Contributions to the stereochemistry of zirconium oxysalts—part IV: syntheses and crystal structures of $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($\text{X} = \text{S}, \text{Se}$), $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Zr}(\text{SeO}_3)_2$

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Received: 26 August 2021 / Accepted: 23 December 2021 / Published online: 25 January 2022
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Abstract

$\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($\text{X} = \text{S}, \text{Se}$), $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Zr}(\text{SeO}_3)_2$ were synthesized at low-hydrothermal conditions from mixtures of $\text{Zr}_2\text{O}_2(\text{CO}_3)(\text{OH})_2$, the respective acids, and minor amounts of water. While $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($\text{X} = \text{S}, \text{Se}$) and $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ form crystals up to several tenths of a mm, $\text{Zr}(\text{SeO}_3)_2$ was mainly obtained as microcrystalline powder, single crystals rarely exceeded 10 μm in size. Samples were investigated by single-crystal X-ray techniques and in the case of $\text{Zr}(\text{SeO}_3)_2$ also by X-ray powder diffraction. The compounds $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($\text{X} = \text{S}, \text{Se}$) crystallize in the $\text{Ce}_2(\text{OH})_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ structure type ($C2/c$, $Z=4$, $a=13.034(2)/13.308(3)$, $b=6.500(1)/6.683(2)$, $c=15.056(3)/15.383(4)$ Å, $\beta=96.27(1)/96.81(1)^\circ$, $V=1267.9(4)/1358.5(6)$ Å³ for $\text{X} = \text{S}/\text{Se}$, respectively). Tetragonal antiprisms $\text{Zr}^{[8]}\text{O}_8$ are edge-connected to dimers that share corners with XO_4 tetrahedra forming a three-dimensional network. $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($Fddd$, $Z=8$, $a=5.498(1)$, $b=11.618(3)$, $c=25.893(6)$ Å, $V=1653.9(6)$ Å³) is isotypic with the respective selenate compound. Occasionally, pseudomerohedral twinning is observed, simulating a larger monoclinic C -centered unit cell. Again, tetragonal antiprisms $\text{Zr}^{[8]}\text{O}_8$ are formed; however, they are corner-linked with SO_4 tetrahedra to $\text{Zr}(\text{SO}_4)_2$ layers interconnected solely by hydrogen bonds. $\text{Zr}(\text{SeO}_3)_2$ crystallizes in $P2_1/c$, $Z=2$; $a=4.9724(3)$, $b=8.5992(5)$, $c=6.9447(3)$ Å, $\beta=110.128(3)^\circ$, $V=278.81(3)$ Å³ (unit cell from powder data) and belongs to the $\beta\text{-Sn}(\text{SeO}_3)_2$ structure type established further for $\text{Ti}(\text{SeO}_3)_2$ and $\text{Pb}(\text{SeO}_3)_2$. Isolated ZrO_6 octahedra share corners with the selenite groups forming a three-dimensional network.

Graphical abstract

Keywords X-ray structure determination · Sulfates · Selenates · Zirconium oxysalts · Twinning

Introduction

The presented work is part of long-term investigations on the crystal chemistry of zirconium oxysalts with $(\text{XO}_4)^{2-}$ or $(\text{XO}_3)^{2-}$ ($\text{X} = \text{S}, \text{Se}$) anions synthesized under mild-hydrothermal conditions below 250 °C. So far, the compounds $\text{Zr}(\text{SeO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Zr}(\text{SeO}_4)_2 \cdot 4\text{H}_2\text{O}$ [1], $\text{Zr}(\text{SeO}_3)(\text{SeO}_4)$, $\text{Zr}_4(\text{SeO}_3)(\text{SeO}_4)_7$, and $\text{Zr}_3(\text{SeO}_3)(\text{SeO}_4)_5 \cdot 2\text{H}_2\text{O}$ [2], as

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well as $M^{2+}\text{Zr}(\text{SO}_4)_3$ with $M = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$ and Cd , and $(\text{Fe}^{3+,2+}, \text{Zr})_2(\text{SO}_4)_3$ [3] were obtained and structurally characterized in detail. The present part IV of this series of studies deals with the two isotopic compounds $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($X = \text{S}, \text{Se}$), as well as with $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Zr}(\text{SeO}_3)_2$.

The crystal structure of $\text{Zr}_2(\text{OH})_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ was originally described by [4] but the experimental localisation of the hydrogen atoms was not possible at that time. The isotopic analogue $\text{Zr}_2(\text{OH})_2(\text{SeO}_4)_3 \cdot 4\text{H}_2\text{O}$ was unknown up to now. This structure type is further reported for $\text{Ce}_2(\text{OH})_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ [5].

$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ was known since 1956, synthesized and crystallographically characterized by Staritzky and Singer [6]. Later on, [7] determined the crystal structure and refined this compound in space group $Fddd$ but without locating hydrogen atoms. $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is also found in nature as the mineral zircosulfate [8]. It is isotopic with $\text{Zr}(\text{SeO}_4)_2 \cdot 4\text{H}_2\text{O}$ [1] as well as with $\text{Hf}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [9]. For $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ three modifications were described so far: (i) The $Fddd$ modification—known for decades—but structurally described only in 2007 [10], is isotopic with the title compound and labelled α -form. (ii) The structure of a second, orthorhombic modification (β -form, space group $Pnma$) was characterized already in 1977 by [11]; it is isotopic with $\text{U}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (mineral name behounekite) [12, 13]. $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is dimorph and crystallizes in the α - $Fddd$ and β - $Pnma$ forms [14, 15]. (iii) Finally, [16] reported a third modification crystallizing in space group $C2/c$. [10] refined both the α - and β -modification of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and discussed the close structural relations based on a geometrical isomerism. They mentioned pronounced similarities between the α -modification and the crystal structure described in space group $C2/c$ with respect to stereochemistry and topology [10, 11, 16].

