Carbon–Sulfur Bond Formation through the Reaction of Sulfur-Bridged Molybdenum Clusters with Acetylene. X-ray Structures of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 7H_2O$ and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu_3\text{-}S_2C_2H_2)(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 7H_2O$

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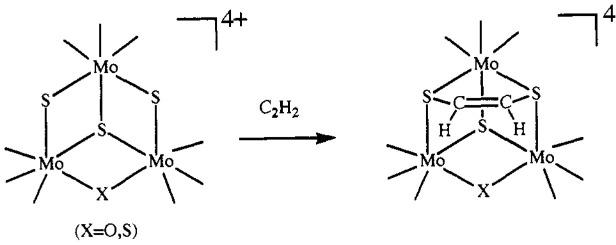
Sulfide (S^{2-}), disulfide (S_2^{2-}), and thiolate (SR^-) ligands combine metal ions to give complex and varied types of metal coordination compounds, and much attention has been paid not only to metal-centered chemistry but also to ligand-centered chemistry because of the interesting characteristics of such compounds and their potential use as catalysts.[1–6]

We describe here the reaction of incomplete cubane-type molybdenum aqua clusters $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (**A**) and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ (**B**) with acetylene to produce clusters with alkenedithiolate ligands $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu_3\text{-}S_2C_2H_2)(H_2O)_9]^{4+}$ (**C**) and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)(\mu_3\text{-}S_2C_2H_2)(H_2O)_9]^{4+}$ (**D**), respectively, with *carbon–sulfur bond formation* as shown in Scheme I. The acetylene addition in **C** was confirmed by the X-ray structure analysis of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu_3\text{-}S_2C_2H_2)(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 7H_2O$ (**C'**). The structure of the starting material $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 7H_2O$ (**A'**) also was reported for comparison. No report has appeared on the reaction of trinuclear metal clusters with acetylene or acetylene derivatives to form carbon-bridging-sulfur bonds.

Examples of *carbon-bridging-sulfur bond formation* through the reaction of sulfur-bridged metal compounds with acetylene and acetylene derivatives are rather limited. Rakowski DuBois and co-workers developed the chemistry of the reaction of dinuclear molybdenum compounds, such as $[\{(C_5H_5)Mo(\mu\text{-}S)(\mu\text{-}SH)\}_2]$, with acetylene.[7] The chemistry of dinuclear sulfur-bridged iron[8] and vanadium[9] compounds has also been reported.

Several other types of carbon–sulfur bond formation have been reported. Stiefel and co-workers[10] and Coucouvanis and co-workers[11] reported addition of activated acetylenes to coordinated polysulfide ligands of molybdenum compounds to form new C–S bonds. Similar reactions have been reported for iron[12] and tungsten[13] compounds. The reaction of sulfur-containing tungsten compounds with organic electrophiles, such as MeN=C=O and $Ph_2C=C=O$,[14] and the reaction of thiols with acetylene using Pd complex catalysts also are interesting.[15] Very recently the reaction of phenylacetylene with the Se–Se bond of $[Fe_2(CO)_6(\mu\text{-}Se_2)]$ was reported.[16]

Scheme I. Reaction of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}X)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (X = O, S) with Acetylene (Aqua ligands and Mo–Mo bonds are omitted for clarity.)



The acetylene adduct **C** was obtained by passing acetylene slowly for several minutes through a green solution of **A**[17] (3.18×10^{-2} M per trimer, 50 mL) in 1 M HCl in a conical flask. The flask was sealed, and the solution turned to dark green immediately, indicating the formation of **C**. After 1 h, the resultant acetylene adduct was absorbed on a Dowex 50W-X2 cation exchanger (diameter 1.0 cm, length 15.0 cm). The resin was washed with 0.1 M HPTS (*p*-toluenesulfonic acid) to remove Cl^- ion, and a dark brownish green solution was obtained by slow elution with 4 M HPTS. Cooling of the solution in a freezer for a couple of weeks gave brownish black crystals. The crystals were analyzed to be $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu_3\text{-}S_2C_2H_2)(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 7H_2O$ (**C'**). Anal. Found (calcd for $Mo_3S_7O_{29}C_{30}H_{62}$): C, 25.84 (25.74); H, 4.24 (4.54). The other acetylene adduct **D** was obtained by a procedure similar to that used for synthesis of **C** by passing acetylene through a green solution of **B**[18] in 1 M HCl. The solution turned immediately to dark green, which indicates the formation of **D**.

