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Reaction of the Mo_3S_4 Cluster with Dimethylacetylenedicarboxylate: An ESR-Active Cluster and an Organometallic Cluster Formed by α,β-Conjugate Addition

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A seven-electron cluster $[Mo_3(\mu_3\text{-}S)\{\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)S\}\{\mu\text{-}SC(CO_2CH_3){=}CH(CO_2CH_3)\}(dtp)_3(\mu\text{-}OAc)]$ [**2**, $S_2P(OC_2H_5)_2^-$; dtp = diethyldithiophosphate] and an organometallic cluster $[Mo_3(\mu_3\text{-}S)\{\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)S\}\{\mu\text{-}SC(CO_2CH_3)CH(OCH_3)(CO_2)\}(dtp)_2(CH_3OH)(\mu\text{-}OAc)]$(Mo–C) (**3**) were obtained by reaction in methanol of the sulfur-bridged trinuclear complex $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(dtp)_3(CH_3CN)(\mu\text{-}OAc)]$ (**1**) with dimethylacetylenedicarboxylate (DMAD). The X-ray structures of **2** and **3** revealed the adduct formation of two DMAD molecules to the respective Mo_3S_4 cores. **2** is paramagnetic and obeys the Curie–Weiss law: the μ_{eff} value at 300 K is 1.90 μ_B. The electron spin resonance signal was observed at 173 K. The density functional theory calculation of **2** demonstrated that the main components of the singly occupied molecular orbitals of α and β spins are Mo d electrons and the main components of lowest unoccupied molecular orbitals are of Mo and the olefin moiety with one C–S bond. A one-electron reversible oxidation process of **2** was observed at $E_{1/2} = -0.11$ V vs Fc/Fc^+. The electronic spectrum of **2** has a peak at 468 nm ($\epsilon = 2170\ M^{-1}\ cm^{-1}$) and shoulders at 640 (918) and 797 (605) nm, and **3** has shoulders at 441 (1740) and 578 (625) nm and a distinct peak at 840 (467) nm. An intermediate $[Mo_3(\mu_3\text{-}S)\{\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)S\}\{\mu\text{-}SC(CO_2CH_3){=}CH(CO_2CH_3)\}(dtp)_3(\mu\text{-}OAc)]^+$ (**4**) is tentatively suggested: a one-electron reduction of **4** gives **2**, and a nucleophilic conjugate addition of CH_3O^- to the α,β-unsaturated carbonyl group of **4** gives **3**.

Many types of terminal/bridging-S/S_2 metal complexes have been reported, and some of the S atoms are very reactive toward metals and organic molecules.[1] We have reported the characteristic properties of S-bridged trinuclear Mo and W clusters with M_3S_4 cores (M = Mo, W), such as the metal incorporation reaction[2] and the adduct formation of acetylene and its derivatives at S atoms in the clusters.[3]

We report here the synthesis and structure of a neutral radical triangular cluster $[Mo_3(\mu_3\text{-}S)\{\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)S\}\{\mu\text{-}SC(CO_2CH_3){=}CH(CO_2CH_3)\}(dtp)_3(\mu\text{-}OAc)]$ (**2**, $S_2P(OC_2H_5)_2^-$; dtp = diethyldithiophosphate) having seven cluster electrons and an organometallic trinuclear cluster $[Mo_3(\mu_3\text{-}S)\{\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)S\}\{\mu\text{-}SC(CO_2CH_3)CH(OCH_3)(CO_2)\}(dtp)_2(CH_3OH)(\mu\text{-}OAc)]$ (**3**). Both clusters were obtained from reaction in methanol of the S-bridged trinuclear complex $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(dtp)_3(CH_3CN)(\mu\text{-}OAc)]$ (**1**) with dimethylacetylenedicarboxylate ($H_3COOCC{\equiv}CCOOCH_3$, DMAD; Scheme 1), with both clusters being air-stable.

