Full Length Research Paper

Hydrothermal synthesis and structural characterization of an organically-templated open-framework trimolybdates

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A new one-dimensional coordination polymer formulated as $[C_2H_{10}N_2]$ $[Mo_3O_{10}]$, **1**, has been synthesized under hydrothermal conditions in the presence of ethylenediamine. The surface morphology of the as-synthesized product reveals colorless rod-like single crystals of **1**. The compound crystallizes in monoclinic space group $P2_1/n$ with a = 8.08 Å, b =14.39 Å, c = 8.89 Å; β = 97.76°, V = 1033.65(12) Å3, Z = 4. The structure is a one-dimensional chain consisting of $[Mo_3O_{10}]^{2-}$ clusters of Mo (VI) octahedral interspersed by the amine molecules. In the infrared spectrum of the compound, the symmetric stretching vibrational mode of the -NH_2 group is observed at 3278 cm^{-1}, while the band at 1604 cm^{-1} is assigned to scissoring mode of the –NH_2 group. The peaks in the spectral range 1913 -2492 and 2962 cm^{-1} are attributed to -CH_2 symmetric and asymmetric stretching vibrations respectively. The absorption bands at 1404 cm^{-1} is due to scissoring, while the one at 1149 cm^{-1} is attributable to twisting modes of - CH_2 group . The characteristic band of the stretching vibrational modes of the Mo=O double bonds is observed at 1018 cm^{-1}, while the vibrational stretching frequency involving single Mo-O bonds is observed at 846 cm^{-1} and the scissoring mode of this bond is at 542 cm^{-1}.

Key words: Hydrothermal synthesis, amine-templated molybdates, molybdenum oxide-organic frameworks, one-dimensional chain.

INTRODUCTION

The great interest in the design of molybdenum(VI) oxide−organic frameworks (MOOFs) is not only due to their applications in such areas as catalysis , magnetism, sorption etc ., but also due to its fascinating structural chemistry (Lysenko et al ., 2010; Pope and Müller, 2001; Senchyk et al., 2014). Various synthetic approaches have been used to isolate highly crystalline samples suitable for structural characterization by X-ray diffraction, but the synthesis of organic−inorganic hybrids using hydrothermal conditions has received special attention in the field of coordination solids based on transition-metal oxides, including transition-metal molybdate complexes (Asnani et al., 2012; Hagrman and Zubieta, 1998; Hagrman et al., 1999; Randy et al., 2001; Hagrman and Zubieta, 2000).

Hydrothermal method is a synthesis pathway in which products are produced using thermal (heat) energy and aqueous solvent. The success of this method is derived from the extremely solvating ability owing to reduced viscosity of the water under these conditions. This allows the dissolution and mixing of the solid reagents thereby minimizing differential solubility problem (Davis, 1992; Barrer, 1982; Francis and O'Hare, 1998). It has been demonstrated that the hydrothermal chemistry of polyoxomolybdates involves many interrelated reaction variables, including the pH, the molybdenum source, and the identities of other reaction species, the temperature, and time (Wu et al., 2002; Xu et al., 2000; Zhang et al., 2007; Zhang et al., 2015; Hubbard et al., 2008). Molybdophosphonates as building blocks or subunits in extended structures have been studied (Hubbard et al., 2008; Armatas et al., 2008; Jones et al., 2010; Armatas et al., 2009).   A molybdenum diphosphonate network structure exhibiting reversible dehydration and selective uptake of methanol have also been reported and it is the first molybdenum diphosphonates in the absence of co-ligands (Ayi et al., 2013).

MATERIALS AND METHODS

The syntheses were carried out in Ace pressure tubes (15 cm^3), purchased from Aldrich Chemical Co., and heated in programmable ovens. The reagents used for syntheses were obtained from Aldrich (Hexaamomoium heptamolybdate tetrahydrate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$; ethylenediamine,) or Epsilon Chime (4-carboxyphenylphosphonic acid) and used without further purification. In a typical synthesis of **1**, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.3088 g, 0.25 mmol) was stirred together with 4-carboxyphenyl phosphonic acid (0.101 g, 0.5 mmol) in 5 cm^3 of distilled water. This was followed by the addition of 0.02 cm^3 of ethylenediamine and the pH of the solution was adjusted to 3 by dropwise addition of 0.2 cm^3 of Conc HCl. The resultant mixture was homogenized for 30 min before transferring into the reaction vessel and heated in an oven at 120°C for 8 h. The product, a crop of colorless crystalline material was washed with distilled water and air-dried.

