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# Hydrates of tin tetrachloride

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The crystal structures of the tri- and tetrahydrate of tin tetrachloride, *viz.* diaquatetrachlorotin(IV) monohydrate, $[SnCl_4(H_2O)_2]\cdot H_2O$, and diaquatetrachlorotin(IV) dihydrate, $[SnCl_4(H_2O)_2]\cdot 2H_2O$, are reported and shown to contain the *cis*-$[SnCl_4(H_2O)_2]$ species and water molecules in both cases. The trihydrate contains chains of the tin species linked by a single hydrogen-bonded water molecule, whilst the tetrahydrate has a three-dimensional network. In addition, there are O—H···Cl interactions present.

## Comment

The literature reports several hydrates of tin tetrachloride, including the tri-, tetra- and pentahydrate, but only the last is commercially available [see Klug & Brasted (1958) and *Gmelins Handbuch der Anorganischen Chemie* (1972)] and it has been structurally characterized using a crystal selected from a commercial bulk sample (Barnes *et al.*, 1980). As part of a systematic study of interactions between main group elements and acyclic and macrocyclic chalcogenoether ligands, we have isolated and structurally characterized several new families of donor–acceptor compounds involving $Sn^{IV}$ halides with thio-, seleno- and telluroether ligands (Levason & Reid, 2001; Levason *et al.*, 2003). In the course of this work, we have also obtained crystals which have been shown to be hydrates of $SnCl_4$. These experiments were carried out under 'anhydrous' conditions and clearly the products arose from small amounts of water in the solvents/reagents or ingress of water from the air during manipulations.

By this route, we have prepared and determined the crystal structures of the tri- and tetrahydrate of tin tetrachloride and this has provided an opportunity to compare the two title structures with that of the pentahydrate and to establish if there are features common to all three hydrates, both in the tin species present and in the nature of the hydrogen bonding. The structure analysis of the pentahydrate (Barnes *et al.*, 1980) did not locate the H atoms, but the O···O and O···Cl distances gave convincing indications of O—H···O and O—H···Cl interactions.

The trihydrate, $SnCl_4\cdot 3H_2O$ or $[SnCl_4(H_2O)_2]\cdot H_2O$, has been isolated on two occasions and contains a *cis*-octahedral $[SnCl_4(H_2O)_2]$ group linked into chains by solvate water molecules through O—H···O hydrogen bonds (Fig. 1). The only initial problem arose from the closeness of the cell $\beta$ parameter to 90° and one of the crystals was shown to be a twin. The data reported are for the non-twin crystal, but the results for the two determinations are essentially identical and gave rise to similar $R$ values. All the H atoms were identified: the tin-bonded water molecules are hydrogen bonded to O3 and by a second hydrogen bond to a Cl atom (Table 1). The hydrate water, in contrast, is hydrogen bonded to Cl, with each H atom involved in a bifurcated hydrogen bond with rather small O—H···Cl angles (121–146°). The Sn—Cl [2.338 (1)–2.401 (1) Å] and Sn—O [2.138 (3) and 2.169 (3) Å] distances are unexceptional.

The tetrahydrate, $SnCl_4\cdot 4H_2O$ or $[SnCl_4(H_2O)_2]\cdot 2H_2O$, like the trihydrate, contains *cis*-octahedral $[SnCl_4(H_2O)_2]$ groups, but with a more complicated three-dimensional network of O—H···O bonds (Fig. 2). Only the H atoms of the bonded water molecules were clearly identified and included in the model, although there was evidence for some H atoms of the

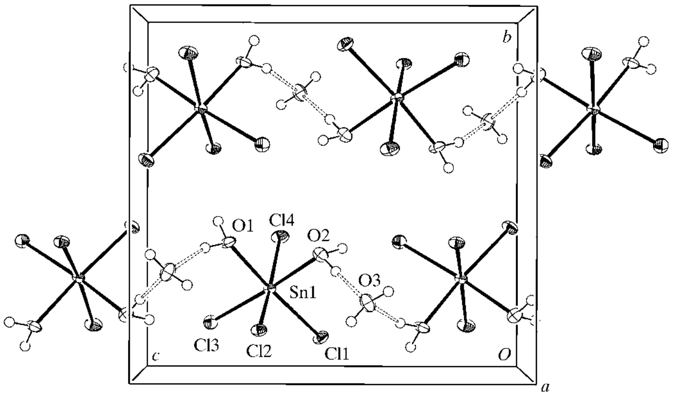

**Figure 1**
Packing diagram for trihydrate $SnCl_4\cdot 3H_2O$, viewed along the $a$ direction. O—H···O hydrogen bonds are shown as dotted lines and displacement ellipsoids are drawn at the 50% probability level.