For $\text{Zr}(\text{SeO}_3)_2$ no crystal structure was reported so far. Its powder pattern (ICDD entry 50–0336 [17]) was indexed with orthorhombic symmetry ($a = 8.568$, $b = 6.488$, $c = 15.277$ Å); space group $Pmmm$ was proposed based on the absence of systematic extinctions, but several Bragg reflections remained unindexed. Since other $M^{4+}(\text{SeO}_3)_2$ phases, i.e. the isotopic compounds $\text{Ti}(\text{SeO}_3)_2$ [18], $\text{Pb}(\text{SeO}_3)_2$, and β - $\text{Sn}(\text{SeO}_3)_2$ [19], show similar powder patterns as $\text{Zr}(\text{SeO}_3)_2$ but crystallize in a smaller monoclinic unit cell, we investigated this compound in detail.

Results and discussion

Selected individual and mean bond lengths and angles as well as bond valences ν (calculated according to [20]) of the four title compounds are listed in Table 1. Details about the hydrogen bonds are compiled in Table 2.

$\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($X = \text{S}, \text{Se}$)

The zirconium atoms in the isotopic compounds $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($X = \text{S}, \text{Se}$) are coordinated by eight oxygen atoms arranged in distorted tetragonal antiprisms. The ligands are represented by the oxygen atoms of two hydroxyl groups (O_h1) and two H_2O molecules (O_w8 , O_w9), as well as by four oxygen atoms of XO_4 tetrahedra ($\text{O}2$, $\text{O}4$, $\text{O}5$, $\text{O}6$). Each two ZrO_8 polyhedra are edge-connected to form dimers. The common O_h1 – O_h1 edges are shortened to ~ 2.34 Å in both compounds due to repulsion of the two tetravalent central atoms. These dimers are corner-linked with two crystallographically different XO_4 tetrahedra (Fig. 1); one has the point symmetry 2, the other is centered on a general position. The oxygen atoms $\text{O}3$ and $\text{O}7$ belong to the XO_4 tetrahedra only; furthermore they act as acceptor atoms of three respectively two hydrogen bonds (Table 2). The hydrogen bond lengths $\text{D} \cdots \text{H} \cdots \text{A}$ are ~ 2.7 Å for the H_2O molecules but somewhat longer for the hydroxyl groups (2.84 and 2.96 Å for $X = \text{S}$ and Se , respectively). Without considering the contributions of hydrogen atoms, the bond valences amount to ~ 1.5 and 1.6 v.u. for the atoms $\text{O}3$ and $\text{O}7$, respectively [20]. The proposed model complies well with calculated bond valences.

Topologically, the crystal structure is formed by $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3(\text{H}_2\text{O})_4$ layers parallel to (101). Eight-membered rings (one corner is concave) and the doubled number of four-membered rings, consisting of alternating Zr atoms and XO_4 tetrahedra, build these layers. All types of rings are linked among each other forming rows parallel to [010]. It should be mentioned that two hydrogen bonds, O_h1 – $\text{H}_h1 \cdots \text{O}3$ and O_w8 – $\text{H}_w2 \cdots \text{O}3$, are running within the eight-membered rings of the layers, whereas adjacent layers are interlinked to make up a three-dimensional framework via the Zr_2O_{14} dimers (at their O_h1 – O_h1 edge) as well as by O_w8 – $\text{H}_w3 \cdots \text{O}7$, O_w9 – $\text{H}_w4 \cdots \text{O}3$, and O_w9 – $\text{H}_w5 \cdots \text{O}7$ hydrogen bonds.

$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$

$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (α -modification) [7, and present study] crystallizes in space group $Fddd$ and represents a structure type which further comprises the crystal structures of $\text{Zr}(\text{SeO}_4)_2 \cdot 4\text{H}_2\text{O}$ [1] and of the sulfates of $M^{4+} = \text{Pu}, \text{Hf}$, or Ce [9, 10, 14]. For $\text{Zr}(\text{SeO}_4)_2 \cdot 4\text{H}_2\text{O}$ the presence of a maximum in the residual electron-density ($9.7 \text{ e } \text{\AA}^{-3}$) was observed at the special position $8a$ (at $1/8 \ 5/8 \ 5/8$) [1]; it was attributed to a partially occupied site Zr2 going along with the formation of vacancies at the Zr1 position [8b, at $5/8 \ 5/8 \ 5/8$]. The occupation factors for the Zr1 and Zr2 atoms were refined to 0.960(1) and 0.040(1), respectively,

Table 1 Selected interatomic bond lengths (Å), angles (°), and bond valences ν (v.u.) for $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($\text{X} = \text{S}, \text{Se}$), $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Zr}(\text{SeO}_3)_2$

