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Layered calcium hydrogen selenite chlorides $\text{Ca}(\text{HSeO}_3)\text{Cl}$ and $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$, the first halides obtained in $\text{CaCl}_2\text{--H}_2\text{SeO}_3\text{--H}_2\text{O}$ system

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Abstract: Synthesis, crystal structures and IR spectra of the first representatives of calcium hydrogen selenite halides are reported. Colourless prismatic crystals of calcium hydrogen selenite chloride $\text{Ca}(\text{HSeO}_3)\text{Cl}$ and corresponding hydrated analogue $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ were produced upon evaporation of aqueous solutions. $\text{Ca}(\text{HSeO}_3)\text{Cl}$ is monoclinic, $P2_1/c$, $a = 7.0031(11)$ Å, $b = 7.7336(12)$ Å, $c = 8.5024(13)$ Å, $\beta = 109.889(3)^\circ$, $V = 433.02(12)$ Å³, $R_1 = 0.039$. $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ is orthorhombic, $Pbca$, $a = 6.222(4)$ Å, $b = 10.413(7)$ Å, $c = 16.875(10)$ Å, $V = 1093.3(12)$ Å³, $R_1 = 0.041$. $\text{Ca}(\text{HSeO}_3)\text{Cl}$ and $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ represent new structure types. In both structures, Ca^{2+} cations adopt mixed-ligand environments formed by oxygen atoms of hydrogen selenite anions (and water molecules for $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$) and chloride ions. Both structures are layered. The crystal structure of $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ demonstrates a rare phenomenon of hydrogen-bonded assembly of water and chloride in the interlayer space.

Keywords: calcium; halides; hydrogen selenites; layered structures.

1 Introduction

The use of ‘lone-pair’ cations and halide anions as a tool for design of low-dimensional inorganic structures has been recognized decades ago [1]. In the meantime, there exist many other structure-driving phenomena

extensively used as important tools in construction of layered materials, whereof probably the most powerful is hydrogen bonding [2]. Protonated lone-pair anions are observed in the structure of $\text{Pb}_2(\text{HASO}_3)\text{Cl}_2$ [3, 4] and a series of layered hydrogen selenites of zinc, cadmium, cobalt, and mostly copper [5–10]. Neutral $[\text{Cu}(\text{HSeO}_3)_2]$ layers are the most common units which are found in three structurally related families: nitrates $(\text{ANO}_3)_n$ $[\text{Cu}(\text{HSeO}_3)_2]$ ($n = 1\text{--}2$, $A = \text{NH}_4, \text{Rb}, \text{Cs}, \text{Tl}$) [11], halides $(\text{AX})[\text{Cu}(\text{HSeO}_3)_2]$ ($A = \text{Na--Cs}, \text{Tl}, \text{NH}_4$; $X = \text{Cl}, \text{Br}$) [12], and more complex $[\text{M}(\text{H}_2\text{O})_4\text{Cl}_2][\text{Cu}(\text{HSeO}_3)_2]$ ($M = \text{Mn}, \text{Co--Zn}$) (Lafont et al. 1995) [13]. Our attempts to look for its new members serendipitously resulted in formation of two novel hydrogen selenite chlorides, namely $\text{Ca}(\text{HSeO}_3)\text{Cl}$ and its hydrate, $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$.

2 Experimental

2.1 Synthesis

We initially attempted to prepare Ca-analogue of the $[\text{M}(\text{H}_2\text{O})_4\text{Cl}_2][\text{Cu}(\text{HSeO}_3)_2]$ chlorides (Lafont et al. 1995). According to previously developed procedure [12], $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, 98%), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich, 99%), and H_2SeO_3 (Aldrich, 98%) were taken in 10:1:3 ratio and dissolved in distilled water. The slight turbidity was eliminated by adding several drops of CF_3COOH . The solutions were left to evaporate for one week. Copper-containing phase precipitated in the form of very small blue grains which looked unlike the expected acicular ones typical for the copper hydro-selenite halides. The blue grains were attached to relatively large, well-faceted colorless crystals investigated during this study. Two kinds of such colorless crystals were selected (Figure 1), one at the start of crystallization and the other at the final stage when evaporation was almost complete. Unit-cell metrics indicated formation of two novel compounds, further identified as $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ and its anhydrous form, $\text{Ca}(\text{HSeO}_3)\text{Cl}$. Attempts to prepare analogous bromides according to similar protocol using Ca and Cu bromides led to a poorly crystalline substance which deliquesced easily in air. Attempts were also made to use Cd^{2+} , Sr^{2+} and Mg^{2+} instead of Ca^{2+} ; new compounds were not observed.

