Sulfur-Bridged Cubane-Type Molybdenum−Gallium Clusters with $Mo_3GaS_4^{n+}$ ($n = 5, 6$) Cores. X-ray Structures of $[Mo_3GaS_4(H_2O)_{12}](CH_3C_6H_4SO_3)_5 \cdot 14H_2O$ and $[Mo_3GaS_4(H_2O)_{12}](CH_3C_6H_4SO_3)_6 \cdot 17H_2O$

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Sulfur-bridged cubane-type molybdenum−gallium clusters $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ (**2**) and $[Mo_3GaS_4(H_2O)_{12}]^{6+}$ (**3**) have been synthesized from $[Mo_3S_4(H_2O)_9]^{4+}$ (**1**) and gallium metal and have been isolated as $\mathbf{2}(pts)_5 \cdot 14H_2O$ (**2·pts**) and $\mathbf{3}(pts)_6 \cdot 17H_2O$ (**3·pts**) (Hpts = *p*-toluenesulfonic acid), whose structures have been characterized by X-ray crystallography. Crystal data for **3·pts**: orthorhombic, space group $Pca2_1$, $a = 11.188(1)$ Å, $b = 30.936(4)$ Å, $c = 23.987(2)$ Å, $V = 8301(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.628$ g cm^{-3}, $D_{obsd} = 1.63$ g cm^{-3}, R (R_w) = 5.8% (6.3%) for 6102 reflections ($I > 3.0\sigma(I)$). Crystal data for **2·pts**: triclinic, space group $P\bar{1}$, $a = 16.406(4)$ Å, $b = 16.743(3)$ Å, $c = 13.173(4)$ Å, $\alpha = 90.64°$, $\beta = 98.40(2)°$, $\gamma = 89.32(2)°$, $V = 3579.2(14)$ Å^3, $Z = 2$, $D_{calcd} = 1.681$ g cm^{-3}, $D_{obsd} = 1.68$ g cm^{-3}, R (R_w) = 6.7% (10.1%) for 7612 reflections ($I > 3.0\sigma(I)$). The Mo−Ga distances (**3·pts**, 3.60[2] Å; **2·pts**, 3.52[2] Å) are much longer than the corresponding Mo−Mo (**3·pts**, 2.679[7] Å; **2·pts**, 2.713[3] Å) distances. At low H^+ concentrations, such as 0.5 M HCl, **2** is stable, and at H^+ concentration higher than 2 M HCl, **2** is oxidized by H^+ to give **3** with evolution of hydrogen gas. Chloride ion plays an important role in the oxidation of **2**. Electronic spectra of **3·pts** and **2·pts** are very similar. Peak positions and ϵ values (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): **3·pts**, 762 (447), 550 (204); **2·pts**, 760 (404), 548 (205). The cyclic voltammogram of **3** shows three reduction processes (the cathodic peak potentials, E_{pc}, are −0.83, −1.20, and −1.74 V, respectively), where the first and second processes are quasi-reversible (the anodic peak potentials, E_{pa}, are −0.55 and −1.00 V, respectively). The reduction current of each process is close to 1:1:3.

Introduction

Metal−sulfur cluster compounds have attracted much interest in chemical, biochemical, and catalytic investigations.[1] A considerable number of metal incorporation reactions have been reported wherein the incomplete cubane-type aqua cluster $[Mo_3S_4(H_2O)_9]^{4+}$ (**1**) reacts with metals to give mixed-metal cubane-type clusters with Mo_3MS_4 cores (M = Fe,[2] Co,[3] Ni,[4] Cu[5] Pd,[6] In,[7] Sn,[8] Sb[9] Hg[3], Pb[10]). The $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ cluster is the first example of this type of compound. Other cubane-type molybdenum−iron clusters with $MoFe_3S_4$ and related cores have extensively been studied as models of nitrogenase.[11]

In addition to direct reaction of **1** with metals or metal ions (e.g., Sn^{2+}),[8] $NaBH_4$ reduction of a solution of **1** and M^{2+} [12] and the reaction of **1** with $[Cr(H_2O)_6]^{2+}$ to give $[Mo_3CrS_4(H_2O)_{12}]^{4+}$,[13] as well as other routes to clusters with $Mo_3M'S_4n$ cores (M′ = Cu,[14a,c,d] M′ = Sb,[14b,c] M′ = W,[15] M′ = Co[16]), have been reported. Metal atom replacement of the incorporated

