A Sandwich Cubane-Type Mo–Sn Cluster: Synthesis and Crystal Structure of $[(H_2O)_9Mo_3OS_3SnS_3OMo_3(H_2O)_9](CH_3C_6H_4SO_3)_8{\cdot}18H_2O$

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A novel sandwich cubane-type mixed-metal Mo–Sn cluster compound $[Mo_6SnO_2S_6(H_2O)_{18}](pts)_8{\cdot}18H_2O$ (A) was synthesized by the reaction of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (B) with tin metal in *p*-toluensulphonic acid (Hpts) solution. The compound A was characterized by the X-ray structure determination and UV–vis spectrum.

Much attention has been paid on the cuboidal Mo–S clusters due to their potential application in biomimetic catalytic processes. A series of trinuclear cuboidal molybdenum aqua ions $[Mo_3O_{4-n}S_n]^{4+}$ ($n = 0 - 4$) have been prepared and characterized,[1] and many derivatives with these cores have been reported.[2] It is known that $[Mo_3S_4]^{4+}$ can react with many transition metals to form cubane-type mixed-metal clusters Mo_3MS_4 (M = Pd, Ni, Fe, Co, etc.), which show interesting reactivity towards small molecules[3] such as alkenes, alkynes, CO, and ^tBuNC. Nevertheless, such kind of reports are very rare for the compounds with the analogous $[Mo_3OS_3]^{4+}$ core, where only a μ-position is different from that in $[Mo_3S_4]^{4+}$. Normally, $[Mo_3OS_3]^{4+}$ is also quite stable in hydrochloric acid, and it can react with many transition metals, and obvious color and spectral changes are observed. However, it is surprisingly difficult to isolate a pure mixed-metal compound. For example, $[Mo_3NiS_4]^{4+}$ is quite stable, but $[Mo_3NiOS_3]^{4+}$ decomposed into the starting material $[Mo_3OS_3(H_2O)_9]^{4+}$ (B) in 1M HCl within 8 h under dinitrogen atmosphere. Such a considerable difference drives us to study the synthesis and properties of these structurally analogous cubane-type clusters. It will be meaningful to understand the influence of different μ-ligands on the geometry and electron structure of these trinuclear Mo–S cluster cations. But till now, only one example with the sandwich-cubane structure $[Mo_6InO_2S_6(H_2O)_{18}](pts)_8{\cdot}30H_2O$ has been synthesized.[4] Here we report the synthesis, X-ray structure and UV–vis spectrum of the sandwich cubane-type Mo–Sn compound, $[(H_2O)_9Mo_3OS_3SnS_3OMo_3(H_2O)_9](pts)_8{\cdot}18H_2O$ (A).

The starting material $[Mo_3OS_3(H_2O)_9]^{4+}$ (B) was prepared according to the literature.[5] Under dinitrogen atmosphere, 0.5 g tin powder was added into a shlenk flask containing (B) (0.5 M per trimer, 10 mL) in 4 M Hpts (*p*-toluenesufonic acid). The color of the solution turned from green to purple within 30 min. After stirred for one day, the mixture was filtered into another shlenk flask to remove the remaining metallic powder. The resulting clear solution was stored in a refrigerator. Dark-purple prism crystals of (A) deposited in a few days.

Compound (A) is highly soluble in water, and little amount of moisture will destroy the crystals. It can also be well dissolved in some organic solvents such as acetone, ethanol and acetonitrile.

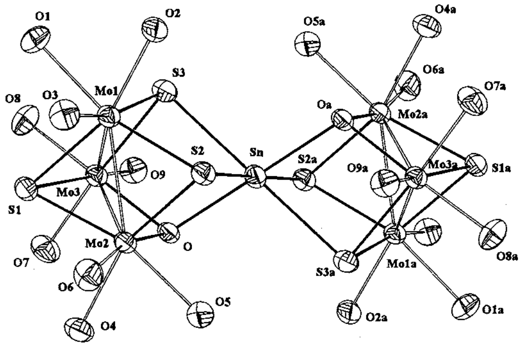

Figure 1. ORTEP drawing of the cation of compound (A). Selected atomic distances(Å): Mo1–Sn = 3.7657(7); Mo2–Sn = 3.4094(7); Mo3–Sn = 3.4046(7); Mo1–Mo2 = 2.6591(10); Mo1–Mo3 = 2.6839(10); Mo2–Mo3 = 2.5920(10); Mo1–S1 = 2.338(2); Sn–O = 2.201(5); Sn–S2 = 2.648(2); Sn–S3 = 2.636(2); Mo1–S2 = 2.347(2); Mo1–S3 = 2.355(2); Mo2–S1 = 2.352(2); Mo2–O = 1.989(5); Mo3–O = 1.983(5); Mo3–S1 = 2.340(2); Mo2–S2 = 2.326(2); Mo3–S3 = 2.333(2).

