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Crystal structure of tin(II) perchlorate trihydrate

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The title compound, $[Sn(H_2O)_3](ClO_4)_2$, was synthesized by the redox reaction of copper(II) perchlorate hexahydrate and metallic tin in perchloric acid. Both the trigonal–pyramidal $[Sn(H_2O)_3]^{2+}$ cations and tetrahedral perchlorate anions lie on crystallographic threefold axes. In the crystal, the cations are linked to the anions by O—H···O hydrogen bonds, generating (001) sheets.

Keywords: crystal structure; low-temperature salt hydrates; perchlorate hydrates; tin(II) salts

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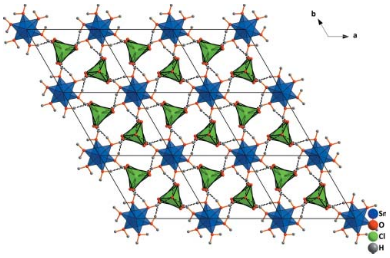
1. Chemical context

The synthesis and powder diffraction data for tin(II) perchlorate trihydrate were described by Davies & Donaldson (1968) and Schiefelbein & Daugherty (1970). With our crystal structure determination, the data of Davies & Donaldson (1968) are confirmed. The interest in the system tin(II)–perchloric acid-water arose from the redetermination of the redox-potential Sn^{2+}/Sn^{4+} in perchloric acid by Gajda *et al.* (2009). There is no solid–liquid diagram for this binary salt–water system known in the literature.



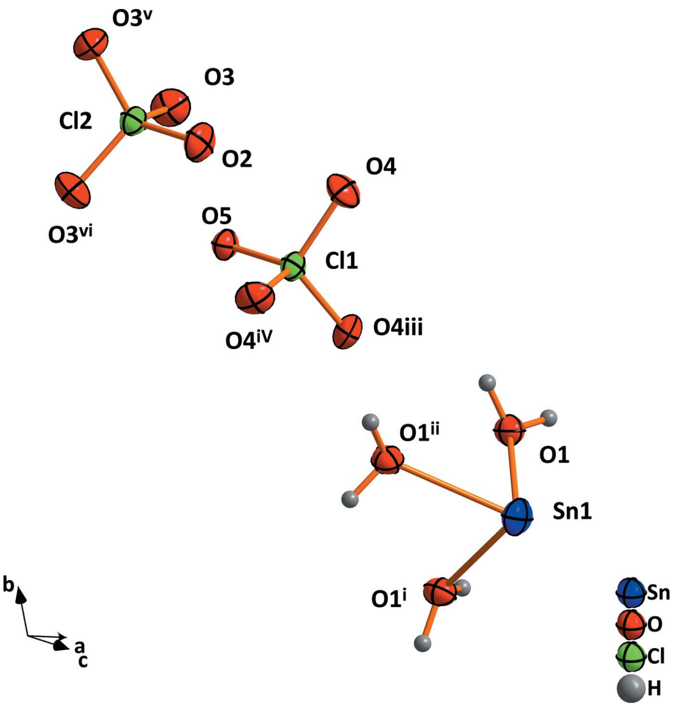


Figure 1
The component ions in tin(II) perchlorate trihydrate with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-x + y, -x, z$; (ii) $-y, x - y, z$; (iii) $1 - x + y, 1 - x, z$; (iv) $1 - y, x - y, z$; (v) $1 - y, 1 + x - y, z$; (vi) $-x + y, 1 - x, z$.]

Table 1
Selected geometric parameters (Å, °).

Sn1—O2	2.201 (7)	Cl2—O1	1.424 (12)
Cl1—O4	1.430 (4)	Cl2—O3	1.426 (5)
Cl1—O5	1.449 (10)		
$O2^{i}$—Sn1—O2	76.9 (3)		

Symmetry code: (i) $-y, x-y, z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2⋯$O4^{ii}$	0.94 (7)	1.95 (8)	2.823 (8)	152 (7)
O2—H2⋯$O3^{iii}$	0.94 (7)	2.46 (8)	2.926 (8)	110 (6)

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

2. Structural commentary

The tin atom lies on a crystallographic threefold rotation axis and is coordinated by three water molecules as a trigonal pyramid (Fig. 1, Table 1). The perchlorate tetrahedra are located in the gaps between the SnO_3 pyramids on their own threefold axes. A similar arrangement of the perchlorate tetrahedra can be observed in the crystal structure of $Ba(ClO_4)_2{\cdot}3H_2O$ (Gallucci & Gerkin, 1988). The difference between the two structures is that the barium atom is sixfold coordinated by oxygen water molecules. All of them are shared between two barium atoms, so that an average of three are bonded to one Ba atom.

