research communications

Crystal structure of tin(IV) chloride octahydrate

Erik Hennings, Horst Schmidt* and Wolfgang Voigt

TU Bergakademie Freiberg, Institute of Inorganic Chemistry, Leipziger Strasse 29, D-09596 Freiberg, Germany. *Correspondence e-mail: horst.schmidt@chemie.tu-freiberg.de

The title compound, $[SnCl_4(H_2O)_2]\cdot 6H_2O$, was crystallized according to the solid–liquid phase diagram at lower temperatures. It is built-up of $SnCl_4(H_2O)_2$ octahedral units (point group symmetry 2) and lattice water molecules. An intricate three-dimensional network of $O-H\cdots O$ and $O-H\cdots Cl$ hydrogen bonds between the complex molecules and the lattice water molecules is formed in the crystal structure.

1. Chemical context

The interest in the stability of tin(IV) salts, especially at lower temperatures, has increased with the recent new determination of the redox potential in aqueous solutions, which is complicated by the presence of chlorido complexes (Gajda *et al.*, 2009). The phase diagram of tin(IV) chloride is not well investigated. Only some points in dilute solutions have been determined by Loomis (1897). For the existing hydrates (R = 8, 5, 4, 3 and 2), Meyerhoffer (1891) described the melting points and the existence fields. The crystal structures of the dihydrate (Semenov *et al.*, 2005), trihydrate (Genge *et al.*, 2004; Semenov *et al.*, 2005), tetrahydrate (Genge *et al.*, 2004; Shihada *et al.*, 2004) and pentahydrate (Barnes *et al.*, 1980; Shihada *et al.*, 2004) have been determined previously. For these salt hydrates, vibrational spectra are also available, classifying all hydrate spectra with point group D_{4h} symmetry (Brune & Zeil, 1962).
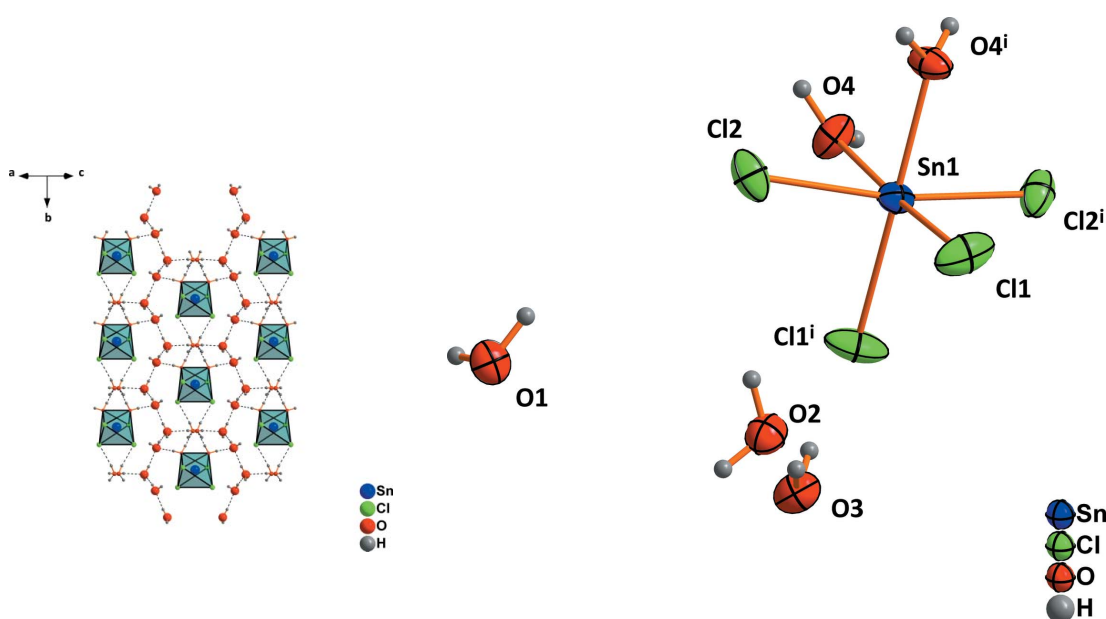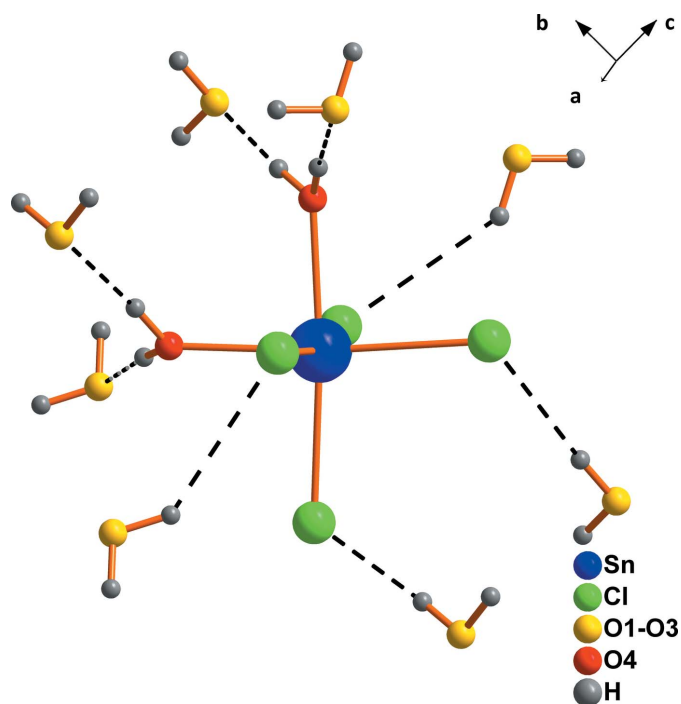

