

Zinc selenium oxochloride,  $\beta$ -Zn<sub>2</sub>-(SeO<sub>3</sub>)Cl<sub>2</sub>, a synthetic polymorph of the mineral sphiiteMats Johansson<sup>a\*</sup> and Karl W. Törnroos<sup>b</sup><sup>a</sup>Inorganic Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden, and  
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Dizinc selenium dichloride trioxide,  $\beta$ -Zn<sub>2</sub>(SeO<sub>3</sub>)Cl<sub>2</sub>, a monoclinic polymorph of the orthorhombic mineral sphiite, has a structure built of distorted ZnO<sub>4</sub>Cl<sub>2</sub> octahedra, ZnO<sub>2</sub>Cl<sub>2</sub> tetrahedra and SeO<sub>3</sub>E tetrahedra (*E* being the 4s<sup>2</sup> lone pair of the Se<sup>IV</sup> ion), joined through shared edges and corners to form charge-neutral layers. The Cl atoms and the Se lone pairs protrude from each layer towards adjacent layers. The main structural difference between the mineral and synthetic polymorphs lies in the packing of the layers.

## Comment

The synthesis and crystal structure determination of the new compound  $\beta$ -Zn<sub>2</sub>(SeO<sub>3</sub>)Cl<sub>2</sub>, (I), a synthetic polymorph of the mineral sphiite (Semenova *et al.*, 1992), is a result of an ongoing investigation of the structural chemistry of selenium and tellurium oxohalides. Transition metal oxohalides containing *p*-element cations, such as Se<sup>IV</sup> or Te<sup>IV</sup>, with stereochemically active lone pairs, frequently show a low-dimensional arrangement of the metal ions. In these compounds, the transition metals tend to bond to both oxygen and the halogen, while the main group elements preferably form bonds only with oxygen. A simple explanation is that the hard Lewis acid Se<sup>IV</sup> prefers the hard Lewis base O<sup>2-</sup>, while the softer Lewis acid Zn<sup>II</sup> accepts both O<sup>2-</sup> and Cl<sup>-</sup> in an oxohalide environment. Some consequences of the different bonding preferences are that only the O atoms bond to both types of cations, and that the Se<sup>IV</sup> lone pairs and the halogen atoms act as 'chemical scissors' by reducing the dimensionality of the crystal structure (Johansson *et al.*, 2000, 2003; Johansson & Törnroos, 2003*a,b*). The aim of the present study was to test this concept of synthesis on the system ZnO<sub>2</sub>-ZnCl<sub>2</sub>-SeO<sub>2</sub>.

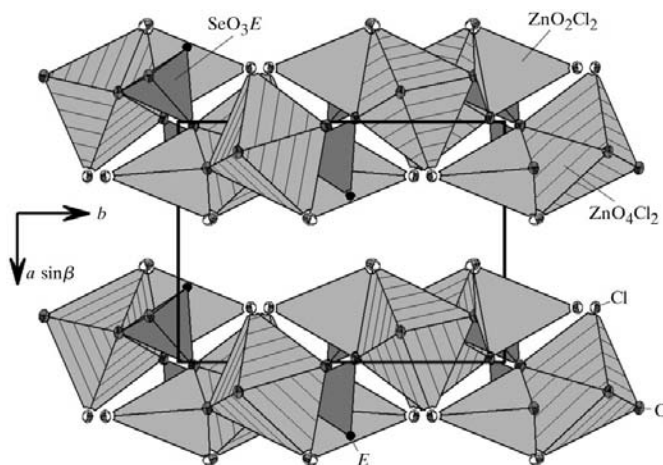
The crystal structure of (I) consists of charge-neutral layers connected only *via* van der Waals interactions (Fig. 1). The Se atom has a typical one-sided threefold coordination owing to the presence of its stereochemically active 4s<sup>2</sup> lone pair (designated *E*), and its coordination polyhedron is therefore a slightly distorted [SeO<sub>3</sub>E] tetrahedron. Atom Zn1 is coordi-

nated by two O atoms and two Cl atoms, forming a distorted [ZnO<sub>2</sub>Cl<sub>2</sub>] tetrahedron, and atom Zn2 is coordinated by four O atoms and two Cl atoms, completing a distorted [ZnO<sub>4</sub>Cl<sub>2</sub>] octahedron (Table 1). The Zn2-Cl2 distance is 2.4306 (4) Å, while the Zn2-Cl1 distance is 2.7645 (5) Å. The latter is quite long, but bond-valence-sum calculations (Brown & Altermatt, 1985) suggest that atom Cl2 should be treated as coordinated by the Zn atom.

