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Syntheses and Characterizations of a Series of Tetradecanuclear Molybdenum(Tungsten)/Copper/Sulfur Heterobimetallic Cluster Compounds

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Using sulfide ion to substitute the weakly copper(I)-philic ligands of $MS_{4-n}{}^{2-}O_n/Cu^+$ compounds, ($M = Mo$, W; $n = 0$, 1), we have prepared and characterized four novel tetradecanuclear clusters having the general formula $[(n\text{-}Bu)_4N]_4[M_4Cu_{10}S_{16}E_2E']H_2O$, ($M = Mo$, $E = E' = O$ for complex **1**; $M = W$, $E = {}^1/_2O + {}^1/_2S$, $E' = O$, for complex **2**; $M = Mo$, $E = S$, $E' = {}^1/_2O + {}^1/_2S$ for complex **3**; $M = W$, $E = E' = S$, for complex **4**). Crystal structures of compounds **1**−**4** were determined; they are isomorphous and crystallized in the orthorhombic space group $Pna2_1$, with $a = 26.6997(2)$ Å, $b = 19.3133(4)$ Å, $c = 21.4577(4)$ Å, $V = 11064.9(3)$ Å^3, $Z = 4$ for $[(n\text{-}Bu)_4N]_4[Mo_4Cu_{10}S_{18}O]\cdot H_2O$ (**3**) and with $a = 26.8141(8)$ Å, $b = 19.4412(6)$ Å, $c = 21.4039(5)$ Å, $V = 11157.8(5)$ Å^3, $Z = 4$ for $[(n\text{-}Bu)_4N]_4[W_4Cu_{10}S_{19}]\cdot H_2O$ (**4**). The cluster cores have approximate σ symmetry. The anions **1**−**4** may be viewed as consisting of one incomplete cubane-like Cu_3MS_3E fragment, one trigonal prism-type Cu_3MS_4, and two butterfly-type Cu_2MS_3E' fragments, bridged by two μ_3-S and one μ_4-S atoms. There are two $(\mu_3\text{-}S)Cu_3$ configurations in the compounds. Infrared, Raman, and UV/vis spectra of the above compounds are discussed, and the main absorption bands are assigned. ^{95}Mo NMR spectra and cylic voltammograms are investigated and compared with those of other compounds, ^{95}Mo NMR spectra show that in the solution there are three kinds of coordination environments of Mo in complexes **1** and **3**, and cyclic voltammograms indicate that complexes **1**−**4** have irreversible electrochemical reductions.

Introduction

The thiometallic anions $[MS_{4-n}]^{2-}$ ($M = Mo$, W; $n = 0$, 1), which have been proved to be useful and versatile reagents,[1] play a key role in bioinorganic and physical chemistry. In this cluster family, Mo/Fe/S clusters were found existing in the active center of some nitrogenase,[2] Mo/Cu/S clusters were recognized to have the biological functions in ruminants,[3] and certain Mo(W)/Cu(Ag)/S clusters were determined to exhibit strong nonlinear third-order optical properties.[4] Mo(W)/Cu/S clusters were widely researched in the past two decades and many different structure configurations have been reported, such as $[(CNCu)MS_3E]^{2-}$,[5] ($M = Mo$, W; $E = S$, O), $[(CuCl)_2WS_4]^{2-}$ [6] (linear), $[(PPh_3)_3Cu_2MS_3O]$[7] (butterfly), $[(CuL)_3MS_4]^{2-}$ [8] (T frame) ($L = Cl$, Br, I), $[(CuCl)_3MOS_3]^{2-}$ [8c] (incomplete cubane-like), $[(CuCl)_3ClMS_4]^{3-}$ [9] (cubane-like), $[(CuBr)_3(\mu_2\text{-}Br)MOS_3]^{3-}$ [10] (half-open cubane-like), $[(Ph_2PCH_2PPh_2)_3Cu_3WS_4]^{+}$ [11] (triprism), $[(CuCl)_4MS_4]^{2-}$ [12] (cross frame), $[(CuCl)_4(\mu_2\text{-}Cl)MS_4]^{3-}$ [9] (a cubane with an extra plane), $[(CuCl)_5(\mu_2\text{-}Cl)_2MS_4]^{4-}$ [13] (double cubane-like), $[(CuCl)_6(\mu_2\text{-}Cl)_3MoS_4]^{5-}$ [14] (cage). However, only a few Mo(W)/Cu/S clusters with pure sulfide ion ligands were reported, such as $[M_4Cu_4S_{12}O_4]^{4-}$ [15] (square-type), $[M_8Cu_{12}S_{28}E_4]^{4-}$ [16] (cage), ($M = Mo$, $E = S$, O;

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M = W, E = O), and $[(\mu_6\text{-S})Cu_6S_6(S_2)_6Mo_6O_6]^{2-}$ [17] (cage). In the system of Mo(W)/Cu/S clusters, the strong σ-donor ligands sulfide ion may substitute the weakly copper(I)-philic ligands halide ion, thus the new structural type of complexes may be synthesized. By this method, the new structural complexes **1**−**4** with pure sulfide ion ligands can be obtained. Recently compounds **1** and **2** were reported briefly;[18] herein, the syntheses and characterizations of compounds **3** and **4** are reported. The formation, ^{95}Mo NMR spectra properties, and cyclic voltammograms of tetradecanuclear heterobimetallic cluster systems are discussed in detail.

Experimental Section

Materials. All experiments were carried out in the air. $(NH_4)_2MS_4$ (M = Mo, W) and $(NH_4)_2WOS_3$ were obtained by published procedures,[19] K_2MoOS_3 was produced by bubbling H_2S gas through an aqueous solution of K_2MoO_4 and KOH, and other chemicals used were purchased.

General Procedure. Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer as KBr pellets. Raman spectra were collected on a Nicolet 910 FT-Raman laser spectrophotometer as CsI pellets. Electronic spectra were obtained on a Shimadzu UV-3000 spectrophotometer in DMF solution between 600 and 200 nm. Cyclic voltammograms were performed on a CV-1B cyclic voltameter. ^{95}Mo NMR spectra were recorded on a Varian Unity-500 spectrometer in DMF solution. Elemental analyses were performed by the Elemental Analysis Laboratories in our institute.

$[(n\text{-Bu})_4N]_4[Mo_4Cu_{10}S_{16}O_3]\cdot H_2O$ (1). A solution of K_2MoOS_3 (1.145 g, 4 mmol), CuBr (1.147 g, 8 mmol) and $(n\text{-Bu})_4NBr$ (1.934 g, 6 mmol) in DMF (9 mL) was stirred for 12 h, and a solution of Li_2S (0.45 g, 10 mmol) in 1.5 mL of water and 3 mL of DMF was added, the reaction mixture was stirred for only 1 min, and then dark precipitate was removed by filtration, 3 mL of *i*-PrOH was added. A 0.90 g (0.35 mmol, 43.8% based on Cu) amount of dark crystals of **1** was obtained by allowing the violet filtrate to stand at room temperature for 1 day. Anal. Calcd (found): C, 29.93 (29.80); H, 5.73 (5.92); N, 2.18 (2.11); Br, 0 (0); S, 19.94 (19.23); Cu, 24.73 (24.56). IR (cm^{-1}): $\nu(M-O_t)$ 894.8 (vs); $\nu(M-(\mu_n\text{-S}))$ ($n = 2, 3, 4$) 462.8 (s), 453.2 (s). Raman (cm^{-1}): $\nu(M-O_t)$ 898.1 (m); $\nu(M-(\mu_n\text{-S}))$ ($n = 2, 3, 4$) 454.5 (s), 419.7 (vs); others 363.8 (w), 280.9 (m), 257.7 (m), 234.6 (m), 184.4 (m), 163.2 (m), 153.6 (m), 132.4 (s). UV (DMF solution): λ_{max}/nm (ϵ/$dm^3\ mol^{-1}\ cm^{-1}$): ν_1 536 (sh) (4.6×10^3); ν_2 416 (1.6×10^4); ν_3 325 (sh) (2.6×10^4), 268 (3.9×10^4).

$[(n\text{-Bu})_4N]_4[W_4Cu_{10}S_{16.5}O_{2.5}]\cdot H_2O$ (2). A procedure similar to that used for complex **1** was employed except that $(NH_4)_2WOS_3$ (1.329 g, 4 mmol) was used instead of K_2MoOS_3. After allowing the red filtrate to stand at room temperature for 3 days, yielding 0.85 g (0.29 mmol, 36.3% based on Cu) of red crystals of **2**. The crystals of **2** can also be obtained by allowing Et_2O vapor to diffuse into the filtrate for 4 days. Anal. Calcd (found): C, 26.26 (26.50); H, 5.03(5.23); N, 1.91 (1.94); Br, 0 (0); S, 18.04 (18.26); Cu, 21.69 (21.53). IR (cm^{-1}): $\nu(M-O_t)$ 914.1 (vs); $\nu(M-S_t)$ 495.6 (s); $\nu(M-(\mu_n\text{-S}))$ ($n = 2, 3, 4$) 453.2 (vs), 426.2 (s). Raman (cm^{-1}): $\nu(M-O_t)$ 915.4 (m); $\nu(M-S_t)$ 491.1 (s); $\nu(M-(\mu_n\text{-S}))$ ($n = 2, 3, 4$) 456.4 (vs), 429.1 (s, sh); others 383.1 (m), 362.7 (w), 325.2 (w), 265.6 (w), 223.0 (w), 205.7 (m), 164.1 (m), 121.4 (s). UV (DMF solution): λ_{max}/nm (ϵ/$dm^3\ mol^{-1}\ cm^{-1}$): ν_1 440 (sh) (1.0×10^4); ν_2 330 (sh) (2.3×10^4); ν_3 278 (4.7×10^4).

