Inorganica Chimica Acta, *216* (1994) 13–14

Inorganica
Chimica Acta
Preliminary Communication

Oxo- and sulfido-bridged sandwich cubane-type molybdenum–indium mixed-metal cluster. Synthesis and X-ray structure of $[(H_2O)_9Mo_3S_3OInOS_3Mo_3(H_2O)_9](CH_3 \cdot C_6H_4 \cdot SO_3)_8 \cdot 30H_2O$

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(Received July 29, 1993, revised October 6, 1993)

Abstract

The aqua cluster $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (**B**) reacts with indium metal in aqueous solution of Hpts to give a novel sandwich cubane-type molybdenum–indium mixed-metal cluster $[(H_2O)_9Mo_3S_3OInOS_3Mo_3(H_2O)_9]^{8+}$ (**C**). The cluster **C** is oxidized in hydrochloric acid to give the starting species **B**, evolution of hydrogen gas being detected. An intermediate is isolated, and is tentatively assigned to $Mo_3In(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2{}^{5+}(aq)$ (**D**). The following reaction pathways are proposed: $2\mathbf{B} + In \rightarrow \mathbf{C}$; $\mathbf{C} + H^+ \rightarrow \mathbf{D} + \mathbf{B} + \frac{1}{2}H_2$; $\mathbf{D} + 2H^+ \rightarrow \mathbf{B} + In^{3+} + H_2$.

Key words Crystal structures, Molybdenum complexes; Indium complexes, Oxo complexes; Sulfido complexes; Cluster complexes

Several metal-incorporation reactions have been reported in which the incomplete cubane-type sulfido-bridged molybdenum aqua cluster $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ (**A**) reacts with metals to give mixed-metal clusters with Mo_3MS_4 cores (M = metals) [1]. It is clear that the bridging sulfurs play an important role for the metal-incorporation reaction, since the corresponding oxo-bridged cluster $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ does not incorporate metals [1a]

We report here the reaction of the oxo- and sulfido-bridged incomplete cubane-type aqua cluster $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (**B**) [2] with indium metal to give a sandwich cubane-type molybdenum–indium mixed-metal cluster $[(H_2O)_9Mo_3S_3OInOS_3Mo_3(H_2O)_9]^{8+}$ (**C**). Nothing has been reported so far on the reactivity of **B** with metals. The usefulness of indium in industry is well recognized, see ref. 1d and refs. therein.

All the procedures were performed under a dinitrogen atmosphere. Several pieces of indium metal (0.53 g) were introduced into a conical flask containing **B** (0.046 M per trimer, 20 ml) in 4 M Hpts (*p*-toluenesulfonic acid), and the mixture was allowed to stand one day at room temperature with stirring. The color of the solution turned from green to red–brown. The solution was filtered to remove the remaining indium metal, and the resulting solution was stored in a refrigerator. After one week, red–brown plate like crystals of $[(H_2O)_9Mo_3S_3OInOS_3Mo_3(H_2O)_9](pts)_8 \cdot 30H_2O$ (**C′**) deposited, which were collected by filtration, and dried by a dinitrogen stream; yield 54%. The high hygroscopicity of **C′** prevented elemental analyses.

The X-ray crystallographic structure investigation† of **C′** revealed the existence of a sandwich cubane-type core $Mo_3S_3OInOS_3Mo_3{}^{8+}$, the indium metal residing on a center of symmetry (Fig. 1). Two long and one short Mo–Mo distances are present: the distance between metal atoms bridged by one oxygen atom and one sulfur atom is shorter than those between metal atoms bridged by two sulfur atoms. The Mo–Mo distances of **C′** are shorter than those of the incomplete cubane-type cluster in $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9](pts)_4 \cdot 7H_2O$ (**B′**) [3] by 0.041–0.072 Å. One long and two short Mo–In distances are present in **C′**, while the three Mo–In distances in the sulfur-bridged mixed-metal cluster $[Mo_3InS_4(pts)_2(H_2O)_{10}](pts)_3 \cdot 13H_2O$ [1d] are not so different from each other (mean, 3.720[18]).