X-ray structure analysis[19] of **C'** revealed clearly the formation of the carbon–sulfur bonds as shown in Figure 1. The carbon–carbon distance in the cluster is 1.321(11) Å, which is closer to that of ethylene (1.339 Å) than to that of acetylene (1.203 Å). The *cis* geometry of the two hydrogen atoms attached to the carbon atoms was disclosed by the X-ray analysis. The bond angles about C1 and C2 are close to 120°, which also indicates the sp^2 character of the orbitals of the two carbon atoms. We succeeded in the crystallization of **A** as $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2$-

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(19) Crystal data: monoclinic system, space group $C2/c$, $a = 37.654(14)$ Å, $b = 10.310(5)$ Å, $c = 32.997(14)$ Å, $\beta = 122.39(3)°$, $V = 10817(8)$ Å^3, $Z = 8$, $D_c = 1.718$ g cm^{-3}, $D_m = 1.72$ g cm^{-3}, $R = 3.85$ for 7131 reflections ($|F_o| \geq 6\sigma|F_o|$). Details will be described elsewhere.

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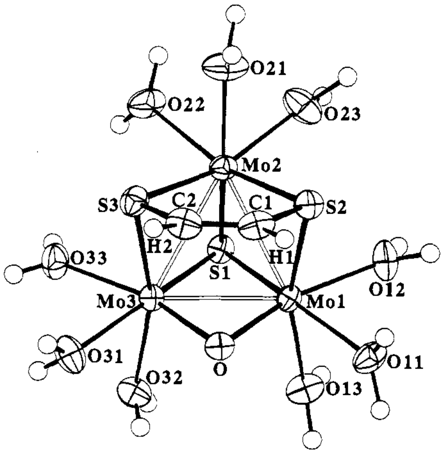

Figure 1. Perspective view of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu_3\text{-}S_2C_2H_2)(H_2O)_9]^{4+}$ in **C′**. Selected atomic distances (Å) and angles (deg): Mo1–Mo2, 2.714(1); Mo1–Mo3, 2.517(1); Mo2–Mo3, 2.745(1); Mo1–S1, 2.353(2); Mo2–S1, 2.329(2); Mo3–S1, 2.350(2); Mo1–S2, 2.404(2); Mo2–S2, 2.350(2); Mo2–S3, 2.349(2); Mo3–S3, 2.410(2); Mo1–O, 1.932(4); Mo3–O, 1.907(4); S2–C1, 1.790(7); S3–C2, 1.793(6); C1–C2, 1.321(11); C1–H1, 0.97; C2–H2, 0.99; S2···S3, 3.183(3); S2–Mo2–S1, 85.1(1); Mo2–S2–C1, 105.6(2); Mo2–S3–C2, 105.8(3); S2–C1–C2, 121.7(4); S3–C2–C1, 121.0(5); S2–C1–H1, 115.5; S3–C2–H2, 114.6; C2–C1–H1, 122.8; C1–C2–H2, 124.0.

$(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 7H_2O$ (**A′**)[20] and determined its structure.[21] The addition of acetylene to **A** causes considerable changes in the core structure of Mo_3OS_3 except in the Mo–μ_3S (S1) distances: elongation of Mo1–S2 and Mo3–S3 bond lengths by ca. 0.15 Å; elongation of Mo2–S2 and Mo3–S3 bond lengths by ca. 0.1 Å; shortening of Mo1–O and Mo3–O bond lengths by more than 0.2 Å; slight elongation (mean 0.025 Å) of the Mo–Mo distances (Mo1–Mo2, Mo2–Mo3) with μ-S's between the metals; and distinct shortening (0.125 Å) of the Mo1–Mo3 distance with μ-O between the metals.[22]

The electronic spectra of **C** and **D** have intense bands in the near infrared region; these spectra are shown in Figure 2 together with those of **A** and **B**. The similarity of the electronic spectra of **C** and **D** indicates that the structures of **C** and **D** are similar to each other. The reactions of acetylene with **A** and **B** in 1 M HCl are fairly fast and are almost completed in several minutes to give **C** and **D**, respectively. Isosbestic points are maintained in both reactions, and no other species were detected by column chromatography, which indicates 100% conversion for both of the reactions.

