

# Crystal Chemistry of Selenates with Mineral-Like Structures. IV. Crystal Structure of $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$ , a New Compound with a Mixed Framework of the Variscite Type

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**Abstract**—The crystal structure of a new compound  $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$  (orthorhombic, *Pbca*,  $a = 9.0411(13)$ ,  $b = 10.246(2)$ ,  $c = 10.3318(15)$  Å,  $V = 957.1(3)$  Å<sup>3</sup>) has been solved by direct methods and refined to  $R_1 = 0.033$  on the basis of 1076 observed reflections with  $|F_{hkl}| \geq 4\sigma|F_{hkl}|$ . The structure contains one independent  $\text{Zn}^{2+}$  cation coordinated by two water molecules and four oxygen atoms of selenate group. The only independent  $(\text{SeO}_4)^{2-}$  tetrahedral oxoanion is tetradentate, sharing its corners with four adjacent  $[\text{Zn}^{2+}\text{O}_2(\text{H}_2\text{O})_4]^{2+}$  octahedrons. The structure can be described as consisting of heteropolyhedral sheets parallel to the (001) plane and linked together into a three-dimensional network. The compound belongs to the variscite structure type and is the first structurally characterized selenate of this group.

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## INTRODUCTION

The first three papers of this series (Krivovichev, 2006a, 2006b, 2006c) were devoted to the crystal structures of mineral-like selenates with low-dimensional complexes. For example, in the structures of  $[\text{Al}(\text{H}_2\text{O})_6]_2(\text{SeO}_4)_3$  and  $[\text{Al}(\text{H}_2\text{O})_6](\text{SeO}_4)(\text{NO}_3)(\text{H}_2\text{O})$ ,  $[\text{Al}^{3+}(\text{H}_2\text{O})_6]^{3+}$  octahedrons and  $(\text{SeO}_4)^{2-}$  tetrahedrons are linked only by hydrogen bonds and do not polymerize with one another. In contrast to aluminoselenates, the structure of  $[\text{Mg}(\text{H}_2\text{O})_4(\text{SeO}_4)]_2(\text{H}_2\text{O})$  contains apex-sharing Mg octahedrons and  $(\text{SeO}_4)^{2-}$  tetrahedrons, which form strongly bent simple chains with the various polyhedrons successively alternating. This publication is devoted to the crystal structure of the newly synthesized compound  $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$ , in which octahedrons and tetrahedrons are linked to form a three-dimensional framework.

## EXPERIMENTAL

Crystals of  $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$  were obtained by means of evaporation from an aqueous solution, which was prepared by dissolving Zn oxide in a 40%  $\text{H}_2\text{SeO}_4$  solution. The single crystal selected for structural analysis was mounted in a STOE IPDS II diffractometer equipped with a flat image plate detector. The unit cell parameters were determined and refined using the least squares technique (Table 1). A correction for absorption was introduced with regard for the shape of the crystal. The structure was solved by direct methods and refined to  $R_1 = 0.033$  ( $wR_2 = 0.075$ ) for 1076 reflections

with  $|F_{hkl}| \geq 4\sigma|F_{hkl}|$ . The final model involved the coordinates and anisotropic displacement parameters for the Zn, Se, and O atoms (Table 2). We managed to localize all positions of hydrogen atoms by using the model of superimposed bonds: the O–H bond lengths were fixed at  $0.96 \pm 0.02$  Å. Table 3 lists the cation–anion bond

**Table 1.** Crystallographic data and refinement parameters for the crystal structure of  $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$

|                                        |                                |
|----------------------------------------|--------------------------------|
| $a$ (Å)                                | 9.0411(13)                     |
| $b$ (Å)                                | 10.246(2)                      |
| $c$ (Å)                                | 10.3318(15)                    |
| $V$ (Å <sup>3</sup> )                  | 957.1(3)                       |
| space group                            | <i>Pbca</i>                    |
| $\mu$ (cm <sup>−1</sup> )              | 12.678                         |
| $Z$                                    | 8                              |
| $D_{\text{calc}}$ (g/cm <sup>3</sup> ) | 3.392                          |
| Crystal size (mm)                      | $0.21 \times 0.20 \times 0.14$ |
| $\lambda$ (Å)                          | 0.71073                        |
| Total Ref.                             | 7558                           |
| Unique Ref.                            | 1158                           |
| Unique $ F_0  \geq 4\sigma_F$          | 1076                           |
| $R_{\text{int}}$                       | 0.093                          |
| $R_\sigma$                             | 0.048                          |
| $R_1$                                  | 0.033                          |
| $wR_2$                                 | 0.075                          |
| $S$                                    | 1.023                          |

