



Syntheses and structures of three *f*-element selenite/hydroselenite compounds

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ABSTRACT

The selenite/hydroselenite compounds $\text{Ce}(\text{SeO}_3)(\text{HSeO}_3)$, $\text{Tb}(\text{SeO}_3)(\text{HSeO}_3) \cdot 2\text{H}_2\text{O}$, and $\text{Cs}[\text{U}(\text{SeO}_3)(\text{HSeO}_3)] \cdot 3\text{H}_2\text{O}$ were synthesized by hydrothermal means at 453 K from the reaction of CeO_2 or Tb_4O_7 or UO_2 with SeO_2 and CsCl (as a mineralizer). $\text{Ce}(\text{SeO}_3)(\text{HSeO}_3)$ crystallizes in the non-centrosymmetric orthorhombic space group $Pca2_1$. The structure comprises a two-dimensional network of interconnected CeO_{10} bicapped distorted square antiprisms and SeO_3 trigonal pyramids. $\text{Tb}(\text{SeO}_3)(\text{HSeO}_3) \cdot 2\text{H}_2\text{O}$ crystallizes in the non-centrosymmetric orthorhombic space group $P2_12_12_1$. The structure features a two-dimensional layer of interconnected TbO_8 distorted square antiprisms and SeO_3 trigonal pyramids. $\text{Cs}[\text{U}(\text{SeO}_3)(\text{HSeO}_3)] \cdot 3\text{H}_2\text{O}$ crystallizes in the centrosymmetric monoclinic space group $P2_1/n$. The structure consists of two-dimensional layers of interconnected UO_7 pentagonal bipyramids and SeO_3 trigonal pyramids. The layers in all three structures are held together by hydrogen-bonding networks.

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1. Introduction

The *f*-element selenite/hydroselenite compounds whose structures are known appear to comprise (1) $\text{Ln}(\text{SeO}_3)(\text{HSeO}_3)$ ($\text{Ln} = \text{La}$ [1], Pr [2]), (2) $\text{Ln}(\text{SeO}_3)(\text{HSeO}_3) \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd}$ [3], Sm [4]), (3) $(\text{NH}_4)[\text{UO}_2(\text{SeO}_3)(\text{HSeO}_3)]$ [5], and (4) $A[\text{UO}_2(\text{SeO}_3)(\text{HSeO}_3)]$ ($A = \text{K}, \text{Rb}, \text{Cs}, \text{Tl}$) [6]. The SeO_3^{2-} and HSeO_3^- anions lack a center of symmetry and each possesses a lone pair of electrons on Se. Unfortunately, this asymmetry does not necessarily lead to non-centrosymmetric crystal structures capable of possessing interesting physical properties: only structure types (1) and (2) belong to non-centrosymmetric space groups. But the presence of both of these groups, with or without additional waters of crystallization, and the high coordination numbers of the *f*-elements lead to unusual crystal structures.

Here we report the syntheses and structures of the three new *f*-element selenite/hydroselenite compounds $\text{Ce}(\text{SeO}_3)(\text{HSeO}_3)$, $\text{Tb}(\text{SeO}_3)(\text{HSeO}_3) \cdot 2\text{H}_2\text{O}$, and $\text{Cs}[\text{U}(\text{SeO}_3)(\text{HSeO}_3)] \cdot 3\text{H}_2\text{O}$.

2. Experimental

2.1. Instrumentation

A Vista-Mpx CCD Simultaneous Varian ICP-OES instrument was used for the determination of Se to *Ln* or U ratios. Three

standards were prepared for each element from ICP standard solutions at approximately 10, 20, and 30 ppm. At least four wavelengths were tested for each element.

A Rigaku Geigerflex Dmax automated powder diffraction station with a $\text{CuK}\alpha$ source and a Ni filter was used to measure the purities of the starting materials and to assess the products of the reactions.

A Cary 1E UV-Vis spectrophotometer with a diffuse reflectance accessory was used to make measurements over the range of 200 nm (6.20 eV) to 800 nm (1.55 eV) at 293 K.