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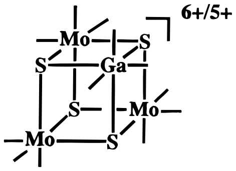
metal atom M′ in the cubane-type $Mo_3M'S_4$ core with Cu^{2+} to give a cluster with an $Mo_3CuS_4{}^{4+}$ core has also been reported,[17] and the existence of a new oxidation state in $Mo_3CuS_4{}^{5+}$ is known.[18] The reactivity of clusters with an Mo_3PdS_4[19] or Mo_3NiS_4[20] core toward small molecules such as CO, alkenes, and alkynes has been described. There are two possible driving forces for the formation of the cubane-type mixed-metal clusters from the incomplete cubane-type aqua cluster **1** and metals. One is the affinity of the metal for the bridging sulfur atoms, and the other is the reducing ability of the metal.[2,4b] In addition, the reaction of **1** with acetylene is known to give a cluster with carbon-sulfur bonds.[21]

Cluster **1** has attracted much attention not only in the synthetic but also in the theoretical area: many molecular orbital calculations have been carried out on **1**, which has six cluster valence electrons, and its model or derivative clusters to elucidate their electronic and magnetic properties and reactivities.[22] In addition to the six-electron clusters, seven-electron clusters with Mo_3S_4 cores have been prepared, their structures have been determined, and comparisons have been made with the six-electron clusters.[23]

We report here the synthesis and characterization of the sulfur-bridged cubane-type molybdenum−gallium clusters $[Mo_3GaS_4(H_2O)_{12}]^{n+}$ (**2**, $n = 5$; **3**, $n = 6$; see structure **I**) obtained



I

from the reaction of cluster **1** with gallium metal. No molybdenum−gallium mixed-metal clusters, especially clusters with Mo_3GaS_4 cores, have been reported to date although the synthesis, structural characterization, and properties of the sulfur-bridged cubane-type gallium cluster $[Ga_4S_4(^tBu)_4]$[24] and many clusters with Mo_4S_4 cores have been reported.[25] A preliminary report of portions of this work has appeared.[26]

Experimental Section

Materials. *p*-Toluenesulfonic acid (Hpts) was used after recrystallization from water. Gallium metal (beads) was purchased from Nakalia Tesque Co. Ltd. The molybdenum cluster $[Mo_3S_4(H_2O)_9]^{4+}$ (**1**) was obtained according to a published procedure.[27]

Electrochemical Measurements. Cyclic voltammetry of the cluster $[Mo_3GaS_4(H_2O)_{12}](pts)_6{\cdot}17H_2O$ (**3·pts**) was performed with a BAS 100B electrochemical analyzer. An acetonitrile/0.1 M tetrabutylammonium hexafluorophosphate mixture was used as solvent, and a glassy-carbon working electrode, an Ag/Ag^+ reference electrode, and a platinum wire counter electrode were employed. The redox potential of the ferrocinium/ferrocene couple was +0.071 V with respect to the reference electrode.

Analytical Measurements. ICP spectrometry was used for the analysis of molybdenum and gallium using a Shimadzu ICPS-500 analyzer. A weighted solid sample of $[Mo_3GaS_4(H_2O)_{12}](pts)_5{\cdot}14H_2O$ (**2·pts**) was dissolved in 3 M HCl, and the amount of H_2 evolved was measured (color change from yellow to brown) using a GASTEC No. 30 instrument.

Syntheses of Compounds. All experiments were carried out under a dinitrogen atmosphere.