$[(n\text{-Bu})_4N]_4[Mo_4Cu_{10}S_{18}O]\cdot H_2O$ (3). A solution of $(NH_4)_2MoS_4$ (1.041 g, 4 mmol), CuBr (1.147 g, 8 mmol), and $(n\text{-Bu})_4NBr$ (1.934 g, 6 mmol) in DMF (15 mL) was stirred for 12 h, and a solution of Li_2S (0.45 g, 10 mmol) in 3 mL of H_2O and 3 mL of DMF was added, the reaction mixture was stirred for another 30 min. The dark precipitate was removed by filtration, and 3 mL of *i*-PrOH was added into the deep purple-black filtrate. A 0.82 g (0.32 mmol, 39.4% based on Cu) amount of black crystals of **3** was obtained by allowing the filtrate to stand at room temperature for 1 week. Anal. Calcd (found): C, 29.56 (29.54); H, 5.66 (5.51); N, 2.15 (2.21); Br, 0 (0); S, 22.15 (21.65); Cu, 24.42 (24.38). IR (cm^{-1}): $\nu(M-O_t)$ 894.8 (s); $\nu(M-S_t)$ 505.3 (vs); $\nu(M-(\mu_n\text{-S}))$ ($n = 2, 3, 4$) 484.1 (s), 462.8 (vs), 451.3 (vs). Raman (cm^{-1}): $\nu(M-O_t)$ 909.6 (w); $\nu(M-S_t)$ 508.5 (s); $\nu(M-(\mu_n\text{-S}))$ ($n = 2, 3, 4$) 454.5 (s), 419.7 (vs); others 373.5 (w), 363.8 (w), 282.8 (m), 273.2 (m), 261.6 (w), 228.8 (m), 188.3 (m), 165.2 (s), 136.2 (s), 124.7 (s). UV (DMF solution): λ_{max}/nm (ϵ/$dm^3\ mol^{-1}\ cm^{-1}$): ν_1 510(8×10^3); ν_2 436 (sh) (1.8×10^4); ν_3 303 (4.1×10^4), 269 (4.4×10^4).

$[(n\text{-Bu})_4N]_4[W_4Cu_{10}S_{19}]\cdot H_2O$ (4). A solution of $(NH_4)_2WS_4$ (1.393 g, 4 mmol), CuBr (1.147 g, 8 mmol), and $(n\text{-Bu})_4NBr$ (1.934 g, 6 mmol) in DMF (6 mL) was stirred for 12 h, a solution of Li_2S (0.45 g, 10 mmol) in 1.5 mL of H_2O and 4 mL of DMF was added, and the resulting reaction mixture was stirred for 2 min. A great amount of brown precipitate was separated out by filtration, and then the precipitate was dissolved in 12 mL of DMF, and the solution was filtered after being stirred for 4 h. After 9 mL of *i*-PrOH was added, the deep red filtrate was allowed to stand at room temperature for 1 day, yielding 0.73 g (0.25 mmol, 30.7% based on Cu) of deep red crystals of **4**. Anal. Calcd (found): C, 25.90 (25.89); H, 4.96(5.05); N, 1.89 (1.96); Br, 0 (0); S, 20.49 (20.13); Cu, 21.39 (21.27). IR (cm^{-1}): $\nu(M-S_t)$ 493.7 (vs); $\nu(M-(\mu_n\text{-S}))$ ($n = 2, 3, 4$) 457.1 (vs), 430.1 (m), 416.6 (m). Raman (cm^{-1}): $\nu(M-S_t)$ 495.0 (vs); $\nu(M-(\mu_n\text{-S}))$ ($n = 2, 3, 4$), 458.3 (s), 441.0 (s), 425.5 (s), 415.9 (m); others 360.0 (w), 273.2 (m), 219.2 (m), 205.7 (w), 163.2 (s), 134.3 (s), 124.7 (s). UV (DMF solution): λ_{max}/nm (ϵ/$dm^3\ mol^{-1}\ cm^{-1}$): ν_1 441 (sh) (1.4×10^4); ν_2 343 (sh) (3.9×10^4); ν_3 300 (sh) (5.3×10^4), 281 (5.5×10^4).

In addition, another two interesting experiments are provided here. (I) When a procedure similar to that of **4** mentioned above except that the molar ratio of starting materials of $(NH_4)_2WS_4$ and CuBr is changed from 1:2 to 1:3, we can also obtain the crystals of **4**. (II) The solution of compound **2** and excess Li_2S in DMF was stirred for over 4 h, then it was filtered, a proper amount of *i*-PrOH was added into the deep red filtrate. The deep red crystals of **4** were also obtained by allowing Et_2O vapor to diffuse into the filtrate. The crystals of these two experiments were identified by X-ray single-crystal analysis and IR spectra.

Crystal Structure Determination. Crystallographic data for compounds **1**−**4** are listed in Table 1. For compound **3**, purple-black prism crystals with dimensions of $0.36 \times 0.36 \times 0.32\ mm^3$ were chosen for study, and for compound **4**, deep red prism crystals with dimensions of $0.40 \times 0.40 \times 0.31\ mm^3$ were chosen. Data were collected at room temperature on a Siemens SMART-CCD area-detector diffractometer with a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.71073$ Å). Intensity data were obtained by using an ω scan technique with scan rates of 10 s/frame and 0.3°/frame, in the range $3.32 < 2\theta < 46.54°$ for **3** and $3.32 < 2\theta < 46.62°$ for **4**. Data reductions, cell refinements, and absorption corrections were performed with SMART, SAINT, and SADABS software, respectively.

For all structural analyses, all calculations were performed on an Indy workstation of Silicon Graphics with the program SHELXTL.[20] The structures were solved by direct methods, and the positions of heavy atoms were obtained from *E* maps. The remaining non-hydrogen atoms were located from successive difference Fourier maps. The refinement of structures was performed by full-matrix least-squares techniques on F^2 using SHELXL93.[21] For **3**, the coordinates of three carbon atoms of cations were obtained from difference Fourier maps and they were fixed in the structure refinement. For **4**, some C−C bonds of cations were restrained to be equal with the deviation of 0.03 Å. The atoms in anions and nitrogen atoms were treated anisotropically; however,

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Table 1. Crystal Data for Compounds **1**−**4**

	1	**2**	**3**	**4**
empirical formula	$C_{64}H_{146}N_4O_4S_{16}Cu_{10}Mo_4$	$C_{64}H_{146}N_4O_{2.5}S_{16.5}Cu_{10}W_4$	$C_{64}H_{146}N_4O_2S_{18}Cu_{10}Mo_4$	$C_{64}H_{146}N_4OS_{19}Cu_{10}W_4$
fw	2567.97	2927.64	2600.09	2967.79
space group	$Pna2_1$	$Pna2_1$	$Pna2_1$	$Pna2_1$
a, Å	26.6097(5)	26.6045(4)	26.6997(2)	26.8141(8)
b, Å	19.1527(3)	19.1580(3)	19.3133(4)	19.4412(6)
c, Å	21.3711(3)	21.3875(1)	21.4577(3)	21.4039(5)
V, Å^3	10 891.7(3)	10 901.0(2)	11 064.9(3)	11 157.8(5)
Z	4	4	4	4
ρ_{calcd}, g/cm^3	1.566	1.784	1.561	1.767
μ, cm^{-1}	26.94	64.58	26.88	63.54
no. of unique reflcns	42 794	41 250	15 675	12 426
no. of obsd reflcns [$I > 2\sigma(I)$]	13184	8926	9284	7402
absolute structure parameter	−0.04(2)	−0.06(2)	0.02(2)	0.00
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0560	0.0821	0.0763	0.0762
$wR_2{}^b$ [$I > 2\sigma(I)$]	0.1393	0.1536	0.1776	0.1583
Goof on F^2	1.231	1.185	1.063	1.044

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR_2 = \{\sum w[(F_o{}^2 - F_c{}^2)^2]/\sum w[(F_o{}^2)^2]\}^{1/2}$, $w = [\sigma^2(F_o{}^2) + (aP)^2 + bP]^{-1}$, $P = (F_o{}^2 + 2F_c{}^2)/3$. **1**, $a = 0.0527$, $b = 49.5023$; **2**, $a = 0.0330$, $b = 237.8371$; **3**, $a = 0.1014$, $b = 4.4613$; **4**, $a = 0.0682$, $b = 87.7697$.

the positions of the hydrogen atoms were generated geometrically (C−H bond fixed at 0.96 Å), assigned isotropic thermal parameters and allowed to ride on their respective parent C atoms before the final cycle of least-squares refinements. Interatomic distances and angles for the cluster cores of **3** and **4** are shown in Tables 2 and 3, respectively.

Results and Discussion

Syntheses of Complexes 1−4. For the syntheses of complexes **1**−**4**, $[MES_3]^{2-}$ (M = Mo, W; E = S, O), CuBr and Bu_4NBr were used as starting reaction materials, and excess Li_2S was added into the reaction solution after the precursor $[MES_3]^{2-}$/CuBr clusters had been formed. The sequence of some Cu(I)-philic ligands of Mo(W)/Cu/S compounds can be described as the following: $S^{2-} > (Py, PPh_3) > X^-$, (X = Cl, Br, I, CN), the former ligands can substitute part or all of the latter ligands, so some small Mo(W)/CuX/S clusters can be assembled together by the way of S^{2-} substituting X^-, thus the larger Mo(W)/Cu/S clusters with pure sulfide ion ligands may be formed. Here the small Mo(W)/CuX/S clusters are used as building block.

