Journal of Solid State Chemistry 219 (2014) 15–20

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Two new helical compounds based on Keggin clusters and N-donor multidentate ligand: Syntheses, structures and properties

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ARTICLE INFO

Article history:
Received 23 April 2014
Received in revised form
3 July 2014
Accepted 5 July 2014
Available online 15 July 2014

Keywords:
Helical chain
Keggin cluster
Polyoxometalate
Hydrothermal synthesis
Photocatalysis

ABSTRACT

Two isostructural polyoxometalate-based inorganic–organic hybrids with 1D helical chain, $[CuH_3L_2(GeMo_{12}O_{40})]\cdot 2H_2O$ (**1**) and $[CuH_3L_2(SiMo_{12}O_{40})]\cdot 2H_2O$ (**2**), where L=2,4,5-tri(4-pyridyl)-imidazole have been synthesized under hydrothermal conditions. It is the first time to use the L ligand to synthesis the Keggin-type polyoxometalate-based inorganic–organic hybrids. The two compounds possess the left- and right-handed helical chains and the POMs as pendants attach in the helical chains through Cu–O bonds. The two compounds have been characterized by elemental analyses, infrared (IR) spectroscopy, powder X-ray diffraction (PXRD), X-ray photoelectron spectra (XPS), thermogravimetric analysis (TGA) and photoluminescent spectroscopy. Moreover, nitrogen adsorption–desorption measurement, electrochemical and photocatalysis properties for degradation of methylene blue (MB) upon a UV irradiation of compound **1** have been examined.

1. Introduction

A helix is a geometric motif which is ubiquitous in nature as well as in human art and architecture. Helicity can be observed in various biology systems [1]. Watson and Crick found out the double-helical structure for DNA in which the two strands are connected by hydrogen bonding between complementary bases [2]. For its potential applications in the fields of asymmetric catalysis, nonlinear optical materials and the aesthetically appealing topologies, many chemists have put great efforts on the rational design and synthesis of artificial helical compounds [3–7]. The most important feature of helix is its chirality, that is, right- (*P*) and left-handed (*M*) helices are non-identical mirror images [8]. The first inorganic double helix self-assembled from simple starting materials under hydrothermally conditions was reported by Haushalter and Zubieta et al. [9].

Polyoxometalate(POM)-based organic–inorganic hybrid compounds [10–16] have attracted a great interest in crystal engineering for their potential applications in catalysis, adsorption, luminescent, electronic, and magnetic materials. In the last two decades, a lot of POMs with changeable structural topologies have been synthesized [17–24]. In this research field, the N-donor organic ligands, transition metal ions, and various kinds of polyoxoanions constitute one of the typical reaction systems to assemble POM-based hybrid compounds [25–34]. Helical compounds based on POMs have attracted more and more attention because of their attractive structural features and potential applications [35–43]. Therefore, the design and construction of helical compounds based on POMs is still a great challenge for both supramolecular and materials chemists.

Recently, Hong et al. pointed out that the use of twisted rigid ligands as structure-directing agents is an effective approach to obtain helical structures with ease [8]. On the basis of this consideration, we chose a multidentate N-donor ligand and a Keggin POM in an attempt to construct helical compounds. Fortunately, we obtained two new compounds, $[CuH_3L_2(GeMo_{12}O_{40})]\cdot 2H_2O$ (**1**) and $[CuH_3L_2(SiMo_{12}O_{40})]\cdot 2H_2O$ (**2**), which are isostructural, possessing the left- and right-handed helical chains. As far as we know, the L ligand is the first time used to synthesize Keggin-type polyoxometalate-based inorganic–organic hybrids.

2. Experimental section

2.1. Materials and methods

2,4,5-tri(4-pyridyl)-imidazole (noted as L) was synthesized by the general method described in the literature [44]. Other reagents were purchased from commercial sources and used as received.

