Inorganic Chemistry Communications 59 (2015) 5–8

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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

Synthesis, structure, and photocatalytic property of a new hybrid compound based on unusual bi-silver-capped polyoxometalates

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ARTICLE INFO

Article history:
Received 28 April 2015
Received in revised form 6 June 2015
Accepted 13 June 2015
Available online 16 June 2015

Keywords:
Bi-silver-capped polyoxometalate
Photocatalytic property
Keggin

ABSTRACT

A new compound based on capped polyoxometalates (POMs), $[Ag(phen)_2]_2(Agphen)_2SiW_{12}O_{40}$ (phen = 1,10-phenanthroline), has been hydrothermally synthesized and characterized by single-crystal X-ray diffraction analysis, infrared spectrum, UV–vis electronic spectrum, elemental analyses, and powder X-ray diffraction pattern. The structural feature of compound 1 is that each $[SiW_{12}O_{40}]^{4-}$ (SiW_{12}) cluster capped by two $(Agphen)^+$ fragments. To the best of our knowledge, the compound 1 represents the first example of hybrid compound based on bi-silver-capped POMs to date. The photocatalytic properties of compound 1 were also investigated in detail and the results of photocatalytic experiment show that compound 1 can be used as a photocatalyst towards the decomposition of organic pollutant methylene blue (MB).

Polyoxometalates (POMs), a large family of metal-oxygen clusters with diversity structures, exhibit versatile applications [1–3], especially in catalysis and electrochemistry. Recently, in the filed of POMs, more and more attention has been focused on the design and synthesis of new POM-based inorganic–organic hybrid compounds with desirable structures and properties. In this field, the hybrid compounds based on capped POMs become extraordinarily promising because of their changeable and controllable structures as well as their predominant properties introduced by capping moieties [4]. These facts have provided a powerful impetus for the creation of novel hybrid compounds based on capped POMs, and thus many significant results have been achieved by the efforts of inorganic chemists [5–27]. An excellent example is that a series of hybrid compounds constructed from bicapped POMs to tetracapped ones were reported by Wang et al. in 2003 [11]. Subsequently, thanks to the work of Peng et al., a novel asymmetrically modified bivanadium-capped Keggin polyoxometalate has been reported [13]. However, the capping metals in these compounds were generally restricted to Mo or V atoms, except for the several examples (see the summarization of these compounds based on capped POMs in Table S1), in which the capping metals are Ni, Sb, Nb, As and Ag atoms. As is well known, Ag^+ ion is widely applied in luminescent, catalytic, and antibacterial materials [28,29]. Further, Ag^+ ion possesses flexible coordination geometries and high affinity to O and N donors, which may easily form covalent links between Ag^+ ions and POMs/ligands [30]. Hence, these properties endow that Ag^+ ions are good synthons as capping metals for construction of novel hybrid compounds based on silver-capped POMs. Nevertheless, to the best of our knowledge, up to now, only one such hybrid compound has been reported Cao et al. in 2008 [31], namely, $\{Ag(phen)_2\}_2\{[Ag(phen)]_2[PMo_{12}O_{40}]\}$ (2), which shows a chain structure based on mono-silver-capped phosphomolybdates and displays fascinating orange luminescent property at ambient temperature (Scheme S1).

Herein, we communicate the preparation and structure of a new hybrid compound based on silver-capped POMs, $[Ag(phen)_2]_2(Agphen)_2SiW_{12}O_{40}$ (phen = 1,10-phenanthroline) (1), which is after the compound 2 reported by Cao et al. [31], but compound 1 is based on bi-silver-capped silicotungstate (see Scheme S1). Furthermore, the photocatalytic property of compound 1 towards photodecomposition of organic pollutant MB was investigated in detail.

