Mishel R. Markovski, Oleg I. Siidra*, Dmitri O. Charkin, Evgeny V. Nazarchuk and
Vasili Yu. Grishaev

# Molecular inorganic polymers: synthesis and crystal structures of KCl·2H$_2$SeO$_3$ and CsCl·H$_2$SeO$_3$

**Abstract:** KCl·2H$_2$SeO$_3$ and CsCl·H$_2$SeO$_3$ have been synthesized using solution evaporation methods from aqueous solution. Both compounds are monoclinic (*P2/n* and *P2$_1$/c*) and demonstrate new structure types. One symmetrically unique SeO(OH)$_2$ molecule is present in each structure. SeO(OH)$_2$ molecules *via* strong hydrogen bonds form chains in KCl·2H$_2$SeO$_3$ and layers in CsCl·H$_2$SeO$_3$. The structures of KCl·2H$_2$SeO$_3$ and CsCl·H$_2$SeO$_3$ can be described as consisting of ionic KCl chains and CsCl layers incorporated into the covalent- and hydrogen-bonded H$_2$SeO$_3$ matrix. To the best of our knowledge, the cases when selenious acid acts as a contributor to the molecular building blocks of salt-inclusion structures are not known to date.

**Keywords:** halides; molecular inorganic polymers; selenious acid; selenite.

## 1 Introduction

Easily accessible by both solution (including hydrothermal) and high-temperature syntheses, selenites are the objects of interest due to the diverse crystal chemistry and attractive physical properties, such as nonlinear optical activity, low-dimensional magnetism of *d*- and *f*-metal derivatives, etc. [1–3]. The use of halides as additional

*Corresponding author: Oleg I. Siidra, Department of Crystallography, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg, Russia; and Kola Science Center, Russian Academy of Sciences, Apatity, 184200 Murmansk Region, Russia, E-mail: o.siidra@spbu.ru
**Mishel R. Markovski and Evgeny V. Nazarchuk,** Department of Crystallography, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg, Russia
**Dmitri O. Charkin and Vasili Yu. Grishaev,** Department of Chemistry, Moscow State University, Leninskie Gory 1, 119991 Moscow, Russia

anions is a successful tool to construct low-dimensional and acentric structures. To date, there are just a few halide-bearing representatives containing protonated selenite anions [4, 5] while those including molecular selenious acid are particularly rare [6].

Studies of salt-acid composites are important for understanding the structural organization and behavior of simple compounds in tailored environments. The crystal structure of selenious acid, first determined in [7], and later refined in [8] helped to understand the role of hydrogen in intermolecular bonding, particularly in case of H$_2$SeO$_3$, which is important for understanding the crystal chemistry of aqueous and/or acidic selenites. The strong effect of the so-called '*hydrogen-bonded network*' phenomenon on the structure formation has been investigated in [9, 10]. This structural organization based on '*weak bonds with strong affinities*' leads to the discovery of many interesting molecular polymers of '*weak bonded entity units*'. Variation of the anion's hydrogen bond donor/acceptor activity is very likely to be a potent instrument in affecting the topology and topological complexity of the resulting structure. Among various choices, halide ions are evidently proper candidates being, on the one hand, already introduced into numerous structures of selenite and hydrogen selenite compounds, and, on the other hand, only moderate-strength acceptors of hydrogen bonds compared to higher-charged sulfate anions.