$\text{Zr}_2(\text{OH})_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$			$\text{Zr}_2(\text{OH})_2(\text{SeO}_4)_3 \cdot 4\text{H}_2\text{O}$		
		ν			ν
Zr–O _h 1	2.0866(7)	0.651	Zr–O _h 1	2.0972(10)	0.633
Zr–O _h 1	2.1482(7)	0.551	Zr–O _h 1	2.1601(10)	0.534
Zr–O5	2.1890(7)	0.494	Zr–O5	2.1955(11)	0.485
Zr–O _w 9	2.1909(7)	0.491	Zr–O _w 9	2.1929(11)	0.489
Zr–O _w 8	2.2031(7)	0.475	Zr–O _w 8	2.1988(10)	0.481
Zr–O6	2.2155(7)	0.460	Zr–O6	2.2138(10)	0.462
Zr–O4	2.2208(7)	0.453	Zr–O4	2.2312(12)	0.441
Zr–O2	2.2238(7)	0.450	Zr–O2	2.2151(10)	0.460
<Zr ^[8] –O>	2.185	Σ 4.026	<Zr ^[8] –O>	2.188	Σ 3.985
S1–O3	1.4705(7) 2×	1.514	Se1–O3	1.6333(10) 2×	1.519
S1–O2	1.4731(6) 2×	1.504	Se1–O2	1.6330(10) 2×	1.520
<S1–O>	1.472	Σ 6.035	<Se1–O>	1.633	Σ 6.079
O3–S1–O3	111.95(6)		O3–Se1–O3	113.71(8)	
O3–S1–O2	108.30(4) 2×		O3–Se1–O2	107.49(5) 2×	
O3–S1–O2	109.03(4) 2×		O3–Se1–O2	108.35(6) 2×	
O2–S1–O2	110.22(6)		O2–Se1–O2	111.52(9)	
<O–S1–O>	109.47		<O–Se1–O>	109.48	
S2–O7	1.4545(7)	1.581	Se2–O7	1.6173(10)	1.586
S2–O4	1.4697(6)	1.517	Se2–O4	1.6290(10)	1.537
S2–O5	1.4762(7)	1.491	Se2–O5	1.6371(10)	1.504
S2–O6	1.4769(7)	1.488	Se2–O6	1.6359(9)	1.508
<S2–O>	1.469	Σ 6.078	<Se2–O>	1.630	Σ 6.135
O7–S2–O4	109.99(4)		O7–Se2–O4	109.94(6)	
O7–S2–O5	111.06(4)		O7–Se2–O5	111.95(6)	
O4–S2–O5	107.12(4)		O4–Se2–O5	105.94(6)	
O7–S2–O6	111.66(4)		O7–Se2–O6	113.11(5)	
O4–S2–O6	108.38(4)		O4–Se2–O6	107.93(5)	
O5–S2–O6	108.49(4)		O5–Se2–O6	107.64(5)	
<O–S2–O>	109.45		<O–Se2–O>	109.42	
$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$			$\text{Zr}(\text{SeO}_3)_2$		
		ν			ν
Zr1–O×4	2.1777(11)	0.509	Zr–O1 2×	2.0429(17)	0.733
Zr1–O _w ×4	2.1801(11)	0.506	Zr–O2 2×	2.0841(17)	0.656
<Zr ^[8] –O>	2.179	Σ 4.061	Zr–O3 2×	2.0847(17)	0.655
			<Zr ^[6] –O>	2.071	Σ 4.087
S–O2×2	1.4602(12)	1.557	Se–O1	1.6820(18)	1.417
S–O1×2	1.4821(11)	1.467	Se–O2	1.6781(17)	1.432
<S–O>	1.471	Σ 6.049	Se–O3	1.6873(17)	1.397
			<Se–O>	1.682	Σ 4.246
O2–S–O2	111.82(10)		O1–Se–O2	100.73(9)	
O1–S–O2×2	110.93(7)		O1–Se–O3	98.40(9)	
O1–S–O2×2	108.03(7)		O2–Se–O3	102.25(9)	
O1–S–O1	107.01(10)		<O–Se–O>	100.46	
<O–S–O>	109.46				

indicating a slight site disorder [1]. In the present study on $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, the highest residual electron density

amounts $2.2 \text{ e } \text{\AA}^{-3}$; it again occurs at the 8a position. This slightly enhanced electron density is not considered to be

Table 2 Selected data for hydrogen bond systems in $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($\text{X} = \text{S}, \text{Se}$) and $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$

	D–H/Å		D–A/Å		D–H...A/°		H–D–H/°	
	X = S	X = Se	X = S	X = Se	X = S	X = Se	X = S	X = Se
$\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$								
$\text{O}_h1\text{--H}_h1\cdots\text{O}3$	0.81(2)	0.76(3)	2.842(1)	2.965(2)	153(2)	155(3)		
$\text{O}_w8\text{--H}_w2\cdots\text{O}3$	0.78(2)	0.80(3)	2.704(1)	2.727(2)	159(2)	162(2)	110(2)	105(2)
$\text{O}_w8\text{--H}_w3\cdots\text{O}7$	0.85(2)	0.86(3)	2.719(1)	2.687(2)	178(2)	174(3)		
$\text{O}_w9\text{--H}_w4\cdots\text{O}3$	0.77(2)	0.83(3)	2.711(1)	2.726(2)	170(2)	176(3)	106(2)	107(3)
$\text{O}_w9\text{--H}_w5\cdots\text{O}7$	0.80(2)	0.74(3)	2.683(1)	2.672(2)	169(2)	172(3)		
$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$								
$\text{O}_w\text{--H}_w1\cdots\text{O}2$	0.78(3)		2.736(2)		157(3)		112(3)	
$\text{O}_w\text{--H}_w2\cdots\text{O}2'$	0.80(3)		2.664(2)		167(3)

Fig. 1 Crystal structure of $\text{Zr}_2(\text{OH})_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ in a projection along the crystallographic b -axis

significant in the final refinements of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. However, a slight disorder cannot be excluded with certainty.

In accordance with an earlier investigation [7], the ZrO_8 polyhedra form antiprisms with point symmetry 222, built up by four oxygen atoms of H_2O molecules and four O1 atoms. The sulfate groups have point symmetry 2. The ZrO_8 polyhedra share four corners—the O1 atoms—with four neighboring sulfate tetrahedra. Vice versa, the sulfate group links between two Zr atoms. Thus eight-membered rings are formed which are linked to $\text{Zr}(\text{H}_2\text{O})_4(\text{SO}_4)_2$ layers running parallel to (001) (Figs. 2, 3a). The remaining two ligands of the sulfate group—atoms O2—act as acceptors of both hydrogen bonds from the H_2O molecule (cf. Table 2). The hydrogen bonds $\text{O}_w\text{--H}_w1\cdots\text{O}2$ are located within the above-mentioned rings, whereas adjacent layers are interconnected only by the hydrogen bond $\text{O}_w\text{--H}_w2\cdots\text{O}2'$. Without the contribution of the hydrogen

bonds, the bond valence calculation gives only 1.56 v.u. for the O2 atom.

Polyhedral bond-length distortions are quite similar for both compounds $\text{Zr}(\text{XO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($\text{X} = \text{S}, \text{Se}$) as well as for $\alpha\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [10]. In $\beta\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (space group $Pnma$) the respective layers are puckered. For detailed discussions, comparisons, and illustrations of the differences and similarities of these two structure types see [10].

