Synthesis and Structure of a Cadmium Selenite-Sulfate Cd₄(SeO₃)₂(SO₄)₂

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Received April 27, 2007

Key Words: Cadmium, Crystal structure, Selenite, Sulfate

Metal selenites have been of research interest to scientists in chemistry and materials because of their novel structures and unusual optical, electrical and magnetic properties, which enable metal selenites to be applied as anisotropic semiconductive coatings, photovoltaic sources, or photovoltaic devices. To date, many metal selenites have been synthesized. Among them, however, no group-12 selenite-sulfate has been reported. Our interest in the selenite-based structures was concerned with the possible role of the stereochemically active lone pair of electrons as an invisible structure-directing agent to prepare unusual structures. The stereochemically active lone pair of electrons in SeIV generally leads to a pyramidal coordination for the selenite species. From synthetic and crystal chemistry viewpoint, it is suggested that this could cause the selenites to result in a noncentrosymmetric structure with interesting physical properties such as nonlinear optical second harmonic generation (SHG). Herein we describe the synthesis, structure and property of cadmium selenite-sulfate, Cd₄(SeO₃)₂(SO₄)₂ (1), which is the first group-12 selenite-sulfates and possesses a novel 3-D structure.

As for the reaction mechanism of preparing the title compound, we proposed a logical process as follows: firstly, the sulfur and selenium were oxidized as SO₄²⁻ and SeO₃²⁻ groups, respectively, then the SO₄²⁻ and SeO₃²⁻ groups bound to the cadmium center to form the result compound. Thus, the following equations may be given: CdBr₂·4H₂O + S + Se → CdBr₂·4H₂O + SO₄²⁻ + SeO₃²⁻ → Cd₄(SeO₃)₂(SO₄)₂ (1).

X-ray diffraction analysis reveals that compound 1 features a 3-D structure with the cadmium atoms in three different coordination environments. An ORTEP drawing of the asymmetric unit of 1 is shown in Figure 1. The four crystallographically independent cadmium atoms are grouped into three kinds of coordination geometries. The Cd₁ and Cd₄ atoms have a distorted octahedral geometry, coordinated to six oxygen atoms from the SeO₃²⁻ and SO₄²⁻ groups. Different from Cd₁ and Cd₄ atoms that are six-coordinated, the Cd₂ atom is coordinated by seven oxygen atoms to form a mono-capped octahedron, and the bond lengths of Cd-O are range from 2.236(4) to 2.572(4) Å with an average value of 2.384(5) Å. The Cd₃ atoms, which are the third kind of coordination geometries of cadmium atoms in 1, are in a distorted square anti-prism environment, coordinated by eight oxygen atoms from the SeO₃²⁻ and SO₄²⁻ groups, yielding a decahedron. In 1, all the bond lengths of Cd-O are in the normal range and comparable with those reported. All the SeIV atoms are three-coordinated by three oxygen atoms in a distorted ψ-SeO₃ tetrahedral geometry with the fourth site occupied by the lone-pair electrons (Figure 2).

Figure 1. ORTEP drawing of 1 with 40% thermal ellipsoids.