Although seven-electron triangular Mo_3S_4 clusters have been established by using mainly electrochemical techniques,[4] only a few of their structures have been determined by X-ray crystallography.[5] The electron spin resonance (ESR)-active cluster **2** is air-stable, and its handling is easy for characterization. The formation of cluster **3** is accompanied with α,β-conjugate addition, and the mechanistic insight into the formation will be interesting because the nucleophilic addition to α,β-unsaturated carbonyl groups (conjugate addition) is one of the most important reactions in organic synthesis and has attracted much attention. Asymmetric 1,4-addition reactions have also been reported using Rh chiral catalysts.[6] Rakowski DuBois and co-workers

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(1) For example, see: (a) Shibahara, T. *Coord. Chem. Rev.* **1993**, *123*, 73–147. (b) Rakowski DuBois, M. *Chem. Rev.* **1989**, *89*, 1–9. (c) Matsumoto, K.; Sugiyama, H. *Acc. Chem. Res.* **2002**, *35*, 915–926. (d) Llusar, R.; Uriel, S. *Eur. J. Inorg. Chem.* **2003**, 1271–1290. (e) Holm, R. H. *Adv. Inorg. Chem.* **1992**, *38*, 1–71. (f) Hidai, M.; Kuwata, S.; Mizobe, Y. *Acc. Chem. Res.* **2000**, *33*, 46–52. (g) Nishioka, T.; Kitayama, H.; Breedlove, B. K.; Shiomi, K.; Kinoshita, I.; Isobe, K. *Inorg. Chem.* **2004**, *43*, 5688–5697. (h) Bana, T. S.; Isobe, K.; Kitayama, H.; Nishioka, T.; Doe, M.; Kinoshita, I. *Organometallics* **2004**, *23*, 5347–5352. (i) Hadjikyriacou, A.; Toupadakis, A.; Koo, S.-M.; Ileperuma, O.; Draganjac, M.; Salifoglou A.; Coucouvanis, D. *Inorg. Chem.* **1983**, *30*, 754–767. (j) Kawaguchi, H.; Yamada, K.; Lang, J.-P.; Tatsumi, K. *J. Am. Chem. Soc.* **1997**, *119*, 10346–10358.

(2) For example, see: (a) Yamauchi, T.; Takagi, H.; Shibahara, T.; Akashi, H. *Inorg. Chem.* **2006**, *45*, 5429–5437. (b) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1986**, *108*, 1342–1343.

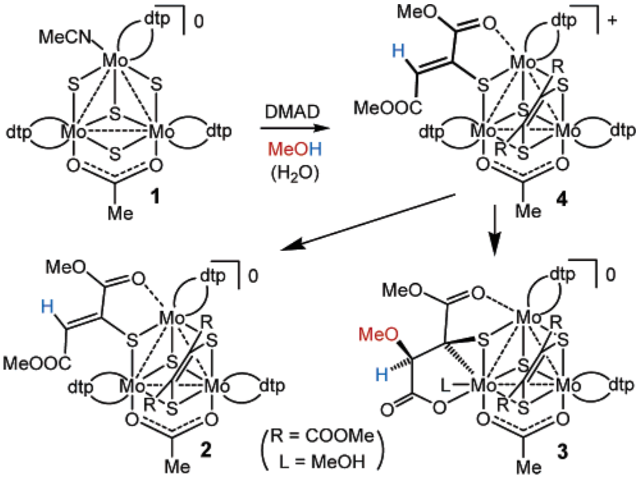
(3) For example, see: (a) Ide, Y.; Maeyama, M.; Shibahara, T. *Inorg. Chem.* **2004**, *43*, 602–612. (b) Ide, Y.; Shibahara, T. *Inorg. Chem. Commun.* **2004**, *7*, 1132–1134. (c) Akashi, H.; Isobe, K.; Shibahara, T. *Inorg. Chem.* **2005**, *44*, 3494–3498. (d) Takagi, H.; Ide, Y.; Shibahara, T. *C. R. Chim.* **2005**, *8*, 985–992.

(4) For example, see: (a) Vergamini, P. J.; Vahrenkamp, H.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6327–6329. (b) Shibahara, T.; Kuroya, H. *Polyhedron* **1986**, *5*, 357–361.

(5) (a) Mizutani, J.; Imoto, H.; Saito, T. *J. Cluster Sci.* **1995**, *6*, 523–532. (b) Cramer, R. E.; Yamada, K.; Kawaguchi, H.; Tatsumi, K. *Inorg. Chem.* **1996**, *35*, 1743–1746.