$[Mo_3GaS_4(H_2O)_{12}]^{6+}$ (3) and $[Mo_3GaS_4(H_2O)_{12}](pts)_6{\cdot}17H_2O$ (3·pts). A mixture of Gallium metal (ca. 2 g, beads) and **1** (0.131 M per trimer, 25 mL in 2 M HCl) was stirred for 1 day at room temperature (ca. 20−25 °C), during which the color of the solution changed from green to dark brown. The resultant solution was filtered, the filtrate was diluted to 10 times its original volume with water, and the unreacted metal was removed. Chromatography was then performed on a Dowex 50W-X2 column (length 30 cm, diameter 2 cm). The resin was washed with 0.1 M HCl, and elution with 2 M HCl yielded a red-brown solution (ca. 200 mL). When the mixture was placed the column, the color of the resin turned black and no distinct bands could be distinguished. Therefore, chromatography was again performed (column length 60 cm, diameter 2 cm). The first (green) and second (brown) bands containing starting material **1** and the cubane-type cluster $[Mo_4S_4(H_2O)_{12}]^{4+}$ (the color of which changes to green on exposure to the air), respectively, were eluted with 1 M HCl. Then the third (brown) and fourth (purple) bands containing **3** (yield 27.5%) and the sandwich cubane-type cluster $[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9]^{8+}$,[28] respectively, were eluted with 2 M HCl.

To obtain crystals of **3·pts**, the solution of **3** in 2 M HCl from the third band was adsorbed onto a short-column cation exchanger, Dowex 50W-X2 (column length 3 cm, diameter 2 cm). The resin was washed with 0.1 M Hpts to remove chloride ion, and slow elution with 4 M Hpts gave a red solution. The concentrated part of the solution was stored in a freezer. After several days, red-brown crystals deposited, which were collected by filtration and washed with ethyl acetate; yield ca. 4% based on the solution **3** in 2 M HCl. Anal. Found (calcd): Mo, 14.03 (14.17); Ga, 3.20 (3.43); C, 24.68 (24.78); H, 5.03 (5.01).

$[Mo_3GaS_4(H_2O)_{12}]^{5+}$ (2) and $[Mo_3GaS_4(H_2O)_{12}](pts)_5{\cdot}14H_2O$ (2·pts). A procedure similar to that used for the synthesis of **3** was followed. A mixture of gallium metal (ca. 2 g, beads) and **1** (0.110 M per trimer, 25 mL in 2 M HCl) was stirred for 1 day in room temperature (ca. 20−25 °C), during which the color of the solution changed from green to dark brown. The resultant solution was filtered,

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Table 1. Summary of Crystal Data, Intensity Collection Details, and Structure Refinement Parameters for $[Mo_3GaS_4(H_2O)_{12}](CH_3C_6H_4SO_3)_6\cdot 17H_2O$ (**3·pts**) and $[Mo_3GaS_4(H_2O)_{12}](CH_3C_6H_4SO_3)_5\cdot 14H_2O$ (**2·pts**)

	3·pts	**2·pts**
formula	$Mo_3GaS_{10}O_{47}C_{42}H_{100}$	$Mo_3GaS_9O_{41}C_{35}H_{87}$
mol wt	2035.36	1810.13
space group	$Pca2_1$	$P\bar{1}$
a, Å	11.188(1)	16.406(4)
b, Å	30.936(4)	16.743(3)
c, Å	23.985(2)	13.173(4)
α, deg	90	90.64(2)
β, deg	90	98.40(2)
γ, deg	90	89.32(2)
V, Å^3	8301(1)	3579(1)
Z	4	2
d_{calcd}, g/cm^3	1.628	1.679
d_{obsd}, g/cm^3	1.63	1.68
λ(Mo Kα),[a] Å	0.710 69	0.710 69
abs coeff, cm^{-1}	11.07	12.38
no. of unique data, $I \geq 3\sigma(I)$	6102	7612
no. of variables	855	844
R (R_w),[b] %	5.8 (6.3)	6.7 (10.1)
goodness of fit	1.45	1.38

[a] Graphite-monochromatized. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 1/[\sigma^2(F_o)]$.

the filtrate was diluted to 10 times its original volume with water, and the unreacted metal was removed. Chromatography was then performed on a Dowex 50W-X2 columm (length 30 cm, diameter 2 cm). The resin was washed with 0.1 M HCl, and elution with a solution containing 0.5 M HCl and 1.5 M NaCl yielded a red-brown solution (ca. 200 mL), to which chromatography was again applied (column length 60 cm, diameter 2 cm). The first (green) and second (brown) bands containing starting material **1** and the cubane-type cluster $[Mo_4S_4(H_2O)_{12}]^{4+}$,[29] respectively, were eluted with a solution containing 0.5 M HCl and 0.5 M NaCl. Then the third (brown) and fourth (purple) bands containing **2** (yield 27%) and the sandwich cubane-type cluster $[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9]^{8+}$,[28] respectively, were eluted with a solution containing 0.5 M HCl and 1.5 M NaCl.

