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Synthesis, crystal structures and third-order nonlinear optical properties of a new family of double incomplete cubane-like clusters $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_3SCu_2X(\mu\text{-}X)]_2$ ($X = Cl^-$, Br^-, SCN^-) and cubane-like clusters $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4(CuX)_2]$ ($X = Br^-$, SCN^-, CN^-)

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Abstract

Reactions of *trans*-$[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}S)_2S_2]$ (**1**) with 2 equiv. of CuX ($X = Cl^-$, Br^-, SCN^-, CN^-) in refluxing acetonitrile resulted in a new set of Mo/Cu/S cluster compounds $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_3SCu_2Cl(\mu\text{-}Cl)]_2$ (**2**), $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4(CuBr)_2]$ (**3**) and $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_3SCu_2Br(\mu\text{-}Br)]_2$ (**4**), $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4(CuSCN)_2]$ (**5**) and $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_3SCu_2(SCN)(\mu\text{-}SCN)]_2$ (**6**) and $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4(CuCN)_2]$ (**7**). Compounds **2**–**7** were fully characterized by elemental analysis, IR, UV–Vis, ^1H NMR and single-crystal X-ray crystallography. Compounds **2**, **4** and **6** consist of two incomplete cubane-like $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_3SCu_2X]$ species bridged by a pair of $\mu\text{-}X^-$ anions while **3**, **5** and **7** contain a cubane-like $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4Cu_2]$ core with each of two terminal X^- coordinated at each copper(I) center. The third-order nonlinear optical (NLO) properties of **2**–**5** and **7** along with $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4(CuCl)_2]$ in CH_2Cl_2 were investigated by using *Z*-scan technique at 532 nm. All these clusters showed strong third-order NLO absorption effects and self-defocusing properties.

Keywords: Molybdenum; Copper; Cluster; Sulfide; Molecular structures; Third-order nonlinear optical properties

1. Introduction

The reactions of thiomolybdates and thiotungstates $[MO_{4-n}S_n]^{2-}$ and $[(\eta^5\text{-}C_5Me_5)MS_3]^-$ (M = Mo, W) with copper(I) salts have been extensively investigated due to their rich chemistry [1–27], and their relations to biological systems [1,5,6,28,29], and electro/photonic materials [11,15,16,24,26,30–39]. However, only a few reactions are involved in the utilization of the disulfido-bridged dimolybdenum clusters $[Cp'_2Mo_2S_4]$ ($Cp' = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5H_4Me$ or $\eta^5\text{-}C_5Me_5$) [40,41]. For example, reactions of a solution containing *trans*-$[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu\text{-}S)_2S_2]$ (**1**) with 2 equiv. of CuCl in toluene gave rise to a cubane-like cluster $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4(CuCl)_2]$ [40].

On the other hand, we have been interested in the synthesis of Mo(W)/Cu/S clusters derived from $[MO_{4-n}S_n]^{2-}$ and $[(\eta^5\text{-}C_5Me_5)MS_3]^-$ (M = Mo, W) [13,14,16–27,30–32,39]. Some of these clusters exhibited good third-order nonlinear

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optical (NLO) properties in solution [16,26,30–32,36,37,39]. In order to expand the chemistry of Mo(W)/Cu/S clusters and screen out clusters with better NLO performances, we have became to adopt other Mo(W)/S precursors including **1** [41–43]. In fact, we have recently reported that treatment of a suspension of **1** in methylene dichloride with 2 equiv. of CuI at ambient temperature afforded an incomplete cubane-like cluster $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_3S(CuI)_2]$ while a *cis*-isomer $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4(CuI)_2]$ could be isolated through heating $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_3S(CuI)_2]$ either in solution or in solid state [41]. Interestingly, both clusters in CH_2Cl_2 showed better NLO effects than those of their cluster precursor **1**. The results encouraged us to further explore reactions of **1** with other copper(I) halides or pseudohalides CuX (X = Cl, Br, SCN, CN) systemically and the third-order NLO properties of the resulting products. In this paper, we report syntheses, crystal structures and third-order NLO properties of a new family of double incomplete cubane-like clusters and cubane-like clusters derived from **1**: $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_3SCu_2Cl(\mu\text{-}Cl)]_2$ (**2**), $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4(CuBr)_2]$ (**3**) and $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_3SCu_2Br(\mu\text{-}Br)]_2$ (**4**), $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4(CuSCN)_2]$ (**5**) and $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_3SCu_2(SCN)(\mu\text{-}SCN)]_2$ (**6**) and $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4(CuCN)_2]$ (**7**).

