Construction of Two Inorganic-organic Hybrid Vanadogermanates Based on Di-Cd-Substituted Ge-V-O Cluster and Transition-metal Complex Bridges Postprint

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Abstract

Two new inorganic-organic hybrid vanadogermanates, H[Cd(en)(phen)(H O)][Cd(en)(phen)]{[Cd(phen)] [Ge V
H O (1) and [Cd(dien)][Cd(dien)] {[Cd(phen)] Ge V O (H O)(OH) } · 0.5H O (2) (en = ethylenediamine, dien = diethylenetriamine, phen = 1,10-phenanthroline), have been synthesized via hydrothermal methods. Their structures were characterized by single-crystal X-ray diffraction, thermogravimetric analysis, powder X-ray diffraction, and infrared spectroscopy. Structural analysis reveals that compound 1 is a rare dimeric structure based on di-Cd-substituted Ge-V-O clusters and bridging transition-metal complexes, while compound 2 is an infinite 1-D chain constructed from di-Cd-substituted Ge-V-O clusters and dinuclear bridging complexes. Magnetic measurements indicate that both 1 and 2 exhibit antiferromagnetic behavior.

Full Text

Preamble

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Abstract

Two inorganic-organic hybrid vanadogermanates, H[Cd(en)(phen)(H O)][Cd(en)(phen)]{[Cd(phen)] [Ge V O (5H O (1) and [Cd(dien)][Cd(dien)] {[Cd(phen)] Ge V O (H O)(OH) }· 6.5H O (2) (en = ethylenediamine, dien = diethylenetriamine, phen = 1,10-phenanthroline), have been synthesized via hydrothermal methods. Their structures were characterized by single-crystal X-ray diffraction, thermogravimetric analysis, powder X-ray diffraction, and infrared spectroscopy. Structural analysis reveals that compound 1 possesses a rare dimeric structure based on di-Cd-substituted Ge-V-O clusters bridged by transition-metal complexes, while compound 2 forms an infinite 1-D chain constructed from di-Cd-substituted Ge-V-O clusters and dinuclear bridging complexes. Magnetic measurements indicate that both compounds exhibit antiferromagnetic behavior. Keywords: vanadogermanates; hydrothermal synthesis; crystal structure; magnetic property. DOI: 10.14102/j.cnki.0254-5861.2011-1741

1. Introduction

Polyoxometalates (POMs) have attracted increasing research attention due to their exceptional properties in catalysis, optics, magnetism, sorption, ion exchange, and other applications [1-4]. Compared with well-studied polyoxomolybdates and polyoxotungstates, polyoxovanadates (POVs) remain relatively underexplored [5-8]. A key feature of polyoxovanadate compounds is the presence of diverse polyhedral building units such as {VO }, {VO }, and {VO }, which can assemble into various vanadium-oxygen clusters through vertex-, edge-, or face-sharing. One of the most effective strategies for developing novel POVs involves incorporating heteroatoms into the cluster frameworks. To date, most research has focused on the incorporation of group 15 elements (As, Sb) into the classic Keggin {V O } cluster anion, yielding vanadoarsenates [9-15] and vanadoantimonates [16-21]. In these structures, {As O }/{Sb O } dimers formed by two vertex-sharing {AsO }/{SbO } trigonal pyramids substitute the VO groups on the {V O } shell.

In contrast to vanadoarsenates and vanadoantimonates, vanadosilicates (VSOs) and vanadogermanates (VGOs) have been investigated much less extensively. Germanium-vanadium oxide clusters based on the {V O } shell primarily include {Ge V O } [7, 22], {Ge V O } [23-24], {Ge V O } [7, 24], and {Ge V O } [7] clusters. These architectures are predominantly constructed from {VO } square pyramids and {Ge O } dumbbell dimers. The {Ge O } units, formed by two vertex-sharing {GeO } tetrahedra, offer advantages over the {AsO } and {SbO } trigonal pyramids. The latter typically favor isolated structures due to the weak coordination capability of the As/Sb lone pairs [25-27].