According to the operation of the above experiments, the crystals of this type reaction are not sensitive to the molar ratio of starting materials of $[MES_3]^{2-}$ and CuBr. The structure determinations of **1**−**4** show that there exist transformations between $[MOS_3]^{2-}$ and $[MS_4]^{2-}$ in the reaction solution, and there are many kinds of configurations of intermediates before the formation of the final stable configuration of production. For the core of MS_4Cu_2, the linear precursor has a reversible butterfly-type configuration; For the core of MS_4Cu_3, the T-frame precursor has a reversible triprism configuration and an incomplete cubane-like configuration. At the end, two butterfly-type clusters of MES_3Cu_2, one incomplete cubane-like cluster of $ME'S_3Cu_3$ and one triprism cluster of MS_4Cu_3, are bridged by three S^{2-} to form the final framework, and all Br^- ligands are detached (M = Mo, W; E, E′ = S, O). The possible reaction pathways are illustrated in Figure 1.

Crystals and Structures of Complexes 1−4. Compounds **1**−**4** are isomorphous, and crystallized in the orthorhombic noncentrosymmetric space group $Pna2_1$. The structure of anions is shown in Figure 2, and selected relevant distances and angles of compounds **1**−**4** (range) are collected in Table 4. The anions of **1**−**4** have approximate σ symmetry, with one mirror plane S3, E′, M1, Cu3, S16, Cu8, S10, S13, and M4. The least-squares crystallographic planes show that the maximum deviation of these nine atoms from the least-squares crystallographic plane is 0.022 Å. The anions of **1**−**4** may be viewed as consisting of two butterfly-type fragments of MES_3Cu_2, one incomplete cubane-like fragment of $ME'S_3Cu_3$, and one triprism fragment of MS_4Cu_3, which are bridged by two μ_3-S and one μ_4-S atoms (M = Mo, E = E′ = O for complex **1**; M = W, E = $^1/_2$O + $^1/_2$S, E′ = O for complex **2**; M = Mo, E = S, E′ = $^1/_2$O + $^1/_2$S for complex **3**; M = W, E = E′ = S for complex **4**). In the butterfly-type fragments of MES_3Cu_2 and the incomplete cubane-like fragment of $ME'S_3Cu_3$, all the terminal atoms are O atoms for compound **1**, and all the terminal atoms are S atoms for compound **4**. For compound **2**, which is produced from $[WOS_3]^{2-}/Cu^+$, some of the terminal O atoms in the incomplete cubane-like fragments of WOS_3Cu_3 are substituted by S atoms; and all of the terminal O atoms of WOS_3Cu_2 and WOS_3Cu_3 can be substituted by S atoms if compound **2** is dissolved in the solution with the presence of excess S^{2-} and it is stirred for more than 2 h. For compound **3**, which is produced from $[MoS_4]^{2-}/Cu^+$, some of the terminal S atoms in the butterfly-type fragments of MoS_4Cu_2 are substituted by O atoms. The crystal structural analysis results indicate that the stabilities of the terminal atoms of S and O in the butterfly-type fragments of MES_3Cu_2 and incomplete cubane-like fragment of $ME'S_3Cu_3$ are quite different: the terminal O atoms are more stable than the terminal S atoms in the butterfly-type fragments of $MoES_3Cu_2$, while the terminal S atoms are more stable than the terminal O atoms in the incomplete cubane-like fragments of $WE'S_3Cu_3$. So the terminal O atoms in tetradecanuclear clusters have the stability sequence as follows: $MoOS_3Cu_2 > MoOS_3Cu_3 > WOS_3Cu_2 > WOS_3Cu_3$, while the stability of terminal S atoms follows the opposite order, $MoS_4Cu_2 < MoS_4Cu_3 < WS_4Cu_2 < WS_4Cu_3$.

There are two (μ_3-S)Cu_3 configurations after the $Cu_6M_2S_{10}$ core portion is linked by two MES_3Cu_2 side groups. This type of (μ_3-S)Cu_3 configuration is a type of distorted tetrahedron whose μ_3-S is close to Cu_3 plane, with Cu−Cu−Cu 56.64(7)−62.79(13)° and Cu−(μ_3-S)−Cu 77.79(15)−84.5(3)°. The Cu−Cu distances (2.675(2)−2.953(2) Å) in (μ_3-S)Cu_3 are longer than 2.55 Å, and this marginal covalent contribution is considered as a dispersion interaction of the d^{10} systems.[22] The Cu−S distances (2.187(9)−2.214(4) Å) in (μ_3-S)Cu_3 are distinctly shorter than the other Cu−S distances (2.218(4)−2.346(7) Å), it indicates that the interactions of Cu−S in (μ_3-S)Cu_3 are much

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(22) (a) Dehnen, S.; Schäfer, A.; Fenske, D.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 746. (b) Kölmel, C.; Ahlrichs, R. *J. Phys. Chem.* **1990**, *94*, 5536.

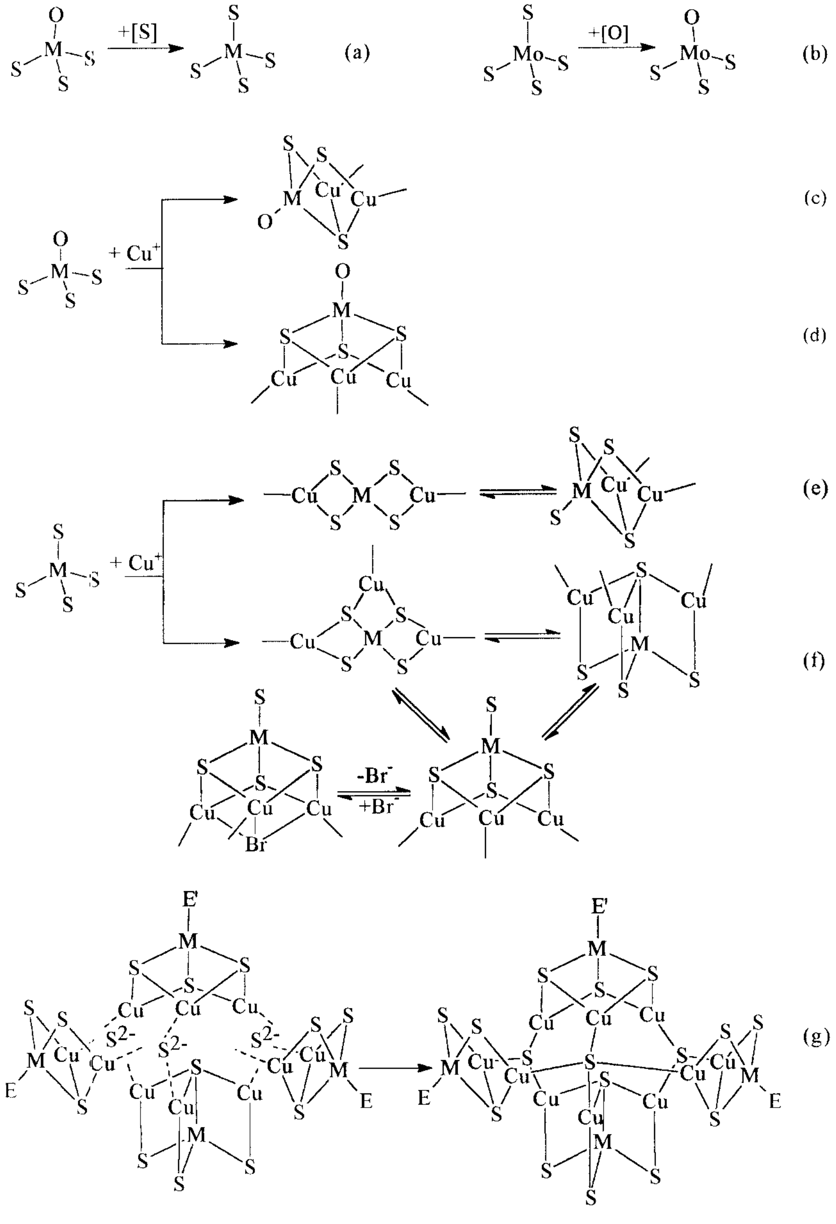


Figure 1. Possible reaction pathways.

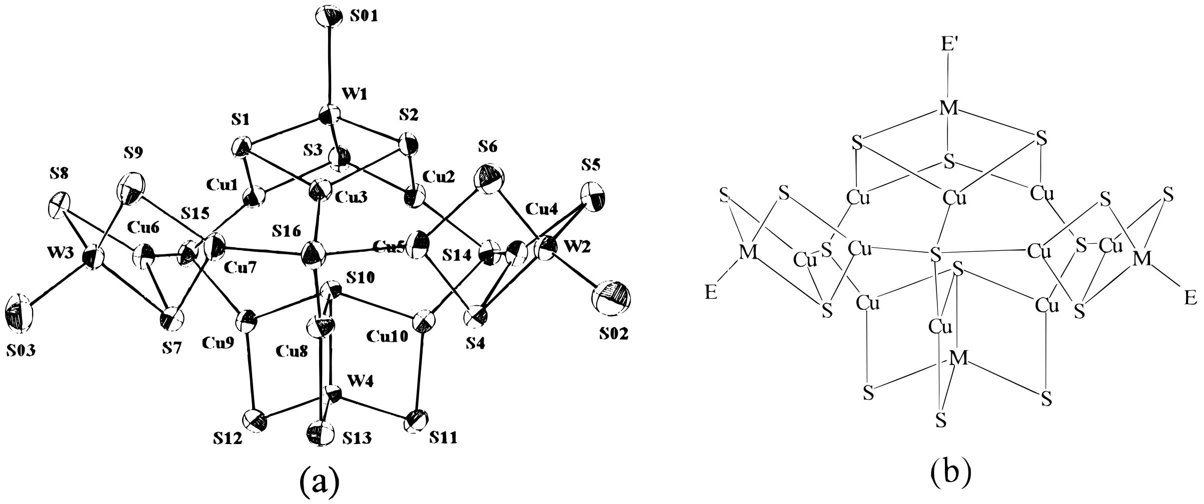


Figure 2. (a) ORTEP diagram of the anion of **1** (20% displacement ellipsoids). (b) Framework of anions of **1**−**4** (M = Mo, E = E′ = O for complex **1**; M = W, E = $^{1}/_{2}$O + $^{1}/_{2}$S, E′ = O for complex **2**; M = Mo, E = S, E′ = $^{1}/_{2}$O + $^{1}/_{2}$S for complex **3**; M = W, E = E′ = S for complex **4**).