To obtain crystals of **2·pts**, the red solution of **2** in 0.5 M HCl and 1.5 M NaCl from the third band was adsorbed onto a short-column cation exchanger, Dowex 50W-X2 (column length 3 cm, diameter 2 cm). Elution using 4 M Hpts gave red-brown crystals of **2·pts**; yield ca. 16% based on the solution in 0.5 M HCl and 1.5 M NaCl. Anal. Found (calcd): Mo, 15.30 (15.90); Ga, 3.74 (3.84); C, 23.36 (23.22); H, 4.71 (4.84).

Structural Determination of $[Mo_3GaS_4(H_2O)_{12}](pts)_6\cdot 17H_2O$ (3·pts) and $[Mo_3GaS_4(H_2O)_{12}](pts)_5\cdot 14H_2O$ (2·pts). A red-brown crystal of **3·pts** and a red-brown crystal of **2·pts** were mounted in glass capillaries, respectively. Crystal data and collection and refinement parameters are summarized in Table 1 (and also in Table S1, Supporting Information). The atomic coordinates and thermal parameters for **3·pts** (Tables S2 and S3) and **2·pts** (Tables S6 and S7) are listed in the Supporting Information. The structures were solved by SHELXS-86, and the remaining non-hydrogen atoms were located from difference maps. Since the space group of **3·pts** is noncentric, the mirror image of the structure initially refined (which gave unweighted and weighted agreement factors of $R = 0.059$ and $R_w = 0.064$) was then tested. It was found to be superior and is the one reported here ($R = 0.058$ and $R_w = 0.063$). All the other calculations were performed using the teXsan crystallographic software package.

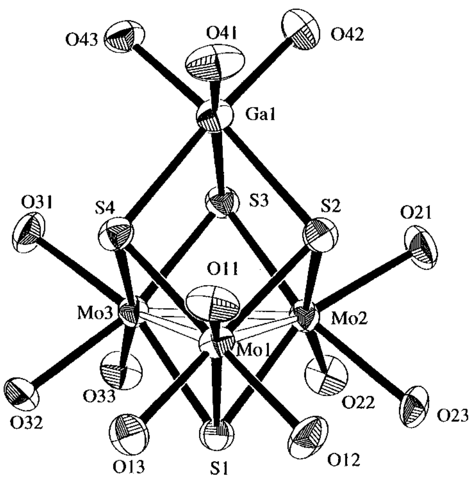

Figure 1. Perspective view of $[Mo_3GaS_4(H_2O)_{12}]^{6+}$ (**3**).

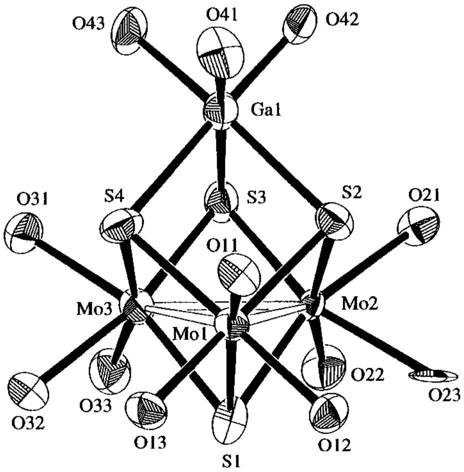

Figure 2. Perspective view of $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ (**2**).

