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Reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with Cobalt and Mercury. Syntheses and X-Ray Structures of Double Cubane-Type Cluster, $[(H_2O)_9Mo_3S_4CoCoS_4Mo_3(H_2O)_9](CH_3\cdot C_6H_4\cdot SO_3)_8\cdot 18H_2O$ and Sandwich Cubane-Type Cluster, $[(H_2O)_9Mo_3S_4HgS_4Mo_3(H_2O)_9](CH_3\cdot C_6H_4\cdot SO_3)_8\cdot 20H_2O$

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Two new clusters, $[(H_2O)_9Mo_3S_4CoCoS_4Mo_3(H_2O)_9](CH_3\cdot C_6H_4\cdot SO_3)_8\cdot 18H_2O$ (**1**) and $[(H_2O)_9Mo_3S_4HgS_4Mo_3(H_2O)_9](CH_3\cdot C_6H_4\cdot SO_3)_8\cdot 20H_2O$ (**2**), have been synthesized by the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$(**3'**) with metallic cobalt and mercury, respectively. The X-ray structure analyses revealed that in **1** two $Mo_3S_4Co(H_2O)_9$ moieties are joined through two cobalt-sulfur bonds, and in **2** a mercury atom was sandwiched by two **3'**s.

Cubane-type mixed metal clusters with $M_3M'S_4$ (M, M'=V, Cr, Fe, Cu, Mo, and W) cores have been studied extensively.[1,2] Recently we reported the reaction of the incomplete cubane-type molybdenum-sulfur aqua clusters, $[Mo_3S_4(H_2O)_9]^{4+}$ (**3'**),[3] with metals (Fe,[4] Ni,[5] Cu,[6] Sn[7]) or metal ion (Sn^{2+})[7] to give mixed metal cubane-type clusters with Mo_3MS_4 cores (M=Fe, Ni, Cu, Sn). We report here syntheses, characterization, and X-ray structures of two kinds of cubane-type mixed metal clusters: a double cubane-type cluster, $[(H_2O)_9Mo_3S_4CoCoS_4Mo_3(H_2O)_9](CH_3\cdot C_6H_4\cdot SO_3)_8\cdot 18H_2O$ (**1**) and a sandwich cubane-type cluster, $[(H_2O)_9Mo_3S_4HgS_4Mo_3(H_2O)_9](CH_3\cdot C_6H_4\cdot SO_3)_8\cdot 20H_2O$ (**2**). No cubane-type compounds with Mo_3CoS_4 or Mo_3HgS_4 cores have been reported so far. The other synthetic methods of mixed-metal clusters with Mo_3MS_4 cores are also known: 1) the reaction of $[Mo_3S_4(dtp)_4(L)]$ (dtp=$S_2P(OEt_2)_2$; L=H_2O, C_3H_3ON (oxazole)) with $SbCl_3$ or CuI.[8-10] 2) the reaction of $[Mo_3S_4(S_2PEt_2)_4]$ with $[W(CO)_3(CH_3CN)_3]$.[11] 3) the reaction of **3'** with metal ions by use of reducing agent.[12]

Synthesis of molybdenum-cobalt cluster **1** is as follows: All the procedures were carried out under a dinitrogen atmosphere. Cobalt (0.20