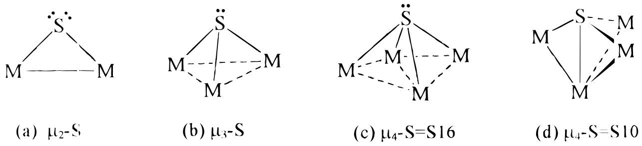
Table 2. Selected Interatoms Distances (Å) and Angles (deg) in **3**

Mo1−S01	2.132(5)	Mo3−Cu7	2.656(2)	Cu2−Cu10	2.772(3)	Cu6−S8	2.221(6)
Mo1−S1	2.246(4)	Mo3−Cu6	2.657(3)	Cu2−Cu4	2.945(3)	Cu6−S7	2.284(6)
Mo1−S3	2.255(5)	Mo4−S12	2.204(5)	Cu3−S16	2.250(5)	Cu6−Cu9	2.907(3)
Mo1−S2	2.256(4)	Mo4−S11	2.212(5)	Cu3−S1	2.273(5)	Cu7−S9	2.233(6)
Mo1−Cu2	2.682(3)	Mo4−S13	2.215(5)	Cu3−S2	2.284(4)	Cu7−S16	2.241(5)
Mo1−Cu1	2.684(3)	Mo4−S10	2.260(4)	Cu3−Cu5	2.693(3)	Cu7−S7	2.266(5)
Mo1−Cu3	2.695(2)	Mo4−Cu10	2.685(2)	Cu3−Cu7	2.727(3)	Cu7−Cu8	2.952(3)
Mo2−S02	2.023(9)	Mo4−Cu9	2.697(3)	Cu3−Cu8	2.893(3)	Cu8−S16	2.229(5)
Mo2−S6	2.210(6)	Mo4−Cu8	2.704(3)	Cu4−S14	2.196(5)	Cu8−S13	2.248(5)
Mo2−S5	2.221(5)	Cu1−S15	2.211(5)	Cu4−S5	2.232(5)	Cu8−S10	2.314(5)
Mo2−S4	2.274(5)	Cu1−S3	2.266(5)	Cu4−S4	2.274(5)	Cu9−S15	2.205(6)
Mo2−Cu4	2.659(3)	Cu1−S1	2.275(6)	Cu4−Cu10	2.898(3)	Cu9−S12	2.215(6)
Mo2−Cu5	2.666(2)	Cu1−Cu9	2.783(3)	Cu5−S16	2.226(5)	Cu9−S10	2.306(4)
Mo3−S03	2.006(10)	Cu1−Cu6	2.943(3)	Cu5−S6	2.256(5)	Cu10−S14	2.216(5)
Mo3−S9	2.218(6)	Cu2−S14	2.199(5)	Cu5−S4	2.274(5)	Cu10−S11	2.225(6)
Mo3−S8	2.230(6)	Cu2−S3	2.276(5)	Cu5−Cu8	2.920(3)	Cu10−S10	2.304(4)
Mo3−S7	2.280(5)	Cu2−S2	2.279(5)	Cu6−S15	2.199(6)		

