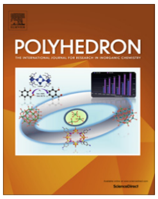
Polyhedron 83 (2014) 60–67

Contents lists available at ScienceDirect

Polyhedron

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



Reactions of Tp*-coordinated thiomolybdate and thiotungstate complexes with different silver salts

Li-Kuan Zhou [a], Quan Liu [a], Bing Wu [a], Hong Yu [a,*], Fei-Long Hu [a], Xin Zhao [a], Shu-Chen Liu [a], Jian-Ping Lang [a,b,*]

[a] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, Jiangsu, People's Republic of China
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 210032, People's Republic of China

ARTICLE INFO

Article history:
Received 7 February 2014
Accepted 8 April 2014
Available online 18 April 2014

Keywords:
Molybdenum
Tungsten
Silver
Cluster
Sulfide

ABSTRACT

Treatment of $[Et_4N][Tp^*MoS(S_4)]$ (Tp^* = hydridotris(3,5-dimethylpyrazol-1-yl)borate) (**1a**) with $[Ag(MeCN)_4]PF_6$ and PPh_3 or Agdca (dca = dicyanamide) afforded two new neutral compounds $[Tp^*MoO(\mu\text{–}O)_2MoO(\mu\text{–}O)_2MoO(\mu\text{–}O)_2OMoTp^*]\cdot 8(MeCN)_{0.5}$ ($\mathbf{2}\cdot 8(MeCN)_{0.5}$) and $[Tp^*Mo(\mu\text{–}S)(\mu\text{–}S_2)(\mu\text{–}S_3)MoTp^*]\cdot DMF$ ($\mathbf{3}\cdot DMF$). Reactions of $[Et_4N][Tp^*WS_3]$ (**1b**) with AgX (X = SCN, NO_3, CN) in the presence of N- or P-donor ligands formed one binuclear cluster $[Et_4N][Tp^*WS(\mu\text{–}S)_2EW(NCS)_2]$ (E = 0.5O + 0.5S) (**4**) and two W/Ag/S clusters $[Tp^*WO(\mu\text{–}S)_2Ag(dppe)]\cdot MeCN$ ($\mathbf{5}\cdot MeCN$) and $[\{Tp^*WS(\mu\text{–}S)(\mu_3\text{–}S)Ag_2(py)_2\}_2(\mu\text{–}CN)_2]$ (**6**). These compounds were characterized by elemental analysis, IR, UV–Vis, ^1H NMR and single-crystal X-ray crystallography. Compound **2** possesses a centrosymmetric tetranuclear structure in which two dinuclear $[Tp^*MoO(\mu\text{–}O)_2MoO]$ units are linked by a pair of μ–O bridges. Compound **3** contains a dimeric structure in which two $[Tp^*Mo]$ units are linked by one μ–S, one $\mu\text{–}S_2$ and one $\mu\text{–}S_3$ bridge. Compound **4** has another dimeric anionic structure in which one $[Tp^*WS]$ unit and one $[(SCN)_2WE]$ unit are linked *via* a pair of μ–S bridges. Compound **5** has a dimeric structure in which one $[Ag(dppe)]^+$ unit is linked by two μ–S atoms of $[Tp^*WO(\mu\text{–}S)_2]^-$ moiety. Compound **6** adopts a centrosymmetric hexanuclear structure in which two unique trinuclear $[Tp^*WS(\mu\text{–}S)(\mu_3\text{–}S)Ag_2(py)_2]$ units are interconnected by a couple of μ–CN bridges. The isolation of **2**–**6** provided an insight into not only the complexity arising from reactions of **1a** and **1b** with Ag(I) salts in the presence or absence of N- or P-donor ligands but also the interesting assembly chemistry of the Mo(W)/Ag/S clusters.

1. Introduction

The M/M′/S (M = Mo, W; M′ = Cu, Ag) clusters remain of great interest owing to their beautiful structural chemistry [1–29], their relevance to biologically-related systems [30,31] and advanced optoelectronic materials [32–35]. To our knowledge, most of them are Mo(W)/Cu/S clusters that are prepared from reactions of tetrathiometallates ($[MS_4]^-$) or Cp^*-coordinated trithiometallates $[PPh_4][Cp^*MS_3]$ ($Cp^* = \eta^5\text{-}C_5Me_5$, M = Mo, W) [36,37] with Cu(I) salts. Only a few belong to the Mo(W)/Ag/S clusters that have been prepared from reactions of $[MS_4]^-$ and $[Cp^*MS_3]^-$ with silver salts [20–29]. It is noted that although some Mo(W)/Ag/S clusters have similar structures to those of their Cu(I) analogues, many of them exhibit quite different topological frameworks from those of Mo(W)/Cu/S clusters [12]. These structural differences among Mo(W)/Cu(Ag)/S clusters may reflect that Ag(I) has different activity toward $[MS_4]^{2-}$ or $[Cp^*MS_3]^-$ from Cu(I). However, studies on the reactivity of Ag(I) towards thiometallates have been slowed down due to the shortage of the suitable Mo(W)/S complexes.