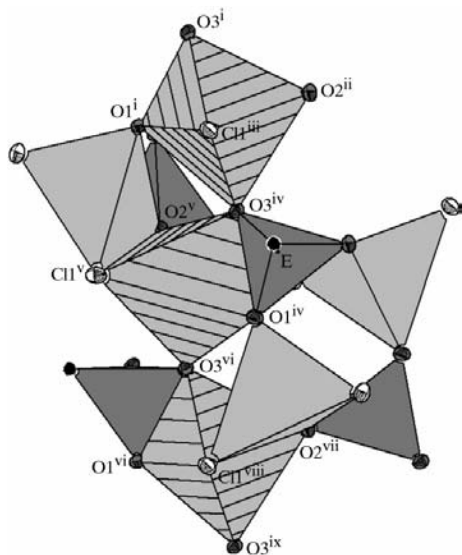
The three different building units, *viz.* the [Zn1O<sub>2</sub>Cl<sub>2</sub>], [Zn2O<sub>4</sub>Cl<sub>2</sub>] and [SeO<sub>3</sub>E] groups, are connected to form infinite (010) layers. Each [ZnO<sub>4</sub>Cl<sub>2</sub>] polyhedron is linked to two others by corner sharing, forming infinite [001] chains within the layers. The chains are separated by [ZnO<sub>2</sub>Cl<sub>2</sub>] and [SeO<sub>3</sub>E] groups, and each [ZnO<sub>4</sub>Cl<sub>2</sub>] polyhedron shares two corners and one edge with three [ZnO<sub>2</sub>Cl<sub>2</sub>] groups, as well as two corners and one edge with three [SeO<sub>3</sub>E] groups (Fig. 2).

The stereochemically active Se lone pairs are located between the layers, pointing in between the protruding Cl atoms of the opposite layer. The shortest cation-anion distances between adjacent layers [Se1...Cl1 = 3.5145 (5) Å, Zn1...Cl1 = 3.6827 (5) Å, Zn1...Cl2 = 4.7786 (5) Å and Zn2...Cl2 = 5.4849 (7) Å] are similar to, or larger than, the cation-cation separations within the layers [Se1...Zn2 = 2.9404 (3) Å, Zn1...Zn2 = 3.2319 (3) Å, Se1...Zn1 = 3.3241 (4) Å, Zn2...Zn2 = 3.8734 (4) Å and Zn1...Zn1 = 4.1349 (5) Å; symmetry codes as in Table 1]. The long inter-layer distances imply that the layers are held together only by dispersion forces. Assuming an Se-E radius of 1.22 Å (Galy *et al.*, 1975), the fractional coordinates for the lone pair *E* (*x* = 0.69, *y* = 0.47, *z* = 0.10) yield E...Cl1 and E...Cl2 contact distances of ~2.72 and ~2.71 Å, respectively.

The orthorhombic (*Pccn*) mineral sphiite shows the same connectivity of the building units within the layers as the synthetic form (I). The main structural difference between the two polymorphs is that every second layer in the mineral structure is rotated 180° around the *a* axis; the layer rotation results in a doubling of the *a* axis.



**Figure 1**  
The layer structure of (I), viewed along [001]. Atomic displacement parameters are given at the 50% probability level. O and Cl atoms are dark grey and white, respectively, and lone pairs (*E*) are black spheres of arbitrary radius.



**Figure 2**

Connectivity of the  $\text{Zn}_2\text{O}_4\text{Cl}_2$  octahedra (striped light grey),  $\text{ZnO}_2\text{Cl}_2$  tetrahedra (light grey) and  $\text{SeO}_3\text{E}$  tetrahedra (dark grey) in (I). [Symmetry codes: (i)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $x - 1, y, z + 1$ ; (iii)  $x - 1, y, z + 1$ ; (iv)  $-x + 1, -y + 1, -z + 1$ ; (v)  $x - 1, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (vi)  $-x + 1, -x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (vii)  $x - 1, y, z$ ; (viii)  $x - 1, y, z$ ; (ix)  $-x + 1, -y + 1, -z$ .]