Recently, we observed formation of two new compounds with peculiar structures, Ca(HSeO$_3$)Cl and Ca(HSeO$_3$)Cl·H$_2$O, among colorless side-products in attempted preparation of Ca–Cu hydroselenite chlorides [11]. This prompted us to take a closer look at the outcomes of some other previous syntheses, including those of (*MX*)[Cu(HSeO$_3$)$_2$] [4]. Colorless, evidently Cu$^{2+}$-free platelets produced upon evaporation of the mother liquor after synthesis of (KCl)[Cu(HSeO$_3$)$_2$] proved to belong to a new compound based on potassium chloride and molecular selenious acid, KCl·2H$_2$SeO$_3$. CsCl·H$_2$SeO$_3$ was prepared in a targeted run. In the current paper, we report their preparation and crystal structures. As certain analogies exist in the structures of protonated selenites and phosphites (e.g., [12]), phosphorous acid was also included in this study.
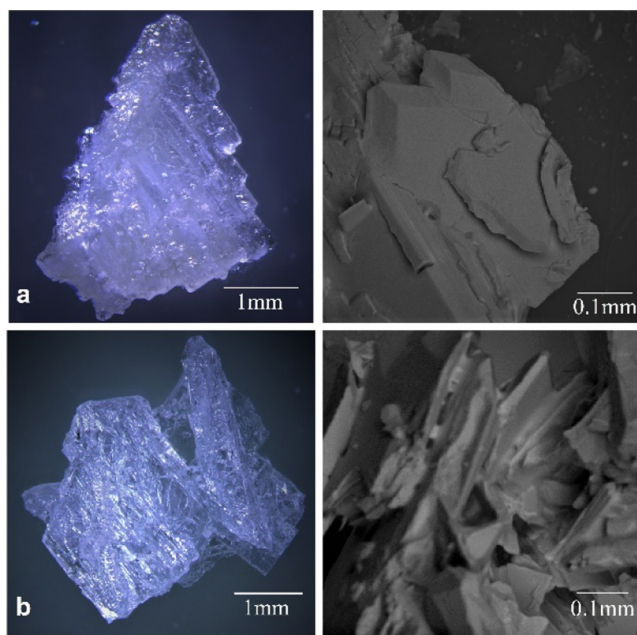
## 2 Experimental

### 2.1 Synthesis

*Caution! Soluble selenium compounds are highly toxic and such experiments should be performed in a properly equipped laboratory by a trained personnel.*

Initially, well-shaped colorless crystals of KCl·2H$_2$SeO$_3$ were collected from the batch used for preparation of (KCl)[Cu(HSeO$_3$)$_2$] [4]. The unit-cell parameters indicated a new compound identified as KCl·2H$_2$SeO$_3$. To prove its identity, 10 mmol KCl and 20 mmol H$_2$SeO$_3$ were dissolved in 20 ml of distilled water and left to evaporate until complete dryness. This protocol produced crystals of different shape (plates of the target phase as well as thick rectangular slabs); PXRD of the sample indicated it to be multiphase. Essentially better (close to 100%) yields were obtained when the solutions were acidified by ~0.2 ml of trifluoroacetic acid, as in the initial experiment. The new compound was obtained in the form of colorless mica-like crystalline masses stable in air within weeks (Figure 1a) yet readily soluble in water.

Attempts were also made to prepare related compounds with other univalent chlorides (NH$_4$Cl, RbCl, CsCl). Applying the same protocols yielded relatively large but very unstable crystals which decomposed rapidly when taken out of mother liquors and subject to X-rays. Good quality data set could be collected for an only one sort of CsCl·H$_2$SeO$_3$ crystals (Figure 1b) taken out of CsCl–H$_2$SeO$_3$ preparation. Attempts to substitute H$_2$SeO$_3$ by H$_3$PO$_3$ (CF$_3$COOH was not added) led only to sequential crystallization of the components.

### 2.2 Single-crystal XRD

Non-hygroscopic platelets of KCl·2H$_2$SeO$_3$ and CsCl·H$_2$SeO$_3$ with dimensions of approximately 0.05 × 0.05 × 0.01 mm, were each mounted on thin glass fiber under microscope. The X-ray diffraction analysis was successfully provided by Bruker APEX II DUO X-ray diffractometer with a micro-focus X-ray tube operated with MoKα radiation at 50 kV and 0.6 mA. The data were integrated and corrected for absorption using a multi-scan type model by Bruker programs APEX and SADABS. The structure solution and refinement was performed by direct methods using SHELXL software package. The positions of hydrogen atoms were ascertained from the difference Fourier maps. $U_{eq}$ value of H1 atom in KCl·2H$_2$SeO$_3$ was constrained to 0.05. The positions of the H atoms in both compounds were constrained to H–O distances of 1.0(1) Å on the final stages of refinement. KCl·2H$_2$SeO$_3$ is monoclinic, $P2/n$, $a$ = 6.2501(6) Å, $b$ = 5.1716(5) Å, $c$ = 12.0380(12) Å, $\beta$ = 103.612(2)°, $V$ = 378.18(6) Å$^3$, $R_1$ = 0.025. CsCl·H$_2$SeO$_3$ is monoclinic, $P2_1/c$, $a$ = 7.9391(3) Å, $b$ = 9.6574(4) Å, $c$ = 7.8275(4) Å, $\beta$ = 109.440(1)°, $V$ = 565.93(4) Å$^3$, $R_1$ = 0.022 (Table 1). Selected bond-lengths are provided in Table 2 and hydrogen bond-lengths are given in Table 3.