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http://dx.doi.org/10.1016/j.jssc.2014.07.005
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The FT-IR spectra were recorded from KBr pellet in the range of 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Elemental analyses of C, H and N were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer and that of Cu and Mo were carried out with a Leaman ICP spectrometer. TG analyses were performed with a Perkin-Elmer TGA7 instrument in N_2 atmosphere at a heating rate of 10 °C min^{-1}. Photoluminescence spectra were measured with pure solid samples at room temperature by using an HITACHI F-7000 instrument. The nitrogen adsorption–desorption experiments were performed on Shimadzu, Micromeritics ASAP 2010 Instrument. The X-ray powder diffraction (PXRD) patterns were recorded on a Siemens D5005 diffractometer with Cu-$K\alpha$ (λ=1.5418 Å) radiation. X-ray photoelectron spectroscopy (XPS) analyses were performed on a VG Escalab 250 spectrometer with an Al $K\alpha$(1486.5 eV) achromatic X-ray source. Electrochemical measurements were carried out on CHI 660C electrochemical workstation at room temperature.

2.2. Syntheses

$[CuH_3L_2(GeMo_{12}O_{40})]\cdot 2H_2O$ (1)

A mixture of *L* (0.03 g, 0.1 mmol), $Cu(CH_3COO)_2\cdot H_2O$ (0.02 g, 0.1 mmol), GeO_2 (0.01 g, 0.1 mmol), $Na_2MoO_4\cdot 2H_2O$ (0.242 g, 1 mmol) and water (10 mL) was placed in a Teflon reactor (18 mL) and heated at 170 °C for 5 days. The initial pH value of the reaction system was about 3. After cooling to room temperature at a rate of 10 °C h^{-1}, red brown crystals of **1** were collected in 44% yield based on L. Anal. Calcd for $C_{36}H_{33}CuGeMo_{12}N_{10}O_{42}$ (*Mr*=2565.13): C, 16.86; H, 1.30; N, 5.46; Cu, 2.48; Mo, 44.88%. Found: C, 16.83; H, 1.24; N, 5.53; Cu, 2.40; Mo, 44.75%. IR (KBr, cm^{-1}): 3527(m), 1627(s), 1606(s), 1509(m), 1485(w), 1422(m), 1253(m), 1194(s), 1128(w), 1062(w), 950(s), 881(s), 804(m), 768(s), 611(w), 505(m).

$[CuH_3L_2(SiMo_{12}O_{40})]\cdot 2H_2O$ (2)

A mixture of *L* (0.06 g, 0.2 mmol), $Cu(CH_3COO)_2\cdot H_2O$ (0.04 g, 0.2 mmol), $Na_2SiO_3\cdot 9H_2O$ (0.284 g, 1 mmol), $Na_2MoO_4\cdot 2H_2O$ (0.242 g, 1 mmol) and water (10 mL) was placed in a Teflon reactor (18 mL) and heated at 170 °C for 5 days. The initial pH value of the reaction system was about 3. After cooling to room temperature at a rate of 10 °C h^{-1}, red brown crystals of **2** were collected in 18% yield based on *L*. Anal. Calcd for $C_{36}H_{33}CuSiMo_{12}N_{10}O_{42}$ (*Mr*= 2520.63): C, 17.15; H, 1.32; N, 5.56; Cu, 2.52; Mo, 45.67%. Found: C, 17.22; H, 1.34; N, 5.53; Cu, 2.49; Mo, 45.75%. IR (KBr, cm^{-1}): 3436 (m), 1627(s), 1607(s), 1510(m), 1485(w), 1422(m), 1252(m), 1194(s), 1128(w), 1063(w), 956(s), 899(s), 832(w), 786(s), 612(w), 506(m).