Three other compounds are quite similar to the mineral sphiite, *viz.*  $\text{CuZn}(\text{TeO}_3)\text{Cl}_2$  (Johnsson & Törnroos, 2003*b*),  $\text{Zn}_2(\text{TeO}_3)\text{Cl}_2$  (Johnsson & Törnroos, 2003*a*) and  $\text{Co}_2(\text{TeO}_3)\text{Br}_2$  (Becker *et al.*, 2006). They all crystallize in the orthorhombic space group *Pccn*. The main structural difference is that the octahedron around the atom corresponding to Zn2 is so distorted that it should rather be regarded as a square pyramid according to the idea that, for a ligand to be regarded as bonded, it should contribute more than 4% of the cation valence (Brown, 2002). A fourth related compound,  $\text{Co}_2(\text{TeO}_3)\text{Cl}_2$  (Becker *et al.*, 2006), crystallizes in the monoclinic space group *P2<sub>1</sub>/m*. However, instead of tetrahedral and octahedral coordination of the metal cations, it contains two types of distorted octahedra, resulting in a completely different connectivity within the layers.

## Experimental

Compound (I) was synthesized by chemical transport reactions in sealed evacuated soda-glass tubes.  $\text{ZnCl}_2$  (Avocado Research Chemicals Ltd, 98+%),  $\text{ZnO}$  (ABCR, 99+%) and  $\text{SeO}_2$  (ABCR, 99+%) were used as starting materials. Equimolar amounts of  $\text{ZnCl}_2$  (0.135 g),  $\text{ZnO}$  (0.081 g) and  $\text{SeO}_2$  (0.110 g) were mixed in a mortar and placed in a glass tube (length  $\sim 5$  cm), which was evacuated and heated at 700 K for 72 h in a muffle furnace. The product appeared as colourless transparent plate-like single crystals, with a maximum size of 0.5 mm, and as a powder. The crystals are hygroscopic. The synthesis product was characterized in a scanning electron microscope (SEM, Jeol 820) with an energy-dispersive spectrometer (EDS, LINK AN10000) on ten different single crystals. Analysis found: Zn 38.0 (17), Se 20.8 (7), Cl 41.2 (23)%. No Si originating from the glass tube was detected.

## Crystal data

$\text{Zn}_2(\text{SeO}_3)\text{Cl}_2$   
 $M_r = 328.60$   
 Monoclinic,  $P2_1/c$   
 $a = 7.6699$  (8) Å  
 $b = 10.2612$  (11) Å  
 $c = 7.6571$  (8) Å  
 $\beta = 100.004$  (2)°

$V = 593.47$  (11) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 15.02$  mm<sup>-1</sup>  
 $T = 123$  (2) K  
 $0.26 \times 0.24 \times 0.02$  mm

## Data collection

Bruker SMART 2K CCD diffractometer  
 Absorption correction: numerical (*SHELXTL/PC*; Sheldrick, 2001*b*)  
 $T_{\min} = 0.026$ ,  $T_{\max} = 0.722$

10582 measured reflections  
 2147 independent reflections  
 2015 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.023$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.013$   
 $wR(F^2) = 0.032$   
 $S = 1.08$   
 2147 reflections

74 parameters  
 $\Delta\rho_{\max} = 0.46$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.39$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

Se1—O3	1.7032 (9)	Zn2—O3 <sup>xii</sup>	2.0075 (9)
Se1—O1	1.7074 (9)	Zn2—O2 <sup>xiii</sup>	2.0487 (10)
Se1—O2	1.7146 (10)	Zn2—O1	2.1265 (10)
Zn1—O1 <sup>x</sup>	1.9833 (9)	Zn2—O3	2.1503 (9)
Zn1—O2	2.0308 (10)	Zn2—Cl2	2.4306 (4)
Zn1—Cl1	2.2225 (4)	Zn2—Cl1 <sup>xiii</sup>	2.7645 (5)
Zn1—Cl2	2.2255 (4)		

Symmetry codes: (x)  $-x + 2, -y + 1, -z + 1$ ; (xi)  $x, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (xii)  $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$ .

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2001*a*); molecular graphics: *SHELXTL/PC* (Sheldrick, 2001*b*); software used to prepare material for publication: *DIAMOND* (Brandenburg, 2006) and *PLATON* (Spek, 2001).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3038). Services for accessing these data are described at the back of the journal.

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