S01−Mo1−S1	110.8(2)	S12−Mo4−Cu10	126.6(2)	S2−Cu3−Cu7	179.2(2)	S9−Cu7−Mo3	53.1(2)
S01−Mo1−S3	110.7(2)	S11−Mo4−Cu10	52.98(15)	Cu5−Cu3−Cu7	104.40(10)	S16−Cu7−Mo3	169.0(2)
S1−Mo1−S3	107.8(2)	S13−Mo4−Cu10	121.5(2)	Mo1−Cu3−Cu7	127.37(10)	S7−Cu7−Mo3	54.50(13)
S01−Mo1−S2	111.6(2)	S10−Mo4−Cu10	54.71(11)	S16−Cu3−Cu8	49.45(14)	S9−Cu7−Cu3	118.9(2)
S1−Mo1−S2	107.6(2)	S12−Mo4−Cu9	52.59(15)	S1−Cu3−Cu8	116.08(14)	S16−Cu7−Cu3	52.75(13)
S3−Mo1−S2	108.1(2)	S11−Mo4−Cu9	126.1(2)	S2−Cu3−Cu8	115.91(14)	S7−Cu7−Cu3	115.8(2)
S01−Mo1−Cu2	129.7(2)	S13−Mo4−Cu9	121.2(2)	Cu5−Cu3−Cu8	62.92(8)	Mo3−Cu7−Cu3	138.16(11)
S1−Mo1−Cu2	119.48(14)	S10−Mo4−Cu9	54.60(11)	Mo1−Cu3−Cu8	131.85(10)	S9−Cu7−Cu8	174.6(2)
S3−Mo1−Cu2	54.05(13)	Cu10−Mo4−Cu9	94.16(8)	Cu7−Cu3−Cu8	63.29(8)	S16−Cu7−Cu8	48.49(14)
S2−Mo1−Cu2	54.12(13)	S12−Mo4−Cu8	124.4(2)	S14−Cu4−S5	128.7(2)	S7−Cu7−Cu8	76.52(15)
S01−Mo1−Cu1	129.3(2)	S11−Mo4−Cu8	125.7(2)	S14−Cu4−S4	124.1(2)	Mo3−Cu7−Cu8	131.01(10)
S1−Mo1−Cu1	54.08(14)	S13−Mo4−Cu8	53.27(15)	S5−Cu4−S4	107.1(2)	Cu3−Cu7−Cu8	61.09(7)
S3−Mo1−Cu1	53.77(13)	S10−Mo4−Cu8	54.69(12)	S14−Cu4−Mo2	176.9(2)	S16−Cu8−S13	136.2(2)
S2−Mo1−Cu1	119.02(13)	Cu10−Mo4−Cu8	87.82(8)	S5−Cu4−Mo2	53.15(14)	S16−Cu8−S10	118.8(2)
Cu2−Mo1−Cu1	83.52(8)	Cu9−Mo4−Cu8	87.46(8)	S4−Cu4−Mo2	54.22(13)	S13−Cu8−S10	105.0(2)
S01−Mo1−Cu3	132.7(2)	S15−Cu1−S3	127.6(2)	S14−Cu4−Cu10	49.23(13)	S16−Cu8−Mo4	171.7(2)
S1−Mo1−Cu3	53.86(13)	S15−Cu1−S1	125.2(2)	S5−Cu4−Cu10	177.8(2)	S13−Cu8−Mo4	52.16(15)
S3−Mo1−Cu3	116.58(14)	S3−Cu1−S1	106.4(2)	S4−Cu4−Cu10	74.93(14)	S10−Cu8−Mo4	52.84(12)
S2−Mo1−Cu3	54.06(11)	S15−Cu1−Mo1	174.0(2)	Mo2−Cu4−Cu10	128.92(10)	S16−Cu8−Cu3	50.08(13)
Cu2−Mo1−Cu3	81.89(7)	S3−Cu1−Mo1	53.39(14)	S14−Cu4−Cu2	47.98(13)	S13−Cu8−Cu3	173.7(2)
Cu1−Mo1−Cu3	81.37(7)	S1−Cu1−Mo1	53.08(12)	S5−Cu4−Cu2	123.1(2)	S10−Cu8−Cu3	68.74(12)
S02−Mo2−S6	110.0(4)	S15−Cu1−Cu9	50.84(15)	S4−Cu4−Cu2	106.19(14)	Mo4−Cu8−Cu3	121.58(9)
S02−Mo2−S5	111.5(3)	S3−Cu1−Cu9	115.1(2)	Mo2−Cu4−Cu2	129.20(9)	S16−Cu8−Cu5	48.99(13)
S6−Mo2−S5	109.7(2)	S1−Cu1−Cu9	117.18(14)	Cu10−Cu4−Cu2	56.64(7)	S13−Cu8−Cu5	126.9(2)
S02−Mo2−S4	110.0(3)	Mo1−Cu1−Cu9	135.03(10)	S16−Cu5−S6	126.9(2)	S10−Cu8−Cu5	98.62(13)
S6−Mo2−S4	108.1(2)	S15−Cu1−Cu6	48.0(2)	S16−Cu5−S4	123.3(2)	Mo4−Cu8−Cu5	128.24(10)
S5−Mo2−S4	107.4(2)	S3−Cu1−Cu6	175.1(2)	S6−Cu5−S4	106.5(2)	Cu3−Cu8−Cu5	55.19(8)
S02−Mo2−Cu4	131.8(3)	S1−Cu1−Cu6	78.37(13)	S16−Cu5−Mo2	167.2(2)	S16−Cu8−Cu7	48.85(13)
S6−Mo2−Cu4	118.2(2)	Mo1−Cu1−Cu6	131.30(10)	S6−Cu5−Mo2	52.55(14)	S13−Cu8−Cu7	127.7(2)
S5−Mo2−Cu4	53.53(13)	Cu9−Cu1−Cu6	60.94(8)	S4−Cu5−Mo2	54.11(12)	S10−Cu8−Cu7	98.62(13)
S4−Mo2−Cu4	54.22(13)	S14−Cu2−S3	128.7(2)	S16−Cu5−Cu3	53.41(13)	Mo4−Cu8−Cu7	128.77(10)
S02−Mo2−Cu5	128.9(3)	S14−Cu2−S2	124.0(2)	S6−Cu5−Cu3	121.4(2)	Cu3−Cu8−Cu7	55.62(8)
S6−Mo2−Cu5	54.16(14)	S3−Cu2−S2	106.7(2)	S4−Cu5−Cu3	115.2(2)	Cu5−Cu8−Cu7	93.66(9)
S5−Mo2−Cu5	119.62(15)	S14−Cu2−Mo1	173.9(2)	Mo2−Cu5−Cu3	139.22(11)	S15−Cu9−S12	134.6(2)
S4−Mo2−Cu5	54.12(13)	S3−Cu2−Mo1	53.35(14)	S16−Cu5−Cu8	49.09(14)	S15−Cu9−S10	119.8(2)
Cu4−Mo2−Cu5	82.07(7)	S2−Cu2−Mo1	53.36(12)	S6−Cu5−Cu8	173.2(2)	S12−Cu9−S10	105.0(2)
S03−Mo3−S9	109.1(4)	S14−Cu2−Cu10	51.37(13)	S4−Cu5−Cu8	75.71(14)	S15−Cu9−Mo4	172.3(2)
S03−Mo3−S8	112.4(4)	S3−Cu2−Cu10	114.6(2)	Mo2−Cu5−Cu8	129.76(10)	S12−Cu9−Mo4	52.20(15)
S9−Mo3−S8	110.5(2)	S2−Cu2−Cu10	116.27(14)	Cu3−Cu5−Cu8	61.89(7)	S10−Cu9−Mo4	53.01(12)
S03−Mo3−S7	110.0(3)	Mo1−Cu2−Cu10	134.32(9)	S15−Cu6−S8	127.8(2)	S15−Cu9−Cu1	51.02(14)
S9−Mo3−S7	107.5(2)	S14−Cu2−Cu4	47.89(13)	S15−Cu6−S7	124.8(2)	S12−Cu9−Cu1	170.8(2)
S8−Mo3−S7	107.2(2)	S3−Cu2−Cu4	175.2(2)	S8−Cu6−S7	107.4(2)	S10−Cu9−Cu1	68.74(13)
S03−Mo3−Cu7	127.3(4)	S2−Cu2−Cu4	77.35(13)	S15−Cu6−Mo3	176.2(2)	Mo4−Cu9−Cu1	121.70(9)
S9−Mo3−Cu7	53.62(15)	Mo1−Cu2−Cu4	130.51(9)	S8−Cu6−Mo3	53.5(2)	S15−Cu9−Cu6	48.6(2)
S8−Mo3−Cu7	120.3(2)	Cu10−Cu2−Cu4	60.83(7)	S7−Cu6−Mo3	54.33(14)	S12−Cu9−Cu6	126.9(2)
S7−Mo3−Cu7	53.99(13)	S16−Cu3−S1	126.7(2)	S15−Cu6−Cu9	48.78(15)	S10−Cu9−Cu6	106.14(13)
S03−Mo3−Cu6	133.1(4)	S16−Cu3−S2	127.1(2)	S8−Cu6−Cu9	176.5(2)	Mo4−Cu9−Cu6	132.88(10)
S9−Mo3−Cu6	117.8(2)	S1−Cu3−S2	105.7(2)	S7−Cu6−Cu9	76.01(14)	Cu1−Cu9−Cu6	62.25(8)
S8−Mo3−Cu6	53.2(2)	S16−Cu3−Cu5	52.60(13)	Mo3−Cu6−Cu9	129.96(11)	S14−Cu10−S11	133.4(2)
S7−Mo3−Cu6	54.45(15)	S1−Cu3−Cu5	179.0(2)	S15−Cu6−Cu1	48.30(14)	S14−Cu10−S10	120.5(2)
Cu7−Mo3−Cu6	82.39(8)	S2−Cu3−Cu5	75.04(13)	S8−Cu6−Cu1	121.6(2)	S11−Cu10−S10	105.5(2)
S12−Mo4−S11	109.7(2)	S16−Cu3−Mo1	178.7(2)	S7−Cu6−Cu1	106.66(15)	S14−Cu10−Mo4	173.5(2)
S12−Mo4−S13	111.8(2)	S1−Cu3−Mo1	52.92(12)	Mo3−Cu6−Cu1	127.88(10)	S11−Cu10−Mo4	52.54(13)
S11−Mo4−S13	112.7(2)	S2−Cu3−Mo1	53.12(12)	Cu9−Cu6−Cu1	56.81(7)	S10−Cu10−Mo4	53.20(11)
S12−Mo4−S10	107.0(2)	Cu5−Cu3−Mo1	127.79(9)	S9−Cu7−S16	126.7(2)	S14−Cu10−Cu2	50.84(13)
S11−Mo4−S10	107.4(2)	S16−Cu3−Cu7	52.46(13)	S9−Cu7−S7	107.5(2)	S11−Cu10−Cu2	171.2(2)
S13−Mo4−S10	108.0(2)	S1−Cu3−Cu7	74.81(13)	S16−Cu7−S7	123.4(2)	S10−Cu10−Cu2	69.69(13)

Table 2 (Continued)

Mo4−Cu10−Cu2	122.84(9)	Mo1−S3−Cu1	72.8(2)	Mo3−S9−Cu7	73.3(2)	Cu4−S14−Cu10	82.1(2)
S14−Cu10−Cu4	48.65(13)	Mo1−S3−Cu2	72.6(2)	Mo4−S10−Cu10	72.08(14)	Cu2−S14−Cu10	77.79(15)
S11−Cu10−Cu4	126.3(2)	Cu1−S3−Cu2	103.8(2)	Mo4−S10−Cu9	72.39(14)	Cu6−S15−Cu9	82.6(2)
S10−Cu10−Cu4	106.36(13)	Cu4−S4−Mo2	71.55(14)	Cu10−S10−Cu9	117.5(2)	Cu6−S15−Cu1	83.7(2)
Mo4−Cu10−Cu4	132.14(10)	Cu4−S4−Cu5	100.5(2)	Mo4−S10−Cu8	72.47(14)	Cu9−S15−Cu1	78.1(2)
Cu2−Cu10−Cu4	62.53(8)	Mo2−S4−Cu5	71.77(15)	Cu10−S10−Cu8	108.1(2)	Cu5−S16−Cu8	81.9(2)
Mo1−S1−Cu3	73.21(14)	Mo2−S5−Cu4	73.3(2)	Cu9−S10−Cu8	107.8(2)	Cu5−S16−Cu7	147.0(2)
Mo1−S1−Cu1	72.8(2)	Mo2−S6−Cu5	73.3(2)	Mo4−S11−Cu10	74.5(2)	Cu8−S16−Cu7	82.7(2)
Cu3−S1−Cu1	100.9(2)	Cu7−S7−Mo3	71.5(2)	Mo4−S12−Cu9	75.2(2)	Cu5−S16−Cu3	74.0(2)
Mo1−S2−Cu2	72.52(14)	Cu7−S7−Cu6	100.6(2)	Mo4−S13−Cu8	74.6(2)	Cu8−S16−Cu3	80.5(2)
Mo1−S2−Cu3	72.82(13)	Mo3−S7−Cu6	71.2(2)	Cu4−S14−Cu2	84.1(2)	Cu7−S16−Cu3	74.8(2)
Cu2−S2−Cu3	101.1(2)	Cu6−S8−Mo3	73.3(2)				



(a) μ_2-S (b) μ_3-S (c) μ_4-S=S16 (d) μ_4-S=S10

Figure 3. Structural types of bridge sulfide ion in the cluster cores.

stronger, and this (μ_3-S)Cu_3 configuration has a stability effect on the core. This type of (μ_3-S)Cu_3 configuration is very common in polynuclear Cu/S compounds,[22] such as $[Cu_{12}S_8]^{4-}$ [23] which has several (μ_3-S)Cu_3 with Cu−(μ_3-S)−Cu 79.75(6)−86.08(6)°, Cu−Cu 2.774(1)−2.950(1) Å, and Cu−S 2.156(2)−2.179(2) Å. However, complexes **1**−**4** are the first series of examples that there exist (μ_3-S)Cu_3 and (μ_4-S)Cu_4 configurations in Mo(W)/Cu/S heterobimetallic clusters.

Each M atom has slightly distorted tetrahedral coordination (106.9(11)−113.7(6)°). There are four types of coordinations for sulfide ion ligands in the cores (shown in Figure 3). For each cluster, M−(μ_2-S) distances are shorter than that of M−(μ_4-S), and the average length of M−(μ_2-S) is shorter than that of M−(μ_3-S). Because of steric effect, the Cu−M4−Cu angles in triprism fragment of MS_4Cu_3 are larger than other Cu−M*−Cu (M* = M1, M2, M3). These interatomic distance and angle characterizations are similar to that of $[M_8Cu_{12}S_{28}O_4]^{4-}$ [16] (M = Mo, W).

