$wR = 0.046$
$S = 1.93$
1296 reflections
50 parameters
H atom fixed but included in calculations
$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{max} = 0.001$

Extinction correction: Larson (1970)
Extinction coefficient: 0.0056 (3)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

U_{iso} for H atom, $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	U_{iso}/U_{eq}
Mn(1)	0	0	0	0.009 (1)
Mn(2)	0	0.2644 (1)	1/2	0.009 (1)
V	0.3793 (1)	0	0.9076 (1)	0.006 (1)
K	0.2622 (1)	1/2	0.7047 (2)	0.017 (1)
O(1)	0.0724 (2)	0	−0.2817 (6)	0.009 (1)
O(2)	0.4145 (1)	0.2318 (3)	0.7767 (4)	0.010 (1)
O(3)	0.2648 (2)	0	0.8200 (6)	0.015 (1)
O(4)	0.4149 (2)	0	0.2436 (6)	0.009 (1)
H	0.1396	0	0.7920	0.050

Table 2. *Selected geometric parameters (Å, °)*

Mn(1)—O(1)	2.101 (3)	K—O(2)	2.786 (2)
Mn(1)—O(2^{i})	2.245 (2)	K—O(3)	3.140 (1)
Mn(2)—O(1^{ii})	2.136 (2)	K—O(2^{vi})	2.786 (2)
Mn(2)—O(2^{iii})	2.226 (2)	K—O(3^{vii})	3.140 (1)
Mn(2)—O(4^{iv})	2.178 (2)	K—O(3^{viii})	2.705 (4)
V—O(2)	1.739 (2)	K—O(3^{iii})	2.753 (3)
V—O(3)	1.678 (3)	K—O(4^{iii})	2.781 (3)
V—O(2^{v})	1.739 (2)	O(1)—H^{ix}	0.993 (2)
V—O(4^{ii})	1.751 (3)		
O(1)—Mn(1)—O(1^{x})	180.0 (1)	O(1^{ii})—Mn(2)—O(4^{iv})	172.1 (1)
O(1)—Mn(1)—O(2^{i})	87.2 (1)	O(1^{x})—Mn(2)—O(4^{iv})	91.4 (1)
O(1^{x})—Mn(1)—O(2^{i})	92.8 (1)	O(2^{iii})—Mn(2)—O(4^{iv})	85.4 (1)
O(2^{i})—Mn(1)—O(2^{iii})	180.0 (1)	O(2^{xii})—Mn(2)—O(4^{iv})	93.8 (1)
O(2^{i})—Mn(1)—O(2^{xi})	85.2 (1)	O(4^{iv})—Mn(2)—O(4^{iii})	96.4 (1)
O(2^{iii})—Mn(1)—O(2^{xi})	94.8 (1)	O(2)—V—O(3)	107.1 (1)
O(1^{ii})—Mn(2)—O(1^{x})	80.7 (1)	O(2)—V—O(2^{v})	110.3 (2)
O(1^{ii})—Mn(2)—O(2^{iii})	94.1 (1)	O(2)—V—O(4^{ii})	112.2 (1)
O(1^{x})—Mn(2)—O(2^{iii})	86.8 (1)	O(3)—V—O(4^{ii})	107.7 (2)
O(2^{iii})—Mn(2)—O(2^{xii})	178.8 (1)		

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

Data collection: *CAD-4 software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 software*. Data reduction: *SHELXTL-Plus XPREP* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus XS*. Program(s) used to refine structure: *SHELXTL-Plus XLS*. Molecular graphics: *SHELXTL-Plus XP*. Software used to prepare material for publication: *SHELXTL-Plus XPUB*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1128). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 286–288

Tin(II) Oxyhydroxide by X-ray Powder Diffraction

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(*Received 30 June 1995; accepted 11 September 1995*)

Abstract

The structure of tin(II) oxide hydroxide, $Sn_6O_4(OH)_4$, has been refined by Rietveld analysis of X-ray powder diffraction data. Atomic parameters based on the isostructural lead analogue were used in the starting model. The structure was refined in the tetragonal space group $P\bar{4}2_1c$ with $a = 7.9268(4)$ and $c = 9.1025(5)$ Å. The title compound forms clusters of $Sn_6O_4(OH)_4$ with the Sn atoms in distorted tetragonal pyramidal coordination geometries. Each Sn atom is coordinated to two bridging oxide O and two bridging hydroxy O atoms. The JCPDS file number for $Sn_6O_4(OH)_4$ is 46-1486.