Both new calcium hydrogen selenite chlorides are stable under ambient conditions. Qualitative electron microprobe analysis (LINK AN-10000 EDS system) in both compounds revealed no elements with the atomic number greater than 11 (Na), other than Cl, Ca, and Se.

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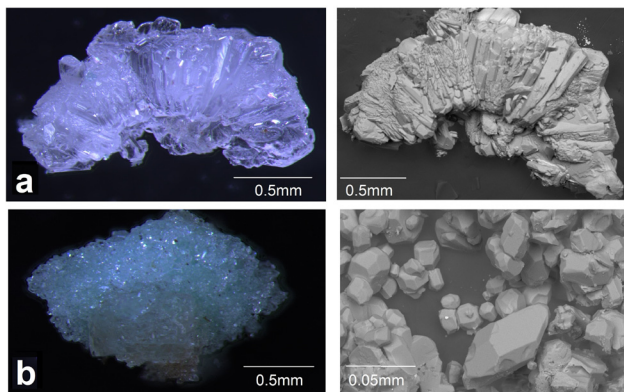


Figure 1: Colorless crystals of $\text{Ca}(\text{HSeO}_3)\text{Cl}$ (a) and $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ (b) under optical microscope and BSE images. Light-green coloration (b) is due to the presence of very small poorly crystalline copper selenites.

2.2 Single-crystal X-ray analysis

Colorless prismatic single crystals of $\text{Ca}(\text{HSeO}_3)\text{Cl}$ and $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ were mounted on thin glass fibers. The X-ray diffraction data were acquired on a Bruker APEX II DUO X-ray diffractometer equipped with a micro-focus X-ray tube operating with $\text{MoK}\alpha$ radiation at 50 kV and 0.6 mA. Both structures were solved by direct methods using SHELXL software package [14]. The positions of hydrogen atoms were ascertained from the difference Fourier maps. U_{eq} value of H1 atom in $\text{Ca}(\text{HSeO}_3)\text{Cl}$ was constrained to 0.01. The constraints of U_{eq} were also applied for H1 and H3 in $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$. Additionally, the positions of the H atoms in $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ were constrained to H–O distances of 1.000(1) Å on the final stages of refinement. $\text{Ca}(\text{HSeO}_3)\text{Cl}$ is

Table 1: Crystallographic data refinement parameters for $\text{Ca}(\text{HSeO}_3)\text{Cl}$ and $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$.

	$\text{Ca}(\text{HSeO}_3)\text{Cl}$	$\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$
Space group	$P2_1/c$	$Pbca$
a (Å)	7.0031 (11)	6.222 (4)
b (Å)	7.7336 (12)	10.413 (7)
c (Å)	8.5024 (13)	16.875 (10)
β (°)	109.889 (3)	
V (Å ³)	433.02 (12)	1093.3 (12)
Z	4	8
Radiation	$\text{MoK}\alpha$	$\text{MoK}\alpha$
Total reflections	2943	6925
Unique reflections	1047	1281
Unique $F^2 \geq 2\sigma(F^2)$	880	811
GoF	1.017	0.950
F_{000}	384	848
Crystal size (mm)	0.07 × 0.06 × 0.10	0.10 × 0.10 × 0.08
μ (cm ⁻¹)	10.324	8.202
D_{calc} (g/cm ³)	3.122	2.691
R_{int}	0.048	0.079
R_1	0.039	0.041
R_1 (all data)	0.048	0.079
wR_2	0.092	0.075
wR_2 (all data)	0.096	0.088

monoclinic, $P2_1/c$, $a = 7.0031(11)$ Å, $b = 7.7336(12)$ Å, $c = 8.5024(13)$ Å, $\beta = 109.889(3)^\circ$, $V = 433.02(12)$ Å³, $R_1 = 0.038$. $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ is orthorhombic, $Pbca$, $a = 6.222(4)$ Å, $b = 10.413(7)$ Å, $c = 16.875(10)$ Å, $V = 1093.3(12)$ Å³, $R_1 = 0.041$ (Table 1). Selected bond-lengths are provided in Table 2.

