Sulfur-Bridged Cubane-Type Molybdenum-Cadmium Clusters with Diethyldithiophosphato or Nitrilotriacetato Ligands

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The metal incorporation reactions of the sulfur-bridged incomplete cubane-type molybdenum clusters in nonaqueous solvent or pure water are reported for the first time. The reaction of the clusters $[Mo_3S_4(dtp)_4(CH_3CN)]$ (**1**) in acetonitrile and $[Mo_3S_4(Hnta)_3]^{2-}$ in pure water with cadmium metal result in the formation of two novel molybdenum-cadmium mixed-metal clusters $[(CH_3CN)(dtp)_4Mo_3S_4CdS_4Mo_3(dtp)_4(CH_3CN)]$ (**3**) and $[(Hnta)_3Mo_3S_4CdS_4Mo_3(Hnta)_3]^{4-}$ (**4**), respectively. Although the clusters **3** and **4** have sandwich cubane-type $Mo_3S_4CdS_4Mo_3{}^{8+}$ cores of the same type, the peak positions of electronic spectra of **3** (856 nm) and **4** (1235 nm) at the longest wavelength are distinctly different from each other.

As an extension of the metal incorporation reaction,[1] we report here the reaction of the sulfur-bridged incomplete cubane-type molybdenum clusters $[Mo_3S_4(dtp)_4(CH_3CN)]$ (**1**)[2] (Hdtp = diethyldithiophosphoric acid) and $[Mo_3S_4(Hnta)_3]^{2-}$ (**2**)[3] (H_3nta = nitrilotriacetic acid) with cadmium metal to give sulfur-bridged sandwich cubane-type molybdenum-cadmium clusters $[(CH_3CN)(dtp)_4Mo_3S_4CdS_4Mo_3(dtp)_4(CH_3CN)]$ (**3**) and $[(Hnta)_3Mo_3S_4CdS_4Mo_3(Hnta)_3]^{4-}$ (**4**), respectively. Cadmium has high affinity toward sulfur, CdS being known well as sulfide, and progress of the metal incorporation reaction has been anticipated. Though many cadmium complexes with sulfur donor ligands have been reported,[4] reports on sulfur bridged mixed-metal clusters containing cadmium are very rare.[5] We have successfully isolated **3** and the cobalt salt of **4**, $[Co(H_2O)_6]_2$ $4{\cdot}22H_2O$ (**4'**) as a solid sample respectively, determined the X-ray structures, and characterized the clusters by means of electronic spectroscopy and molecular orbital calculations.

The compounds **3** and **4'** were synthesized under a dinitrogen atmosphere. Several pieces of cadmium metal were introduced into a conical flask containing **1** in acetonitrile, and the mixture was allowed to stand one day at room temperature with stirring. The color of the solution turned from brown to dark brown. The solution was filtered to remove the remaining cadmium metal, and the resulting solution was stored in a refrigerator. After several months, dark brown tabular crystals of **3** deposited, which were collected by filtration; yield 0.3%.[6] To synthesize **4'**, a procedure similar to that used for the synthesis of **3** was adopted. Cadmium metal was added to sodium salt of **2** in pure water. During stirring, the color of the solution turned from green to orange in a few hours. The remaining cadmium metal was removed, and pH of the solution was adjusted to 1.2 with dilute HCl.[7] Cobalt(II) chloride hexahydrate was added to the solution, and orange cubic crystals of **4'** deposited after one week, which were collected by filtration; yield 23%.

The X-ray structure analyses of **3** (Figure 1)[8] and **4'** (Figure 2)[9] revealed the existence of sandwich cubane-type $Mo_3S_4CdS_4$-$Mo_3{}^{8+}$ cores. **3** and the cluster anion of **4'** have crystallographic

