Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 4027–4035
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Formation of new organometallic W/Cu/S clusters from reactions of $[\{(\eta^5\text{-}C_5Me_5)WS_3\}_3Cu_7(MeCN)_9](PF_6)_4$ with donor ligands. Crystal structures and optical limiting properties of $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3(Py)_6](PF_6)_2$, $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3Br(PPh_3)_3](PF_6)$, and $[(\eta^5\text{-}C_5Me_5)WS_3Cu_4(Py)Cl(dppm)_2](PF_6)_2$

Hong Yu [a,*], Wen-Hua Zhang [a], Zhi-Gang Ren [a], Jin-Xiang Chen [a], Chun-Lan Wang [a], Jian-Ping Lang [a,b,*], Hendry Izaac Elim [c], Wei Ji [c]

[a] *Key Laboratory of Organic Chemistry of Jiangsu Province, School of Chemistry and Chemical Engineering, Suzhou University, No. 1 Shizi Street, Suzhou 215006, Jiangsu, PR China*
[b] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, Fujian, PR China*
[c] *Department of Physics, National University of Singapore, 2 Science Drive 3, 117542 Singapore*

Received 3 April 2005; received in revised form 28 May 2005; accepted 2 June 2005
Available online 14 July 2005

Abstract

Treatment of a preformed cluster $\{(\eta^5\text{-}C_5Me_5)WS_3\}_3Cu_7(MeCN)_9](PF_6)_4$ (**1**) in MeCN with excess pyridine afforded a tetranuclear cationic cluster $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3(Py)_6](PF_6)_2$ (**2**). On the other hand, reactions of **1** with excess PPh_3 under the presence of LiBr gave rise to the other tetranuclear cationic cubane-type cluster $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3Br(PPh_3)_3](PF_6)$ (**3**) while analogous reactions of **1** with dppm and LiCl followed by addition of excess pyridine generated an intriguing pentanuclear cationic cluster $[(\eta^5\text{-}C_5Me_5)WS_3Cu_4(Py)Cl(dppm)_2](PF_6)_2$ (**4**). Compounds **2**–**4** were fully characterized by spectroscopy and X-ray crystallography. The cluster dication of **2** adopts an incomplete WS_3Cu_3 cubane-like structure while the cluster cation of **3** contains a WS_3Cu_3Br cubane-like structure. The structure of the cluster dication of **4** consists of an unique WS_3Cu_4Cl framework in which an open cubane-like WS_3Cu_3Cl fragment and a $Cu(dppm)_2$ fragment are connected by one Cu–Cl bond and two Cu–dppm–Cu bridges. The optical limiting (OL) properties of the MeCN solutions of **1**–**4** were investigated with 7-ns laser pulses at 532 nm.

Keywords: Tungsten cluster; Copper cluster; Sulfide cluster; Crystal structures; Optical limiting properties

1. Introduction

In the past decades, synthesis of Mo(W)/Cu/S clusters has attracted much interest due to their interesting chemistry [1–11], and their potential applications in biological systems [1,4,10] and electro/photonic materials [7,8f,9f,9g,11]. There are several approaches to the construction of the Mo(W)/Cu/S clusters. The first one is the "one-pot" synthesis, in which thiometallates (e.g. $[MO_{4-n}S_n]^{2-}$ (M = Mo, W; n = 1–4) and $[(\eta^5\text{-}C_5Me_5)MS_3]^-$ (M = Mo, W)) were mixed with Cu(I) salts or complexes in organic solvents to generate various Mo(W)/Cu/S clusters, which could be found in

* Corresponding authors. Tel.: +86 512 65213506; fax: +86 512 65224783.
E-mail addresses: yuhong@suda.edu.cn (H. Yu), jplang@suda.edu.cn (J.-P. Lang).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.06.003

