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Inorganic Chemistry Communications 8 (2005) 841–845

INORGANIC CHEMISTRY COMMUNICATIONS

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Templated synthesis of a chiral solid: Synthesis and characterization of $\{Co(H_2N(CH_2)_2NH_2)_3\}[V_3O_9] \cdot H_2O$, containing a new type of chiral vanadium oxide chain

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Received 10 May 2005; accepted 2 June 2005
Available online 10 August 2005

Abstract

Synthesis and characterization of a novel chiral solid, $\{Co(H_2N(CH_2)_2NH_2)_3\}[V_3O_9] \cdot H_2O$ (**1**), containing chiral vanadium oxide chains constructed from corner sharing tetrahedral $\{VO_4\}$ units and propagated by a twofold screw axis are described. The resulting $[\{V_3O_9\}^{3-}]_n$ chains host dissymmetric $\{Co(H_2N(CH_2)_2NH_2)_3\}^{3+}$ species, which functions as an optically active template. The synthesis of **1** demonstrates the potential application of an optically active complex compound of D_3 symmetry as a chiral template in the synthesis of chiral chemical systems with extended structures. Crystal data for $C_6H_{26}CoN_6O_{10}V_3$, **1**: Orthorhombic space group $P2_12_12_1$ (No. 19), $a = 8.183(4)$ Å, $b = 12.638(6)$ Å, $c = 18.039(7)$ Å, $V = 1865.6(14)$ Å^3, $Z = 4$, $D_{calcd} = 1.973$ Mg m^{-3}, $R_1 = 0.0297$ (all data), $wR_2 = 0.0681$.

Keywords: Chiral structure; Vanadium oxide; Templated synthesis; Crystal structure; Magnetic properties

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The design and synthesis of extended solids with chiral structures is of intense current interest. Chiral surfaces are considered promising heterogeneous catalysts for stereospecific chemical transformations [1–3]. Insoluble chiral catalysts offer tremendous advantages over homogeneous catalysts to achieve these chemical conversions. They can be easily separated from the reactants and products, allow straightforward catalyst recycling, avoid metal contamination commonly associated with homogeneous catalysis, and offer inexpensive catalysts that can be modified. However, chiral catalysis on solid surfaces is practically nonexistent in current industrial processes due mainly to the unavailability of suitable extended structure chiral solids/materials.

We are currently exploring the design and synthesis of extended structure solids with porous and open framework structures [4–9]. One of the several possible ways to generate open structures is to use structure directing templates that can impose unique constraints during the construction of the structures. We reasoned that the use of optically active templates may direct the synthesis of chiral structures. Since a number of molecular complexes of the type $\{M(L–L)_3\}$ (M = transition metal such as Mn, Fe, Co, Ni, etc.; L–L = chelating bidentate ligands such as, ethylenediamine, oxalate, 2,2′-bipyridine, 1,10,-phenanthroline, etc.) of chiral point group symmetry D_3 are known, they can possibly be employed to explore the potential of this approach. If

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doi:10.1016/j.inoche.2005.06.009

successful, a templated synthesis approach that uses a single enantiomer of the template can be especially valuable for preparing chiral solids, which are rare and difficult to make.

During our ongoing effort we have prepared a novel solid composed of chiral crystals containing vanadium oxide chains templated with a dissymmetric complex cation. This report describes the synthesis of the composite material, $[\{Co(H_2N(CH_2)_2NH_2)_3\}\{V_3O_9\}]\cdot H_2O$ (**1**), and its characterization by infrared spectroscopy, thermogravimetry, elemental analysis, manganometric titration, bond valance sum calculations, temperature dependent magnetic susceptibility measurement and complete single crystal X-ray structure analysis [10,11].

Ethylenediamine (7.50 mmol) was slowly added to a stirred slurry of V_2O_5 (1.25 mmol) in water (15.00 ml) contained in a 50-ml round bottom flask maintained at 80–84 °C. To the resulting clear brownish yellow solution of pH 7.40, $CoSO_4.7H_2O$ (1.87 mmol) was added. The reaction mixture was refluxed for 24 h to yield light orange rod-shaped crystals. The crystals were filtered along with a black powdery impurity from the colorless mother liquor. The mixture was washed thoroughly with cold water and dried in air at room temperature. The light orange crystals were separated mechanically from the black impurity to give ~375 mg (~91.2% based on vanadium) of $[\{Co(H_2N(CH_2)_2NH_2)_3\}\{V_3O_9\}]\cdot H_2O$ (**1**). Anal. Calcd. for $[Co(en)_3V_3O_9]\cdot H_2O$ (**1**): C, 13.00; H, 4.73; N, 15.16; Co, 10.64; V, 27.58. Found: C, 12.40; H, 4.80; N, 14.14; Co, 9.08; V, 27.97%. Prominent IR bands (KBr pellet, 4000–400 cm^{-1}): 3517 (m), 3466 (m), 3125 (s), 3039 (s), 1631 (sh), 1599 (m), 1577 (m) 1461 (m), 1330 (w), 1218 (w), 1144 (m), 1054 (m), 946 (s), 908 (vs), 891 (sh),797 (m), 746 (s), 643 (s).