The aqua cluster **C′** dissolved in hydrochloric acid decomposes to give the starting material **B**, where the presence of an intermediate species can be detected by the observation of a UV–Vis spectral change, while the aqua cluster **C′** dissolved in 1–4 M Hpts is rather

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†X-ray diffraction data were collected from a crystal mounted in a glass capillary on a Mac Science MXC 18 diffractometer at the Analytical Center of Okayama University of Science The structure solution and refinement were performed by SHELXS-86 and teXsan, respectively. An empirical absorption correction using the program DIFABS was applied Crystal data triclinic system, space group $P\bar{1}$, $a = 17.964(2)$, $b = 19.147(3)$, $c = 10.070(1)$ Å, $\alpha = 95.15(1)$, $\beta = 100.44(1)$, $\gamma = 111.68(1)$, $V = 3118.6(8)$ Å^3, $Z = 1$, $D_c = 1.677$ g cm^{-3}, $R(R_w) = 5.6(6.6)$%. See also ‘Supplementary material’.

SSDI 0020-1693(93)03726-Q

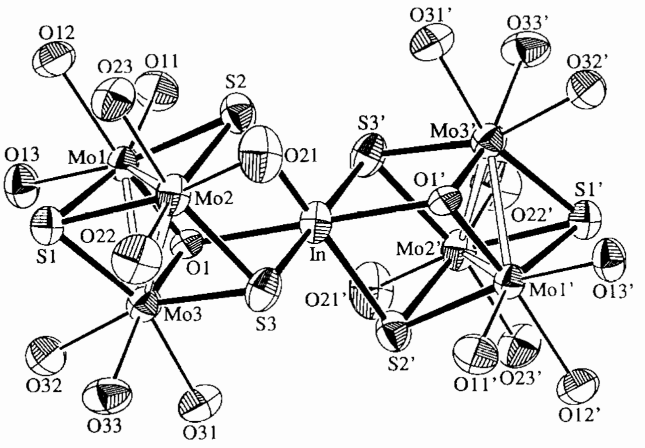

Fig. 1 ORTEP drawing of the cation of C′. Selected atomic distances (Å) Mo1–Mo2, 2.651(2); Mo1–Mo3, 2.570(2), Mo2–Mo3, 2.659(2); Mo1–In, 3.488(1); Mo2–In, 3.810(1); Mo3–In; 3.450(1); Mo*k*–S*k*′ (*k*, *k*′ = 1–3), 2.332[5]; Mo*k*–O1 (*k* = 1, 3; mean), 1.988[8]; In–S*k* (*k* = 2, 3; mean), 2.67[3], In–O1, 2.295(6), Mo–O(H_2O), 2.20[2]. (The primed atoms are related to the unprimed ones by a center of symmetry.)

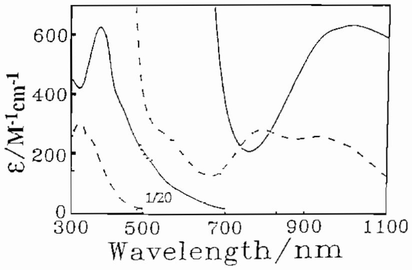

Fig. 2. UV–Vis spectra: —— $[(H_2O)_9Mo_3S_3OInOS_3Mo_3(H_2O)_9]^{8+}$ (**C**) in 1 M Hpts; - - - $[Mo_3OS_3(H_2O)_9]^{4+}$ (**B**) in 1 M Hpts; – - – $Mo_3InOS_3{}^{5+}(aq)$ (**D**) in 1 M NaCl/0.1 M HCl.

stable. The higher the concentration of hydrochloric acid, the faster the decomposition reaction: in 1 M HCl the decomposition is complete within 30 min.

