Contributions to the stereochemistry of zirconium oxysalts—part IV: syntheses and crystal structures of $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3\cdot4\text{H}_2\text{O}$ ($\text{X} = \text{S, Se}$), $\text{Zr}(\text{SO}_4)_2\cdot4\text{H}_2\text{O}$, 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
$\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3\cdot4\text{H}_2\text{O}$ ($\text{X} = \text{S, Se}$), $\text{Zr}(\text{SO}_4)_2\cdot4\text{H}_2\text{O}$, 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 $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3\cdot4\text{H}_2\text{O}$ ($\text{X} = \text{S, Se}$) and $\text{Zr}(\text{SO}_4)_2\cdot4\text{H}_2\text{O}$ 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 $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3\cdot4\text{H}_2\text{O}$ ($\text{X} = \text{S, Se}$) crystallize in the $\text{Ce}_2(\text{OH})_2(\text{SO}_4)_3\cdot4\text{H}_2\text{O}$ 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, $\beta = 96.27(1)$ / $96.81(1)$°, $V = 1267.9(4)$ / $1358.5(6)$ Å$^3$ 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 $\text{XO}_4$ tetrahedra forming a three-dimensional network. $\text{Zr}(\text{SO}_4)_2\cdot4\text{H}_2\text{O}$ ($Fddd$, $Z = 8$, $a = 5.498(1)$, $b = 11.618(3)$, $c = 25.893(6)$ Å, $V = 1653.9(6)$ Å$^3$) 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 $\text{SO}_4$ 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, $\beta = 110.128(3)$°, $V = 278.81(3)$ Å$^3$ (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 $\text{ZrO}_6$ 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 $(\text{XO}_3)^{2-}$ ($\text{X} = \text{S, Se}$) anions synthesized under mild-hydrothermal conditions below 250 °C. So far, the compounds $\text{Zr}(\text{SeO}_3)_2\cdot\text{H}_2\text{O}$ and $\text{Zr}(\text{SeO}_3)_2\cdot4\text{H}_2\text{O}$ [1], $\text{Zr}(\text{SeO}_3)(\text{SeO}_4)_2$, $\text{Zr}_4(\text{SeO}_3)(\text{SeO}_4)_7$, and $\text{Zr}_5(\text{SeO}_3)(\text{SeO}_4)_5\cdot2\text{H}_2\text{O}$ [2], as

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

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 isotypic 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].

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

For $\text{Zr(SeO}_4\text{)}_2$ 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 $\text{Pmmm}$ was proposed based on the absence of systematic extinctions, but several Bragg reflections remained unindexed. Since other $\text{M}^{4+}(\text{SeO}_4)_2$ phases, i.e. the isotypic compounds $\text{Ti(SeO}_4)_2$ [18], $\text{Pb(SeO}_4)_2$, and $\beta$-$\text{Sn(SeO}_4)_2$ [19], show similar powder patterns as $\text{Zr(SeO}_4)_2$ 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 $\nu$ (calculated according to [20]) of the four title compounds are listed in Table 1. Details about the hydrogen bonds are compiled in Table 2.

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**Zr$_2$(OH)$_2$(XO$_4$)$_3$·4H$_2$O (X=S, Se)**