An X-ray quality crystal of $[\{Co(H_2N(CH_2)_2NH_2)_3\}\{V_3O_9\}]\cdot H_2O$ of approximate dimensions $0.22 \times 0.12 \times 0.06\ mm^3$ was selected. The crystal was immersed in hydrocarbon oil and mounted on a thin glass fiber in the low-temperature stream of a Bruker SMART CCD diffractometer. Preliminary unit cell parameters and crystal orientation were determined by standard procedures [12]. A full sphere of diffraction data was collected in 30s 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 [13] and corrected for absorption (and other effects) with SADABS [14]. 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 [15] package. A summary of the crystal data and details of the intensity data collection and structure refinement are given in a footnote; full details have been deposited [16].

X-ray diffraction quality single crystals of $[\{Co(H_2N(CH_2)_2NH_2)_3\}\{V_3O_9\}]\cdot H_2O$ (**1**) are obtained in high yield by the reaction of $CoSO_4\cdot 7H_2O$ with the yellowish-brown solution obtained by the addition of ethylenediamine into an aqueous slurry of V_2O_5 at 80–82 °C. The compound can also be prepared in high yield by using different sources of cobalt, such as $CoMoO_4\cdot H_2O$ or $CoCl_2.6H_2O$ in place of $CoSO_4\cdot 7H_2O$ in the reaction. It is readily synthesized in crystalline form both by refluxing the reaction mixture and by hydrothermal reactions.

Crystals of **1** are stable in air and insoluble in cold and hot water and in common organic solvents. The light orange color of the crystals of **1** is indicative of an oxidized species. The results of the manganometric titration, magnetic moment measurement and bond valence sum calculation reveal the presence of three V^V and one Co^{III} per formula unit of the compound. This indicates that charge balance is achieved by the oxidation of Co^{II} to Co^{III} during the course of the reaction. The oxidation of the cobalt, presumably by molecular oxygen, proceeds even in the presence of a reducing agent, hydrazinium sulfate.

The infrared spectrum of $[\{Co(H_2N(CH_2)_2NH_2)_3\}\{V_3O_9\}]\cdot H_2O$ (**1**) exhibits a number of absorption bands in the 1700–400 cm^{-1} region. Many of these bands are attributable to the fundamental vibration modes of the ethylenediamine [17–19]. Broad bands between 3637 and 3313 cm^{-1} with maxima around 3578 and 3466 cm^{-1} are assigned to asymmetric and symmetric O–H stretching, respectively, and the shoulder at 1631 cm^{-1} due to H–O–H bending of the water of crystallization. The strong and sharp bands at 946 and 908 cm^{-1} and a shoulder at 891 cm^{-1} are assigned to asymmetric and symmetric V–O stretching vibrations from the terminal {V–O} moieties. Furthermore a broad band between 836 and 709 cm^{-1} with maxima at 797 and 746 cm^{-1} and a strong and sharp band at 643 cm^{-1} are attributed to asymmetric and symmetric {V–O–V} stretching of the vanadium oxide chains. The positions of the bands and their assignments are consistent with literature reports [20–22].

Thermogravimetric analysis of **1** revealed a first weight loss of 2.83% occurring between 70 and 110 °C. This corresponds to the loss of one water molecule (calculated 3.25%) per formula unit. This is followed by a loss of 48.81% weight in three successive steps in the temperature range 259–643 °C. This corresponds to removal of the three ethylenediamine molecules and five oxygen atoms from the vanadium oxide chain. The loss of network oxygen atoms in this temperature range suggests that the compound may have undergone a phase transformation. The infrared spectrum of the black amorphous residue, which differs significantly from that of any known vanadium oxide phase, indicates the formation of a mixed metal oxide phase or a mixture of simple metal oxide phases.

Crystallographic data for **1** are summarized in a footnote [16]. Selected bond angles and bond lengths are