Figure 1
The building units in tin(IV) chloride octahydrate [symmetry code: (i) $-x, y, -z + \frac{1}{2}$]. Displacement ellipsoids are drawn at the 50% probability level.

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1B···O2^i	0.84 (1)	1.90 (2)	2.729 (3)	169 (6)
O2—H2B···O3^{ii}	0.84 (1)	2.04 (2)	2.825 (3)	157 (5)
O2—H2A···O1^{iii}	0.84 (1)	1.94 (2)	2.762 (3)	168 (5)
O1—H1A···Cl3^{iv}	0.84 (1)	2.68 (3)	3.389 (2)	143 (4)
O3—H3A···O2	0.84 (1)	1.95 (2)	2.763 (3)	163 (4)
O3—H3B···Cl1^v	0.83 (1)	2.43 (1)	3.260 (2)	173 (4)
O4—H4B···O1^{vi}	0.83 (1)	1.77 (1)	2.598 (3)	176 (4)
O4—H4A···O3^{vii}	0.84 (1)	1.80 (1)	2.635 (3)	176 (4)

Symmetry codes: (i) $-x+1, y, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (iii) $x-\frac{1}{2}, y+\frac{1}{2}, z$; (iv) $-x+1, -y+1, -z+1$; (v) $-x, y, -z+\frac{1}{2}$; (vi) $x-1, y+1, z$; (vii) $x, y+1, z$.

2. Structural commentary

The tin(IV) ion in tin(IV) chloride octahydrate is situated on a twofold rotation axis and is coordinated by four Cl atoms and two water molecules in a *cis*-octahedral geometry (Fig. 1), as was observed before for the tetra- and pentahydrate (Shihada *et al.*, 2004). In addition, three water molecules (O1, O2 and O3) are located around the octahedra as non-coordinating water molecules. Every water molecule of the first coordination sphere is connected with two water molecules of the second shell by hydrogen bonds. The chlorine atoms form only one hydrogen bond towards 'free' water molecules of the second shell (Fig. 2).

