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THE CRYSTAL STRUCTURE OF DI-μ_3-OXO-BIS(μ-MONOCHLOROACETATO-*O,O'*)BIS(MONOCHLOROACETATO)-TETRAKIS[DIMETHYLTIN(IV)]

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Summary

The crystal structure analysis of $\{[(CH_3)_2SnO_2CCH_2Cl]_2O\}_2$ is reported. The compound consists of dimeric units located on symmetry centers; the dimers are weakly bonded to form rows oriented in the *a* direction. The two tin atoms of the structural unit have different environments; but the coordination numbers cannot be assigned.

Introduction

There is much interest in the structural reports, dealing with chemical and physical properties of compounds of the type $[(R_2SnX)O(R_2SnY)]_2$, (tetraorganostannoxanes) where X and Y are two equal or two different monodentate or bidentate ligands [1–12]. In the absence of structural data, the geometry and stereochemistry about the tin atoms is usually elucidated by spectroscopic techniques, but this is often impossible owing to the high number of variables present. One way to avoid such difficulties is to obtain first data for a series of homologous derivatives. A few complexes having $X = Y = O_2CCH_3$, O_2CCF_3, O_2CCCl_3 and $R = CH_3$, n-C_4H_9, $CH_2{=}CH$ have been prepared and examined by X-ray analysis [6–9]. The investigated crystal structures are very similar to each other, but different interpretations were offered in respect of the coordination about the two non-equivalent tin atoms of the dimeric compounds.

We describe below the crystal structure of $\{[(CH_3)_2SnO_2CCH_2Cl]_2O\}_2$.

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Experimental

The title compound was prepared by a published method [13]. Crystals for X-ray analysis were obtained by recrystallization from a $CHCl_3$/n-hexane mixture. They were not protected after mounting, but there was no evidence of deterioration during data collection.

Crystal data, $C_{16}H_{32}O_{10}Cl_4Sn_4$, triclinic, $P\bar{1}$, a 11.426(8), b 10.190(8), c 7.667(6) Å, α 112.17(4), β 89.98(5), γ 107.68(6)°, V 781.0 Å^3, T 298 K, D_m 2.12, D_c 2.13 g cm^{-3}, Z = 1; Cu-K_α radiation, λ 1.5418 Å, μ(Cu-K_α) 305.2 cm^{-1}. Lattice and orientation parameters were obtained by least-squares treatment of 25 symmetry related reflections. Intensity data were measured by use of the ϑ-2ϑ scan method with a Philips PW 1100 computer-controlled four-circle diffractometer, with a graphite monochromator. The intensities were corrected for Lorentz and polarization effects. Absorption corrections were applied during data reduction. The data were scaled to give 722 independent $F(h\ k\ l)$ values for which I was greater than $2\sigma(I)$. The positions of the tin atoms were determined from a three-dimensional Patterson synthesis. A difference electron-density synthesis, based upon the signs for Sn, revealed the position of all the non-hydrogen atoms. Five cycles of isotropic refinement with unit weights reduced the R value to 0.130. Three more cycles with anisotropic temperature factors for Sn and Cl reduced R to 0.099. Hydrogens were not included in the calculations. The weighting scheme used in the final calculations was of the form $W^{-1} = a_i|F_c|^i$; the a_i parameters were calculated using the program PESO [14]. All the calculations were carried out by use of the SHELX-76 program [15] on a CDC Cyber-76 computer. Scattering factors are from ref. 16. Atomic parameters are listed in Table 1. Lists of the observed and calculated structure factors and thermal parameters are available from the authors on request.