In the past decades, we have been interested in the chemistry and third-order nonlinear optical (NLO) properties of Mo(W)/Cu(Ag)/S clusters prepared from $[MS_4]^{2-}$ and $[Cp^*MS_3]^-$ (M = Mo, W) complexes [6,10–20,25–27]. Recently, we have embarked on employing two new Mo(W)/S synthons $[Et_4N][Tp^*MoS(S_4)]$ (Tp^* = hydridotris(3,5-dimethylpyrazol-1-yl)borate) (**1a**) and $[Et_4N][Tp^*WS_3]$ (**1b**) [38] for the synthesis of Mo(W)/Cu/S clusters [39–48]. It seems that complex **1a** or **1b** also showed different reactivity towards Cu(I) from $[MS_4]^{2-}$ or $[Cp^*MS_3]^-$, and some cluster frameworks were unprecedented in the chemistry of the previous thiometallates. Previously, we reported reactions of **1b** with AgSCN in MeCN, which did not yield our expected W/Ag/S cluster but a neutral binuclear W/S complex $[(Tp^*WS_2)_2(\mu\text{–}S_2)]$ [42]. Being aware of the fact that the reactivity of **1a** or **1b** towards

---

* Corresponding authors. Address: College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, Jiangsu, People's Republic of China (J.-P. Lang). Tel.: +86 512 6588 2865; fax: +86 512 6588 0328.

E-mail address: jplang@suda.edu.cn (J.-P. Lang).

http://dx.doi.org/10.1016/j.poly.2014.04.010
0277-5387/© 2014 Elsevier Ltd. All rights reserved.

Ag(I) has been less explored and our continuing ambition to expand new structural chemistry of Mo(W)/Ag/S clusters, we carried out reactions of **1a** or **1b** with five silver(I) salts ($[Ag(MeCN)_4]ClO_4$, Agdca (dca = dicyanamide), AgSCN, $AgNO_3$ and AgCN) in the presence or absence of N-, or P-donor ligands. One tetranuclear Mo/O cluster $[Tp^*MoO(\mu\text{–}O)_2MoO(\mu\text{–}O)_2MoO(\mu\text{–}O)_2OMoTp^*]\cdot 8(MeCN)_{0.5}$ (**2**$\cdot 8(MeCN)_{0.5}$), one binuclear Mo/S cluster $[Tp^*Mo(\mu\text{–}S)(\mu\text{–}S_2)(\mu\text{–}S_3)MoTp^*]\cdot$DMF (**3**·DMF), one binuclear W/S cluster $[Et_4N][Tp^*WS(\mu\text{–}S)_2EW(NCS)_2]$ (E = 0.5O + 0.5S) (**4**), one binuclear W/Ag/S cluster $[Tp^*WO(\mu\text{–}S)_2Ag(dppe)]\cdot$MeCN (**5**·MeCN), and one hexanuclear cluster $[\{Tp^*WS(\mu\text{–}S)(\mu_3\text{–}S)Ag_2(py)_2\}_2(\mu\text{–}CN)_2]$ (**6**) were isolated therefrom (Scheme 1). In this article, we report their synthesis and structural characterization.

