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

Chinyere A. Anyama, Grace E. Iniama, Joseph O. Ogar and Ayi A. Ayi*

Inorganic Materials Chemistry Laboratory, Department of Pure and Applied Chemistry, University of Calabar, P. M. B. 1115, Calabar, Nigeria.

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A new one-dimensional coordination polymer formulated as [C₂H₁₀N₂][Mo₃O₁₀]₄, 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 P2₁/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 [Mo₃O₁₀]₄²⁻ clusters of Mo (VI) octahedral interspersed by the amine molecules. In the infrared spectrum of the compound, the symmetric stretching vibrational mode of the –NH₂ group is observed at 3278 cm⁻¹, while the band at 1604 cm⁻¹ is assigned to scissoring mode of the –NH₂ group. The peaks in the spectral range 1913 -2492 and 2962 cm⁻¹ are attributed to -CH₂ 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 -CH₂ 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).

*Corresponding author. E-mail: ayiayi72@gmail.com, a.anyama@chem.unical.edu.ng. Author(s) agree that this article remain permanently open access under the terms of the Creative Commons Attribution License 4.0 International License.
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 cm³), purchased from Aldrich Chemical Co., and heated in programmable ovens. The reagents used for syntheses were obtained from Aldrich (Hexamammonium heptamolybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O; ethylenediamine,) or Epsilon Chime (4-carboxyphenylphosphonic acid) and used without further purification. In a typical synthesis of 1, (NH₄)₂Mo₇O₂₄·4H₂O (0.3088 g, 0.25 mmol) was stirred together with 4-carboxyphenyl phosphonic acid (0.101 g, 0.5 mmol) in 5 cm³ of distilled water. This was followed by the addition of 0.2 cm³ of ethylenediamine and the pH of the solution was adjusted to 3 by dropwise addition of 0.2 cm³ 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 structure and 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 molybdocarboxyphosphonate frameworks. During the investigation of the (NH₄)₆Mo₇O₂₄·4H₂O·HCl Carboxyphenylphosphonic acid–ethylenediamine–H₂O–system, a new inorganic-organic hybrid material, (C₂H₉N₂) (Mo₅O₁₀) 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 π-orbital to an antibonding π-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 π-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 P2₁/m (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(1) 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 (MoO₂)₄²⁻ 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.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Empirical formula               | C₂H₁₀N₂Mo₃O₁₀                               |
| 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 x 0.05 x 0.02                        |
| Theta range for data collection | 2.97 to 29.96°                            |
| Index ranges                    | -22 ≤ h ≤ 27; -14 ≤ k ≤ 13; -11 ≤ l ≤ 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 F²            |
| Data / restraints / parameters  | 1902 / 0 / 156                             |
| Goodness-of-fit on F²           | 0.902                                      |
| Final R indices (I > 2 (h))     | R₁ = 0.0390, wR₂ = 0.0405                  |
| R indices (all data)            | R₁ = 0.0571, wR₂ = 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 -NH₂ asymmetric stretching involved in N-H…O hydrogen bond formation. The symmetric stretching vibrational mode of the -NH₂ group is observed at 3278 cm⁻¹, while
the band at 1604 cm\(^{-1}\) is assigned to scissoring mode of the \(-\text{NH}_2\) group. The peaks in the spectral range 1913 - 2492 and 2962 cm\(^{-1}\) are attributed to \(-\text{CH}_2\) 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 \(-\text{CH}_2\) 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$_3$O$_{10}$)$^{2-}$ clusters interspersed by the ethylenediammonium cation.

Figure 5. The infrared spectrum of (C$_2$H$_{10}$N$_2$) (Mo$_3$O$_{10}$), 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$_2$H$_{10}$N$_2$) (Mo$_3$O$_{10}$), 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$_3$O$_{10}$)$^{2-}$ 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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REFERENCES

Armatas NG, Allis DG, Prosirvin A, Carnutu G, O'Connor CJ, Dunbar K, Zubieta J (2008). Molybdophosphonate clusters as building blocks in the oxomolybdate-organophosphonate/Cobalt(II)-organinoimine system. Structural influences of secondary metal coordination preferences and phosphonate tether lengths. Inorg. Chem. 47:832.

Armatas NG, Ouellette W, Whitenack K, Pelcher J, Liu H, Romaine E, O'Connor CJ, Zubieta J (2009). Construction of Metal-Organic Oxides from molybdophosphonates clusters and copper bipyridine building blocks. Inorg. Chem. 48:8897-8910.

Asnani M, Kumar K, Duraisamy T, Ramanan A (2012). Crystallization of organically templated phosphomolybdate cluster-based solids from aqueous solution. J. Chem. Sci. 124:1275-1286.

Ayi AA, Burrows AD, Mahon MF, Sebastian VM (2013). A molybdenum diphasophonate network structure exhibiting reversible dehydration and selective uptake of methanol. Cryst. Eng. Comm. 15:9301-9303

Barrer RM (1962). Hydrothermal Chemistry of Zeolites, Academic press, London.