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$)

Atom	x/a	y/b	z/c
Sn(1)	9920(3)	3240(5)	−871(7)
Sn(2)	6945(3)	4184(5)	−400(7)
Cl(1)	7007(18)	7896(19)	−3522(37)
Cl(2)	6795(20)	246(23)	2626(45)
O(1)	8797(37)	4575(43)	−321(59)
O(2)	6674(42)	1773(55)	−1419(68)
O(3)	8110(59)	1161(69)	−2333(93)
O(4)	7718(35)	6615(41)	876(54)
O(5)	5922(44)	6943(53)	1002(73)
C(1)	151(59)	2740(71)	−3756(93)
C(2)	150(70)	2718(85)	1471(98)
C(3)	6508(48)	4078(59)	2363(80)
C(4)	6641(55)	4099(68)	−3132(95)
C(5)	6949(65)	697(79)	−1868(99)
C(6)	6286(61)	−770(72)	−2934(95)
C(7)	7057(55)	7391(67)	989(90)
C(8)	7778(62)	9039(74)	1976(99)

TABLE 2

SELECTED BOND LENGTHS AND ANGLES FOR $\{[(CH_3)_2SnO_2CCH_2Cl]_2O\}_2$, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

About Sn(1)		About Sn(2)	
Bond lengths (Å)			
O(1)–Sn(1)	2.07(1)	O(1)–Sn(2)	2.03(1)
O(1)′–Sn(1)	2.10(1)	O(4)–Sn(2)	2.17(1)
O(3)–Sn(1)	2.36(2)	O(2)–Sn(2)	2.20(2)
C(1)–Sn(1)	2.11(3)	C(3)–Sn(2)	2.21(3)
C(2)–Sn(1)	2.09(3)	C(4)–Sn(2)	2.09(3)
O(4)′–Sn(1)	2.66(2)	O(5)–Sn(2)	3.09(2)
		O(5)′–Sn(2)	3.18(2)
Interbond angles (°)			
O(1)–Sn(1)–O(1)′	77.1(7)	O(1)–Sn(2)–O(4)	77.7(7)
O(1)–Sn(1)–O(3)	87.2(8)	O(1)–Sn(2)–O(2)	88.6(9)
O(3)–Sn(1)–O(1)′	163.5(8)	O(2)–Sn(2)–O(4)	164.3(7)
O(3)–Sn(1)–C(1)	79.8(9)	O(2)–Sn(2)–C(3)	86.3(9)
O(3)–Sn(1)–C(2)	94.5(9)	O(2)–Sn(2)–C(4)	93.4(8)
C(1)–Sn(1)–C(2)	145.6(8)	C(3)–Sn(2)–C(4)	158.5(9)
	Sn(1)–O(1)–Sn(1)′	102.9(7)	
	Sn(1)–O(1)–Sn(2)	134.7(6)	
	Sn(1)′–O(1)–Sn(2)	121.8(7)	

Discussion

Bond lengths and angles are given in Table 2 and the structure is shown in Fig. 1. The molecular structure is almost identical to those reported in references 6–9, even though the packing is different. Sn(1), which has been regarded as pentacoordinated, could be described as six-coordinated. The environment of Sn(2) is quite different; its coordination has been described as distorted trigonal bipyramidal, but, as pointed out by Fagliani, et al. [9], in $\{[(CH_3)_2SnO_2CCF_3]_2O\}_2$, two more neighbouring oxygen atoms have to be taken into account, O(5) at 3.09 Å from Sn(2) and O(5)′ at 3.18 Å from Sn(2). If we adopt the arguments used for homologous or similar compounds in the papers quoted the following observation can be made: (a) the first contact distance mentioned raises the question of whether the involved chloroacetate group is weakly chelated, and (b) the second contact distance suggests the possibility of weak bonds between adjacent dimers giving rows elongated in the *a* direction. In the case of O(5) we note that such a feature is always present not only in all these tetraorganostannoxanes but also in other tin-acetate derivatives [17–19], where the relevant Sn...O distance ranges from 2.85 to 3.11 Å; as an example, the acetate group has been assumed by Zubieta et al. [19] to be weakly chelated. In the case of O(5) there are many examples of structures of organotin compounds where even far larger Sn...O distances (e.g., 3.7–3.8 Å) have been taken with confidence to indicate weak bridging (see, for instance, ref. 20 and therein quoted papers). The considerable enlargement of the bond angle C(3)–Sn(2)–C(4), 158.5°, is noteworthy; this probably allows a more efficient electronic interaction between Sn(2) and the O(5)′ atom which points towards Sn(2) almost in the direction of the Sn(2)–O(1) bond (the angle O(1)–Sn(2)–O(5)′ 171°). Thus a very distorted octahedral coordination