Two kinds of S atoms are present in the cores: S_M (S_M is on behalf of the S atoms in the MOS_3 and MS_4 moieties, M = Mo, W) and bridge S_B (S_B = S14, S15, S16). These two kinds of S atoms have different coordination angles. For example, S_B−Cu−S_M angles (118.8(2)−136.5(3)°) are larger than S_M−Cu−S_M (103.4(2)−107.5(2)°), and M−S_M−Cu angles (71.2(2)−75.5(3)°) slightly vary.

There are two groups of M−Cu lengths: one is in the butterfly-type subunit of MES_3Cu_2, whose M/Cu coordination molar ratio is 1:2; another is in the incomplete cubane-like subunit of $ME'S_3Cu_3$ and one triprism subunit of MS_4Cu_3, whose M/Cu coordination molar ratio is 1:3. The lengths in the first group of M−Cu are shorter than in the second. W−Cu distances of these compounds are shown in Table 5. It indicates that M−Cu lengths are related to coordination molar ratio M:Cu, ligands and configuration.

IR and Raman Spectra. In general, the absorptions around 900 cm^{-1} in IR and Raman spectra are attributed to the M−O_t stretching vibrations, and those in the range of 400−500 cm^{-1}, to the M−S stretching vibrations (M = Mo, W).[25] An obvious red-shift trend for the M−S stretching vibration is observed as the corresponding sulfur atom is more bonded, the sequence for the M−S stretching vibration frequences is as the following: M−S_t > M−(μ_2-S) > M−(μ_3-S) > M−(μ_4-S). This is consistent with the sequences of their bond lengths. So the absorptions around 500 cm^{-1} can be attributed to the M−S_t stretching vibrations. In the range of 120−380 cm^{-1} of Raman spectra, the absorption of ν(Cu−S) is in the high wave frequencies, and that of $\delta(MES_3)$ is in the low. For the isostructural Mo(W)/Cu/S compounds, the M−S_t and M−O_t stretching vibrations have frequencies as the following: ν(Mo−S_t) > ν(W−S_t), ν(Mo−O_t) < ν(W−O_t). This is consistent with the results of reference.[25]

UV−Visible Spectra. Because **1**−**4** are the complexes of $[MES_3]^{2-}/Cu^+$ with pure S^{2-} ligands, the three strong absorption bands (ν_1, ν_2, ν_3) are attributed to ligand-to-metal charge-transfer transitions within the $MoES_3$ units (E = S, O).[25] It also shows that the ν_1 bands are shifted in the direction of longer wavelength in Mo(W)/Cu/S clusters after coordination of copper(I) to $MoES_3$ moieties. In addition, the Mo/Cu/S compounds absorption bands of ν_1 and ν_2 show red-shifts correspondingly when they are compared with isostructural W/Cu/S compounds.

^{95}Mo NMR Spectra. The previous research of ^{95}Mo NMR spectroscopy shows that the ^{95}Mo chemical shift decreases monotonically as the value of x or n increases in $[(LCu)_x MoO_nS_{4-n}]^{2-}$ (L = RS^-, CN^-, Cl^-, Br^-, I^-) species, while it slightly alters as the nature of the L ligand attached to the Cu atom is changed,[5c,8c] thus ^{95}Mo NMR spectra can clearly identify the value of x when n is given, and it can also identify the value of n when that of x is known, it provides an effective measure to distinguish and identify the configurations of Mo/Cu/S clusters in the solution. Compounds **1** and **3** were examined by ^{95}Mo NMR (shown in Table 6), which indicated that there are three different kinds of coordination environments of Mo in each complex in solution. These ^{95}Mo chemical shifts agree well with the corresponding values of x and n in $[(LCu)_x MoO_nS_{4-n}]^{2-}$, thus they can be attributed easily. For complex **1**, the chemical shifts of 1224, 877, and 481 ppm may be attributed to that of MoS_4Cu_3, $MoOS_3Cu_2$, and $MoOS_3Cu_3$ fragments, respectively; For complex **3**, the chemical shifts of 1547, 1216, and 1154 ppm are associated with MoS_4Cu_2, MoS_4Cu_3, and $MoOS_3Cu_2$ fragments, respectively. Complexes **1** and **3** are the first example of Mo−Cu−S clusters which have three kinds of coordination environments of Mo. ^{95}Mo NMR peaks have narrow line with (30 hertz), and do not shift in position during the recording of these spectra, suggesting that these two compounds are stable in DMF solution.

Cyclic Voltammetry. All the complexes exhibit the similar redox behaviors. Compared with the other Mo(W)/Cu/S compounds, complexes **1**−**4** have more irreversible electrochemical reductions between 0.11 and −1.28 V (shown in Table 7), which may be related with the state that every cluster core

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Table 3. Selected Interatoms Distances (Å) and Angles (deg) in **4**