## 3 Results and discussion

The new compound KCl·2H$_2$SeO$_3$ represents a new structure type. One symmetrically independent K$^+$ cation is symmetrically coordinated by six O and two Cl atoms (Figure 2, Table 2). One unique SeO(OH)$_2$ molecule is present in the structure of KCl·2H$_2$SeO$_3$. It has a typical trigonal pyramidal coordination environment with Se$^{4+}$ cation in the apex. Se1–O2 (1.7387(15) Å) and Se1–O3 (1.7532(15) Å) bonds are significantly elongated (Table 2), in comparison with Se1–O1 (1.6541(14) Å). SeO(OH)$_2$ molecules *via* hydrogen bonds form chains shown in Figure 3a. Strong O–H···O hydrogen bonding is observed between the OH groups and the terminal O1 atoms of the molecules. Note,



**Figure 1:** Colorless crystals of KCl·2H$_2$SeO$_3$ (a) and CsCl·H$_2$SeO$_3$ (b) under optical microscope and BSE images.

**Table 1:** Crystallographic data and refinement parameters for KCl·2H$_2$SeO$_3$ and CsCl·H$_2$SeO$_3$.

|  | KCl·2H$_2$SeO$_3$ | CsCl·H$_2$SeO$_3$ |
|---|---|---|
| $a$ (Å) | 6.2501(6) | 7.9391(3) |
| $b$ (Å) | 5.1716(5) | 9.6574(4) |
| $c$ (Å) | 12.0380(12) | 7.8275(4) |
| $\beta$ (°) | 103.612(2) | 109.440(1) |
| $V$ (Å$^3$) | 378.18(6) | 565.93(4) |
| Radiation | MoKα | MoKα |
| Total reflections | 6636 | 10152 |
| Unique reflections | 1766 | 3078 |
| Unique $|F_o| \geq 4\sigma_F$ | 1297 | 2518 |
| GooF | 1.028 | 1.042 |
| Space group | $P2/n$ | $P2_1/c$ |
| Crystal size (mm) | 0.05 × 0.05 × 0.01 | 0.05 × 0.05 × 0.01 |
| $\mu$ cm$^{-1}$ | 10.654 | 13.335 |
| $D_{calc}$ (g/cm$^3$) | 2.920 | 3.490 |
| $R_{int}$ | 0.035 | 0.027 |
| $R_1$ | 0.025 | 0.022 |
| $R_1$(all data) | 0.041 | 0.033 |
| w$R_2$ | 0.049 | 0.044 |
| w$R_2$ (all data) | 0.054 | 0.046 |

**Table 2:** Selected interatomic distances (Å) for KCl·2H₂SeO₃ and CsCl·H₂SeO₃.

| KCl·2H₂SeO₃ | | CsCl·H₂SeO₃ | |
|---|---|---|---|
| K1–O3 | 2.9237(15)×2 | Cs1–O1 | 3.1359(11) |
| K1–O2 | 3.0112(18)×2 | Cs1–O3 | 3.2345(12) |
| K1–O2 | 3.0271(18)×2 | Cs1–O3 | 3.2873(12) |
| K1–Cl1 | 3.1251(3)×2 | Cs1–Cl1 | 3.3976(4) |
| | | Cs1–Cl1 | 3.4037(4) |
| Se1–O1 | 1.6541(14) | Cs1–O2 | 3.4359(13) |
| Se1–O2 | 1.7387(15) | Cs1–Cl1 | 3.4508(4) |
| Se1–O3 | 1.7532(15) | Cs1–O2 | 3.5141(11) |
| H1–O2 | 1.00(1) | Se1–O1 | 1.6561(10) |
| H2–O3 | 0.98(1) | Se1–O3 | 1.7518(12) |
| | | Se1–O2 | 1.7579(11) |
| | | | |
| | | H1–O2 | 0.97(1) |
| | | | |
| | | H2–O3 | 0.98(1) |