Figure 2
The coordination of tin(IV) in the second coordination shell of tin(IV) chloride octahydrate [symmetry code: (i) $-x, y, -z+\frac{1}{2}$]. Hydrogen bonds are shown as dashed lines.
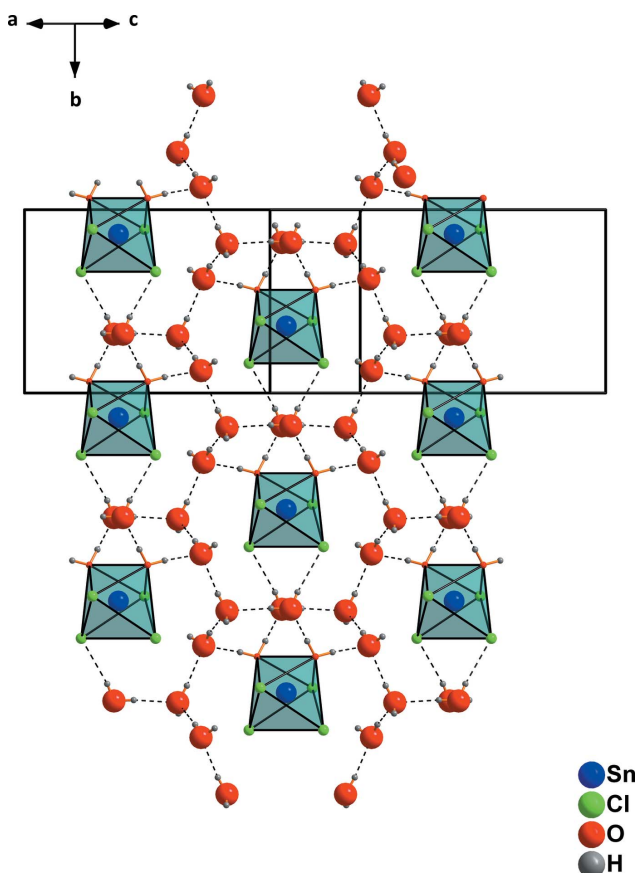
Figure 3
Formation of chains by water molecules O1 and O2 (bold). Dashed lines indicate hydrogen bonds.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[SnCl_4(H_2O)_2]\cdot6H_2O$
M_r	404.62
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	200
a, b, c (Å)	16.0224 (15), 7.8530 (8), 12.6766 (12)
β (°)	119.739 (7)
V (Å^3)	1384.9 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.63
Crystal size (mm)	$0.34 \times 0.23 \times 0.12$
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Integration (Coppens, 1970)
T_{min}, T_{max}	0.492, 0.731
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13041, 1600, 1451
R_{int}	0.030
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.049, 1.11
No. of reflections	1600
No. of parameters	92
No. of restraints	12
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.01, -0.71

Computer programs: *X-AREA* and *X-RED* (Stoe & Cie, 2009), *SHELXS97* and *SHELXL2012* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

3. Supramolecular features

Having a larger view of the crystal structure in direction [001] (Fig. 3), it becomes obvious that these non-coordinating water molecules form chains between the octahedrally coordinated tin(IV) ions. These water molecules (O1 and O2) are connected *via* hydrogen bonds (Table 1) and the chains are oriented along the *b*-axis direction. Considering all types of hydrogen bonding, a three-dimensional network between the complex molecules and the lattice water molecules results.

4. Database survey

For crystal structure determination of other tin(IV) chloride hydrates, see: Shihada *et al.* (2004); Semenov *et al.* (2005); Genge *et al.* (2004); Barnes *et al.* (1980).

5. Synthesis and crystallization

Tin(IV) chloride octahydrate was crystallized from an aqueous solution of 53.39 wt% $SnCl_4$ at 263 K after 2 d. For preparing this solution, tin(IV) chloride pentahydrate (Acros Organics, 98%) was used. The content of Cl^- was analysed by titration with $AgNO_3$. The crystals are stable in their saturated solution over a period of at least four weeks.

The samples were stored in a freezer or a cryostat at low temperatures. The crystals were separated and embedded in perfluorinated ether for X-ray diffraction analysis

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms were placed in the positions indicated by difference Fourier maps. Distance restraints were applied for the geometries of all water molecules, with O—H and H—H distance restraints of 0.84 (1) and 1.4 (1) Å, respectively.

References

Barnes, J. C., Sampson, H. A. & Weakley, T. J. R. (1980). *J. Chem. Soc. Dalton Trans.* pp. 949–953.

Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Brune, H. A. & Zeil, W. (1962). *Z. Phys. Chem. Neue Folge*, **32**, 384–400.

