



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Review Article

Investigation of electronic structure of tri- and tetranuclear molybdenum clusters by X-ray photoelectron and emission spectroscopies and quantum chemical methods



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ARTICLE INFO

Article history:

Received 5 April 2017

Received in revised form 11 September 2017

Accepted 15 September 2017

Available online 19 September 2017

Keywords:

Sulfide cluster

Molybdenum

Thiourea

Bipyridine

X-ray photoelectron spectroscopy

X-ray emission spectroscopy

Quantum chemical calculations

DFT method

ABSTRACT

Charge state studies of compounds $[\text{Mo}_3\text{S}_4(\text{tu})_8(\text{H}_2\text{O})]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ (**1**), $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{dbbpy})_3]\text{Cl} \cdot 5\text{H}_2\text{O}$ (**2**), $[\text{Mo}_3\text{S}_4(\text{CuCl})\text{Cl}_3(\text{dbbpy})_3][\text{CuCl}_2]$ (**3**), containing $\{\text{Mo}_3\text{S}_4\}^{4+}$ and $\{\text{Mo}_3\text{CuS}_4\}^{5+}$ cluster cores bearing terminal thiourea (tu) or 4,4'-di-*tert*-butyl-2,2'-bipyridine (dbbpy) ligands, have been performed by X-ray photoelectron and X-ray emission spectroscopies combined with quantum chemical calculations. The best agreement between theory and experiments has been obtained using the B3LYP method. According to the experimental and calculated data, the Mo atoms are in the oxidation state 4+ for all compounds. The energies and shapes of the Cu2p lines indicate formal oxidation states of Cu as 1+. The coordination of Cu(I) to the cluster $\{\text{Mo}_3\text{S}_4\}$ in **3** does not lead to significant changes in the charge state of the molybdenum atoms and the $\{\text{Mo}_3\text{S}_4\}$ unit can be considered as a tridentate metallothia crown ether.

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1. Introduction

Triangular chalcogenide clusters of molybdenum and tungsten with the $\{\text{M}_3\text{Q}_4\}^{4+}$ (M = Mo, W) core and their heterometallic cuboidal

clusters $\{\text{M}_3\text{Q}_4\text{M}'\}^{n+}$ represent a large and well-studied family of coordination compounds [1–4]. Their relevance to optics, molecular electronics and catalysis has been demonstrated [5–9]. Three (or four, respectively) metal atoms in these clusters are bridged with chalcogenide ligands (typically, sulfide ligands). Other coordination sites are occupied with terminal ligands (mostly mono- or bidentate ligands) (Fig. 1).

Functionalization of the $\{\text{Mo}_3\text{S}_4\}$ cluster by heterocyclic diimines such as 2,2'-bipyridine, 1,10-phenanthroline produces homoleptic

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