10.1021/ic0617285 CCC: $37.00

Scheme 1. Reaction of **1** with DMAD to give **2** and **3**



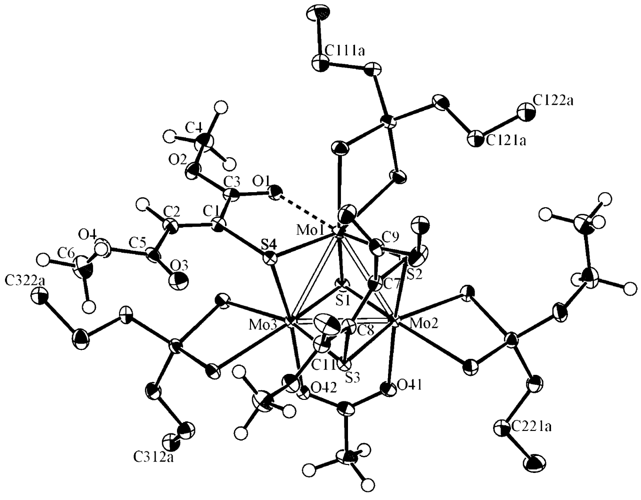


Figure 1. ORTEP drawing of **2** at the 50% probability level. Bond distances (Å) and angles (deg): Mo1−Mo2, 2.7544(2); Mo1−Mo3, 2.6821(3); Mo2−Mo3, 2.7276(3); Mo1−O1, 2.1965(18); S2−C7, 1.778(2); S3−C8, 1.779(2); S4−C1, 1.774(2); O1−C3, 1.241(3); C1−C2, 1.330(4); C1−C3, 1.478(3); C2−C5, 1.486(4); C7−C9, 1.508(3); C7−C8, 1.342(4); C8−C11, 1.484(3); Mo2−Mo1−Mo3, 60.209(8); Mo1−Mo2−Mo3, 58.582(7); Mo1−Mo3−Mo2, 61.209(8); C2−C1−C3, 120.3(2); C1−C2−C5, 125.1(2); C8−C7−C9, 123.7(2); C7−C8−C11, 120.0(2).

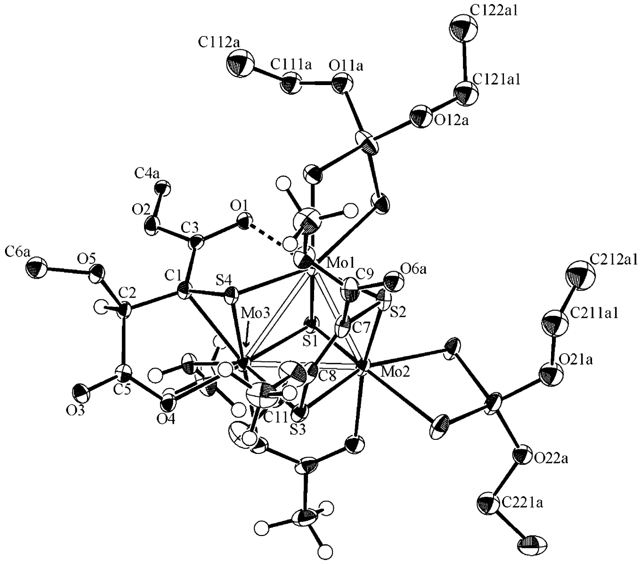


Figure 2. ORTEP drawing of **3** at the 50% probability level. Bond distances (Å) and angles (deg): Mo1−Mo2, 2.6173(4); Mo1−Mo3, 2.8004(3); Mo2−Mo3, 2.8003(3); Mo1−O1, 2.198(2); Mo3−C1, 2.223(3); S2−C7, 1.793(3); S3−C8, 1.788(3); S4−C1, 1.760(3); O1−C3, 1.246(3); O5−C2, 1.424(3); C1−C2, 1.507(4); C1−C3, 1.461(4); C2−C5, 1.537(4); C7−C9, 1.500(4); C7−C8, 1.350(4); C8−C11, 1.496(4); Mo2−Mo1−Mo3, 62.137(10); Mo1−Mo2−Mo3, 62.141(10); Mo1−Mo3−Mo2, 55.722(9); Mo3−C1−S4, 72.40(13); Mo3−C1−C2, 111.5(2); Mo3−C1−C3, 111.71(17); C2−C1−C3, 119.2(3); O5−C2−C1, 109.3(2); O5−C2−C5, 112.0(2); C1−C2−C5, 110.0(2); C8−C7−C9, 124.6(2); C7−C8−C11, 124.1(2).

reported $[(MoCp)_2(S_2CH_2)(S_2CCH_3)]^+$ having a Mo−C bond formed by the reaction of $(CpMoS)_2(S_2CH_2)$ or its S-protonated species with acyl halides or nitriles.[7]

To a suspension of cluster **1** (50.3 mg, 4.69×10^{-2} mmol, MW = 1071.85) in methanol (1.9 mL, containing 0.3% H_2O) was added under a N_2 atmosphere a 4.0-fold excess of DMAD (0.20 mL, a 0.928 mmol solution in methanol, 1.86×10^{-1} mmol). Stirring the resultant green-brown solution at room temperature for a day gave a brown powder of **2**, which was filtered in air with a yield of 32.8 mg (53%). Recrystallization of the powder of **2** from methanol/acetone (2/1) gave brown platelike crystals of **2** with a yield of 23.8 mg (39%).[8] Slow evaporation of the filtrate obtained by filtering the powder of **2** in air gave a small amount of crystals of $\mathbf{3}\cdot 0.25CH_3OH$ (0.7 mg, 1%).[9] Use of a 10-fold excess of DMAD gave **2** (37%) and **3** (22%) in lower and higher yields, respectively, and use of a 2-fold excess of DMAD gave only **3** (11%).