Comment

Tin(II) oxyhydroxide is readily precipitated from mildly alkaline aqueous solutions of stannous salts. Preparation of single crystals of this compound has proved particularly difficult. A single-crystal study has been performed (Howie & Moser, 1968, 1973) which identified a tetragonal structure (space group *P*4/*mnc*) and the presence of discrete $Sn_6O_4(OH)_4$ clusters; however, no atomic coordinates were published. The structure of $Pb_6O_4(OH)_4$ has been determined by powder neutron diffraction (Hill, 1985) and similarities in the X-ray powder diffraction data for these two compounds indicate that they are isostructural. Structure refinement of $Sn_6O_4(OH)_4$ has been carried out as part of a general study of tin and lead cluster formation in aqueous solution.

The original single-crystal study of $Sn_6O_4(OH)_4$ (Howie & Moser, 1968) suggested that the compound crystallizes in the centrosymmetric space group *P4/mnc*. However, this assignment assumes that the hydroxy and oxide O atoms are equivalent and the H atoms are disordered over a general position. The neutron diffraction study on the isostructural lead compound $Pb_6O_4(OH)_4$ (Hill, 1985) showed that the introduction of H atoms into the refinement breaks the centre of symmetry and makes the hydroxy and oxide O atoms crystallographically non-equivalent. The crystal structure of $Sn_6O_4(OH)_4$ has, therefore, been refined in the space group $P\bar{4}2_1c$ using the atomic parameters of the lead analogue as a starting model.

The structure of the title compound may be described as $Sn_6O_4(OH)_4$ clusters, packed in a pseudo body-centred arrangement, with intercluster hydrogen bonding between hydroxy and oxide O atoms (Fig. 1). The large neutral $Sn_6O_4(OH)_4$ cluster seen in the present work is in contrast to the cationic $[Sn_3(OH)_4]^{2+}$ cluster observed in the structure of $Sn_3(OH)_4(NO_3)_2$ (Johnston, Grimes & Abrahams, 1995). Unlike the smaller $[Sn_3(OH)_4]^{2+}$ cluster, where Sn has essentially trigonal pyramidal coordination geometry, in the present structure Sn adopts distorted tetragonal pyramidal coordination geometry. The tetragonal pyramidal coordination environment for Sn atoms in this structure is more typical of Sn^{II} in oxide systems (Donaldson & Grimes, 1984).

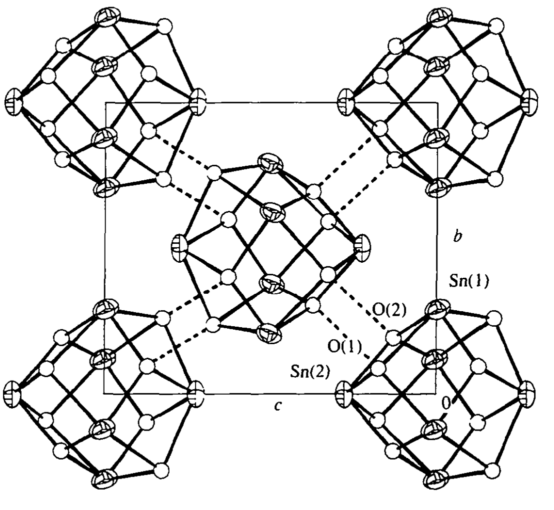

Fig. 1. Unit-cell projection down the *a* axis of $Sn_6O_4(OH)_4$ showing 50% probability displacement ellipsoids for Sn atoms.