Incorporating secondary transition-metal (TM) ions into POV skeletons can generate intriguing structures with special properties, yet TM-substituted POVs remain relatively unexplored. Notable examples include {[(en) Cd Ge V O (OH) (H O)][Cd(en)] }·6H O reported in 2010 [23], {(CdX) Ge V O (H O)[V (H O)] (GeO) }·8H O (X = en, 1,2-dap) reported by Yang's group in 2014 [28], and {[Cd(en)][Cd(en)] Ge V O (OH) } {[Cd(en)(H O)] }·en·2H O prepared by Liu's group in 2016 [29]. Recently, our group reported two novel transition-metal-substituted vanadogermanates, [Cd(en)(H O)][Cd(en)][Cd(en)]{[Cd(en)] [Ge V O . (O 2H O and [Cd(en)][Cd(en)] {[Cd(en)] [Ge V O (OH)]}·10H O [30]. Inspired by these results, we sought to further explore this system.

Herein, we report the hydrothermal syntheses, crystal structures, and magnetic properties of two new transition-metal-substituted vanadogermanates: H[Cd(en)(phen)(H O)][Cd(en)(phen)]{[Cd(phen)] [Ge V O (OH)]}·5H O (1) and [Cd(dien)][Cd(dien)] {[Cd(phen)] Ge V O (H O)(OH) }·6.5H O (2). Compound 1 features an uncommon dimeric structure based on di-Cd-substituted Ge-V-O clusters bridged by transition-metal complexes, while compound 2 displays an infinite 1-D chain structure built from di-Cd-substituted Ge-V-O clusters and dinuclear bridging complexes.

2. Experimental

2.1 Materials and Measurements

All chemicals of analytical grade were purchased from commercial sources and used without further purification. Elemental analyses for C, H, and N were performed on a Vario EL III elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded on a computer-automated Bruker D8 Advance diffractometer with Cu-K radiation (= 1.54056 Å) at room temperature, scanning from 5° to 50° (2) at 0.02° increments. Fourier-transform infrared (FT-IR) spectra (4000–400 cm ^{1}) were obtained on a Nicolet iS10 spectrometer using KBr pellets. Thermogravimetric (TG) analysis was conducted on a NETZSCH PC409 simultaneous thermal analyzer from 20 to 1000 °C at 10 °C/min under flowing N atmosphere. Magnetic susceptibility data were collected on a Quantum Design MPMS SQUID VSM magnetometer at 2–300 K under an external magnetic field of 1 kOe.

2.2 Synthesis

During our investigation, we found that pH value, temperature, and reaction time significantly affect product formation and crystal growth. Extensive parallel experiments demonstrated that crystals of 1 and 2 are highly sensitive to reaction pH, with optimal ranges of 8.8-9.0 for 1 and 8.5-8.8 for 2. Additionally, reaction temperature plays a critical role; neither compound could be obtained when the temperature deviated from 160–180 °C. The optimal reaction time was determined to be 3–5 days.

2.2.1 Synthesis of 1 A mixture of NH VO (0.0345 g, 0.29 mmol), GeO (0.0384 g, 0.37 mmol), CdCl ·2.5H O (0.0242 g, 0.11 mmol), phen (0.0306 g, 0.17 mmol), en (0.1 mL), and H O (5 mL) was stirred for 0.5 h, then transferred to a

25 mL Teflon-lined stainless-steel autoclave and sealed. The mixture was heated at 170 °C for 4 days and cooled to room temperature. Brown block-shaped crystals were isolated by filtration, washed with distilled water, and dried at ambient temperature (Yield: 0.0711 g, 46% based on GeO). Elemental analysis (%) calcd. for H C N O V Ge Cd (3366.97): C, 18.55; N, 4.99; H, 2.02. Found: C, 18.30; N, 5.01; H, 2.33. IR (KBr, cm ^{1}): 3438(s), 3275(w), 3048(w), 1617(m), 1574(m), 1516(m), 1427(s), 1350(w), 1145(w), 1103(w), 984(s), 793(s), 729(m), 668(m), 542(m).