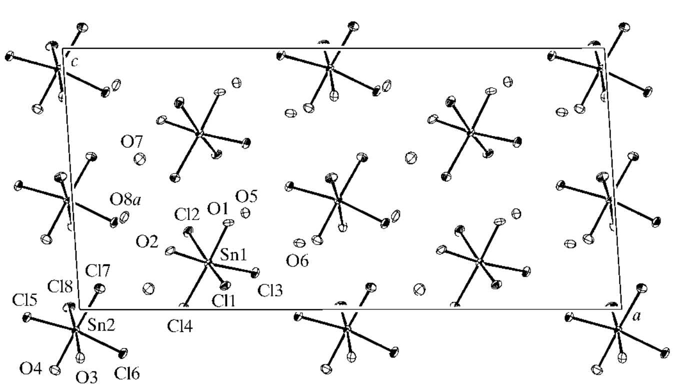

**Figure 2**
Packing diagram for tetrahydrate $SnCl_4\cdot 4H_2O$, viewed along the $b$ direction. H atoms are only included in the model for atoms O1 to O4, but are excluded from the diagram for clarity. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: ($a$) $x, 1 - y, \frac{1}{2} + z$.]

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hydrate waters, but this was not convincing. All eight H atoms of the coordinated water molecules are involved in hydrogen bonding, with H1 and H8 forming O—H···Cl linkages, the remainder forming O—H···O linkages (Table 2). Judged solely by distance (no H atoms being available), O5···O6 [2.745 (8) Å] and O7···O8*a* [2.966 (9) Å; symmetry code: (*a*) $x, 1 - y, \frac{1}{2} + z$] form O—H···O hydrogen bonds. Short chains of hydrogen-bonded O atoms linking $[SnCl_4(H_2O)_2]$ groups are easily recognized [*e.g.* O1···O5···O6···O4*b*; symmetry code: (*b*) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$]. The Sn—Cl [2.359 (2)–2.397 (2) Å] and Sn—O [2.106 (5)–2.137 (6) Å] distances are again unexceptional.

The structure of the pentahydrate, $SnCl_4{\cdot}5H_2O$ (Barnes *et al.*, 1980), again shows the *cis*-$[SnCl_4(H_2O)_2]$ moiety linked into chains parallel to *c* through three hydrate water molecules. There is further O—H···O linking to a parallel chain (Fig. 3) and, judged by O···Cl distances, there is additional weak hydrogen bonding between the double chains. Finally, the $[SnCl_4(H_2O)_2]$ unit has been found in a number (*ca* six) of complexes of crown ethers and similar molecules [see Cusack *et al.* (1984) and Junk & Raston (2004)]. Four examples are hydrates and involve hydrogen bonding between the tin residue and the hydrate water and organic O atoms. Surprisingly, one example (Hough *et al.*, 1986) contains the *trans*-$[SnCl_4(H_2O)_2]$ group, with the rest containing the by now familiar *cis* geometric isomer.

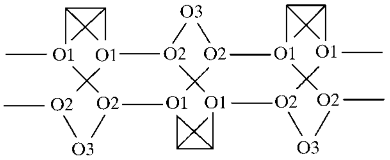

**Figure 3**
Schematic diagram of the O—H···O hydrogen bonding in pentahydrate $SnCl_3{\cdot}5H_2O$, showing the double chains. The O atoms shown are O1, which is part of $[SnCl_4(H_2O)_2]$, and the hydrate atoms O2 and O3.

## Experimental

Crystals were obtained serendipitously during attempts to crystallize $SnCl_4$ complexes of dithioether and tetrathia-macrocycles from $CH_2Cl_2$. Removal of the bulk thioether complex by filtration and slow evaporation of the residual filtrate unexpectedly yielded crystals of the tri- and tetrahydrate of $SnCl_4$.

## Trihydrate $SnCl_4{\cdot}3H_2O$

*Crystal data*

$[SnCl_4(H_2O)_2]{\cdot}H_2O$
$M_r = 314.54$
Monoclinic, $P2_1/c$
$a = 6.362$ (3) Å
$b = 11.071$ (4) Å
$c = 11.895$ (4) Å
$\beta = 90.22$ (2)°
$V = 837.8$ (6) Å$^3$
$Z = 4$

$D_x = 2.494$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 23.0$–24.9°
$\mu = 4.26$ mm$^{-1}$
$T = 150$ (2) K
Block, colourless
0.48 × 0.28 × 0.20 mm

*Data collection*

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min} = 0.268$, $T_{max} = 0.427$
1549 measured reflections
1475 independent reflections
1356 reflections with $I > 2\sigma(I)$

$R_{int} = 0.011$
$\theta_{max} = 25.0°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 14$
3 standard reflections every 200 reflections
intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.082$
$S = 1.07$
1475 reflections
92 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 1.1933P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.83$ e Å$^{-3}$
$\Delta\rho_{min} = -2.44$ e Å$^{-3}$

