

## Synthesis, Vibrational Spectra, and X-Ray Crystal Structure of Di- $\mu$ -hydroxo-bis[bromodichloro(tetrahydrofuran)tin(IV)]-Tetrahydrofuran (1/2) †

David Tudela\* and Vicente Fernández

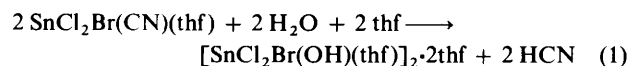
Departamento de Química Inorgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, Canto Blanco, 28049 Madrid, Spain

Angel Vegas

Instituto de Química Inorgánica 'Elhuyar', CSIC, Serrano, 113, 28006 Madrid, Spain

Colourless crystals of  $[\text{SnCl}_2\text{Br}(\text{OH})(\text{thf})]_2 \cdot 2\text{thf}$  were obtained by careful hydrolysis of  $\text{SnCl}_2\text{Br}(\text{CN})(\text{thf})$  in tetrahydrofuran (thf) solution. The crystal structure has been solved and refined to  $R = 0.046$ , based on 3 087 observed reflections. The structure consists of centrosymmetric dimeric molecules in which the tin atoms are *fac*-octahedrally co-ordinated by three halides [ $\text{Sn}-\text{X}$  2.426(1), 2.411(2), and 2.446(2) Å; X = disordered Cl and Br], two bridging OH groups [ $\text{Sn}-\text{O}$  2.086(5) and 2.066(4) Å], and a thf molecule [ $\text{Sn}-\text{O}$  2.211(4) Å]. Two additional thf molecules are hydrogen bonded to the OH groups [ $\text{O}(2) \cdots \text{O}(3)$  2.587(6) Å]. Vibrational spectra are consistent with the dimeric framework with OH bridges, the rather strong hydrogen bonds, and the existence of two different types of thf molecules.

Bridging through hydroxy or alkoxy groups appears to give high stability to tin(IV) compounds and the crystal structures of some such dimeric compounds containing a  $\text{Sn}_2\text{O}_2$  ring have been reported.<sup>1,2</sup> The centrosymmetric molecules  $[\text{SnX}_3(\text{OR})(\text{ROH})]_2$  (X = Cl or Br, R = H;<sup>3</sup> X = Cl, R =  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ )<sup>5</sup> which contain a *fac*-octahedral arrangement of ligand atoms in the  $\text{X}_3\text{SnO}_3$  polyhedron belong to this type of structure, and a feature that they all have in common is that the bridging group is the anion of the co-ordinated molecule. However, no such compound with different co-ordinated and bridging groups has been fully characterized, although some compounds of composition  $\text{SnCl}_3(\text{OEt})\cdot\text{L}$  probably belong to this group as suggested by i.r. data.<sup>6</sup> In this work we describe the crystal structure of a closely related hydroxy-bridged compound in which the co-ordinated ligand is a tetrahydrofuran (thf) molecule instead of water. This compound,  $[\text{SnCl}_2\text{Br}(\text{OH})(\text{thf})]_2 \cdot 2\text{thf}$ , has been prepared by careful hydrolysis of the cyanide derivative  $\text{SnCl}_2\text{Br}(\text{CN})(\text{thf})$ <sup>7</sup> according to reaction (1).



### Experimental

All operations were carried out under dry nitrogen. The compound  $\text{SnCl}_2\text{Br}(\text{CN})(\text{thf})$  was prepared as previously reported<sup>7</sup> and peroxide-free thf was dried over sodium and distilled before use. The i.r. and Raman spectrometers have been previously described.<sup>8</sup>

A thf solution containing  $\text{SnCl}_2\text{Br}(\text{CN})(\text{thf})$  and the stoichiometric amount of water was heated to boiling and then allowed to cool to room temperature. The solution was concentrated *in vacuo* and cooled to  $-20^\circ\text{C}$ , yielding colourless crystals of  $[\text{SnCl}_2\text{Br}(\text{OH})(\text{thf})]_2 \cdot 2\text{thf}$  which were removed from the supernatant liquid and washed with dry hexane, m.p. ca.  $120^\circ\text{C}$  (decomp.) (Found: Br, 18.55; Cl, 16.45; Sn, 27.55.  $\text{C}_8\text{H}_{17}\text{BrCl}_2\text{O}_3\text{Sn}$  requires Br, 18.00; Cl, 17.00; Sn, 27.00%). I.r.