The zirconium atoms in the isotypic compounds $\text{Zr}_2(\text{OH})_2(\text{XO}_4)_3\cdot 4\text{H}_2\text{O}$ ($X=\text{S, Se}$) are coordinated by eight oxygen atoms arranged in distorted tetragonal antiprisms. The ligands are represented by the oxygen atoms of two hydroxyl groups (O$_{\text{1}}$,O$_{\text{2}}$) and two H$_2$O molecules (O$_{\text{3}}$,O$_{\text{4}}$), as well as by four oxygen atoms of XO$_4$ tetrahedra (O$_{\text{5}}$,O$_{\text{6}}$,O$_{\text{7}}$,O$_{\text{8}}$). Each two ZrO$_8$ polyhedra are edge-connected to form dimers. The common O$_{\text{1}}$–O$_{\text{1}}$ 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 O$_3$ and 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 D–H···A are ~2.7 Å for the H$_2$O molecules but somewhat longer for the hydroxyl groups (2.84 and 2.96 Å for X=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 O$_3$ and 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$_{\text{b}}$–H$_{\text{a}}$···O$_{\text{1}}$ and O$_{\text{b}}$–H$_{\text{a}}$···O$_{\text{2}}$, are running within the eight-membered rings of the layers, whereas adjacent layers are interlinked to make up a three-dimensional framework via the $\text{Zr}_2$O$_4$ dimers (at their O$_{\text{1}}$–O$_{\text{1}}$ edge) as well as by O$_{\text{8}}$–H$_{\text{w}}$···O$_{\text{7}}$, O$_{\text{9}}$–H$_{\text{w}}$···O$_{\text{3}}$, and O$_{\text{9}}$–H$_{\text{w}}$···O$_{\text{7}}$ hydrogen bonds.

**Zr(SO$_4$)$_2$·4H$_2$O**

$\text{Zr(SO}_4\text{)}_2\cdot 4\text{H}_2\text{O}$ ($\alpha$-modification) [7, and present study] crystallizes in space group $\text{Fddd}$ and represents a structure type which further comprises the crystal structures of $\text{Zr(SO}_4\text{)}_2\cdot 4\text{H}_2\text{O}$ [1] and of the sulfates of $\text{M}^{4+}$=Pu, Hf, or Ce [9, 10, 14]. For $\text{Zr(SO}_4\text{)}_2\cdot 4\text{H}_2\text{O}$ the presence of a maximum in the residual electron-density (9.7 eÅ$^{-3}$) was observed at the special position 8a (at 1/8 5/8 5/8) [1]; it was attributed to a partially occupied site $\text{Zr}_2$ going along with the formation of vacancies at the $\text{Zr}_1$ 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.
indicating a slight site disorder [1]. In the present study on Zr(SO₄)₂·4H₂O, the highest residual electron density amounts 2.2 e Å⁻³; it again occurs at the 8a position. This slightly enhanced electron density is not considered to be
significant in the final refinements of Zr(SO_4)_2·4H_2O. 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 O_1 atoms. The sulfate groups have point symmetry 2. The ZrO_8 polyhedra share four corners—the O_1 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 Zr(H_2O)_4(SO_4)_2 layers running parallel to (001) (Figs. 2, 3a). The remaining two ligands of the sulfate group—atoms O_2—act as acceptors of both hydrogen bonds from the H_2O molecule (cf. Table 2). The hydrogen bonds O_w–H_1···O2 are located within the above-mentioned rings, whereas adjacent layers are interconnected only by the hydrogen bond O_w–H_2···O2. Without the contribution of the hydrogen bonds, the bond valence calculation gives only 1.56 v.u. for the O_2 atom.

Polyhedral bond-length distortions are quite similar for both compounds Zr(XO_4)_2·4H_2O (X = S, Se) as well as for α-Ce(SO_4)_2·4H_2O [10]. In β-Ce(SO_4)_2·4H_2O (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. γ-Ce(SO_4)_2·4H_2O, 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 Å, b = 5.633 Å, 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 γ-Ce(SO_4)_2·4H_2O must be doubted. Very likely, the phase investigated by [16] actually is the modification α-Ce(SO_4)_2·4H_2O. 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 Zr(SO_4)_2·4H_2O with its remarkable twinning behavior (see chapter on single-crystal X-ray diffraction in the experimental part), it seems very likely that crystals of α-Ce(SO_4)_2·4H_2O might be twinned in the same way as described herein, thus simulating a monoclinic C-centered