2. Experimental

2.1. Materials and instruments

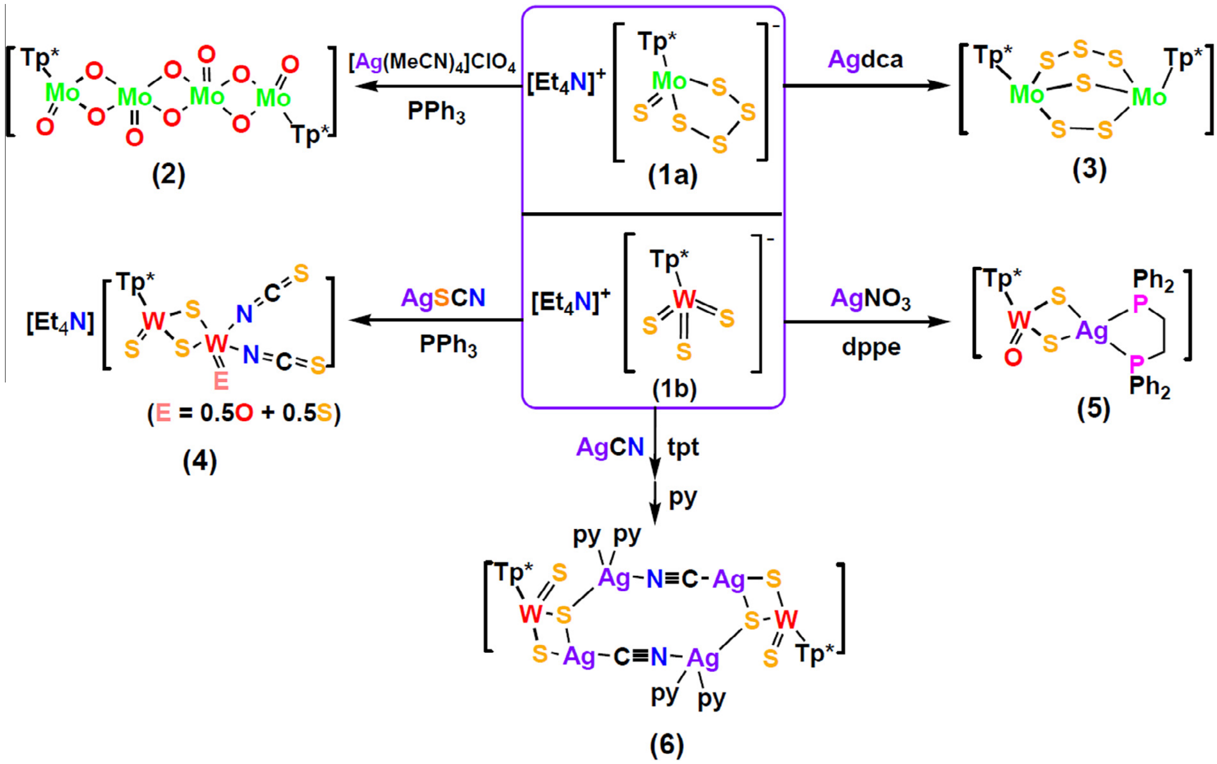
All manipulations were carried out under an argon atmosphere using standard Schlenk-line techniques. Compounds **1a** and **1b** were prepared according to the literature method [38]. All the solvents were pre-dried over activated molecular sieves and refluxed over the appropriate drying agents under argon. Other chemicals and reagents were obtained from commercial sources and used as received. Elemental analyses for C, H and N were performed on a Carlo-Erba CHNO-S microanalyzer. IR spectra were recorded on a Varian 1000 FT–IR spectrometer as KBr disks (4000–400 cm^{-1}). UV–Vis spectra were measured on a Varian Cary-50 UV–Visible spectrophotometer. ^1H NMR spectra were recorded at ambient temperature on a Varian UNITY plus–400 spectrometer. Chemical shifts were referenced to TMS in $CDCl_3$ or to the deuterated dimethyl sulfoxide (DMSO–d_6) signal.

2.2. Synthesis of $[Tp^*MoO(\mu\text{–}O)_2MoO(\mu\text{–}O)_2MoO(\mu\text{–}O)_2OMoTp^*]\cdot 8(MeCN)_{0.5}$ (**2**$\cdot 8(MeCN)_{0.5}$)

To a dark green solution of **1a** (14 mg, 0.02 mmol) in MeCN (10 mL) was added a solution containing $[Ag(MeCN)_4]ClO_4$ (22 mg, 0.06 mmol) and PPh_3 (16 mg, 0.06 mmol) in 5 mL of CH_2Cl_2. The resulting mixture was stirred at room temperature for 30 min and filtered. Diethyl ether (10 mL) was carefully layered onto the filtrate to form orange blocks of **2**$\cdot 8(MeCN)_{0.5}$ after several weeks. These crystals were collected by filtration, washed thoroughly with Et_2O, firmly ground and dried *in vacuo* for several hours to give pure **2**. Yield: 4.5 mg (20% based on Mo). *Anal.* Calc. for $C_{30}H_{44}B_2N_{12}O_{10}Mo_4$: C, 31.66; H, 3.90; N, 14.77. Found: C, 31.82; H, 3.81; N, 14.34%. IR: 2974 (w), 2539 (w), 1628 (s), 1542 (m), 1451 (w), 1383 (w), 1209 (m), 977 (s), 859 (m), 572 (m), 464 (m) cm^{-1}. UV–Vis (DMF, λ_{max}(nm(ε M^{-1} cm^{-1}))): 312 (8850). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 2.35 (s, 18H, CH_3 in Tp*), 2.97 (s, 18H, CH_3 in Tp*), 5.89 (s, 6H, CH in Tp*). The B–H proton was not located.

2.3. Synthesis of $[Tp^*Mo(\mu\text{–}S)(\mu\text{–}S_2)(\mu\text{–}S_3)MoTp^*]\cdot$DMF (**3**·DMF)

To a dark green solution of **1a** (14 mg, 0.02 mmol) in MeCN (10 mL) was added Agdca (17 mg, 0.1 mmol) in 5 ml of DMF. The mixture was stirred to generate a red precipitate immediately and was allowed to continue stirring for 1 h. The precipitate was filtered, washed with MeCN and Et_2O, and re-dissolved in 5 mL CH_2Cl_2. Diethyl ether (10 mL) was carefully layered onto the brown-red filtrate to yield red prisms of **3**·DMF after several weeks. These crystals were collected by filtration, washed thoroughly with Et_2O, firmly ground and dried *in vacuo* for several hours to give pure **3**. Yield: 4 mg (20%) based on Mo. *Anal.* Calc. for $C_{30}H_{44}B_2Mo_2N_{12}S_6$:



Scheme 1. Reactions of **1a** or **1b** with Ag(I) salts in the absence or presence of N- or P-donor ligands.