2.3 Infrared spectroscopy

IR spectra (Figure 2) of $\text{Ca}(\text{HSeO}_3)\text{Cl}$ and $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ were obtained from powdered samples mixed with dried KBr, pelletized and analyzed at room temperature using an Bruker Vertex 70 FTIR spectrometer with a resolution of 4 cm⁻¹. In general, both compounds demonstrate similar spectra. Selenite ion vibrations are observed in the region 430–855 cm⁻¹ [15, 16]. Both spectra have peaks

Table 2: Selected interatomic distances (Å) and bond-valence sums (in *v.u.*) for $\text{Ca}(\text{HSeO}_3)\text{Cl}$ and $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$. Symmetry transformations used to generate equivalent atoms are shown in footnotes a–f.

	$\text{Ca}(\text{HSeO}_3)\text{Cl}$	$\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$	
Ca1–O2 ^a	2.389 (4)	Ca1–O2	2.346 (4)
Ca1–O1 ^b	2.393 (4)	Ca1–O1 ^d	2.369 (4)
Ca1–O2 ^c	2.405 (4)	Ca1–OW1	2.378 (5)
Ca1–O1	2.415 (4)	Ca1–O2 ^e	2.455 (4)
Ca1–OH1 ^c	2.680 (4)	Ca1–O1 ^f	2.455 (4)
Ca1–OH1	2.693 (4)	Ca1–Cl1	2.777 (2)
Ca1–Cl1 ^c	2.845 (2)	Ca1–OH1 ^e	2.834 (5)
Ca1–Cl1	2.859 (2)	Ca1–OH1 ^f	2.935 (6)
BVS Ca	2.05	BVS Ca	2.01
Se1–O2	1.660 (3)	Se1–O2	1.655 (4)
Se1–O1	1.664 (3)	Se1–O1	1.664 (4)
Se1–OH1	1.801 (4)	Se1–OH1	1.798 (4)
BVS Se	3.85	BVS Se	3.87

^a– $x, 0.5 + y, 0.5 - z$; ^b– $x, -y, 1 - z$; ^c– $x, 0.5 - y, 0.5 + z$; ^d– $1.5 - x, -0.5 + y, z$; ^e– $0.5 + x, y, 1.5 - z$; ^f– $1 - x, -0.5 + y, 1.5 - z$.

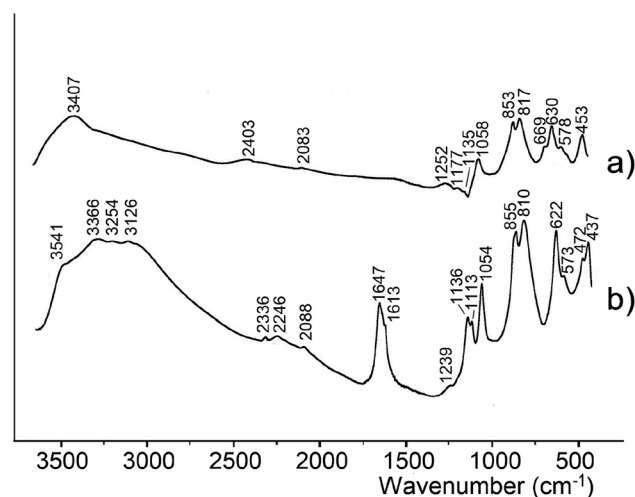


Figure 2: Infrared absorption spectra of $\text{Ca}(\text{HSeO}_3)\text{Cl}$ (a) and $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ (b).

corresponding to O–H vibrations. The peaks at 2336, 2246 (in $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$) and 2403 (in $\text{Ca}(\text{HSeO}_3)\text{Cl}$) cm^{-1} indicate hydrogen bonding. The main differences between the spectra are the O–H and H–O–H vibrations at 1613, 1647 cm^{-1} and 3126, 3254, 3336 and 3541 cm^{-1} of water molecules which are indeed present in the spectrum of $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ but not $\text{Ca}(\text{HSeO}_3)\text{Cl}$.

