

UC Irvine

UC Irvine Previously Published Works

Title

An inorganic-organic hybrid material with a novel oxometallic framework: Hydrothermal synthesis and characterization of [Zn₃O₃(C₁₃H₁₄N₂)₃]V₆O₁₅

Permalink

<https://escholarship.org/uc/item/3dc257dv>

Journal

Inorganic Chemistry Communications, 12(11)

ISSN

1387-7003

Authors

Khan, M Ishaque
Deb, Sangita
Doedens, Robert J

Publication Date

2009-11-01

DOI

10.1016/j.inoche.2009.08.032

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed



An inorganic–organic hybrid material with a novel oxometallic framework: Hydrothermal synthesis and characterization of $[\text{Zn}_3\text{O}_3(\text{C}_{13}\text{H}_{14}\text{N}_2)_3]\text{V}_6\text{O}_{15}$

M. Ishaque Khan^{a,*}, Sangita Deb^a, Robert J. Doedens^{b,*}

^a Department of Biological, Chemical and Physical Sciences, Illinois Institute of Technology, Chicago, IL 60616, USA

^b Department of Chemistry, University of California, Irvine, CA 92697, USA

ARTICLE INFO

Article history:

Received 17 February 2009

Accepted 30 August 2009

Available online 4 September 2009

Keywords:

Hybrid material

Oxometalate motifs

Crystal structure

Framework-structure

Solid-state NMR model compound

ABSTRACT

A new hybrid material $[\text{Zn}_3\text{O}_3(\text{C}_{13}\text{H}_{14}\text{N}_2)_3]\text{V}_6\text{O}_{15}$ (**1**) with extended framework structure has been synthesized hydrothermally and characterized by vibrational spectroscopy, thermogravimetry and complete single crystal X-ray diffraction analysis. The compound has a complex three-dimensional covalent framework structure. It exhibits a fully oxidized novel oxometallic framework containing 10-membered $\{\text{V}_4\text{ZnO}_5\}$ oxometalate rings and 4,4'-trimethylene dipyridine ligands ($\text{C}_{13}\text{H}_{14}\text{N}_2$) that connect pairs of crystallographically equivalent zinc atoms. The extended structure of **1** may also be viewed as containing a framework of corner-sharing $\{\text{VO}_4\}$ and $\{\text{ZnO}_2\text{N}_2\}$ polyhedra together with 4,4'-trimethylene dipyridine ligands linking zinc centers. The hybrid material is thermally stable up to 323 °C. It contains metal centers and coordination geometry that make it a potentially attractive model compound for investigating the structures of metallo-organic biomolecules by use of solid state NMR spectroscopic techniques. Crystal data for $\text{C}_{39}\text{H}_{42}\text{N}_6\text{O}_{18}\text{V}_6\text{Zn}_3$: monoclinic $P2_1$, $a = 10.9894(9)$ Å, $b = 18.1493(15)$ Å, $c = 13.0903(11)$ Å, $\beta = 109.8880(10)^\circ$, $V = 2455.1(4)$ Å³, $Z = 2$, $D_{\text{calc.}} = 1.873$ Mg/m³.

© 2009 Elsevier B.V. All rights reserved.

Design and synthesis of functional materials has attracted considerable attention in recent years [1]. This has led to a new class of inorganic–organic hybrid materials with rich topological diversity and potential applications in catalysis, gas storage, sorption and photochemistry [2–5]. Hybrid materials have shown excellent laser efficiencies and photostabilities [6], fast photochromic responses [7], as well as high and stable optical responses [8]. These materials can also be used as pH sensors [9] and many of them have shown attractive gas storage capacity [10–14].

We have been interested in the design and synthesis of inorganic–organic hybrid framework materials by combining metal–organic moieties and oxometalate motifs. We have successfully employed synthetic strategies using metal–organic complexes as linkers to cross-link vanadium oxide chains and layers to generate a series of open-framework hybrids and neutral networks. The metal–organic complex also provides the charge balance required to generate a neutral framework [15–21]. In this approach the organic components act as ligands to secondary transition metal centers giving rise to bimetallic, organically templated hybrid materials. Here we report a new hybrid material containing a novel oxometallic framework $[\text{Zn}_3\text{O}_3(\text{C}_{13}\text{H}_{14}\text{N}_2)_3]\text{V}_6\text{O}_{15}$ (**1**) which was prepared hydrothermally and characterized by FT-IR, elemental analysis, manganometric titration, thermogravimetric analysis and complete single crystal X-ray diffraction analysis.