Characterization

The surface morphology of the as-synthesized compound was determined using computer controlled polarized PZPZ300T-8M electron microscope. The ultraviolet-visible measurements were recorded with the help of Thermo Scientific Evolution 201 UV-vis spectrophotometer. The Infrared spectra were recorded on a Shimadzu IR affinity-1 from 400 to 4000 cm^{-1}.

Crystal structure

"X-ray diffraction data was collected on an Oxford Diffraction Gemini diffractometer fitted with an Atlas CCD detector using Mo-Kα radiation of wavelength 0.71073 Å at 150 K". The crystal structure and refinement parameters are given in Table 1. "The structure was solved using SHELXS-97 and refined using full-matrix least squares in SHELXL-97 (Sheldrick, 2008). The final refinements were generally straight forward with all non-hydrogen atoms refined anisotropically in the final least squares run, and hydrogen atoms included at calculated positions".

RESULTS AND DISCUSSION

We were interested in isolating Mo (VI) oxide cluster as a building block in the preparation of molybdo-carboxyphosphonate frameworks. During the investigation of the $(NH_4)_6Mo_7O_{22} \cdot 4H_2O$ –HCl Carboxyphenylphosphonic acid–ethylenediamine–H_2O–system, a new inorganic-organic hybrid material, $(C_2H_{10}N_2)$ (Mo_3O_{10}) constructed from molybdenum (VI) oxide with encapsulated ethylenediammonium ions was isolated. The carboxyphenylphosphonic acid was added into the reactant mixture with the aim of obtaining molybdenum organophosphonate frameworks, but was not incorporated into the final product. The ethylenediamine added to the synthetic gel exerts a significant structural role in controlling the architecture of the molybdenum oxide phase formed as well as compensating the metal oxide anionic charge. The addition of the HCl helps in maintaining acidic pH before and after the reaction. It is only in an acidic medium that the amine component gets protonated. A portion of the soluble reactant precursor was taken out for UV-Vis measurement.   The UV-Vis spectrum of the reactants in aqueous solution is presented in Figure 1. The spectrum exhibits three absorption bands at 279, 284 and 286 nm. The strong band at 279 and 284 nm are attributable to π- π* transitions. These transitions involves moving electron from a bonding pi-orbital to an antibonding pi-orbital and is said to occur at high energy region of 35,842 to 35211 cm^{-1}. The broad band at 286 nm corresponds to n – π* transitions, which involve moving an electron from a non-bonding electron pair to an antibonding pi-orbital and is found to occur at lower energy region of 34,364 to 34,965 cm^{-1}

The surface structure and morphology of the as-synthesized product reveals colorless rod-like crystals (Figure 2). The crystal data and structure refinement parameter for compound **1 is** presented in Table 1. The compound crystallizes in monoclinic space group $P2_{1/n}$ (No. 14) with a = 8.08 Å, b =14.39 Å, c = 8.89 Å; β = 97.76°.   The asymmetric unit (Figure 3) consists of Molybdenum center in octahedral coordination by six oxygen atoms, and protonated amine. The bridging Mo-O bond lengths in the range of 1.592(16) to 1.693(15) Å are shorter compared with the terminal Mo-O bonds (1.994(5) to 2.429(14) Å) and the O(1)-Mo(1)-O(#2) bond angles in the range of 158.10 to 170.3997° are in good agreement with similar reported compounds (Hubbard et al., 2008; Ayi et al., 2013). The structure is a one-dimensional chain consisting of $(Mo_3O_{10})^{2-}$ clusters interspersed by the ethylenediammonium cation (Figure 4), which also serves to compensate the framework negative charge of -2.

