

Preliminary communication

THE CRYSTAL STRUCTURE OF DICHLORODIMETHYLTIN(IV) 1/1 TETRAMETHYLUREA ADDUCT

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Summary

The results of a single crystal X-ray diffraction study of dichlorodimethyltin(IV) 1/1 tetramethylurea adduct are reported. The compound is five-coordinated with a distorted trigonal bipyramidal geometry.

In a previous study, a series of inorganic tin(IV) compounds with general formula $\text{SnX}_4 \cdot 2\text{L}$ (L = urea or thiourea, X = Cl, Br or I) was described [1]. The presence of *cis*-octahedral tin was demonstrated by the crystal structures of $\text{SnBr}_4 \cdot 2(1,3\text{-diethylurea})$ and $\text{SnCl}_4 \cdot 2(1,3\text{-diethylthiourea})$ and extended to the whole series by IR data and calculations of the steric angles on the basis of Zahrobski's model. We have prepared and characterized a large number of adducts of organotin(IV) halides with urea or thiourea derivatives, and preliminary data on the crystal structure of $\text{Me}_2\text{SnCl}_2 \cdot \text{tmu}$ (tmu = tetramethylurea) are reported below since to the best of our knowledge this is the first structural determination for a complex containing a urea derivative bonded to our organotin centre.

The compound was obtained adding the stoichiometric quantity of tmu to a solution of Me_2SnCl_2 in methyl ethyl ketone. Addition of pentane gave a white powder, which was filtered off, washed, and dried under vacuum. The elemental analysis agrees with the formula $\text{Me}_2\text{SnCl}_2 \cdot \text{tmu}$ (Found: C, 25.0;

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H, 5.5; Cl, 21.2; N, 8.4. $C_7H_{18}Cl_2N_2OSn$ calcd.: C, 25.0; H, 5.4; Cl, 21.1; N, 8.3%). Crystals suitable for X-ray study were obtained by slow evaporation of the ketone.

The crystals are monoclinic with $a = 16.241(9)$, $b = 9.624(6)$, $c = 8.659(5)$ Å $\beta = 96.8(3)^\circ$, $Z = 4$; $U = 1344.0$ Å³, D_o and $D_c = 1.64$ and 1.66 g cm⁻³, $F(000) = 664$, space group $P2_1/n$. Intensity data were collected using a Philips PW 1100 four-circle diffractometer in the range $4 < 2\theta < 50^\circ$ with Mo- K_α radiation. Using the criterion $I > 3\sigma(I)$, 2036 of the 2687 recorded intensities were independent and observable. Lorentz and polarization corrections were applied. The structure was solved using a three-dimensional Patterson-Fourier synthesis. A full-matrix least-squares refinement on F was computed and the function $\sum w[|F_o| - |F_c|]^2$ in which $w = 1$ was minimized. The SHELX program [2] and the usual scattering factors [3] were used. The non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were located from a difference Fourier map but not refined. The final R value is 0.038. Fractional atomic coordinates are reported in Table 1. Tables of observed and calculated structure factors can be obtained from the authors.

The crystal structure is shown in Fig. 1. The tin atom has a distorted trigonal bipyramidal geometry with the urea oxygen and one chlorine atom in the axial positions. This geometry is similar to that in $Me_2SnCl_2 \cdot$ salicylaldehyde, which contains an axial carbonyl oxygen [4]. The IR spectrum of our compound is consistent with an O-bonded tmu. Its $\nu(CN)$ band is found as a shoulder at ca. 1540 cm⁻¹ with a positive shift of 35 cm⁻¹ from the free tmu, while the $\nu(CO)$ is at 1554 with a negative shift of ca. 90 cm⁻¹. The distortion in the