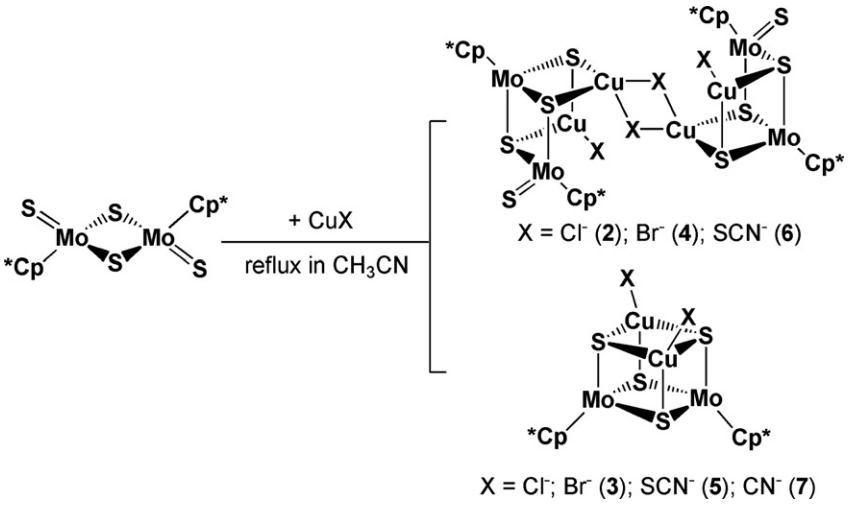
2. Results and discussion

2.1. Synthesis and spectral characterization of 2–7

Treatment of **1** with 2 equiv. of CuCl in refluxing CH_3CN followed by a standard workup afforded the known single cubane-like cluster $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4(CuCl)_2]$ (33% yield) and a new double incomplete cubane-like cluster **2** (51% yield) (Scheme 1). Similar reactions of **1** with 2 equiv. of CuBr produced **3** and **4** in 46% and 30% yields, respectively. It is noticed that the double incomplete cubane-like cluster **2** or **4** gradually underwent the *trans*-to-*cis* isomerization [41] to form the cubane-like cluster $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_4(CuX)_2]$ (X = Cl, Br (**3**)) during the reaction period. For example, reactions of **4** in refluxing CH_3CN for 20 h followed by column chromatography on silica gave rise to a mixture of **3** (38% yield) and **4** (57% yield). Continuous heating of this solution of **4** did not significantly increase the yield of **3** (41% yield) but **4** (48% yield) became decomposed after a heating period of 40 h and some unknown species occurred in the ^1H NMR spectra. Similar phenomena were once observed in their iodide analogue [41], though **2** or **4** may be cleaved into 2 equiv. of incomplete cubane-like $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_3S(CuX)_2]$ clusters before the isomerization.

Intriguingly, analogous reactions of **1** with 2 equiv. of CuSCN gave rise to the single cubane-like cluster **5** in 31% yield coupled with the double incomplete cubane-like cluster **6** (~2% yield) (Scheme 1). In the case of CuCN, no expected double incomplete cubane-like cluster $[(\eta^5\text{-}C_5Me_5)_2Mo_2(\mu_3\text{-}S)_3SCu_2(CN)(\mu\text{-}CN)]_2$ but only the cubane-like cluster **7** was isolated in 23% yield. In both cases, the yield for the double incomplete cubane-cluster was quite low, which may be attributed to the formation of a large amount of insoluble dark brown solids during the reaction. Short reaction time (2–3 h) or running the reactions at low temperatures (e.g. 0 °C) did not improve the yield for the double incomplete cubane-like cluster **6**. It is understandable that both SCN^- and CN^- are versatile bridging ligands that may link some Mo/Cu/S cluster species existed in the reaction mixture to form certain kinds of insoluble Mo/Cu/S cluster-based coordination polymers [18,27,44]. In fact, the IR spectra revealed that these solids contained the SCN^- (2118/2073 cm^{-1}) or CN^- (2129/2117 cm^{-1}) stretching vibrations and the bridging Mo–S vibration at 427 or 453 cm^{-1}. X-ray fluorescence analysis conformed that these samples contained Mo, Cu and S elements (Mo:Cu:S = 2:2:6 for X = SCN^- and 2:2:4 for X = CN^-). However, numerous attempts to grow their single crystals to elucidate their actual compositions failed.

Compounds **2**–**7** are readily soluble in CH_2Cl_2 or $CHCl_3$, slightly soluble in CH_3CN, benzene or acetone,



Scheme 1.