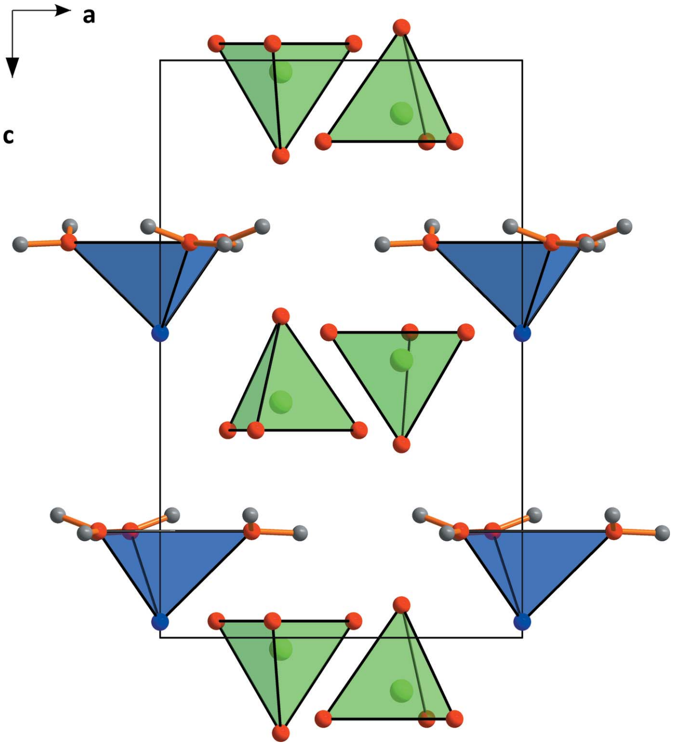


Figure 2
The unit-cell packing in tin(II) perchlorate trihydrate with the ions shown in polyhedral representation.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Sn(H_2O)_3](ClO_4)_2$
M_r	371.44
Crystal system, space group	Hexagonal, $P6_3$
Temperature (K)	180
a, c (Å)	7.0701 (10), 9.7631 (15)
V ($Å^3$)	422.64 (16)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.70
Crystal size (mm)	0.70 × 0.52 × 0.22
Data collection	
Diffractometer	STOE IPDS 2
Absorption correction	Integration (Coppens, 1970)
T_{min}, T_{max}	0.116, 0.441
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	792, 788, 742
R_{int}	0.152
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.689
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.093, 1.08
No. of reflections	792
No. of parameters	52
No. of restraints	1
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.85, −0.90
Absolute structure	Classical Flack (1983) method preferred over Parsons & Flack (2004) because s.u. lower
Absolute structure parameter	−0.04 (14)

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

The different coordination of Sn^{2+} in comparison with Ba^{2+} is caused by the lone-pair effect. It requires more space, so the distance to the next oxygen atoms is larger than in the barium salt structure. The perchlorate tetrahedra are connected by O—H⋯O hydrogen bonds (Table 2) with the water molecules

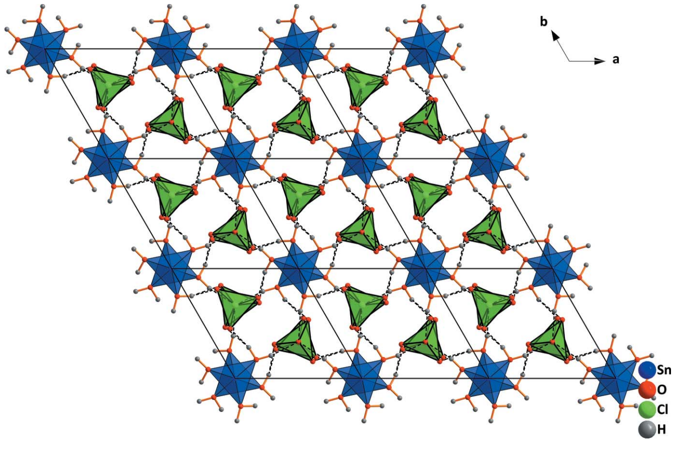


Figure 3
Larger view of the crystal structure of tin(II) perchlorate trihydrate viewed down [001]. Dashed lines indicate hydrogen bonds.

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coordinated at the tin atoms (Figs. 2 and 3), forming sheets parallel to (001).

4. Database survey

For properties, thermal behavior and powder diffraction data for tin(II) perchlorate trihydrate, see: Schiefelbein & Daugherty (1970) and Davies & Donaldson (1968). For crystal structure determinations of other divalent perchlorate trihydrates, see: Gallucci & Gerkin (1988) for the barium salt and Hennings *et al.* (2014) for the strontium salt.

5. Synthesis and crystallization

$Sn(ClO_4)_2·3H_2O$ was prepared by reaction of copper(II) perchlorate hexahydrate (15 g, Alfa Aesar, reagent grade) and elemental tin (12.04 g, VEB Feinchemikalien) in perchloric acid (50 ml, 60%, Merck, pA). After stirring the solution for 2 h the precipitated copper was filtered off and the solution was transferred into a freezer at 253 K for crystallization. All crystals are stable in the saturated aqueous solution over a period of at least four weeks.

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

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The H atoms were placed in the positions indicated by difference Fourier maps. No further constraints were applied.

