Hydrothermal Synthesis and Crystal Structure of a Meso-Helical Chain Based on Lindqvist Polyoxometalates

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A new Lindqvist polyoxometalate-based hybrid compound with a helical chain structure, $[Cu(bipy)_2][W_6O_{19}]$ (**1**), (bipy = 2,2′-bipyridine), has been hydrothermally synthesized and characterized by elemental analysis, infrared spectroscopy, thermogravimetry, and single-crystal X-ray diffraction. The compound crystallizes in the space group $C2/c$ of the monoclinic system. In **1**, the $[W_6O_{19}]^{2-}$ anions are connected alternately with $[Cu(bipy)_2]^{2+}$ subunits to form a meso-helical chain. To our knowledge, this structure represents the first example of a helical chain structure consisting of the hexatungstate anion $[W_6O_{19}]^{2-}$. The electrochemical properties of the title compound have been studied.

Key words: Polyoxometalate, Lindqvist, Helical Structure, Hydrothermal Synthesis

Introduction

Over the past decade, the rapid progress of exploring organic-inorganic hybrid materials is driven by the interest in their intriguing variety of architectures and their potential applications in biochemistry, catalysis, molecular absorption, and as electron-conductive, optical, and magnetic materials [1 – 5]. Among the large amount of reported work, the rational synthesis of organic-inorganic hybrid compounds containing helical arrays is currently of particular interest [6 – 8]. Helical structures are ubiquitous in nature and an essence of life, so helical structures have received much attention in coordination and materials chemistry. Many chemists have put great efforts on the rational design and synthesis of artificial helical compounds which also show significance in multidisciplinary areas such as biology, optical devices, and asymmetric catalysis [9 – 11].

Polyoxometalates (POMs) [12 – 15], as one kind of significant metal oxide clusters with a variety of topologies and great potential in the above applications [16 – 19], have recently been employed as functional secondary building blocks (SBUs) for constructing inorganic–organic hybrids with various metal–organic coordination fragments. The helical compounds based on POMs have attracted more and more attention due to their attractive structural features and potential applications. Many helical compounds based on POMs as connectors have been successfully synthesized, including Keggin POMs [20 – 22], polyvanadates [23 – 27], Anderson-type POMs [28 – 30], isopolymolybdates [31 – 35], and others [36 – 39]. However, no helical compounds based on the Lindqvist $[M_6O_{19}]^{2-}$ (M = W, Mo) clusters have been reported, where O atoms have two different coordination numbers (6 terminal and 12 μ_2-O atoms). They offer smart sites to link metal centers or metal complex units, and

their globular surface makes their coordination sites more flexible to adjust to steric hindrance, which is in favor of the formation of helical motifs or other attractive structures.

Herein, we present the synthesis and crystal structure of a novel organic–inorgainc hybrid compound $[Cu(bipy)_2][W_6O_{19}]$ (**1**), (bipy = 2,2′-bipyridine). Compound **1** is the first meso-helical chain structure based on Lindqvist POMs.

Experimental

Materials and methods

All reagents were purchased and used without further purification. Elemental analyses of C, H and N were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer, and that of W and Cu on a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded on KBr pellets with a Nicolet 170SX FT-IR spectrophotometer in the range 400 – 4000 cm^{-1}. The thermogravimetric (TG) analysis was performed with a Perkin-Elmer TGA7 instrument in an atmosphere of nitrogen at a heating rate of 10 °C min^{-1}. A CHI660 electrochemical workstation was used for control of the electrochemical measurements and data collection. A conventional three-electrode system was used, with a carbon paste electrode (CPE) as a working electrode, commercial Ag/AgCl as reference electrode and a twisted platinum wire as counter electrode.

Synthesis of [Cu(bipy)$_2$][W$_6$O$_{19}$]

$Na_2WO_4{\cdot}2H_2O$ (0.26 g, 0.8 mmol), $Cu(NO_3)_2{\cdot}3H_2O$ (0.10 g, 0.4 mmol), bipy (0.08 g, 0.5 mmol), and methanol (2 mL) were dissolved in 12 mL distilled water and stirred at room temperature for 30 min. The pH was adjusted to 1.7 with 1 M oxalic acid, and then the mixture was transferred to an 18 mL Teflon-lined reactor and kept under autogeneous pressure at 160 °C for 5 d. After the reactor was slowly cooled to room temperature over a period of 10 °C/h, green block-shaped crystals of **1** were obtained. The crystals were picked out, washed with distilled water, and dried at room temperature (31 % yield based on W). Anal. for $C_{20}H_{16}CuN_4O_{19}W_6$ (1782.96): calcd. C 13.47, H 0.90, N 3.14, Cu 3.56, W 61.87; found C 13.35, H 1.03, N 3.29, Cu 3.47, W 61.96 (%).

