



Polyoxometalates functioned as ligands: Synthesis and crystal structure of a new hybrid compound constructed from metatungstate and metal complex units

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ABSTRACT

A new organic–inorganic hybrid compound, $[\text{Zn}(\text{bpy})_3]_{1.5}[\text{H}_3\text{W}_{12}\text{O}_{40}\text{Zn}(\text{bpy})_2(\text{H}_2\text{O})] \cdot 0.5\text{H}_2\text{O}$ (bpy = 2,2'-bipyridine) has been synthesized hydrothermally from ZnCl_2 , $\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}]$, and 2,2'-bipyridine, and has been analyzed using X-ray crystallography, thermogravimetric analysis and UV–Vis spectroscopy. The compound contains an anionic complex $[\text{H}_3\text{W}_{12}\text{O}_{40}\text{Zn}(\text{bpy})_2(\text{H}_2\text{O})]^{3-}$ in which α -metatungstate ion $[\text{H}_3\text{W}_{12}\text{O}_{40}]^{5-}$ coordinated to a $[\text{Zn}(\text{bpy})_2(\text{H}_2\text{O})]^{2+}$ unit through a bridging oxo group.

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Polyoxometalates (POMs) have been extensively studied due to their so-called “value-adding properties” [1] such as redox properties, photochemical response, ionic charge, conductivity and ionic weights, and their wide applications in catalysis, medicine and magnetic materials [2]. It has been shown that POMs, with well defined structures and their size typically of a few nanometers, have similar properties to aggregates of various metal oxides [3]. For example, similar to some metal oxides that can participate in catalytic processes as oxygen and multielectron relays, polytungstate anions are able to sensitize the photochemical reduction of oxygen and water [4–6]. In aqueous solution, $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ can act as electron carriers in the photoreduction of water by chloroplasts [7]. Thus, POMs have attracted significant attention as building blocks of new functional materials in recent years. A popular strategy for developing new hybrid materials is the self-assembly of metal–organic complexes and POMs, essentially because POMs are able to function as multidentate, totally inorganic, and oxidatively resistant ligands for redox-active ions [8,9] or other functional active centers. The recent success in the development of organic–inorganic hybrids from metatungstate ions as inorganic ligands [10–13] further demonstrated the feasibility of this strategy. Our interest is to investigate the assembly of new compounds using POMs as ligands to metal–organic complexes and to study their optical properties. Here, we reported the hydrothermal synthesis and

characterization of a α -Keggin anion supported zinc–bpy complex $[\text{Zn}(\text{bpy})_3]_{1.5}[\text{H}_3\text{W}_{12}\text{O}_{40}\text{Zn}(\text{bpy})_2(\text{H}_2\text{O})] \cdot 0.5\text{H}_2\text{O}$ (**1**).

Compound **1** was initially synthesized [14] hydrothermally as a minor phase from a mixture of ZnCl_2 , $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 2,2'-bipyridine and water at 160 °C for 96 h. The major phase is $[\text{Zn}(\text{bpy})_3]_2[\text{ZnW}_{12}\text{O}_{40}\text{Zn}(\text{bpy})_2] \cdot \text{H}_2\text{O}$ [13]. We subsequently rationalized the synthesis of **1** by using $[\text{Zn}(\text{bpy})_3]^{2+}$, $[\text{Zn}(\text{bpy})_2]^{2+}$ and $\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}]$ as starting materials. The preformed $[\text{Zn}(\text{bpy})_3]^{2+}$ / $[\text{Zn}(\text{bpy})_2]^{2+}$ would prevent the incorporation of Zn^{2+} into the center of $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ to form $[\text{ZnW}_{12}\text{O}_{40}]^{6-}$. Thus we can synthesize **1** in high yield (~70% based on W). A single crystal X-ray diffraction study [15] of **1** at 193 K revealed that its structure consists of $[\text{H}_3\text{W}_{12}\text{O}_{40}\text{Zn}(\text{bpy})_2(\text{H}_2\text{O})]^{3-}$ anions (as shown in Fig. 1) and $[\text{Zn}(\text{bpy})_3]^{2+}$ cations. The anion $[\text{H}_3\text{W}_{12}\text{O}_{40}\text{Zn}(\text{bpy})_2(\text{H}_2\text{O})]^{3-}$ consists of a Keggin α - $[\text{H}_3\text{W}_{12}\text{O}_{40}]^{5-}$ anion coordinated by a $[\text{Zn}(\text{bpy})_2(\text{H}_2\text{O})]^{2+}$ complex. The well-known Keggin α - $[\text{H}_3\text{W}_{12}\text{O}_{40}]^{5-}$ anion can be described as an assembly of 12 edge- and corner-shared WO_6 octahedra, which form four W_3 “triads”. At the center of the Keggin anion, a tetrahedral cavity is formed by the four W_3 “triads”. As usual, each W atom is displaced towards the unshared oxygen of its WO_6 octahedron, with the coordination geometry at the W site defined by one terminal oxo group, two pairs of bridging μ_2 -oxo groups and one bridging μ_3 -oxo group with the $\text{W}-\text{O}_t$ 1.700(9)–1.752(9) Å, $\text{W}-\text{O}_{\mu_2}$ 1.747(9)–2.023(9) Å, and $\text{W}-\text{O}_{\mu_3}$ 2.175(8)–2.349(8) Å. This geometry signifies a short multiple bond to that oxygen atom, thus reduces its basicity. In fact, the terminal oxygen atoms at the entire “surface” of the Keggin structure are very weakly basic. Nonetheless, in the title

