



A new method for the synthesis of organic–polyoxometallate hybrid compounds

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ABSTRACT

The reaction of the Na₂MoO₄ or Na₂WO₄ salt with organic amine and PCl₅, SiCl₄ or TiCl₄ in hydrochloric acid medium under hydrothermal conditions yields organic–polyoxometallate hybrid compounds, with the following reaction formula: Na₂MO₄ + Lewis-base + XCl_n + HCl → (Lewis-baseH)_m(XM₁₂O₄₀) + NaCl + H₂O (M = Mo or W; X = P, Si, Ti; n = 3–5). By using this method, four new complexes, [(CH₃)₂NH]₃[H₃PW₁₂O₄₀] (1), (C₂H₅OH)₃(H₃PMo₁₂O₄₀) (2), [DMDA]₂[H₄SiW₁₂O₄₀]·H₂O (3) (DMDA = 1 N,3 N-dimethyl-1,3-diazolidine) and [(DAN)₆][H₄TiW₁₂O₄₀]·4H₂O (DAN = 4,4'-dianiline) (4), were obtained, and their crystal structures are reported. Thermal analysis of 1, 2 and 4 has been carried out. The thermal analysis indicates that the Keggin anion skeleton begins to decompose at about 300 °C. The possibility of constructing hydrogen-bond interactions by association between the polyoxometallate and the organic compound is explored. The roles of solvents and organic groups in the formation of specific crystalline architectures are discussed. The crystal structure of [H₄TiW₁₂O₄₀], a hetero-transition-metal Keggin polyoxometallate with a square-plane TiO₄, has been reported. Four architectures developed by hydrogen-bond associations of different Keggin polyoxometallates and organic bearing N–H or O–H donor functions are described. The selected organic modules (4,4'-dianiline, 1,3-dimethylimidazolidine, dimethylamine and ethanol) possess hydrogen-donor functions to allow them to act as bridges between polyoxometallate groups. Depending on the nature of the donor group, the number of hydrogens available for bonding, the geometric features and the sizes of the organic modules, diverse assembling patterns have been observed ranging from one-dimensional to three-dimensional networks. For all the networks, H₃O⁺ and H⁺ act as actual linkers between the molecular units.

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1. Introduction

Hybrid organic–inorganic compounds have attracted increasing interest in recent years due to the possibility of combining the different characteristics of the components to get unusual structures, properties or applications [1]. Polyoxometallates (POMs) are one of the most widely used inorganic components [2,3]. The chemistry of POMs is a rapidly growing field because these nanomolecular entities exhibit a unique combination of tunable properties, including composition, size, shape, charge density, redox potentials and solubility [4–6]. The main goal in the synthesis of POMs is to discover novel species with unexpected structures and properties. The formation of hybrid compounds between polyoxometallates and organic or metal–organic species has significant potential in many areas of polyoxometallate chemistry, ranging from applications in catalysis and material science to biologically relevant environments [7]. The preparation of such organic–polyoxometallate hybrid compounds with predesigned structure and trait requires synthetic pro-

cedures that should be as simple as possible. A perusal of the known methods for such preparations reveals that there is a relative paucity of synthetic approaches available, and in all, one can discern two general approaches [8]. The first type of synthetic method involves the creation of hybrid materials *via* electrostatic interactions between anionic polyoxometallates and cationic species that can be organic or metal organics, such as [R_nN]X + H₄SiMo₁₂O₄₀ or [ML_n]X + Na₃(PW₁₂O₄₀) (M = metal, L = ligands) [9–13]. Since the negative charge of the polyoxometallate anion is polarized over the entire structure, the hybrid compounds formed generally have little element of design. These compounds are sometimes insoluble, especially with more rigid cations, although solubility can often be obtained in apolar solvents or using surfactants. The second type of method involves a covalent, site-selective link between an organic moiety and the polyoxometallate. One of the most notable methodologies is the reaction of amines with polyoxometallates *via* the substitution of terminal oxo moieties by organoimines [14–19].

