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$SrZn(SeO_3)_2$ Containing Novel ZnO_{4+2} Bicapped Tetrahedra

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Introduction

The structures of inorganic solids containing the $[Se^{IV}O_3]^{2-}$ selenite ion are of interest because of the asymmetric coordination polyhedron adopted by this species.[1] This effect can be rationalized[2] in terms of the stereochemically active (nonbonded) lone pair of electrons possessed by Se^{IV}, which invariably leads to pyramidal coordination for the $[SeO_3]^{2-}$ species. It is hoped that this may lead to a tendency for selenites to crystallize in noncentrosymmetric structures with consequent interesting physical properties, such as nonlinear optical second harmonic generation (SHG).[3] We have recently observed nonregular coordination environments for Zn^{2+} in combination with selenite ions. One of the ZnO_6 octahedra in $Zn_3(SeO_3)_3{\cdot}H_2O$[4] is extremely distorted, with four short bonds of normal length (i.e., roughly corresponding to a Zn−O distance of about 2.05 Å as expected on the basis of ionic radii sums)[5] and two very long bonds ($d > 2.45$ Å) in the cis configuration. In the organically templated selenite $(CN_3H_6)_4[Zn_3(SeO_3)_5]$,[6] one of the ZnO_4 tetrahedra is highly distorted with an O−Zn−O bond angle of greater than 130°, although the Zn−O bond lengths are normal. To some extent, these zinc coordination environments can be understood in terms of the way the ZnO_6 or ZnO_4 and SeO_3 groups are fused together and the fact that Zn^{2+} lacks any strong preference for a particular coordination environment.[4] Another example of novel zinc geometry occurs in the layered phases $A_2Zn_3As_2O_2$ (A = Ba or Sr) which contain square-planar ZnO_4 moieties.[7]

Here, we report the hydrothermal synthesis and single-crystal structure of the first strontium zinc selenite, $SrZn(SeO_3)_2$. This phase contains a new type of zinc coordination that can be described as a “bicapped tetrahedron”.

Experimental Section

Synthesis and Characterization. $SrCO_3$ (0.300 g, 2 mmol), ZnO (0.162 g, 4 mmol), SeO_2 (0.445 g, 4 mmol), and 8 mL of H_2O were sealed in a 23-mL capacity Teflon-lined steel bomb. The mixture was heated at 150 °C for 7 days. Upon removal from the oven and cooling over 1 day, the resulting solids (wt = 0.64 g) were recovered by vacuum filtration and washed with water. These consisted of colorless ingot-shaped crystals of the title compound (visually estimated yield = 30% of the mixture) and peach and white powders. EDAX measurements confirmed the 1:1:2 Sr/Zn/Se ratio in the crystalline phase and indicated that ZnO and possibly $ZnSeO_3$ were also present in the mix. A suitable single crystal of $SrZn(SeO_3)_2$ (ca. 0.14 × 0.03 × 0.03 mm) was then mounted for structural analysis.

Table 1. Crystallographic Parameters for $SrZn(SeO_3)_2$

$SrSe_2ZnO_6$	fw 406.92
monoclinic	space group $P2_1/n$ (No. 14)
$a = 4.4836(3)$ Å	$b = 14.7576(10)$ Å
$c = 9.4267(7)$ Å	$\beta = 95.273(2)°$
$V = 621.08(8)$ Å^3	$Z = 4$
$\lambda = 0.710\,73$ Å	$\rho_{calc} = 4.35$ g/cm^3
$\mu = 241.3$ cm^{-1}	R1^a = 0.047
wR2^b = 0.109	

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

Table 2. Selected Geometrical Data (Å, deg) for $SrZn(SeO_3)_2$[a]

Zn1−O1a	1.960(5)	O6−Zn1−O3	169.2(2)
Zn1−O4b	2.017(5)	O2−Zn1−O3	67.83(17)
Zn1−O6	2.045(5)	O1a−Zn1−O4	89.49(18)
Zn1−O2	2.062(5)	O4b−Zn1−O4	151.5(2)
Zn1−O3	2.443(6)	O6−Zn1−O4	64.77(17)
Zn1−O4	2.607(5)	O2−Zn1−O4	80.39(17)
O1a−Zn1−O4b	109.1(2)	O3−Zn1−O4	117.43(18)
O1a−Zn1−O6	110.7(2)	Se1−O1−Zn1c	126.1(3)
O4b−Zn1−O6	88.02(19)	Se1−O2−Zn1	104.0(2)
O1a−Zn1−O2	136.3(2)	Se1−O3−Zn1	91.1(2)
O4b−Zn1−O2	98.8(2)	Se2−O4−Zn1d	117.7(2)
O6−Zn1−O2	103.0(2)	Se2−O4−Zn1	88.13(19)
O1a−Zn1−O3	80.07(19)	Zn1d−O4−Zn1	151.5(2)
O4b−Zn1−O3	87.7(2)	Se2−O6−Zn1	110.3(2)

[a] Symmetry transformations used to generate equivalent atoms: (a) $x - 1/2, -y + 3/2, z - 1/2$; (b) $x + 1, y, z$; (c) $x + 1/2, -y + 3/2, z + 1/2$; (d) $x - 1, y, z$.

