

## Synthesis and Structure of a Cadmium Selenite-Sulfate $\text{Cd}_4(\text{SeO}_3)_2(\text{SO}_4)_2$

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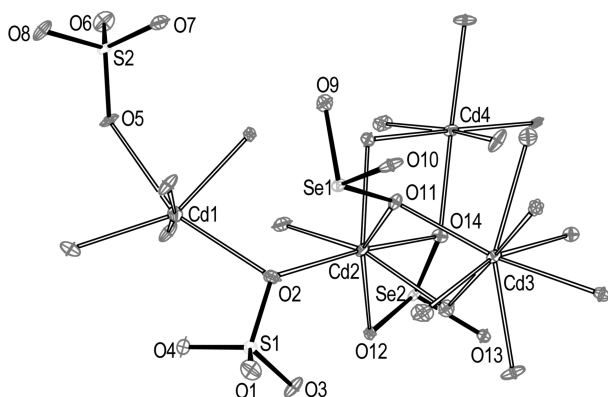
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Metal selenites have been of research interest to scientists in chemistry and materials<sup>1</sup> because of their novel structures and unusual optical, electrical and magnetic properties, which enable metal selenites to be applied as anisotropic semiconductive coatings, photovoltage sources, or photoelectric devices.<sup>2</sup> To date, many metal selenites have been synthesized.<sup>3</sup> 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  $\text{Se}^{\text{IV}}$  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).<sup>4</sup> Herein we describe the synthesis, structure and property of cadmium selenite-sulfate,  $\text{Cd}_4(\text{SeO}_3)_2(\text{SO}_4)_2$  (**1**), which is the first group-12 selenite-sulfates and possesses a novel 3-D structure.

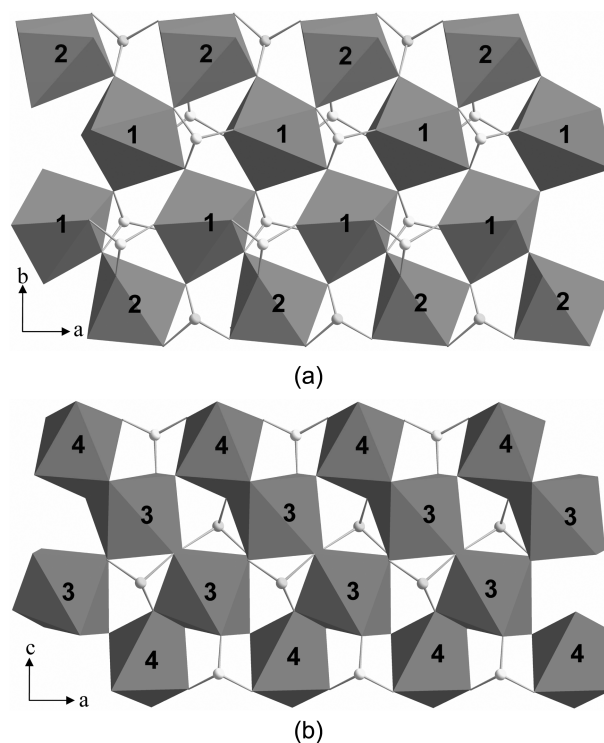
As for the reaction mechanism of preparing the title compound, we proposed a logical process as follows: firstly, the sulfur and selenium were oxidized as  $\text{SO}_4^{2-}$  and  $\text{SeO}_3^{2-}$  groups, respectively, then the  $\text{SO}_4^{2-}$  and  $\text{SeO}_3^{2-}$  groups bound to the cadmium center to form the result compound. Thus, the following equations may be given:  $\text{CdBr}_2 \cdot 4\text{H}_2\text{O} + \text{S} + \text{Se} \rightarrow \text{CdBr}_2 \cdot 4\text{H}_2\text{O} + \text{SO}_4^{2-} + \text{SeO}_3^{2-} \rightarrow \text{Cd}_4(\text{SeO}_3)_2(\text{SO}_4)_2$  (**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