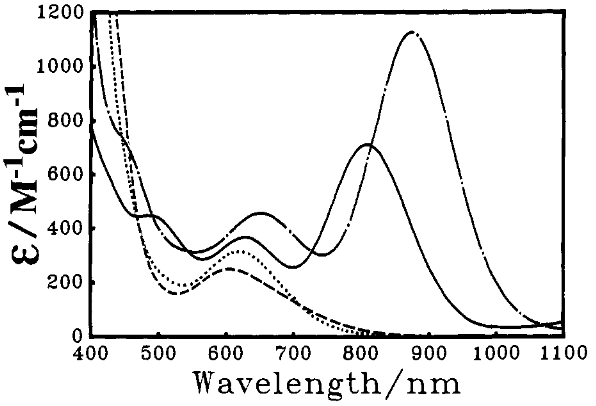

Figure 2. Electronic spectra. (- - -) $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (**A**) in 1 M HCl; (···) $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ (**B**) in 1 M HCl; (—) $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu_3\text{-}S_2C_2H_2)(H_2O)_9]^{4+}$ (**C**) obtained by passing acetylene through **A** in 1 M HCl; and (– · –) $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)(\mu_3\text{-}S_2C_2H_2)(H_2O)_9]^{4+}$ (**D**) obtained by passing acetylene through **B** in 1 M HCl.

Derivatives of the aqua clusters **A** and **B** with $Mo_3(\mu_3\text{-}S)(\mu\text{-}X)(\mu\text{-}S)_2$ cores (X = O, S) also react with acetylene and acetylene derivatives not only in aqueous solution but also in organic solvents.[23] The carbon–sulfur bonds formation may lead to new synthetic routes to sulfur-containing organic compounds, and the use of unsymmetrical acetylene derivatives possibly gives optically isomeric clusters. Further work is in progress to characterize the unusual reactivity of the clusters.

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Supplementary Material Available: Listings of crystallographic details, atomic coordinates, thermal parameters, bond distances, and bond angles, and an ORTEP figure of **A′** (36 pages). Ordering information is given on any current masthead page.

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(20) A procedure similar to that used for the preparation of $[Mo_3S_4(H_2O)_9](CH_3C_6H_4SO_3)_4\cdot 9H_2O$ was applied: Akashi, H.; Shibahara, T.; Kuroya, H. *Polyhedron* **1990**, *9*, 1671–1676.

(21) Crystal data: triclinic system, space group $P\bar{1}$, a = 15.397(6) Å, b = 15.806(5) Å, c = 11.922(7) Å, α = 100.94(4)°, β = 108.57(4)°, γ = 76.04(3)°, V = 2648.8(22) Å^3, Z = 2, D_c = 1.722 g cm^{-3}, D_m = 1.72 g cm^{-3}, R = 4.90 for 8830 reflections ($|F_o| \geq 6\sigma|F_o|$). Details will be described elsewhere.

(22) The same atom numbering scheme as used for **C′** was employed. Selected atomic distances (Å) and angles (deg): Mo1–Mo2, 2.692(1); Mo1–Mo3, 2.642(1); Mo2–Mo3, 2.718(2); Mo1–S1, 2.342(2); Mo2–S1, 2.341(2); Mo3–S1, 2.338(2); Mo1–S2, 2.258(2); Mo2–S2, 2.246(2); Mo2–S3, 2.260(2); Mo3–S3, 2.254(2); Mo1–O, 2.150(3); Mo3–O, 2.129(4); S2···S3, 3.347(2); S2–Mo2–S1, 95.9(1).

(23) For example, reaction of $[Mo_3S_4Cl_4(H_2O)_2(PPh_3)_3]\cdot 3THF$ with acetylene and 1-butyn-3-ol in acetonitrile causes large characteristic absorption peaks at 944 and 930 nm, respectively. Reaction of $[Mo_3S_4(H_2O)_9](pts)_4\cdot 9H_2O$ with acetylene in acetonitrile causes an absorption peak at 897 nm.