Single-Crystal X-ray Study. The structure of $SrZn(SeO_3)_2$ was determined by standard methods, using a Bruker SMART 1000 CCD area detector diffractometer (Mo Kα radiation, $\lambda = 0.710\,73$ Å, $T = 25 \pm 2$ °C). An empirical absorption correction (range of transmission factors = 0.520−0.928) was applied with SADABS.[8] The structure was solved by direct methods using SHELXS-97[9] and refined by full-matrix least-squares analysis using SHELXL-97,[9] as summarized in Table 1. The largest difference Fourier peak (2.85 e Å^{-3}) is close to selenium. The crystallochemical considerations and the charge-balancing criterion did not indicate the need for any protons to be included in this structure.

Results and Discussion

Selected bond-distance and bond-angle data for $SrZn(SeO_3)_2$ are presented in Table 2, and the structure is illustrated in Figures 1 and 2. There are 10 unique atoms in $SrZn(SeO_3)_2$, all of which occupy general positions. The zinc atom has four nearest-neighbor [d(Zn−O) < 2.06 Å] O atoms in an approximately tetrahedral arrangement, although the O1−Zn1−O2 bond angle of 136.3(2)° is particularly obtuse. There are two further O atoms associated with zinc, with d(Zn−O) = 2.44 and 2.61 Å. These distances are far longer than the nominal ionic radii sum[5] of 1.96 Å for tetrahedral Zn^{2+} and O^{2-} but are much shorter than the typical nonbonded contacts of 3 Å or more. If only the four nearest-neighbor O atoms are considered, the bond valence sum[10] (BVS) of 1.71 for Zn is significantly lower than the expected 2.00. Including the two more distant oxygen atoms

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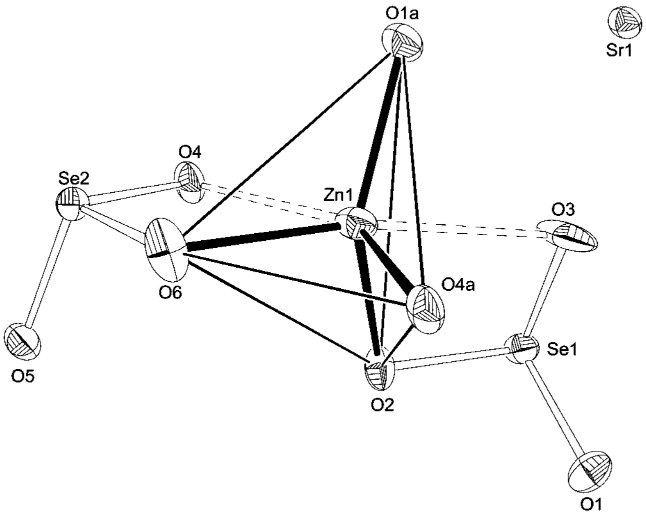

Figure 1. Fragment of $SrZn(SeO_3)_2$ showing the atom labeling scheme (50% thermal ellipsoids). O1a and O4b are symmetry-generated atoms (see Table 2). The four nearest-neighbor O atoms around zinc (O1a, O2, O4a, and O6) form a distorted tetrahedron, as outlined with thin black lines. The long Zn−O3 and Zn−O4 bonds (dashed lines) project through the tetrahedral faces defined by atoms O1a, O2, and O4a and atoms O1a, O2, and O6, respectively.

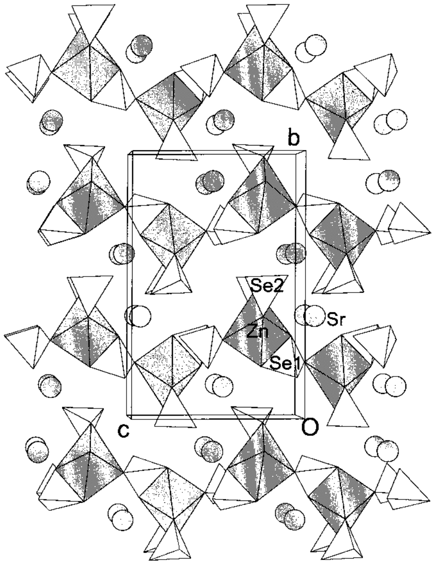

Figure 2. Packing diagram for $SrZn(SeO_3)_2$ viewed down [100] in a polyhedral representation. The SeO_3 pyramids (light shading) are represented by SeO_3E tetrahedra, where the dummy atom E, geometrically placed at 1.0 Å from selenium, represents the Se^{IV} lone pair. Strontium cations are represented by spheres of an arbitrary radius.