Figure 5 gives the infrared spectrum of compound **1**. In this spectrum, the two peaks at 3657 and 3780 cm^{-1}

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

Empirical formula	$C_2H_{10}N_2Mo_3O_{10}$
Formula weight	254.91
Temperature / K	150(2)
Wavelength / Å	0.7107
Crystal system	Monoclinic
Space group	*P2(1)/n (No.14)*
Unit cell dimensions	a = 8. 08(8)Å, alpha = 90°
	b = 14.39(3)Å, beta = 97.76(4)°
	c = 8.89(4)Å, gamma = 90°
Volume / Å³	1033.65(12)
Z	*4*
Density (calculated) / g cm⁻³	1.972
Absorption coefficient / mm⁻¹	1.595
F(000)	1502
Crystal size / mm	0.18 × 0.05 × 0.02
Theta range for data collection	2.97 to 29.96°
Index ranges	$-22 \leq h \leq 27$; $-14 \leq k \leq 13$; $-11 \leq l \leq 12$
Reflections collected	6916
Independent reflections	2442 (*R*(int) = 0.0284)
Reflections observed (>2)	1502
Data Completeness	0.905
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.94878
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1902 / 0 / 156
Goodness-of-fit on F^2	0.902
Final R indices (*I* > 2 (*I*))	R_1 = 0.0390 wR_2 = 0.0405
R indices (all data)	R_1 = 0.0571 wR_2 = 0.0587
Largest diff. peak and hole / e Å⁻³	0.988 and -1.057
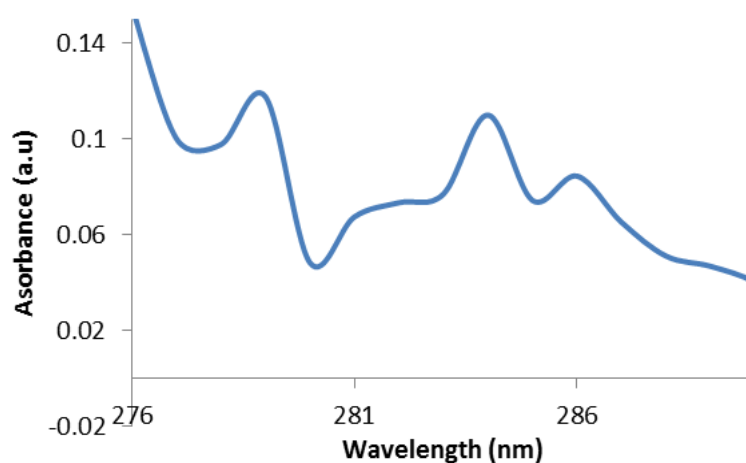
Figure 1. UV-Vis spectrum of the reactant mixture in aqueous solution for the synthesis of **1**.