2.3. X-ray crystallography

The simple-crystal samples with suitable size were sealed in capillaries. The X-ray diffraction data of compounds **1** and **2** were collected on a Bruker Smart Apex II diffractometer with graphite monochromatic Mo-$K\alpha$ radiation (λ=0.71073 Å) at 293 K with ω scans. Multi-scan absorption corrections were applied. The structures were solved by direct methods and refined by full matrix least squares on F^2 using the SHELXTL crystallographic software package [45]. The positions of hydrogen atoms on the carbon atoms were calculated theoretically. Crystal data and structure refinements for compounds **1** and **2** are presented in Table 1. CCDC-996688 (for **1**) and -996689 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1
Crystal data and structure refinements for compounds **1** and **2**.

	1	**2**
Formula	$C_{36}H_{33}CuGeMo_{12}N_{10}O_{42}$	$C_{36}H_{33}CuSiMo_{12}N_{10}O_{42}$
FW	2565.13	2520.63
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*
a (Å)	15.8681(6)	15.864(3)
b (Å)	15.1661(6)	15.159(3)
c (Å)	24.9681(10)	25.011(5
α (°)	90.000	90.000
β (°)	94.5290(10)	94.514(2)
γ (°)	90.000	90.000
V ($Å^3$)	5990.0(4)	5996.2(19)
Z	4	4
D_c (g cm^{-3})	2.844	2.792
F(0 0 0)	4880	4808
$R_{(int)}$	0.0195	0.0240
GOF on F^2	1.066	1.022
$R_1[I > 2\sigma(I)]$	0.0204	0.0221
ωR_2 (all data)	0.0513	0.0525

3. Results and discussion

3.1. Crystal structure description

Structure of $[CuH_3L_2(GeMo_{12}O_{40})]\cdot 2H_2O$ (**1**)

X-ray single-crystal diffraction analyses revealed that compounds **1** and **2** are isostructural except that the polyoxoanion in **2** is $[SiMo_{12}O_{40}]^{4-}$. Therefore, we will discuss the structure of **1** as an example in detail. Compound **1** crystallizes in the monoclinic space group *P*2(1)/*c*. The asymmetric unit contains one Cu(I) ion, two protonated *L* ligands (L^1 and L^2)(Fig. S2a), one $[GeMo_{12}O_{40}]^{4-}$ cluster, and two lattice water molecules (Fig. 1). The Cu(I) center is four-coordinated with three pyridyl nitrogen atoms from three different *L* ligands and one terminal oxygen atoms from $[GeMo_{12}O_{40}]^{4-}$ anion, exhibiting a distorted tetrahedral coordination geometry. The oxidation state of Cu(I) center was confirmed by the BVS calculations [46] and the typical coordination environment of Cu(I) ion as well as XPS measurements. It is worth mentioning that the *L* ligands in **1** display two types of coordination modes, that is, L^1 acts as a monodentate ligand coordinating with one Cu(I) ion and L^2 acts as a bidentate ligand connecting two Cu(I) ions, forming the left- and right-handed helical chains along *b* axis with a screw pitch of 15.166 Å (Fig. S2b). The POMs as pendants attach in the helical chains through Cu–O bonds [47–52]. The adjacent helical chains prossessing the same handedness are linked by multiple intermolecular hydrogen bonds between the $GeMo_{12}$ clusters, water molecules and the *L* ligands (Fig. S3, Table S3), generating a 2D layer parallel *ab* plane. The adjacent 2D layers prossessing the different handedness of helical chains are linked alternately through hydrogen bonds to form a 3D supermolecular network (Fig. 2).

3.2. Characterization

3.2.1. XRPD and XPS characterization

The XRPD patterns for **1** and **2** are presented in Figs. S4 and Fig. S5 (Supporting information). The diffraction peaks of both simulated and experimental patterns match well, indicating the phase purities of these two compounds.

The XPS spectra of compounds **1** and **2** are shown in Fig. S6 in the Supporting Information. The XPS spectra show two peaks at 932.9 and 953.2 eV in **1**, 932.7 and 953.3 eV in **2** attributed