X-Ray crystallography

Crystallographic data for **1** were measured on a Rigaku R-AXIS RAPID IP diffractometer with monochromatic Mo K_α radiation ($\lambda = 0.71073$ Å) at 293 K. The structure of **1** was solved by Direct Methods and refined by full-matrix least-squares on F^2 using the SHELXTL crystallographic software package [40, 41]. The organic hydrogen atoms were generated geometrically. During the refinement, the restraint command 'ISOR' was used to refine the atoms C4, O3 and O4 with ADP or NPD problems. The refinement was based altogether on 18 restraints. The crystal and structure refinement data of **1** are summarized in Table 1.

CCDC 916644 contains 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.

Results and Discussion

Description of the structure

Single-crystal X-ray diffraction analysis has revealed that **1** is constructed from $[W_6O_{19}]^{2-}$ anions, Cu^{2+} cations and bipy ligands, as shown in Fig. 1. The W atoms are in the oxidation state +VI and the Cu atoms in the oxidation state +II, confirmed by BVS calculations [42], coordination environments and the green crystal color.

Table 1. Crystal data and numbers pertinent to data collection and structure refinement of **1**.

Empirical formula	$C_{20}H_{16}CuN_4W_6O_{19}$
M_r	1782.96
Color, habit	green, block
Crystal size, mm^3	$0.21 \times 0.21 \times 0.11$
Crystal system	monoclinic
Space group	$C2/c$
a, Å	21.044(4)
b, Å	7.830(2)
c, Å	21.178(4)
β, deg	118.94(3)
V, $Å^3$	3053.9(14)
Z	4
D_{calcd}, g cm^{-3}	3.88
T, K	293 (2)
μ(Mo K_α), mm^{-1}	23.3
$F(000)$, e	3156.0
hkl range	±27, ±10, ±27
Absorption correction	empirical
Refl. measured / unique / R_{int}	3504 / 3111 / 0.0676
Param. refined	215
$R_1/wR_2[I > 2\sigma(I)]$[a,b]	0.0440 / 0.0836
R_1/wR_2 (all data)[a,b]	0.0519 / 0.0867
GoF (F^2)[c]	1.098
$\Delta\rho_{fin}$(max / min), e $Å^{-3}$	5.03 / – 3.77

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; [b] $wR_2 = \left[\sum w\left(F_o^2 - F_c^2\right)^2/\sum w\left(F_o^2\right)^2\right]^{1/2}$, $w = \left[\sigma^2(F_o^2) + (AP)^2 + BP\right]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] GoF= $\left[\sum w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})\right]^{1/2}$.

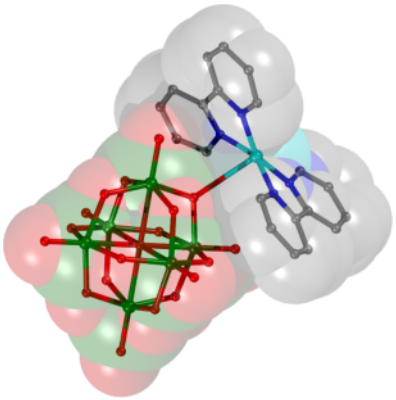

Fig. 1 (color online). View of the basic structural unit of **1**. All hydrogen atoms are omitted for clarity.

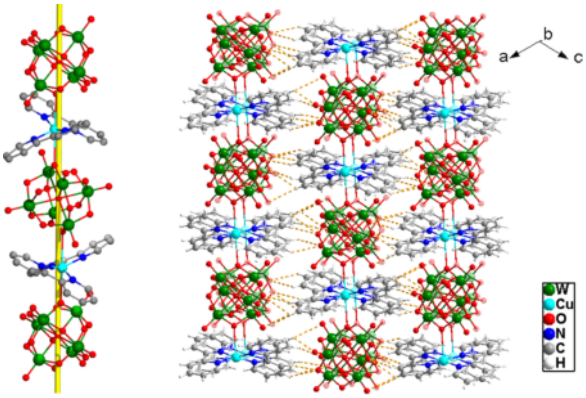

Fig. 2 (color online). (left) Meso-helical chains constructed from $[W_6O_{19}]^{2-}$ clusters and $Cu[Cu(bipy)_2]^{2+}$ subunits and (right) their 3D supramolecular framework (orange bonds represent the hydrogen bonding interactions in the framework).