Results and Discussion

Syntheses and Properties of Molybdenum–Gallium Clusters with Mo_3GaS_4 Cores. Through the reaction of **1** with gallium in hydrochloric acid, we have obtained two clusters with Mo_3GaS_4 cores, **2** and **3**, whose charges are 5+ and 6+, respectively. We propose tentatively the following reaction mechanism for the formation of **2** and **3**:

$$[Mo_3S_4(H_2O)_9]^{4+} + Ga + 3H_2O \rightarrow [Mo_3GaS_4(H_2O)_{12}]^{4+} \quad (1)$$

$$[Mo_3GaS_4(H_2O)_{12}]^{4+} + H^+ \rightarrow [Mo_3GaS_4(H_2O)_{12}]^{5+} + {}^1/_2H_2 \quad (2)$$

$$[Mo_3GaS_4(H_2O)_{12}]^{5+} + H^+ \rightarrow [Mo_3GaS_4(H_2O)_{12}]^{6+} + {}^1/_2H_2 \quad (3)$$

$$[Mo_3GaS_4(H_2O)_{12}]^{6+} + {}^1/_3Ga \rightarrow [Mo_3GaS_4(H_2O)_{12}]^{5+} + {}^1/_3Ga^{3+} \quad (4)$$

We have not detected the 4+ species, and we assume that the oxidation of the 4+ species by H^+ is very rapid to give the 5+ species **2**. At low H^+ concentrations, such as 0.5 M HCl, **2** is stable. At H^+ concentrations higher than 2 M HCl, **2** is oxidized by H^+ to give the 6+ species **3**: semiquantitative analysis of hydrogen gas evolved supports eq 3. Chloride ion plays an important role in the oxidation of **2**, since **2** is stable even in 4 M Hpts: coordination of chloride ion to the cluster core appears to prompt the oxidation. At the initial stages of the synthetic procedures for both **2** and **3**, 2 M HCl was used, where **2** survived, and we assume that eq 4 is operative and **2**

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(29) Sakane, G.; Shibahara, T. Unpublished results.

Table 2. Interatomic Distances (Å) and Angles (deg) in $[Mo_3GaS_4(H_2O)_{12}](CH_3C_6H_4SO_3)_6 \cdot 17H_2O$ (**3·pts**)[a]

Mo1−Mo2	2.674(2)	Ga1−S2	2.518(4)
Mo1−Mo3	2.692(2)	Ga1−S3	2.491(4)
Mo2−Mo3	2.672(2)	Ga1−S4	2.477(4)
mean	2.679[6]	mean	2.50[1]
Mo1−Ga1	3.618(2)	Mo1−O11	2.22(1)
Mo2−Ga1	3.625(2)	Mo1−O12	2.23(1)
Mo3−Ga1	3.566(2)	Mo1−O13	2.189(8)
mean	3.60[2]	Mo2−O21	2.231(9)
Mo1−S1	2.327(4)	Mo2−O22	2.188(9)
Mo2−S1	2.332(4)	Mo2−O23	2.201(9)
Mo3−S1	2.338(4)	Mo3−O31	2.206(9)
mean	2.332[3]	Mo3−O32	2.174(8)
		Mo3−O33	2.186(9)
Mo1−S2	2.340(4)	mean	2.20[1]
Mo1−S4	2.330(4)		
Mo2−S2	2.346(4)	Ga1−O41	1.95(1)
Mo2−S3	2.332(4)	Ga1−O42	2.01(1)
Mo3−S3	2.329(4)	Ga1−O43	2.011(9)
Mo3−S4	2.333(4)	mean	1.99[2]
mean	2.335[4]		
Mo2−Mo1−Mo3	59.72(4)	S1−Mo1−S2	109.8(1)
Mo1−Mo2−Mo3	60.48(4)	S1−Mo1−S4	108.9(1)
Mo1−Mo3−Mo2	59.80(4)	S1−Mo2−S2	109.5(1)
mean	60.0[2]	S1−Mo2−S3	109.5(1)
Mo2−Mo1−Ga1	68.48(4)	S1−Mo3−S3	109.4(1)
Mo3−Mo1−Ga1	66.97(4)	S1−Mo3−S4	108.4(1)
Mo1−Mo2−Ga1	68.18(4)	mean	109.3[2]
Mo3−Mo2−Ga1	67.01(4)	S2−Mo1−S4	86.2(1)
Mo1−Mo3−Ga1	69.01(4)	S2−Mo2−S3	86.2(1)
Mo2−Mo3−Ga1	69.37(4)	S3−Mo3−S4	87.7(1)
mean	68.2[4]	mean	86.7[5]
Mo1−Ga1−Mo2	42.97(3)	S2−Ga1−S3	79.3(1)
Mo1−Ga1−Mo3	43.74(3)	S2−Ga1−S4	79.4(1)
Mo2−Ga1−Mo3	43.25(3)	S3−Ga1−S4	81.1(1)
mean	43.3[2]	mean	79.9[6]

[a] The estimated deviation in brackets is calculated as being equal to $[\sum\Delta_i^2/n(n-1)]^{1/2}$, in which Δ_i is the deviation of the ith (of n) value from the arithmetic mean of the n values.

