ELSEVIER

Synthesis and crystal structure of two supramolecular compounds constructed from amantadine and polyoxometalate

Jing Yang, Kunlin Huang, Zhifa Pu, Yun Gong, Hui Li, Changwen Hu *

Department of Chemistry, The Institute for Chemical Physics, Beijing Institute of Technology, Beijing 100081, People's Republic of China

Abstract

Two organic–inorganic hybrid compounds based on amantadines and polyoxometalates formulated as $(C_{10}H_{18}N)_4(H_2V_{10}O_{28}) \cdot 2DMF \cdot 2H_2O$ (**1**) and $(C_{10}H_{18}N)_3(PMo_{12}O_{40})$ (**2**), were synthesized and structurally characterized by elemental analysis, single-crystal X-ray diffraction analysis, IR, UV and TGA. Compounds **1** and **2** consist of protonated amantadines together with different polyoxometalates, $[H_2V_{10}O_{28}]^{4-}$ and $[PMo_{12}O_{40}]^{3-}$, respectively. There are hydrogen bonding interactions and electrostatic attractions between polyoxometalates and amantadines in **1** and **2**. Polyoxometalates are linked through amantadines into a two-dimensional network via hydrogen bonds in the two compounds. The two-dimensional framework is further extended into supramolecular network by hydrophobic interaction of amantadines between adjacent layers. The crystal packing patterns of the two compounds reveal various supramolecular framework.
© 2006 Elsevier B.V. All rights reserved.

1. Introduction

Crystal engineering of organic–inorganic hybrid materials has provoked significant interest because these materials exhibit synergetic properties such as electrical, magnetic and optical properties [1]. A remarkable area is the exploitation of polyoxometalate (POMs) as building blocks to construct the solid-state materials with organic substrates [2–13]. Furthermore, POMs are having a large impact in many different disciplines of current interest, such as catalysis (e.g. photochemical dehydrogenations of organic substrates), medicine (e.g. anti-viral and anti-tumor drugs), and material sciences [14]. Most of these POMs have discrete structure of definite size and shape belonging to well-known structural types, such as the Lindquist (e.g. $[Mo_6O_{19}]^{2-}$), Keggin (e.g. $[PMo_{12}O_{40}]^{3-}$) or Dawson (e.g. $[P_2Mo_{18}O_{62}]^{6-}$) types. Adamantaneamine chloride (1-aminoadamantane hydrochloride), a drug in the aminoadamantane series, has been used to design organic–inorganic compounds [15–20]. The nucleophilic characteristic of the POMs allows specific assembly with electrophilic fragment and it is expected to produce hybrid

materials via OH···O or NH···O hydrogen-bonding interactions. Taking into account of this, a motivation for design and synthesis of organic–inorganic hybrid compounds containing POMs and amantadines, has been put forward.

To the best of our knowledge, the vanadium-containing POMs present a wide range interesting topology and structure, however, there is no report on compound consisting of amantadine and vanadium–oxygen framework of the prototype $[H_nV_{10}O_{28}]^{(6-n)-}$ [21–35]. In this paper, we report two supramolecular assemblies: $(C_{10}H_{18}N)_4(H_2V_{10}O_{28}) \cdot 2DMF \cdot 2H_2O$ (**1**) and $(C_{10}H_{18}N)_3(PMo_{12}O_{40})$ (**2**). In this work, based on the same organic groups (amantadine) in compounds **1** and **2**, their different hydrogen bonding interactions and molecular arrays have been discussed due to their different POMs. The synthesis of the two organic–inorganic hybrid materials may not only provide hybrid compounds, but also advance the understanding of hybrid material.

2. Experimental

2.1. General procedures

All chemicals purchased were of reagent grade and used without further purification. C, H, N elemental analyses were performed on Perkin–Elmer 2400 CHN elemental analyzer. Infrared spectra were recorded as KBr pellets on a Nicolet 170SXFT/IR spectrometer. The UV spectra were measured on

---

* Corresponding author. Tel./fax: +86 10 62828869.
  E-mail address: cwhu@bit.edu.cn (C. Hu).

a UV-1901 spectrometer in the range of 190–400 nm (DMF as solvent for compound **1** and water for compound **2**). TG analyses were carried out in nitrogen atmosphere between 30 and 800 °C at a heating rate of 10 °C·min^{-1} on a ZRY-2P simultaneous thermal analyzer.

2.2. Synthesis

2.2.1. Synthesis of $(C_{10}H_{18}N)_4(H_2V_{10}O_{28})\cdot 2DMF\cdot 2H_2O$ (1)

A mixture of 0.2 mmol of adamantaneamine chloride, 0.4 mmol of $NaVO_3$, 4 mL H_2O and 4 mL DMF was stirred for a few seconds at ambient temperature, yielding a white suspension. The pH of the reaction mixture was carefully adjusted to three by adding 1.0 M aqueous hydrochloric acid. The bright orange precipitate that was formed upon adjusting pH value was filtered and the filtrate was kept in air at room temperature. Two weeks later orange crystals were isolated (yield: ca. 90% based on V). Elemental analyses: calc: C, 31.53; H, 5.26; N, 4.80%; found: C, 31.50; H, 5.27; N, 4.77%.