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**Table 2.** Atomic coordinates and displacement parameters ( $\text{\AA}^2$ ) for the crystal structure of  $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$ 

| Atom | <i>x</i>   | <i>y</i>   | <i>z</i>     | $U_{\text{eq}}$ | $U_{11}$    |
|------|------------|------------|--------------|-----------------|-------------|
| Se   | 0.03414(5) | 0.63943(4) | 0.15244(4)   | 0.0099(2)       | 0.0099(3)   |
| Zn   | 0.16041(6) | 0.33082(5) | 0.12911(5)   | 0.0145(2)       | 0.0146(3)   |
| O1   | 0.0031(4)  | 0.4830(3)  | 0.1459(3)    | 0.0157(6)       | 0.0138(14)  |
| O2   | 0.0061(4)  | 0.6961(3)  | 0.2995(3)    | 0.0177(7)       | 0.0172(16)  |
| O3   | 0.2057(4)  | 0.6647(3)  | 0.1078(3)    | 0.0180(7)       | 0.0136(16)  |
| O4   | 0.2305(4)  | 0.3895(3)  | 0.3078(3)    | 0.0196(7)       | 0.0188(17)  |
| O5   | −0.0807(4) | 0.7134(3)  | 0.0531(3)    | 0.0185(7)       | 0.0230(17)  |
| O6   | 0.3409(4)  | 0.4313(4)  | 0.0470(4)    | 0.0258(8)       | 0.0216(18)  |
| H1   | 0.190(9)   | 0.321(6)   | 0.361(6)     | 0.05(2)         | 0.0099(3)   |
| H2   | 0.379(8)   | 0.399(7)   | −0.034(4)    | 0.05(2)         | 0.0146(3)   |
| H3   | 0.334(3)   | 0.408(9)   | 0.327(7)     | 0.05(2)         | 0.0138(14)  |
| H4   | 0.388(14)  | 0.513(7)   | 0.073(13)    | 0.14(5)         | 0.0172(16)  |
| Atom | $U_{22}$   | $U_{33}$   | $U_{23}$     | $U_{13}$        | $U_{12}$    |
| Se   | 0.0069(2)  | 0.0127(2)  | −0.00036(13) | 0.00017(13)     | 0.00024(14) |
| Zn   | 0.0122(3)  | 0.0166(3)  | −0.00178(18) | −0.00170(19)    | 0.0012(4)   |
| O1   | 0.0076(15) | 0.0259(16) | 0.0006(11)   | 0.0006(12)      | −0.0008(13) |
| O2   | 0.0190(16) | 0.0168(14) | −0.0021(12)  | 0.0015(12)      | 0.0039(13)  |
| O3   | 0.0104(14) | 0.0299(17) | −0.0026(12)  | 0.0064(13)      | −0.0015(12) |
| O4   | 0.0220(17) | 0.0181(14) | 0.0005(12)   | −0.0014(13)     | −0.0048(14) |
| O5   | 0.0159(15) | 0.0166(14) | −0.0034(11)  | −0.0043(12)     | 0.0100(14)  |
| O6   | 0.0174(17) | 0.038(2)   | 0.0044(15)   | 0.0083(15)      | −0.0045(15) |
| H1   | 0.0069(2)  | 0.0127(2)  | −0.00036(13) | 0.00017(13)     | 0.00024(14) |
| H2   | 0.0122(3)  | 0.0166(3)  | −0.00178(18) | −0.00170(19)    | 0.0012(2)   |
| H3   | 0.0076(15) | 0.0259(16) | 0.0006(11)   | 0.0006(12)      | −0.0008(13) |
| H4   | 0.0190(16) | 0.0168(14) | −0.0021(12)  | 0.0015(12)      | 0.0039(13)  |

lengths in the structure, and Table 4 summarizes the principal geometric parameters of the hydrogen bonding system, which were calculated from the refined coordinates of hydrogen atoms.