Table 3. Interatomic Distances (Å) and Angles (deg) in $[Mo_3GaS_4(H_2O)_{12}](CH_3C_6H_4SO_3)_5 \cdot 14H_2O$ (**2·pts**)[a]

Mo1−Mo2	2.708(2)	Ga1−S2	2.546(3)
Mo1−Mo3	2.713(1)	Ga1−S3	2.534(4)
Mo2−Mo3	2.718(2)	Ga1−S4	2.521(3)
mean	2.713[3]	mean	2.534[7]
Mo1−Ga1	3.519(2)	Mo1−O11	2.213(7)
Mo2−Ga1	3.549(2)	Mo1−O12	2.217(7)
Mo3−Ga1	3.494(2)	Mo1−O13	2.186(7)
mean	3.52[2]	Mo2−O21	2.23(1)
Mo1−S1	2.338(3)	Mo2−O22	2.19(2)
Mo2−S1	2.278(3)	Mo2−O23	2.20(1)
Mo3−S1	2.330(3)	Mo3−O31	2.207(7)
mean	2.32[2]	Mo3−O32	2.222(7)
		Mo3−O33	2.186(8)
Mo1−S2	2.315(3)	mean	2.206[5]
Mo1−S4	2.312(3)		
Mo2−S2	2.290(3)	Ga1−O41	2.06(1)
Mo2−S3	2.283(3)	Ga1−O42	1.93(1)
Mo3−S3	2.311(3)	Ga1−O43	2.03(1)
Mo3−S4	2.308(3)	mean	2.01[4]
mean	2.303[5]		
Mo2−Mo1−Mo3	60.18(4)	S1−Mo1−S2	105.8(1)
Mo1−Mo2−Mo3	59.99(4)	S1−Mo1−S4	107.5(1)
Mo1−Mo3−Mo2	59.83(4)	S1−Mo2−S2	108.7(1)
mean	60.0[1]	S1−Mo2−S3	107.9(1)
Mo2−Mo1−Ga1	68.06(4)	S1−Mo3−S3	105.2(1)
Mo3−Mo1−Ga1	66.75(4)	S1−Mo3−S4	107.8(1)
Mo1−Mo2−Ga1	66.89(4)	mean	107.2[6]
Mo3−Mo2−Ga1	66.23(4)	S2−Mo1−S4	91.7(1)
Mo1−Mo3−Ga1	67.74(4)	S2−Mo2−S3	90.5(1)
Mo2−Mo3−Ga1	68.38(4)	S3−Mo3−S4	92.4(1)
mean	67.3[3]	mean	91.5[6]
Mo1−Ga1−Mo2	45.06(3)	S2−Ga1−S3	79.5(1)
Mo1−Ga1−Mo3	45.51(3)	S2−Ga1−S4	81.9(1)
Mo2−Ga1−Mo3	45.39(3)	S3−Ga1−S4	82.6(1)
mean	45.3[1]	mean	81.3[9]

[a] The estimated deviation in brackets is calculated as being equal to $[\sum\Delta_i^2/n(n-1)]^{1/2}$, in which Δ_i is the deviation of the ith (of n) value from the arithmetic mean of the n values.

can exist in the presence of gallium metal even in 2 M HCl. Attempts to synthesize **2** at lower H^+ concentrations (e.g., 0.5 M HCl) were unsuccessful: no reaction of **1** with gallium metal was observed. Reaction of **1** with gallium in 2 M Hpts at room temperature gave mainly the cubane-type molybdenum cluster $[Mo_4S_4(H_2O)_{12}]^{4+}$, while reaction of **1** with indium metal in 4 M Hpts was observed to give clusters with Mo_3InS_4 cores.[7] The temperature of the reaction of **1** with gallium was kept at 20−25 °C. At temperatures lower than 5 °C, no reaction was observed, and at high temperatures (ca. 100 °C), the formation of the molybdenum cluster $[Mo_4S_4(H_2O)_{12}]^{4+}$ was observed (13%).