W1−S01	2.158(9)	W3−Cu7	2.675(3)	Cu2−Cu10	2.783(5)	Cu6−S8	2.254(8)
W1−S3	2.218(9)	W3−Cu6	2.684(4)	Cu2−Cu4	2.939(5)	Cu6−S7	2.289(9)
W1−S1	2.235(7)	W4−S11	2.202(8)	Cu3−S16	2.249(9)	Cu6−Cu9	2.890(5)
W1−S2	2.246(7)	W4−S12	2.214(8)	Cu3−S2	2.288(8)	Cu7−S16	2.244(8)
W1−Cu1	2.694(4)	W4−S13	2.216(9)	Cu3−S1	2.306(7)	Cu7−S9	2.258(9)
W1−Cu2	2.699(4)	W4−S10	2.276(7)	Cu3−Cu7	2.699(5)	Cu7−S7	2.291(9)
W1−Cu3	2.704(4)	W4−Cu10	2.709(4)	Cu3−Cu5	2.721(5)	Cu7−Cu8	2.920(5)
W2−S02	2.085(14)	W4−Cu9	2.714(3)	Cu3−Cu8	2.892(5)	Cu8−S16	2.244(10)
W2−S6	2.227(10)	W4−Cu8	2.724(4)	Cu4−S14	2.193(11)	Cu8−S13	2.276(10)
W2−S5	2.238(11)	Cu1−S15	2.187(9)	Cu4−S5	2.229(10)	Cu8−S10	2.325(8)
W2−S4	2.269(8)	Cu1−S3	2.288(8)	Cu4−S4	2.294(10)	Cu9−S15	2.213(8)
W2−Cu5	2.679(3)	Cu1−S1	2.291(9)	Cu4−Cu10	2.899(6)	Cu9−S12	2.231(10)
W2−Cu4	2.685(5)	Cu1−Cu9	2.769(5)	Cu5−S16	2.219(8)	Cu9−S10	2.346(7)
W3−S03	2.107(12)	Cu1−Cu6	2.950(5)	Cu5−S6	2.254(10)	Cu10−S14	2.213(9)
W3−S9	2.205(9)	Cu2−S14	2.213(9)	Cu5−S4	2.275(9)	Cu10−S11	2.227(9)
W3−S8	2.226(9)	Cu2−S3	2.267(8)	Cu5−Cu8	2.934(5)	Cu10−S10	2.326(7)
W3−S7	2.259(8)	Cu2−S2	2.315(10)	Cu6−S15	2.201(9)		
S01−W1−S3	109.8(4)	S11−W4−Cu10	52.7(2)	Cu7−Cu3−W1	104.2(2)	S16−Cu7−W3	167.5(3)
S01−W1−S1	110.3(3)	S12−W4−Cu10	126.2(3)	Cu5−Cu3−W1	127.4(2)	S9−Cu7−W3	52.3(2)
S3−W1−S1	108.9(3)	S13−W4−Cu10	121.7(3)	S16−Cu3−Cu8	49.9(2)	S7−Cu7−W3	53.4(2)
S01−W1−S2	110.8(3)	S10−W4−Cu10	54.8(2)	S2−Cu3−Cu8	116.4(3)	S16−Cu7−Cu3	53.2(2)
S3−W1−S2	108.6(3)	S11−W4−Cu9	126.7(3)	S1−Cu3−Cu8	116.2(2)	S9−Cu7−Cu3	121.4(3)
S1−W1−S2	108.4(3)	S12−W4−Cu9	52.7(2)	Cu7−Cu3−Cu8	62.85(15)	S7−Cu7−Cu3	115.4(3)
S01−W1−Cu1	128.5(3)	S13−W4−Cu9	121.8(2)	Cu5−Cu3−Cu8	131.1(2)	W3−Cu7−Cu3	139.2(2)
S3−W1−Cu1	54.5(2)	S10−W4−Cu9	55.2(2)	W1−Cu3−Cu8	62.94(14)	S16−Cu7−Cu8	49.4(2)
S1−W1−Cu1	54.5(2)	Cu10−W4−Cu9	94.31(11)	S14−Cu4−S5	127.2(4)	S9−Cu7−Cu8	174.0(3)
S2−W1−Cu1	120.7(2)	S11−W4−Cu8	124.6(2)	S14−Cu4−S4	126.5(4)	S7−Cu7−Cu8	76.1(2)
S01−W1−Cu2	129.6(3)	S12−W4−Cu8	125.4(3)	S5−Cu4−S4	106.3(4)	W3−Cu7−Cu8	129.5(2)
S3−W1−Cu2	53.9(2)	S13−W4−Cu8	53.7(3)	S14−Cu4−W2	176.1(3)	Cu3−Cu7−Cu8	61.81(12)
S1−W1−Cu2	120.1(2)	S10−W4−Cu8	54.5(2)	S5−Cu4−W2	53.2(3)	S16−Cu8−S13	136.5(3)
S2−W1−Cu2	54.9(2)	Cu10−W4−Cu8	87.84(13)	S4−Cu4−W2	53.5(2)	S16−Cu8−S10	118.9(3)
Cu1−W1−Cu2	83.89(12)	Cu9−W4−Cu8	88.17(12)	S14−Cu4−Cu10	49.1(2)	S13−Cu8−S10	104.5(3)
S01−W1−Cu3	132.5(3)	S15−Cu1−S3	129.7(4)	S5−Cu4−Cu10	176.3(4)	S16−Cu8−W4	171.8(3)
S3−W1−Cu3	117.7(2)	S15−Cu1−S1	124.9(3)	S4−Cu4−Cu10	77.4(2)	S13−Cu8−W4	51.7(2)
S1−W1−Cu3	54.7(2)	S15−Cu1−W1	174.0(3)	W2−Cu4−Cu10	130.5(2)	S10−Cu8−W4	52.9(2)
S2−W1−Cu3	54.1(2)	S3−Cu1−W1	52.1(2)	S14−Cu4−Cu2	48.5(2)	S16−Cu8−Cu3	50.0(2)
Cu1−W1−Cu3	82.61(11)	S1−Cu1−W1	52.5(2)	S5−Cu4−Cu2	121.5(3)	S13−Cu8−Cu3	173.4(3)
Cu2−W1−Cu3	81.99(12)	S15−Cu1−Cu9	51.4(2)	S4−Cu4−Cu2	107.6(2)	S10−Cu8−Cu3	68.9(2)
S02−W2−S6	107.9(6)	S3−Cu1−Cu9	115.4(3)	W2−Cu4−Cu2	127.7(2)	W4−Cu8−Cu3	121.8(2)
S02−W2−S5	113.7(6)	S1−Cu1−Cu9	117.2(2)	Cu10−Cu4−Cu2	56.94(13)	S16−Cu8−Cu7	49.4(2)
S6−W2−S5	110.2(4)	W1−Cu1−Cu9	134.26(15)	S16−Cu5−S6	126.2(4)	S13−Cu8−Cu7	126.8(3)
S02−W2−S4	110.4(5)	S15−Cu1−Cu6	48.0(2)	S16−Cu5−S4	125.0(3)	S10−Cu8−Cu7	98.9(2)
S6−W2−S4	107.7(3)	S3−Cu1−Cu6	176.0(3)	S6−Cu5−S4	106.5(3)	W4−Cu8−Cu7	128.2(2)
S5−W2−S4	106.9(4)	S1−Cu1−Cu6	78.4(2)	S16−Cu5−W2	168.9(3)	Cu3−Cu8−Cu7	55.35(13)
S02−W2−Cu5	126.0(5)	W1−Cu1−Cu6	130.6(2)	S6−Cu5−W2	52.8(3)	S16−Cu8−Cu5	48.5(2)
S6−W2−Cu5	53.8(3)	Cu9−Cu1−Cu6	60.61(13)	S4−Cu5−W2	53.8(2)	S13−Cu8−Cu5	127.8(3)
S5−W2−Cu5	120.3(3)	S14−Cu2−S3	128.8(4)	S16−Cu5−Cu3	53.0(2)	S10−Cu8−Cu5	98.6(2)
S4−W2−Cu5	54.0(2)	S14−Cu2−S2	125.5(3)	S6−Cu5−Cu3	117.8(3)	W4−Cu8−Cu5	128.8(2)
S02−W2−Cu4	135.0(6)	S3−Cu2−S2	104.6(3)	S4−Cu5−Cu3	117.0(3)	Cu3−Cu8−Cu5	55.67(13)
S6−W2−Cu4	117.1(3)	S14−Cu2−W1	174.0(3)	W2−Cu5−Cu3	138.1(2)	Cu7−Cu8−Cu5	93.9(2)
S5−W2−Cu4	52.9(3)	S3−Cu2−W1	52.2(2)	S16−Cu5−Cu8	49.3(2)	S15−Cu9−S12	134.8(3)
S4−W2−Cu4	54.4(3)	S2−Cu2−W1	52.6(2)	S6−Cu5−Cu8	175.3(3)	S15−Cu9−S10	120.0(3)
Cu5−W2−Cu4	82.21(12)	S14−Cu2−Cu10	51.0(2)	S4−Cu5−Cu8	77.4(2)	S12−Cu9−S10	104.8(3)
S03−W3−S9	109.9(5)	S3−Cu2−Cu10	115.9(3)	W2−Cu5−Cu8	131.2(2)	S15−Cu9−W4	172.7(3)
S03−W3−S8	111.1(4)	S2−Cu2−Cu10	117.9(3)	Cu3−Cu5−Cu8	61.39(12)	S12−Cu9−W4	52.1(2)
S9−W3−S8	109.8(4)	W1−Cu2−Cu10	134.8(2)	S15−Cu6−S8	129.3(3)	S10−Cu9−W4	52.8(2)
S03−W3−S7	109.9(4)	S14−Cu2−Cu4	47.9(3)	S15−Cu6−S7	124.9(3)	S15−Cu9−Cu1	50.6(2)
S9−W3−S7	108.5(3)	S3−Cu2−Cu4	176.2(3)	S8−Cu6−S7	105.7(3)	S10−Cu9−Cu1	69.5(2)
S8−W3−S7	107.6(3)	S2−Cu2−Cu4	79.0(2)	S15−Cu6−W3	176.2(3)	W4−Cu9−Cu1	122.27(14)
S03−W3−Cu7	128.4(4)	W1−Cu2−Cu4	131.3(2)	S8−Cu6−W3	52.7(2)	S15−Cu9−Cu6	48.9(2)
S9−W3−Cu7	54.1(2)	Cu10−Cu2−Cu4	60.81(13)	S7−Cu6−W3	53.3(2)	S12−Cu9−Cu6	126.0(3)
S8−W3−Cu7	120.6(2)	S16−Cu3−S2	126.6(3)	S15−Cu6−Cu9	49.3(2)	S10−Cu9−Cu6	106.2(2)
S7−W3−Cu7	54.5(2)	S16−Cu3−S1	128.4(3)	S8−Cu6−Cu9	178.0(3)	W4−Cu9−Cu6	131.7(2)
S03−W3−Cu6	131.9(4)	S2−Cu3−S1	104.5(3)	S7−Cu6−Cu9	75.7(2)	Cu1−Cu9−Cu6	62.79(13)
S9−W3−Cu6	118.2(3)	S16−Cu3−Cu7	53.0(2)	W3−Cu6−Cu9	128.8(2)	S14−Cu10−S11	135.3(4)
S8−W3−Cu6	53.7(2)	S2−Cu3−Cu7	179.2(3)	S15−Cu6−Cu1	47.5(2)	S14−Cu10−S10	119.4(3)
S7−W3−Cu6	54.4(2)	S1−Cu3−Cu7	76.0(2)	S8−Cu6−Cu1	123.9(3)	S11−Cu10−S10	104.8(3)
Cu7−W3−Cu6	82.66(11)	S16−Cu3−Cu5	178.8(3)	S7−Cu6−Cu1	106.3(2)	S14−Cu10−W4	172.2(3)
S11−W4−S12	109.8(3)	S2−Cu3−Cu5	52.7(2)	W3−Cu6−Cu1	128.8(2)	S11−Cu10−W4	51.9(2)
S11−W4−S13	111.4(3)	S1−Cu3−Cu5	52.2(2)	Cu9−Cu6−Cu1	56.60(12)	S10−Cu10−W4	53.1(2)
S12−W4−S13	112.1(3)	Cu7−Cu3−Cu5	127.8(2)	S16−Cu7−S9	127.3(4)	S14−Cu10−Cu2	51.0(2)
S11−W4−S10	107.4(3)	S16−Cu3−W1	52.0(2)	S16−Cu7−S7	124.1(3)	S11−Cu10−Cu2	170.8(3)
S12−W4−S10	107.7(3)	S2−Cu3−W1	75.3(2)	S9−Cu7−S7	105.6(3)	S10−Cu10−Cu2	68.4(2)
S13−W4−S10	108.2(3)	S1−Cu3−W1	178.7(3)				

Table 3 (Continued)

W4−Cu10−Cu2	121.42(15)	W1−S3−Cu2	74.0(3)	W3−S9−Cu7	73.6(3)	Cu4−S14−Cu10	82.3(3)
S14−Cu10−Cu4	48.6(3)	W1−S3−Cu1	73.4(3)	W4−S10−Cu10	72.1(2)	Cu2−S14−Cu10	77.9(3)
S11−Cu10−Cu4	126.7(3)	Cu2−S3−Cu1	104.6(3)	W4−S10−Cu8	72.6(2)	Cu1−S15−Cu6	84.5(3)
S10−Cu10−Cu4	105.4(2)	W2−S4−Cu5	72.2(3)	Cu10−S10−Cu8	108.3(3)	Cu1−S15−Cu9	78.0(3)
W4−Cu10−Cu4	132.2(2)	W2−S4−Cu4	72.1(3)	W4−S10−Cu9	71.9(2)	Cu6−S15−Cu9	81.8(3)
Cu2−Cu10−Cu4	62.25(14)	Cu5−S4−Cu4	101.0(3)	Cu10−S10−Cu9	116.7(3)	Cu5−S16−Cu7	82.2(3)
W1−S1−Cu1	73.0(2)	Cu4−S5−W2	73.9(3)	Cu8−S10−Cu9	108.2(3)	Cu5−S16−Cu8	146.7(4)
W1−S1−Cu3	73.1(2)	W2−S6−Cu5	73.4(3)	W4−S11−Cu10	75.4(3)	Cu7−S16−Cu8	81.2(3)
Cu1−S1−Cu3	101.6(3)	W3−S7−Cu7	72.0(2)	W4−S12−Cu9	75.3(3)	Cu5−S16−Cu3	75.0(3)
W1−S2−Cu3	73.2(2)	W3−S7−Cu6	72.3(2)	W4−S13−Cu8	74.6(3)	Cu7−S16−Cu3	80.1(3)
W1−S2−Cu2	72.5(3)	Cu7−S7−Cu6	101.2(3)	Cu4−S14−Cu2	83.7(4)	Cu8−S16−Cu3	73.8(3)
Cu3−S2−Cu2	100.7(3)	W3−S8−Cu6	73.6(3)				