Table 1. Fractional atomic co-ordinates ( $\times 10^4$ ) for  $[\text{SnCl}_2\text{Br}(\text{OH})(\text{thf})]_2 \cdot 2\text{thf}$  with estimated standard deviations in parentheses. X represents Cl or Br

Atom	X/a	Y/b	Z/c
Sn	912.7(4)	391.3(3)	3 983.6(4)
X(1)	364(2)	1 646(1)	2 505(2)
X(2)	2 854(2)	1 055(1)	5 870(2)
X(3)	2 652(2)	9 712(1)	3 038(2)
O(1)	9 199(5)	9 748(3)	2 238(5)
O(2)	9 273(4)	648(2)	4 838(4)
C(1)	-2 100(9)	134(6)	1 236(9)
C(2)	-3 034(10)	-546(7)	440(10)
C(3)	-2 007(12)	-1 264(7)	519(10)
C(4)	-749(10)	-1 142(5)	1 819(10)
O(3)	-2 894(6)	1 654(3)	3 651(8)
C(5)	-4 381(9)	1 451(6)	3 410(13)
C(6)	-5 116(12)	2 188(8)	3 493(19)
C(7)	-4 056(13)	2 872(7)	3 948(16)
C(8)	-2 666(10)	2 531(6)	3 966(15)
H(2)	8 219	1 073	4 385

(Nujol): 2 270s br  $[\nu(\text{OH})]$ , 1 043vs, 1 009vs  $[\nu_{\text{asym}}(\text{COC})]$ , 877vs, 843vs  $[\nu_{\text{sym}}(\text{COC})]$ , 511s, 490(sh)  $[\nu(\text{SnOSn})]$ , 328vvs  $[\nu(\text{SnCl})]$ , and 230m  $[\nu(\text{SnBr})]$   $\text{cm}^{-1}$ . Raman: 342vs, 334(sh), 322(sh), 243m  $[\nu(\text{SnCl})]$ , 233m  $[\nu(\text{SnBr})]$ , and 194mw  $[\nu(\text{SnO})]$   $\text{cm}^{-1}$ .

An irregular fragment of a larger crystal was mounted into a glass capillary which was sealed off.

*Crystal Data.*— $\text{C}_{16}\text{H}_{34}\text{Br}_2\text{Cl}_4\text{O}_6\text{Sn}_2$ ,  $M = 861.5$ , monoclinic,  $a = 9.715(1)$ ,  $b = 15.844(2)$ ,  $c = 9.989(1)$  Å,  $\beta = 109.76(1)^\circ$ ,  $U = 1 447$  Å<sup>3</sup> (by least-squares refinement on diffractometer angles for 25 centred reflections,  $\lambda = 0.7107$  Å), space group  $P2_1/c$  (no. 14),  $Z = 2$ ,  $D_c = 1.98$  g  $\text{cm}^{-3}$ . Colourless, air-sensitive prisms. Approximate crystal dimensions  $0.30 \times 0.34 \times 0.39$  mm,  $\mu(\text{Mo-K}\alpha) = 50.03$   $\text{cm}^{-1}$ ,  $F(000) = 832$ .

*Data Collection and Processing.*—Philips PW 1100 diffractometer,  $\omega/2\theta$  mode with  $\omega$  scan width =  $1.40^\circ$ ,  $\omega$  scan speed  $1.8^\circ \text{min}^{-1}$ , graphite-monochromated  $\text{Mo-K}\alpha$  radiation; 4 520 reflections measured ( $2 \leq \theta \leq 30^\circ$ ), 4 258 unique, of them 3 097 with  $I \geq 2\sigma(I)$ . Absorption correction was not applied

† Supplementary data available (No. SUP 56427, 5 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

**Table 2.** Interatomic distances (Å) and angles (°) for  $[\text{SnCl}_2\text{Br}(\text{OH})(\text{thf})]_2 \cdot 2\text{thf}$ , with estimated standard deviations in parentheses. Primed and unprimed atoms are related by a centre of symmetry