The centrosymmetric $[W_6O_{19}]^{2-}$ anion has the well-known Lindqvist structure and consists of a central oxygen atom which is encompassed by six metal atoms in an octahedral geometry with the polyhedra sharing edges. There exist three kinds of oxygen atoms in the cluster, namely, the terminal oxygen O_t, the double-bridging oxygen O_b, and the central oxygen atoms O_c. Thus, the W–O bond lengths can be grouped into three sets: W–O_t 1.694(8) – 1.704(8) Å, W–O_b 1.901(7) – 1.951(7) Å and W–O_c 2.3215(7) – 2.3309(5) Å. Compared with W–O bond lengths of Lindqvist isopolyanion salts, the W–O bond lengths in **1** are not significantly changed [43].

There is one crystallographically independent Cu ion in **1** exhibiting an octahedral coordination geometry with four nitrogen atoms from two bipy ligands and two oxygen atoms from two $[W_6O_{19}]^{2-}$ anions. The bond lengths around the Cu atoms are 2.747(9) Å for the Cu–O bonds, and in the range of 1.958(9) – 1.971(8) Å for the Cu–N bonds. The angles are 178.53(7)° for N–Cu–N, and in the range 81.8(4) – 153.7(3)° for O–Cu–O. It should be noted that the distances are shorter than the sum of the van der Waals radii of Cu and O (2.95 Å) [44 – 46], implying a long-range coordinative bond.

The $[W_6O_{19}]^{2-}$ anions are connected by the $[Cu(bipy)_2]^{2+}$ cations, and the resulting structure is a meso-helical chain along the [101] direction with a pitch of 10.724 Å. The $[W_6O_{19}]^{2-}$ anions are located along a hypothetical 2_1 screw axis displaced by a rotation of 90°, while the $[Cu(bipy)_2]^{2+}$ subunits are periodically surrounding the 2_1 screw axis (Fig. 2, left). To our knowledge, such a meso-helical structure was rarely shown for POM systems [32, 47 – 49]. Furthermore, there are hydrogen bonding interactions [C1–H1A···O1: 2.936 Å; C5–H5A···O1: 2.878 Å; C5–H5A···O5: 2.764 Å; C7–H5A···O7: 2.814 Å; C10–H10A···O7: 2.598 Å] between the oxygen atoms of the $[W_6O_{19}]^{2-}$ clusters and the hydrogen atoms of the bipy molecules, forming a 3D supramolecular framework (Fig. 2, right).

IR spectrum

As shown in Fig. 3, in the 400 – 2000 cm^{-1} region of the IR spectrum for **1**, the characteristic peaks at 956/932, 795, 567, and 441 cm^{-1} are attributed to $\nu(W-O_a)$, $\nu(W-O_b-W)$, $\delta(W-O_b-W)$, and $\delta(W-O_c)$ of the $[W_6O_{19}]^{2-}$ polyoxoanion, respectively, similar to the IR spectrum of $(TBA)_2[M_6O_{19}]$ [50]. The bands in the 1000 – 1700 cm^{-1} region can be assigned to characteristic peaks of the bipy ligands. The vibration of $\nu(-N{=}C)$ at 1580 cm^{-1} for the free ligand is shifted to 1607 cm^{-1} for **1**, showing the occurrence of a coordinate binding of bipy to a copper atom.

Thermal analysis

The TG experiment was performed under a N_2 atmosphere with a heating rate of 10 °C min^{-1} in the temperature range of 25 – 600 °C (Fig. 4). No weight

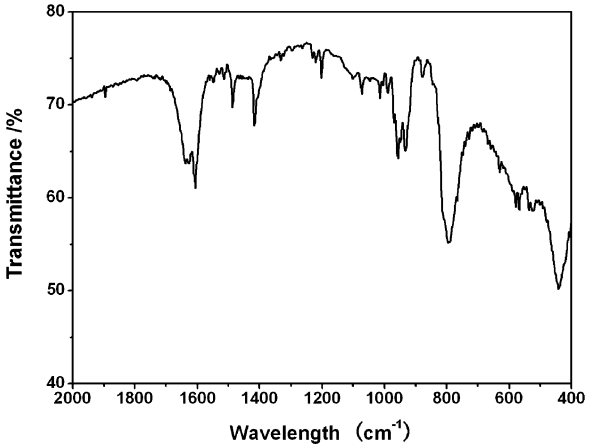

Fig. 3. The IR spectrum of **1**.

