Journal of Molecular Structure 1049 (2013) 212–219

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

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

A 2D hydrogen-bonded supramolecular framework based on acyclic water tetramer clusters and tetraprotonated triethylenetetramine molecules templated by molybdenum(V) phosphates

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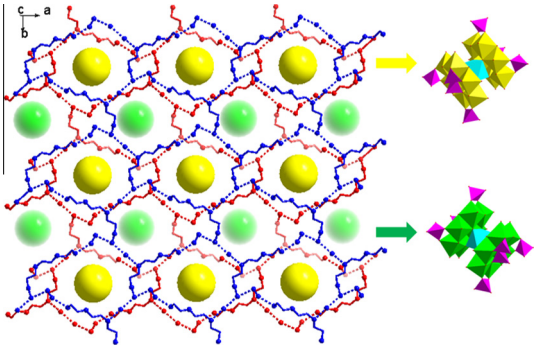
HIGHLIGHTS

- A tetraprotonated triethylenetetramine molecule is bonded with three water tetramers *via* H-bonds and vice versa.
- A new 2D H-bonded supramolecular framework is formed with hexagon pores.
- Two symmetry-operation related standing and lying style POMs present as template.
- The standing and lying style POMs are wrapped between the layers, resulting in a 3D entity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 April 2013
Received in revised form 6 June 2013
Accepted 6 June 2013
Available online 25 June 2013

Keywords:
Sodium molybdenum(V) phosphate
Crystal structure
Supramolecular self-assembly
Hydrogen bonding
Triethylenetetramine

ABSTRACT

A new 2D hydrogen-bonded supramolecular framework based on acyclic water tetramer clusters and tetraprotonated triethylenetetramine (denoted by H_4TETA) molecules is formed in a new sodium molybdenum(V) phosphate compound, $[H_4TETA]_4\left\{Na\left[Mo^{V}_{12}(OH)_6(HPO_4)(PO_4)_7O_{24}\right]\right\}\cdot 11H_2O$ (**1**), which is hydrothermally prepared and characterized thoroughly. Single crystal X-ray diffraction analysis reveals that the 2D supramolecular framework is composed of unique kind of "hexagon" pores each of which is formed by the connection of alternate acyclic water tetramer cluster and H_4TETA molecules *via* hydrogen-bonding interactions. In between the 2D frameworks the $\left\{Na\left[Mo^{V}_{12}(OH)_6(HPO_4)(PO_4)_7O_{24}\right]\right\}^{16-}$ anions partially infix sideling into the hexagon pores through H-bonding interaction with standing style anions sandwiched in one interlayer and the lying style ones in another interlayer alternately, and consequently a 3D sandwich type supramolecular entity is resulted. Moreover, the electrochemical properties and preliminary catalytic properties toward rhodamine B degradation of the compound **1** are also investigated.

1. Introduction

It is well known that water plays vital roles in many biological and chemical processes [1,2]. Extensive studies have been carried out on various small water clusters in recent years including trimer, tetramer, pentamer, hexamer and octamer from both the theoretical and experimental aspects [3–9] because the investigations of hydrogen-bonded small water clusters help us to understand not only the nature of bulk water but also the roles of water clusters in stabilizing and functionalizing the host network [10–12]. On the other hand, a lot of work has been done on low molecular weight amines regarding to their chemical changes under various conditions like the well known saltification, acylation, oxidization,

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http://dx.doi.org/10.1016/j.molstruc.2013.06.032

nitrosylation reactions and so on [13], but a little effort has been made to understand their non-covalent interactions with water molecules/clusters and the consequent possible water–amine assembly under diverse environmental conditions. Indeed, this nonbonding structural information is very important to understand the anomalous behavior, chemical and physical properties such as surface tension, viscosity, boiling point and solubility of the resulting mixture system [14,15].

Following our previous efforts to explore the possible interactions, structure assemblies and stabilities of water and low molecular weight amines in different environments [16], we herein report a new 2D hydrogen-bonded supramolecular framework based on acyclic water tetramer clusters and tetraprotonated triethylenetetramine molecules templated by molybdenum(V) phosphates in a new compound $[H_4TETA]_4\left\{Na\left[Mo^{V}_{12}(OH)_6(HPO_4)(PO_4)_7O_{24}\right]\right\}\cdot 11H_2O$ (**1**) which was prepared under hydrothermal conditions and characterized by elemental analyses, single-crystal X-ray diffraction, IR, UV–vis spectroscopy, TG–DTA and XRD analysis. Moreover, the catalytic activity and electrochemical properties of the compound **1** were also investigated.

2. Experimental

2.1. Materials and apparatus

All chemicals were purchased commercially and used without further purification. Elemental analyses for C, H, and N were performed on a Perkin–Elmer Vario El element analyzer and analyses for Mo, P, Fe and Na on a Jarrel-ASH ICAP-9000 ICP spectrometer. Infrared spectrum was recorded at room temperature on a Nicolet 470 FT-IR spectrophotometer as KBr pellet in the 4000–400 cm^{-1} region. UV–vis spectrum was obtained by using a Shimadzu UV-2550 spectrometer equipped with a diffuse reflectance accessory in the 200–800 nm range using $BaSO_4$ as the reference. TG–DTA analysis was performed on a Perkin–Elmer TGA 7 instrument in flowing air with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction measurements were performed on a Rigaku-Dmax 2500 diffractometer at a scanning rate of 15° min^{-1} in the 2θ range from 5° to 90°, with graphite monochromatized Cu Kα radiation (λ = 0.15405 nm). Cyclic voltammetry measurements were carried out on a CHI 660B electrochemical station.