The role of gallium metal in the metal incorporation reaction is unique. Reaction of **1** with such metals as magnesium ($Mg^{2+/0}$, $E° = -2.36$ V), aluminum ($Al^{3+/0}$, $E° = 1.68$ V), and zinc ($Zn^{2+/0}$, $E° = -0.76$ V) and rare-earth metals (e.g., $La^{3+/0}$, $E° = -2.38$ V) having stronger reducing ability than gallium ($Ga^{3+/0}$, $E° = -0.56$ V) gives molybdenum clusters with the sandwich cubane-type $Mo_3S_4MoS_4Mo_3$ or cubane-type Mo_4S_4 cores, while iron ($Fe^{2+/0}$, $E° = -0.44$ V), cobalt ($Co^{2+/0}$, $E° = -0.28$ V), nickel ($Na^{2+/0}$, $E° = -0.26$ V), indium ($In^{3+/0}$, $E° = -0.34$ V), and other metals having weaker reducing ability than gallium give mixed-metal clusters with Mo_3MS_4 cores (M = metals other than Mo). No sandwich cubane-type $[(H_2O)_9Mo_3S_4GaS_4Mo_3(H_2O)_9]^{n+}$ clusters have been detected, while molybdenum−indium $[(H_2O)_9Mo_3S_4InS_4Mo_3(H_2O)_9]^{n+}$ clusters have been isolated, though the charge n of the cluster is not certain at present.[29]

X-ray Structures of $[Mo_3GaS_4(H_2O)_{12}](pts)_6 \cdot 17H_2O$ (3·pts) and $[Mo_3GaS_4(H_2O)_{12}](pts)_5 \cdot 14H_2O$ (2·pts). The structures of the cations of **3·pts** and **2·pts** are shown in Figures 1 and 2, respectively. Both cluster cations have an approximate symmetry of C_{3v}. A statistical disorder was observed between Mo2 and Ga1 of the cation of **2·pts**, and the following occupancy factors were used for the disordered atoms: Mo2, 0.75; Mo4, 0.25; Ga1, 0.75; Ga2, 0.25. Atoms with smaller occupancy factors, Mo4 and Ga2, are omitted in Figure 2 for clarity. Selected interatomic distances and angles of **3·pts** and **2·pts** are collected in Tables 2 and 3, respectively.

The Mo−Ga distances (**3·pts**, 3.60[2] Å; **2·pts**, 3.52[0] Å) are much longer than the corresponding Mo−Mo (**3·pts**, 2.679[7] Å; **2·pts**, 2.713[3] Å) distances, similar to the case of $[Mo_3InS_4(pts)_2(H_2O)_{10}]^{3+}$ having an $Mo_3InS_4^{5+}$ core (Mo−Mo, 2.681[7] Å; Mo-In, 3.72[2] Å)[7] and distinctly different from the case of $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ (Mo−Mo, 2.767[7] Å; Mo−Fe, 2.67[1] Å). The Mo−Ga and Mo−Mo distances in **2·pts** are slightly shorter and longer, respectively, than the corresponding distances in **3·pts**.

Electronic Spectra and Electrochemistry. Electronic spectra of **3·pts** in 2 M HCl and **2·pts** in 0.5 M HCl are shown in Figure 3. The corresponding peak positions and ϵ values (λ_{max}, nm (ϵ, M^{-1} cm^{-1})) are very similar for both compounds: **3·pts**, 762 (447), 550 (204); **2·pts**, 760 (404), 548 (205). The spectrum of **2·pts** in 2 M HCl is identical to that of **3·pts** in 2 M HCl in the visible region. The spectra of **2** and **3** are very similar to that of $[Mo_3InS_4(pts)_2(H_2O)_{10}]^{3+}$ (λ_{max} 758, 552 nm).[7]