A further modification, i.e. $\gamma\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, was described in literature [16] in space group $C2/c$. However, already in Ref. [10] the authors note that “The packing features adopted by the monoclinic form are very similar to the one adopted by the α -form”, and the respective structure layers were compared in their Fig. 3, but not further discussed in detail. A transformation of the unit-cell parameters listed by [16] for the space group $C2/c$ according to $[1/3 \ 0 \ 2/3 \ / \ 0 \ 1 \ 0 \ / \ 1/3 \ 0 \ -4/3]$ results in the cell parameters $a = 11.988$, $b = 5.633$, $c = 26.614$ Å, $\alpha = 90.00$, $\beta = 90.03$, $\gamma = 90.00^\circ$; they fit with those given by [10] for the orthorhombic modification of $\alpha\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $a = 5.6587(1)$, $b = 12.0469(2)$, $c = 26.7201(3)$ Å. Applying the same transformation to the atomic coordinates of the two Ce and three S atom positions results in overlapping Ce...Ce distances < 0.009 Å and S...S distances < 0.015 Å. For the O atoms the situation is not that clear as obviously some misprints occur already for the atomic coordinates published in space group $C2/c$ [16]: e.g. O16...O16 (1.21 Å), O13...O18 (2.13 Å), O18...S2 (1.95 Å), although the published H atom positions are conspicuous (see also comments to Figs. 2 and 3). As a consequence, the existence of the structure type of $\gamma\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ must be doubted. Very likely, the phase investigated by [16] actually is the modification $\alpha\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. This close similarity is evident also in our Figs. 2 and 3a, 3b. In the light of the present investigations on the crystal structure of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ with its remarkable twinning behavior (see chapter on single-crystal X-ray diffraction in the experimental part), it seems very likely that crystals of $\alpha\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ might be twinned in the same way as described herein, thus simulating a monoclinic C -centered

Fig. 2 Crystal structure of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in a projection along the crystallographic a -axis. The monoclinic cell choice published for ‘ $\gamma\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ’ in [16] is shown with dashed lines for comparison.

son. Note: to comply with at least approximately with the bond lengths and figures given in [16], the coordinates of O16, O18, H7, H8, H11, and H12 had to be corrected

pseudo cell. This assumption is further corroborated by our observation of respective twinning also in $\text{Zr}(\text{SeO}_4)_2 \cdot 4\text{H}_2\text{O}$, alongside with untwinned single crystals [1].

$\text{Zr}(\text{SeO}_3)_2$

The atomic arrangement in $\text{Zr}(\text{SeO}_3)_2$ consists of isolated ZrO_6 octahedra, sharing all corners with trigonal pyramidal selenite groups as illustrated in Fig. 4. Four- and six-membered rings consisting of alternating Zr atoms and selenite groups are formed, linked to tubes running parallel to [100]. The Se atoms of the selenite groups point into these tubes to give space for the lone-pair electrons. The compound is isotypic with $\text{Ti}(\text{SeO}_3)_2$ [18], $\text{Pb}(\text{SeO}_3)_2$, and $\beta\text{-Sn}(\text{SeO}_3)_2$ [19], a comparison is given in Table 3. It has to be noted that the unit cell volumes of $\text{Zr}(\text{SeO}_3)_2$ and $\text{Pb}(\text{SeO}_3)_2$ are rather similar, while the mean Zr–O bond length resembles more closely that of the SnO_6 polyhedron. Actually, based on the single-crystal data, the mean M^{4+} –O bond lengths in this group obey a strict linear correlation with their respective ionic radii. The comparatively high cell volume of $\text{Zr}(\text{SeO}_3)_2$ could be induced by the clearly extended M –O–Se angles, which in turn are negatively correlated with the octahedral bond angle distortion σ_{oct}^2 (Table 3). As outlined in the section on X-ray powder diffraction, a

previous description of $\text{Zr}(\text{SeO}_3)_2$ with orthorhombic symmetry (space group $Pmmm$) from powder data [17] and the respective ICDD entry 50–0336 have to be revised.

Analysis of structural similarities

The title compounds and isotypic analogues were geometrically analyzed with the program COMPSTRU as summarized in Table 4 (for details see the experimental section). For the isotypic compounds $M_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($M = \text{Zr}$; $X = \text{S}, \text{Se}$ [this work]; $M = \text{Ce}$, $X = \text{S}$ [5]) the X1 atom (located on a twofold axis, but sharing only two corners with ZrO_8 -polyhedra) exhibits a larger average shift compared to the X2 atom (on a general position, but three corners shared). However, the X_2O_4 tetrahedra show a more pronounced rotation. The average shifts of the O atoms belonging to the XO_4 tetrahedra in both the Zr compounds amount 0.1520 and 0.1439 Å. Interestingly, these shifts are marginally smaller than the difference between the S/Se–O bond lengths (0.1610 Å). The locations of the H atoms are corroborated, with a displacement between the compounds $M = \text{Zr}$; $X = \text{S}, \text{Se}$ of only 0.034–0.146 Å. For the structure pairs $M = \text{Zr}$ and Ce , $X = \text{S}$, a significant deviation of the O_w positions is evident (0.148 and

Fig. 3 Single polyhedral sheets in the structures of **a** $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in a projection onto (001) compared to **b** ‘monoclinic $\gamma\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ’ according to [16] in a projection onto (2 0 1). Note: to comply at least approximately with the bond lengths and figures given in [16], the coordinates of atoms O16, O18, H7, H8, H11, and H12 had to be corrected

0.160 Å). Again, the smaller shift of the S2 atom is notable. In case of the $\alpha\text{-}M(\text{XO}_4)_2 \cdot 4\text{H}_2\text{O}$ structure type (space group $Fddd$), the smallest degree of lattice distortion and the closest structural similarity are verified between the Zr- and Hf-sulfates. For the selenites $M(\text{SeO}_3)_2$ ($M = \text{Zr}, \text{Sn}, \text{Ti}, \text{Pb}$) the M atoms are strictly localized due to their point symmetry mmm , but a pronounced shift and rotation of the selenite group is observed. Compared to $\text{Zr}(\text{SeO}_3)_2$, the lattice distortion is large for the Ti-compound but consistently smaller for the Sn- and Pb-representatives; however, the ratios of the corresponding lattice parameters are inverse proportional.