Figure 2. Polyhedral view of 1 shows two kinds of quadruple-chain structures: (a) polyhedra corner-share to each other; (b) polyhedra corner-share and edge-share to each other. Yellow: S, green: Se. Numbers are the crystallographically distinct cadmium atoms.
which are similar to those found in the references. The Se-O distances range between 1.671(4) and 1.713(5) Å, which are comparable to those reported in other metal selenites. The S1 and S2 atoms have a four-coordinated tetrahedral geometry, coordinated by four oxygen atoms with the S-O bond lengths between 1.446(5) and 1.508(5) Å, which is normal for a SO$_4^{2-}$ moiety. The Cd1-centered octahedra link to each other via SO$_4^{2-}$ moieties, yielding a Cd1 chain along a axis (Figure 2). While the Cd2-centered one-face centred octahedra connect together via SeO$_3^{2-}$ groups to form a Cd2 chain along a axis. Two Cd1 chains interconnect through corner-share to construct a double chain, of which both sides are connected by two Cd2 chains via corner-shared oxygen atoms and bridging SO$_4^{2-}$ moieties, yielding a quadruple 2-1-1-2 chain running along a axis, as shown in Figure 2(a). Interestingly, in I, there is another quadruple 4-3-3-4 chain, which is different from the quadruple 2-1-1-2 chain. The Cd3-centered octahedra connect to each other via SeO$_3^{2-}$ groups to form a Cd3 chain along a axis. Two Cd3 chains interconnect to each other via edge-share to form a Cd3 double chain. The Cd4-centered octahedra link to each other via SO$_4^{2-}$ moieties, yielding a Cd4 chain along a axis. Each Cd3 double chain is connected by two Cd4 chains via corner-share, edge-share and SO$_4^{2-}$ moieties, constructing a quadruple 4-3-3-4 chain running along a axis [Figure 2(b)]. In a word, in the quadruple 2-1-1-2 chain, the polyhedra are interconnected via corner-share and SO$_4^{2-}$ moieties, while in the quadruple 4-3-3-4 chain, the polyhedra are interconnected via corner-share, edge-share and SO$_4^{2-}$ moieties. Each quadruple 2-1-1-2 chain interconnects to four 4-3-3-4 chains through corner-share, edge-share, SeO$_3^{2-}$ and SO$_4^{2-}$ moieties to build a 3-D structure, as shown in Figure 3.

A noteworthy feature of I is the MO$_8$ decahedron, which is the first example in metal selenites, although many MO$_8^{11}$ MO$_8^{7}$ MO$_8^{6}$ and MO$_8^{9}$ polyhedra in metal selenites have been reported. Another structural feature of I derives from the fact that there are three kinds of coordination geometries of cadmium (six-, seven- and eight-coordination geometries) coexist in the structure, which is not common in cadmium-containing compounds.

To our knowledge, only one metal selenite-sulfate, in which the metal is molybdenum, has been documented so far, although several metal selenate-sulfates have been reported. Therefore, compound I is the first group-12 metal selenite-sulfates and the second example of metal selenite-sulfates.

For the structure of I, a Flack x parameter of $-0.00(1)$ was calculated, indicating a correct absolute structure. Results of the bond valence calculations indicate that all the cadmium atoms are in +2 oxidation state (Cd1: 1.939, Cd2: 2.001, Cd3: 1.950, Cd4: 2.241). The calculated bond valences are 4.093 and 4.084 for Se1 and Se2, respectively, suggesting that Se1 and Se2 atoms are in +4 oxidation state. All the S atoms are in +6 oxidation state, which is consistent with the bond valence calculation (S1: 6.099, S2: 5.948).

Optical absorption spectrum of compound I reveals an optical gap of 1.62 eV (Figure 4), which suggests that compound I may be a semiconductor and is consistent with the color of the crystals. The gradual slope of the optical absorption edge is indicative of the existence of indirect transition. The energy band gap of I is comparable with those of CdTe (1.5 eV), GaAs (1.4 eV) and CuInS$_2$ (1.55 eV), all of them are highly efficient photovoltaic materials.

In summary, the first example of group-12 selenite-sulfates, Cd$_4$(SeO$_3$)$_2$(SO$_4$)$_2$ (I), has been synthesized via hydrothermal reaction. The transparent and acentric nature of I suggests that it may have nonlinear optical property. Future investigations on the relationship between the crystal structure and the properties in this field are in progress.

**Experimental Section**

All reactants of A.R. grade were obtained commercially and used without further purification. The UV-vis spectra were recorded at room temperature on a computer-controlled PE Lambda 900 UV-vis spectrometer equipped with an integrating sphere in the wavelength range 190-2500 nm. BaSO$_4$ plate was used as a reference (100% reflectance), on which the finely ground powder of the samples were coated.  

![Figure 3](image-url)  
Figure 3. Polyhedral representation of the 3-D structure of I. Yellow: S, green: Se. Numbers are the crystallographically distinct cadmium atoms.

![Figure 4](image-url)  
Figure 4. The solid-state diffuse reflectance spectrum of I.
The absorption spectra were calculated from reflection spectra by the Kubelka-Munk function: \( \alpha = \beta S = (1 - R)^2/2R \), \( \alpha \) is the absorption coefficient, \( S \) is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 \( \mu m \), and \( R \) is the reflectance.

\[
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\text{CdSeO}_2\text{Se}_2\text{SO}_4 & : & 2.421(5) \\
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