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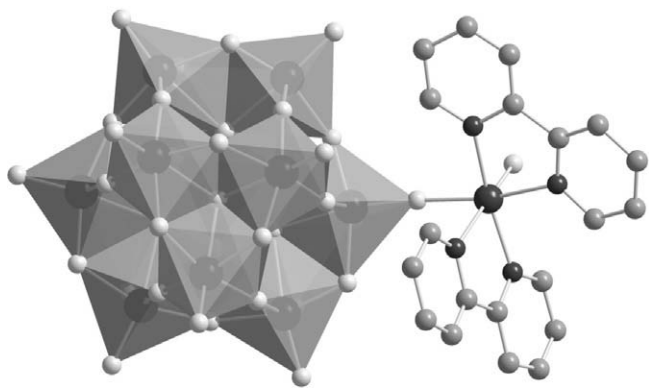


Fig. 1. A polyhedron and Ball-and-Stick representation of the anionic complex $[\text{H}_3\text{W}_{12}\text{O}_{40}\text{Zn}(\text{bpy})_2(\text{H}_2\text{O})]^{3-}$ in compound **1** showing the coordination of the Keggin ion bridged to $[\text{Zn}(\text{bpy})_2(\text{H}_2\text{O})]^{2+}$ through a terminal oxygen atom.

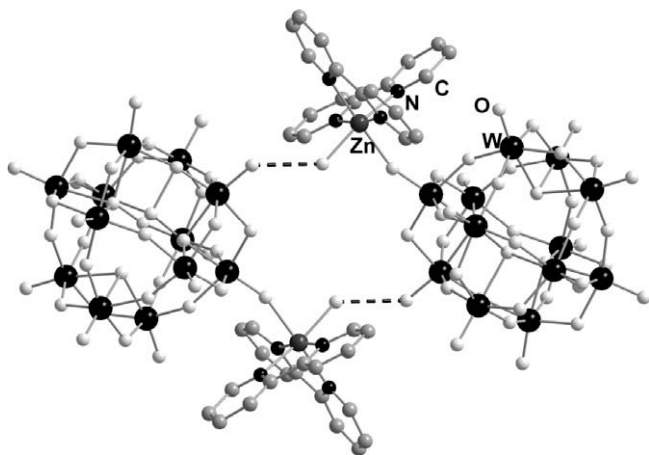


Fig. 2. A Ball-and-Stick representation of the dimer structure formed between two anionic complexes $[\text{H}_3\text{W}_{12}\text{O}_{40}\text{Zn}(\text{bpy})_2(\text{H}_2\text{O})]^{3-}$ through hydrogen bonds.