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supporting information

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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(II) perchlorate trihydrate

Crystal data

$[Sn(H_2O)_3](ClO_4)_2$
M_r = 371.44
Hexagonal, $P6_3$
a = 7.0701 (10) Å
c = 9.7631 (15) Å
V = 422.64 (16) Å^3
Z = 2
F(000) = 355.8
D_x = 2.919 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 14633 reflections
θ = 2.1–29.6°
μ = 3.70 mm^{-1}
T = 180 K
Prism, colourless
0.70 × 0.52 × 0.22 mm

Data collection

STOE IPDS 2
diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
Absorption correction: integration
(Coppens, 1970)
T_{min} = 0.116, T_{max} = 0.441
792 measured reflections
788 independent reflections
742 reflections with $I > 2\sigma(I)$
R_{int} = 0.152
θ_{max} = 29.3°, θ_{min} = 3.3°
$h = -7 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.093
S = 1.08
792 reflections
52 parameters
1 restraint
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0771P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −0.90 e Å^{-3}
Extinction correction: *SHELXL*,
$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.62 (5)
Absolute structure: Classical Flack (1983)
method preferred over Parsons & Flack (2004)
because s.u. lower.
Absolute structure parameter: −0.04 (14)

Special details

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

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
Sn1	0.0000	0.0000	0.9724 (6)	0.0280 (4)
O2	0.2529 (5)	0.1712 (6)	0.8156 (8)	0.0239 (8)
O3	0.5340 (6)	0.6895 (7)	−0.0288 (9)	0.0311 (10)
Cl1	0.6667	0.3333	0.0921 (2)	0.0182 (5)
Cl2	0.3333	0.6667	0.0195 (3)	0.0197 (5)
O1	0.3333	0.6667	0.1653 (12)	0.0295 (18)
O4	0.8132 (6)	0.5490 (7)	0.1408 (7)	0.0280 (10)
O5	0.6667	0.3333	−0.0564 (10)	0.0204 (16)
H1	0.386 (19)	0.209 (16)	0.83 (2)	0.06 (3)*
H2	0.246 (11)	0.293 (10)	0.783 (8)	0.017 (17)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn1	0.0337 (4)	0.0337 (4)	0.0164 (5)	0.0169 (2)	0.000	0.000
O2	0.0197 (15)	0.0232 (14)	0.030 (2)	0.0113 (12)	−0.0002 (19)	0.001 (2)
O3	0.0264 (16)	0.0359 (18)	0.034 (2)	0.0178 (15)	0.009 (3)	0.005 (3)
Cl1	0.0200 (7)	0.0200 (7)	0.0146 (12)	0.0100 (3)	0.000	0.000
Cl2	0.0202 (7)	0.0202 (7)	0.0187 (13)	0.0101 (3)	0.000	0.000
O1	0.038 (3)	0.038 (3)	0.013 (5)	0.0190 (15)	0.000	0.000
O4	0.0301 (18)	0.0236 (17)	0.028 (2)	0.0118 (14)	−0.003 (2)	−0.010 (2)
O5	0.023 (2)	0.023 (2)	0.016 (4)	0.0114 (11)	0.000	0.000

Geometric parameters (Å, º)

Sn1—O2^{i}	2.201 (7)	Cl1—O5	1.449 (10)
Sn1—O2^{ii}	2.201 (7)	Cl2—O1	1.424 (12)
Sn1—O2	2.201 (7)	Cl2—O3^{v}	1.426 (5)
Cl1—O4	1.430 (4)	Cl2—O3^{vi}	1.426 (5)
Cl1—O4^{iii}	1.430 (4)	Cl2—O3	1.426 (5)
Cl1—O4^{iv}	1.430 (4)		
O2^{i}—Sn1—O2^{ii}	76.9 (3)	O4^{iv}—Cl1—O5	109.4 (3)
O2^{i}—Sn1—O2	76.9 (3)	O1—Cl2—O3^{v}	109.3 (4)
O2^{ii}—Sn1—O2	76.9 (3)	O1—Cl2—O3^{vi}	109.3 (4)
O4—Cl1—O4^{iii}	109.5 (3)	O3^{v}—Cl2—O3^{vi}	109.6 (4)
O4—Cl1—O4^{iv}	109.5 (3)	O1—Cl2—O3	109.3 (4)
O4^{iii}—Cl1—O4^{iv}	109.5 (3)	O3^{v}—Cl2—O3	109.6 (4)

O4—Cl1—O5	109.4 (3)	O3^{vi}—Cl2—O3	109.6 (4)
O4^{iii}—Cl1—O5	109.4 (3)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O4^{vii}	0.94 (7)	1.95 (8)	2.823 (8)	152 (7)
O2—H2···O3^{viii}	0.94 (7)	2.46 (8)	2.926 (8)	110 (6)

Symmetry codes: (vii) −*x*+1, −*y*+1, *z*+1/2; (viii) −*x*+*y*, −*x*+1, *z*+1.