A Bio-Rad FTS-40 FTIR instrument was used for infrared measurements. KBr was ground and dried prior to use. Samples were pressed in a KBr pellet. Measurements were made over the range 400–4000 cm^{-1} at 293 K. KBr was used as a standard.

EDX measurements were made on selected single crystals with an Hitachi S-3500 SEM.

2.2. Syntheses

2.2.1. General procedures

The following reagents were used as obtained: CeO_2 (Aldrich, 99.999%), Tb_4O_7 (Alfa Aesar, 99.9%), UO_2 (Strem, 99.8%), SeO_2 (Aldrich, 99.8%), and CsCl (Aldrich or Strem, 99.9%). On the basis of powder diffraction measurements CeO_2 , UO_2 , and SeO_2 were pure, and Tb_4O_7 consisted of different Tb/O phases with a molar range for O–Tb of 1.75–1.82 to 1.

Reaction mixtures were loaded into fused-silica tubes in an Ar-filled glove box. 0.35 mL of deionized water was added to each tube. The tubes were frozen in liquid N_2 , evacuated to 0.013 Pa,

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and flame-sealed. Tubes were loaded into a 2 L high-pressure reaction vessel containing water to balance the pressure created inside the tubes during reaction. The reaction vessel containing the tubes was then loaded into a computer-controlled furnace. When heated to 453 K, the pressure inside the reaction vessel reached 5.8 MPa. All crystals were washed free of chloride salts with deionized water and then dried with acetone. Single crystals for analytical measurements were selected by hand.

Although the nature of the redox processes is unknown it is clear from the products isolated from these reactions that Ce and Tb were both reduced to their +3 oxidation states whereas U was oxidized to its +6 oxidation state.

2.2.2. $Ce(SeO_3)(HSeO_3)$

The reaction mixture consisted of 0.037 mmol of CeO_2 , 0.074 mmol of SeO_2 , and 0.074 mmol of CsCl (used as a mineralizer to aid in crystal growth). The sample was heated to 453 K in 24 h, kept at 453 K for 72 h, and cooled at 9 K/h to 293 K. Colorless transparent plates of $Ce(SeO_3)(HSeO_3)$ crystallized in approximately 5% yield. The remaining material from the synthesis was primarily $Ce(SeO_3)(HSeO_3)$ powder. EDX: Ce and Se present; Cs and Cl absent. ICP: Se:Ce = 1.96(3):1. IR (cm^{-1}): 441, 685, 748, 874, and 1139.

2.2.3. $Tb(SeO_3)(HSeO_3) \cdot 2H_2O$

The reaction mixture consisted of 0.10 mmol of Tb_4O_7 , 0.08 mmol of SeO_2 , and 0.08 mmol of CsCl. The sample was heated to 453 K in 24 h, kept at 453 K for 72 h, and cooled at 1.3 K/h to 293 K. Colorless transparent plates of $Tb(SeO_3)(HSeO_3) \cdot 2H_2O$ crystallized in approximately 40% yield. The remaining material from the synthesis was unreacted Tb_4O_7 and $Tb(SeO_3)(HSeO_3) \cdot 2H_2O$ powder. EDX: Tb and Se present; Cs and Cl absent. ICP: Se:Tb = 2.02(3):1. IR (cm^{-1}): 454, 672, 777, 895, 1223, 1639, and 3316.

2.2.4. $Cs[U(SeO_3)(HSeO_3)] \cdot 3H_2O$

The reaction mixture consisted of 0.037 mmol of UO_2 , 0.074 mmol of SeO_2 , and 0.074 mmol of CsCl. The sample was heated to 453 K in 24 h, kept at 453 K for 72 h, and cooled at 3 K/h to 293 K. $Cs[U(SeO_3)(HSeO_3)] \cdot 3H_2O$ crystallized as yellow plates in approximately 40% yield. The byproducts were $[UO_2][SeO_3]$ and two types of uranium oxide. EDX: Cs, U, and Se present; Cl absent.

ICP: Se:U = 1.98(3):1. IR (cm^{-1}): 464, 665, 793, 895, 1166, 1642, 3396. UV–Vis: 429 nm.