Compound 1 was hydrothermally synthesized with a mixture of $H_4[SiW_{12}O_{40}]\cdot 12H_2O$, $AgNO_3$, and phen in water at 160 °C for 3 days (Supplementary material). And compound 1 crystallizes in the triclinic space group $P\bar{1}$ (Supplementary material). Single-crystal X-ray diffraction analysis reveals that compound 1 consists of a silicotungstate polyanion SiW_{12}, four Ag^+ cations and six phen ligands, as shown in Fig. 1. The SiW_{12} polyanion exhibits the well-known α-Keggin type structure, consisting of central SiO_4 tetrahedron corner-sharing four triad $\{W_3O_{13}\}$ clusters. The central atom Si is disorderly surrounded by a cube of eight oxygen atoms, with each oxygen site half-occupied. There are two crystallographically independent Ag atoms in structure of compound 1, which exhibit an identical six-coordination in distorted octahedral geometries, but their coordination environments are entirely different. Namely, the Ag(1) is coordinated by two nitrogen atoms from a phen molecule and four oxygen atoms from a SiW_{12} polyanion. While the Ag(2) is coordinated by four nitrogen atoms from two phen molecules and two oxygen atoms from a SiW_{12} polyanion. The

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http://dx.doi.org/10.1016/j.inoche.2015.06.010
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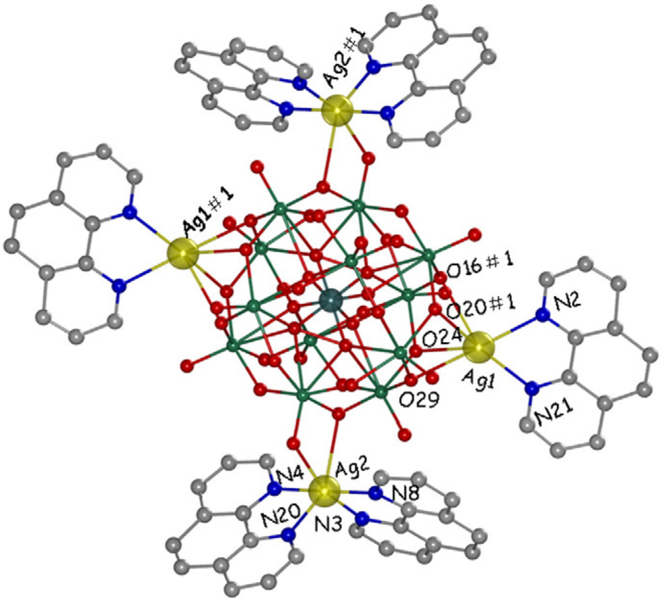

Fig. 1. View of the basic structural unit and the coordination environments for the SiW_{12} cluster and Ag^+ ions in 1 (symmetry codes: #1: 1-x, 2-y, −z;). All the hydrogen atoms attached to phen molecules are omitted for clarity.

bond lengths and angles around the Ag ions are in the ranges of 1.96(2)—2.36(2) Å (Ag—N), 2.31(2)—2.58(2) Å (Ag—O), 72.1(8)—178.8(8)° (N—Ag—N) and 84.5(7)—173.5(8)° (N—Ag—O).

An interesting structural feature of compound 1 is its bi-silver-capped silicotungstate polyanion, which can be described in detail as follows: as mentioned above, the Ag(1) atom is coordinated by two nitrogen atoms from one phen molecule to form a $[\text{Ag(1)phen}]^+$ coordination fragment, while the Ag(2) atom is coordinated by four nitrogen atoms from two phen molecules to give birth to a $[\text{Ag(2)(phen)}_2]^+$ coordination fragment. Each $[\text{Ag(1)phen}]^+$ coordination fragment is further coordinated by four bridging oxygen atoms from a SiW_{12} polyanion to construct square pyramidal motives, and there are two such square pyramidal motives capping on the two opposite points of each SiW_{12} polyanion. Consequently, a novel bi-silver-capped silicotungstate polyanion $[(\text{Agphen})_2SiW_{12}O_{40}]^{2-}$ is obtained (Fig. 2). Herein, in the structure of polyanion $[(\text{Agphen})_2SiW_{12}O_{40}]^{2-}$, capping silver atoms may play a great role in inducing the polyanion to polarize and making the surface of polyanion modified by other transition metal complexes with ease. And thus, the $[(\text{Agphen})_2SiW_{12}O_{40}]^{2-}$ polyanion is further modified by two $[(\text{Agphen})_2]_2^{2+}$ (Fig. 1). Furthermore, there exist π···π interactions between the almost parallel phen rings from adjacent $[\text{Ag(1)phen}]^+$ coordination fragments. And the centroid–centroid distance is 3.65 Å (see Fig. S1), which is usual ranges of π···π interactions [32]. As a result, a 1D supramolecular chain is formed (Fig. 3).