3 Results and discussion

According to its size, Ca^{2+} is probably too large to contribute to the family of $[\text{M}(\text{H}_2\text{O})_4\text{Cl}_2][\text{Cu}(\text{HSeO}_3)_2]$ copper hydrogen selenites. The obtained copper-free compounds are distantly structurally related to calcium hydrogen selenites [16]. $\text{Ca}(\text{HSeO}_3)\text{Cl}$ and $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ are the first hydrogen selenite halides of Group 2 elements. Their structures, as expected, differ essentially from those of the transition metal hydrogen selenite family. The very small crystals of copper selenites (not investigated) were probably formed after crystallization of the calcium compounds, as they had been found on the surface of calcium hydroselenite chlorides.

The crystal structure of anhydrous $\text{Ca}(\text{HSeO}_3)\text{Cl}$, apart from the only one H position, contains two symmetrically independent cation and three symmetrically independent anion positions. All atoms reside in general positions. The protonated selenite anion has a distorted triangular pyramidal shape; the Se–O distances are 1.660(3), 1.664(3) and 1.801(4) Å, the latter corresponding to the Se–OH bond (the O–H distance is 0.97(5) Å). The Ca^{2+} resides in an irregular eight-vertex polyhedron (Figure 3a) formed by oxygen atoms of the HSeO_3^- species (including those of OH groups) and Cl^- anions. The Ca–Cl distances are in the range 2.845(2)–2.859(2) Å. The distances to hydroxyl

oxygens (2.680(4) and 2.693(4) Å), are, as expected, longer than those to non-protonated counterparts (2.389(4)–2.415(4) Å).

In the structure of $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$, all atoms also reside in general positions. Apart from three H positions, there are two cationic and five anionic positions. The HSeO_3^- anions exhibit very similar geometry with Se–O distances of 1.655(4), 1.664(4), and 1.798(4) Å. The Ca^{2+} in $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ is also eight-coordinated but with one chlorine and seven oxygen atoms (Figure 3b). The Ca–Cl bond is shorter (2.777(2) Å) and Ca– H_2O distance is 2.378(5) Å. Ca– H_2O bond-length values are in a good agreement with those observed in CaCl_2 hydrates: 2.315 Å in sinjarite $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ [17] and 2.354–2.468 Å in ghiaraita $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ [18]. The protonated oxygen atoms are at larger distances from the Ca^{2+} (2.834(5)–2.935(5) Å) in comparison to their non-protonated counterparts (2.346(4)–2.455(4) Å). Calculated bond valence sums for cations (Table 2) [19], are in agreement with expected oxidation states.

Both $\text{Ca}(\text{HSeO}_3)\text{Cl}$ (Figure 4a) and $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ (Figure 5a) form centrosymmetric layered structures, comprised of edge- and vertex-sharing irregular CaX_8 polyhedra decorated by hydroselenite groups. In the structure of anhydrous $\text{Ca}(\text{HSeO}_3)\text{Cl}$, the $\text{CaO}_4(\text{OH})_2\text{Cl}_2$ irregular polyhedra share O–O and Cl–O edges; they are arranged in an alternative “up-down” orientation along the *b* axis (Figure 4b). The Se atoms of the HSeO_3^- groups from one layer are facing Cl atoms from the other; the ‘lone pairs’ of Se^{4+} are directed into the interlayer space. $\text{Ca}(\text{HSeO}_3)\text{Cl}$ is distantly related to the previously reported $\text{Cd}(\text{HSeO}_3)\text{NO}_3$ (Pbca, $a = 6.359(1)$, $b = 8.945(2)$, $c = 16.648(4)$ Å, $V = 946.96$ Å³) [14]. This is not surprising considering that the ionic radii of Ca^{2+} (1.12 Å) and Cd^{2+} (1.10 Å) are close and