A mixture of NH_4VO_3 (1 mmol), 4,4'-tmdp (1 mmol), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (0.5 mmol), $\text{C}_2\text{H}_5\text{OH}$ (85.76 mmol, 5 ml), H_2O (555.5 mmol, 10 ml) was placed in a 23 ml teflon-lined Parr reaction vessel and stirred continuously for 10 min. The reaction mixture (pH = 5.1) was then treated hydrothermally at 125 °C for 5 days. The reaction was then cooled to room temperature for 24 h and colorless crystals of **1**, which were covered with a black shiny impurity were isolated from the yellow mother liquor.

The following modified synthetic method gave a higher yield of **1** in purer form. A mixture of NH_4VO_3 (1 mmol), 4,4'-tmdp (1 mmol), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (0.5 mmol), $\text{HO}_2\text{C}(\text{CH}_2)_4\text{COOH}$ (adipic acid, 0.5 mmol) and H_2O (833.3 mmol, 15 ml) was sealed in a 23 ml teflon-lined Parr reaction vessel, stirred continuously for 10 min and treated hydrothermally at 125 °C for 5 days. This reaction mixture yielded colorless crystals covered by a small amount of black shiny impurity and yellow mother liquor.

Use of the adipic acid ($\text{C}_6\text{H}_{10}\text{O}_4$), which is not incorporated in the final product, in the reaction mixture increased the purity of the compound (**1**) considerably (by decreasing the black impurity). It is possible that adipic acid helps to maintain suitable pH for the formation of the product in better yield and purity. Addition of ethanol to the reaction mixture (in addition to adipic acid) gave a similar result. Our study shows that under hydrothermal condition pH and temperature influence vanadate speciation. We have already reported the synthesis of $[\{\text{Co}_2(4,4'\text{-tmdp})_4\}\text{V}_4\text{O}_{12}]$ [21].

The crystals of compound **1** are insoluble in most common solvents, such as H_2O , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and CH_3CN and are stable in

* Corresponding authors. Tel.: +1 312 5673431 (M.I. Khan).
E-mail address: khan@iit.edu (M.I. Khan).

air. The infrared spectrum of **1** show distinct bands in the 3130–3016 cm^{-1} and 2949–2864 cm^{-1} region which can be attributed to aromatic C–H stretching and the asymmetric CH_2 stretching respectively. Strong bands in the region 1619 cm^{-1} are assigned to C=C and C=N ring vibrations. Prominent bands observed at 969, 934, 885 and 844 cm^{-1} are due to the ($\text{V}-\text{O}_t$) and ($\text{V}-\text{O}-\text{V}$) stretching vibrations. Elemental analysis of $\text{C}_{39}\text{H}_{42}\text{N}_6\text{O}_{18}\text{V}_6\text{Zn}_3$, **1** showed (calc.: C, 33.83; H, 3.03; N, 6.06 Found: C, 34.09; H, 2.94; N, 6.03).

Compound **1** crystallizes in the monoclinic space group $P2_1$, with two formula units of stoichiometry $\text{C}_{39}\text{H}_{42}\text{N}_6\text{O}_{18}\text{V}_6\text{Zn}_3$ per unit cell. A summary of the crystal data and details of the intensity data collection and structure refinement are given in a footnote [22–26]. Full details have been deposited [27]. The compound has a novel structure composed of inorganic and organic motifs. The structure may be viewed as containing a framework of corner-sharing VO_4 and ZnO_2N_2 polyhedra together with 4,4'-trimethylene dipyridine ligands linking pairs of Zn^{2+} ions. Views of the asymmetric unit and of the oxometallate framework of **1** are shown in Figs. 1 and 2, respectively. A view of the unit cell contents of **1** is shown in

Fig. 3. All bond angles and bond distances are within their expected ranges.

The compound has a complex three-dimensional structure that contains a 10-membered V_4ZnO_5 ring. The ring atoms V2 and V3 are linked to the two non-ring zinc atoms by V2–O8–Zn2 and V3–O9–Zn3 bridges. Two 4,4'-trimethylene dipyridine molecules connect pairs of crystallographically equivalent zinc atoms. For Zn2 and Zn3, the linked Zn atoms are separated by pure unit cell translations parallel to the *c*-axis, while for Zn1 the relationship combines a twofold screw operation about *b* with a unit cell translation along *c*. The two non-ring vanadium atoms, V5 and V6, are part of a V_2O_7 grouping that forms V5–O7–Zn2 and V6–O10–Zn3 bridges to the two non-ring zinc atoms. Finally, the ring vanadium atoms V1 and V4 form bridges through O6 and O11, respectively, to V_2O_7 groupings in other asymmetric units.