The X-ray structure of (A) has been characterized[6] and the ORTEP drawing of its cation is shown in Figure 1 together with selected atomic distances. The crystal structure of (A), like that of $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ and $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$, shows the typical sandwich cubane-type framework,[7] and it is heavily distorted because of the existence of O and Oa, which are on the trans-positions around the Sn atom. Sn resides in the center of symmetry, integrates two Mo_3OS_3 units via four Sn–S bonds and two Sn–O bonds. There are two types of Mo atoms in compound (A): Mo1 is coordinated with three μ_3-S, Mo2(Mo3) with two μ_3-S and one μ_3-O. All these Mo atoms are octahedrally coordinated.

The Mo–Sn distances are between 3.405–3.766 Å. It seems that there is not direct bonding between them. The coordination of Mo1 and Mo2 (Mo3) to a varied number of μ_3-S and μ_3-O lead to the different Mo–Sn and Mo–Mo distances: the bond lengths of Mo2–Sn and Mo3–Sn are much shorter than that of Mo1–Sn by 0.357–0.361 Å; the Mo2–Mo3 distance is shorter than Mo1–Mo2 and Mo1–Mo3 by 0.067–0.092 Å. The average Mo–Mo distances of (A) is similar to those of $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$ and shorter than those of $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ by 0.043 Å.

We assume that Sn in compound (A) has the same oxidation-state Sn(IV) as that in $[Mo_6SnS_8(H_2O)_{18}]^{8+}$, since these two compounds are synthesized in a similar way, and they have similar structural and spectral feature.

The UV–vis spectrum of (A) is shown in Figure 2, which was measured between 200–1000 nm with reference to 0.2 M Hpts. The spectrum shows four absorption peaks (λ_{max}/nm): (a)

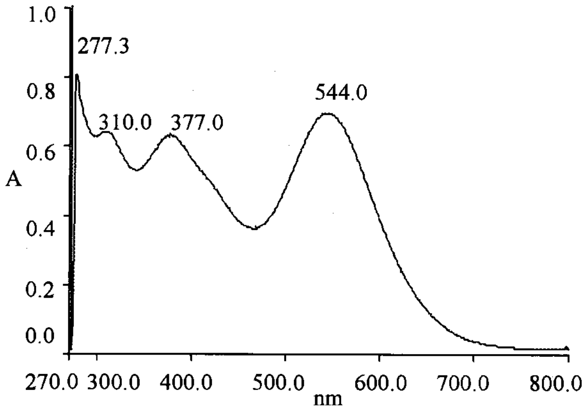

Figure 2. UV-vis spectrum of $[Mo_6SnO_2S_6(H_2O)_{18}]^{4+}$ in 0.2 M Hpts.

277.3, (b) 310.0, (c) 377.0 and (d) 544.0. There is an abrupt decrease near the absorption 277.3 nm, which might be due to the small concentration difference of Hpts between the sample and reference solution (Hpts has strong absorption in the UV region). Whether it is the absorption by the sample is under investigation. Absorptions (c) 377.0 and (d) 544.0 are similar to those of $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ (in 2 M Hpts),[8] and considerably different from those of $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$, which has only two absorption peaks[4] (nm): 374 and 1000. The crystals of (A) and the aqueous HCl solution are more air-sensitive than that of the all-S analogue $[Mo_6SnS_8(H_2O)_{18}]^{8+}$. They are easily decomposed when exposed in air. There is possible partial oxidation during the spectral measurement. The HCl solution decomposes within a few hours in air with the color change from purple into yellowish green. It may follow the route: $[Mo_6SnO_2S_6(H_2O)_{18}]^{8+}$ to $[Mo_3SnOS_3(H_2O)_9]^{6+}$ to $[Mo_3OS_3(H_2O)_9]^{4+}$. This process can be monitored by UV–vis spectra: peaks (c) and (d) go down obviously in 3 h, while (a) and (b) can withstand much longer. Comparatively, this decomposition is not so quick in 4 M Hpts.

If the synthesis is rationally designed, more mixed-metal cluster compounds can be synthesized from the precursor $[Mo_3OS_3]^{4+}$. Further study on the synthesis and reaction of these compounds is in progress.

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6 Data collections were performed on Siemens SMART CCD diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). Crystal data were corrected with SADABS programs. The structure was refined with Siemens SHELXL-97 softwares. The crystal data of compound (A): $C_{56}H_{56}O_{62}S_{14}Mo_6Sn$, triclinic $P\bar{1}$, Fw = 2864.18, a = 12.3706(2) Å, b = 15.1691(3) Å, c = 15.8375(3) Å, α = 99.2630(10)°, β = 99.9900(10)°, γ = 107.0150(10)°, V = 2727.03(9) Å^3, Z = 1. The final R_1 = 0.0641 and wR = 0.1540 for 7575 observed reflections ($I > 2\sigma$).
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