superimposed on the water peak can be attributed to -NH₂asymmetricstretching involved in N-H…O hydrogen bond formation . The symmetric stretching vibrational mode of the -NH₂ group is observed at 3278 cm⁻¹, while
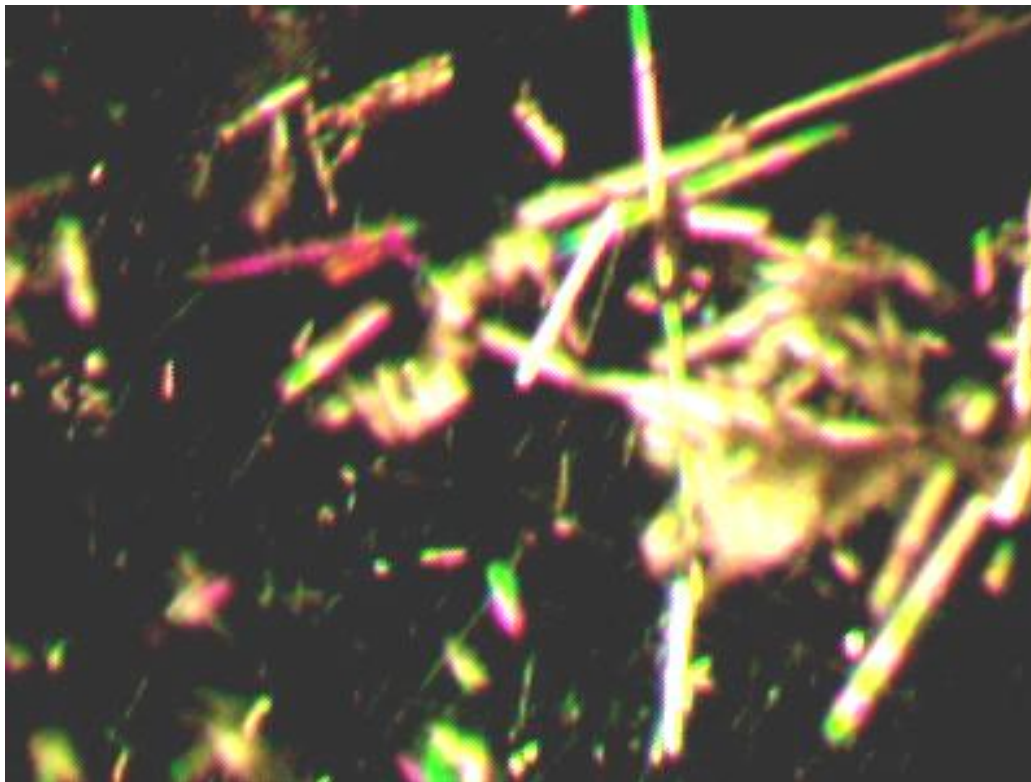
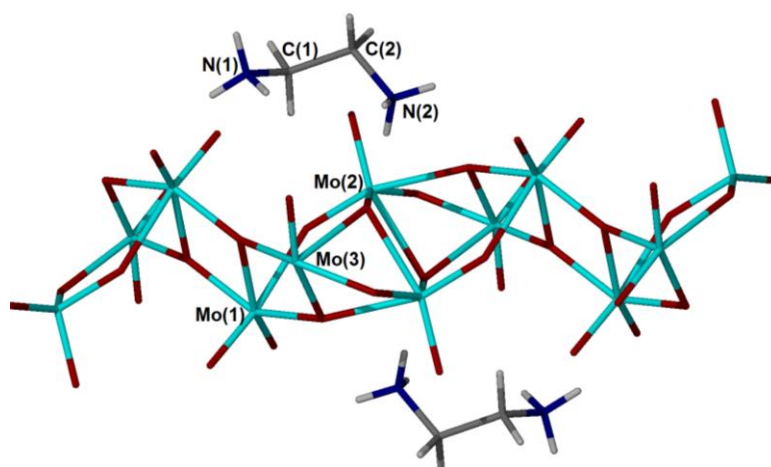**Figure 2.** Optical microscopic image of the as-synthesized compound **1**.

Figure 3. The structure of **1** showing the coordination environment of Mo and the encapsulated amine molecule.

the band at 1604 cm^{-1} is assigned to scissoring mode of the –NH$_2$ group. The peaks in the spectral range 1913 - 2492 and 2962 cm^{-1} are attributed to -CH$_2$ symmetric and asymmetric stretching vibrations respectively. The absorption bands at 1404 cm^{-1} is due to scissoring, while the one at 1149 cm^{-1} is attributable to twisting modes of - CH$_2$ group . The characteristic band of the