**Table 3:** Hydrogen bond lengths (Å) for KCl·2H₂SeO₃ and CsCl·H₂SeO₃.

| O–H | $d$(O-H) | H···A | $d$(H···A) |
|---|---|---|---|
| **KCl·2H₂SeO₃** | | | |
| O2–H1 | 0.995(1) | O1 | 1.622(1) |
| O3–H2 | 0.981(1) | Cl1 | 2.742(1) |
| O3–H2 | 0.981(1) | O1 | 1.797(1) |
| **CsCl·H₂SeO₃** | | | |
| O2–H1 | 0.968(1) | Cl1 | 2.956(1) |
| O2–H1 | 0.968(1) | O1 | 1.755(1) |
| O3–H2 | 0.984(1) | O1 | 1.629(1) |

non-protonated O1 atoms do not coordinate K⁺ cations but are "employed" only in hydrogen bonding between the molecules. The chains are packed in layers parallel to *ab* plane. Vertices of SeO(OH)₂ trigonal pyramids are inversed one relative to the other and each point in the direction of Cl ions, in accordance with the well-known phenomenon of halophilicity (Figure 3b). The K⁺ and Cl⁻ form one-dimensional infinite $\frac{1}{\infty}$[Cl – K – Cl] chains running along the *a* axis (Figure 3c). The Cl⁻ anions have only two K⁺ neighbors at distances of 3.1251(3) Å, i.e., very similar to those in NaCl-type halides; given essentially smaller number of such contacts and relatively short Cl···H contacts these may be considered as weakly bonding [13, 14] with bifurcated OH···(O, Cl) hydrogen bonds.

The crystal structure of CsCl·H₂SeO₃ has a pronounced 2*D* character. The Cs⁺ cations center irregular 8-vertex CsO₅Cl₃ polyhedra (Figure 2). SeO(OH)₂ molecules have similar geometry (Table 2) as in KCl·2H₂SeO₃. The bond

lengths in the SeO(OH)₂ molecule are typical for the double and single Se−O bonds [15]. In CsCl·H₂SeO₃, all three oxygen atoms of the SeO(OH)₂ molecule are bonded to the cesium cations. Similar to the structure of KCl·2H₂SeO₃, the structure of CsCl·H₂SeO₃ (Figure 4a) can be described as consisting of two types of nets shown in Figure 4a and b. CsCl complexes form layers, as well as SeO(OH)₂ molecules are interconnected one with each other *via* strong O−H···O hydrogen bonding into layered arrangement. The 'lone pairs' on Se⁴⁺ cations are projected towards the Cl⁻ anions. This arrangement distantly resembles the one observed in the structure of Mn₉Bi(SeO₃)₈Cl₅ [16].

In both structures, the 'lone-pair cation – chloride' combination provides the pronounced two-dimensional character of the structure. This differs two novel compounds described herein from other co-crystals of relatively weak inorganic acids and salts which form more or less isotropic hydrogen-bonded frameworks. Introducing cations preferring more regular coordination and ionic bonding favors formation of salt-inclusion structures. The structures of KCl·2H₂SeO₃ and CsCl·H₂SeO₃ can be described as consisting of ionic KCl chains and CsCl layers incorporated into the covalent- and hydrogen-bonded H₂SeO₃ matrix. To the best of our knowledge, the cases when selenious acid acts as a contributor to the molecular building blocks of salt-inclusion structures are not known to date. The only hitherto reported metal halide – selenious acid co-crystal is CoCl₂·H₂SeO₃·2H₂O [6] wherein the H₂SeO₃ molecules behave as terminal ligands and do not form any hydrogen bonds. We believe that more representatives may be formed by varying the nature of salt components. The weaker phosphorous acid is probably a too poor hydrogen bond donor to contribute to such structures. Hydrogen bonding is more commonly used in construction of organic frameworks; the studied structures indicate that this may be also possible among pure inorganics. In addition, the size of alkali cation plays a prominent role in structure formation: the composition and structure of K and Cs compounds, obtained under very similar conditions, differ drastically. Very low chemical stability of the corresponding Rb compound suggests a yet different composition (possibly a low-melting hydrate).