## RESULTS

The structure of  $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$  contains one crystallographically independent cation  $\text{Zn}^{2+}$ . Figure 1 shows its coordination in a sphere 5 Å in radius. As can be seen, the  $\text{Zn}^{2+}$  cation is coordinated by two water molecules in *cis* position relative to each other and by the four oxygen atoms of adjacent selenate groups. The only symmetrically independent tetrahedral oxoanion  $(\text{SeO}_4)^{2-}$  is tetradentate, i.e., is linked with four adjacent  $[\text{Zn}^{2+}\text{O}_2(\text{H}_2\text{O}_4)]^{2+}$  octahedrons.

Figure 2a shows a projection of the structure on the (100) plane. The structure can be viewed as consisting of mixed heteropolyhedral sheets, which are shown in Fig. 2b. The sheets are parallel to the (001) plane and are linked into a three-dimensional framework. The topology of this framework can be most easily compre-

hended using the graphical approach to the topological description of heteropolyhedral complexes (this approach was proposed in our earlier publications (Krivovichev, 2004, 2005)). In application to the structure in question, this approach implies (1) the symbolic representation of tetrahedrons and octahedrons as black and white apexes, respectively, and (2) the linking of two apexes by a line only if the polyhedrons corresponding to these apexes share an oxygen atom. The

**Table 3.** Cation–anion bond length ( $\text{\AA}$ ) for the crystal structure of  $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$ 

|        |          |                      |          |
|--------|----------|----------------------|----------|
| Se–O1  | 1.629(3) | Zn–H <sub>2</sub> O4 | 2.042(3) |
| Se–O3  | 1.639(3) | Zn–O5                | 2.066(3) |
| Se–O5  | 1.645(3) | Zn–O3                | 2.101(3) |
| Se–O2  | 1.646(3) | Zn–H <sub>2</sub> O6 | 2.107(4) |
| ⟨Se–O⟩ | 1.640    | Zn–O1                | 2.118(3) |
|        |          | Zn–O2                | 2.172(3) |
|        |          | ⟨Zn–O⟩               | 2.101    |

**Table 4.** Geometric parameters of the hydrogen bonding system in the crystal structure of  $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$ 

| D–H                      | $d(\text{D–H}), \text{\AA}$ | $d(\text{H}\cdots\text{A}), \text{\AA}$ | $\angle\text{DHA}, \text{\AA}$ | $d(\text{D}\cdots\text{A}), \text{\AA}$ | A  |
|--------------------------|-----------------------------|-----------------------------------------|--------------------------------|-----------------------------------------|----|
| $\text{H}_2\text{O4–H1}$ | 0.963                       | 1.726                                   | 167.62                         | 2.675                                   | O5 |
| $\text{H}_2\text{O4–H3}$ | 0.973                       | 1.737                                   | 164.54                         | 2.688                                   | O1 |
| $\text{H}_2\text{O6–H2}$ | 0.967                       | 2.230                                   | 170.29                         | 3.168                                   | O2 |
| $\text{H}_2\text{O6–H4}$ | 0.973                       | 2.533                                   | 164.43                         | 3.479                                   | O2 |

Note: D is the donor of the hydrogen bond (a water molecule), A is the acceptor of the hydrogen bond (a water molecule or an oxygen atom of the selenate group), and  $\angle\text{DHA}$  is the angle between the D–H and  $\text{H}\cdots\text{A}$  directions at the hydrogen atom.

result of this procedure is a black-and-white graph whose topology describes that of the structural complex. For example, the black-and-white graph displayed in Fig. 2c symbolizes the topology of the linkage of the octahedrons and tetrahedrons within the sheet shown in Fig. 2b. Finally, it is important to elucidate the configuration of the three-dimensional framework in the structure. This can be readily done by designating the directions of bonds between sheets in the two-dimensional graph (U for up and D for down) relative to the graph plane. As can be seen, the graph in Fig. 2c is made up of hexagonal rings with bonding oriented as DUDDUU.

Fig. 2d shows the linkage structure of the two-dimensional graph with an adjacent graph into a three-dimensional structure, which describes the topology of the mixed framework of the  $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$  structure.