Sn-X(1)	2.426(1)	Sn...Sn'	3.353(1)	O(1)-C(1)	1.45(1)	O(3)-C(5)	1.42(1)
Sn-X(2)	2.411(2)	O(2)...O(2')	2.450(5)	O(1)-C(4)	1.48(1)	O(3)-C(8)	1.42(1)
Sn-X(3)	2.446(2)	O(2)...O(3)	2.587(6)	C(1)-C(2)	1.46(1)	C(5)-C(6)	1.39(2)
Sn-O(2)	2.086(5)	O(2)-H(2)	1.18	C(2)-C(3)	1.50(2)	C(6)-C(7)	1.46(2)
Sn-O(2')	2.066(4)	O(3)...H(2)	1.42	C(3)-C(4)	1.46(1)	C(7)-C(8)	1.45(2)
Sn-O(1)	2.211(4)						
X(1)-Sn-X(2)	94.08(6)	X(2)-Sn-O(2)	95.7(1)	O(2)-Sn-O(2')	72.3(2)	C(5)-O(3)-C(8)	109.3(7)
X(1)-Sn-X(3)	99.42(6)	X(2)-Sn-O(2')	95.6(1)	Sn-O(2)-Sn'	107.7(2)	O(3)-C(5)-C(6)	108.4(8)
X(2)-Sn-X(3)	91.94(6)	X(3)-Sn-O(1)	85.8(1)	C(1)-O(1)-C(4)	108.1(5)	C(5)-C(6)-C(7)	109(1)
X(1)-Sn-O(1)	86.9(1)	X(3)-Sn-O(2)	165.1(1)	O(1)-C(1)-C(2)	107.5(7)	C(6)-C(7)-C(8)	106(1)
X(1)-Sn-O(2)	92.8(1)	X(3)-Sn-O(2')	94.3(1)	C(1)-C(2)-C(3)	104.6(8)	C(7)-C(8)-O(3)	106.7(8)
X(1)-Sn-O(2')	162.9(1)	O(2)-Sn-O(1)	86.4(2)	C(2)-C(3)-C(4)	106.7(8)	O(2)-H(2)...O(3)	168
X(2)-Sn-O(1)	177.7(1)	O(1)-Sn-O(2')	84.0(2)	C(3)-C(4)-O(1)	106.3(7)		

because of the irregular shape of the crystal. A correction for crystal decay, *ca.* 7%, was applied during processing.

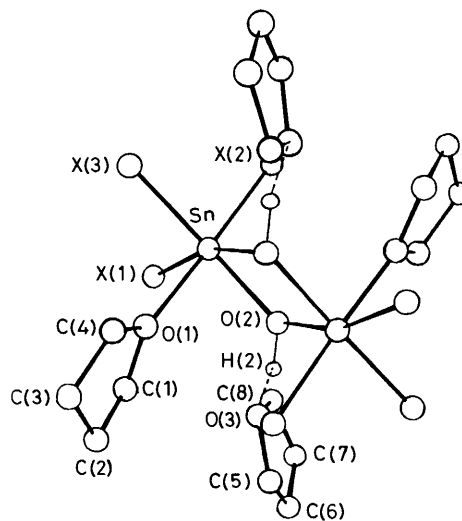
**Structure Analysis and Refinement.**—Heavy-atom method (Sn) followed by normal Fourier synthesis which did not allow us to distinguish Cl and Br. Full-matrix least-squares refinement. Cl atoms were supposed to exist at the three halide positions and their population parameters were allowed to vary freely in the least-squares calculations. Ten strong reflections probably affected by extinction or counting errors were excluded in further refinements. The H atom of the OH group was located by difference synthesis but the remainder were placed at calculated positions and held invariant in the last refinements. The thermal motion was considered anisotropic for Sn, Cl, O, and C and isotropic for H. Unit weights were applied to every reflection. The final *R* value was 0.046 for the observed reflections only. The final atomic parameters are listed in Table 1. The values obtained for the population parameters of the Cl atoms were 1.371(7), 1.267(7), and 1.426(7) for X(1), X(2), and X(3) respectively, corresponding to a total of 69 electrons, equivalent to 2 Cl and 1 Br per tin atom. Programs used and sources of scattering factor data are given in ref. 9.

## Results and Discussion

The structure consists of centrosymmetric dimeric molecules (Figure) with the tin atoms linked through two bridging OH groups. The facial octahedral co-ordination is completed by three halides (disordered Cl and Br) and a thf molecule. Two additional thf molecules connect with the dimeric molecule through hydrogen bonds involving the OH groups. These discrete units, shown in the Figure, are held together by van der Waals forces. The interatomic distances and angles are collected in Table 2.