2.2.2. Synthesis of $(C_{10}H_{18}N)_3(PMo_{12}O_{40})$ (2)

A mixture of adamantaneamine chloride (0.3 mmol), $H_3PMo_{12}O_{40}$ (0.1 mmol), $NaVO_3$ (0.3 mmol) and H_2O (7 mL) was sealed in a 15 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 3 days. After the mixture was slowly cooled to room temperature, dark red crystals were isolated by filtration and washed with distilled water (yield: ca. 90% based on Mo). Elemental analyses: calc: C, 15.80; H, 2.37; N, 1.84%; found: C, 15.82; H, 2.35; N, 1.85%.

2.3. X-ray crystallography

The structures of **1** and **2**, were determined by single crystal X-ray diffraction. XRD data of **1** and **2** were collected at 298 K on a Bruker-AXS CCD area detector-equipped diffractometer with Mo Kα ($\lambda = 0.07103$ Å) radiation. A total of 8623 (5688 unique, $R_{int} = 0.0280$) reflections of **1** ($-11 \leq h \leq 12$, $-13 \leq k \leq 13$, $-18 \leq l \leq 11$, $2.03 < \theta < 25.01$) and a total of 16,355 (5663 unique, $R_{int} = 0.0805$) reflections of **2** ($-16 \leq h \leq 16$, $-20 \leq k \leq 13$, $-17 \leq l \leq 17$, $1.86 < \theta < 25.01$) were measured. An empirical absorption correction from ψ scan was applied. All the structures were solved by direct methods and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon, oxygen and nitrogen atoms were located in the calculated positions. The hydrogen atoms attached to the $[V_{10}O_{28}]$ cluster in **1** could not be located. The least-squares refinement cycles on F2 were performed until the model converged. All calculations were performed using the SHELXTL-97 program [36,37]. The crystallographic details of **1** and **2** are summarized in Table 1. Selected bond lengths and angles of **1** and **2** are listed in Tables 2 and 4, respectively. Distances and angles involving weak interactions between POMs and selected hydrogen bonds of **1** and **2** are shown in Tables 3 and 5, respectively.

3. Results and discussion

3.1. Synthesis

Compound **1** was prepared by solvent evaporation under room temperature. By plenty of parallel experiments, it was found that the species of solvents were crucial for the crystallization of **1**. DMF was chosen for its high boiling point and could slow down the volatile speed of mixture. The parallel experiments showed that carrying out the reaction with the pH value in the range of 2–6 did not alter the products,

Table 1
Crystal data and structure refinement parameters for **1** and **2**

	$C_{46}H_{92}N_6O_{32}V_{10}$, **1**	$C_{30}H_{54}Mo_{12}N_3O_{40}P$, **2**
Empirical formula		
Color	Yellow	Red
Formula weight	1750.66	2279.01
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2(1)/c$
a (Å)	10.925(2)	13.466(3)
b (Å)	11.298(3)	16.888(4)
c (Å)	15.219(3)	14.437(3)
α (°)	81.961(3)	90
β (°)	79.301(3)	94.734(3)
γ (°)	62.585(3)	90
V (Å^3)	1635.2(6)	3271.8(12)
Z	1	2
ρ_{calc} (g cm^{-3})	1.778	2.313
μ (mm^{-1})	1.452	2.332
$F(000)$	896	2188
Number of restraints	3	491
Goodness-of-fit on F^2	0.998	1.017
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0395$	$R_1 = 0.0695$
	$wR_2 = 0.1002$	$wR_2 = 01707$
R indices (all data)	$R_1 = 0.0606$	$R_1 = 0.1580$
	$wR_2 = 0.1146$	$wR_2 = 0.2233$

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $\omega R_2 = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega(F_o^2)^2]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths			
V(1)–O(5)	1.676(2)	V(3)–O(1)	2.016(2)
V(1)–O(2)	1.686(2)	V(3)–O(4)#1	2.102(2)
V(1)–O(1)	1.883(2)	V(3)–O(3)	2.289(2)
V(1)–O(3)#1	2.066(2)	V(4)–O(12)	1.594(2)
V(1)–O(4)	2.074(2)	V(4)–O(7)#1	1.817(2)
V(1)–O(3)	2.111(2)	V(4)–O(13)	1.850(2)
V(2)–O(6)	1.605(3)	V(4)–O(9)	1.941(2)
V(2)–O(8)	1.762(2)	V(4)–O(2)	2.022(2)
V(2)–O(7)	1.831(2)	V(4)–O(3)	2.351(2)
V(2)–O(1)	1.998(2)	V(5)–O(14)	1.593(3)
V(2)–O(4)#1	2.126(2)	V(5)–O(13)	1.816(2)
V(2)–O(3)#1	2.288(2)	V(5)–O(10)	1.842(2)
V(3)–O(11)	1.603(2)	V(5)–O(8)#1	1.932(2)
V(3)–O(9)	1.760(2)	V(5)–O(5)#1	2.073(2)
V(3)–O(10)	1.834(2)	V(5)–O(3)	2.345(2)
Bond angles			
O(2)–V(1)–O(3)#1	163.61(10)	O(1)–V(3)–O(4)#1	73.90(9)
O(1)–V(1)–O(3)#1	83.51(9)	O(13)–V(4)–O(2)	154.76(10)
O(6)–V(2)–O(3)#1	170.95(11)	O(9)–V(4)–O(2)	82.21(10)
O(1)–V(2)–O(3)#1	75.48(9)	O(14)–V(5)–O(3)	173.93(11)
O(11)–V(3)–O(4)#1	99.75(11)	O(5)#1–V(5)–O(3)	72.53(9)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y, -z$.