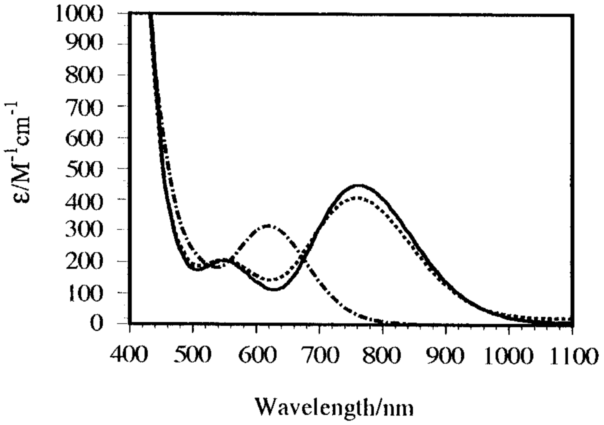

Figure 3. Electronic spectra of cubane-type clusters with $Mo_3GaS_4{}^{n+}$ (n = 5, 6) cores and of an incomplete cubane-type cluster with an $Mo_3S_4{}^{4+}$ core: (—) $[Mo_3GaS_4(H_2O)_{12}](pts)_6{\cdot}17H_2O$ (**3·pts**) in 2 M HCl; (···) $[Mo_3GaS_4(H_2O)_{12}](pts)_5{\cdot}14H_2O$ (**2·pts**) in 0.5 M HCl; (−•−) $[Mo_3S_4(H_2O)_9](pts)_4{\cdot}9H_2O$ (**1·pts**) in 2 M HCl.

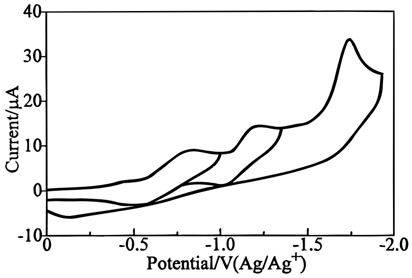

Figure 4. Cyclic voltammogram of $[Mo_3GaS_4(H_2O)_{12}]^{6+}$ (**3**, 0.3 mM) at a glassy carbon electrode in acetonitrile/0.1 M tetrabutylammonium hexafluorophosphate. Scan rate: 100 mV s^{-1}.

In contrast to the very small spectral differences between **2** and **3** with Mo_3GaS_4 cores, the electronic spectra of the cubane-type molybdenum clusters $[Mo_4S_4(edta)_2]^{n-}$ (n = 2−4), where the charges of the Mo_4S_4 cores are 6+, 5+, and 4+, respectively, differ greatly.[25a] The electronic structures of **2** and **3** were investigated by using the spin-polarized discrete variational (DV)−Xα method, C_{3v} symmetry being applied for both clusters. The degree of spin polarization of **3** having odd electrons is very small. In the molecular orbitals of **2** and **3**, HOMO and next to HOMO orbitals and LUMO and next to LUMO orbitals consist mainly of Mo 4d atomic orbitals and the HOMO−LUMO gaps are very close to each other, which may be the reason for the similarity of the electronic spectra.[30]

The cyclic voltammogram of **3** (Figure 4) shows three reduction processes (the cathodic peak potentials, E_{pc}, are −0.83, −1.20, and −1.74 V, respectively), where the first and second processes are quasi-reversible (the anodic peak potentials, E_{pa}, are −0.55 and −1.00 V, respectively), but the third one is irreversible. The spectrum obtained by means of convolution and semi-integration of the voltammogram showed that the ratio of the height of each process is close to 1:1:3. The formal oxidation states of the metals in **3** are assigned tentatively as $Mo^{IV}Mo^{III}{}_2$ and Ga^{III}, and the those after the three reduction processes, as $Mo^{III}{}_3$ and Ga^0. The cyclic voltammogram of the molybdenum−iron cluster $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ shows three consecutive one-electron reduction processes; the cathodic peak potentials, E_{pc}, are −0.91, −1.47, and −1.81 V, respectively,[2b] and these potentials are very similar to those in the cyclic voltammogram of **3**. Detailed research will be required to assign the oxidation states of metals in each reduction process of **3**.

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Supporting Information Available: Figures showing valence state molecular orbital energy levels and atomic components for **2** and **3** (3 pages). X-ray crystallographic files, in CIF format, for compounds **3·pts** and **2·pts** are available on the Internet only. Ordering and access information is given on any current masthead page.

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