Conclusion

The crystal structures of the oxysalts $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($X = \text{S}, \text{Se}$), $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Zr}(\text{SeO}_3)_2$ were studied by single-crystal X-ray diffraction, $\text{Zr}(\text{SeO}_3)_2$ also by powder techniques. The $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ compounds ($X = \text{S}, \text{Se}$) are isotypic with $\text{Ce}_2(\text{OH})_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ and crystallize in space group $C2/c$. $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (space group $Fddd$) is isotypic with the respective selenate as well as with $\alpha\text{-}M(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($M = \text{Ce}, \text{Pu}, \text{Hf}$). It often shows pseudomerohedral twinning, simulating a monoclinic

Fig. 4 Crystal structure of $\text{Zr}(\text{SeO}_3)_2$ in a projection approximately along the crystallographic a -axis

C-centered cell. By analogy, we postulate that the previously proposed γ -modification of $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (space group $C2/c$ [16]) is most probably identical with α - $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. Finally, $\text{Zr}(\text{SeO}_3)_2$ is monoclinic (space group $P2_1/c$) and belongs to the structure type

known for $\text{Ti}(\text{SeO}_3)_2$, $\text{Pb}(\text{SeO}_3)_2$, and β - $\text{Sn}(\text{SeO}_3)_2$. A previous indexing of $\text{Zr}(\text{SeO}_3)_2$ with orthorhombic symmetry (space group $Pmmm$) from powder data [17] and the respective ICDD entry 50-0336 have to be revised.

At the time we started our investigations of zirconium oxysalts [1], more than a dozen of purely inorganic zirconium sulfates, but no selenates or selenites had been structurally described in the literature. In the course of our studies [1–3] and present work, we were as yet able to synthesize and characterize seven zirconium sulfates as well as seven zirconium compounds containing $[\text{SeO}_4]$ and/or $[\text{SeO}_3]$ anions with interesting stereochemical properties. Currently, in continuation of our research program, the investigation of eight new zirconium oxysalts is in progress. Usually, respective Zr-sulfates and -selenates were found to be isotypic. Besides, the rare element hafnium, substituting zirconium in nature (it is found e.g. as a solid solution with Zr in the mineral zircon, ZrSiO_4) is also expected to form isotypic compounds as reported for zirconium. While a series of respective hafnium sulfates are listed in the ICDD database, no hafnium selenates or selenites are evident so far. It is most likely that a thorough study on this class of compounds will be promising, too.

Table 3 Crystal data compared for $\text{Ti}(\text{SeO}_3)_2$ [18], β - $\text{Sn}(\text{SeO}_3)_2$ [19], $\text{Zr}(\text{SeO}_3)_2$ [present work], and $\text{Pb}(\text{SeO}_3)_2$ [19]. #: left column represents values obtained by Rietveld refinement

Compound	$\text{Ti}(\text{SeO}_3)_2$	$\text{Sn}(\text{SeO}_3)_2$	$\text{Zr}(\text{SeO}_3)_2^{\#}$		$\text{Pb}(\text{SeO}_3)_2$
$a/\text{\AA}$	4.741	4.784	4.9724(3)	4.963(1)	4.811
$b/\text{\AA}$	8.2554	8.529	8.5992(5)	8.592(2)	8.768
$c/\text{\AA}$	6.7547	6.943	6.9447(3)	6.939(2)	7.079
$\beta/^\circ$	110.57	111.01	110.128(3)	110.09(1)	110.10
$V/\text{\AA}^3$	247.52	264.43	278.81(3)	277.9(1)	280.4
$\langle M^{VI}-O \rangle / \text{\AA}$	1.937	2.040	2.056	2.071	2.121
$\langle \text{Se}-O \rangle / \text{\AA}$	1.708	1.697	1.710	1.682	1.702
σ_{oct}^2	10.68	22.60	12.50	4.42	38.38
$\langle M-O-\text{Se} \rangle / ^\circ$	136.4	132.8	141.4	142.5	131.4

Table 4 Comparison of the title compounds with isotypic crystal structures (for details see the experimental section)

Compounds [this work]	Compared with	S	$d_{\text{max}}/\text{\AA}$	$d_{\text{av}}/\text{\AA}$	Δ
$\text{Zr}_2(\text{OH})_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$	$\text{Zr}_2(\text{OH})_2(\text{SeO}_4)_3 \cdot 4\text{H}_2\text{O}$ [this work]	0.0133	0.1817	0.1013	0.023
	$\text{Ce}_2(\text{OH})_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$ [5]	0.0213	0.1601	0.0780	0.020
$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [7]	0.0021	0.0299	0.0129	0.014
	$\text{Zr}(\text{SeO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Zr2 omitted) [1]	0.0158	0.1362	0.0830	0.017
	$\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [10]	0.0181	0.1033	0.0685	0.018
	$\text{Hf}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [9]	0.0007	0.1048	0.0247	0.005
	$\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [11]	0.0150	0.1170	0.0531	0.031
$\text{Zr}(\text{SeO}_3)_2$	$\text{Sn}(\text{SeO}_3)_2$ [19]	0.0151	0.3596	0.2482	0.128
	$\text{Ti}(\text{SeO}_3)_2$ [18]	0.0239	0.2673	0.1747	0.065
	$\text{Pb}(\text{SeO}_3)_2$ [19]	0.0149	0.3783	0.2558	0.170

Experimental

Synthesis

The investigated zirconium oxysalts were obtained by low-hydrothermal synthesis from mixtures of $\text{Zr}_2\text{O}_2(\text{CO}_3)(\text{OH})_2$ with concentrated H_2SO_4 , H_2SeO_4 , or H_2SeO_3 , respectively, and a few tenths of a cm^3 water filled in Teflon-lined steel vessels of about 5 cm^3 volume (filling level $\leq 25\%$). The autoclaves were heated up to a maximum of 220°C within several hours, kept at this temperature for one week and finally cooled down slowly to room temperature.

In case of $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($X = \text{S}, \text{Se}$) and $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ colorless crystals up to several tenth of a mm formed; they were separated from the remaining liquid, washed in methanol, dried, and embedded in silicone grease. $\text{Zr}(\text{SeO}_3)_2$ was obtained mainly as a very fine-grained white powder, only occasionally crystals with up to $10 \mu\text{m}$ were obtained; the largest one found was used for the single-crystal X-ray investigation. By variation of reaction conditions (ratio of precursor reagents, temperature, cooling rate, pH value) no significant effect on the grain size of the precipitate could be achieved. In literature, the formation of zirconium selenite only as nanoparticles or microcrystals [21, 22] by reaction of $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and SeO_2 at room temperature has been described.