Comparison with the structure of the lead analogue indicates that O(1) is the hydroxy O atom. This assignment is reflected in longer Sn—O(1) distances. Sn(1) has one short and one intermediate Sn—O contact, and one long and one intermediate Sn—O(H) contact. Sn(2) has two intermediate length contacts to oxide O atoms and two longer contacts to hydroxy O atoms. This coordination pattern is similar to that observed in the lead structure. The Sn—O bond lengths can be compared with the value of 2.224 (8) Å observed in blue-black SnO (Pannetier & Denes, 1980) and 2.15–2.28 Å in $Sn_3(OH)_4(NO_3)_2$ (Johnston *et al.*, 1995). The longer distances to the hydroxy O atom, 2.38–2.52 Å, are longer than those normally encountered in Sn^{II} oxide systems and must be regarded as possessing a high degree of ionic character. They are, however, comparable with the distances in $Sn(H_2PO_4)_2$ (Herak, Prelesnik, Curic & Vasic, 1978) of 2.21–2.47 Å.

The intercluster contact distances indicate hydrogen bonding between the hydroxy O(1) and the oxide O(2) atoms on neighbouring clusters. The non-bonding electron pairs on the Sn atoms remain stereochemically active and prevent close approach of adjacent O atoms from neighbouring clusters. The lone pairs on Sn(1) point towards those on an Sn(1) atom on a neighbouring cluster. Sn(2) atoms behave in a similar fashion. The Sn···Sn intercluster distances are Sn(1)···Sn(1) 3.826 (3) and Sn(2)···Sn(2) 4.083 (3) Å. These distances may allow for some orbital overlap between Sn atoms; however, the lone pairs appear to remain localized and stereochemically active.

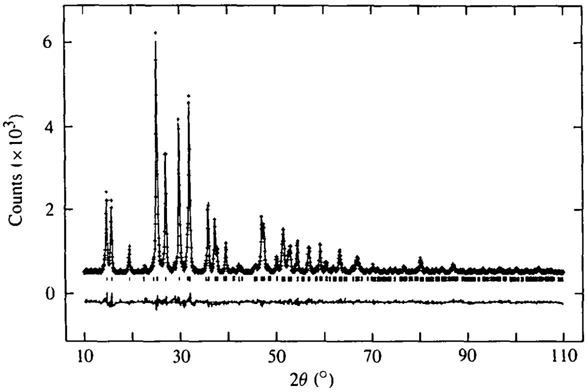

Fig. 2. Fitted diffraction profile for $Sn_6O_4(OH)_4$ showing calculated (line), observed (plus signs) and difference (lower) profiles. Reflection positions are indicated by markers.

Experimental

A powdered sample of $Sn_6O_4(OH)_4$ was prepared under nitrogen using previously degassed solutions. Approximately 50 g of analytical grade copper(II) sulfate pentahydrate was dissolved in 400 ml of distilled water and 20 ml of concentrated sulfuric acid. The solution was boiled with 50 g of analytical grade metallic tin until it became colourless and the deposited copper was covered with a grey coating of tin. The resultant tin(II) sulfate solution was filtered and treated with 280 ml of 1:1 ammonia (density 0.880 g cm^{-3})–water solution to precipitate the title compound. The precipitate was repeatedly centrifuged with successive portions of distilled water until no odour of ammonia was detectable. The resultant paste was vacuum filtered and dried under vacuum at 298 K.

Crystal data

$Sn_6O_4(OH)_4$
$M_r = 844.16$
Tetragonal
$P\bar{4}2_1c$
$a = 7.9268\ (4)$ Å
$c = 9.1025\ (5)$ Å
$V = 571.94\ (8)$ Å^3
$Z = 2$
$D_x = 4.904$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 464 reflections
$\theta = 5$–$55°$
$\mu = 105.6$ mm^{-1}
$T = 298$ K
Powder
White

Data collection

Siemens D-5000 X-ray diffractometer
Flat-plate $\theta/2\theta$ scans
Graphite monochromator

Step size: 0.02°
Scan time/step: 12 s
Range: 10–110° 2θ

Refinement

Refinement on profile intensities
Rietveld method
$R_{\rm wp} = 0.0436$
$R_{\rm p} = 0.0332$
$R_{\rm ex} = 0.0384$
$\chi^2 = 1.286$

