Crystal structure of tin tetrabromodioxane, $\text{SnBr}_4 \cdot (\text{C}_4\text{H}_8\text{O}_2)$, a one dimensional polymer of Sn(IV)

M. Bauer^I, J. Kouvetakis^{*I} and T. L. Groy^{II}^I Arizona State University, Goldwater Center for Science and Engineering, Department of Chemistry and Biochemistry, Tempe, AZ 85287-1604, USA^{II} Arizona State University, Department of Chemistry and Biochemistry, Tempe, AZ 85287-1604, USA

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Abstract

$\text{C}_4\text{H}_8\text{Br}_4\text{O}_2\text{Sn}$, orthorhombic, *Pbcn* (No. 60), $a = 8.7678(6)$ Å, $b = 11.2927(7)$ Å, $c = 11.1746(7)$ Å, $V = 1106.4$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.032$, $wR_{\text{ref}}(F^2) = 0.078$, $T = 298$ K.

Source of material

$\text{SnBr}_4 \cdot (\text{dioxane})$ is prepared by reaction of SnBr_4 with a large excess of dry dioxane at room temperature. Crystallization at 253 K yields a pure crystalline amber solid with the correct chemical formula as determined by mass spectrometry, as well as IR and NMR spectroscopies.

Discussion

Recently we have utilized reactions of SnD_4 with Ge_2H_6 to produce highly metastable diamond cubic $\text{Ge}_{1-x}\text{Sn}_x$ semiconductors with Sn concentrations up to 20 at. % using chemical vapor deposition (CVD) methods [1]. The bandgaps of these materials are intermediate to those of elemental Ge ($E_g = 0.70$ eV) and α -Sn ($E_g = 0.1$ eV) and decrease monotonically with Sn concentration indicating that this material will have important applications in

Si-based infrared optoelectronics and microelectronics devices. Pure SnD_4 is unstable and decomposes at room temperature to give the H_2 and Sn byproducts. Nevertheless mixtures of the compound in H_2 have the necessary stability to be used in CVD of $\text{Ge}_{1-x}\text{Sn}_x$. Ongoing work to further stabilize SnD_4 by formation of Lewis acid-base adducts with common bases such as dioxane has led to the formation of the new compound $\text{SnBr}_4 \cdot (\text{dioxane})$. This is currently used as the starting material for synthesis of the corresponding hydride $\text{SnH}_4 \cdot (\text{dioxane})$ and the perdeuterated derivative $\text{SnD}_4 \cdot (\text{dioxane})$. Adducts of Sn(IV) halides with neutral Lewis bases have been previously detected by solution NMR [2].

The Sn(II) adduct with composition $\text{SnCl}_2 \cdot (\text{dioxane})$ is known and its structure has been determined. The structure shows that the compound is a linear polymer in which the Sn atoms are linked by dioxane ligands [2]. The central metal is four fold coordinated by two Cl ligands and the two oxygen atoms of the dioxane linkages. The Sn—O bond distances are 2.527(5) Å, which are substantially longer than those observed for $\text{SnBr}_4 \cdot (\text{dioxane})$ (2.347(4) Å). The latter value is considered to be normal and similar values have been observed in the structures of tin(II) chloride dihydrate [3]. The title structure is comprised of one dimensional polymeric sinusoidal chains running parallel to the *c*-axis, having a period equal to the *c*-axis length, as shown in the figure. The chains have a modulation direction down the *b*-axis, with an amplitude of one half of the *b*-axis length. The crystal is stabilized through interpolymer C2—H—Br1 associations. These associations occur through both hydrogens on the C2 carbon and their nearest neighboring Br1 atoms, with H—Br1 distances of 2.95 Å and 3.06 Å. However, these distances are based on idealized hydrogen positions [4].

Table 1. Data collection and handling.

Crystal:	amber block, size 0.13 × 0.16 × 0.18 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	167.12 cm ⁻¹
Diffractometer, scan mode:	Bruker SMART APEX, ω
$2\theta_{\text{max}}$:	50.06°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	8210, 982
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 848
$N(\text{param})_{\text{refined}}$:	51
Program:	SHELXTL [4]

* Correspondence author (e-mail: JKouvetakis@ASU.edu)

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(1A)	8d	0.1912	0.1366	0.4824	0.039
H(1B)	8d	0.2072	−0.0017	0.4723	0.039
H(2A)	8d	0.1384	0.0507	0.6663	0.039
H(2B)	8d	−0.0085	0.1140	0.6174	0.039

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Sn(1)	4c	0	0.21422(4)	1/4	0.0246(3)	0.0206(3)	0.0223(3)	0	0.0009(2)	0
Br(1)	8d	0.01686(7)	0.35769(6)	0.41992(7)	0.0485(4)	0.0418(4)	0.0525(5)	−0.0017(3)	−0.0041(3)	−0.0257(3)
Br(2)	8d	0.28001(6)	0.17569(5)	0.22884(6)	0.0254(4)	0.0427(4)	0.0396(4)	0.0001(3)	0.0043(2)	0.0064(2)
O(1)	8d	0.0198(4)	0.0611(3)	0.3911(4)	0.039(2)	0.032(2)	0.026(2)	−0.017(2)	−0.010(2)	0.010(2)
C(1)	8d	0.1354(6)	0.0625(5)	0.4851(5)	0.031(3)	0.040(4)	0.026(3)	−0.011(2)	−0.008(2)	0.009(2)
C(2)	8d	0.0615(6)	0.0489(4)	0.6039(5)	0.039(3)	0.024(3)	0.034(3)	−0.007(2)	−0.006(3)	0.003(2)

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