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Synthesis and Characterization of the Cubane-Type Molybdenum–Indium Mixed-Metal Cluster $[Mo_3InS_4(pts)_2(H_2O)_{10}]^{3+}$

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It is well-known that indium metal is very useful as a component of low melting alloys and of intermetallic compound semiconductors, such as InSb, InAs, and InP, and that the metal is important as a dopant in the manufacturing of p-type Ge and Si semiconductors.[1] However, the chemistry of indium has not been fully developed, and coordination compounds of indium are very few.

We have recently developed a new type of reaction in which the incomplete cubane-type sulfur-bridged molybdenum cluster $[Mo_3S_4(H_2O)_9]^{4+}$ (A) incorporates metals to give cubane-type mixed-metal clusters with Mo_3MS_4 cores (M = Fe,[2,3] Co,[4] Ni,[5] Cu,[6] Sn,[7] Hg,[4] etc.). In this paper, we describe the synthesis and characterization of a molybdenum–indium mixed-metal cubane-type cluster, $[Mo_3InS_4(pts)_2(H_2O)_{10}]^{3+}$ (B) (Hpts = *p*-toluenesulfonic acid), prepared by the reaction of the aqua ion A with metallic indium, together with the X-ray structure of the *p*-toluenesulfonate salt of B.

The compound $[Mo_3InS_4(pts)_2(H_2O)_{10}](pts)_3 \cdot 13H_2O$ (B′) was synthesized under a dinitrogen atmosphere. Indium plate (0.62 g) was added to the green aqua ion A (2.7×10^{-2} M, 20 mL; In/A = 10) in 4 M Hpts, which was stirred for 2 days at room temperature. The resultant red-brown solution was filtered to remove unreacted indium metal and was stored in a refrigerator (ca. −5 °C) for 2 days. Brown needlelike crystals were obtained, yield 0.55 g (57%).[8]

The X-ray analysis[9] of B′ revealed the existence of a cubane-type core $Mo_3InS_4^{5+}$ and coordination of two pts^- anions to the indium in the cluster (Figure 1). The cluster B may be regarded as an indium complex with the ligands H_2O, pts^-, and A, when the molybdenum cluster A functions as a ligand having three ligating sulfur atoms. No cubane-type mixed-metal clusters with Mo_3InS_4 cores have been reported so far. Almost all compounds made up of molybdenum, indium, and sulfur (and some other elements) are intercalation compounds that consist of Chevrel phase Mo_6S_8 (or closely related Chevrel phase clusters)[10] or MoS_2[11] and indium. Very recently a discrete cluster [{Cp(CO)$_3$-

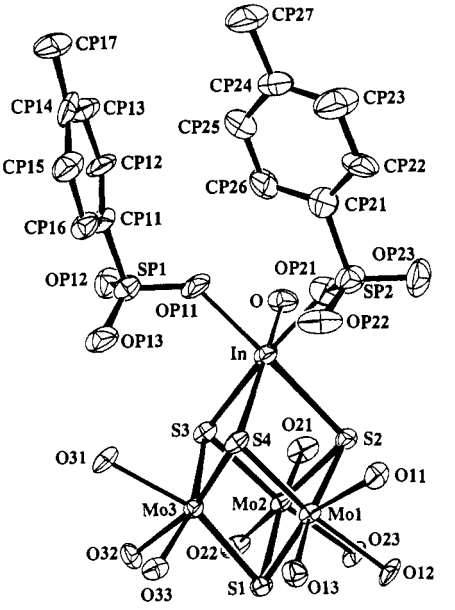

Figure 1. Perspective view of $[Mo_3InS_4(pts)_2(H_2O)_{10}]^{3+}$ (B). Selected bond distances (Å): Mo1–Mo2, 2.691(2); Mo1–Mo3, 2.681(2); Mo2–Mo3, 2.675(2); Mo1–In, 3.705(5); Mo2–In, 3.714(3); Mo3–In, 3.740(3); Mo*n*–S1 (*n* = 1–3, mean), 2.340[6]; Mo*n*–S*n*′ (*n* = 1–3, *n*′ = 2–4, mean), 2.342[6]; In–S*n* (*n* = 2–4, mean), 2.645[14]; Mo–O(H_2O, mean), 2.202[21]; In–O(H_2O, mean), 2.216(13); In–O(pts, mean), 2.174[19].