Table 4. Summary of Relevant Distances (Å) and Angles (deg) in Compounds **1**−**4** (Range)

	1	**2**	**3**	**4**
Cu−Cu	2.675(2)−2.953(2)	2.718(5)−2.937(6)	2.693(3)−2.952(3)	2.699(5)−2.950(5)
M−Cu (in MES_3Cu_2)	2.660(2)−2.677(2)	2.670(4)−2.692(4)	2.656(2)−2.666(2)	2.679(3)−2.685(5)
M−Cu (in $MESCu_3$)	2.682(2)−2.713(2)	2.693(4)−2.724(4)	2.682(3)−2.704(3)	2.694(4)−2.724(4)
M−(μ_2-S)	2.206(4)−2.231(4)	2.198(9)−2.235(10)	2.204(5)−2.230(6)	2.202(8)−2.238(11)
M−(μ_3-S)	2.262(4)−2.278(3)	2.229(10)−2.275(9)	2.246(4)−2.280(5)	2.218(9)−2.246(7)
M−(μ_4-S)	2.261(3)	2.255(8)	2.260(4)	2.276(7)
Cu−S (in (μ_3-S)Cu_3)	2.202(4)−2.214(4)	2.196(9)−2.202(10)	2.196(5)−2.216(5)	2.167(9)−2.213(9)
other Cu−S	2.218(4)−2.316(3)	2.211(9)−2.335(8)	2.221(6)−2.314(5)	2.219(8)−2.346(7)
Cu−(μ_3-S)−Cu (in (μ_3-S)Cu_3)	78.06(11)−83.50(13)	78.1(3)−83.6(3)	77.79(5)−84.1(2)	77.9(3)−84.5(3)
Cu−Cu−Cu (in (μ_3-S)Cu_3)	56.84(5)−62.79(6)	57.02(13)−62.66(14)	56.64(7)−62.53(8)	56.60(12)−62.79(13)
S_M−M−S_M and S_M−M−E	106.90(11)−112.5(3)	107.1(3)−112.2(4)	107.0(2)−112.7(2)	107.4(3)−113.7(6)
M−S_M−Cu	71.48(10)−75.10(12)	71.5(3)−75.5(3)	71.2(2)−75.2(2)	71.9(3)−75.4(3)
S_M−Cu−S_M	103.69(7)−107.20(13)	103.4(2)−107.3(3)	105.0(2)−107.5(2)	104.5(3)−106.5(3)
S_B−Cu−S_M	119.30(13)−136.03(15)	119.0(3)−136.3(4)	118.8(2)−136.2(2)	118.9(3)−135.6(3)
Cu−M*−Cu (M* = M1, M2, M3)	82.31(5)−83.80(6)	82.23(13)−84.24(12)	81.37(7)−83.52(8)	81.99(12)−83.82(12)
Cu−M4−Cu	87.66(6)−94.04(6)	87.73(13)−94.39(13)	87.46(8)−94.16(8)	87.84(13)−94.31(11)

Table 5. Summary of W−Cu Lengths in Certain W−Cu−S Compounds

	W−Cu lengths (Å)	structural type	ref
portion of W/Cu = 1:2			
2, in WOS_3Cu_2	2.670(4)−2.692(4)		this work
4, in WS_4Cu_2	2.679(3)−2.685(5)		this work
$[PPh_4]_2[WS_4Cu_2Cl_2]$	2.614(4)−2.625(4)	linear	6
$[WS_4Cu_2(PPh_3)_3]\cdot 0.8CH_2Cl_2$	2.670(3)−2.809(3)	linear	24
portion of W/Cu = 1:3			
2, in $WE'S_3Cu_3$ and WS_4Cu_3	2.693(4)−2.724(4)		this work
4, in WS_4Cu_3	2.694(4)−2.724(4)		this work
$[PPh_4]_2[WS_4Cu_3Cl_3]\cdot H_3CN$	2.627(2)−2.638(2)	T-frame	8b
$[NPr_4]_2[WOS_3Cu_3Cl_3]$	2.647(2)−2.651(2)	incompete cubane-like	9
$[(Ph_2PCH_2PPh_2)_3Cu_3WS_4]ClO_4$	2.790(3)−2.834(3)	triprism	11
$[WS_4Cu_3Cl(PPh_3)_3]$	2.695(2)−2.734(2)	cubane-like	24
$[WOS_3Cu_3Cl(PPh_3)_3]$	2.721(2)−2.763(2)	cubane-like	24
$[NEt_4]_3[[WS_4Cu_3Cl_4]\cdot NEt_4Cl$	2.770(7)−2.833(6)	cubane-like	9

Table 6. ^{95}Mo NMR Spectra Data (ppm)

	solvent	δ(Mo)[a]	ref
$(NH_4)_2MoS_4$	CH_3CN	2207 (<10)	5c
$[Ph_4P]_2[(BrCu)_2MoS_4]$	DMF	1632 (600)	8c
$[(n\text{-}Pr)_4N]_2[(ClCu)_2MoS_4]$	DMF	1618 (250)	8c
$[(n\text{-}Pr)_4N]_2[(CNCu)_2MoS_4]$	CH_3CN	1616 (250)	5c
$[(n\text{-}Pr)_4N]_2[(PhSCu)_2MoS_4]$	CH_3CN	1700 (250)	26
$[Ph_4P]_2[(BrCu)_3MoS_4]$	DMF	1272 (250)	8c
$[Ph_4P]_2[(BrCu)_3MoS_4]$	DMF	1234 (200)	8c
$[(n\text{-}Pr)_4N]_2[(ICu)_3MoS_4]$	CH_3CN	1282 (170)	8c
$(NH_4)_2MoOS_3$	CH_3CN	1587 (<10)	5c
$[Ph_4P]_2[(PhSCu)_2MoOS_3]$	DMF	892 (100)	8c
$[Ph_4P]_2[(ClCu)_3MoOS_3]$	CH_2Cl_2	474 (20)	8c
$[(n\text{-}Bu)_4N]_4[Mo_4Cu_{10}S_{16}O_3]\cdot H_2O$ (**1**)	DMF	1224, 877, 481 (30)	this work
$[(n\text{-}Bu)_4N]_4[Mo_4Cu_{10}S_{18}O]\cdot H_2O$ (**3**)	DMF	1547, 1216, 1154 (30)	this work

[a] Relative to external 2 M Na_2MoO_4 in D_2O, effective pH 11; line widths in parentheses (in Hz).

in the solution is composed of several Mo(W)/Cu/S fragments so they have rich reduction behavior. According to the previous research of cyclic voltammetry of Mo(W)/Cu/S complexes,[6,10,27,28] the anodic wave of about 1.18 v is attributed to the irreversible oxidation of MES_3 (M = Mo, W; E = S, O) groups, and the E_4(red) and E_5(red) cathodic waves are associated with the irreversible reductions of M^{VI}, and the quasireversible redox

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Table 7. Cyclic Voltammograms Data [V]

	E_1(ox)	E_2(ox)	E_2(red)	E_3(ox)	E_3(red)	E_4(red)	E_5(red)	ref
$[(\mu_2\text{-Br})Br_3Cu_3MoOS_3]^{3-}$		0.50	0.42	−0.36				10a
$[(AsPh_3)_3Cu_3BrWOS_3]$		0.52	0.40		−1.53			27
$[BrCl_2Cu_3MoOS_3]^{2-}$		0.51	0.40		0.18	−1.75		28
$[Cl_3Cu_3WS_4]^{2-}$	0.93	0.45			0.30			6
$[(CN)_2Cu_2WS_4]^{2-}$	1.25				0.02			6
$[Mo_4Cu_{10}S_{16}O_3]^{4-}$ (**1**)	1.18	0.74	0.65		0.05	−0.51	−0.84	this work
$[W_4Cu_{10}S_{16.5}O_{2.5}]^{4-}$ (**2**)	1.16	0.75	0.70		0.11	−0.60	−1.22	this work
$[Mo_4Cu_{10}S_{18}O]^{4-}$ (**3**)	1.22	0.75	0.68		0.11	−0.72	−1.28	this work
$[W_4Cu_{10}S_{19}]^{4-}$ (**4**)	1.19	0.72	0.63			−0.68	−1.20	this work

couples at about 0.74 and 0.65 V and the E_3(red) cathodic wave are attributed to the redox behavior of Cu^I.

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Supporting Information Available: Complete listings of crystallographic data, atomic positional parameters and their estimated standard deviations bond distances and angles, and anisotropic displacement parameters (28 pages). Ordering information is given on any current masthead page.

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