2.3. Structure determinations

Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 153 K on a Bruker Smart-1000 CCD diffractometer [7]. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by recollecting 50 initial frames at the end of the data collection. Data were collected by a scan of 0.3° in ω in groups of 606 frames at ϕ settings of 0° , 90° , 180° , and 270° , respectively. The exposure time was 15 s/frame. The collection of the intensity data was carried out with the program SMART [7]. Cell refinement and data reduction were carried out with the use of the program SAINT [7]. The dimensions of each data crystal were measured with a Leitz microscope equipped with a calibrated micrometer eyepiece; face-indexed absorption corrections were performed numerically with the use of the program XPREP [8]. Then the program SADABS [7] was employed to make incident beam and decay corrections.

Each structure was solved with the direct-methods program SHELXS and refined with the least-squares program SHELXL [8].

$Ce(SeO_3)(HSeO_3)$ crystallizes with eight formula units in space group $Pca2_1$. All non-hydrogen atoms were refined anisotropically. The two independent H atoms, located in a difference electron density map, were refined isotropically. The Flack parameter of 0.39(1) is indicative of enantiomeric twinning. The structure could not be solved in the centrosymmetric space group $Pcam$.

$Tb(SeO_3)(HSeO_3) \cdot 2H_2O$ crystallizes with four formula units in space group $P2_12_12_1$. The Flack parameter of 0.42(4) is indicative of enantiomeric twinning. Non-hydrogen atoms were refined anisotropically, except for atoms O4, O5, and O6. The five independent H atoms, located in a difference electron density map, were fixed in idealized positions ($O-H = 0.82 \text{ \AA}$) [8].

$Cs[U(SeO_3)(HSeO_3)] \cdot 3H_2O$ crystallizes with four formula units in space group $P2_1/n$. Non-hydrogen atoms were refined anisotropically, except for atom O3. The seven independent H atoms, located in a difference electron density map, were fixed in idealized positions ($O-H = 0.82 \text{ \AA}$).

Additional crystallographic details are presented in Table 1 and Supplementary material. Tables 2–5 present selected metrical data.

Table 1

Crystal data and structure refinement for $Ce(SeO_3)(HSeO_3)$, $Tb(SeO_3)(HSeO_3) \cdot 2H_2O$, and $Cs[UO_2(SeO_3)(HSeO_3)] \cdot 3H_2O^a$.

	$Ce(SeO_3)(HSeO_3)$	$Tb(SeO_3)(HSeO_3) \cdot 2H_2O$	$Cs[UO_2(SeO_3)(HSeO_3)] \cdot 3H_2O$
Formula weight	395.05	449.88	711.92
Space group	$Pca2_1$	$P2_12_12_1$	$P2_1/n$
<i>a</i> (Å)	8.3875(5)	6.6017(5)	8.673(2)
<i>b</i> (Å)	7.0906(5)	6.9449(5)	10.452(3)
<i>c</i> (Å)	18.965(1)	16.255(1)	13.235(4)
β (deg)	90	90	105.147(4)
<i>V</i> (Å ³)	1127.9(1)	745.3(1)	1158.1(6)
<i>Z</i>	8	4	4
ρ_c (g/cm ³)	4.653	4.010	4.083
μ (cm ⁻¹)	209.35	192.60	234.39
<i>R</i> (<i>F</i>) ^b	0.0181	0.0353	0.0496
<i>R</i> _w (<i>F</i> _o ²) ^c	0.0438	0.0750	0.134
<i>q</i>	0.02	0.026	0.073

^a For all three compounds *T* = 153(2) K and $\lambda(MoK\alpha) = 0.71073 \text{ \AA}$.

^b $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.

^c $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (q \times F_o^2)^2$ for $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

Table 2
Selected distances (Å) and angles (deg) in Ce(SeO₃)(HSeO₃).