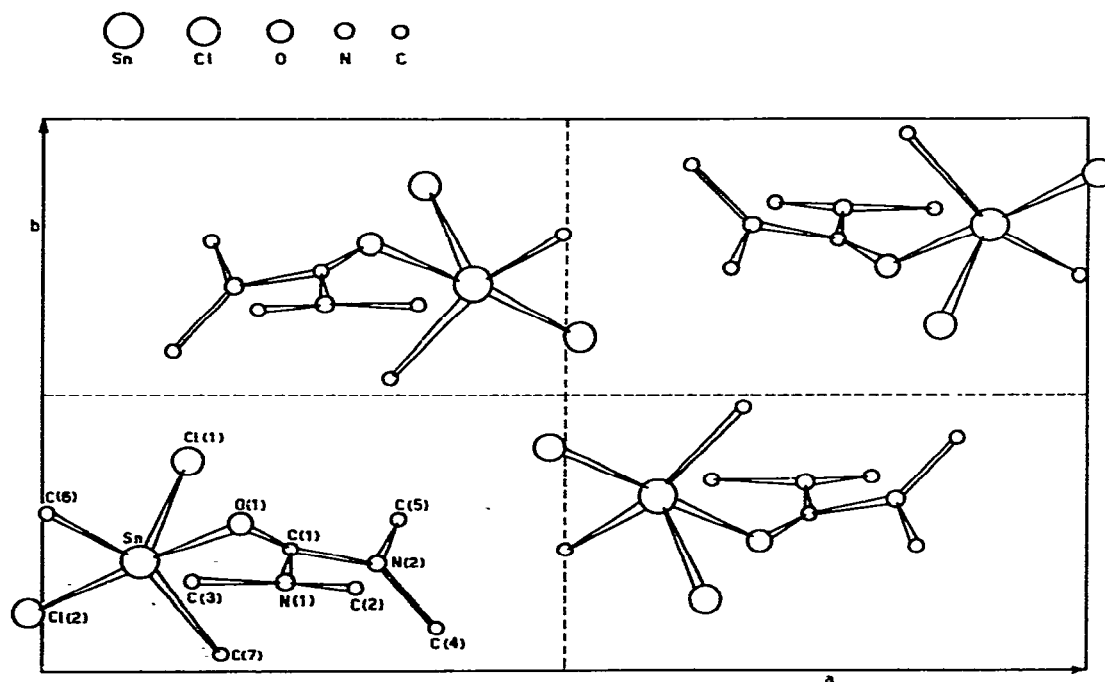


Fig. 1. Perspective view of $Me_2SnCl_2 \cdot$ tmu.

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Distances			
Sn—Cl(1)	2.372(2)	C(1)—N(1)	1.335(8)
Sn—Cl(2)	2.497(2)	N(1)—C(2)	1.465(9)
Sn—C(6)	2.100(7)	N(1)—C(3)	1.479(9)
Sn—C(7)	2.107(7)	C(1)—N(2)	1.356(8)
Sn—O(1)	2.357(4)	N(2)—C(4)	1.47(1)
O(1)—C(1)	1.269(7)	N(2)—C(5)	1.45(1)
(b) Angles			
Cl(1)—Sn—Cl(2)	94.4(1)	Sn—O(1)—C(1)	132.6(4)
Cl(1)—Sn—C(6)	104.5(3)	C(1)—C(1)—N(2)	120.8(6)
Cl(1)—Sn—O(1)	89.4(1)	C(1)—N(2)—C(5)	120.1(6)
Cl(1)—Sn—C(7)	107.2(3)	C(5)—N(2)—C(4)	114.8(7)
Cl(2)—Sn—C(6)	95.2(2)	C(4)—N(2)—C(1)	123.4(7)
Cl(2)—Sn—O(1)	176.2(1)	N(2)—C(1)—N(1)	119.6(6)
Cl(2)—Sn—C(7)	92.7(2)	C(1)—N(1)—C(2)	123.5(6)
C(6)—Sn—O(1)	83.3(3)	C(2)—N(1)—C(3)	115.6(6)
C(6)—Sn—C(7)	146.6(3)	C(3)—N(1)—C(1)	117.7(6)
O(1)—Sn—C(7)	86.7(3)	N(1)—C(1)—O(1)	119.6(6)

equatorial positions is large (cf. Table 2), while the O—Sn—Cl angle is nearly regular. The tin atom is displaced by 0.15 Å from the equatorial plane towards the axial chlorine atom, even if this Sn—Cl bond length is larger (by 0.12 Å) than the equatorial ones. The two Sn—C(Me) bond distances are equal and in good agreement with the literature range of values [5]. The $\nu_{\text{as}}(\text{Sn—C})$ and $\nu_{\text{s}}(\text{Sn—C})$ absorptions, 568 and 518 cm^{-1} , respectively, are practically unaffected by coordination of the tmu ligand.

As for $\text{Me}_2\text{SnCl}_2 \cdot \text{salicylaldehyde}$, our compound is present as discrete molecules, while some association between neighbouring molecules has been suggested for the related Me_2SnCl_2 [6]. The structural difference between our compound and Me_2SnCl_2 is illustrated by the spacings Sn···Sn (4.71 and 4.2 Å respectively) and Sn···Cl (3.66 and ca. 4.2 Å vs. 3.54 Å in Me_2SnCl_2). This confirms [4] that the distortion of the C—Sn—C angles is due to a large tin 5s orbital contribution to the Sn—C bond [7] and not to association [6].

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References

- 1 S. Calogero, U. Russo, G. Valle, P.W.C. Barnard and J.D. Donaldson, *Inorg. Chim. Acta*, in press.
- 2 G. Sheldrick, *SHELX76 System of computing programs*, University of Cambridge, 1976.
- 3 *International Tables for X-ray Crystallography*, 2nd Edn., Kynoch Press, Birmingham, 1974, vol. 4.
- 4 D. Cunningham, I. Douek, M.J. Frazer, M. McPartlin and J.D. Matthews, *J. Organometal. Chem.*, **90** (1975) C23.
- 5 J.A. Zubieta, J.J. Zuckerman, in S.J. Lippard (Ed.), *Progress in Inorganic Chemistry*, Interscience Publ., New York, vol. 24, 1978, p. 251.
- 6 A.G. Davies, H.J. Milledge, D.C. Puxley and P.J. Smith, *J. Chem. Soc. A*, (1970) 2862.
- 7 R.S. Tobias, *Inorg. Chem.*, **9** (1970) 1296.