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MÖSSBAUER AND SINGLE CRYSTAL X-RAY STUDIES OF POLYMERIC DIMETHYLCHLOROTIN ACETATE

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Summary

The solid state structure of dimethylchlorotin acetate has been investigated by Mössbauer spectroscopy and single crystal X-ray analysis. Tin-119 Mössbauer spectra have been recorded at 80 K and 300 K, and the measured isomer shift and quadrupole splitting parameters have been correlated with the crystallographic data. The crystal structure has been determined using heavy-atom methods in conjunction with least-squares refinement of data measured on a two-circle X-ray diffractometer. Crystals are orthorhombic, space group $Pna2_1$, with four formula weights in a cell having the dimensions a = 9.315(3), b = 11.061(3), c = 7.656(2) Å and U = 788.78 Å^3. The observed and calculated densities are 2.07 and 2.05 mg m^{-3}, respectively. The structure was refined using 842 observed reflections to give conventional discrepancy factors of R = 0.040 and R' = 0.044. The crystal structure is composed of Me_2ClSn units bridged by acetate ligands giving rise to polymeric chains which run along the a direction. The tin atom is in a distorted trigonal bipyramidal environment consisting of two axial oxygen atoms distanced 2.165(6) and 2,392(7) Å from the metal, and equatorial positions occupied by two methyl groups and a chlorine atom. Distortions within the coordination polyhedron may be attributed to a further weak but apparently significant tin—oxygen interaction (Sn—O 2.782(7) Å), resulting in the tin atom becoming six-coordinate.

Introduction

Dimethylchlorotin acetate is a simple analogue of the chlorotin carboxylates observed in our recent studies of the changes occurring to organotin stabilisers

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during the thermal degradation of PVC [1]. The Mössbauer quadrupole splitting parameter measured at 80 K agrees with the previously published value (ΔE_Q = 3.56 mm s^{-1} [2]) and suggests that the tin atom is five or six coordinate. The Mössbauer spectrum has also been recorded at 300 K, and this has been taken as evidence for a polymeric structure [3—5]. However, this cannot be taken as conclusive as a number of unassociated compounds have given absorption at room temperature [5]. Therefore, in order to determine the exact tin coordination a single crystal X-ray analysis has been undertaken.

Experimental

Dimethylchlorotin acetate was prepared by the addition of equivalent amounts (0.009 mol) of dimethyltin dichloride and triphenyltin acetate to 150 cm^3 chloroform. Complete dissolution was achieved upon boiling, and reduction of the volume of the solution to 75 cm^3 led to the formation of colourless crystals upon cooling. Subsequent analysis confirmed the crystals to be dimethylchlorotin acetate (found: C, 19.60; H, 3.66; Cl, 14.43; $C_4H_9ClO_2Sn$ calcd.: C, 19.71; H, 3.69; Cl, 14.57%; M.pt. 179—181°C, lit. value 185°C [6].

Mössbauer data

The Mössbauer spectra were recorded at 80 K and 300 K using a constant acceleration Mössbauer spectrometer [7] with a room temperature 10 mCi ^{119m}Sn barium stannate source. A continuous flow cryostat with helium exchange gas was used to cool the sample to 80 K. The measured Mössbauer parameters (Table 1) were determined by computer fitting the data using Lorentzian line shapes [8].

Crystal data

$C_4H_9ClO_2Sn$, M_r 243.3, orthorhombic, $Pna2_1$, a = 9.315(3), b = 11.061(3), c = 7.656(2) Å, U = 788.78 Å, Z = 4, D_c = 2.05, D_m = 2.07 mg m^{-3}, μ(Mo-K_α) = 3.247 mm^{-1}, $F(000)$ = 464.