**Table 1**
Hydrogen-bonding geometry (Å, °) for trihydrate $SnCl_4{\cdot}3H_2O$.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···O3$^{i}$ | 0.82 (2) | 1.91 (3) | 2.678 (5) | 156 (6) |
| O1—H2···Cl2$^{ii}$ | 0.84 (5) | 2.44 (3) | 3.238 (3) | 158 (6) |
| O2—H3···Cl3$^{iii}$ | 0.85 (5) | 2.35 (6) | 3.188 (4) | 172 (7) |
| O2—H4···O3 | 0.83 (6) | 1.85 (3) | 2.675 (5) | 169 (8) |
| O3—H5···Cl3$^{iv}$ | 0.84 (6) | 2.56 (4) | 3.286 (4) | 144 (5) |
| O3—H5···Cl2$^{iii}$ | 0.84 (6) | 2.80 (6) | 3.309 (4) | 121 (5) |
| O3—H6···Cl1$^{v}$ | 0.83 (6) | 2.59 (5) | 3.315 (4) | 146 (7) |
| O3—H6···Cl1$^{vi}$ | 0.83 (6) | 2.91 (6) | 3.425 (4) | 122 (6) |

Symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iv) $1 + x, \frac{1}{2} - y, z - \frac{1}{2}$; (v) $1 + x, y, z$; (vi) $1 - x, -y, 1 - z$.

## Tetrahydrate $SnCl_4{\cdot}4H_2O$

*Crystal data*

$[SnCl_4(H_2O)_2]{\cdot}2H_2O$
$M_r = 332.55$
Monoclinic, *Cc*
$a = 23.987$ (4) Å
$b = 6.714$ (6) Å
$c = 11.580$ (3) Å
$\beta = 93.77$ (2)°
$V = 1860.9$ (18) Å$^3$
$Z = 8$

$D_x = 2.374$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 23.6$–24.9°
$\mu = 3.85$ mm$^{-1}$
$T = 150$ (2) K
Block, colourless
0.42 × 0.34 × 0.28 mm

*Data collection*

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min} = 0.241$, $T_{max} = 0.340$
1717 measured reflections
1717 independent reflections
1704 reflections with $I > 2\sigma(I)$

$\theta_{max} = 25.0°$
$h = -28 \rightarrow 28$
$k = -7 \rightarrow 0$
$l = 0 \rightarrow 13$
3 standard reflections every 200 reflections
intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.074$
$S = 1.13$
1717 reflections
164 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.94$ e Å$^{-3}$
$\Delta\rho_{min} = -2.23$ e Å$^{-3}$
Absolute structure: Flack (1983)
Flack parameter = 0.11 (3)

**Table 2**
Hydrogen-bonding geometry (Å, °) for tetrahydrate $SnCl_4 \cdot 4H_2O$.

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---|---|---|---|---|
| $O1-H1 \cdots Cl1^{i}$ | 0.84 | 2.42 | 3.223 (5) | 162 |
| $O1-H2 \cdots O5^{ii}$ | 0.84 | 1.78 | 2.600 (8) | 164 |
| $O2-H3 \cdots O8^{iii}$ | 0.85 | 1.89 | 2.703 (7) | 158 |
| $O2-H4 \cdots O7^{iv}$ | 0.84 | 1.83 | 2.653 (8) | 165 |
| $O3-H5 \cdots O8^{ii}$ | 0.84 | 1.86 | 2.680 (8) | 162 |
| $O3-H6 \cdots O6^{v}$ | 0.84 | 1.89 | 2.672 (8) | 154 |
| $O4-H7 \cdots O6^{vi}$ | 0.83 | 1.83 | 2.653 (8) | 167 |
| $O4-H8 \cdots Cl8^{vii}$ | 0.83 | 2.49 | 3.256 (6) | 153 |

Symmetry codes: (i) $x, -y, \frac{1}{2}+z$; (ii) $x, y-1, z$; (iii) $x, 1-y, \frac{1}{2}+z$; (iv) $x, -y, z-\frac{1}{2}$; (v) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (vi) $x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$; (vii) $x, 1-y, z-\frac{1}{2}$.

For the trihydrate, all the H atoms were located from a difference electron-density map and refined using restraints on the O—H bond distances (0.84 Å). H atoms were given a common refined displacement parameter. For the tetrahydrate, a difference electron-density map showed a number of peaks for potential H atoms, of which the eight of the tin-bonded water molecules were the most convincing, with reasonable O—H, H—O—H and H—O—Sn geometry. Inclusion of these with restraints (DFIX) gave a satisfactory model. The H atoms on the hydrate water molecules were incomplete, with poor H—O—H angles (in two cases where both H atoms were located), and refinement calculations gave unsatisfactory intermolecular H···H distances. Accordingly, these H atoms were excluded from the model. The Flack (1983) parameter for the tetrahydrate was determined from a small number of reflections, which makes the absolute structure determination of the chosen crystals less reliable. The H atoms were fixed in the final cycle as the shift/error values were small but failing to converge probably due to the large correlation coefficients between the H-atom coordinates.

For both compounds, data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1307). Services for accessing these data are described at the back of the journal.

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