compound, the Keggin anion acts as a ligand to a cation $[\text{Zn}(\text{bpy})_2(\text{H}_2\text{O})]^{2+}$ to form a hybrid $[\text{H}_3\text{W}_{12}\text{O}_{40}\text{Zn}(\text{bpy})_2(\text{H}_2\text{O})]^{3-}$ anionic complex through a bridging μ_2 -oxo group (O(1)). This results in a longer W–O(1) (1.752(9) Å) bond length compared with other W–O_t (1.700(9)–1.730(9) Å) bond lengths. This observation complies with reports of other compounds containing Keggin units such as $[\text{XW}_{12}\text{O}_{40}]^{n-}$ (X = Zn, P) coordinated unidentately to metal complexes [12,13]. In the cation $[\text{Zn}(\text{bpy})_2(\text{H}_2\text{O})]^{2+}$, the slightly distorted octahedral coordination geometry of Zn atom is defined by four nitrogen from two bpy ligands, one oxygen from a water molecule and a terminal oxygen from a Keggin unit, with Zn–O 2.120(9)–2.123(9) Å and Zn–N 2.12(1)–2.14(1) Å. Two anionic units $[\text{H}_3\text{W}_{12}\text{O}_{40}\text{Zn}(\text{bpy})_2(\text{H}_2\text{O})]^{3-}$ form a dimer through hydrogen bonding between the coordinated water molecule on Zn atoms and oxygen of a cluster (Fig. 2). For the cationic complexes $[\text{Zn}(\text{bpy})_3]^{2+}$ in compound **1**, there are two distinct Zn^{2+} sites, each of them is coordinated by six nitrogen atoms from three bpy ligands, with Zn–N 2.06(2)–2.32(2) Å. These two cationic complexes $[\text{Zn}(\text{bpy})_3]^{2+}$ are enantiomers to each other. Bond valence sum calculations show all tungsten atoms are in their highest oxidation states (+6) [16]. Charge balance consideration suggests that there are three hydrogen ions in the $[\text{H}_3\text{W}_{12}\text{O}_{40}]^{5-}$ unit. Very interestingly, it is also reported that Keggin anions may bidentately bond to a $[\text{Zn}(\text{bpy})_2]^{2+}$ complex [13]. The successful synthesis of compound **1** further demonstrated the flexible coordinative properties

of POMs in the formation of organic–inorganic composite materials.

The thermogravimetric analysis of **1** under N_2 atmosphere shows there are several steps of mass losses in the temperature range of 40–700 °C. The first weight loss of 1.07% before 120 °C corresponds to the removal of 2.5 water molecules per formula unit (calc. 1.11%). The total mass loss (23.4%) observed in the temperature range of 270–700 °C can be attributed to the removal of bpy ligands (calc. 25.03%).

UV–Vis Diffuse Reflectance (DRS) Spectra on solid samples of **1** were obtained with a Varian Cary 100 UV–Vis spectrophotometer employing the integration sphere diffuse reflectance attachment. The broad band at around 257 nm and the band at 289 nm can be attributed to ligand-to-metal charge-transfer (LMCT) transitions (O → W) [17]. The bands around 200–330 nm with a maximum at approximately 263 nm on UV spectra are characters of Keggin-type POMs [18]. The corresponding UV–Vis DRS electronic edge energy (E_g) value of the title compound is 3.5 eV, which is typical for Keggin compounds. Furthermore, it appears that the position of the UV–Vis DRS band maxima and the E_g value of the Keggin are not affected by its coordination to a Zn complex, although the band position changes. The π – π^* ligand transition of $[\text{Zn}(\text{bpy})_3]^{2+}$, which is located at 311 nm [19], is mixed with the LMCT transitions of the Keggin ion.

Supplementary material

CCDC 734741 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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dried in air. Yields: ca. 70% based on W. Anal. Calc. (%) for **1**: C, 19.25; H, 1.44; N, 4.49. Found: C, 20.06; H, 1.52; N, 4.40.

- [15] Crystal data for **1**, monoclinic, space group *C2/c*, colorless crystal, $a = 46.672(9) \text{ \AA}$, $b = 14.294(3) \text{ \AA}$, $c = 26.201(5) \text{ \AA}$, $\beta = 90.37(3)^\circ$, $V = 17479(6) \text{ \AA}^3$, $Z = 4$, $D_{\text{caled}} = 3.082 \text{ Mg/cm}^3$, $\mu = 16.487 \text{ mm}^{-1}$, $R(\text{int}) = 0.0874$, 153,441 reflections measured, 19,925 unique. Diffraction intensities for **1** were collected on a Nonius kappa CCD diffractometer equipped with graphite monochromated Mo $K\alpha$ radiation with a radiation wavelength of 0.71073 \AA . The structure was solved by direct methods and refined on F^2 by weighted full

matrix least squares using the SHELXTL-97 program package [20]. Non-hydrogen atoms were refined with anisotropic displacement parameters. The organic hydrogen atoms were found in difference maps but subsequently placed at calculated positions and refined using a riding model.

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