Coppens, P. (1970). In *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 255–270. Copenhagen: Munksgaard.

Gajda, T., Sipos, P. & Gamsjäger, H. (2009). *Monatsh. Chem.* **140**, 1293–1303.

Genge, A. R. J., Levason, W., Patel, R., Reid, G. & Webster, M. (2004). *Acta Cryst.* C**60**, i47–i49.

Loomis, E. H. (1897). *Phys. Rev. (Series I)*, **4**, 273–296.

Meyerhoffer, M. (1891). *Bull. Soc. Chem. Paris*, **3**, 85–86.

Semenov, S. N., Maltsev, E. Y., Timokhin, I. G., Drozdov, A. A. & Troyanov, S. I. (2005). *Mendeleev Commun.* **15**, 205–207.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Shihada, A.-F., Abushamleh, A. S. & Weller, F. (2004). *Z. Anorg. Allg. Chem.* **630**, 841–847.

Stoe & Cie (2009). *X-AREA* and *X-RED*. Stoe & Cie, Darmstadt, Germany.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Crystal structure of tin(IV) chloride octahydrate

Erik Hennings, Horst Schmidt and Wolfgang Voigt

Computing details

Data collection: *X-AREA* (Stoe & Cie, 2009); cell refinement: *X-AREA* (Stoe & Cie, 2009); data reduction: *X-RED* (Stoe & Cie, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2012* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Tin(IV) chloride octahydrate

Crystal data

[SnCl$_4$(H$_2$O)$_2$]·6H$_2$O	$F(000) = 792$
$M_r = 404.62$	$D_x = 1.941$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 16.0224\,(15)$ Å	Cell parameters from 13366 reflections
$b = 7.8530\,(8)$ Å	$\theta = 1.8$–29.6°
$c = 12.6766\,(12)$ Å	$\mu = 2.63$ mm^{-1}
$\beta = 119.739\,(7)$°	$T = 200$ K
$V = 1384.9\,(2)$ Å^3	Plate, colourless
$Z = 4$	$0.34 \times 0.23 \times 0.12$ mm

Data collection

Stoe IPDS 2T diffractometer	13041 measured reflections
Radiation source: fine-focus sealed tube	1600 independent reflections
Detector resolution: 6.67 pixels mm^{-1}	1451 reflections with $I > 2\sigma(I)$
rotation method scans	$R_{int} = 0.030$
Absorption correction: integration (Coppens, 1970)	$\theta_{max} = 27.5$°, $\theta_{min} = 2.9$°
	$h = -22 \rightarrow 21$
$T_{min} = 0.492$, $T_{max} = 0.731$	$k = -10 \rightarrow 10$
	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.021$	$w = 1/[\sigma^2(F_o^2) + (0.0133P)^2 + 4.9358P]$
$wR(F^2) = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.001$
1600 reflections	$\Delta\rho_{max} = 1.01$ e Å^{-3}
92 parameters	$\Delta\rho_{min} = -0.71$ e Å^{-3}
12 restraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Sn1	0.0000	0.86619 (3)	0.2500	0.02527 (8)
Cl3	0.17022 (5)	0.89264 (10)	0.37662 (6)	0.04076 (17)
O4	−0.00709 (13)	1.0623 (3)	0.35862 (18)	0.0342 (4)
Cl1	0.01591 (7)	0.66227 (10)	0.12053 (8)	0.0504 (2)
O1	0.83339 (14)	0.1224 (3)	0.35849 (18)	0.0341 (4)
O2	0.24917 (15)	0.3119 (3)	0.34936 (19)	0.0377 (4)
O3	0.11311 (15)	0.3211 (3)	0.4228 (2)	0.0380 (4)
H4A	0.030 (2)	1.146 (3)	0.376 (3)	0.057 (11)*
H4B	−0.0574 (14)	1.086 (4)	0.359 (3)	0.044 (9)*
H3B	0.085 (3)	0.414 (3)	0.414 (4)	0.070 (13)*
H3A	0.145 (3)	0.326 (6)	0.387 (4)	0.082 (15)*
H1A	0.837 (3)	0.169 (5)	0.420 (2)	0.063 (12)*
H2A	0.270 (4)	0.405 (3)	0.341 (5)	0.100 (18)*
H2B	0.291 (3)	0.251 (5)	0.404 (3)	0.099 (18)*
H1B	0.805 (4)	0.190 (6)	0.299 (4)	0.14 (2)*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn1	0.03433 (13)	0.02255 (12)	0.02383 (12)	0.000	0.01815 (10)	0.000
Cl3	0.0320 (3)	0.0591 (4)	0.0315 (3)	0.0162 (3)	0.0161 (3)	0.0064 (3)
O4	0.0290 (9)	0.0348 (10)	0.0440 (10)	−0.0046 (8)	0.0220 (8)	−0.0141 (9)
Cl1	0.0809 (6)	0.0363 (4)	0.0615 (5)	−0.0147 (4)	0.0563 (5)	−0.0188 (3)
O1	0.0356 (10)	0.0410 (11)	0.0311 (9)	0.0046 (8)	0.0206 (8)	−0.0013 (8)
O2	0.0387 (11)	0.0412 (11)	0.0372 (10)	−0.0055 (9)	0.0218 (9)	−0.0020 (9)
O3	0.0369 (10)	0.0334 (10)	0.0508 (12)	−0.0016 (8)	0.0273 (10)	−0.0054 (9)