4999 observables
33 parameters
$(\Delta/\sigma)_{\rm max} = -0.10$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$U_{\rm iso}$ for O atoms, $U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for Sn atoms.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
Sn(1)	0.1218 (2)	0.2917 (2)	−0.0038 (6)	0.027 (1)
Sn(2)	0	0	0.2757 (2)	0.032 (3)
O(1)	0.2606 (17)	0.090 (2)	0.1730 (15)	0.019 (3)
O(2)	−0.097 (3)	0.1945 (19)	0.1277 (15)	0.019

Table 2. *Bond lengths, significant contact distances* (Å) *and angles* (°)

Sn(1)—O(1)	2.52 (2)	Sn(2)—O(1)	2.38 (1)
Sn(1)—O($1^{\rm i}$)	2.29 (2)	Sn(2)—O($1^{\rm iii}$)	2.38 (1)
Sn(1)—O(2)	2.25 (2)	Sn(2)—O(2)	2.19 (2)
Sn(1)—O($2^{\rm ii}$)	1.99 (2)	Sn(2)—O($2^{\rm iii}$)	2.19 (2)
O(1)···O($2^{\rm iv}$)	2.73 (2)	Sn(2)···Sn($2^{\rm vi}$)	4.083 (3)
Sn(1)···Sn($1^{\rm v}$)	3.826 (3)		
O(1)—Sn(1)—O($1^{\rm i}$)	132.9 (6)	Sn($1^{\rm i}$)—O(2)—Sn(2)	114.7 (8)
O(1)—Sn(1)—O($2^{\rm ii}$)	75.3 (6)	O(1)—Sn(1)—O(2)	77.3 (6)
O($1^{\rm i}$)—Sn(1)—O($2^{\rm ii}$)	75.4 (6)	O($1'$)—Sn(1)—O(2)	75.8 (6)
O(1)—Sn(2)—O($1^{\rm iii}$)	133.7 (7)	O(2)—Sn(1)—O($2''$)	105.1 (8)
O(1)—Sn(2)—O(2)	81.5 (7)	O(1)—Sn(2)—O($2'''$)	70.3 (7)
Sn(1)—O(1)—Sn($1^{\rm ii}$)	94.7 (5)	O(2)—Sn(2)—O($2'''$)	104.0 (8)
Sn($1^{\rm ii}$)—O(1)—Sn(2)	97.9 (6)	Sn(1)—O(1)—Sn(2)	93.6 (5)
Sn(1)—O(2)—Sn($1^{\rm i}$)	113.3 (6)	Sn(1)—O(2)—Sn(2)	107.3 (9)

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

The structure of the title compound was refined by Rietveld analysis. A starting model based on the isostructural lead compound in space group $P\bar{4}2_1c$ was used. The scale factor, three background parameters and pseudo-Voigt peak-shape parameters were refined first, followed by unit-cell and zero-point-correction parameters. Refinement continued with variation of the atomic and displacement parameters. Anisotropic displacement parameters were refined for Sn atoms only and the O-atom isotropic displacement parameters were tied. A fully absorbing flat-plate sample was assumed and no preferred orientation correction was found to be necessary. The H atom was not located and attempts to refine the H-atom position from the neutron study of the lead analogue were unsuccessful.

Program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 1987). Molecular graphics: *SNOOPI* (Davies, 1983).

We gratefully acknowledge the SERC for an award to SRJ, and Professor J. D. Donaldson for helpful discussions.

Lists of powder diffraction data, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1120). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 288–290

Sodium Hexanitroruthenate(II) Monohydrate

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(*Received 18 April 1995; accepted 30 August 1995*)

Abstract

Crystals of sodium hexanitroruthenate(II) monohydrate, $Na_4[Ru(NO_2)_6].H_2O$, are composed of $[Ru(NO_2)_6]^{4-}$ complex anions, Na^+ cations and water molecules. The structure is compared with those of other hexanitroruthenate(II) complexes.

Acta Crystallographica Section C
ISSN 0108-2701 © 1996