Ce(1)–O(5)	2.470(4)
Ce(1)–O(7)	2.494(4)
Ce(1)–O(9)	2.504(4)
Ce(1)–O(3)	2.523(4)
Ce(1)–O(5)	2.542(4)
Ce(1)–O(8)	2.553(3)
Ce(1)–O(2)	2.649(4)
Ce(1)–O(4)	2.668(4)
Ce(1)–O(2)	2.716(4)
Ce(1)–O(1)	2.813(4)
Ce(2)–O(11)	2.485(4)
Ce(2)–O(3)	2.491(3)
Ce(2)–O(1)	2.508(4)
Ce(2)–O(7)	2.527(4)
Ce(2)–O(2)	2.541(3)
Ce(2)–O(11)	2.600(4)
Ce(2)–O(8)	2.616(4)
Ce(2)–O(10)	2.703(4)
Ce(2)–O(8)	2.711(4)
Ce(2)–O(9)	2.777(4)
Se(1)–O(1)	1.673(4)
Se(1)–O(3)	1.713(3)
Se(1)–O(2)	1.731(4)
Se(2)–O(4)	1.658(4)
Se(2)–O(5)	1.670(4)
Se(2)–O(6)	1.782(4)
Se(3)–O(9)	1.685(4)
Se(3)–O(7)	1.718(4)
Se(3)–O(8)	1.732(4)
Se(4)–O(11)	1.666(4)
Se(4)–O(10)	1.680(4)
Se(4)–O(12)	1.762(4)
O(6)–(6A)	0.93(8)
O(12)–H(12A)	1.06(6)
O(1)–Se(1)–O(3)	106.2(2)
O(1)–Se(1)–O(2)	95.0(2)
O(3)–Se(1)–O(2)	97.0(2)
O(4)–Se(2)–O(5)	97.4(2)
O(4)–Se(2)–O(6)	98.8(2)
O(5)–Se(2)–O(6)	100.7(2)
O(9)–Se(3)–O(7)	106.2(2)
O(9)–Se(3)–O(8)	95.6(2)
O(7)–Se(3)–O(8)	97.1(2)
O(11)–Se(4)–O(10)	96.5(2)
O(11)–Se(4)–O(12)	102.1(2)
O(10)–Se(4)–O(12)	95.4(2)
Se(2)–O(6)–H(6A)	102(5)
Se(4)–O(12)–H(12A)	108(3)

Table 3
Selected distances (Å) and angles (deg) in Tb(SeO₃)(HSeO₃) · 2H₂O.

Tb(1)–O(1)	2.290(6)
Tb(1)–O(7)	2.363(7)
Tb(1)–O(5)	2.368(6)
Tb(1)–O(4)	2.383(7)
Tb(1)–O(3)	2.387(7)
Tb(1)–O(2)	2.390(7)
Tb(1)–O(3)	2.432(7)
Tb(1)–O(2)	2.452(7)
Se(1)–O(1)	1.679(6)
Se(1)–O(2)	1.713(7)
Se(1)–O(3)	1.719(7)
Se(2)–O(4)	1.680(7)
Se(2)–O(5)	1.699(6)
Se(2)–O(6)	1.758(7)
O(1)–Se(1)–O(2)	102.2(3)
O(1)–Se(1)–O(3)	102.2(3)
O(2)–Se(1)–O(3)	92.7(3)
O(4)–Se(2)–O(5)	101.7(3)
O(4)–Se(2)–O(6)	97.2(3)
O(5)–Se(2)–O(6)	98.2(3)
Se(2)–O(6)–H(6A)	89.3(5)

Table 4
Selected distances (Å) and angles (deg) in Cs[UO₂(SeO₃)(HSeO₃)] · 3H₂O.

U(1)–O(8)	1.774(9)
U(1)–O(7)	1.790(9)
U(1)–O(3)	2.354(8)
U(1)–O(1)	2.369(9)
U(1)–O(5)	2.378(9)
U(1)–O(4)	2.387(8)
U(1)–O(2)	2.392(8)
Cs(1)–O(8)	3.041(8)
Cs(1)–O(4)	3.090(8)
Cs(1)–O(10)	3.093(9)
Cs(1)–O(5)	3.113(9)
Cs(1)–O(6)	3.113(9)
Cs(1)–O(1)	3.237(9)
Cs(1)–O(9)	3.289(11)
Cs(1)–O(7)	3.323(8)
Cs(1)–O(10)	3.335(9)
Cs(1)–O(2)	3.354(8)
Se(1)–O(1)	1.669(9)
Se(1)–O(2)	1.695(8)
Se(1)–O(3)	1.705(8)
Se(2)–O(4)	1.677(8)
Se(2)–O(5)	1.680(10)
Se(2)–O(6)	1.768(9)
O(1)–Se(1)–O(2)	99.7(4)
O(1)–Se(1)–O(3)	103.2(4)
O(2)–Se(1)–O(3)	99.2(4)
O(4)–Se(2)–O(5)	102.6(4)
O(4)–Se(2)–O(6)	95.8(4)
O(5)–Se(2)–O(6)	100.1(5)
Se(2)–O(6)–H(6A)	107.3(8)