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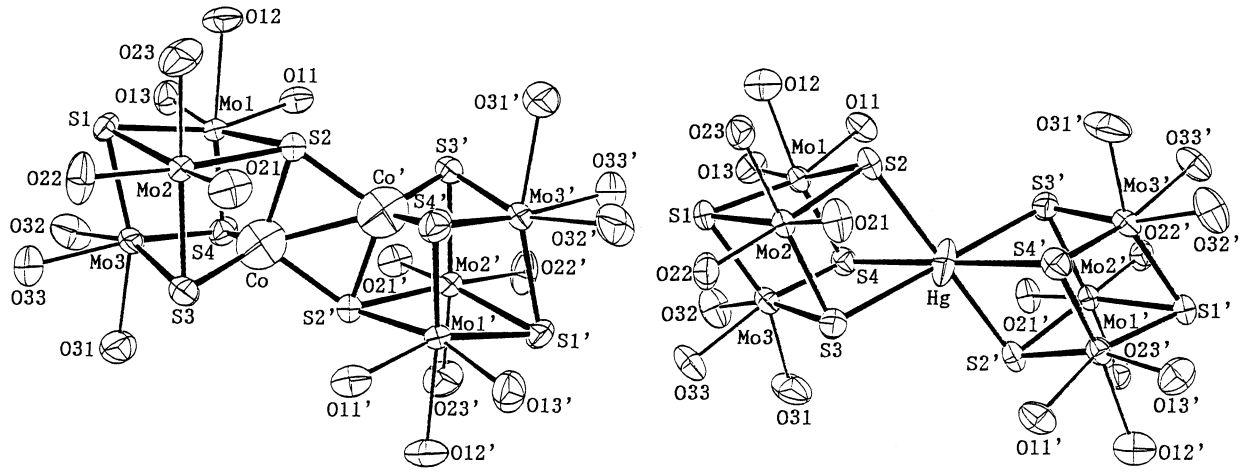
g, powder) was introduced to a conical flask containing the aqua ion **3'** (0.05 M per trimer, 25 mL; M=mol dm^{-3}) in 2 M HCl. The color of the solution turned from green to brown within a couple of days. After a week the solution was filtered and Dowex 50W-X2 column chromatography was applied (ϕ2 cm x 80 cm). The order of elution is as follows: cobalt ion (with 0.5 M HCl), the green aqua ion **3'** (with 1 M HCl), and dark brown $[(H_2O)_9Mo_3S_4CoCoS_4Mo_3(H_2O)_9]^{8+}$ (**1'**, with 2 M HCl; yield 45%).[13] The dark brown solution was absorbed on the cation exchanger again and eluted with 4 M HPTS (p-toluenesulfonic acid). The resultant solution was kept in a freezer. Black-brown crystals were obtained after a week. The aqua ion in 2 M HCl or in 2 M HPTS is very air sensitive and turns to **3'** and Co^{2+}.

The molybdenum-mercury cluster **2** was synthesized by introducing mercury (3 g) into a conical flask containing **3'** (0.1 M per trimer in 4 M HPTS, 25 mL). The color of the solution turned from green to purple within several hours. After three days at room temperature, the remaining mercury was removed from the solution, which was kept in a freezer to give a purple columnar crystals after a few days.[14]

X-Ray structure analyses[15] of **1** and **2** revealed the existence of a double cubane-type $Mo_3S_4CoCoS_4Mo_3$ core in which two Mo_3S_4Co moieties are



$[(H_2O)_9Mo_3S_4CoCoS_4Mo_3(H_2O)_9]^{8+}$ $[(H_2O)_9Mo_3S_4HgS_4Mo_3(H_2O)_9]^{8+}$

Fig. 1. Perspective view of $[(H_2O)_9Mo_3S_4CoCoS_4Mo_3(H_2O)_9]^{8+}$ (**1'**) in **1** and $[(H_2O)_9Mo_3S_4HgS_4Mo_3(H_2O)_9]^{8+}$ (**2'**) in **2** with selected bond distances (Å). **1**: Mo1-Mo2, 2.748(2); Mo1-Mo3, 2.752(2); Mo2-Mo3, 2.733(2); Mo1-Co, 2.639(4); Mo2-Co, 2.668(6); Mo3-Co, 2.621(5); Co-Co', 2.498(10); Mo-S1 (av.), 2.343[9]; Mo-S (S2, S3, S4; av.), 2.308[13]; Co-S (S2, S3, S4; av.), 2.105[14]; Mo-H_2O (av.), 2.200[29]. **2**: Mo1-Mo2, 2.720(2); Mo1-Mo3, 2.715(2); Mo2-Mo3, 2.703(2); Mo1-Hg, 3.726(2); Mo2-Hg, 3.881(2); Mo3-Hg, 3.892(2); Mo-S1 (av.), 2.331[6]; Mo-S (S2, S3, S4; av.), 2.296[5]; Mo-H_2O (av.), 2.172[27].

joined through two cobalt-sulfur bonds, and a sandwich cubane-type $Mo_3S_4HgS_4Mo_3$ core in which a mercury atom was sandwiched by two Mo_3S_4's, respectively as shown in Fig. 1.