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

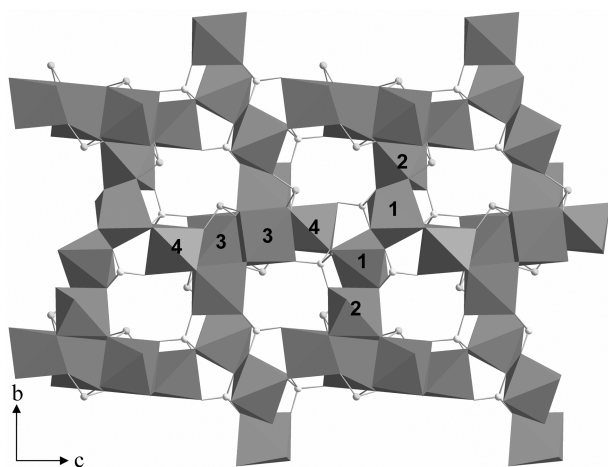
the asymmetric unit of **1** is shown in Figure 1. The four crystallographically independent cadmium atoms are grouped into three kinds of coordination geometries. The Cd1 and Cd4 atoms have a distorted octahedral geometry, coordinated to six oxygen atoms from the  $\text{SeO}_3^{2-}$  and  $\text{SO}_4^{2-}$  groups. Different from Cd1 and Cd4 atoms that are six-coordinated, the Cd2 atom is coordinated by seven oxygen atoms to form 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  $\text{SeO}_3^{2-}$  and  $\text{SO}_4^{2-}$  groups, yielding a decahedron. In **1**, all the bond lengths of Cd-O are in the normal range and comparable with those reported.<sup>3e,5</sup> All the  $\text{Se}^{\text{IV}}$  atoms are three-coordinated by three oxygen atoms in a distorted  $\psi$ - $\text{SeO}_3$  tetrahedral geometry with the fourth site occupied by the lone-pair electrons (Figure 2),



**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.<sup>6</sup> The Se-O distances range between 1.671(4) and 1.713(5) Å, which are comparable to those reported in other metal selenites.<sup>3,7</sup> 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  $\text{SO}_4^{2-}$  moiety. The Cd1-centered octahedra link to each other *via*  $\text{SO}_4^{2-}$  moieties, yielding a Cd1 chain along *a* axis (Figure 2). While the Cd2-centered one-face centred octahedra connect together *via*  $\text{SeO}_3^{2-}$  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  $\text{SO}_4^{2-}$  moieties, yielding a quadruple 2-1-1-2 chain running along *a* axis, as shown in Figure 2(a). Interestingly, in **1**, there is another quadruple 4-3-3-4 chain, which is different from the quadruple 2-1-1-2 chain. The Cd3-centered decahedra connect to each other *via*  $\text{SeO}_3^{2-}$  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*  $\text{SO}_4^{2-}$  moieties, yielding a Cd4 chain along *a* axis. Each Cd3 double chain is connected by two Cd4 chains *via* corner-share, edge-share and  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  moieties, while in the quadruple 4-3-3-4 chain, the polyhedra are interconnected *via* corner-share, edge-share and  $\text{SO}_4^{2-}$  moieties. Each quadruple 2-1-1-2 chain interconnects to four 4-3-3-4 chains through corner-share, edge-share,  $\text{SeO}_3^{2-}$  and  $\text{SO}_4^{2-}$  moieties to build a 3-D structure, as shown in Figure 3.

A noteworthy feature of **1** is the  $\text{MO}_8$  decahedron, which is the first example in metal selenites, although many  $\text{MO}_4$ ,<sup>3f</sup>  $\text{MO}_5$ ,<sup>7</sup>  $\text{MO}_6$ ,<sup>8</sup> and  $\text{MO}_7$ ,<sup>9</sup> polyhedra in metal selenites have been reported. Another structural feature of **1** derives from the fact that there are three kinds of coordination geometries of cadmium (six-, seven- and eight-coordination geometries)



**Figure 3.** Polyhedral representation of the 3-D structure of **1**. Yellow: S, green: Se. Numbers are the crystallographically distinct cadmium atoms.

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,<sup>10</sup> has been documented so far, although several metal selenate-sulfates have been reported.<sup>11</sup> Therefore, compound **1** is the first group-12 metal selenite-sulfates and the second example of metal selenite-sulfates.

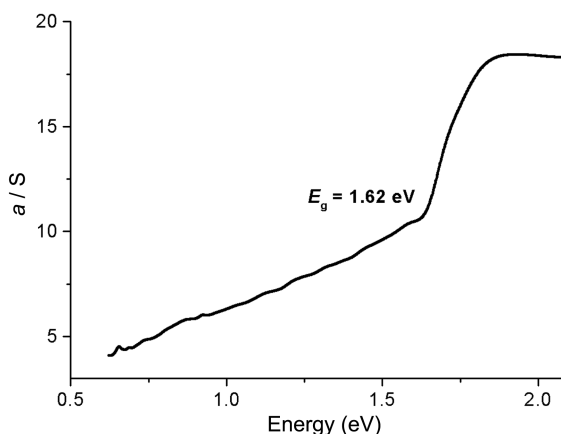
For the structure of **1**, a Flack *x* parameter of  $-0.00(1)$  was calculated, indicating a correct absolute structure.<sup>12</sup> Results of the bond valence calculations indicate that all the cadmium atoms are in +2 oxidation state (Cd1: 1.939, Cd2: 2.001, Cd3: 1.950, Cd4: 2.241).<sup>13</sup> 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 **1** reveals an optical gap of 1.62 eV (Figure 4), which suggests that compound **1** may be a semiconductor and is consistent with the color of the crystals.<sup>14</sup> The gradual slope of the optical absorption edge is indicative of the existence of indirect transition.<sup>15</sup> The energy band gap of **1** is comparable with those of CdTe (1.5 eV), GaAs (1.4 eV) and CuInS<sub>2</sub> (1.55 eV), all of them are highly efficient photovoltaic materials.<sup>16</sup>