Currently, we are interested in exploring the applicability of Keggin–POM complexes in the preparation of new hybrid compounds [20]. The polyoxometallates with Keggin structures exhibit potent anti-HIV activity and some of them are under pre-clinical evaluations for the treatment of HIV [21,22]. It is therefore vital

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to design and synthesize novel metallates with different structural characteristics in order to explore their properties. It is well known that POMs have the ability to conjugate with organic molecules [23]. Such anions are interesting because of their high electron acceptor capability and organic component as a donor [24]. In this paper we present a *new simple* synthetic methodology whereby organic amines, even neutral solvent molecules, can react with common compounds such as Na_2MoO_4 or Na_2WO_4 and PCl_5 , SiCl_4 , TiCl_4 , etc. in hydrochloric acid medium under hydrothermal conditions to yield the polyoxometallate-amine or small organic molecule adduct. By this method, we have synthesized four Keggin structure complexes and obtained their single-crystal structures, in particular that of **4**. Among Keggin-type compounds, their formula can be generally expressed as $[\text{XM}_{12}\text{O}_{40}]^{n-}$ ($\text{M} = \text{W}, \text{Mo}$; $\text{X} = \text{P}, \text{Si}, \text{B}, \text{Ge}, \text{As}, \text{S}, \text{Al}, \text{Co}, \text{Fe}, \text{Cu}, \text{V}, \text{Zn}, \text{and Ni}$), and most studies are focused on main-group atom-centered polyoxoanions, while the transition-metal-centered Keggin-type compounds are rarely explored [25–28]. The synthesis of TMX–Keggin-type heteropoly-molybdates remains a challenge. Zhang, etc. reported DFT studies of hetero-transition-metal Keggin structures, and suggested the properties of TMX–Keggin compounds could be substantially different from those of main-group MGX–Keggin compounds [29]. So far, we have only obtained one TMX–Keggin compound, $[(\text{DAN})_6][\text{H}_4\text{TiW}_{12}\text{O}_{40}]\cdot 4\text{H}_2\text{O}$ (**4**), and have not obtained any other TMX–Keggin compounds such as V, Cr, Fe, Co, Ni, etc. But we believe this new synthetic methodology may be useful to synthesize TMX–Keggin compounds.

Although it is well known that PCl_5 , SiCl_4 or TiCl_4 are easy to hydrolyze in hydrous solvents, we don't think Keggin compounds are formed only by PO_4^{3-} , SiO_4^{4-} or TiO_3^{2-} . In fact, PCl_5 , SiCl_4 or TiCl_4 are all liquids, and we put all the reactants into a Teflon-lined reactor as quickly as possible when liquid PCl_5 , SiCl_4 or TiCl_4 are added. In addition, H_4SiO_4 and H_3TiO_3 are not dissolved in water solution. We have only found a few Keggin compounds that are reported as being synthesized directly from Na_2MoO_4 , NH_4VO_3 , Lewis-base, H_3PO_4 or Na_2HPO_4 [30,31]. To the best of our knowledge, there are no reports about synthesizing Keggin compounds by using PCl_5 , SiCl_4 or TiCl_4 directly. We conclude that the Keggin compounds could also be synthesized using XCl_n ($\text{X} = \text{P}, \text{As}, \text{Sb}, \text{Si}, \text{Se}, \text{Ti}, \text{Zr}, \text{Hf}, \text{V}, \text{Nb}, \text{Ta}, \text{Cr}, \text{Fe}, \text{Co}, \text{Ni}, \text{etc.}$), Na_2MoO_4 or Na_2WO_4 , and a Lewis-base as reactants in a Teflon-lined autoclave at a temperature above 120 °C. Starting from commercially available reactants, the four Keggin compounds **1–4** were obtained. The reported method is shown to be very flexible and the work-up procedure is simple. Mild reaction conditions, simple purification, short reaction period, the stability and cheapness of the reagents are features of this new procedure. Moreover, extrapolation of this method to the application of TMX–Keggin compounds is currently under investigation. The electrochemical property of a **2**-bulk modified carbon paste electrode (**2**-CPE) has been studied, and the results indicate that **2**-CPE has good electrocatalytic activities toward the reduction of bromate.

2. Experimental section

2.1. Chemicals and measurement

Thermogravimetry (TG) and differential thermal gravimetric (DTG) analyses were recorded on an SDT 2980 simultaneously for the samples of 10 mg under a nitrogen atmosphere (150 ml/min) at a heating rate of 10 °C/min. Electrochemical measurements were using an Autolab PGSTAT-30 digital potentiostat/galvanostat, (EcoChemie BV, Utrecht, Netherlands). A three-electrode cell was used in the experiments. The working electrode was modified CPE. The counter electrode was a platinum wire. The reference electrode was $\text{Ag}|\text{AgCl}, \text{KCl} (1 \text{ M})|$, and all the potentials reported

in this work were measured relative to this electrode (236.3 mV/SHE at 25 °C). 0.1 M, pH 4.0 Britton–Robinson (B–R) buffer solution was used as the supporting electrolyte. All the solutions were deaerated with pure nitrogen for 30 min and kept under nitrogen atmosphere during the experiments. All the measurements were performed at room temperature (25 ± 2 °C).