## DISCUSSION

The compound  $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$  belongs to the variscite structural type, which comprises several other minerals and inorganic compounds with the general formula  $\text{M}(\text{TO}_4)(\text{H}_2\text{O})_2$  (where  $\text{M} = \text{Fe}, \text{Al}, \text{Ga}, \text{or In}$  and  $\text{T} = \text{P or As}$ ). This type also includes such minerals

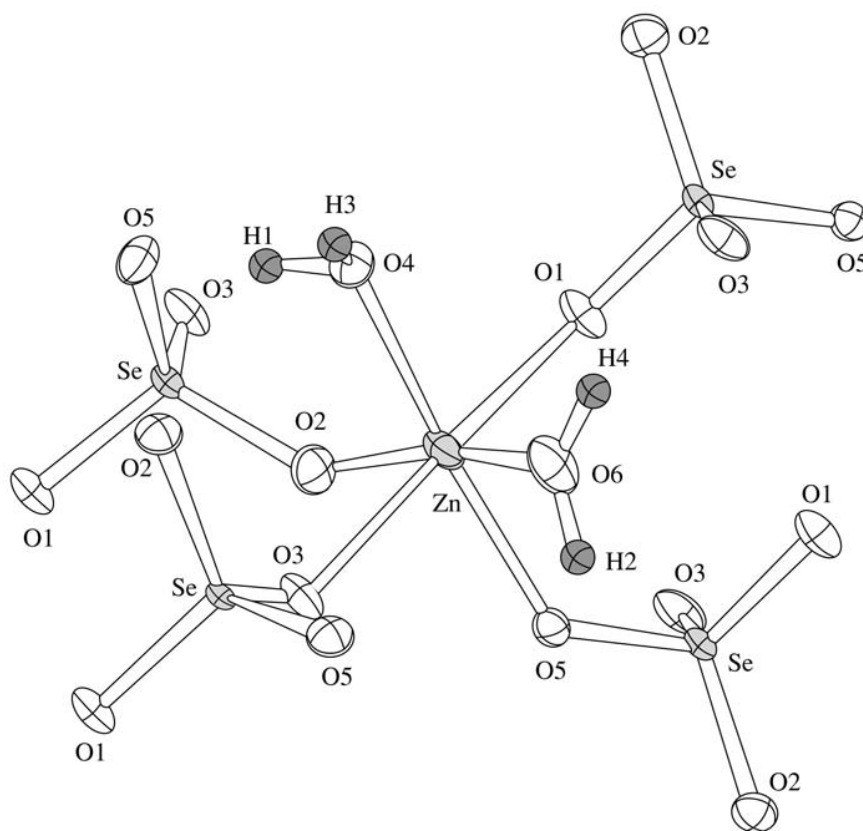


**Fig. 1.** Coordination of the  $\text{Zn}^{2+}$  cation within a sphere 5 Å in radius in the structure of  $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$ . Thermal vibration ellipsoids are drawn at a 50% probability level.