Thermogravimetric analysis of compound **1** showed that it is stable up to 323 °C. The compound loses weight in two consecutive steps. The first weight loss of 28.43% (calc. 28.63%) is observed at 323 °C. This corresponds to the loss of two ligand molecules. The second weight loss of 30.93% (calc. 30.48%), which corresponds

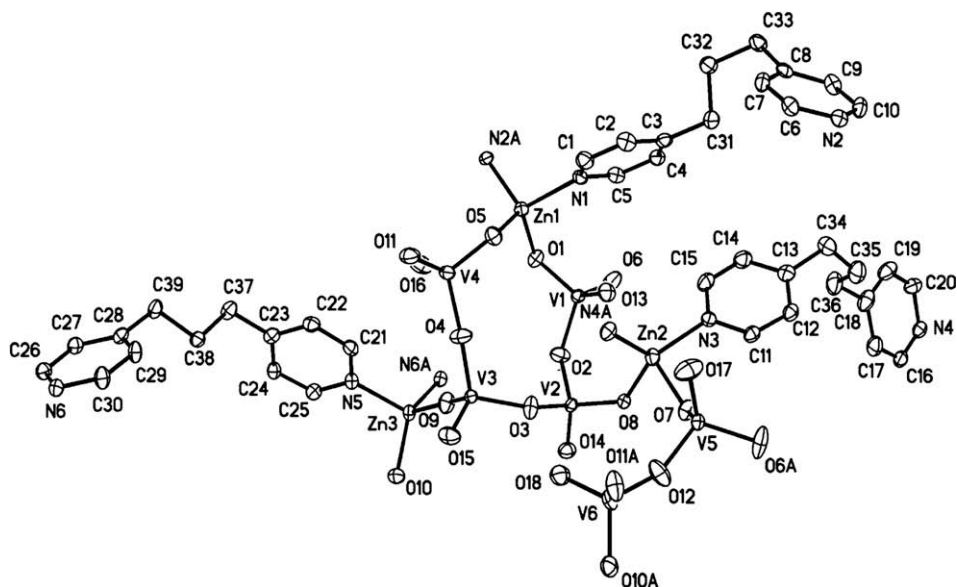


Fig. 1. A view of the asymmetric unit (plus a few additional atoms to complete the metal coordination polyhedra) in the crystals of $[\text{Zn}_3\text{O}_3(\text{C}_{13}\text{H}_{14}\text{N}_2)_3]\text{V}_6\text{O}_{15}$ (**1**) with displacement ellipsoids and atom labels.

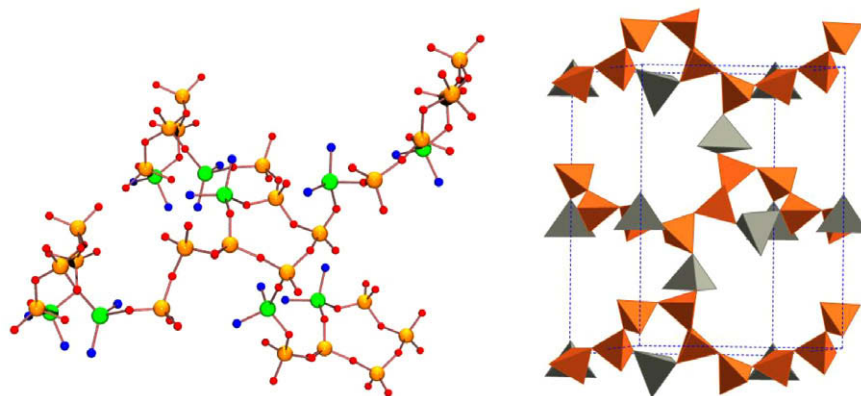


Fig. 2. A portion of the structure framework in $[\text{Zn}_3\text{O}_3(\text{C}_{13}\text{H}_{14}\text{N}_2)_3]\text{V}_6\text{O}_{15}$ (**1**) (left) and a polyhedral diagram of the structure framework (right). (Carbon and hydrogen atoms are omitted for clarity. Color code: V, golden yellow; Zn, green/gray; O, red; N, blue). (For interpretation of color in Fig. 2, the reader is referred to the web version of this article.)