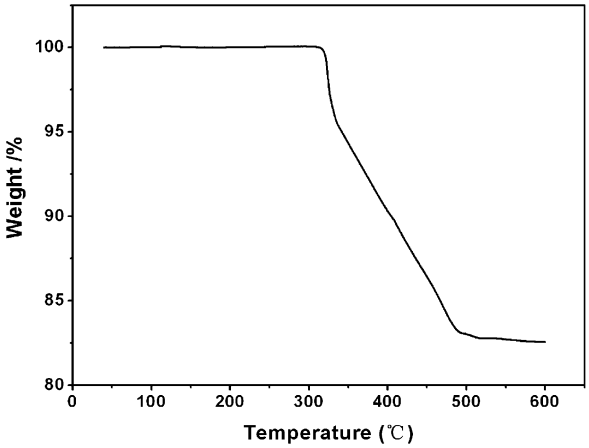

Fig. 4. The TG curve of **1**.

loss was observed below 312 °C, which demonstrates that the title compound possesses good thermal stability. In range of 312 – 522 °C, a weight loss of 17.5 % (calcd. 17.5 %) is observed, which is consistent with the loss of bipy molecules.

*Voltammetric behavior of **1**-CPE in aqueous electrolyte*

Compound **1** is insoluble in water and common organic solvents. Thus, a bulk-modified carbon paste electrode (CPE) can be used to study the electrochemical properties. The cyclic voltammetric behavior of **1**-CPE in 1 M H_2SO_4 solution at different scan rates was recorded. As shown in Fig. 5a, in the potential range of -0.5 to 0.6 V, there exists one pair of reversible redox peaks with half-wave potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ at -0.116 V (II–II′), corresponding to the one-electron reductive process of W^{VI} in **1**. In addition, there is one irreversible anodic peak (I) at $+0.23$ V, which is assigned to a Cu(II)/Cu(I) redox process [51]. When the scan rates are varied from 20 to 120 $mV \cdot s^{-1}$, the peak potentials change gradually: the cathodic peak potentials shift toward the negative direction and the corresponding anodic peak potentials to the positive direction with increasing scan rates. The peak currents are proportional to the scan rate as shown in Fig. 5b, which indicates that the redox processes are

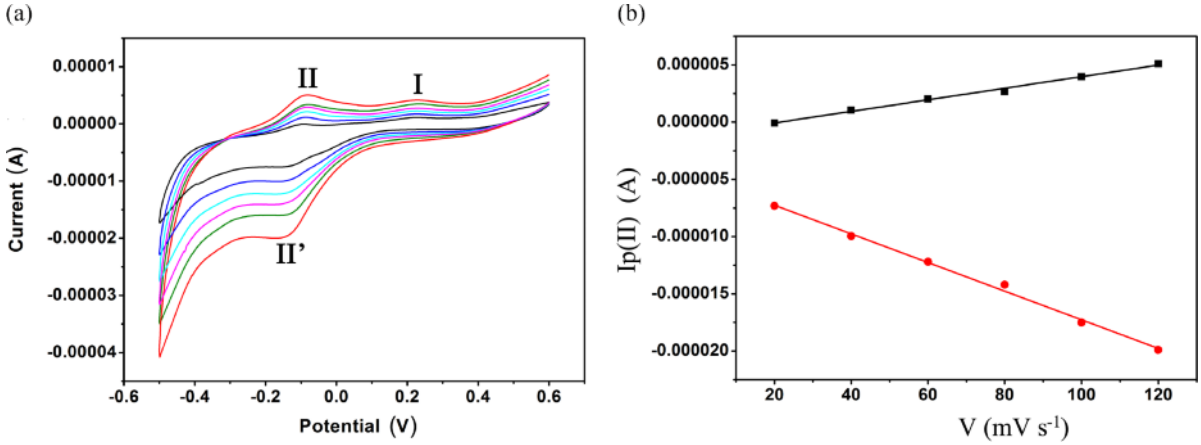

Fig. 5. The cyclic voltammograms of **1**-CPE (a) in 1 M H_2SO_4 at different scan rates (from inner to outer: 20, 40, 60, 80, 100, and 120 $mV \cdot s^{-1}$). The dependence of anodic peak (II) and cathodic peak (II′) currents on scan rates for **1**-CPE (b).

surface-controlled, and the exchange rate of electrons is fast.

Conclusions

A new meso-helical chain structure built of Lindqvist $[W_6O_{19}]^{2-}$ clusters linked by copper complexes $[Cu(bipy)_2]^{2+}$ has been synthesized, which represents the first example of helical structures based on $[W_6O_{19}]^{2-}$ clusters. The results suggest that more other new compounds with a helical structure can be prepared by this synthetic strategy.

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