Single-crystal X-ray diffraction data and structure refinement

Selected fragments of $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($X = \text{S}, \text{Se}$), $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, and a tiny chip of $\text{Zr}(\text{SeO}_3)_2$ were prepared for single-crystal X-ray investigations. Data collections were performed on a Bruker APEXII diffractometer equipped with a CCD area detector, an Incoatec Micro-focus Source I μ S (30 W, multilayer mirror, Mo-K α), and an Oxford Cryosystems Cryostream 800 Plus LT device; the crystal-detector distance was 40 mm. $\text{Zr}(\text{SeO}_3)_2$ was studied at room temperature, all other samples at 200 K to avoid decomposition and improve the location of the hydrogen atoms. Several sets of ϕ - and ω -scans with 2° scan-width were combined to achieve respective full-sphere data. For data handling including integration and absorption correction (evaluation of

multi-scans) the Bruker Apex3 suite was used [23]. For $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($X = \text{S}, \text{Se}$) the atomic coordinates reported by [4] were taken as starting parameters and the crystal structures were refined by full-matrix least-squares techniques (Shelxl [24]). The positions of the hydrogen atoms were revealed from final difference Fourier maps. Crystal parameters as well as a summary on the data collections and structure refinements are given in Table 5, final atomic positions are compiled in Table 6.

It has to be noted that for $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ standard indexing of the ‘single-crystal’ reflex positions led to a monoclinic *C*-centered unit cell ($a = 34.815(5)$, $b = 5.497(1)$, $c = 14.190(3) \text{ \AA}$, $\beta = 114.00(1)^\circ$, $V = 2481.0(8) \text{ \AA}^3$, $Z = 12$). This unit cell closely resembles that proposed for $\gamma\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [16] ($a = 35.813$, $b = 5.633$, $c = 14.597 \text{ \AA}$, $\beta = 113.73^\circ$, $V = 2695.7 \text{ \AA}^3$), which is one of three modifications reported for $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in literature [10, 16]. A refinement of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in space group *C2/c* using a modified atomic model (see comments in captions to Figs. 2 and 3) published for $\gamma\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ was performed. Moreover, *pseudomerohedral* twinning was considered (the transformation matrix $\begin{bmatrix} 1 & 0 & 2 & / & 0 & -1 & 0 & / & 0 & 0 & -1 \end{bmatrix}$ gave $a = 34.838$, $b = 5.497$, $c = 14.190 \text{ \AA}$, $\beta = 114.09^\circ$); the twin components were 72(1) and 28(1) %, respectively. At a first glance, the refinement gave a reasonable result ($R1 = 0.028$). However, an evaluation of the refined atomic arrangement (via the ADDSYMM tool implemented in the program PLATON [25]) revealed the presence of “non-space group” translation vectors. A further analysis of the collected data with the program CELL_NOW [26] indicated the tentative presence of a twinned crystal with *F*-centered orthorhombic unit cell. A transformation of the atom coordinates formerly obtained in space group *C2/c* by the transformation matrix $\begin{bmatrix} 1/3 & 0 & 2/3 & / & 0 & 1 & 0 & / & 1/3 & 0 & -4/3 \end{bmatrix}$ resulted in the hitherto known unit cell and an atomic arrangement based on space-group symmetry *Fddd*, also known for $\alpha\text{-Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [10]. Finally, the observed reflection pattern is best described by an orthorhombic unit cell ($a = 5.498$, $b = 11.618$, $c = 25.893 \text{ \AA}$, $Z = 8$) and assuming a twinning (twin matrix $\begin{bmatrix} 1 & 0 & 0 & / & 0 & 2/3 & 1/3 & / & 0 & -5/3 & 2/3 \end{bmatrix}$). The conclusive structure refinement, starting with the atomic positions given in [1, 10], is based on a new processing of the measured reflection intensities of both orthorhombic twin components (Bruker APEX3 program suite [23], a reflection file in format HKLF5 from program TWINABS [27]). The orthorhombic crystal-structure model was refined

Table 5 Relevant crystal data and details of the single-crystal intensity measurements and structure refinements for $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($\text{X} = \text{S}, \text{Se}$), $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Zr}(\text{SeO}_3)_2$

Crystal data	$\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$		$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	$\text{Zr}(\text{SeO}_3)_2$
	S	Se		
Space group	$C2/c$	$C2/c$	$Fddd$	$P2_1/c$
$a/\text{\AA}$	13.034(2)	13.308(3)	5.498(2)	4.963(1)
$b/\text{\AA}$	6.500(1)	6.683(2)	11.618(3)	8.592(2)
$c/\text{\AA}$	15.056(3)	15.383(4)	25.893(6)	6.939(2)
$\beta/^\circ$	96.27(1)	96.81(1)		110.09(1)
$V/\text{\AA}^3$	1267.9(4)	1358.5(6)	1653.9(6)	277.9(1)
Z	4	4	8	2
$\rho_{\text{calc}}/\text{g cm}^{-3}$	3.021	3.508	2.855	4.125
$\mu(\text{MoK}\alpha)/\text{mm}^{-1}$	2.25	9.68	1.90	15.03
Crystal size/ mm^3	$0.20 \times 0.20 \times 0.17$	$0.15 \times 0.10 \times 0.08$	$0.20 \times 0.05 \times 0.025$	$0.02 \times 0.01 \times 0.0075$
Data collection and refinement				
$2\theta_{\text{max}}/^\circ$	80	80	80	72
Unique data	3995	4285	1453	1185
Data with $F_o > 4\sigma(F_o)$	3855	3869	1322	1035
Variables	126	126	45	44
$R1$ [for $F_o > 4\sigma(F_o)$]/all data ^a	0.016 / 0.017	0.020 / 0.024	0.027 / 0.032	0.025 / 0.034
$wR2$ [for all F_o] ^a	0.036	0.038	0.056	0.038
a, b^b	0.012, 1.35	0.005, 3.0	0.018, 8.47	0.01, 0.32
$\Delta\rho_{\text{min/max}}/e \text{\AA}^{-3}$	− 0.63 / 0.52	− 1.11 / 0.80	− 0.92 / 2.23	− 0.84 / 0.76

^a $R1 = \Sigma F_o - F_c / \Sigma F_o$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)]^{1/2}$

^b $w = 1 / [\sigma^2(F_o^2) + (a \times P)^2 + b \times P]$; $P = \{\max \text{ of } (0 \text{ or } F_o^2)\} + 2F_c^2 / 3$

satisfactorily to $R1 = 0.027$ with twin components of 73(1) and 27(1)%.