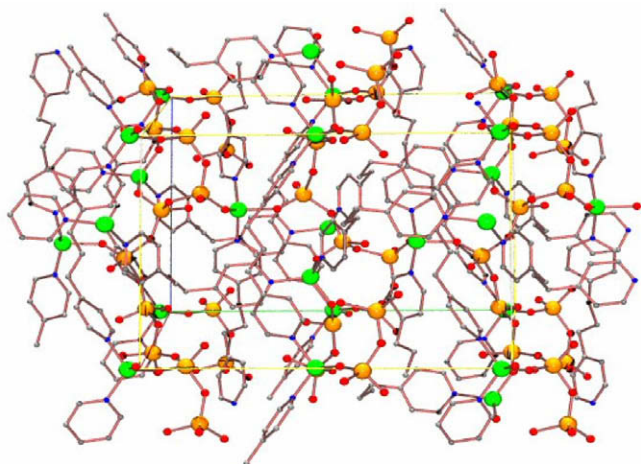


Fig. 3. A packing diagram of the $[\text{Zn}_3\text{O}_3(\text{C}_{13}\text{H}_{14}\text{N}_2)_3]\text{V}_6\text{O}_{15}$ (**1**) (color code: V, golden yellow; Zn, green; O, red; N, blue). (For interpretation of color in Fig. 2, the reader is referred to the web version of this article.)

to the loss of 14 oxygen atoms and one ligand, starts at ~ 473 °C and continues until 952 °C. The IR spectrum of the blackish residue left after TGA study showed a broad band at 1638 cm^{-1} . This clearly indicates a complete decomposition of the framework structure (after heating up to 1000 °C) and formation of a mixed metal oxide – $\{\text{Zn}/\text{V}/\text{O}\}$ – phase which has not been further characterized.

Recent years have seen increased interest in the use of NMR spectroscopy to study the structure and coordination chemistry of metal ions in biological systems to understand the role of metal ions in chemical and biological processes in living organisms [28–30]. The hybrid material described here contains fully oxidized metal centers in suitable coordination geometry that make it a potentially attractive model compound for investigating the structures of metallo-biomolecules by use of solid state NMR techniques.

In conclusion, a new inorganic–organic hybrid material containing a novel framework has been synthesized hydrothermally and characterized. The combination of hydrothermal method with metal–organic complexes and oxometallic motifs provides a powerful tool for design and development of functional hybrid materials. The structures of such materials can ‘in principle’ be modified/tailored by changing the organic and/or oxometallic components along with variations in pH and temperature of the reactions. However, precise design and synthesis of materials with predictable structures is still in its infancy.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2009.08.032.