(1) For example: III-V Compound Semiconductors and Semiconductor Properties of Superionic Materials; Willarson, R. K., Beer, A. C., Eds.; *Semiconductors and semimetals Vol. 26*; Academic Press: Boston, MA, 1988.
(2) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1986**, *108*, 1342–1343.
(3) Katada, M.; Akashi, H.; Shibahara, T.; Sano, H. *J. Radioanal. Nucl. Chem. Lett.* **1990**, *145* (2), 143–149.
(4) Shibahara, T.; Akashi, H.; Yamasaki, M.; Hashimoto, K. *Chem. Lett.* **1991**, 689–692.
(5) Shibahara, T.; Yamasaki, M.; Akashi, H.; Katayama, T. *Inorg. Chem.* **1991**, *30*, 2693–2699.
(6) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1988**, *110*, 3313–3314.
(7) Akashi, H.; Shibahara, T. *Inorg. Chem.* **1989**, *28*, 2906–2907.
(8) Anal. Found (calcd for B′): C, 23.46 (23.34); H, 4.57 (4.53).
(9) X-ray data were collected on a Mac Science MXC 18 diffractometer at the Analytical Center of Okayama University of Science. The structure was solved as described in ref 5. Crystal data: triclinic system, space group $P\bar{1}$, a = 16.807(8) Å, b = 23.393(13) Å, c = 9.301(3) Å, α = 91.23(4)°, β = 103.58(4)°, γ = 76.95(4)°, V = 3460.9(27) Å^3, Z = 2, D_c = 1.729 g cm^{-3}, D_m = 1.73 g cm^{-3}, R = 7.49% for 5907 reflections ($|F_o| \geq 4\sigma|F_o|$). The structure was solved by direct methods (SHELXS) and refined by least squares. No absorption correction was applied. Details will be described elsewhere.

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$Mo\}_4In_4S_4]$ was reported, which had a cubane-type In_4S_4 core and four Mo–In bonds.[12]

The cluster B has two absorption peaks in the visible region, as shown in Figure 2 [λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 552 (192), 758 (510) in 2 M Hpts], and returns to A on exposure to air.

The charge of the core Mo_3InS_4 is five, while that of the cores of the clusters $[Mo_3FeS_4(H_2O)_{10}]^{4+}$,[2,3] $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$,[4] $[Mo_3NiS_4(H_2O)_{10}]^{4+}$,[5] and $[\{Mo_3CuS_4(H_2O)_9\}_2]^{8+}$ [6] obtained from the aqua ion A and the corresponding metals is four. Binding energies (eV) of molybdenum ($3d_{3/2}$ = 233.2 and $3d_{5/2}$ = 230.2) and indium ($3d_{3/2}$ = 453.0 and $3d_{5/2}$ 445.4) were measured by XPS of B′ (Cls = 285.0 eV) so that the oxidation states of molybdenum and indium atoms could be determined. For comparison, those of molybdenum atoms in $[Mo_3S_4(H_2O)_9](pts)_4 \cdot 9H_2O$ (A′; $3d_{3/2}$ = 233.7 and $3d_{5/2}$ = 230.7), $[Mo_3FeS_4(H_2O)_{10}](pts)_4 \cdot 7H_2O$ (C′; $3d_{3/2}$ = 233.2 and $3d_{5/2}$ = 230.2), and $[Mo_3NiS_4(H_2O)_{10}](pts)_4 \cdot 7H_2O$ (D′; $3d_{3/2}$ = 233.3 and $3d_{5/2}$ = 230.3) and those of indium in $InCl_3$ ($3d_{3/2}$ = 454.3 and $3d_{5/2}$ = 446.7) were also obtained.[13] The binding energies of molybdenum in B′, C′, and D′ are similar to each other, and those of indium in B′ are slightly smaller than those of indium in $InCl_3$. Since the oxidation state "three" of indium is more common than the oxidation state "two",[14] the following formal oxidation states of metals in B′ are assigned tentatively: "Mo_3 (4,3,3); In (3)" rather than "Mo_3 (4,4,3); In (2)".