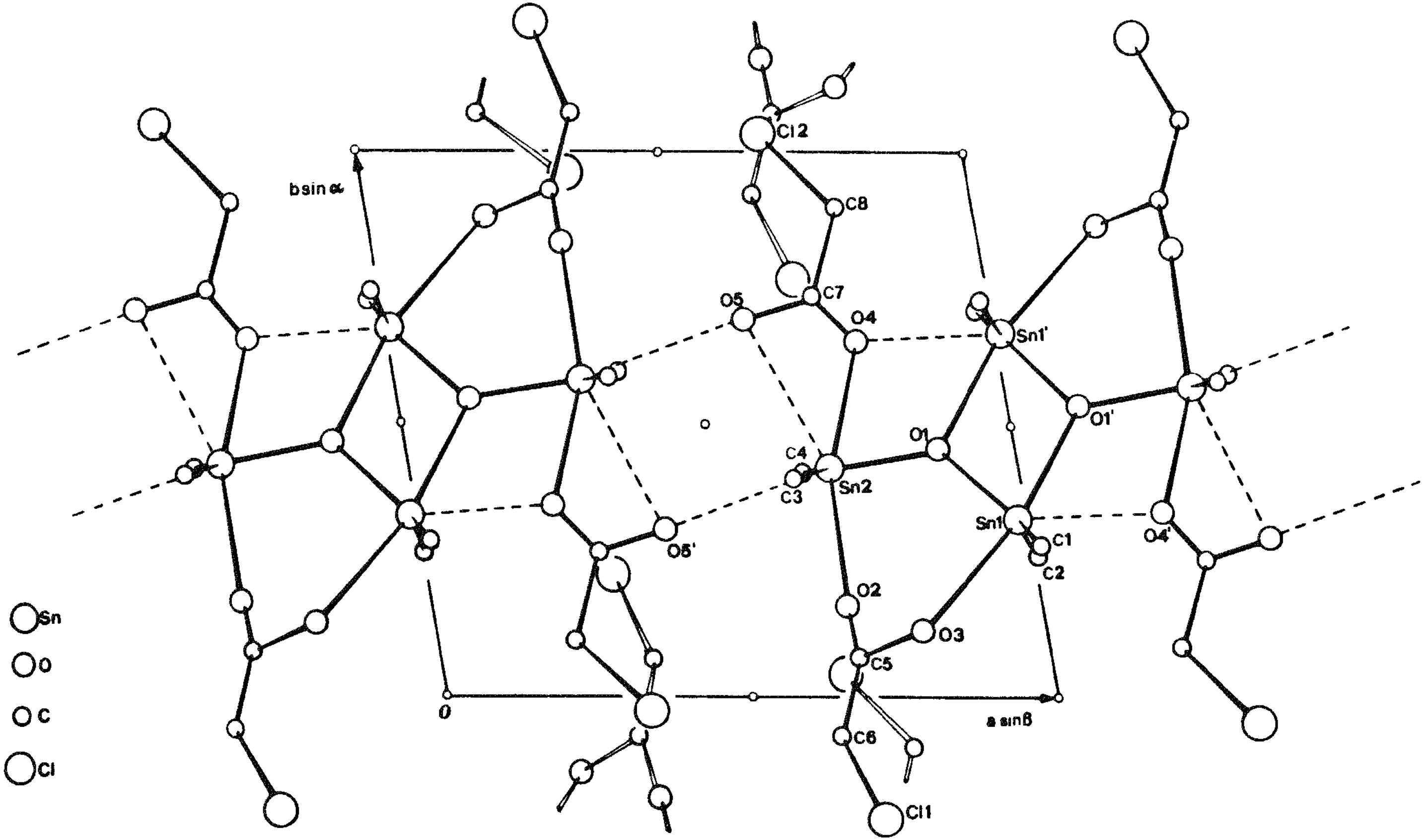

Fig. 1. Structure of $\{[(CH_3)_2SnO_2CCH_2Cl]_2O\}_2$ as viewed along the c axis The atoms are labelled as indicated in the Tables.