It is worth noting that in our experiments it was necessary to suppress dissociation of selenious acid to achieve high yields of KCl·2H₂SeO₃ and CsCl·H₂SeO₃. A very similar pattern was observed by [6] who noticed contamination of their target compound Co(H₂O)₂Cl₂(H₂SeO₃) by hydrates of Co(HSeO₃)Cl when no extra strong acid (HCl in their case) was present. The simplest chemical explanation is in partial loss of volatile HCl upon evaporation of the mother liquor: though a weaker acid, H₂SeO₃ is negligibly
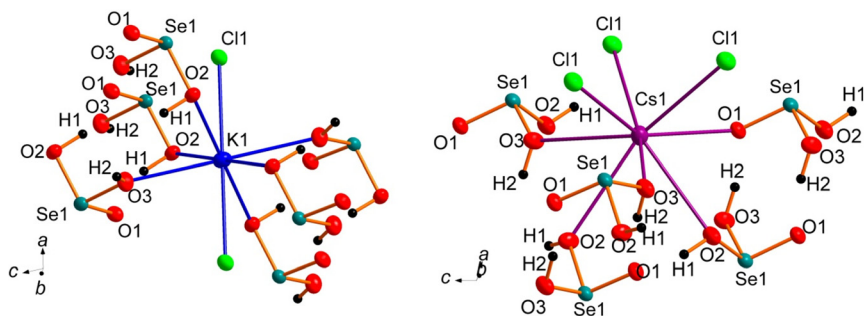
**Figure 2:** Coordination environments of K⁺ and Cs⁺ in crystal structures of KCl·2H₂SeO₃ and CsCl·H₂SeO₃, respectively.
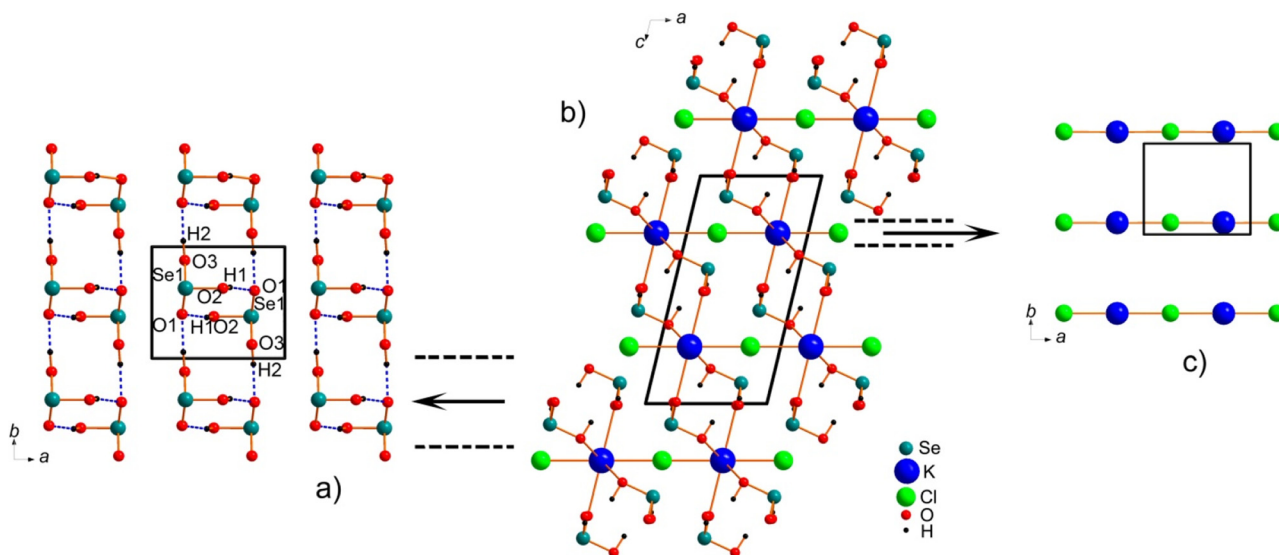