Table 2 Selected data for hydrogen bond systems in Zr_2(OH)_2(XO_4)_3·4H_2O (X = S, Se) and Zr(SO_4)_2·4H_2O

|                | D–H/Å   | D–A/Å   | D–H–A/° | H–D–H/° |
|----------------|---------|---------|---------|---------|
| Zr_2(OH)_2(XO_4)_3·4H_2O |         |         |         |         |
| O_1–H_1···O3  | 0.81(2) | 0.76(3) | 2.842(1)| 2.965(2)| 153(2) | 155(3) |
| O_8–H_2···O3  | 0.78(2) | 0.80(3) | 2.704(1)| 2.727(2)| 159(2) | 162(2) |
| O_w–H_3···O7  | 0.85(2) | 0.86(3) | 2.719(1)| 2.687(2)| 178(2) | 174(3) |
| O_9–H_4···O3  | 0.77(2) | 0.83(3) | 2.711(1)| 2.726(2)| 170(2) | 176(3) |
| O_9–H_5···O7  | 0.80(2) | 0.74(3) | 2.683(1)| 2.672(2)| 169(2) | 172(3) |
| Zr(SO_4)_2·4H_2O |         |         |         |         |
| O_w–H_1···O2  | 0.78(3) | 2.736(2)| 157(3)  | 112(3)  |
| O_w–H_2···O2' | 0.80(3) | 2.664(2)|         |         |

Fig. 1 Crystal structure of Zr_2(OH)_2(SO_4)_3·4H_2O in a projection along the crystallographic b-axis.
pseudo cell. This assumption is further corroborated by our observation of respective twinning also in Zr(SeO₄)₂·4H₂O, alongside with untwinned single crystals [1].

**Zr(SeO₃)₂**

The atomic arrangement in Zr(SeO₃)₂ consists of isolated ZrO₆ 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 Ti(SeO₃)₂ [18], Pb(SeO₃)₂, and β-Sn(SeO₃)₂ [19], a comparison is given in Table 3. It has to be noted that the unit cell volumes of Zr(SeO₃)₂ and Pb(SeO₃)₂ are rather similar, while the mean Zr–O bond length resembles more closely that of the SnO₆ polyhedron. Actually, based on the single-crystal data, the mean M⁴⁺–O bond lengths in this group obey a strict linear correlation with their respective ionic radii. The comparatively high cell volume of Zr(SeO₃)₂ could be induced by the clearly extended M–O–Se angles, which in turn are negatively correlated with the octahedral bond angle distortion σoct (Table 3).

As outlined in the section on X-ray powder diffraction, a previous description of Zr(SeO₃)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 M₂(OH)₂(XO₄)₃·4 H₂O (M = Zr; X = S, Se [this work]; M = Ce, X = S [5]) the X1 atom (located on a twofold axis, but sharing only two corners with ZrO₆-polyhedra) exhibits a larger average shift compared to the X2 atom (on a general position, but three corners shared). However, the X2O₄ tetrahedra show a more pronounced rotation. The average shifts of the O atoms belonging to the XO₄ tetrahedra 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 = Zr; X = S, Se of only 0.034–0.146 Å. For the structure pairs M = Zr and Ce, X = S, a significant deviation of the O₆ positions is evident (0.148 and...
0.160 Å). Again, the smaller shift of the S2 atom is notable. In case of the \( \alpha\)-\( M\)(\( XO_4\))\(_2\)\( \cdot\)4\( H_2\)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 \( M\)(SeO\(_3\))\(_2\) (\( M\) = Zr, Sn, Ti, 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 Zr(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 Zr\(_2\)(OH)\(_2\)(\( XO_4\))\(_3\)\( \cdot\)4\( H_2\)O (\( X\) = S, Se), Zr(SeO\(_4\))\(_2\)\( \cdot\)4\( H_2\)O, and Zr(SeO\(_3\))\(_2\) were studied by single-crystal X-ray diffraction, Zr(SeO\(_3\))\(_2\) also by powder techniques. The Zr\(_2\)(OH)\(_2\)(\( XO_4\))\(_3\)\( \cdot\)4\( H_2\)O compounds (\( X\) = S, Se) are isotypic with Ce\(_2\)(OH)\(_2\)(SO\(_4\))\(_3\)\( \cdot\)4\( H_2\)O and crystallize in space group \( C2/c\). Zr(SeO\(_4\))\(_2\)\( \cdot\)4\( H_2\)O (space group \( Fddd\)) is isotypic with the respective selenate as well as with \( \alpha\)-M(SeO\(_3\))\(_2\)\( \cdot\)4\( H_2\)O (\( M\) = Ce, Pu, Hf). It often shows pseudomerohedral twinning, simulating a monoclinic...
C-centered cell. By analogy, we postulate that the previously proposed γ-modification of Ce(SO₄)₂·4H₂O (space group C₂/c [16]) is most probably identical with α-Ce(SO₄)₂·4H₂O. Finally, Zr(SeO₃)₂ is monoclinic (space group P₂₁/c) and belongs to the structure type known for Ti(SeO₃)₂. Pb(SeO₃)₂, and β-Sn(SeO₃)₂. A previous indexing of Zr(SeO₃)₂ with orthorhombic symmetry (space group Pmnm) 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 [SeO₄] and/or [SeO₃] 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, ZrSiO₄) 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 Ti(SeO₃)₂ [18], β-Sn(SeO₃)₂ [19], Zr(SeO₃)₂ [present work], and Pb(SeO₃)₂ [19]. #: left column represents values obtained by Rietveld refinement.