Geometric parameters (Å, º)

Sn1—O4	2.1064 (18)	Sn1—Cl3	2.3906 (7)
Sn1—O4ⁱ	2.1064 (18)	Sn1—Cl1	2.3954 (7)
Sn1—Cl3ⁱ	2.3906 (7)	Sn1—Cl1ⁱ	2.3954 (7)
O4—Sn1—O4ⁱ	86.01 (12)	Cl3ⁱ—Sn1—Cl1	94.12 (3)
O4—Sn1—Cl3ⁱ	87.81 (6)	Cl3—Sn1—Cl1	92.55 (3)
O4ⁱ—Sn1—Cl3ⁱ	84.90 (5)	O4—Sn1—Cl1ⁱ	88.99 (6)
O4—Sn1—Cl3	84.90 (5)	O4ⁱ—Sn1—Cl1ⁱ	174.47 (6)
O4ⁱ—Sn1—Cl3	87.81 (6)	Cl3ⁱ—Sn1—Cl1ⁱ	92.55 (3)
Cl3ⁱ—Sn1—Cl3	170.03 (4)	Cl3—Sn1—Cl1ⁱ	94.12 (3)

O4—Sn1—Cl1	174.47 (6)	Cl1—Sn1—Cl1ⁱ	96.09 (4)
O4ⁱ—Sn1—Cl1	88.99 (6)		

Symmetry code: (i) −*x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*B*···O2ⁱⁱ	0.84 (1)	1.90 (2)	2.729 (3)	169 (6)
O2—H2*B*···O3ⁱⁱⁱ	0.84 (1)	2.04 (2)	2.825 (3)	157 (5)
O2—H2*A*···O1^{iv}	0.84 (1)	1.94 (2)	2.762 (3)	168 (5)
O1—H1*A*···Cl3^v	0.84 (1)	2.68 (3)	3.389 (2)	143 (4)
O3—H3*A*···O2	0.84 (1)	1.95 (2)	2.763 (3)	163 (4)
O3—H3*B*···Cl1ⁱ	0.83 (1)	2.43 (1)	3.260 (2)	173 (4)
O4—H4*B*···O1^{vi}	0.83 (1)	1.77 (1)	2.598 (3)	176 (4)
O4—H4*A*···O3^{vii}	0.84 (1)	1.80 (1)	2.635 (3)	176 (4)

Symmetry codes: (i) −*x*, *y*, −*z*+1/2; (ii) −*x*+1, *y*, −*z*+1/2; (iii) −*x*+1/2, −*y*+1/2, −*z*+1; (iv) *x*−1/2, *y*+1/2, *z*; (v) −*x*+1, −*y*+1, −*z*+1; (vi) *x*−1, *y*+1, *z*; (vii) *x*, *y*+1, *z*.