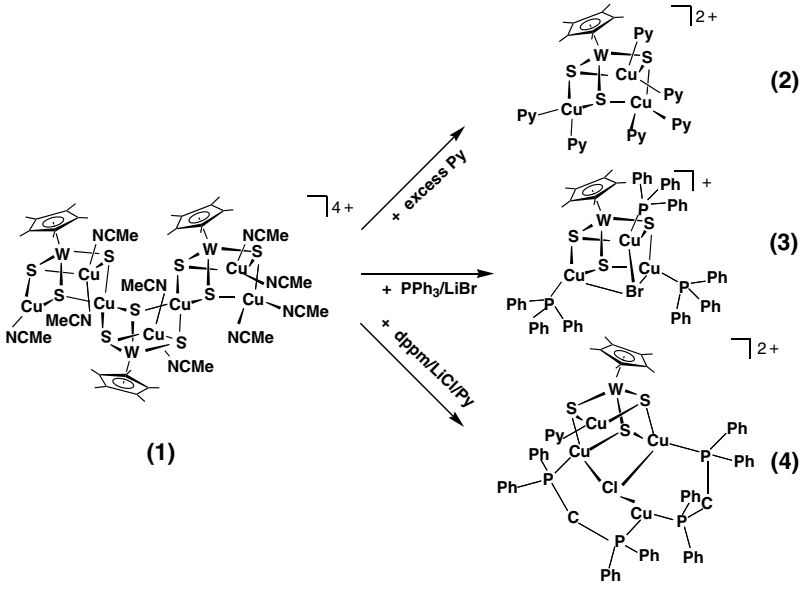
numerous literatures [1–9,11]. The second one is that a preformed small Mo(W)/Cu/S cluster is used to react with certain donor ligands (e.g. S^{2-}, 4,4′-bipy), yielding larger clusters or polymeric clusters [3,5c,6b,9e–9g]. The third one, which is less explored, is involved in the formation of a smaller cluster from the reaction of a preformed cluster with donor ligands (e.g. 2,2′-bipy and PPh_3) [9c,9e,12]. For example, reaction of $[NEt_4]_4[WS_4Cu_5Cl_7]$ with 2,2′-bipyridine and PPh_3 afforded $[WS_4Cu_3Cl(2,2'\text{-bipy})]_n$ and $[WS_4Cu_3(PPh_3)_3Cl]$, respectively [12a]. In the two reactions, the $[WS_4Cu_5]$ framework was turned into a smaller incomplete WS_4Cu_3 cubane-shaped core.

On the other hand, we have been interested in the preparation and third-order non-linear optical properties of Mo(W)/Cu/S clusters over the last ten years [8b,8c,8e,8f,9]. We once communicated an interesting reaction in which $[\{(\eta^5\text{-}C_5Me_5)WS_3\}_3Cu_7(MeCN)_9](PF_6)_4$ (**1**) reacted with 1,4-pyrazine (1,4-pyz) under the presence of LiCl, forming an interesting 2D polymer $\{[(\eta^5\text{-}C_5Me_5)WS_3Cu_3Cl(MeCN)(1,4\text{-pyz})](PF_6)\}_\infty$ [9e]. In this reaction, the triple incomplete cubane-like $[W_3S_9Cu_7]$ framework of **1** was turned into a smaller incomplete WS_3Cu_3 cubane-like framework. In addition, we are involved in the construction of Mo(W)/Cu/S clusters from some preformed clusters with luminescent or optical limiting properties [9g,9f]. As discussed later in this paper, the solution of compound **1** exhibited slightly better optical limiting (OL) performance than that of C_{60}. Therefore, is it possible to use **1** as a useful precursor to make other new W/Cu/S clusters with better OL properties via its reactions with other donor ligands? With the question in mind, we carried out reactions of **1** with Py, PPh_3, and dppm, and some in the presence of LiX (X = Cl, Br). Three novel smaller W/Cu/S clusters $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3(Py)_6](PF_6)_2$ (**2**) $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3Br(PPh_3)_3](PF_6)$ (**3**) and $[(\eta^5\text{-}C_5Me_5)WS_3Cu_4(Py)Cl(dppm)_2](PF_6)_2$ (**4**) were produced in relatively high yields. Furthermore, we have also examined the OL properties of **1**–**4** in acetonitrile with 7-ns laser pulses at 532 nm. Herein, we report their preparation and structural characterization along with their OL properties in solution.

2. Results and discussion

2.1. Synthesis and spectral characterization

As shown in Scheme 1, reaction of **1** in MeCN with excess Py formed a homogeneous solution, from which $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3(Py)_6](PF_6)_2$ (**2**) was isolated as dark red plates in 65% yield. We once reported that lithium halide sometimes proved to be useful in making cluster-based supramolecular compounds [9e,9f]. For example, reactions of $[PPh_4][(\eta^5\text{-}C_5Me_5)WS_3Cu_3(CN)_3]$ with 1,4-pyrazine under the presence of LiCl yielded a supramolecular cube $[\{(\eta^5\text{-}C_5Me_5)WS_3Cu_3\}_8Cl_8(CN)_{12}Li_4]$ [9f]. In the structure of this compound, each chloride interacts weakly with three copper atoms of the $(\eta^5\text{-}C_5Me_5)WS_3Cu_3$ core, which may stabilize the resulting cluster framework. However, analogous reaction of **1** in MeCN with excess Py in the presence of LiCl (4 equiv.) gave rise to the same cluster **2** in 60% yield. When excess PPh_3 was added into the acentonitrile solution of **1**, it formed a clear red solution, from which a red product was isolated after a workup. According to its elemental analysis, X-ray fluorescence analysis and IR spectrum, we tentatively assumed its chemical formula to be $[(\eta^5\text{-}C_5Me_5)WS_3Cu_3(PPh_3)_3](PF_6)_2$. Interest-



Scheme 1.