| Compound | Ti(SeO₃)₂ | Sn(SeO₃)₂ | Zr(SeO₃)₂ | Pb(SeO₃)₂ |
|----------|-----------|-----------|-----------|-----------|
| a/Å      | 4.741     | 4.784     | 4.972(3)  | 4.963(1)  | 4.811     |
| b/Å      | 8.2554    | 8.529     | 8.599(5)  | 8.592(2)  | 8.768     |
| c/Å      | 6.7547    | 6.943     | 6.944(7)  | 6.939(2)  | 7.079     |
| β / °    | 110.57    | 111.01    | 110.12(3) | 110.09(1) | 110.10    |
| V/Å³     | 247.52    | 264.43    | 278.81(3) | 277.9(1)  | 280.4     |
| <M⁻⁶⁻O⁻>/Å | 1.937    | 2.040     | 2.056     | 2.071     | 2.121     |
| <Se–O>/Å  | 1.708     | 1.697     | 1.710     | 1.682     | 1.702     |
| σ_{oct}² | 10.68     | 22.60     | 12.50     | 4.42      | 38.38     |
| <M–O–Se>/° | 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_{max}/Å | d_{min}/Å | Δ |
|-----------------------|---------------|---|-----------|-----------|---|
| Zr₂(OH)₂(SO₄)₂·4H₂O   | Zr₂(SeO₄)₂·4H₂O [this work] | 0.0133 | 0.1817 | 0.1013 | 0.023 |
| Ce₂(SeO₄)₂·4H₂O       | Ce₂(SO₄)₂·4H₂O [5] | 0.0213 | 0.1601 | 0.0780 | 0.020 |
| Zr(SeO₄)₂·4H₂O        | Zr(SeO₄)₂·4H₂O [7] | 0.0021 | 0.0299 | 0.0129 | 0.014 |
| Zr(SeO₄)₂·4H₂O       | Zr(SeO₄)₂·4H₂O (Zr2 omitted) [1] | 0.0158 | 0.1362 | 0.0830 | 0.017 |
| Ce₂(SO₄)₂·4H₂O       | Ce₂(SO₄)₂·4H₂O [10] | 0.0181 | 0.1033 | 0.0685 | 0.018 |
| Hf(SO₄)₂·4H₂O        | Hf(SO₄)₂·4H₂O [9] | 0.0097 | 0.1048 | 0.0247 | 0.005 |
| Pu(SO₄)₂·4H₂O        | Pu(SO₄)₂·4H₂O [11] | 0.0150 | 0.1170 | 0.0531 | 0.031 |
| Zr₂(SeO₄)₂·4H₂O      | Sn(SeO₄)₂     | 0.0151 | 0.3596 | 0.2482 | 0.128 |
| Ti(SeO₄)₂            | Ti(SeO₄)₂     | 0.0239 | 0.2673 | 0.1747 | 0.065 |
| Pb(SeO₄)₂            | Pb(SeO₄)₂     | 0.0149 | 0.3783 | 0.2558 | 0.170 |
**Experimental**