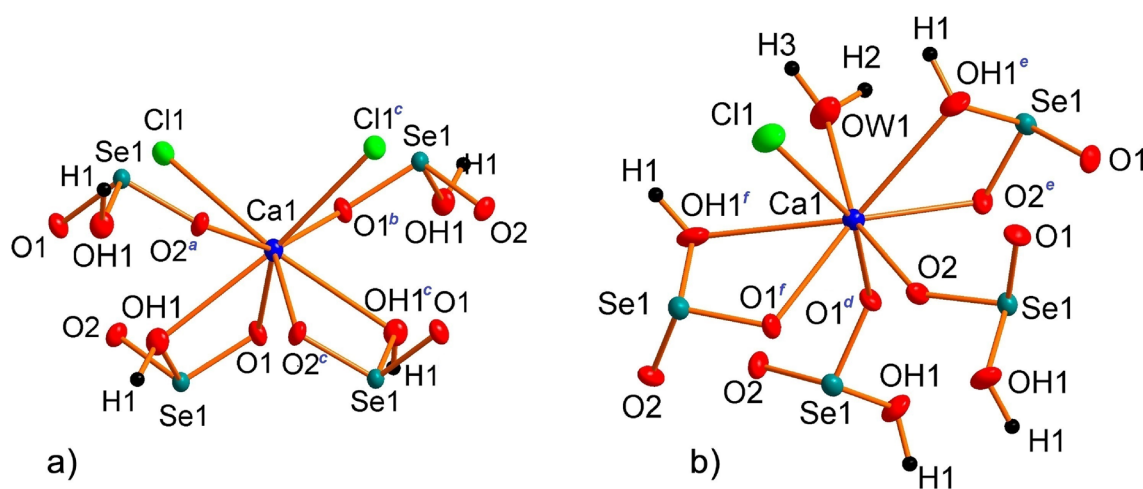


Figure 3: Mixed-ligand coordination of Ca^{2+} cation in the crystal structure of $\text{Ca}(\text{HSeO}_3)\text{Cl}$ (a) and $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ (b). Symmetry transformations used to generate equivalent atoms are given in Table 2 caption.

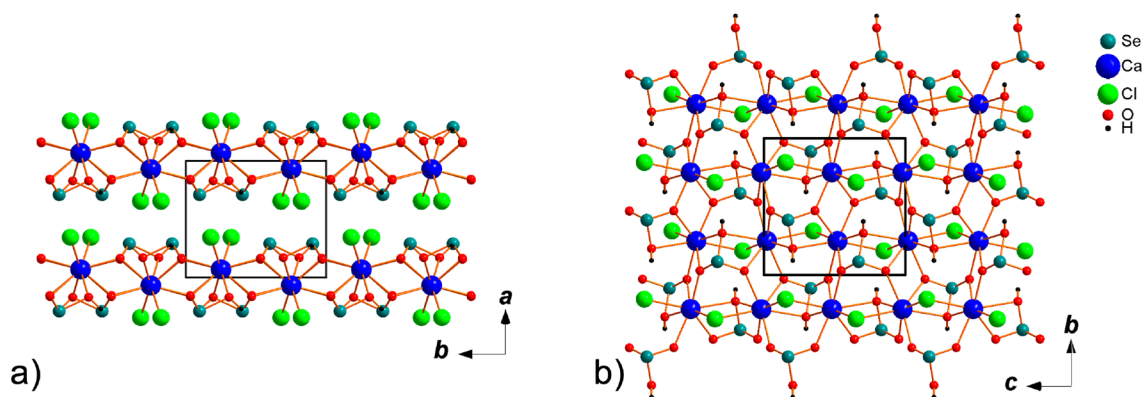


Figure 4: General projections of the crystal structure of $\text{Ca}(\text{HSeO}_3)\text{Cl}$ along the c axis (a) and the layer along the a axis (b).