could be attributed to Sn(1) whereas Sn(2) could be seven-coordinate.

In spite of the discussion of details, the outstanding feature is that the geometrical parameters about Sn(1) and Sn(2) when only the five unambiguously bonded atoms are considered are almost identical (see Table 2), and this is why for this series of tetraorganostannoxanes the Mössbauer measurements show a very broad signal which makes it impossible to distinguish the two differently-coordinated tin atoms [11,21]. The only information which can be derived by Mössbauer spectroscopy concerns the different contribution to the Δ's values of the X ligands once the corresponding molecular residue is retained; this was demonstrated in our earlier report [21].

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References

1 P. Pfeiffer and O. Brach, Z. Anorg. Chem., 87 (1914) 229.
2 D.L. Alleston, A.G. Davies, M. Hancock and R.F.M. White, J. Chem. Soc., (1963) 5469.
3 R. Okawara, Proc. Chem. Soc., (1961) 383.
4 Y.M. Chow, Inorg. Chem., 10 (1971) 673.
5 Z.V. Zvonkova, Acta Crystallogr. A, 21 (1966) 155.
6 Z.V. Zvonkova, Z.P. Povet'eva, V.M. Vozzennikov, V.P. Gluskova, V.I. Jakovenko and A.N. Khvatkina, Acta Crystallogr. A, 21 (1966) 155.
7 C.D. Garner, B. Hughes and T.J. King, Inorg. Nucl. Chem. Lett., 12 (1976) 859.
8 R. Graziani, G. Bombieri, E. Forsellini P. Furlan, V. Peruzzo and G. Tagliavini, J. Organomet. Chem., 43 (1977) 125.
9 R. Fagliani, J.P. Johnson, J.D. Brown and R. Birchall, Acta Crystallogr. B, 34 (1978) 3743.
10 P.J. Smith, J. Organomet. Chem. Libr., 12 (1981) 97.
11 P.G. Harrison, M.J. Begley and K.C. Molloy, J. Organomet. Chem., 186 (1980) 213.
12 R.C. Mehrotra and R. Bohra, Metal Carboxylates, Academic Press Inc., London, 1983.
13 V. Peruzzo and G. Tagliavini, J. Organomet. Chem., 66 (1974) 437.
14 G. Bandoli and D.A. Clemente, J. Chem. Soc., Perkin Trans. II, (1976) 413.
15 G.M. Sheldrick, SHELX-76 Program for Crystal Structure Determination, Cambridge University, England, 1975.
16 (a) D.T. Cromer and J.T. Waber, Acta Crystallogr., 18 (1965) 104; (b) D.T. Cromer, Acta Crystallogr., 18 (1965) 17.
17 N.W. Alcock and R.E. Timms, J. Chem. Soc. A, (1968) 1876.
18 S. Calogero, P. Ganis, V. Peruzzo and G. Tagliavini, J. Organomet. Chem., 191 (1980) 381.
19 J.A. Zubieta and J.J. Zuckerman, in S.J. Lippard (Ed.), Progress in Inorganic Chemistry, Vol. 24, Wiley, New York, 1978 and ref. therein.
20 P.G. Harrison, K. Lambert and T.J. King, J. Chem. Soc., Dalton Trans., (1983) 363.
21 S. Calogero, P. Furlan, V. Peruzzo and G. Tagliavini, J. Organomet. Chem., 128 (1977) 177.