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Crystal structures of tin(IV) chloride hydrates

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As determined by single crystal X-ray crystallography, $SnCl_4{\cdot}2H_2O$ and $SnCl_4{\cdot}3H_2O$ have a molecular structure with *cis*-$[SnCl_4(H_2O)_2]$ units linked to each other by a system of hydrogen bonds.

The interaction of tin tetrachloride with water under variable conditions produces a number of hydrates, which were described[1] in 1891. The crystallization of a concentrated aqueous solution at 60–83 °C leads to a trihydrate, at 56–63 °C, to a tetrahydrate, at 19–56 °C, to a pentahydrate, and below 19 °C, to an octahydrate. Based on nuclear quadrupole resonance (NQR), Mössbauer and Raman spectroscopy, the existence of the molecular species $[SnCl_4(H_2O)_2]$ in di-, tri- and pentahydrates has been supposed.[2] Due to the presence of a single line in the NQR spectra of these compounds, the *trans*-geometry of $[SnCl_4(H_2O)_2]$ was suggested in accordance with the Raman spectra. However, the crystal structure determination for $SnCl_4{\cdot}5H_2O$, $SnCl_4{\cdot}4H_2O$ and $SnCl_4{\cdot}6H_2O$ revealed the *cis*-geometry of the coordination environment,[3,4] although the influence of non-coordinated water molecules on Sn–Cl bonds really takes place. The further nuclear quadrupole resonance study of the pentahydrate also indicated two chemically nonequivalent chlorine sites comprising three non-coordinated water molecules.[5] Surprisingly, results of the X-ray structural study were not given.[3] We report here the results of X-ray single-crystal structure determination for di- and trihydrates.

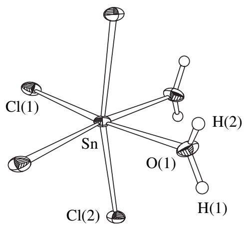

Figure 1 $[SnCl_4(H_2O)_2]$ unit in **1** and **2**.

Large colourless prismatic crystals of $SnCl_4{\cdot}2H_2O$ **1** were prepared by a long-time storage of anhydrous tetrachloride, due to the interaction of $SnCl_4$ vapour (6.4 Torr at 298 K) with the moisture of air. A similar method for the preparation of the dihydrate at room temperature was reported.[6] Heating a sealed ampoule with non-dried $SnCl_4$ at 80–90 °C produces colourless needles of the trihydrate. Both compounds are highly hydroscopic. The crystallographic data are presented in Table 1, and selected interatomic distances are listed in Table 2. The complexes have a molecular structure containing $[SnCl_4(H_2O)_2]$

Table 1 Crystallographic data for **1** and **2**.

Compound	$H_4Cl_4O_2Sn$ **1**	$H_6Cl_4O_3Sn$ **2**
Formula weight	296.52	314.54
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbcn*	$P2_1/c$
a/Å	9.215(3)	6.357(2)
b/Å	7.257(2)	11.065(3)
c/Å	11.076(3)	11.885(3)
β	90	90.17(1)
V/Å^3	740.7(4)	836.0(4)
Z	4	4
d_{calc}/g cm^{-3}	2.659	2.449
u(MoKα)/mm^{-1}	4.801	4.270
F(000)	552	592
Crystal size/mm	0.80×0.76×0.46	0.70×0.10×0.10
λ(MoKα)/Å	0.71073	0.71073
T/K	130	150
θ_{max}/°	31.90	26.73
Collected reflections	3352	1842
Unique reflections	1223	1741
Reflections with $I > 2\sigma(I)$	1167	1541
Number of parameters	42	96
Extinction coefficient	0.032(2)	0.0048(5)
GOOF	1.151	1.159
R_1 $[F^2 > 2\sigma(F^2)]$ / wR_2 (all)	0.0294 / 0.0681	0.0333 / 0.0709
Remaining electron density (min / max)/e Å^{-3}	−2.632 / 1.402	−1.170 / 0.668