stretching vibrational modes of the Mo=O double bonds is observed at 1018 cm^{-1} and compares well with similar compounds in the literature (Hubbard et al., 2008). The vibrational stretching frequency involving single Mo-O bonds is observed at 846 cm^{-1} while the scissoring mode of this bond is at 542 cm^{-1}. The various assignments are made on the basis of similar work in the literature (Asnani
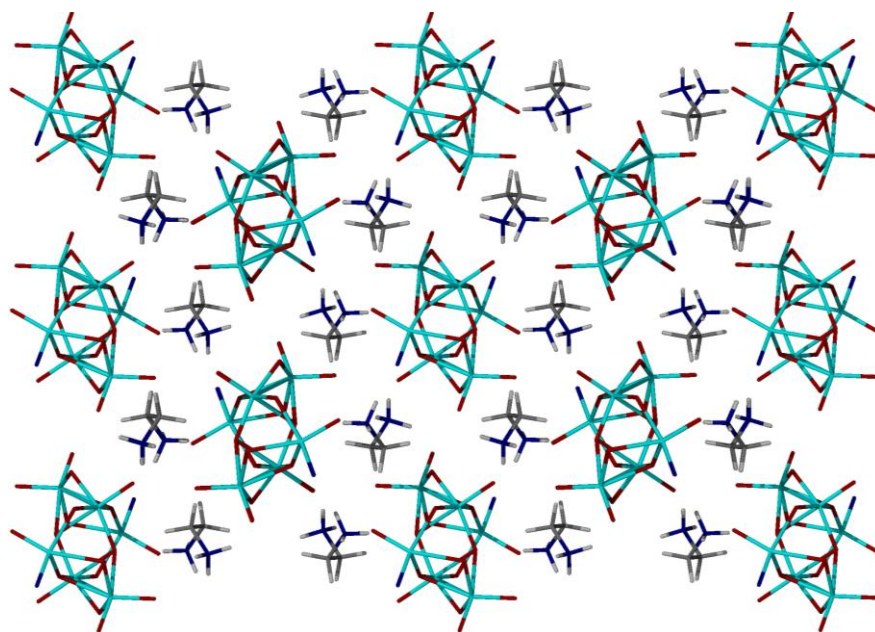
Figure 4. Structure of **1** viewed along the (100) direction showing the $(Mo_3O_{10})^{2-}$ clusters interspersed by the ethylenediammonium cation.

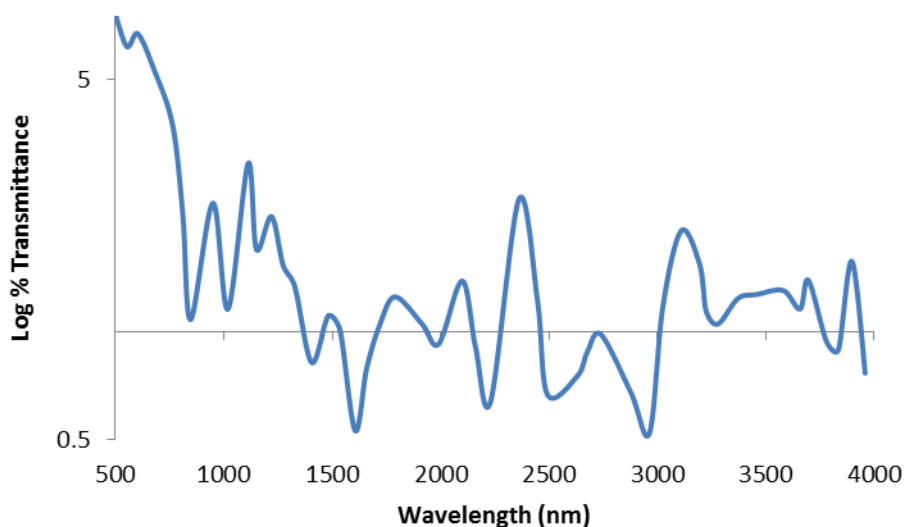**Figure 5.** The infrared spectrum of $(C_2H_{10}N_2) (Mo_3O_{10})$, **1** .

et al., 2012; Hagrman and Zubieta, 1998; Hubbard et al., 2008; Sierka et al., 2007).

Conclusion

In conclusion, a new one-dimensional coordination polymer formulated as $(C_2H_{10}N_2) (Mo_3O_{10})$, has been synthesized under hydrothermal conditions in the presence of ethylenediamine. The surface structure and morphology of the as-synthesized product reveals colorless rod-like crystals. The structure is a one-dimensional chain consisting of $(Mo_3O_{10})^{2-}$ clusters of Mo (VI) octahedral interspersed by the amine molecules. In the IR spectrum, the two peaks at 3657 and 3780 cm[1] superimposed on the water peak can be attributed to $-NH_2$ asymmetric stretching involved in N-H…O hydrogen bond formation . The protonated organic amine interacts with the inorganic frameworks through multiple hydrogen bonds of the type N-H…O. Efforts are

under way to use this compound as a building block in designing Mo (VI) oxide-carboxyphosphonate framework materials.

Conflict of Interest

The authors declare that there is no conflict of interest in publishing this article.

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