The X-ray structure of **2** revealed the adduct formation of two DMAD molecules to the Mo_3S_4 core, as shown in Figure 1. The C1−C2 and C7−C8 distances indicate their double-bond character. The short Mo1−O1 distance indicates the coordination of O1 to Mo1, although C3−O1 has a double-bond character. The X-ray structure of **3** (Figure 2) clearly indicates that the addition of the CH_3O^- group to C2 and the Mo3−C1 bond formation make the C1−C2 distance much longer than that of **2**. The three Mo−Mo distances in **2** differ slightly from each other, while the three Mo−Mo distances in **3** are divided into one short [2.6173(4) Å] and two long [2.8003(3) and 2.8004(3) Å] ones. The elongation of Mo1−Mo3 and Mo2−Mo3 in **3** is probably due to the increase of the coordination number of Mo3 (from 6 to 7), and it is difficult to discuss the effect of the addition of a seventh electron to the Mo_3S_4 core in this case.[5]

The electronic spectra of **2** and **3** are shown in Figure 3 together with that of **1**. **2** has a peak at 468 nm (ϵ = 2170 M^{-1} cm^{-1}) and shoulders at 640 (918) and 797 (605) nm, and **3** has shoulders at 441 (1740) and 578 (625) nm and a distinct peak at 840 (467) nm.

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(6) For example, see: (a) Hayashi, T. *Synlett* **2001**, 879−887. (b) Bolm, C.; Hildebrand, J. P.; Muniz, K.; Hermanns, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 3284−3308. (c) Fagnou, K.; Lauten, M. *Chem. Rev.* **2003**, *103*, 169−196. (d) Hayashi, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 13−21.

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(8) Anal. Found (calcd for $Mo_3S_{10}P_3O_{16}C_{26}H_{46}$, MW = 1315.98): C, 23.70 (23.73); H, 3.42 (3.52). The electronic spectrum of the powder sample guaranteed the purity.

(9) Anal. Found (calcd for $Mo_3S_8P_2O_{15}C_{22}H_{36}$, MW = 1146.80): C, 22.84 (23.04); H, 2.84 (3.16). The crystals effloresce very easily to give a powder sample, and the methanol of crystallization was not included in the calculation.

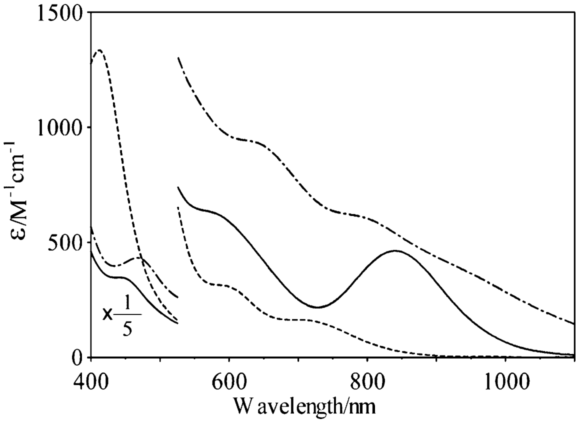

Figure 3. Electronic spectra of **1**−**3** in methanol: (- - -) **1**; (− • − • −) **2**; (—) **3**.

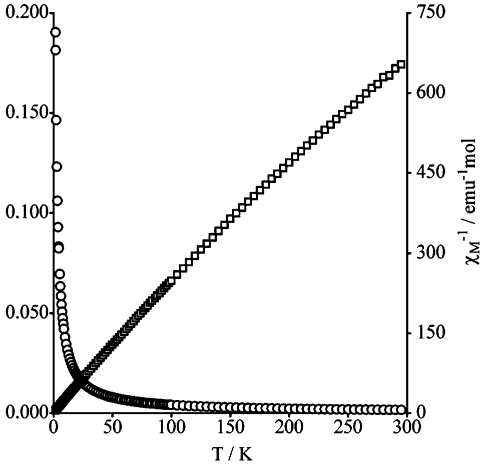

Figure 4. Temperature dependence of the magnetic susceptibility of **2**: χ_M vs *T* plot (○) and χ_M^{-1} vs *T* plot (□) for **2** (10 000 G; 1.9−300 K).