2.2. Hydrothermal synthesis of $[H_4TETA]_4\left\{Na\left[Mo^{V}_{12}(OH)_6(HPO_4)(PO_4)_7O_{24}\right]\right\}\cdot 11H_2O$ (*1*)

Compound **1** was synthesized from a mixture of Na_2MoO_4 (0.302 g, 1.23 mmol), CuCl (0.112 g, 1.13 mmol), triethylenetetramine (1.0 mL), H_3PO_4 (0.7 mL, 85%) and 8.0 mL of H_2O with pH approximately 6.66. The mixture was stirred for 30 min at room temperature, then was transferred to a Teflon-lined autoclave (23 mL) and kept at 160 °C for 3 days. After slow cooling to room temperature, with resulting pH 6.77, red block-like crystals of compound **1** (*ca.* 0.09 g, 29.8% based on Mo) were collected under microscope, washed with distilled water and dried at room temperature. Anal. Calcd. for $C_{24}H_{117}N_{16}NaMo_{12}O_{73}P_8$: C, 8.95; H, 3.66; N, 6.95; Na, 0.71; Mo, 35.75; P, 7.69. Found: C, 9.03; H, 3.09; N, 7.01; Na, 0.71; Mo, 36.03; P, 7.72.

2.3. Single-crystal X-ray diffraction

Suitable single crystals of compound **1** were mounted on a glass fiber with vaseline and used for data collection on a Bruker SMART APEX CCD diffractometer at 298(2) K with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) using φ and ω scan techniques. An empirical absorption correction by SADABS was applied to the intensity data [17]. The structure was solved by direct methods, successive Fourier difference synthesis, and refined by full-matrix least-squares techniques on $|F|^2$ using the SHELXL-97 software [18,19]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. The hydrogen atoms bonded to C and N atoms were introduced at calculated positions as riding atoms, and attempt on location of other hydrogen atoms bonded to water O atoms and O atoms of the anion which show lack of valence were given up but they were included in the final refinement cycles. A summary of the crystallographic data and structural determination parameters for compound **1** are given in Table 1, the selected bond lengths and bond angles in Table 2.

Table 1
Crystal data and structure refinement for compound **1.**

Empirical formula	$C_{24}H_{117}NaMo_{12}N_{16}O_{73}P_8$
Formula weight	3220.37
Crystal system	Monoclinic
Space group	*P*2(1)/*n*
a	15.9865(9) Å
b	16.7685(10) Å
c	17.2040(9) Å,
α	90.00°
β	97.957(10)°
γ	90.00°
Volume	4567.5(4) $Å^3$
Z	2
Density (calculated)	2.342 Mg/m^3
Absorption coefficient	1.858 mm^{-1}
F(000)	3184
Shape	Block
Color	Red
Crystal size (mm^3)	0.10 × 0.10 × 0.10
Index ranges	$-24 \leqslant h \leqslant 21$ $-25 \leqslant k \leqslant 19$ $-15 \leqslant l \leqslant 26$
Reflections collected	43,755
Independent reflections	17,141 [*R* (int) = 0.0370]
Data/restraints/parameters	17,141/36/609
Goodness-of-fit on F^2	1.022
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0461, *wR*2 = 0.1169
R indices (all data)	*R*1 = 0.0659, *wR*2 = 0.1266
Largest diff. peak and hole (e $Å^{-3}$)	1.517 and −1.325

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

Moiety	Bond distance	Moiety	Bond angle
Mo1–O17	2.031(3)	O15–Mo1–O14	106.69(12)
Mo1–O6	2.603(3)	O29–Mo1–O16	70.75(9)
Mo2–O7	2.114(3)	O5–Mo2–O8	166.96(12)
Mo2–O6	1.945(3)	O7–Mo2–O8	72.04(10)
Mo3–O25	2.342(3)	O11–Mo3–O26	160.83(11)
Mo3–O10	2.102(3)	O10–Mo3–O25	72.46(10)
Mo4–O24	1.684(3)	O24–Mo4–O8	169.69(13)
Mo4–O1	2.083(3)	O7–Mo4–O8	70.57(9)
Mo5–O21	1.682(3)	O21–Mo5–O16	168.98(12)
Mo5–O16	2.281(3)	O29–Mo5–O16	70.78(9)
Mo6–O14	1.949(3)	O13–Mo6–O25	169.20(12)
Mo6–O13	1.680(3)	O10–Mo6–O25	72.36(10)
C1–N4	1.450(6)	O11#1–Na1–O11	180.00(13)
O(2)–P(3)	1.494(3)	O30–Na1–O23#1	82.27(9)
O(4)–P(3)	1.602(3)	O17–Mo1–Mo6	132.28(8)
Na1–O11	2.276(3)	P1–O25–Mo6	125.47(15)
Na1–O23#1	2.325(3)	O2–P3–O4	104.42(19)
Na1–O30	2.268(2)	O2–P3–O1	113.35(18)
O(31)–P(1)	1.517(3)	O7–Mo4–O8	70.7(10)

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

2.4. Fabrication of carbon paste modified electrode of compound *1*

As the compound **1** is insoluble in any of familiar and common solvents like DMF, H_2O, EtOH and DMSO, its electrochemical prop-