Table 5
The hydrogen bonding schemes.^a

D	H	A	D–H	H...A	D...A	<D–H...A
Ce(SeO ₃)(HSeO ₃)						
O6	H6A	O10	0.93	1.709	2.539	147
O6	H6A	O4	0.93	2.584	3.067	113
O12	H12A	O6	1.06	1.593	2.645	174
Tb(SeO ₃)(HSeO ₃) · 2H ₂ O ^b						
O6	H6A	O6	0.82	2.585	3.396	177
O7	H7A	O5	0.82	2.214	2.810	133
O7	H7B	O8	0.82	1.858	2.651	164
O8	H8A	O1	0.82	2.141	2.850	144
O8	H8A	O2	0.82	2.449	3.162	146
O8	H8B	O5	0.82	2.309	2.974	142
Cs[U(SeO ₃)(HSeO ₃)] · 3H ₂ O ^b						
O6	H6A	O11	0.82	1.815	2.641	180
O9	H9A	O3	0.82	2.021	2.835	169
O9	H9B	O11	0.82	2.332	3.149	169
O10	H10A	O2	0.82	2.063	2.885	179
O10	H10B	O9	0.82	1.925	2.750	180
O11	H11A	O7	0.82	2.134	2.952	174
O11	H11B	O10	0.82	1.970	2.777	167

^a D = donor atom; A = acceptor atom.^b In the Tb and U structures the positions of the H atoms were located in difference electron density syntheses but these positions could not be refined and thus they were idealized. As a result, the metrical details of the hydrogen bonding schemes are subject to considerable uncertainty.

3. Results and discussion

3.1. Syntheses

Crystals of the three compounds Ce(SeO₃)(HSeO₃), Tb(SeO₃)(HSeO₃) · 2H₂O, and Cs[UO₂(SeO₃)(HSeO₃)] · 3H₂O were prepared

in approximate yields of crystals of 5%, 40%, and 40%, respectively, by hydrothermal reactions of CeO_2 , Tb_4O_7 , or UO_2 with SeO_2 and CsCl at 453 K. No attempt was made to optimize yields. Although the experimental conditions appear to be the same, we synthesized yellow plates of $\text{Cs}[\text{UO}_2(\text{SeO}_3)(\text{HSeO}_3)] \cdot 3\text{H}_2\text{O}$ whereas earlier [6] yellow needles of $\text{Cs}[\text{UO}_2(\text{SeO}_3)(\text{HSeO}_3)]$ [6] were synthesized.

3.2. Crystal structures

3.2.1. $\text{Ce}(\text{SeO}_3)(\text{HSeO}_3)$

This compound is isostructural to $\text{Ln}(\text{SeO}_3)(\text{HSeO}_3)$ ($\text{Ln} = \text{La}$ [1], Pr [2]). Its structure consists of a two-dimensional network of interconnected CeO_{10} bicapped distorted square antiprisms and SeO_3 trigonal pyramids that propagate in the ab plane (Fig. 1). These independent layers are held together by hydrogen bonds (Table 5). Each layer consists of $\text{Ce}(1)(\text{SeO}_3)(\text{HSeO}_3)$ and $\text{Ce}(2)(\text{SeO}_3)(\text{HSeO}_3)$ chains that run along the a -axis. The CeO_{10} antiprisms (Fig. 2) edge share within the chains and face share between the chains. The two independent SeO_3 groups, containing atoms $\text{Se}(1)$ and $\text{Se}(3)$, act as bridges for the CeO_{10} antiprisms both within and between the chains. The two independent HSeO_3 groups, containing atoms $\text{Se}(2)$ and $\text{Se}(4)$, bridge the CeO_{10} antiprisms within the chains.