For the refinement of $\text{Zr}(\text{SeO}_3)_2$ (see also next section) the unit-cell setting and the atom labelling scheme were chosen in accordance to literature on the isotypic compounds $M(\text{SeO}_3)_2$ with $M = \text{Ti}, \text{Sn}$, and Pb [18, 19].

Furthermore, the title compounds and isopointal analogues were geometrically analyzed with the program COMPSTRU [28, 29]. It allows a comparison between the configurations of crystal-structure pairs by the degree of lattice distortion (S), the maximal displacement between the atomic positions of the paired atoms (d_{max}), the arithmetic mean of the displacement between the atomic positions (d_{av}), and the similarity as a function of the differences in atomic positions and the ratios of the corresponding lattice parameters (Δ). The results are compiled in Table 4. The atom labels for the structure types under discussion refer to those given in Table 6.

Powder X-ray diffraction work

Microcrystalline powder of $\text{Zr}(\text{SeO}_3)_2$ was studied at ambient conditions on a Bruker D8-Advance Eco diffractometer

system, equipped with a $\text{CuK}\alpha$ -optimized LynxEye XE-T position sensitive detector with an angular opening of 3.29° 2θ , primary Ni-filter, fixed divergence slit ($\text{FDS} = 0.3^\circ$), 2.5° soller slits for primary and secondary beam path, a fixed anti-scatter knife edge improved by an in-house variable anti-scatter screen and sample ϕ -spinning (15 min^{-1}). Sample diameter and FDS setting avoided beam spill in the angular range of the first occurring peak at $\sim 17^\circ 2\theta$. Data were collected from 5 to $125^\circ 2\theta$ with $\sim 0.01^\circ 2\theta$ step size and an overall measurement time of 200 min (equivalent to an accumulated step counting time of 330 s), thus leading to an I_{max} of $\sim 35,000$ counts. The ambient temperature within the Eco-system enclosure was about $30(2)^\circ\text{C}$. Identification and characterization of crystalline phases was undertaken using the program EVA [30]. Consecutively, the advanced qualitative data treatment based on indexing [31], whole powder pattern decomposition [32], and structure refinement [33] was done with the program TOPAS [34]. The atomic coordinates of the isotypic compounds $M(\text{SeO}_3)_2$ with $M = \text{Ti}, \text{Sn}$, and Pb [18, 19] were used as starting structural parameters.

For the preliminary data evaluation, a Pawley refinement based on the orthorhombic unit cell given in literature [17] was performed, clearly demonstrating a misfit of

Table 6 Atomic coordinates and displacement parameters for $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3 \cdot 4\text{H}_2\text{O}$ ($\text{X} = \text{S}, \text{Se}$), $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($Fddd$ cell choice 2—origin at $\bar{1}, 1/8, 1/8, 1/8$ from 222), and $\text{Zr}(\text{SeO}_3)_2$ (e.s.d.'s in parentheses)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso/eq}}$
$\text{Zr}_2(\text{OH})_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$				
Zr	0.10516(2)	0.01833(2)	0.08425(2)	0.00395(2)
S1	0	0.72059(4)	0.25	0.00505(4)
S2	0.20987(2)	0.51943(3)	0.06601(2)	0.00506(3)
O _h 1	0.04124(5)	0.12106(9)	−0.04102(4)	0.00699(9)
O2	0.07286(5)	0.85022(10)	0.20680(4)	0.01004(10)
O3	0.05937(5)	0.59400(10)	0.31841(4)	0.01029(10)
O4	0.14316(5)	0.35141(10)	0.09087(5)	0.01074(10)
O5	0.14390(5)	0.70299(10)	0.04928(5)	0.01053(10)
O6	0.25145(5)	0.46268(9)	−0.01805(4)	0.00807(9)
O7	0.29189(5)	0.55667(12)	0.13774(4)	0.01193(11)
O _w 8	−0.01148(5)	0.20046(10)	0.14502(5)	0.01124(10)
O _w 9	0.23601(5)	0.03167(12)	0.18862(4)	0.01240(11)
H _h 1	0.0600(16)	0.220(3)	−0.0677(14)	0.037(5)
H _w 2	−0.0122(17)	0.320(4)	0.1500(15)	0.043(6)
H _w 3	−0.0721(16)	0.153(3)	0.1430(14)	0.033(5)
H _w 4	0.2922(16)	0.062(3)	0.1835(13)	0.026(4)
H _w 5	0.2320(17)	0.025(3)	0.2409(15)	0.033(5)
$\text{Zr}_2(\text{OH})_2(\text{SeO}_4)_3 \cdot 4\text{H}_2\text{O}$				
Zr	0.10282(2)	0.02137(2)	0.08437(2)	0.00488(2)
Se1	0	0.70891(3)	0.25	0.00579(3)
Se2	0.20979(2)	0.52077(2)	0.06382(2)	0.00556(3)
O _h 1	0.04098(7)	0.11692(14)	−0.04047(6)	0.00775(14)
O2	0.07904(8)	0.84640(17)	0.20251(6)	0.01343(18)
O3	0.06639(8)	0.57528(16)	0.32501(7)	0.01303(17)
O4	0.13151(8)	0.35029(15)	0.09055(7)	0.01266(17)
O5	0.14154(8)	0.72165(15)	0.04030(7)	0.01222(16)
O6	0.25379(7)	0.44774(14)	−0.02587(6)	0.00903(15)
O7	0.29762(8)	0.55824(18)	0.14421(6)	0.01407(18)
O _w 8	−0.01132(8)	0.18992(16)	0.14652(7)	0.01214(17)
O _w 9	0.23155(8)	0.04326(19)	0.18704(7)	0.01521(19)
H _h 1	0.056(2)	0.213(4)	−0.0616(18)	0.034(7)
H _w 2	−0.0178(19)	0.308(4)	0.1485(16)	0.026(6)
H _w 3	−0.072(2)	0.144(4)	0.1427(17)	0.032(7)
H _w 4	0.292(2)	0.058(4)	0.1817(16)	0.029(7)
H _w 5	0.2276(19)	0.040(4)	0.2343(17)	0.022(6)
$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$				
Zr	5/8	5/8	5/8	0.00810(5)
S	7/8	7/8	0.68275(2)	0.00911(4)
O1	0.84559(19)	0.76692(8)	0.64537(4)	0.02104(19)
O2	1.11021(19)	0.85383(9)	0.71628(4)	0.02072(18)
O _w	0.4183(2)	0.56897(9)	0.55959(4)	0.02057(19)
H _w 1	0.337(5)	0.517(2)	0.5606(10)	0.049(8)
H _w 2	0.400(4)	0.604(2)	0.5330(10)	0.039(7)
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} B_{iso}
$\text{Zr}(\text{SeO}_3)_2$: Single-crystal (upper row) and powder (Rietveld) data (lower row)				
Zr	0.5	0.5	0.5	0.00820(6)
	0.5	0.5	0.5	0.731(19)