Electronic spectra of **1'**, **2'**, and **3'** are shown in Fig. 2 and λ_{max},nm (ε/M^{-1} cm^{-1} per Mo) are as follows: **1'** in 2 M HPTS 360(2310), 450(1450), 790(1170); **1'** in 2 M HCl 360 (1790), 445(1420), 796(1120); **2'** in 2 M HCl 372 (2160), 556 (3140). As for **1'** there is only a little spectrum difference by the change of solvent. From this and the behavior on the cation exchanger (see above), it is estimated that the cluster **1'** exists as a double cubane-type cluster in both 2 M HPTS and 2 M HCl in contrast to the case of the molybdenum-copper double cubane-type cluster, $[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9]^{8+}$ which dissociates in diluted HCl.[6] The molybdenum-mercury compound **2'** has a very intense peak in the visible region, which can be used for the determination of mercury.[16]

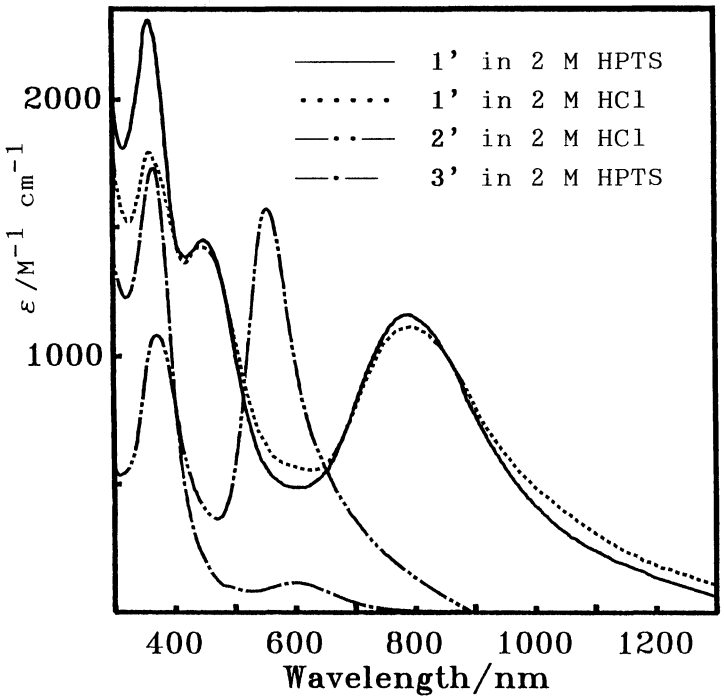


Fig. 2. Electronic spectra.

Including these two new clusters **1** and **2**, totally seven mixed-metal aqua clusters with single cubane-type Mo_3MS_4 (M=Fe, Ni, Sn), double cubane-type $Mo_3S_4MMS_4Mo_3$ (M=Co, Cu), or sandwich cubane-type $Mo_3S_4MS_4Mo_3$ (M=Sn, Hg) cores have been synthesized from the incomplete cubane-type aqua ion **3'** and the joining metals or metal ion (Sn^{2+}) so far. These reactions can be regarded as reductive addition of metals or metal ion to the $Mo_3{}^{IV}S_4$ core except the case of $Mo_3S_4HgS_4Mo_3$, where the formal oxidation state of mercury is estimated to be zero because of the long Hg-S distances.[17] The high affinity between mercury and sulfur is presumed to be the main factor for the formation of the cluster **2**.

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13) Anal: Mo/Co=3.06

14) Anal(Found): Mo, 17.95(18.64); Hg, 6.37(6.95); C, 21.86(21.87); H, 4.16(4.31)%.

15) Crystal data: **1**; triclinic system, space group $P\bar{1}$, a=15.310(4) Å, b=16.699(6)Å, c=12.080(4) Å, α=96.21(3)°, β=108.52(2)°, γ=101.97(3)°, V=2814.1(17) Å^3, Z=1, D_c=1.751 g cm^{-3}, D_m=1.72 g cm^{-3}, $2\theta_{max}$=50°, R=9.46% for 5996 reflections ($F_o \geq 8\sigma(F_o)$). **2**; triclinic system, space group $P\bar{1}$, a=14.503(3) Å, b=18.483(4) Å, c=14.185(3) Å, α=93.06(2)°, β=122.14(1)°, γ=72.89(2)°, V=3051.9(13) Å^3, Z=1, D_c=1.680 g cm^{-3}, $2\theta_{max}$=45°, R=7.53% for 6151 reflections ($F_o \geq 8\sigma(F_o)$). Eighteen and twenty waters of crystallization were found for **1** and **2**, respectively. Intensity data were collected and structures were solved for both crystals as described in Ref. 3b. Lists of atomic coordinates, thermal parameters, bond distances and angles for **1** and **2** can be obtained from the author (T. S.) on request. Details will be published elsewhere.

16) H. Aikoh and T. Shibahara, to be published.

17) If the mercury were cationic, the mercury-sulfur distances should be shorter. The oxidation state of cobalt in **1** is supposed to be +II.

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