An intermediate was isolated by the ion exchange technique using Dowex 50W-X2, and was tentatively assigned as $Mo_3In(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2{}^{5+}(aq)$ (**D**). The intermediate **D** is further oxidized by hydrogen ions in the presence of chloride ions. Evolution of hydrogen gas was detected in the reaction. The electronic spectra of **C** (λ_{max} (nm) (ϵ (M^{-1} cm^{-1})): 1000 (633), 374 (12 500)) and **D** (923 (258), 784 (279), 550sh (262), 333 (6000)) are shown in Fig. 2 together with that of **B**.

The following reaction pathways are plausible, where the presence of chloride ion accelerates the oxidation reactions by hydrogen ions in the second and third steps: coordination of chloride ion(s) to **C** and **D** seems to cause negative shifts of the redox potentials of **C** and **D**, which enables hydrogen ions to oxidize the clusters.

$$2\mathbf{B} + In \longrightarrow \mathbf{C} \quad (1)$$

$$\mathbf{C} + H^+ \longrightarrow \mathbf{D} + \mathbf{B} + \tfrac{1}{2}H_2 \quad (2)$$

$$\mathbf{D} + 2H^+ \longrightarrow \mathbf{B} + In^{3+} + H_2 \quad (3)$$

The aqua ion **B** differs from **A** only by one bridging atom, and the two ions are similar to each other in stability toward air-oxidation, color, and behavior on column chromatography. However, while the reaction product of **B** with indium metal in 4 M Hpts is the sandwich cubane-type cluster **C**, the corresponding reaction product of **A** in the same conditions is the single cubane-type cluster $[Mo_3InS_4(pts)_2(H_2O)_{10}]^{3+}$ [1d]*. Apparently the indium-incorporated cluster **C** with μ-O has more a positive redox potential than that of the corresponding sulfur-bridged cluster $[(H_2O)_9Mo_3S_4InS_4Mo_3(H_2O)_9]^{8+}$.

Currently we are comparing the reactivities of A and B to probe further the roles of oxygen and sulfur in the two incomplete cubane-type molybdenum clusters.

Supplementary material

Tables of crystallographic data, atomic coordinates, thermal parameters, atomic distances and angles of **C**′ are available from author T.S. on request.

Acknowledgements

Y.Y. thanks the Inoue Foundation for Science for financial support. This work was partly supported by a Grand-in-Aid for Scientific Research (Nos. 04640587, 04241102) from the Ministry of Education, Science and Culture.

References

1 (a) M = Fe: T. Shibahara, H. Akashi and H. Kuroya, *J. Am. Chem. Soc.*, *108* (1986) 1342; (b) M = Ni: T. Shibahara, M. Yamasaki, H. Akashi and T. Katayama, *Inorg. Chem.*, *30* (1991) 2693; (c) M = Pd: T. Murata, H. Gao, Y. Mizobe, F. Nakano, S. Motomura, T. Tanase, S. Yano and M. Hidai, *J. Am. Chem. Soc.*, *114* (1992) 8287; (d) M = In: G. Sakane and T. Shibahara, *Inorg. Chem.*, *32* (1993) 777

2 (a) T. Shibahara, H. Miyake, K. Kobayashi and H. Kuroya, *Chem. Lett.*, (1986) 139; (b) T. Shibahara and H. Akashi, *Inorg. Synth.*, *29* (1992) 260

3 T. Shibahara, G. Sakane and S. Mochida, *J. Am. Chem. Soc.*, *115* (1993) 10408.

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*In low acid concentration (0.1 M Hpts), the reaction product of A with indium metal is the sandwich cubane-type $[(H_2O)_9Mo_3S_4InS_4Mo_3(H_2O)_9]^{n+}$ (n = 7 or 8) aqua cluster. The core structure $Mo_3S_4InS_4Mo_3$ has been determined by X-ray structure analysis. However, the charge (7+ or 8+) has not been determined yet because of the disorder of some of the pts anions.