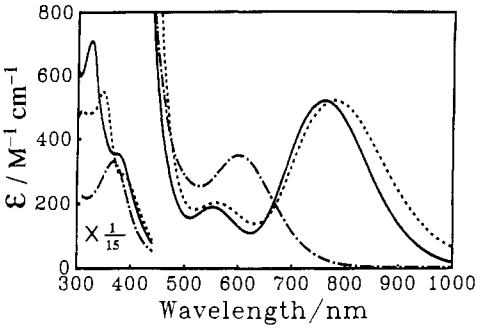

Figure 2. UV–visible spectra: —, $[Mo_3InS_4(pts)_2(H_2O)_{10}]^{3+}$ (B) in 2 M Hpts; ···, $[Mo_3InS_4(pts)_2(H_2O)_{10}]^{3+}$ (B) in 1 M HCl; – · –, $[Mo_3S_4(H_2O)_9]^{4+}$ (A) in 2 M Hpts.

We assume an intermediate $Mo_3S_4InS_4Mo_3^{8+}(aq)$ and hydrogen-ion-oxidation of it as follows:[15]

$$Mo_3S_4InS_4Mo_3^{8+}(aq) + H^+ \rightarrow Mo_3InS_4^{5+}(aq) + A + {}^1/_2H_2$$

The isolation of the intermediate species is in progress.

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Supplementary Material Available: Listings of crystallographic details, atomic coordinates and thermal parameters, and bond distances and angles (Tables S1–S3) and infrared spectra of A′, B′, and D′ (Figure S1) (9 pages). Ordering information is given on any current masthead page.

(10) For example: (a) Tarascon, J. M.; Hull, G. W. *Mat. Res. Bull.* **1986**, *21*, 859–869. (b) Selwyn, L. S.; McKinnon, W. R.; Le Page, Y. *Phys. Rev. B* **1990**, *42*, 10427–10432. (c) Tarascon, J. M.; DiSalvo, F. J.; Waszczak, J. V.; Hull, G. W., Jr. *Phys. Rev. B* **1985**, *31*, 1012–1021. (d) Tarascon, J. M.; Waszczak, J. V.; DiSalvo, F. J. *Solid State Commun.* **1985**, *53*, 849–855. (e) Yomo, S.; Hor, P. H.; Meng, R. L.; Chu, C. W.; Wu, M. K.; Tarascon, J. M. *Phys. B + C (Amsterdam)* **1985**, *135*, 248–251. (f) Wakihara, M.; Satoh, K.; Hinode, H.; Taniguchi, M. *J. Less-Common Met.* **1990**, *157*, 281–288.

(11) For example: (a) Srivastava, S. K. *Mater. Res. Bull.* **1991**, *6*, 631–639. (b) Astava, S. K. S.; Avasthi, B. N. *Synth. Met.* **1985**, *11*, 193–205. (c) Srivastava, S. K.; Avasthi, B. N.; Mathur, B. K. *J. Mater. Sci. Lett.* **1984**, *3*, 671–673.

(12) Merzweiler, K.; Rudolph, F.; Brands, L. *Z. Naturforsch.* **1992**, *47b*, 470–476.

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

(14) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; p 208.

(15) A corresponding tin compound $[(H_2O)_9Mo_3S_4SnS_4Mo_3(H_2O)_9]^{8+}$ has been isolated: see ref 7.