2.2.2 Synthesis of 2 A mixture of NH VO (0.0200 g, 0.17 mmol), GeO (0.0380 g, 0.36 mmol), CdCl ·2.5H O (0.0800 g, 0.35 mmol), phen (0.0300 g, 0.17 mmol), dien (0.2 mL), and H O (5 mL) was stirred for 0.5 h, then transferred to a 25 mL Teflon-lined stainless-steel autoclave and sealed. The mixture was heated at 170 °C for 4 days and cooled to room temperature. Brown block-shaped crystals were isolated by filtration, washed with distilled water, and dried at ambient temperature (Yield: 0.0448 g, 29% based on GeO). Elemental analysis (%) calcd. for H C N O . V Ge Cd (3436.44): C, 13.98; N, 6.52; H, 2.59. Found: C, 14.01; N, 6.57; H, 2.98. IR (KBr, cm ^{1}): 3422(w), 3352(w), 3276(w), 2924(w), 2876(w), 1589(m), 1516(m), 1426(m), 1341(w), 1143(w), 1101(w), 984(s), 790(s), 728(w), 669(m), 552(m).

2.3 Single-Crystal X-Ray Crystallography

X-ray diffraction data for 1 and 2 were collected on a Bruker APEX II CCD diffractometer at 296(2) K using a fine-focus 2.0 kW sealed tube X-ray source (MoK radiation, = 0.71073 Å) operating at 50 kV and 30 mA. Empirical absorption corrections were applied based on equivalent reflections. Structures were solved by direct methods and refined on F^2 using full-matrix least-squares with SHELXS-97 and SHELXL-97 programs. All hydrogen atoms attached to carbon, nitrogen, and oxygen were placed geometrically. All non-hydrogen atoms were refined anisotropically except O7w, O8w, and O9w in compound 1. Final formulas were determined by combining single-crystal X-ray diffraction with elemental and thermogravimetric analyses. To balance the charge of 1, one proton was added; this proton could not be located and was assumed to be delocalized over the structure, a common phenomenon in POM chemistry. Crystal data and structure refinement details are summarized in Table 1 .

3. Results and Discussion

3.1 Crystal Structure of 1

Single-crystal X-ray diffraction analysis reveals that 1 crystallizes in the triclinic P space group. Its molecular structure consists of one di-Cd-substituted Ge-V-O cluster {[Cd(phen)] [Ge V O (OH)]} (1a), one decorative [Cd(en)(phen)(H O)]^{2} group, one [Cd(en)(phen)]^{2} fragment, and five lattice water molecules. As shown in Fig. 1a [Figure 1: see original paper]-1b, a notable feature of 1a is that two [Cd(phen)]^{2} groups replace two VO groups located between the Ge O units of the reported {Ge V O (OH) } polyanion with rhombicuboctahedral topology [31], generating a new {Cd Ge V O (OH) } cluster that adopts the -{Ge V O (OH) } configuration [30]. Each 1a cluster is further decorated by one [Cd(phen)(en)(H O)]^{2} group to form the unprecedented cluster {[Cd(phen)(en)(H O)][Cd(phen)] [Ge V O (OH)]}^{3} .

In 1, four unique Cd^{2} ions exhibit two distinct coordination environments: trigonal prismatic CdO N (Cd(1), Cd(2)) and distorted octahedral CdO N (Cd(3), Cd(4)). The Cd(1) and Cd(2) ions in 1a are coordinated by two N atoms from one phen ligand and four bridging O atoms from two adjacent VO tetragonal pyramids of 1a. In contrast, both Cd(3) and Cd(4) are chelated by two different nitrogen-containing organic ligands. Cd(4) is defined by one O atom from a VO polyhedron, one coordinated water molecule, one en ligand, and one phen ligand. Cd(3) is surrounded by one en ligand, one phen molecule, and two O atoms (Fig. 1c), forming a [CdO (en)(phen)] fragment. Notably, one O atom in the [CdO (en)(phen)] fragment originates from a GeO tetrahedron (O(27)) in 1a, while the other comes from a VO tetragonal pyramid (O(11)) of a neighboring symmetry-related 1a cluster.

