)	1.172	1.030
<i>R</i> ₁ ^b > (<i>wR</i> ₂ ^c), %	0.0731 (0.1980)	0.0680 (0.1592)

^a Mo K α radiation. ^b $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$. ^c $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

Molecular orbitals were visualized using “Gauss View”, and geometry optimized molecular structures were shown with Diamond 3.1e. Gas phase geometry optimization and population analysis of the molecular orbitals were carried out at the density-functional theory (DFT) level. The method used was Becke’s three-parameter hybrid-exchange functional,^{12a} the nonlocal correlation provided by the Lee, Yang, and Parr expression,^{12b} and the Vosko, Wilk, and Nuair 1980 local correlation functional (III) (B3LYP).¹² A 6–31G*+ basis set¹³ was used for S, P, C, N, and H atoms. The LANL2DZ basis set¹⁴ and LANL2 pseudopotentials of Hay and Wadt¹⁵ were used for the Mo atom. The optimized minima were characterized by harmonic-vibration frequency calculations with the same method and basis set in which the minimum has no imaginary frequency. For the geometry optimization of complexes **1**, **2**, and **3**, the initial geometry was taken from corresponding crystal structures.

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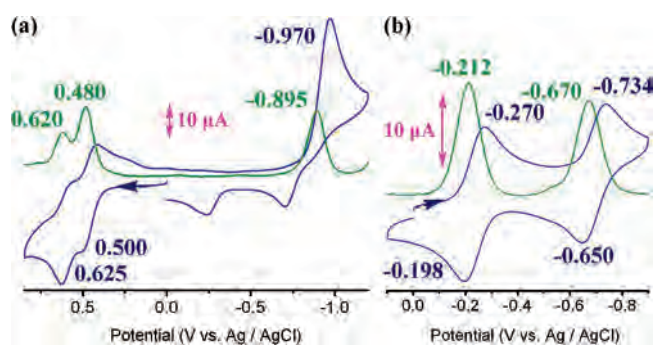


Figure 2. Cyclic voltammograms (blue line, scan rate = 100 mV/sec) and differential pulse polarograms (green line, scan rate = 20 mV/sec, pulse width = 50 ms, pulse period = 200 ms, pulse amplitude = 50 mV) for complexes **1** (a) and **2** (b) in acetonitrile and DMF, respectively.

Results and Discussion

Synthesis and Reactivity of Compounds. The chemical reactions of complex $[\text{Mo}^{\text{IV}}\text{O}(\text{mnt})_2]^{2-}$ suggest that its molybdenyl group, $\{\text{Mo}^{\text{IV}}=\text{O}\}$, behaves like the carbonyl group.^{16,17} Thus, the $\{\text{Mo}=\text{O}\}$ group can easily be protonated with the addition of an acid (HX) which may yield a $\{\text{Mo}^{\text{IV}}(\text{OH})(\text{X})\}$ moiety, and when the counteranion X is a non coordinating anion like methanesulfonate, the species responds to hydrolysis to yield the stable tris¹⁸ species $[\text{Mo}^{\text{IV}}(\text{mnt})_3]^{2-}$ in 67% yield (based on the molybdenum). Its formation can be near quantitative on the addition of one

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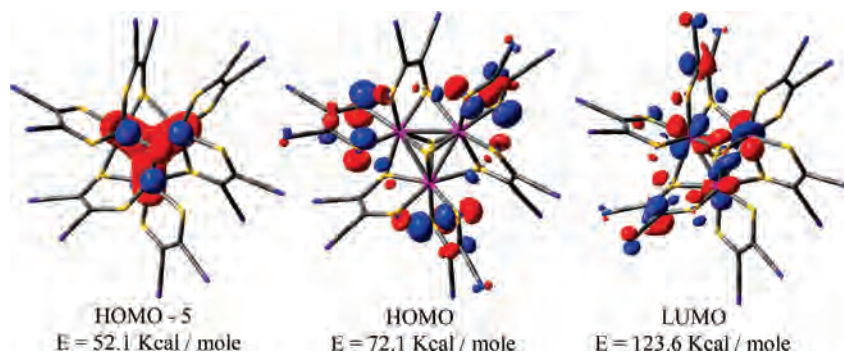


Figure 3. Pictorial representation for the selected molecular orbitals of complex **1**. Isosurface cut off value = 0.04. Color code for atoms: pink, Mo; yellow, S; blue, N; gray, C.