Table 2 provides selected interatomic distances and angles. The range of $\text{Ce}-\text{O}$ distances in $\text{Ce}(\text{SeO}_3)(\text{HSeO}_3)$, 2.470(4)–2.813(4) Å (Table 2), is within the range of the $\text{La}-\text{O}$ distances in the isostructural $\text{La}(\text{SeO}_3)(\text{HSeO}_3)$ compound (2.51(1)–2.84(1) Å) and the $\text{Pr}-\text{O}$ distances in the isostructural $\text{Pr}(\text{SeO}_3)(\text{HSeO}_3)$ compound (2.47(1)–2.77(1) Å).

The $\text{Se}-\text{O}$ distances are normal. As expected, the longest are the $\text{Se}-\text{O}(\text{H})$ distances $\text{Se}(2)-\text{O}(6)$ and $\text{Se}(4)-\text{O}(12)$ and the next longest are the tetrahedrally coordinated atoms $\text{O}2$ and $\text{O}8$ of the SeO_3 groups. Specifically, the $\text{Se}-\text{O}(\text{H})$ distances are 1.782(4) and 1.762(4) Å whereas the remaining $\text{Se}-\text{O}$ distances range from 1.658(4) to 1.732(4) Å.

3.2.2. $\text{Tb}(\text{SeO}_3)(\text{HSeO}_3) \cdot 2\text{H}_2\text{O}$

This compound is isostructural to $\text{Ln}(\text{SeO}_3)(\text{HSeO}_3) \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd}$ [3], Sm [4]). Its structure consists of a two-dimensional layer of interconnected TbO_8 distorted square antiprisms (Fig. 2) and SeO_3 trigonal pyramids that propagate in the ab plane (Fig. 3). The independent layers are connected through an extended hydrogen bonding scheme involving the HSeO_3 groups and H_2O molecules (Table 5). Each layer consists of individual TbO_8 chains along the b -axis (Fig. 3). The TbO_8 antiprisms edge share within the chains but do not interact directly between chains. The $\text{Se}(1)\text{O}_3$ group bridges three different Tb atoms within a chain and connects to another Tb atom in a different chain. The $\text{Se}(2)\text{O}_3$ group bridges Tb atoms within a Tb chain.

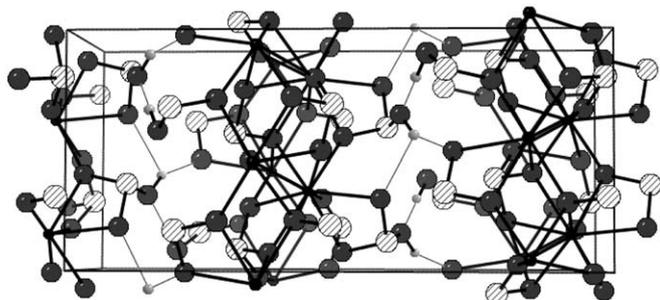


Fig. 1. The structure of $\text{Ce}(\text{SeO}_3)(\text{HSeO}_3)$ viewed down [010]. The small black balls are Ce; the hollow striped balls are Se; the larger black balls are O; and the small gray balls are H.