The geometrical details of the planar  $\text{Sn}_2\text{O}_2$  rings agree with the results for other related molecules containing the same  $\text{Sn}_2\text{O}_2$  system.<sup>2,3</sup> The Sn-X bond lengths are intermediate between the expected values for Sn-Cl and Sn-Br bonds which are of the order of 2.36 and 2.50 Å respectively.<sup>3</sup> The Sn-O(1) bond length, involving the co-ordinated thf molecule, is significantly longer than those found in  $[\text{SnCl}_3(\text{OH})(\text{H}_2\text{O})]_2$  or  $[\text{SnBr}_3(\text{OH})(\text{H}_2\text{O})]_2$  containing co-ordinated water,<sup>3</sup> indicating that water bonds to tin more strongly than does thf. This fact can explain the very hygroscopic nature of our compound, and suggests that only the stoichiometric amount of water should be used in reaction (1); otherwise, hydrolysis can continue until total substitution of co-ordinated thf by water.

The geometry of the O(2)-H(2)...O(3) hydrogen bond is expressed in Table 2. The O(2)...O(3) contact distance [2.587(6) Å] corresponds to a rather strong hydrogen bond,



**Figure.** Molecular structure of  $[\text{SnCl}_2\text{Br}(\text{OH})(\text{thf})]_2 \cdot 2\text{thf}$  showing the atomic-numbering scheme. X represents the disordered Cl and Br atoms. Dotted lines indicate hydrogen bonds

which agrees with the assignment of the i.r. band at  $2\,270\text{ cm}^{-1}$  to the  $\nu(\text{OH})$  stretching vibration on the basis of the frequency-distance relationships reported by Novak.<sup>10</sup>

The appearance of four i.r. C-O-C stretching bands at  $1\,043$ ,  $1\,009$ ,  $877$ , and  $843\text{ cm}^{-1}$  agrees with the two different types of thf molecules found in the structure determination. The i.r. spectrum also shows evidence of the dimeric framework with OH bridges, because of the presence of two bands at  $511$  and  $490\text{ cm}^{-1}$ , assigned to the Sn-O-Sn stretching mode. This mode appears in the range  $480\text{--}530\text{ cm}^{-1}$  for dimeric compounds containing bridging alkoxy groups.<sup>6</sup>

## Acknowledgements

We thank Professor S. Garcia-Blanco (Instituto Rocasolamo CSIC) for the use of the diffractometer.

## References

- J. A. Zubieta and J. J. Zuckerman, *Prog. Inorg. Chem.*, 1978, **24**, 251; P. A. Cusack, P. J. Smith, J. D. Donaldson, and S. M. Grimes, 'A Bibliography of X-Ray Crystal Structures of Tin Compounds,' International Tin Research Institute, Middlesex, Publication No. 588, 1981.
- K. A. K. Nasser, M. B. Hossain, D. Van der Helm, and J. J. Zuckerman, *Inorg. Chem.*, 1983, **22**, 3107.

- 3 J. C. Barnes, H. A. Sampson, and T. J. R. Weakley, *J. Chem. Soc., Dalton Trans.*, 1980, 949.
- 4 G. Stern and R. Mattes, *Z. Anorg. Allg. Chem.*, 1963, **322**, 319.
- 5 M. Webster and P. H. Collins, *Inorg. Chim. Acta*, 1974, **9**, 157.
- 6 R. C. Paul, V. Nagpal, and S. L. Chadha, *Inorg. Chim. Acta*, 1972, **6**, 335.
- 7 D. Tudela, V. Fernandez, and J. D. Tornero, *Inorg. Chem.*, 1985, **24**, 3892.
- 8 D. Tudela, V. Fernandez, and J. D. Tornero, *J. Chem. Soc., Dalton Trans.*, 1985, 1281.
- 9 A. Vegas, A. Perez-Salazar, A. J. Banister, and R. G. Hey, *J. Chem. Soc., Dalton Trans.*, 1980, 1812.
- 10 A. Novak, *Struct. Bonding (Berlin)*, 1974, **18**, 177.

*Received 20th May 1985; Paper 5/839*