It is well known that POMs often show photocatalytic activity in decomposition of waste organic molecules so as to purify the water resources. Accordingly, we selected an organic dye methylene blue (MB) as a model pollutant to evaluate its photodecomposition under UV irradiation. Before we did the photocatalytic experiments, the characterizations of infrared spectrum, UV–vis electronic spectrum, elemental analyses, and powder X-ray diffraction pattern had been performed (please see details in Supplementary material). As shown in Fig. 4, the absorption peaks of MB aqueous solution decreased gradually and the decolorization of MB aqueous solution became obvious with increasing time under UV irradiation with compound 1. The decomposition rate of MB (K) can be expressed as $K = (C_0 - C) / C_0$, where C_0 represents the UV–vis absorption intensity of MB at the initial time and C is the intensity at a given time. It can be seen that the photocatalytic decomposition rate is 70.25% for compound 1. In contrast, the rates of photocatalytic decomposition without compound 1 is 13.15%, after UV irradiation for the same time, which reveals that the formation of organic–inorganic hybrid compound based on POMs could improve the photocatalytic decomposition rate of MB. The degradation of the MB dye occurs by the hydroxyl radicals and the superoxides (see the photocatalytic mechanisms in Supplementary material).

In summary, a new hybrid compound based on silver-capped POMs has been obtained from hydrothermally synthesis method. The compound 1 represents the first example of hybrid compound based on bi-silver-capped POMs to date. Also, there exist π···π interactions in its structure, which have an important influence on linking the low-dimensional entities into a supramolecular chain. In addition, compound 1 shows good photocatalytic activity towards the decomposition of organic pollutant methylene blue. With hindsight, we can imagine that more new hybrid compounds based on capped POMs could be prepared by replacement of capping metallic-organic segments and/or by

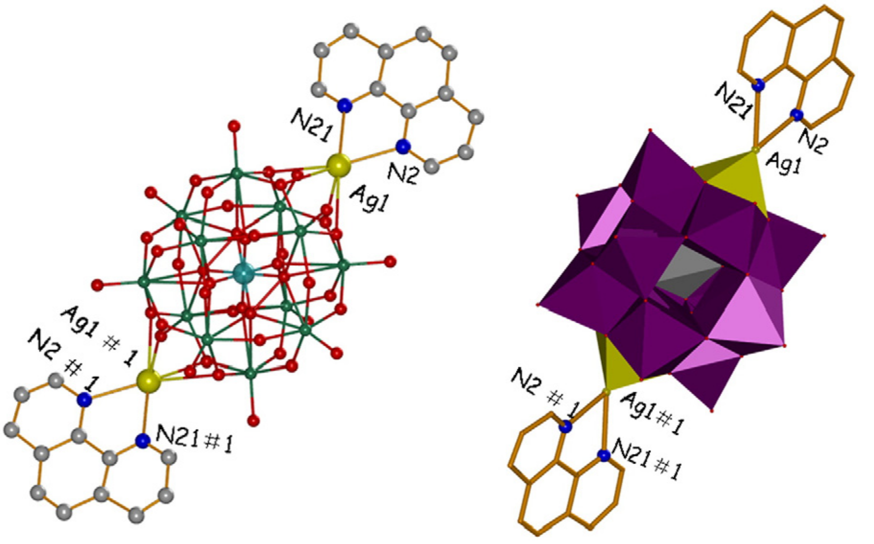

Fig. 2. Combined ball/stick/polyhedral representation of bi-silver-capped silicotungstate polyanion $[(\text{Agphen})_2SiW_{12}O_{40}]^{2-}$ in 1.