References

- [1] C. Sanchez, G.J.D.A. Soler-Illia, F. Ribot, T. Lalot, C.R. Mayer, V. Cabuil, *Chem. Mater.* 13 (2001) 3061.
- [2] J.P. Jolivet, M. Henry, J. Livage, *Metal Oxide Chemistry and Synthesis: From Solution to Solid State*, Wiley, New York, 2000.
- [3] W.P. Griffith, *Trans. Met. Chem.* 16 (1991) 548.
- [4] M.H.D. Linden, *Handbook of Batteries*, McGraw-Hill, New York, 1995.
- [5] A. Müller, F. Peters, M.T. Pope, D. Gatteschi, *Chem. Rev.* 98 (1998) 239.
- [6] M. Faloss, M. Canva, P. Georges, A. Brun, F. Chaput, J.P. Boilot, *Appl. Opt.* 36 (1997) 6760.
- [7] B. Schaudel, C. Guermeur, C. Sanchez, K. Nakatani, J.A. Delaire, *J. Mater. Chem.* 7 (1997) 61.
- [8] B. Lebeau, S. Brasselet, J. Zyss, C. Sanchez, *Chem. Mater.* 9 (1997) 012.
- [9] C. Rottman, G. Grader, Y. De Hazan, S. Melchior, D. Avnir, *J. Am. Chem. Soc.* 121 (1999) 8533.
- [10] N.L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O’Keeffe, O.M. Yaghi, *Science* 300 (2003) 1127.
- [11] T. Dören, L. Sarkisov, O.M. Yaghi, R.Q. Snurr, *Langmuir* 20 (2004) 2683.
- [12] J.L.C. Rowsell, A.R. Millward, K.S. Park, O.M. Yaghi, *J. Am. Chem. Soc.* 126 (2004) 5666.
- [13] B.L. Chen, N.W. Ockwig, A.R. Millward, D.S. Contreras, O.M. Yaghi, *Angew. Chem. Int. Ed.* 44 (2005) 4745.
- [14] A.R. Millward, O.M. Yaghi, *J. Am. Chem. Soc.* 127 (2005) 17998.
- [15] M.I. Khan, S. Cevik, R.J. Doedens, in: T. Yamase, M.T. Pope (Eds.), *Polyoxometalate Chemistry for Nano-Composite Design*, Kluwer Academic, New York, 2002, pp. 27–38.
- [16] M.I. Khan, S. Giri, S. Ayesch, R.J. Doedens, *Inorg. Chem. Commun.* 7 (2004) 721.
- [17] M.I. Khan, S. Cevik, R.J. Doedens, *Chem. Commun.* (2001) 930.
- [18] M.I. Khan, S. Tabassum, R.J. Doedens, *Chem. Commun.* (2003) 532.
- [19] M.I. Khan, E. Yohannes, R.C. Nome, S. Ayesch, V.O. Golub, C.J. O’Connor, R.J. Doedens, *Chem. Mater.* 16 (2004) 5273.
- [20] M.I. Khan, E. Yohannes, V.O. Golub, C.J. O’Connor, R.J. Doedens, *Chem. Mater.* 19 (2007) 4890.
- [21] M.I. Khan, S. Deb, R.J. Doedens, *Inorg. Chem. Commun.* 9 (2006) 25.
- [22] Crystallographic data were collected at low temperature on a Bruker SMART-1 K CCD diffractometer. Crystals were immersed in hydrocarbon oil and mounted on a thin glass fiber in a cold nitrogen stream. Preliminary unit cell parameters and crystal orientation were determined by standard procedures [23]. A full sphere of diffraction data was collected in frames separated by 0.3° increments in ω . The first 50 frames were remeasured at the end of data collection as a check on crystal decay. The data were processed with the program SAINT [24] and corrected for absorption (and other effects) with SADABS [25]. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. All calculations were performed by use of the SHELXTL [26] package. Full details of the crystal structure analysis have been deposited [27]. Crystal data for $\text{C}_{39}\text{H}_{42}\text{N}_6\text{O}_{18}\text{V}_6\text{Zn}_3$, **1**: colorless, crystal dimensions: $0.37 \times 0.22 \times 0.05\text{ mm}^3$, monoclinic, space group $P2_1$, $a = 10.9894(9)\text{ \AA}$, $b = 18.1493(15)\text{ \AA}$, $c = 13.0903(11)\text{ \AA}$, $\beta = 109.8880(10)^\circ$, $V = 2455.1(4)\text{ \AA}^3$, $Z = 2$, $D_{\text{calc.}} = 1.873\text{ Mg/m}^{-3}$, $\mu(\text{Mo K}\alpha) = 2.603\text{ mm}^{-1}$. Data collection $T = 171(2)\text{ K}$. Of the 27,142 reflections measured ($-14 \leq h \leq 14$, $-23 \leq k \leq 24$, $-17 \leq l \leq 17$), 11,865 [$R_{\text{int}} = 0.0266$] independent reflections were used to solve the structure. Based on these data and 649 refined parameters, final $R_1 = 0.0274$ (all data), $wR_2 = 0.0559$, and the goodness-of-fit on F^2 is 1.026.
- [23] SMART, Version 4.210, Siemens Analytical X-Ray Systems, Madison, WI, 1997.
- [24] SAINT, Version 6.36A, Bruker AXS, Madison, WI, 2001.
- [25] G.M. Sheldrick, SADABS, Version 2.10, University of Göttingen, Göttingen, Germany, 2002.
- [26] G.M. Sheldrick, SHELXTL Version 6.12, Bruker AXS, Madison, WI, 2001.
- [27] Details of the crystallographic data for **1** have been deposited (CCDC reference number: $[\text{Zn}_3\text{O}_3(\text{C}_{13}\text{H}_{14}\text{N}_2)_3]\text{V}_6\text{O}_{15}$ (**1**), CCDC 720104) with the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB21EZ, UK (deposit@CCDC.cam.ac.uk).
- [28] K. Srikant, R.W. Schurko, I. Hung, A. Ramamoorthy, *Mater. Sci. Technol.* 19 (2003) 1191.
- [29] S.K. Kidambi, D.K. Lee, A. Ramamoorthy, *Inorg. Chem.* 42 (2003) 3142.
- [30] A.S. Lipton, R.W. Heck, P.D. Ellis, *J. Am. Chem. Soc.* 126 (2004) 4735.