All V centers in 1 adopt a distorted VO square-pyramidal geometry. V-O bond lengths for terminal O atoms range from 1.588(8) to 1.633(7) Å, while bridging O atoms fall in the 1.903(7)-2.015(7) Å range. Ge-O distances span 1.708(7)-1.781(8) Å. Bond valence sum (BVS) calculations [32] indicate that all V atoms are in the +4 oxidation state (3.96-4.31), as are all Ge atoms (3.95-4.06) in 1 (Table 2). Additionally, BVS values for terminal O atoms (O(2), O(5), O(6), O(9), O(12), O(15), O(20)) connected to Ge atoms range from 0.99 to 1.08, confirming these as OH groups.

The most intriguing structural feature of 1 is that [Cd(en)(phen)(H O)]-decorated 1a clusters can be interconnected by two [CdO (en)(phen)] fragments to form a dimeric aggregate (Fig. 1d). While some POM dimeric compounds based on POM building blocks bridged by transition-metal complexes have been reported [29], dimeric aggregates containing mixed-ligand chelated transition-metal complexes are rare. Thus, compound 1 not only enriches dimeric POM chemistry but also provides a feasible synthetic approach for assembling poly(vanadogermanate) aggregates from discrete clusters.

3.2 Crystal Structure of 2

The molecular structure of 2 contains a di-Cd-substituted Ge-V-O cluster {[Cd(phen)] [Ge V O (OH)]} (2a, Fig. 2a [Figure 2: see original paper]-2b), one [Cd(dien)]^{2} group, two [Cd(dien)]^{2} units, and 6.5 lattice water molecules. The structure and configuration of 2a resemble those of 1a, differing only in the number of hydroxyl groups (six in 2a versus seven in 1a). Ge-O/V-O bond distances for terminal O atoms range from 1.706(1)-1.743(2)/1.593(8)-1.616(5) Å, while bridging O atoms span 1.713(3)-1.799(1)/1.923(2)-2.009(4) Å. BVS calculations (Table 3) confirm that all V atoms are +4 (4.03–4.22) and all Ge atoms are +4 (4.02–4.09) in 2.

Three unique Cd^2 ions (Cd(1), Cd(2), Cd(3)) in 2 exhibit three different coordination geometries: distorted trigonal bipyramidal CdO N for Cd(1), trigonal prismatic CdO N for Cd(2), and pentagonal bipyramidal CdON for Cd(3). Cd(1) is coordinated by three N atoms from one dien ligand (Cd–N: 2.269(8)–2.416(8) Å) and two -O atoms from GeO tetrahedra of two neighboring 2a clusters. Interestingly, two symmetry-related Cd(1) ions are interconnected through two shared -O atoms, forming a centrosymmetric dinuclear complex [Cd O (en) (phen)] (Fig. 2c). Cd(2) is defined by two N atoms from one phen ligand (Cd–N: 2.339(7)–2.410(8) Å) and four -O atoms from the 2a cluster (Cd–O: 2.264(5)–2.331(6) Å). Cd(3) is surrounded by six N atoms from two dien ligands (Cd–N: 2.380(1)–2.47(2) Å) and one O atom from a VO tetragonal pyramid of 2a (Cd–O: 2.618(9) Å), forming a decorative [CdO(dien)] unit on the cluster exterior.

Notably, the 2a clusters undergo further assembly. As shown in Fig. 2c, each 2a cluster links to two neighboring clusters through two dinuclear [Cd O (dien)] complexes via Ge–O–Cd bonds, generating an infinite 1-D chain (Fig. 2d). The successful construction of this 1-D chain further demonstrates that tetrahedral {GeO } groups are superior to {AsO } and {SbO } trigonal pyramids for building extended polyoxovanadate structures.

3.3 PXRD Analysis

The PXRD patterns of 1 and 2 (Fig. 3 [Figure 3: see original paper]) show excellent agreement between experimental and simulated patterns, confirming good phase purity for both compounds.