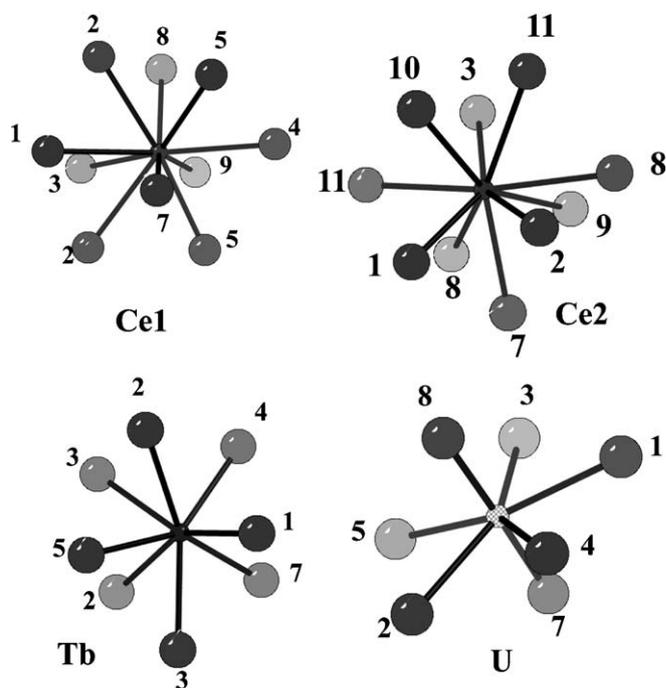


Fig. 2. The coordination spheres of Ce in $\text{Ce}(\text{SeO}_3)(\text{HSeO}_3)$, Tb in $\text{Tb}(\text{SeO}_3)(\text{HSeO}_3) \cdot 2\text{H}_2\text{O}$, and U in $\text{Cs}[\text{U}(\text{SeO}_3)(\text{HSeO}_3)] \cdot 3\text{H}_2\text{O}$.

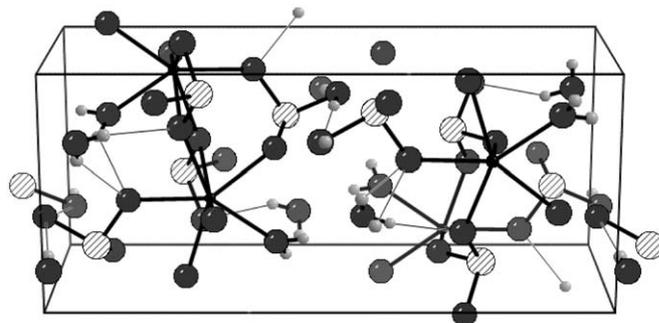


Fig. 3. The structure of $\text{Tb}(\text{SeO}_3)(\text{HSeO}_3) \cdot 2\text{H}_2\text{O}$ viewed approximately along [100]. The smaller black balls are Tb; the hollow striped balls are Se; the larger black balls are O; and the small gray balls are H.

Table 3 provides selected interatomic distances and angles. These data are in excellent agreement with those for the isostructural compounds $\text{Ln}(\text{SeO}_3)(\text{HSeO}_3) \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Nd}$, Sm). The range of $\text{Tb}-\text{O}$ distances in $\text{Tb}(\text{SeO}_3)(\text{HSeO}_3) \cdot 2\text{H}_2\text{O}$, 2.290(6)–2.452(7) Å (Table 3), is similar to those of 2.260–2.548 Å in $\text{Tb}_2\text{O}(\text{SeO}_3)_2$ [9].

The $\text{Se}-\text{O}$ distances are normal. The longest is the $\text{Se}(2)-\text{O}(6)(\text{H})$ distance (1.758(7) Å). The remaining $\text{Se}-\text{O}$ distances range from 1.679(6) to 1.719(7) Å. The longest of these involve atoms $\text{O}2$ and $\text{O}3$ of the SeO_3 group that are connected to two Tb atoms and one Se atom, and the shortest involve atoms $\text{O}1$ of the SeO_3 group and $\text{O}4$ and $\text{O}5$ of the HSeO_3 group that are involved in $\text{Tb}-\text{O}-\text{Se}$ bonding.

3.2.3. $\text{Cs}[\text{UO}_2(\text{SeO}_3)(\text{HSeO}_3)] \cdot 3\text{H}_2\text{O}$

The structure of the $[\text{UO}_2(\text{SeO}_3)(\text{HSeO}_3)]^{1-}$ anion in $\text{Cs}[\text{UO}_2(\text{SeO}_3)(\text{HSeO}_3)] \cdot 3\text{H}_2\text{O}$ is very similar to those in $(\text{NH}_4)[\text{UO}_2(\text{SeO}_3)(\text{HSeO}_3)]$ [5] and $\text{A}[\text{UO}_2(\text{HSeO}_3)(\text{SeO}_3)]$ ($\text{A} = \text{K}$, Rb , Cs , Tl) [6]. The presence of water in the present compound provides a