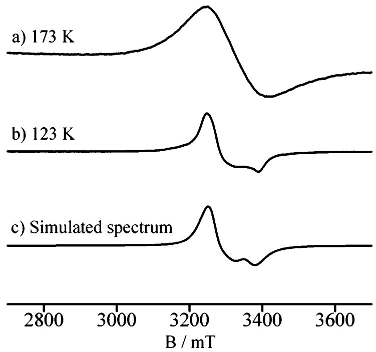

Figure 5. ESR spectra of **2** in dichloromethane.

The magnetic measurement showed that **2** is paramagnetic and obeys the Curie−Weiss law, as shown in Figure 4. The μ_{eff} value at 300 K is 1.90 μ_B, which is close to the spin-only formula of d^1 configuration complexes. The ESR spectra of **2** in dichloromethane are shown in Figure 5. The simulated spectrum c with ($g_1 = 2.008$, $g_2 = 1.998$, and $g_3 = 1.951$) is in good agreement with the signal b at 123 K.

A hybrid density functional theory (DFT) calculation of **2** based on the B3LYP theory with LanL2Dz (Mo) and 3-21g** (others) basis sets at spin multiplicity 2 was carried out by using the *Gaussian03* program package.[10] The main components of the singly occupied molecular orbitals (SOMOs) of α and β spins are Mo d electrons, and the main components of lowest unoccupied molecular orbitals are Mo and the olefin moiety with one C−S bond. The Mulliken spin density of the optimized structure of **2** shows that the unpaired electron delocalizes over three Mo atoms.

A one-electron oxidation process of **2** was observed at $E_{1/2} = -0.11$ V vs Fc/Fc$^+$. The molecular orbital calculation of **2** denies the possibility that the oxidation may occur on the dithiolene moiety, μ_3-SC(CO_2CH_3)═C(CO_2CH_3)S,[3d] because the main components of the SOMOs are made up of Mo atoms.

For the formation of **2** and **3**, we tentatively suggest the presence of an intermediate $[Mo_3(\mu_3\text{-}S)\{\mu_3\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)S\}\{\mu\text{-}SC(CO_2CH_3){=}CH(CO_2CH_3)\}(dtp)_3(\mu\text{-}OAc)]^+$ (**4**; see Scheme 1), whose fundamental framework is close to those of $[W_3(\mu_3\text{-}S)(\mu_3\text{-}SCH{=}CHS)(\mu\text{-}SCH{=}CH_2)(NCS)_9]^{4-}$[3a] and $[Mo_3(\mu_3\text{-}S)(\mu_3\text{-}SC(COOH){=}C(COOH)S)(\mu\text{-}SC(COOH){=}CH(COOH))(Hnta)_3]^-$:[3d] **2** is a one-electron-reduction product of **4**. For the formation of **2**, DMAD works not only as an adduct-formation reagent but also as a reducing reagent, while DMAD is usually an electron-deficient symmetrical alkynic diester useful as a dienophile in cycloaddition reactions, such as the Diels−Alder reaction:[11] the low solubility of **2** in methanol might be the driving force for DMAD to serve as a reductant to reduce complex **4**. A nucleophilic conjugate addition of CH_3O^- to the α,β-unsaturated carbonyl group of **4** gives **3**. The coordination of the carbonyl O to the Mo (C═O···Mo; see Scheme 1) of **4** will enhance the reactivity of the α,β-unsaturated moiety. Nitrosyl tetrafluoroborate oxidation of an acetonitrile solution of **2** gave a greenish-brown solution. Probably this solution contains the intermediate **4** because the addition of sodium methoxide to the resultant solution gave a brown solution, the spectrum of which was very close to that of **3**. Further work is in progress to characterize the unusual reactivity of **2** and **4**.

Crystallographic data of **2** (CCDC 600046) and **3** (CCDC 620578) are available upon request from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (tel +44 1223 336408, fax +44 1223 336033).

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Supporting Information Available: Experimental details of the synthesis and characterization (DFT, NMR, and electrochemistry) of **2** and **3** and electronic spectra of the $NOBF_4$ oxidation product of **2** with and without $NaOCH_3$ in acetonitrile. This material is available free of charge via the Internet at http://pubs.acs.org.

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