Table 6 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} B_{iso}
Se	0.15072(5)	0.12962(3)	0.34232(3)	0.01114(6)
	0.15044(22)	0.12802(11)	0.34179(10)	1.024(17)
O1	0.2664(4)	0.3141(2)	0.3474(3)	0.0198(4)
	0.2528(10)	0.3180(5)	0.3443(5)	1.22(11)
O2	0.6133(4)	0.05359(2)	0.2407(3)	0.0189(4)
	0.6028(10)	0.5316(5)	0.2374(5)	1.31(11)
O3	0.1408(4)	0.6411(2)	0.3727(3)	0.0183(3)
	0.1492(12)	0.6371(5)	0.3709(6)	1.70(10)

Fig. 5 Rietveld plot after the structure refinement of $Zr(SeO_3)_2$. Data: observed (black), calculated (red) and difference (gray). The lower tick marks (blue) represent the peak positions of $Zr(SeO_3)_2$ (color figure online)

calculated and observed peak positions (e.g. *d*-values: 4.09, 3.16, 3.14 Å). The corresponding intensity-unconstrained refinement using the monoclinic cell with space group $P2_1/c$ revealed a satisfactory fit with $R_{wp}=7.1\%$ and a GOF of 1.81. The consecutive Rietveld refinement based on the structural model gave a criterion of fit with $R_{wp}=27.7\%$, invoking a preferred orientation model along [001] and [012] the refinement converged with $R_{wp}=10.1\%$, a value close to the previous Pawley refinement. The refined structural parameters of the Rietveld refinement are given in Table 6, the final Rietveld plot is shown in Fig. 5. X-ray powder-diffraction data are listed in Table 7.

Further details of the crystal-structure investigations may be obtained from the joint CCDC/FIZ Karlsruhe online deposition service: <https://www.ccdc.cam.ac.uk/structures/> by quoting the deposition number CSD-2122296 (S), 2122297 (Se) for $Zr_2(OH)_2(XO_4)_3 \cdot 4H_2O$ ($X=S, Se$), 2122298 for $Zr(SO_4)_2 \cdot 4H_2O$, and 2122299 for $Zr(SeO_3)_2$. An extended Table 6 including anisotropic displacement parameters is available as supplementary information.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00706-021-02887-4>.

Table 7 X-ray powder-diffraction data (d in Å) for $\text{Zr}(\text{SeO}_3)_2$

I_{obs}	I_{cal}	d_{obs}	d_{cal}	h	k	l
63	26	5.197	5.1957	0	1	1
20	21	4.301	4.2996	0	2	0
34	53	4.104	4.1030	1	1	0
7	10	4.073	4.0719	1	1	-1
98	71	3.590	3.5895	0	2	1
100	100	3.249	3.2489	1	0	-2
28	36	3.163	3.1627	1	2	0
39	55	3.149	3.1484	1	2	-1
72	74	3.079	3.0783	1	1	1
66	24	3.049	3.0485	0	1	2
21	19	2.624	2.6240	0	3	1
14	7	2.598	2.5979	0	2	2
5	6	2.443	2.4427	1	3	0
8	8	2.437	2.4361	1	3	-1
9	20	2.381	2.3882	2	1	-1
4	6	2.324	2.3239	1	0	2
3	5	2.253	2.2528	2	1	0
9	8	2.244	2.2434	1	1	2
4	6	2.232	2.2323	2	1	-2
4	3	2.219	2.2181	1	1	-3
2	4	2.163	2.1631	1	3	1
7	4	2.153	2.1521	2	2	-1
50	22	2.107	2.1072	0	1	3
5	10	2.052	2.0515	2	2	0
9	6	2.045	2.0444	1	2	2
5	4	2.025	2.0252	1	2	-3
17	25	1.953	1.9527	1	4	0
4	6	1.914	1.9137	2	1	-3
6	6	1.807	1.8068	2	2	1
11	8	1.795	1.7947	0	4	2
15	11	1.792	1.7919	1	3	-3
10	12	1.786	1.7856	2	2	-3
6	7	1.663	1.6630	0	5	1
8	11	1.648	1.6484	2	0	2
8	11	1.635	1.6353	2	3	1
13	10	1.624	1.6244	2	0	-4
4	6	1.581	1.5814	2	4	0
10	8	1.578	1.5781	1	4	2
10	13	1.574	1.5742	2	4	-2
3	8	1.556	1.5562	3	0	0
8	4	1.524	1.5243	0	2	4
5	9	1.517	1.5168	3	1	-3
5	4	1.496	1.4956	1	3	3
2	5	1.428	1.4281	3	3	-1
9	7	1.397	1.3967	1	0	4
4	4	1.376	1.3764	1	5	-3
7	5	1.368	1.3689	1	6	-1
7	7	1.299	1.2989	0	4	4

Acknowledgements This study was financially supported by University Vienna grants IS526001 and IP532010. We are grateful to three anonymous reviewers for their helpful comments.

Funding Open access funding provided by University of Vienna.

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