**Figure 3:** Arrangement of H₂SeO₃ molecules (blue dotted line = suggested hydrogen bonds) KCl·2H₂SeO₃ (a). General projection of the crystal structure of KCl·2H₂SeO₃ along the *b* axis (b) and KCl complexes (c).
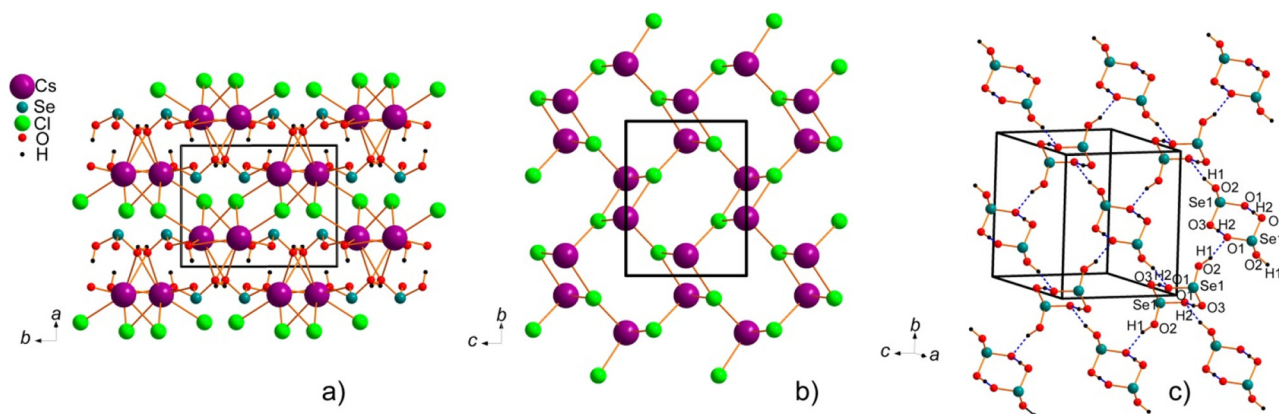


**Figure 4:** General projection of the crystal structure of CsCl·H₂SeO₃ along the *c* axis (a). Arrangement of layered CsCl complexes (b) and H₂SeO₃ molecules (blue dotted line = suggested hydrogen bonds) (c).

volatile at room temperature. Therefore, variation of synthesis conditions may occasionally occur to be an important factor. Note that CF₃COOH is probably a better choice since at increasing concentrations of HCl upon evaporation, various chlorometallate and chloroselenate complexes are readily formed instead of the target compounds

[4]. In one of our experiments aimed at the production of (CsCl)[Co(HSeO$_3$)$_2$] with 10× excess of CsCl, only Cs$_2$CoCl$_4$ [17] was produced.

In conclusion, we would like to note that suggested-to-be-side products of some syntheses may occasionally prove to be of interest both in their composition and structure, derivatives of selenious acid forming a promising yet mostly unexplored family. Investigations are currently underway aimed at its further studies and development.

# References

1. Kim S. H., Yeon J., Halasyamani P. S. Noncentrosymmetric polar oxide material, Pb$_3$SeO$_5$: synthesis, characterization, electronic structure calculations and structure-property relationships. *Chem. Mater.* 2009, *21*, 5335.

2. Berdonosov P. S., Kuznetsova E. S., Dolgikh V. A. Transition metal selenite halides: a fascinating family of magnetic compounds. *Crystals* 2018, *8*, 159.

3. Markovski M. R., Siidra O. I., Charkin D. O., Vladimirova V. A., Tsirlin A. A., Grishaev V. V. Li$_2$(Se$_2$O$_5$)(H$_2$O)$_{1.5}$·CuCl$_2$, a salt-inclusion diselenide structurally based on tetranuclear Li$_4$ complexes. *Dalton Trans.* 2020, *49*, 7790.