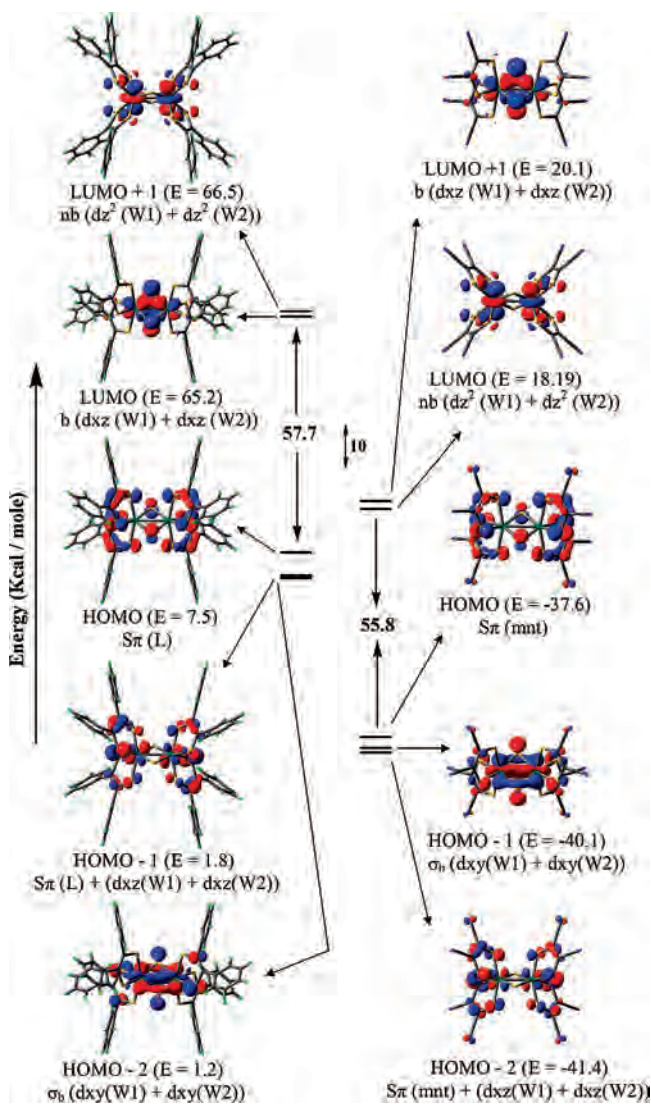


Figure 4. Relative energy diagram for the selected molecular orbitals of complexes **2** (right) and **3**^{23a} (left). Isosurface cut off value = 0.04. Color code for atoms: teal, W; yellow, S; blue, N; gray, C; green, H. L = 1,2-diphenylethylenedithiolate.

equivalent of free mnt^{19} anion into the reaction medium.²⁰ When acidification was carried out in the presence of various

thiols, a series of thiol bridged dimeric M(IV) (M = Mo/W) complexes were obtained²¹ without involving a metal–metal bond (Scheme 1). However, the reactivity is completely changed with the replacement of thiols by H₂S. The trinuclear Mo^{IV} cluster complex, [Et₄N]₄[Mo^{IV}₃(μ_3 -S)₂(mnt)₆]·CH₃CN (**1**) (Figure 1a) was directly synthesized by the addition of methanesulphonic acid in a H₂S saturated dichloromethane solution of the starting complex, [Et₄N]₂[Mo^{IV}(O)(mnt)₂].¹⁷ Under identical condition, the tungsten analogue of the starting material yielded a binuclear W^V complex, [PNP]₂[W^V₂(μ_2 -S)₂(mnt)₄] (**2**) (Scheme 1b, PNP, bis(triphenylphosphoranylidene) ammonium mono cation). Formation of **1** and **2** (Scheme 1) in contrast to the thiol bridged dimeric complexes²¹ indicates that the hypothetical species, {M^{IV}(OH)(SR)} (R = Ph, CH₂Ph, CH₂CH₃, CH₂CH₂OH, H), upon elimination of water under a protic environment may generate the highly reactive pentacoordinated species {M^{IV}(SR)} (R = Ph, CH₂Ph, CH₂CH₃, CH₂CH₂OH). This, on dimerization, yielded hexacoordinated, thiol bridged M^{IV} dimeric complexes²¹ (M = Mo/W). When R = H, the {M^{IV}(SH)} species seems to proceed to further deprotonation in forming the reactive building unit, {M^{IV}(S-)} (M = Mo), which rearranges to yield **1**. When M = W, the reaction becomes more complicated (Scheme 1). H₂S is known to be auto-oxidized to produce polysulfide and elemental sulfur,²² which are capable to oxidize²⁰ W^{IV} to W^V, and the system may be stabilized by dimerization involving bridging ligands which are possibly assisted by W^V–W^V bond formation to yield **2**.