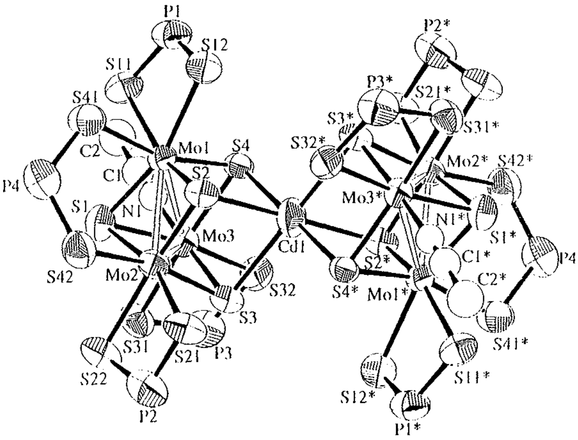

Figure 1. ORTEP drawing of **3**. Selected interatomic distances (Å) and angles (°): Mo1-Mo2, 2.724(5); Mo1-Mo3, 2.744(4); Mo2-Mo3, 2.732(5); Cd1-S2, 2.63(1); Cd1-S3, 2.721(9); Cd1-S4, 2.723(9); Mo1-S1, 2.34(1); Mo2-S1, 2.33(1); Mo3-S1, 2.34(1); Mo1-S2, 2.32(1); Mo1-S4, 2.33(1); Mo2-S2, 2.341(9); Mo2-S3, 2.30(1); Mo3-S3, 2.29(1); Mo3-S4, 2.337(9); Cd1-S2-Mo1, 94.1(3); Cd1-S2-Mo2, 93.9(3); Cd1-S3-Mo2, 92.6(3); Cd1-S3-Mo3, 94.2(3); Cd1-S4-Mo1, 91.8(3); Cd1-S4-Mo3, 93.0(3). The OC_2H_5 groups are omitted for clarity.

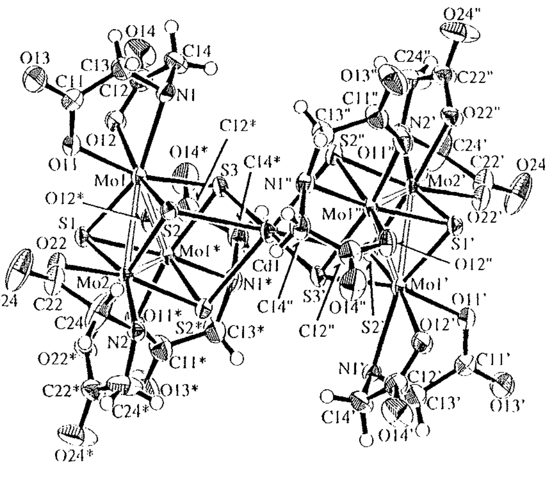

Figure 2. ORTEP drawing of the anion of **4'**. Selected interatomic distances (Å) and angles (°): Mo1-Mo2, 2.7195(4); Mo1-Mo1', 2.7216(5); Cd1-S2, 2.8195(9); Cd1-S3, 2.715(1); Mo1-S1, 2.3403(9); Mo2-S1, 2.347(1); Mo1-S2, 2.3275(8); Mo1-S3, 2.3426(9); Mo2-S2, 2.3314(9); Cd1-S2-Mo1, 96.96(3); Cd1-S2-Mo2, 98.76(3); Cd1-S3-Mo1, 99.49(4); Cd1-S3-Mo1*, 99.49(4). The CH_2CO_2H groups are omitted for clarity.

C_i and C_{2h} symmetry, respectively. The Cd-Mo distances in **3** (3.652[9] Å) are distinctly shorter than the corresponding ones in **4'** (3.886[12] Å), and both the Cd-Mo distances are much longer than the Mo-Mo distances in **3** (2.734[6] Å) and **4'** (2.7203[6] Å). The Cd-S-Mo angels in **3** (91.8 ~ 94.2°) are smaller than those in **4'** (96.96 ~ 99.49°).

The electronic spectrum of **3** in acetonitrile has peaks at 410 nm (ε 14200 ($M^{-1}cm^{-1}$); 1 M = 1 mol dm^{-3}) and 856 (8060), and the peaks of **4'** in 0.06 M HCl are at 310 (16300), 400 (19700), and 1235 (10800) (Figure 3). Although the clusters **3** and **4** have similar sandwich cubane-type $Mo_3S_4CdS_4Mo_3^{8+}$, the electronic spectrum peak positions of **3** (856 nm) and **4'** (1235 nm) at the longest wavelength are distinctly different from each other.

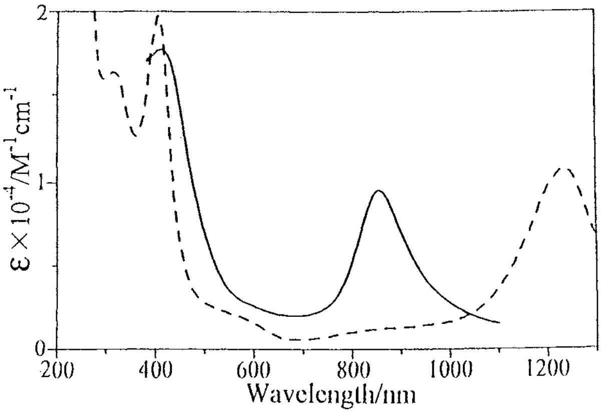

Figure 3. Electronic spectra of molybdenum-cadmium clusters: ——— **3** in acetonitrile; — — — **4'** in 0.06 M HCl.