4. Charkin D. O., Markovski M. R., Siidra O. I., Nekrasova D. O. Influence of the alkali cation size on the Cu$^{2+}$ coordination environments in (*AX*)[Cu(HSeO$_3$)$_2$] (*A* = Na, K, NH$_4$, Rb, Cs; *X* = Cl, Br) layered copper hydrogen selenite halides. *Z. für Kristallogr. Cryst. Mater.* 2019, *234*, 739.

5. Markovski M. R., Charkin D. O., Siidra O. I., Nekrasova D. O. Copper hydroselenite nitrates (*A*$^+$NO$_3$)$_n$[Cu(HSeO$_3$)$_2$] (*A* = Rb$^+$, Cs$^+$ and Tl$^+$, *n* = 1, 2) related to Ruddlesden - popper phases. *Z. für Kristallogr. Cryst. Mater.* 2019, *234*, 749.

6. Ben Hamida M., Wickleder M. S. Selenious acid as a ligand: molecular and crystal structure of [Co(H$_2$O)$_2$Cl$_2$(H$_2$SeO$_3$)$_2$]. *Z. Anorg. Allg. Chem.* 2005, *631*, 2306.

7. Wells A. F., Bailey M. The structures of inorganic oxy-acids: the crystal structure of selenious acid. *J. Chem. Soc.* 1949, *278*, 1282.

8. Krebs Larsen F., Lehmann M. S., Søtofte I. A neutron diffraction study of selenious acid H$_2$SeO$_3$. *Acta Chem. Scand.* 1971, *25*, 1233.

9. Novak A. Hydrogen bonding in solids correlation of spectroscopic and crystallographic data. *Struct. Bond* 1974, *18*, 177.

10. Unterderweide K., Engelen B., Boldt K. Strong hydrogen bonds in acid selenites: correlation of infrared spectroscopic and structural data. *J. Mol. Struct.* 1994, *322*, 233.

11. Markovski M. R., Siidra O. I., Charkin D. O., Grishaev V. V. Layered calcium hydrogen selenite chlorides Ca(HSeO$_3$)Cl and Ca(HSeO$_3$)Cl(H$_2$O), the first halides obtained in CaCl$_2$–H$_2$SeO$_3$–H$_2$O system. *Z. für Kristallogr. Cryst. Mater.* 2020; https://doi.org/10.1515/zkri-2020-0054 In this issue.

12. Boldt K., Engelen B., Panthöfer M., Unterderweide K. Stereochemical equivalence of P$^{III}$-bonded hydrogen atoms and Se(IV) lone electron pairs in Sr(H$_2$PO$_3$)$_2$ and Sr(HSeO$_3$)$_2$. *Eur. J. Inorg. Chem.* 2000, *9*, 2071; https://doi.org/10.1002/1099-0682(200009)2000:9<2071.

13. Ghosh A. K., Ghoshal D., Ribas J., Mostafa G., Chaudhuri N. R. Hydrogen-bonded, assembly of water and chloride in a 3D supramolecular host. *Cryst. Growth Des.* 2006, *6*, 36.

14. Dai J-X., Wu F-H., Yao W-R., Zhang Q-F. One-dimensional hydrogen-bonded chloride-hydrate assembly {[(H$_2$O)$_4$Cl$_2$]$^{2-}$}$_\infty$. *Z. Naturforsch.* 2007, *B62*, 491.

15. Pollitt S., Weil M. Polymorphism of H$_2$SeO$_3$, NaHSeO$_4$ and Na$_5$H$_3$(SeO$_4$)$_4$(H$_2$O)$_2$, and Re-refinement of the crystal structure of Te$_2$O$_4$(OH)$_2$. *Z. Anorg. Allg. Chem.* 2014, *640*, 1622.

16. Kovrugin V. M., Colmont M., Siidra O. I., Charkin D. O., Aliev A., Krivovichev S. V., Mentré O. Synthesis and structural variety of first Mn and Bi selenites and selenite chlorides. *Z. für Kristallogr. Cryst. Mater.* 2019, *234*, 141.

17. Figgis B. N., Reynolds P. A., White A. H. Charge density in the CoCl$_4$$^{2-}$ ion: a comparison with spin density and theoretical calculations. *J. Chem. Soc. Dalton Trans.* 1987, 1737–1745, https://doi.org/10.1039/dt9870001737.