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Concerning the Identity of the Pb-Containing Heterometallic Product Obtained on Reacting $[Mo_3S_4(H_2O)_8]^{4+}$ with Pb Metal

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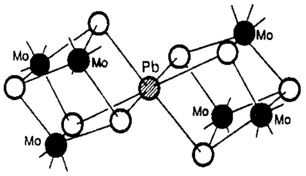
Brorson et al. reported recently the preparation of a Pb-containing derivative of $[Mo_3S_4(H_2O)_9]^{4+}$ and assigned a formula $[Mo_3PbS_4(H_2O)_{9+x}]^{4+}$ to their product.[1] This is however in conflict with our findings[2] that the product is a corner-shared double cube $[Mo_6PbS_8(H_2O)_{18}]^{8+}$.



We report further experiments, which confirm our earlier assignment, and comment on some of the difficulties encountered in such studies. Rigorous air-free (N_2) techniques are essential at all times.

UV−vis spectra[1,2] indicate that the same Pb cube was obtained in both laboratories. Absorption coefficients (ϵ) were obtained by air oxidation and quantitative determination of $[Mo_3S_4(H_2O)_9]^{4+}$ as the only identifiable Mo-containing product.[3] The ϵ values for the Pb cube reported by Brorson et al.[1] in 2 M Hpts (*p*-toluenesulfonic acid) can be doubled to give those applying for a double cube, peak positions λ/nm (ϵ/M^{-1} cm^{-1} per Mo_6) at 391 (14.6×10^3) and 755 (2.96×10^3). These are in good agreement with our values of 392 (14.6×10^3), and 757 (2.73×10^4) for the double cube.[2] In neither study is there any evidence for the coexistence of two different Pb-containing clusters. Analyses and Mo:Pb ratios in particular are of key importance therefore, as well as the overall charge indicated by cation-exchange chromatography (Dowex 50W-X8 was used in both laboratories).

The preparative procedure used in the present studies was to syphon $[Mo_3S_4(H_2O)_9]^{4+}$ (1 mM; 15 mL) in 0.50 M Hpts[4] onto Pb shot, which was left to react for ∼30 min. A Dowex column (1 × 12 cm) was then loaded and washed in turn with 0.50 and 1.0 M Hpts (both 100 mL amounts). An excess of green $[Mo_3S_4(H_2O)_9]^{4+}$ separated as a quite distinct band and was eluted first using 2.0 M Hpts. Its identity was confirmed from the UV−vis spectrum with 248 (8219), 366 (5550), and 603 (362), ϵ's per Mo_3 assumed to be the same in 2 M $HClO_4$ and in 2 M Hpts.[3] No other product was eluted until much higher concentrations of Hpts (in this work 4 M) were used. No elution was observed with similar volumes of 4 M $HClO_4$.

We are concerned that, in the experiments of Brorson et al.,[1] elution of the Pb product occurs prior to $[Mo_3S_4(H_2O)_9]^{4+}$ with 2.0 M Hpts and have tried to understand this observation. It is known that cations e.g. La^{3+} (0.25 M) at pH ≥ 1 can displace 4+ or more highly charged species not shifted with 1 M acid,[5,6] and can only suggest that some such effect is relevant with high concentrations of $[Mo_3S_4(H_2O)_9]^{4+}$ displacing the more highly charged Pb cube. However we have never observed this behavior on >10 occasions that elution has been carried out. We note that because of the very strong absorbance of the Pb cube it is difficult to detect and quantify by UV−vis spectrophotometry any $[Mo_3S_4(H_2O)_9]^{4+}$ component.