Davis, Lobo (1992). Zeolite and molecular sieve synthesis, J. Chem. Mat. 4:756-768.

Francis RJ, O’Hare D (1998). The kinetics and mechanisms of the crystallization of microporous materials. J. Chem. Soc. Dalton Trans. 1998:3133-3148.

Hagrmann D, Zubieta J (1998). Organic-inorganic composite oxide phase: one-dimensional molybdenum oxide chains entrained within a three-dimensional complex cationic framework in (Cu2(triazolate)4(H2O)2)MoO3. Chem. Commun. 1998:2005-2006.

Hagrmann PJ, Hagrmann D, Zubieta J (1999). Organic-Inorganic hybrid Materials: From “Simple” Coordination Polymers to Organodiamine- Templated Molybdenum oxide. Angew. Chem. Int. Ed. 38:2638-2684.

Hagrmann PJ, Zubieta J (2000). Solid-state coordination chemistry: Influences of {M(terpyridyl)(Cu, Ni(II))} subunits on molybdenum oxide structures. Inorg. Chem.39: 5218–5224.

Hubbard DJ, Johnston AR, Casalongue HS, Sarjeant AN, Norquist AJ. (2008). Synthetic Approaches for Noncentrosymmetric Molybdates. Inorg. Chem. 47:8518-8525.

Jones S, Liu H, Schmidtko K, O’Connor CC, Zubieta J. (2010). A bimetallic oxide (Cu(bpy))4MoO3(O2PCH2CH2PO3)4n chains. Inorg. Chem. Comm. 13:298.

Lysenko AB, Senchyk GA, Lincke J, Lässig D, Fokin AA, Butova ED, Schreiner PR, Krautscheid H, Domasevitch KV (2010). Metal oxide-organic frameworks (MOOFs), a new series of coordination hydrids constructed from molybdenum (VI) oxide and bipicolic 2,3-triazole linkers. Dalton Trans. 39:4223–4231.

Pope MT, Müller A (2001). Polyoxometalate Chemistry from Topology via Self-Assembly to Applications. Kluwer Academic: Dordrecht, Netherlands.

Randy S, Farig J, Zubieta J (2001). Influences of secondary metal–ligand subunits on molybdenum oxide structures: the hydrothermal syntheses and structures of (M(tpytrz)4MoO3) (M = Fe, Co, Ni, Zn; tpytrz = tripicyltripyrazine), (Ni(tpytrz)4MoO3) and (Zn(tpytrz)4MoO3). Dalton Trans. 23:3446-3452.

Senchyk GA, Lysenko AB, Babaryk AA, Rusanov EB, Krautscheid H, Neves P, Valente AA, Gonçalves IS, Krämer KW, Liu SX, Decurtn S, Domasevitch KV (2014). Triazolyl-Based Copper–Molybdate Hybrids: From Composition Space Diagram to Magnetism and Catalytic Performance. Inorg. Chem. 53:10112–10121

Sheldrick GM (2008). A short history of SHELX: The Crystallographic Program System. Acta Cryst. 64:112.

Stacchiola D, Sierka M, Todorova TK, and Sauer J, Kaya S, Valente AA, Goncalves IS, Krämer KW, Liu SX, Decurtins H, Krautscheid H, Domasevitch KV (2014). Triazolyl-Based Copper–Molybdate Hybrids: From Composition Space Diagram to Magnetism and Catalytic Performance. Inorg. Chem. 53:10112–10121

Wu CD, Lu CZ, Zhuang H, Huang JS (2002). Hydrothermal assembly of a novel three-dimensional framework formed by (GdMo4O12)8 anions and nine coordinated Gd4+ cations. J. Am. Chem. Soc. 124:3836-3837.

Xu Y, Xu QJ, Zhang K, Zhang Y, You XZ (2000). Keggin unit supported transition metal complexes: Hydrothermal synthesis and Characterization of (Ni(2,2'-bipy)3(11.5(PW12O40)Ni(2,2'-bipy)3(H2O))0.5(H2O) and (Co(1,10'-phen)3)5 (PMo12O40Co(1,10'- phen)3(H2O))0.5H2O. Chem. Commun. 2:153-154.

Zhang JW, Kan XM, Li XL, Luan J, Wang XL (2015). Transition metal carboxylate coordination polymers with amide-bridged polypyrlyridine co ligands: assemblies and properties. Cryst. Eng. Comm. 17:3881-3907

Zhang YY, Qi Y, Zhang Y, Liu ZY, Zhao YF, Liu ZM (2007). Synthesis, structure and magnetic properties of a new iron phosphonate-oxalate with 3D framework: (Fe(O2PCH2CH2O)3(0.5)(H2O)). Mat. Res. Bull. 42:1531.