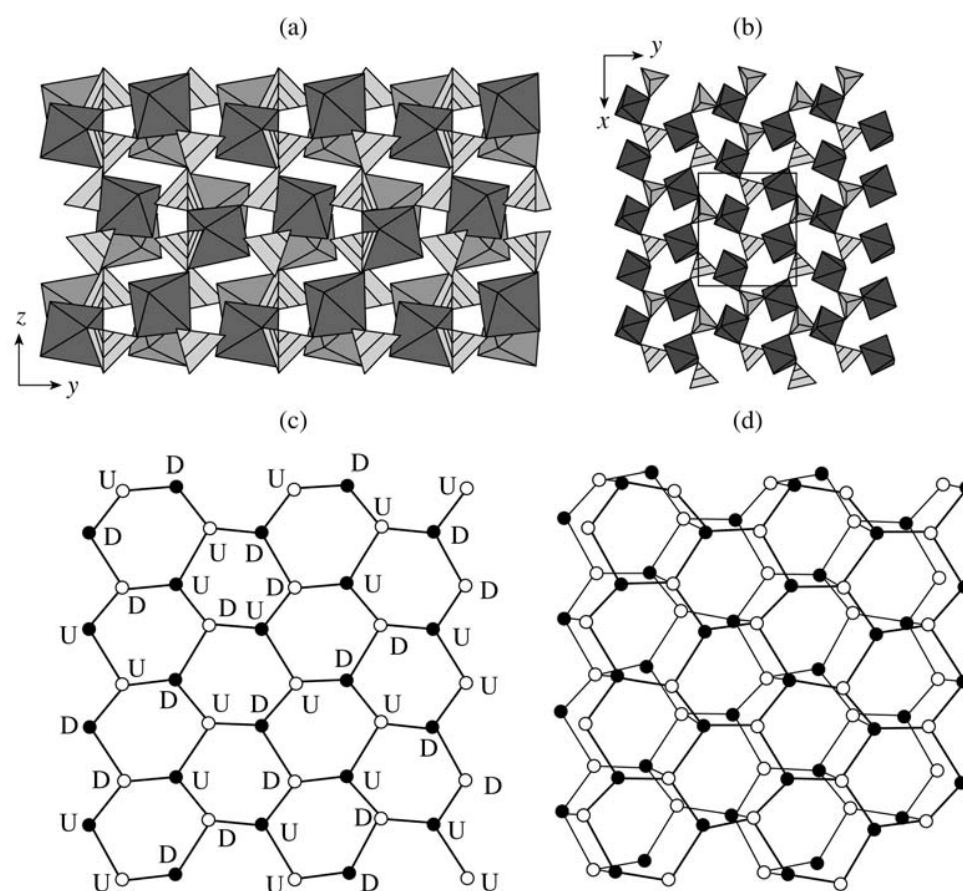


**Fig. 2.** (a) Projection of the  $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$  crystal structure on the (100); (b) sheet of octahedra and tetrahedra parallel to the (001) plane and (c) its black-and-white graph with the direction of links to neighboring sheets; (d) schematic representation of the linkage of adjacent two-dimensional graphs into a three-dimensional graph.

as scorodite, mansfieldite, yanomaite, variscite itself, and strengite. The crystallographic parameters of these compounds are listed in Table 5. It should be mentioned that the occurrence of hydrous selenates of bivalent

metals isostructural to scorodite was first described as long ago as 1939 (Kokkoros, 1939), but the compound  $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$  is the first in this group for which direct structural data were obtained. Detailed topologi-

**Table 5.** Crystallographic parameters for compounds of general composition  $\text{M}(\text{TO}_4)(\text{H}_2\text{O})_2$ , belonging to the scorodite structural type (space group  $Pbca$ )

| Mineral     | Formula                                         | $a$ (Å) | $b$ (Å) | $c$ (Å) | Reference            |
|-------------|-------------------------------------------------|---------|---------|---------|----------------------|
| Scorodite   | $\text{Fe}(\text{AsO}_4)(\text{H}_2\text{O})_2$ | 10.278  | 8.937   | 9.996   | Hawthorne, 1976      |
| Yanomaite   | $\text{In}(\text{AsO}_4)(\text{H}_2\text{O})_2$ | 10.478  | 9.100   | 10.345  | Tang et al., 2001    |
| Mansfeldite | $\text{Al}(\text{AsO}_4)(\text{H}_2\text{O})_2$ | 10.116  | 8.822   | 9.825   | Harrison, 2000       |
| Variscite   | $\text{Al}(\text{PO}_4)(\text{H}_2\text{O})_2$  | 9.882   | 8.561   | 9.630   | Kniep et al., 1977   |
| Strengite   | $\text{Fe}(\text{PO}_4)(\text{H}_2\text{O})_2$  | 9.867   | 8.705   | 10.097  | Song et al., 2002    |
|             | $\text{Ga}(\text{PO}_4)(\text{H}_2\text{O})_2$  | 9.926   | 8.619   | 9.762   | Loiseau et al., 1998 |
|             | $\text{Ga}(\text{AsO}_4)(\text{H}_2\text{O})_2$ | 10.160  | 8.862   | 9.941   | Dick, 1997           |
|             | $\text{In}(\text{PO}_4)(\text{H}_2\text{O})_2$  | 10.327  | 8.842   | 10.187  | Xu et al., 1995      |
|             | $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$ | 10.332  | 9.041   | 10.246  | This publication     |

Note: The unit cell parameters of  $\text{Zn}(\text{SeO}_4)(\text{H}_2\text{O})_2$  are exchanged to conform to those of other members of the group.

cal descriptions of frameworks in the structure of variscite and other aluminophosphates were presented by Bennett et al. (1986).

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