units (Figure 1) linked together by a system of intermolecular hydrogen bonds. The tin atom in $[SnCl_4(H_2O)_2]$ is situated at the centre of a slightly distorted octahedron formed by four chlorine atoms and two water molecules in the *cis* position. A similar *cis* geometry is present in the structures of $[SnCl_4(OPCl_3)_2]$,[7] $[SnCl_4(DMSO)_2]$,[8] $[SnCl_4(H_2O)_2]\cdot 3H_2O$[3] and $[SnCl_4(NCMe)_2]$.[9] It can be attributed to a small size of the donor ligands. On the contrary, the complexes with bulky ligands such as Et_2O and THF usually have a *trans* geometry.[10,11] Meanwhile, in $[SnCl_4(H_2O)_2]$(15-crown-5) with a crown ether as an outer-sphere ligand, water molecules occupy *trans* positions in the coordination sphere of the tin atom.[12]

The similarity in Sn–O and Sn–Cl bond distances in **1** despite the large difference of atomic radii of oxygen and chlorine shows the relative weakness of Sn–OH_2 bonds. The repulsion of chlorine atoms results in an increase in the Cl(1)–Sn–Cl(1) angle from 90 to 96.9°; the angle Cl(2)–Sn–Cl(2′) decreased from 180 to 167.0°, and O(1)–Sn–O(1′) was 82.1°. The significant difference in Sn–Cl(1) (2.408 Å) and Sn–Cl(2) (2.336 Å) bond distances could be explained by the participation of Cl(1) in the formation of two hydrogen bonds with the adjacent fragments, O(1)–H(1)···Cl(1) 3.186 Å and O(1)–H(2)···Cl(1′) 3.208 Å, which are slightly shorter than that in the structure of the pentahydrate (O–H···Cl 3.22 and 3.31 Å). The packing of the molecules depends on the system of H-bonds. The molecules in **1** are arranged in approximately hexagonal layers parallel to the *xy*0 plane. Hydrogen bonds link the molecules within the layers and in the *c* direction resulting in a three-dimensional framework (Figure 2).

The structure of $[SnCl_4(H_2O)_2]\cdot H_2O$ **2** contains similar distorted octahedral *cis*-$[SnCl_4(H_2O)_2]$ units. The average Sn–Cl bond (2.37 Å) is similar to that in **1** and the difference between Sn–Cl(4) [2.337(1) Å] and the remaining Sn–Cl bond distances [2.378–2.397(1) Å] reflects the participation of all Cl atoms except Cl(4) in hydrogen bonds. In particular, the Cl(1) and Cl(3) atoms form one O–H···Cl bond each (3.314 and 3.236 Å, respectively), whereas the Cl(2) atom acts as an acceptor in two H-bonds with distances of 3.193 and 3.277 Å. The structure of the pentahydrate is also characterised by the similar dependence of Sn–Cl distances on the number of H-bonds. The water molecule non-coordinated by a tin atom forms four H-bonds with four $[SnCl_4(H_2O)_2]$ units linking them in layers oriented parallel to the *x*0*z* plane (Figure 3). The coordinated water molecules also participate in H-bonding thus forming a three-dimensional framework.

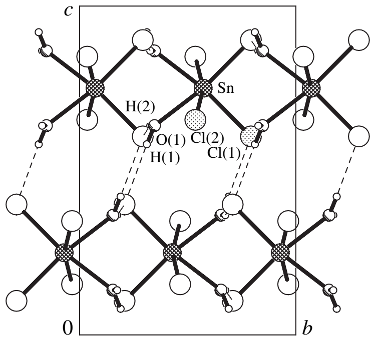

Figure 2 Layers of $[SnCl_4(H_2O)_2]$ molecules in the structure of **1**.

Table 2 Environments of tin atoms and hydrogen bonds (Å) in the structures of **1** and **2**.

Distance	1	2
Sn–O(1)	2.168(2)	2.139(4)
Sn–O(2)		2.160(4)
Sn–Cl(1)	2.4085(7)	2.380(1)
Sn–Cl(2)	2.3362(8)	2.397(1)
Sn–Cl(3)		2.378(1)
Sn–Cl(4)		2.337(1)
O(1)–H(1)···Cl(1)	3.186(2)	
O(1)–H(2)···Cl(1)	3.208(2)	
O(1)–H(1)···Cl(3)		3.236(5)
O(1)–H(2)···O(3)		2.676(6)
O(2)–H(3)···O(3)		2.668(6)
O(2)–H(4)···Cl(2)		3.193(4)
O(3)–H(5)···Cl(1)		3.314(4)
O(3)–H(6)···Cl(2)		3.277(5)