**Synthesis**

The investigated zirconium oxysalts were obtained by low-hydrothermal synthesis from mixtures of Zr\(_2\)O\(_2\)(CO\(_3\))\(_2\)(OH)\(_2\) with concentrated \(\text{H}_2\text{SO}_4\), \(\text{H}_2\text{SeO}_4\), or \(\text{H}_2\text{SeO}_3\), 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 Zr\(_2\)(OH)\(_2\)(XO\(_4\))\(_3\)-4H\(_2\)O \((X = \text{S, Se})\) and Zr(SO\(_4\))\(_2\)-4H\(_2\)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. Zr(SeO\(_3\))\(_2\) was obtained mainly as a very fine-grained white powder, only occasionally crystals with up to 10 µm were obtained; the largest one found was used for a single-crystal X-ray investigation. 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 Zr(SO\(_4\))\(_2\)-4H\(_2\)O standard indexing of the ‘single-crystal’ reflex positions led to a monoclinic \(C\)-centered unit cell \((a = 34.815(5)\ Å, b = 5.497(1)\ Å, c = 14.190(3)\ Å, \beta = 114.00(1)°, V = 2481.0(8)\ Å\(^3\))\,\ Z = 12\). This unit cell closely resembles that proposed for \(\gamma\)-Ce(SO\(_4\))\(_2\)-4H\(_2\)O \[16\] \((a = 35.813, b = 5.633, c = 14.597\ Å, \beta = 113.73°, V = 2695.7\ Å\(^3\))\, which is one of three modifications reported for Ce(SO\(_4\))\(_2\)-4H\(_2\)O in literature \[10, 16\]. A refinement of Zr(SO\(_4\))\(_2\)-4H\(_2\)O in space group C2/c using a modified atomic model (see comments in captions to Figs. 2 and 3) published for \(\gamma\)-Ce(SO\(_4\))\(_2\)-4H\(_2\)O was performed. Moreover, pseudomerohedral twinning was considered (the transformation matrix \[1 0 2 / 0 −1 0 / 0 0 \ −1\] gave \(a = 34.838, b = 5.497, c = 14.190\ Å, \beta = 114.09°\); 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 ADDSYM 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 \[1/3 0 2/3 / 0 1 0 / 1/3 0 −4/3\] resulted in the hitherto known unit cell and an atomic arrangement based on space-group symmetry \(Fddd\), also known for \(\alpha\)-Ce(SO\(_4\))\(_2\)-4H\(_2\)O \[10\]. Finally, the observed reflection pattern is best described by an orthorhombic unit cell \((a = 5.498, b = 11.618, c = 25.893\ Å, \ Z = 8)\) and assuming a twinning (twin matrix \[1 0 0 / 0 2/3 1/3 / 0 −5/3 2/3\]). 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.
For the refinement of \( \text{Zr(SeO}_3\text{)}_2 \) (see also next section) the unit-cell setting and the atom labelling scheme were chosen in accordance to literature on the isotypic compounds \( M(\text{SeO}_3\text{)}_2 \) with \( M = \text{Ti}, \text{Sn}, \) and \( \text{Pb} \) \[18, 19\]. 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 (\( d_{\text{max}} \)), the arithmetic mean of the displacement between the atomic positions (\( d_{\text{av}} \)), and the similarity as a function of the differences in atomic positions and the ratios of the corresponding lattice parameters (\( \Delta \)). 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 \( \text{Zr(SeO}_3\text{)}_2 \) was studied at ambient conditions on a Bruker D8-Advance Eco diffractometer system, equipped with a CuK\( \alpha \)-optimized LynxEye XE-T position sensitive detector with an angular opening of 3.29° 2\( \theta \), primary Ni-filter, fixed divergence slit (FDS = 0.3°), 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 \( \varphi \)-spinning (15 min\(^{-1}\)). Sample diameter and FDS setting avoided beam spill in the angular range of the first occurring peak at ~ 17° 2\( \theta \). Data were collected from 5 to 125° 2\( \theta \) with ~ 0.01° 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 \( I_{\text{max}} \) of ~ 35,000 counts. The ambient temperature within the Eco-system enclosure was about 30(2) °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 \( M(\text{SeO}_3\text{)}_2 \) with \( M = \text{Ti}, \text{Sn}, \) and \( \text{Pb} \) \[18, 19\] 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 satisfactorily to \( R_1 = 0.027 \) with twin components of 73(1)% and 27(1)%.