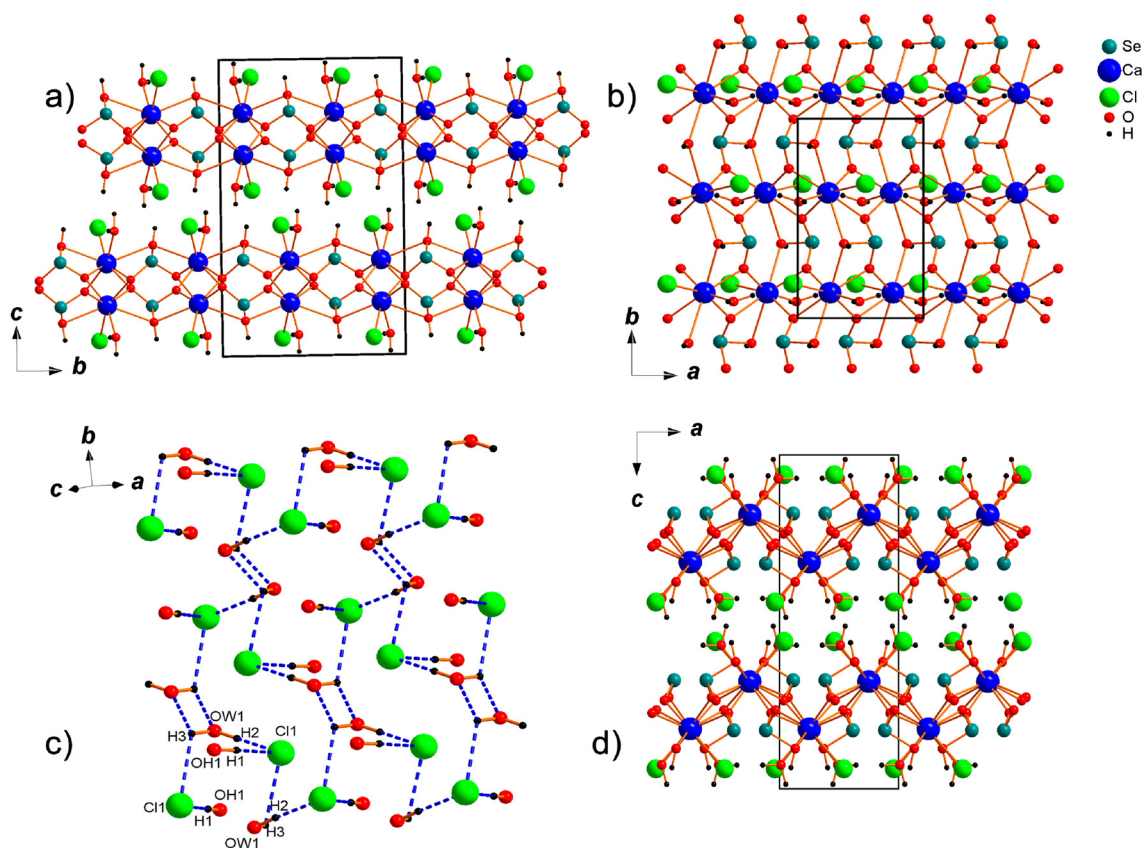


Figure 5: General projections of the crystal structure of $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ along the a axis (a) and the layer along the c axis. (b) Assembly of hydroxyl, chloride and water in the interlayer (blue dotted line is for suggested hydrogen bonds) (c). General projection of the crystal structure of $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ along the b axis (d).

nitrate has long been recognized as a crystal chemical analog of halides, except F^- [11].

The addition of water molecule to $\text{Ca}(\text{HSeO}_3)\text{Cl}$ results in the total rearrangement of the structural architecture. The layers in the structure of $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ (Figure 5a, b) can be described as decorated by the OH^- , Cl^- and H_2O ligands. Note, Cl atom forms only one relatively weak bond

of 0.33 valence units with Ca. Hydroxyl anions, water molecules and chlorine atoms are assembled into a loose hydrogen-bonded net (Figure 5c). Such hydrogen-bonded water-chloride assemblies are relatively rare in inorganic compounds [20]. Therefore, hydration of $\text{Ca}(\text{HSeO}_3)\text{Cl}$ into $\text{Ca}(\text{HSeO}_3)\text{Cl}(\text{H}_2\text{O})$ changes the interlayer interaction from halophilic to hydrogen bonding. This may be the reason

why no bromide analog, has not been successfully synthesized yet, as Br⁻ with its more diffuse valence shell is less effective [21] in hydrogen bonding. It is also of interest, that Se vertices of the HSeO₃⁻ pyramidal anions are pointing toward the ‘inner’ surfaces of corrugations (Figure 5d). Their ‘lone pairs’ do not significantly contribute to the 2D character of the structure.

Compared to the previously reported structures comprising protonated lone-pair anions, the HSeO₃⁻ anions are weakly involved in the hydrogen bonding in Ca(HSeO₃)Cl. The OH groups of the HSeO₃⁻ anions are oriented toward inside the layer. However, in hydrate Ca(HSeO₃)Cl(H₂O), the O–H bonds of the HSeO₃⁻ anions are oriented into the interlayer which results in the formation of complex hydrogen bonding system. Similar, relatively strong hydrogen bonding with hydrogenselenite anion is observed in the structure of Ca(HSeO₃)₂(H₂O) [16]. Further investigations involving other protonated ‘lone-pair’ anions are necessary to find the trends in crystal chemistry of this yet mostly unexplored family.

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