On washing/eluting Dowex columns with HCl, banding of $[Mo_3S_4(H_2O)_9]^{4+}$ followed by the Pb cube is again observed. However separation of the two is not as clean due to Cl^- complexing. Also the color of the Pb cube eluted with 2 M HCl is green rather than blue-green. The Pb cube prepared by reacting $[Mo_3S_4(H_2O)_9]^{4+}$ (14 mM) in 2 M $HClO_4$ with Pb shot gives similar column behavior. In our previous study inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses was carried out on 2 M HCl but not 4 M Hpts eluted solutions of the Pb cube. We therefore carried out analyses on the latter (diluted to 2 M Hpts) and obtained a Mo:Pb ratio of 5.9:1.0. A sample eluted with 2 M HCl gave Mo:Pb of 6.3:1 in agreement with the previous determination (6.1:1).[2] ICP-AES analyses of Brorson et al.[1] on an Hpts solution gave a Mo:Pb ratio of 2.9. In our experience greater care is required with ICP-AES analyses on Hpts solutions, when it is particularly important to make up calibrant solutions with the same acid background.

Finally stoichiometry measurements[7] were carried out for the reaction of Pb cube (0.1 mM in Mo_6) eluted with 4 M Hpts, using $[Fe(H_2O)_6]^{3+}$ (∼2 mM) as oxidant (770 mV), $I = 2.00$M (Hpts) at 25 °C. Titration was by adding aliquots of oxidant from a 0.5 mL Hamilton microsyringe. Both solutions were in 2 M Hpts, and the absorbance changes were monitored at 747 nm. The stoichiometry obtained was 1.90 mol of oxidant per Mo_6. Similarly for solutions of Pb cube in 2 M HCl (787 nm) and 2 M $HClO_4$ (757 nm), stoichiometries of 1.94 and 1.87 were obtained per mole of $[Co(dipic)_2]^-$ as oxidant (747 mV), dipic = 2,6-dicarboxylatopyridine. These indicate reactions for the double cube as in (1) (M = Fe, Co). The product from the

$$Mo_6PbS_8{}^{8+} + 2\ M^{III} \rightarrow 2\ Mo_3S_4{}^{4+} + Pb^{2+} + 2\ M^{II} \quad (1)$$

reaction in 2 M Hpts was loaded onto a Dowex column after dilution to 0.5 M Hpts, and the colorless solution collected during loading gave a white precipitate with iodate, consistent

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[2] Saysell, D. M.; Huang, Z.-X.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1996**, 2623.

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[4] Use of Aldrich *p*-toluenesulfonic acid, which is a white crystalline material, is recommended. Other commercial samples are sometimes pink in color.

[5] Patel, A.; Richens, D. T. *Inorg. Chem.* **1991**, *30*, 3789.

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[7] Saysell, D. M.; Sokolov, M. N.; Sykes, A. G. In *Sulfur Coordinated Transition Metal Complexes*; ACS Symposium Series No. 653; Matsumoto, K., Stiefel, E. I., Eds.; American Chemical Society: Washington, DC, 1996; pp 216−224.

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with formation of Pb^{2+}.[8] Oxidation to Pb^{IV} is unlikely in view of the reduction potential reported for the Pb^{IV}/Pb^{II} couple (1.67 V).[9,10] Had the single-cube formula $[Mo_3PbS_4(H_2O)_{9+x}]^{4+}$ applied, then for an equivalent absorbance change 2 mol of $[Mo_3PbS_4(H_2O)_{9+x}]^{4+}$ would have to be considered, and the equation would read as (2). Stoichiometries of 4:1 would apply,

$$2\,Mo_3PbS_4^{\,4+} + 4\,M^{III} \rightarrow 2\,Mo_3S_4^{\,4+} + 2Pb^{2+} + 4\,M^{II} \qquad (2)$$

whereas values close to 2:1 are observed in keeping with (1).

We conclude therefore from these additional studies on the elution behavior, ICP-AES analyses, and stoichiometry that the formula of the product is that of the corner-shared double cube $[Mo_6PbS_8(H_2O)_{18}]^{8+}$, with no evidence for the single cube as reported by Brorson et al.[1,13] Note however in the case of Sn that two derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ are obtained, $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ (reaction with Sn) and $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ (addition of Sn^{2+}).[11,12]

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(12) Shibahara, T.; Akashi, H. *Inorg. Chem.* **1989**, *28*, 2906.

(13) Note added in proof: Brorson et al. have published a correction, *Inorg. Chem.* **1997**, *36*, 264, in which they now accept the cluster formulation as $[MO_6PbS_8(H_2O)_{18}]^{8+}$.