3.4 FT-IR Analysis

IR spectra of 1 and 2 are presented in Fig. 4 [Figure 4: see original paper]. NH and CH stretching bands appear at 3383–3312 and 2975–2890 cm ^{1}, respectively, while absorption peaks at 1609–1570 cm ^{1} correspond to NH bending vibrations, confirming the presence of amino groups. A broad band at 3462–3391 cm ^{1} arises from OH stretching. Peaks at 1536–1401 and 738–705 cm ^{1} are assigned to the phen ligand. Strong peaks at 1016–896 cm ^{1} belong to V=O stretching vibrations, while those at 879–743 cm ^{1} likely correspond to Ge-O stretching of GeO tetrahedra [23]. Peaks at 2386–2289 cm ^{1} are attributed to asymmetric CO stretching vibrations.

3.5 TG Analysis

TG curves for 1 and 2 are shown in Fig. 5 [Figure 5: see original paper]. For 1, a 5.92% weight loss from 20–300 °C corresponds to removal of five H O molecules and two en ligands (calcd: 6.24%). A second weight loss of ~4.40% from 300–500 °C is assigned to loss of seven hydroxyl groups and one coordinated water ligand (calcd: 4.06%). Subsequent weight loss of ~21.27% from 500–813 °C results from decomposition of four phen molecules (calcd: 21.38%). For 2, a 7.87% weight loss from 20–125 °C corresponds to departure of 7.5 water molecules and six hydroxyl groups (calcd: 6.90%). An 11.23% loss from 125–415 °C arises from loss of four dien molecules (calcd: 12.01%). A final weight loss of ~10.49% from 415–585 °C is attributed to decomposition of two phen ligands (calcd: 10.50%).

3.6 Magnetic Properties

Variable-temperature magnetic susceptibilities of 1 and 2 were measured from 2–300 K under an external field of 1 kOe (Figs. 6 and 7). At room temperature, the experimental T values for 1 and 2 are both 1.36 cm^3 · K · mol^{1} per formula unit, significantly lower than the theoretical value of 4.5 cm^3 · K · mol^{1} for twelve uncoupled V ions (g = 2.00). Upon cooling, T values decrease gradually to 1.08 cm^3 · K · mol^{1} at 48 K for 1 and 1.25 cm^3 · K · mol^{1} at 35 K for 2. Further cooling causes abrupt decreases, reaching minima of 0.07 and 0.09 cm^3 · K · mol^{1} at 2 K for 1 and 2, respectively. These behaviors indicate antiferromagnetic coupling within the clusters [33]. Structurally, V · · · V pairs with double O bridges show distances of 2.852–3.025 Å in 1 and 2.847–3.027 Å in 2, consistent with antiferromagnetic coupling [23, 34]. Additionally, the temperature dependence of reciprocal susceptibility (1/) follows the Curie-Weiss law from 220–9 K for 1 and 245–5 K for 2, with Weiss constants of -8.61 K and -1.07 K, and Curie constants of 1.26 and 1.27 cm^3 · K · mol^{1}, respectively, further supporting antiferromagnetic interactions between V ions. Thus, both compounds exhibit expected antiferromagnetic properties.

4. Conclusion

We have successfully synthesized two new inorganic-organic hybrid vanadogermanates under hydrothermal conditions. Structural analysis reveals that compound 1 is a rare dimeric structure based on di-Cd-substituted Ge-V-O clusters {[Cd(en)(phen)(H O)][Cd(phen)] [Ge V O (OH)]}^{3} bridged by transition-metal complexes [CdO (en)(phen)]^2 , while compound 2 forms an infinite 1-D chain constructed from di-Cd-substituted Ge-V-O clusters {[Cd(phen)] [Ge V O (OH)]} and dinuclear complex [Cd (dien) O] bridges. Magnetic studies confirm antiferromagnetic coupling between metal ions within the clusters. This work not only expands the structural diversity of inorganic-organic hybrid vanadogermanates but also demonstrates significant potential for creating novel functional materials by linking discrete transition-metal-substituted Ge–V–O clusters with various transition-metal complex bridges.

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