Electronic structure of **4** was investigated by the discrete variational (DV)-Xα method.[10] The structural parameters of **4** were idealized to D_{3d} symmetry. The atomic coordinates for **4** were obtained from X-ray structure of **4'**. The calculated HOMO($64a_{1g}$)-LUMO($61a_{2u}$) gap (1.010 eV, 1228 nm) is in excellent agreement with the value obtained from the peak position at the longest wavelength in **4'** (1235 nm). HOMO consists mainly of Cd 5s and Mo 4d atomic orbitals, LUMO consists mainly of Cd $5p_z$, Mo 4d, and μ_3-S 3p atomic orbitals, and the contribution of nitrilotriacetato ligands to the HOMO and LUMO is small.

We have also calculated the electronic structures of two kinds of the bare $Mo_3S_4CdS_4Mo_3^{8+}$ cores, where atomic coordinates were obtained from X-ray structures of **3** and **4'**. The calculated HOMO($33a_{1g}$)-LUMO($30a_{2u}$) gaps for **3** (1.37 eV, 902 nm) and **4** (1.16 eV, 1070 nm) are in good agreement with the values obtained from the peak positions of electronic spectra at the longest wavelengths in **3** and **4'**, respectively. It seems that clusters having shorter Cd-Mo distance show larger HOMO-LUMO gaps of the electronic structures.

In the metal incorporation reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ in acidic aqueous solution,[1,11] the use of metals, such as Mg, Al, Zn, and rare earth metals, having strong reducing power resulted in the partial disintegration of the Mo_3S_4 core to give the sandwich cubane-type cluster $[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9]^{8+}$, where no metal incorporation reaction has occurred.[12]

Present research has made clear that the metal incorporation reaction proceeds even in nonaqueous solvent or pure water if suitable ligands are used. In these solvents, the strong reducing power of the above-mentioned metals to be incorporated will change substantially, and we hope that this becomes a new route for the synthesis of mixed metal clusters with Mo_3MS_4 cores. By employing this new method, we have already started the syntheses of molybdenum-zinc clusters.

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References and Notes

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4 For example, 6-coordinate cadmium complexes with sulfur donor ligands, see: a) [6 monodentate ligands] R. Petrova, O. Angelova, and J. Macíček, *Acta Crystallogr., Sec. C*, **1997**, 565. b) [3 bidentate ligands] J. Sola, P. González-Duarte, J. Sanz, I. Casals, T. Alsina, I. Sobrados, A. Alvarez-Larena, J.-F. Piniella, and X. Solans, *J. Am. Chem. Soc.*, **115**, 10018 (1993). c) [2 tridentate ligands] R. S. Glass, L. K. Steffen, D. D. Swanson, G. S. Wilson, R. de Gelder, R. A. G. de Graaff, and J. Reedijk, *Inorg. Chim. Acta*, **207**, 241 (1993).

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6 We suppose that the yield of **3** in acetonitrile is almost 100%, because the absorption spectrum is the same as that of crystals of **3** dissolved in acetonitrile.

7 pH adjustment is important to get good crystals for X-ray crystallography.

8 Crystal data for **3**: Formula $CdMo_6S_{12}P_8O_{16}N_2C_{36}H_{86}$, M_w = 2508.5, monoclinic, space group $P2_1/n$, a = 21.14(2) Å, b = 13.787(2) Å, c = 16.189(2) Å, β = 108.42(5)°, V = 4475(3) Å^3, Z = 2, D_C = 1.862 g cm^{-3}, D_O = 1.87 g cm^{-3}, R (R_w) = 8.6 (12.0)% for 2305 reflections ($I \geq 2.0\ \sigma(I)$).

9 Crystal data for **4'**: Formula $CdMo_6Co_2S_8O_{70}C_{36}H_{110}$, M_w = 2809.7, monoclinic, space group $C2/m$, a = 17.0170(6) Å, b = 16.9893(8) Å, c = 16.7230(5) Å, β = 103.026(2)°, V = 4710.3(3) Å^3, Z = 1, D_C = 1.981 g cm^{-3}, D_O = 1.99 g cm^{-3}, R (R^w) = 3.3 (5.3)% for 3909 reflections ($I \geq 3.0\ \sigma(I)$).

10 Numerical atomic orbitals (Cd, 1s-5p; Mo, 1s-5p; S, 1s-3d; O, 1s-2p; N, 1s-2p; C, 1s-2p; H, 1s) were used as a basis set for the MO calculations. The Slater exchange parameter was chosen to be α = 0.7 for all atoms. The sample points were taken up to 100000 points. Self-consistency within 0.0001 e was obtained for the orbital populations.

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