2.2. Synthesis of the four compounds

2.2.1. Synthesis of compound $[(\text{CH}_3)_2\text{NH}]_3[\text{H}_3\text{PW}_{12}\text{O}_{40}]$ (**1**)

A mixture of Na_2WO_4 (0.6 g, 2 mmol), PCl_5 (0.1 g, 0.5 mmol) and $(\text{CH}_3)_2\text{NH}$ water solution (50%, 0.5 mL, 5 mmol) was neutralized to pH < 3.0 with 10% HCl (20 ml) and sealed in a 30 ml Teflon-lined reactor, which was heated to 120 °C for two days. After cooling to room temperature, colorless prism crystals were isolated. Yield about 35% based on Na_2WO_4 . *Anal. Calc.* for $\text{C}_6\text{H}_{24}\text{N}_3\text{O}_{40}\text{PW}_{12}$: C, 2.39; H, 0.80, N, 1.39. Found: C, 2.19; H, 0.97, N, 1.32%.

2.2.2. Synthesis of compound $(\text{C}_2\text{H}_5\text{OH})_3(\text{H}_3\text{PMo}_{12}\text{O}_{40})$ (**2**)

A mixture of Na_2MoO_4 (0.4 g, 2 mmol), PCl_5 (0.1 g, 0.5 mmol) and ethanol solvent was neutralized to pH 3.0 with 10% HCl (20 ml) and sealed in a 30 ml Teflon-lined reactor, which was heated to 120 °C for two days. After cooling to room temperature, colorless prism crystals were isolated. Yield about 40% based on Na_2MoO_4 . *Anal. Calc.* for $\text{C}_6\text{H}_{21}\text{Mo}_{12}\text{O}_{43}\text{P}$: C, 3.67; H, 1.07. Found: C, 3.49; H, 0.98%.

2.2.3. Synthesis of compound $(\text{DMDA})_2(\text{H}_4\text{SiW}_{12}\text{O}_{40})\cdot \text{H}_2\text{O}$ (**3**)

A mixture of Na_2WO_4 (0.6 g, 2 mmol), SiCl_4 (0.2 mL, 1.8 mmol) and ethylenediamine (0.2 g, 3.3 mmol) in methanol solvent was neutralized to pH < 1.0 with 30% HCl and sealed in a 30 ml Teflon-lined reactor, which was heated to 120 °C for two days. After cooling to room temperature, light yellow needle crystals were isolated. Yield about 20% based on SiCl_4 . *Anal. Calc.* for $\text{C}_{10}\text{H}_{30}\text{N}_4\text{O}_{41}\text{SiW}_{12}$: C, 3.88; H, 0.97, N, 1.81. Found: C, 3.65; H, 0.97, N, 1.78%.

2.2.4. Synthesis of compound $(\text{DAN})_6(\text{H}_4\text{TiW}_{12}\text{O}_{40})\cdot 4\text{H}_2\text{O}$ (**4**)

A mixture of Na_2WO_4 (0.6 g, 2 mmol), TiCl_4 (0.2 mL, 1.8 mmol) and 4,4'-dianiline (0.5 g, 2.7 mmol) was neutralized to pH < 3.0 with 10% HCl (20 ml) and sealed in a 30 ml Teflon-lined reactor, which was heated to 120 °C for two days. After cooling to room temperature, red prism crystals were isolated. Yield about 12% based on Na_2WO_4 . *Anal. Calc.* for $\text{C}_{72}\text{H}_{84}\text{N}_{12}\text{O}_{44}\text{TiW}_{12}$: C, 21.20; H, 2.06, N, 4.12. Found: C, 21.09; H, 1.97, N, 3.97%.

2.3. Preparation of **2**-CPE

The traditional carbon paste electrode (CPE) was prepared by hand-mixing of graphite powder with paraffin oil at a ratio of 70:30 (w/w) in an agate mortar. The title complex was employed to fabricate modified carbon paste electrodes due to its insolubility. The modified CPE was fabricated as follows: 0.3 g of graphite powder and 0.03 g of **2** were mixed and ground together using an agate mortar and pestle for about 30 minutes to achieve an even, dry mixture. Paraffin oil (0.1 mL) was added to the mixture and stirred with a glass rod. Then the homogenized mixture was used to fill a glass tube (3 mm inner diameter) to a depth of 0.8 cm. Electrical contact was established with a copper rod and the surface of **2**-CPE was polished on a piece of weighing paper to a mirror finish just before use.

The different quantity ratios of graphite powder and **2** were investigated to determine the optimum preparation conditions. We investigated graphite powder and title complex ratios of 20:1, 14:1, 10:1, 8:1 and 5:1 (w/w), and found the 10:1 ratio to be optimal. When the amount of **2** was too low, the electrochem-

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