For the refinement of \( \text{Zr(SeO}_3\text{)}_2 \) (see also next section) the unit-cell setting and the atom labelling scheme were chosen in accordance to literature on the isotypic compounds \( M(\text{SeO}_3\text{)}_2 \) with \( M = \text{Ti}, \text{Sn}, \) and \( \text{Pb} \) \[18, 19\]. 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 (\( d_{\text{max}} \)), the arithmetic mean of the displacement between the atomic positions (\( d_{\text{av}} \)), and the similarity as a function of the differences in atomic positions and the ratios of the corresponding lattice parameters (\( \Delta \)). The results are compiled in Table 4. The atom labels for the structure types under discussion refer to those given in Table 6.

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| Table 5 | Relevant crystal data and details of the single-crystal intensity measurements and structure refinements for \( \text{Zr}_2(\text{OH}_2(\text{XO}_4)_3\cdot 4\text{H}_2\text{O} \) \( X = \text{S}, \text{Se}, \) \( \text{Zr(SeO}_3\text{)}_2\cdot 4\text{H}_2\text{O}, \) and \( \text{Zr(SeO}_3\text{)}_2\) |
|---|---|---|---|
| **X** | **Zr(\text{OH}_2(\text{XO}_4)_3\cdot 4\text{H}_2\text{O}** | **Zr(\text{SO}_4)_2\cdot 4\text{H}_2\text{O** | **Zr(\text{SeO}_3)_2** |
| **Space group** | **C2/c** | **C2/c** | **Fddd** | **P2_1/c** |
| **a/Å** | 13.034(2) | 13.308(3) | 5.498(2) | 4.963(1) |
| **b/Å** | 6.500(1) | 6.683(2) | 11.618(3) | 8.592(2) |
| **c/Å** | 15.056(3) | 15.383(4) | 25.893(6) | 6.939(2) |
| **β/°** | 96.27(1) | 96.81(1) | 110.09(1) | |
| **V/Å³** | 1267.9(4) | 1358.5(6) | 1653.9(6) | 277.9(1) |
| **Z** | 4 | 4 | 8 | 2 |
| **ρ_{calc}/g cm^{-3** | 3.021 | 3.508 | 2.855 | 4.125 |
| **μ(\text{MoK}_α)/mm^{-1** | 2.25 | 9.68 | 1.90 | 15.03 |
| **Crystal size/mm³** | 0.20×0.20×0.17 | 0.15×0.10×0.08 | 0.20×0.05×0.025 | 0.02×0.01×0.0075 |
| **Data collection and refinement** | 2\( θ_{\text{max}}\) | 80 | 80 | 80 |
| **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]** | 0.016 / 0.017 | 0.020 / 0.024 | 0.027 / 0.032 | 0.025 / 0.034 |
| **wR2 [for all \( F_o²]²** | 0.036 | 0.038 | 0.056 | 0.038 |
| **a, b** | 0.012, 1.35 | 0.005, 3.0 | 0.018, 8.47 | 0.01, 0.32 |
| **Δρ_{min} / Δρ_{max}/Å^{-3**} | − 0.63 / 0.52 | − 1.11 / 0.80 | − 0.92 / 2.23 | − 0.84 / 0.76 |
Table 6  Atomic coordinates and displacement parameters for Zr₂(OH)₂(XO₄)₃·4H₂O (X = S, Se), Zr(SO₄)₂·4H₂O (Fddd cell choice 2—origin at 1/8 1/8 1/8 from 222), and Zr(SeO₃)₂ (e.s.d.'s in parentheses)