raises the Zn BVS to 1.93. This novel geometry can be visualized (Figure 1) as a bicapped tetrahedron or a ZnO_{4+2} grouping. The validity of regarding this geometry as fundamentally tetrahedral is supported by an IVTON[11] analysis of the displacement of the zinc atom from its geometric best center. For the four nearest-neighbor O atoms, the Zn displacement is only 0.06 Å, whereas for the intrinsically asymmetric situation including all six of the O neighbors, the Zn atom is displaced off-center by 0.32 Å. Both a short and a long Zn−O vertex (O2 + O3 and O4 + O6, respectively) serve to fuse the zinc atom to two nearby selenite groups by "edge sharing".

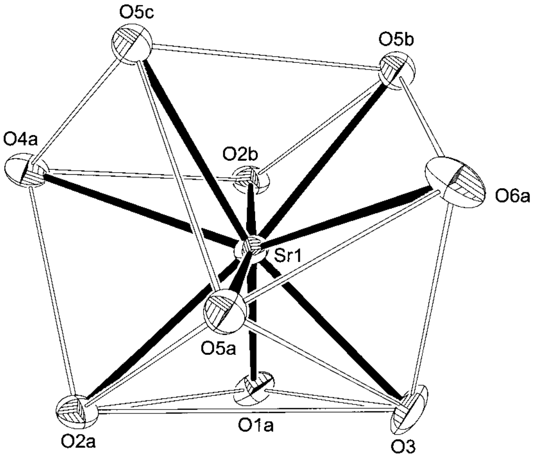

Figure 3. Ninefold strontium coordination in $SrZn(SeO_3)_2$ with short (d < 3.6 Å) O···O contacts indicated by open lines (50% thermal ellipsoids). The labels O1a and so forth refer to symmetry-generated atoms.

Both of the $[SeO_3]^{2-}$ groups adopt their usual pyramidal geometry [$d_{av}(Se-O) = 1.698(5)$ Å], with the Se^{IV} lone pair of electrons presumed to occupy the fourth tetrahedral vertex. The O−Se−O bond angles show no particular distortions (spread of values = 96.2−102.4°) and are within the range observed previously for inorganic selenites.[12] The strontium cation has nine O-atom neighbors with $d(Sr-O) < 3.1$ Å [$d_{av} = 2.700(5)$ Å, BVS = 2.03 (expected 2.00)] in an irregular coordination (Figure 3). The next-nearest-neighbor O atom is some 3.85 Å distant. Of the six oxygen atoms, O1, O2, O3, and O6 participate in Zn−O−Se bridges ($\theta_{av} = 107.9°$). O4 is bonded to two Zn neighbors and one Se neighbor, and O5 is part of a terminal Se−O grouping. All of the O atoms also make one or more bonds to nearby strontium cations.

The packing of these polyhedral building units can be visualized in terms of infinite chains of vertex-linked ZnO_{4+2} units propagating along the a direction. The $Se2-O_3$ groups are grafted onto the Zn/O chains. In turn, the $Se1-O_3$ groups cross-link the chains along the c direction into highly contorted infinite sheets of the nominal formula $[Zn(SeO_3)_2]^{2-}$, which propagate normal to [010]. The charge-balancing strontium cations occupy the interlayer regions and serve to fuse the sheets into an infinite structure. When viewed down [100] (Figure 2), there appear to be significant voids present at ($y = 0$, $z = 0$) and symmetry-equivalent locations. However, these are probably associated with the Se^{IV} lone pairs and do not represent space accessible to other chemical species.

Conclusion

In summary, hydrothermal synthesis has led to a strontium zinc selenite containing novel ZnO_{4+2} bicapped tetrahedra as a structural building unit. A few other recent studies have revealed zinc-containing phases to possess Zn−O bond lengths in the range of 2.5−2.7 Å. The ZnO_6 group with one Zn−O bond length of 2.61 Å in $CsNa_3Zn_7(PO_4)_6$ can be viewed as an axially distorted octahedron tending to a square-based pyramid.[13] Essentially, the same situation occurs in $Zn_3(PO_4)_2 \cdot H_2O$, where the long axial Zn−O bond length is 2.56 Å.[14] $Ba_2KZn_3(B_3O_6)$-

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$(O(B_3O_6)_2)$, determined by a medium-resolution crystal structure [$R(F) \approx 0.21$],[15] contains a ZnO_5 moiety with a Zn−O separation of 2.61 Å. This irregular grouping could be described as very distorted trigonal-bipyramidal or singly capped tetrahedral.

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Supporting Information Available: Full crystallographic details in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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