The Sn–Cl(2) bond distances in **1** and **2** are close to those in anhydrous $SnCl_4$ (2.31 Å) and to the shortest Sn–Cl(1) distance in an adduct with acetonitrile (2.339 Å).[9] In this adduct, the Sn–Cl(2) distance is shorter (2.355 Å) than that in **1** and **2**. This can arise from the nature of the acetonitrile molecule, which demonstrates weaker interaction with chlorine atoms. The angle O(1)–Sn–O(1′) in **1** (82.1°) is larger than that in $[SnCl_4(NCMe)_2]$ (76.7°). Bond distances Sn–O in **1** and **2** (2.14–2.17 Å) are longer than that in the pentahydrate $[SnCl_4(H_2O)_2]\cdot 3H_2O$ (2.098 Å). Analogous data for the trihydrate were published recently.[13] The crystals were prepared by the hydration of tin chloride with a small amount of water.

The crystallographic studies of $SnCl_4$ di- and trihydrates proved an incorrect interpretation of spectral data for the same compounds.[3,4] It is interesting to investigate these compounds using Raman spectra recorded for well-characterised samples and to study the chlorohydroxo complexes of tin(IV), of which only $[Sn_2Cl_6(OH)_2(H_2O)_2]$ has been reported.[3,14]

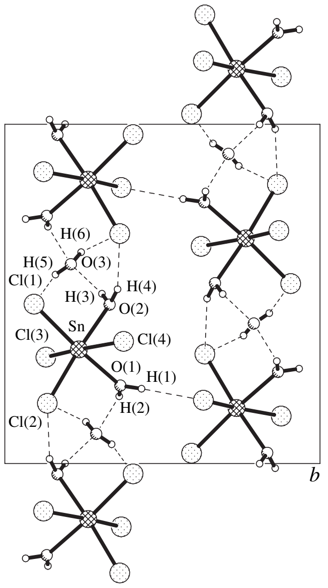

Figure 3 Layers of $[SnCl_4(H_2O)_2]$ molecules in the structure of **2**.

References

1 W. Meyerhoffer, *Bull. Soc. Chim. Fr.*, 1891, **6**, 855.

2 H. Negita, T. Okuda and M. Mishima, *Bull. Chem. Soc. Jpn*., 1969, **42**, 2509.

3 J. C. Barnes, H. A. Sampson and T. J. R. Weakley, *J. Chem. Soc., Dalton Trans*., 1980, 949.

4 A.-F. Shihada, A. S. Abushamleh and F. Weller, *Z. Anorg. Allg. Chem*., 2004, **630**, 841.

5 D. K. Oh, Y. M. Kwon, C. Rhee, C. E. Lee and J.-K. Kang, *J. Chem. Phys*., 1998, **109**, 3176.

6 *Cationic Polymerization Related Complexes, Proc. Conf*., Univ. Coll. N. Staffordshire, Engl., 1952, p. 26.

7 C.-I. Branden, *Acta Chem. Scand*., 1963, **17**, 759.

8 J. M. Kisenyi, G. R. Willey and M. G. B. Drew, *Acta Crystallogr., Sect. C*, 1985, **41**, 700.

9 M. Webster and H. E. Blayden, *J. Chem. Soc. (A)*, 1969, 2443.

10 A. V. Yatsenko, L. A. Aslanov , M. Yu. Burtsev and E. A. Kravchenko, *Zh. Neorg. Khim.*, 1991, **36**, 2031 (*Russ. J. Inorg. Chem*., 1991, **36**, 1986).

11 G. R. Willey, T. J. Woodman, R. J. Deeth and W. Errington, *Main Group Metal Chemistry*, 1998, **21**, 583.

12 G. Valle, A. Cassol and U. Russo, *Inorg. Chim. Acta*, 1984, **82**, 81.

13 A. R. J. Genge, W. Levason, R. Patel, G. Reid and M. Webster, *Acta Crystallogr*., 2004, **C60** (4), i47.

14 T. S. Cameron, O. Knop and B. R. Vincent, *Can. J. Chem*., 1985, **63**, 759.

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