In summary, the first example of group-12 selenite-sulfates,  $\text{Cd}_4(\text{SeO}_3)_2(\text{SO}_4)_2$  (**1**), has been synthesized *via* hydrothermal reaction. The transparent and acentric nature of **1** 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.  $\text{BaSO}_4$  plate was used as a reference (100% reflectance), on which the finely ground powder of the samples were coated.



**Figure 4.** The solid-state diffuse reflectance spectrum of **1**.

**Table 1.** Summary of crystallographic data and structure analysis

Formula	Cd <sub>4</sub> O <sub>14</sub> S <sub>2</sub> Se <sub>2</sub>	$V(\text{Å}^3)$	1241.5(3)
$F_w$	895.64	$Z$	4
Crystal system	orthorhombic	Reflections collected	8091
Space group	$P2_12_12_1$	Independent	2190
$a(\text{Å})$	5.3524(7)	$\mu(\text{mm}^{-1})$	13.036
$b(\text{Å})$	14.595(2)	$T(\text{K})$	293(2)
$c(\text{Å})$	15.892(2)	$R1, wR2$	0.0197, 0.0461

**Table 2.** Selected bond lengths (Å)

Cd1-O2	2.421(5)	Cd3-O9#3	2.508(4)
Cd1-O3#1	2.261(5)	Cd3-O9#5	2.506(4)
Cd1-O4#2	2.264(4)	Cd3-O10#3	2.395(4)
Cd1-O5	2.528(4)	Cd3-O11	2.322(4)
Cd1-O8#3	2.302(4)	Cd3-O11#5	2.415(4)
Cd1-O12#1	2.236(4)	Cd3-O13#6	2.431(4)
Cd2-O2	2.263(4)	Cd3-O14#6	2.556(4)
Cd2-O7#3	2.414(4)	Cd4-O1#7	2.233(4)
Cd2-O9#3	2.236(4)	Cd4-O5#8	2.275(4)
Cd2-O11	2.572(4)	Cd4-O8#9	2.332(4)
Cd2-O12	2.455(5)	Cd4-O10#5	2.217(4)
Cd2-O13#1	2.305(4)	Cd4-O13#1	2.343(4)
Cd2-O14	2.440(4)	Cd4-O14	2.230(4)
Cd3-O6#4	2.342(4)		

Symmetry codes: #1  $x-1, y, z$ ; #2  $x-1/2, -y+3/2, -z+3$ ; #3  $x+1, y, z$ ; #4  $-x+3/2, -y+2, z+1/2$ ; #5  $x+1/2, -y+5/2, -z+3$ ; #6  $x-1/2, -y+5/2, -z+3$ ; #7  $-x+5/2, -y+2, z-1/2$ ; #8  $-x+2, y+1/2, -z+5/2$ ; #9  $-x+1, y+1/2, -z+5/2$ .

The absorption spectra were calculated from reflection spectra by the Kubelka-Munk function:<sup>17</sup>  $\alpha/S = (1 - R)^2/2R$ ,  $\alpha$  is the absorption coefficient,  $S$  is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5  $\mu\text{m}$ , and  $R$  is the reflectance.

**Cd<sub>4</sub>(SeO<sub>3</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> (1).** CdBr<sub>2</sub>·4H<sub>2</sub>O (1 mmol, 344 mg), S (2 mmol, 64 mg) and Se (2 mmol, 158 mg) were ground into fine powders in an agate mortar and loaded into a pyrex tube, then added 0.1 mL water. The tube was flame-sealed under a 10<sup>-3</sup> Torr atmosphere and subsequently placed into a furnace. The tube was heated from room temperature to 450 °C in 6 hrs and kept at this temperature for 6 days, followed by cooling to 100 °C at a rate of 6 °C/h to promote crystal growth and then power off.

X-ray diffraction data were collected on Bruker APEX-II X-ray diffractometer with graphite monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ Å}$ ) using  $\phi$  and  $w$  scan techniques. APEX2 software was used for data reduction and multi-scan absorption correction. The structure was solved by the direct methods using the Siemens SHELXTL<sup>TM</sup> Version 5 package of crystallographic software. The difference Fourier maps based on the atomic positions yield all atoms. The structure was refined using a full-matrix least-squares refinement on  $F^2$ . All atoms were refined anisotropically. The summary of crystallographic data and structure analysis is listed in Table 1. The selected bond lengths are listed in Table 2.

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