X-ray Structure Description. Both complexes have been structurally characterized (Figure 1), and the leading structural parameters are summarized in Table 1. Complex **1** contains an equilateral {Mo₃} triangle bi capped by two μ_3 bridging sulfide ligands. The Mo–Mo distance (2.84 Å) in **1** is larger than that reported (2.71 Å) for the complex [Mo₃S₅(PMe₃)₆]^{5b,c} but lies in the range of 2.73–2.83 Å found in Mo₃S₄ type cluster complexes.^{3a,b} The Mo–S(μ_3) distances for the two μ_3 S (Mo–S(1)_{average} = 2.36 Å and Mo–S(2)_{average} = 2.44 Å) are different and the distances of two μ_3 S from the plane containing three molybdenum atoms

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are 1.71 and 1.81 Å, respectively. The cluster core contains three μ_2 bridging sulfurs which are provided by alternate maleonitriledithiolate (mnt) ligands. The Mo– μ_2 S–Mo angle lies in the range 67.89–68.45°. On the other hand, complex **2** contains a dimeric core (Figure 1) with two μ_2 S and a weak or negligible W–W bond (2.93 Å) where each W atom is hexacoordinated. The W– μ_2 S distance is 2.32 Å and the W– μ_2 S–W angle is 78.26°, which are quite similar to the distances and angles found in similar type of complexes reported earlier.²³

Electrochemistry. The electrochemical properties of **1** and **2** have been investigated by cyclic voltammetry and by differential pulse polarography (Figure 2). The trinuclear cluster (**1**) exhibited two consecutive one electron irreversible oxidations at $E_{pa} = 0.500$ and 0.625 V, respectively. **1** shows one irreversible reduction at $E_{pc} = -0.970$ V showing instability of the complex under reduction. Coulometric analysis of **1** was thwarted because of a preadsorption process on the platinum electrode; nevertheless, the current response using ferrocene as internal standard at the same concentration suggested this process at $E_{pc} = -0.970$ V to be a two electron process. Complex **2** exhibited two consecutive one electron reversible reductions at $E_{1/2} = 0.234$ V ($\Delta E_{pp} = 72$ mV) and 0.692 V ($\Delta E_{pp} = 84$ mV). No oxidative response was found up to 1.2 V (not shown). A similar tungsten complex, [Et₄N]₂[W₂(μ_2 S)₂(S₂C₂Ph₂)₄] (**3**),^{23a} was reported to have accessible irreversible oxidation with apparently no easy reduction process.

Theoretical Calculations. To understand the electrochemical responses of the synthesized complexes, a gas phase DFT calculation was performed using the Gaussian 03 program.¹¹ The molecular orbitals responsible for metal–metal bonding are the HOMO-5 and the HOMO-1 for complexes **1** and **2**, respectively. In complex **1**, the ligand based highest occupied molecular orbital (HOMO, Figure 3) is associated with the observed irreversible oxidations. The LUMO of complex **1** is predominantly metal centered (48.70%) and originates from the bonding interaction of one μ_3 S ($S\pi$) and mainly metal d_z^2 at one Mo center along with antibonding

interactions of the same μ_3 S ($S\pi$) with two other Mo centers, which are mainly metal $d_{x^2-y^2}$ in character. This is exhibited by the apparent two electron reduction at $E_{pc} = -0.970$ V. Further reduction beyond -1.2 V has not been scanned. In complex **2**, the ligand centered HOMO (Figure 4) is too deeply buried energetically to respond any oxidation process up to 1.2 V. In contrast, for complex **3**, its HOMO is relatively accessible (Figure 4) energetically and so it responds to an easy oxidation.^{23a} Interestingly, the LUMO of **2** is predominantly metal in character (55.11%) and non bonding, and therefore, it responds to two successive reversible reduction processes without affecting the overall stability of the complex. In contrast, **3** possesses a weakly bonding LUMO to affect the W–W bonding, but this reduction is energetically not readily accessible. The relative energy diagram for **2** and **3** (Figure 4) thus correlates the difference in redox response observed by cyclic voltammetric studies of these two similar compounds.

Conclusion

We have synthesized a new electron precise, six-electron, sulfide-bicapped trinuclear Mo^{IV} cluster containing all sulfur coordination where each Mo atom is seven coordinated and retains the oxidation state of +4. The formation of a binuclear tungsten(V) complex under identical reaction conditions with one electron oxidation of each W^{IV} center has been rationalized. The redox chemistry of these complexes has been explained and correlated with theoretical calculations at the DFT level.

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Supporting Information Available: Geometry optimized structures for **1**, **2**, and **3**, comparative structural parameters for the structures determined from X-ray and geometry optimized structures for **1** and **2**, XYZ coordinates for the geometry optimized structures of **1**, **2** and **3**^{23a} (PDF), and crystallographic data (in CIF format) for the complexes **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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