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

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Publication Date
2009-11-01

DOI
10.1016/j.inoche.2009.08.032

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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 organic moieties and oxometalate motifs. We 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].

A new hybrid material [ZnO2(C13H14N2)3]V6O15 (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 \{V2ZnO5\} oxometalate rings and 4,4′-trimethylene dipyridine ligands (C13H14N2) that connect pairs of crystallographically equivalent zinc atoms. The extended structure of 1 may also be viewed as containing a framework of corner-sharing \{VO4\} and \{ZnO2\} 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 \[\text{Co}_{2}(4,4'-\text{tmdp})_{4}\text{V}_{2}\text{O}_{12}\] [21]. 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 \[\text{Co}_{2}(4,4'-\text{tmdp})_{4}\text{V}_{2}\text{O}_{12}\] [21].

A mixture of NH4VO3 (1 mmol), 4,4′-tmdp (1 mmol), ZnSO4·7H2O (0.5 mmol), C2H5OH (85.76 mmol, 5 ml), H2O (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 NH4VO3 (1 mmol), 4,4′-tmdp (1 mmol), ZnSO4·7H2O (0.5 mmol), HO2C(CH2)6COOH (adipic acid, 0.5 mmol) and H2O (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 (C6H10O4), 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 [[Co2(4,4′-tmdp)4]V2O12] [21].

The crystals of compound 1 are insoluble in most common solvents, such as H2O, CH3OH, C2H5OH and CH3CN and are stable in...
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 (V–O\(_1\)) and (V–O–V) stretching vibrations. Elemental analysis of C\(_{39}\)H\(_{42}\)N\(_6\)O\(_{18}\)V\(_6\)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 C\(_{39}\)H\(_{42}\)N\(_6\)O\(_{18}\)V\(_6\)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\(_2\)N\(_2\) 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\(_4\)ZnO\(_5\) 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\(_2\)O\(_2\) 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\(_2\)O\(_7\) 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
to the loss of 14 oxygen atoms and one ligand, starts at around 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 and continues until 952 °C.

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.

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[22] Crystalographic 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 θ. 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 F² 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 C₁₇₅H₁₄₅N₆O₁₈V₆Zn₃: colorless, a = 10.9894(9) Å, b = 18.1493(15) Å, c = 13.0903(11) Å, β = 109.8880(10)°, V = 2455.14(4) Å³, Z = 2, D_cal. = 1.873 Mg/m³, μ(Mo Kα) = 2.603 mm⁻¹. Data collection T = 17(2) K. Of the 27,142 reflections measured (−14 ≤ h ≤ 14, −23 ≤ k ≤ 24, −17 ≤ l ≤ 17), 11,865 [R(int) = 0.0266] independent reflections were used to solve the structure. Based on these data and 649 refined parameters, final R₁ = 0.0274 (all data), wR₂ = 0.0559, and the goodness-of-fit on F² is 1.0256.
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