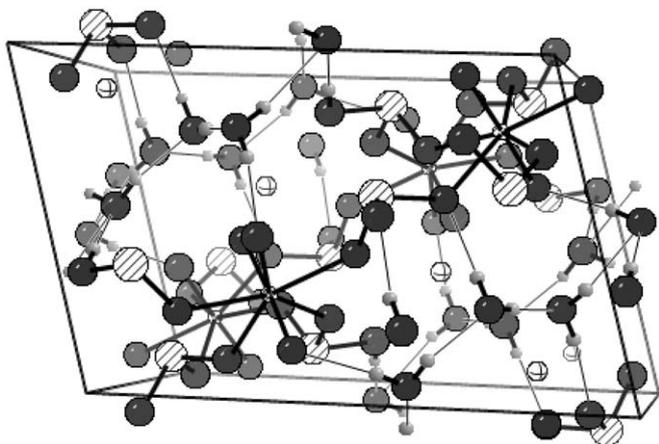


Fig. 4. The structure of $\text{Cs}[\text{U}(\text{SeO}_3)(\text{HSeO}_3)] \cdot 3\text{H}_2\text{O}$ viewed approximately along [010]. The small hollow hatched balls are U; the hollow equatorial balls are Cs, the hollow striped balls are Se; the large black balls are O; and the small gray balls are H.

different packing from that in $A[\text{UO}_2(\text{HSeO}_3)(\text{SeO}_3)]$ ($A = \text{K}, \text{Rb}, \text{Cs}, \text{Tl}$). The structure consists of a two-dimensional layer of interconnected UO_7 pentagonal bipyramids (Fig. 2) and SeO_3 trigonal pyramids that propagate in the ab direction (Fig. 4). The UO_7 pentagonal bipyramids are not directly connected to one another within the layer, but rather are bridged by either a single SeO_3 group or by a SeO_3 and a HSeO_3 group. Four UO_7 pentagonal bipyramids form a channel along the c -axis. There is a zigzag chain of Cs atoms that runs through these channels along the c -axis. Each layer of $[\text{UO}_2(\text{SeO}_3)(\text{HSeO}_3)]^{1-}$ is separated by a layer of water molecules (Table 5). Table 4 provides selected interatomic distances and angles. These data are in excellent agreement with those for the compound $\text{Cs}[\text{UO}_2(\text{HSeO}_3)(\text{SeO}_3)]$. The $\text{U}-\text{O}(\text{UO}_2)$ distances in $\text{Cs}[\text{UO}_2(\text{SeO}_3)(\text{HSeO}_3)] \cdot 3\text{H}_2\text{O}$ of 1.774(9) and 1.790(9) Å (Table 4) are similar to those of 1.783(4)–1.787(4) Å in $\text{Cs}[\text{UO}_2(\text{HSeO}_3)(\text{SeO}_3)]$. The $\text{U}-\text{O}(\text{Se})$ distances of 2.354(8) to 2.392(8) Å are within the range seen in $\text{Cs}[\text{UO}_2(\text{HSeO}_3)(\text{SeO}_3)]$, 2.324(4)–2.419(4) Å. These distances are consistent with the values of 1.79(3) and 2.37(10) Å derived from an extensive tabulation of well-refined crystal structures containing uranyl pentagonal bipyramids [10]. The longest Se–O bond involves atom

O6 of the Se–O–H group (1.768(9) Å); the remaining Se–O distances range from 1.669(9) to 1.705(8) Å.

Supplementary material

Crystallographic files in CIF format for $\text{Ce}(\text{SeO}_3)(\text{HSeO}_3)$, $\text{Tb}(\text{SeO}_3)(\text{HSeO}_3) \cdot 2\text{H}_2\text{O}$, and $\text{Cs}[\text{U}(\text{SeO}_3)(\text{HSeO}_3)] \cdot 3\text{H}_2\text{O}$ have been deposited with FIZ Karlsruhe as CSD numbers 420178, 420180, and 420179, respectively. These data may be obtained free of charge by contacting FIZ Karlsruhe at +49 7247 808 666 (fax) or crysdata@fiz-karlsruhe.de (email).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2009.03.016](https://doi.org/10.1016/j.jssc.2009.03.016).

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