|       | x       | y       | z       | U_{iso} |
|-------|---------|---------|---------|---------|
| 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) | 0.26501(2) | 0.00506(3) |
| O₁    | 0.04124(5) | 0.12106(9) | 0.08425(2) | 0.00699(9) |
| O₂    | 0.07286(5) | 0.85022(10) | 0.26501(2) | 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) | 0.55676(12)| 0.13774(4) | 0.01193(11) |
| O₈    | 0.05601(5) | 0.03167(12)| 0.18351(3) | 0.0264(4)   |
| O₉    | 0.06000(16)| 0.220(3)   | 0.00775(14)| 0.037(5)    |
| H₁    | 0.056(2)  | 0.213(4)  | 0.00775(14)| 0.037(5)    |
| H₂    | 0.0721(16)| 0.153(3)  | 0.1430(14) | 0.033(5)    |
| H₃    | 0.2922(16)| 0.062(3)  | 0.18351(3) | 0.0264(4)   |
| H₄    | 0.2320(17)| 0.025(3)  | 0.24091(15)| 0.033(5)    |
| 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)  |
| O₁    | 0.04098(7) | 0.11792(14)| 0.00775(14)| 0.037(5)    |
| 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)| 0.14421(6) | 0.01407(18) |
| O₇    | 0.29762(8) | 0.55824(18)| 0.00775(14)| 0.037(5)    |
| O₈    | 0.01132(8) | 0.18992(16)| 0.14652(7) | 0.01214(17) |
| O₉    | 0.23155(8) | 0.04326(19)| 0.18704(7) | 0.01521(19) |
| H₁    | 0.056(2)  | 0.213(4)  | 0.00775(14)| 0.037(5)    |
| H₂    | 0.00178(19)| 0.308(4)  | 0.1485(16) | 0.026(6)    |
| H₃    | 0.072(2)  | 0.144(4)  | 0.1427(17) | 0.032(7)    |
| H₄    | 0.292(2)  | 0.058(4)  | 0.1817(16) | 0.029(7)    |
| H₅    | 0.2276(19)| 0.040(4)  | 0.2343(17) | 0.022(6)    |

|       | x       | y       | z       | U_{iso} |
|-------|---------|---------|---------|---------|
| Zr    | 0.5     | 0.5     | 0.5     | 0.00820(6) |
| S     | 0.5     | 0.5     | 0.5     | 0.731(19)  |

Zr(SeO₃)₂: Single-crystal (upper row) and powder (Rietveld) data (lower row)
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 P2₁/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$_4$)$_3$·4H$_2$O ($X = S, Se$), 2122298 for Zr(SO$_4$)$_2$·4H$_2$O, 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.

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### Table 6 (continued)

|   | $x$     | $y$     | $z$     | $U_{eq}$ |
|---|---------|---------|---------|---------|
| 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) |
Table 7 X-ray powder-diffraction data (d in Å) for Zr(SeO$_3$)$_2$

| $I_{\text{obs}}$ | $I_{\text{cal}}$ | $d_{\text{obs}}$ | $d_{\text{cal}}$ | $h$ | $k$ | $l$ |
|------------------|------------------|------------------|------------------|-----|-----|-----|
| 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  |
| 5                | 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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