Data collection and reduction

A crystal, approximate dimensions 0.16 × 0.40 × 0.48 mm was selected and mounted with the a axis coincident with the rotation (ω) axis of a Stoë Stadi-2 two circle diffractometer. With monochromated Mo-K_α radiation and using the

TABLE 1

^{119m}Sn MÖSSBAUER DATA OF DIMETHYLCHLOROTIN ACETATE

Temperature (K)	Isomer shift δ (mm s^{-1}) [a] ±0.02 mm s^{-1}	Quadrupole splitting ΔE_Q (mm s^{-1}) ±0.02 mm s^{-1}	Full width at half weight Γ (mm s^{-1})
80	1.38	3.56	1.12
300	1.34	3.70	0.87

R_{80} = 0.032 (ratio of total normalised area at 300 K to total normalised area at 80 K).
[a] Relative to $BaSnO_3$.

TABLE 2

FRACTIONAL POSITIONAL PARAMETERS ($\times 10^5$ FOR Sn; $\times 10^4$ FOR REMAINING ATOMS) WITH e.s.d.'s FOR NON-HYDROGEN ATOMS IN PARENTHESES

Atom	*x*	*y*	*z*
Sn	57335(5)	32330(4)	0
Cl	7536(3)	4750(2)	−89(14)
O(1)	2751(9)	3105(9)	−11(27)
O(2)	4179(6)	4687(5)	−65(38)
C(1)	2941(10)	4231(7)	−150(25)
C(2)	1666(11)	5072(9)	−54(53)
C(3)	5480(34)	2777(15)	1530(29)
C(4)	5316(31)	2553(17)	−2600(26)
H(21)	2047	5789	−197
H(22)	1149	4972	1200
H(23)	906	4873	−1080
H(31)	4610	2304	3163
H(32)	6148	2138	1841
H(33)	6115	3243	3501
H(41)	4421	2060	−3145
H(42)	5952	2933	−3644
H(43)	5972	1947	−1835

background-ω scan-background technique, 958 unique reflections were measured, of which 842 had $I \geqslant 3.0\sigma(I)$ and were considered to be observed. [The net intensity $I = T - B$, where T = scan count, B = mean background count over the scan width; $\sigma(I) = (T + Bc/2t)^{1/2}$ where c = scan time, t = time for background measurement at each end of the scan.] Corrections for Lorentz and polarisation effects were applied to the data, but no corrections for absorption were made.

TABLE 3

BOND DISTANCES (Å) AND ANGLES (°)

Symmetry code
none x, y, z; (′) $0.5 + x, 0.5 - y, z$; (″) $-0.5 + x, 0.5 - y, z$

Bond distances

Sn—Cl	2.375(2)	Sn—C(4)	2.163(18)
Sn—O(1)	2.782(7)	O(1)—C(1)	1.262(10)
Sn—O(1′)	2.392(7)	O(2)—C(1)	1.260(9)
Sn—O(2′)	2.165(6)	C(1)—C(2)	1.511(12)
Sn—C(3)	2.015(21)		

Bond angles

Cl—Sn—O(1)	137.9(2)	O(2)—Sn—C(3)	97.4(11)
Cl—Sn—O(1′)	83.2(2)	O(2)—Sn—C(4)	96.7(10)
Cl—Sn—O(2)	87.0(2)	C(3)—Sn—C(4)	140.9(6)
Cl—Sn—C(3)	106.7(7)	Sn—O(1)—Sn″	144.7(1)
Cl—Sn—C(4)	110.3(7)	Sn—O(1)—C(1)	79.0(7)
O(1)—Sn—O(1′)	138.9(2)	Sn″—O(1)—C(1)	136.2(7)
O(1)—Sn—O(2)	50.9(2)	Sn—O(2)—C(1)	108.4(7)
O(1)—Sn—C(3)	82.7(10)	O(1)—C(1)—O(2)	121.3(6)
O(1)—Sn—C(4)	78.5(10)	O(1)—C(1)—C(2)	119.5(8)
O(1′)—Sn—O(2)	170.1(2)	O(2)—C(1)—C(2)	118.0(8)
O(1′)—Sn—C(3)	86.6(10)		
O(1′)—Sn—C(4)	85.6(9)		

Structure determination and refinement

Systematic absences do not distinguish between space groups $Pna2_1$ and $Pnma$. $Pnma$ would require the molecule to have mirror symmetry ($Z = 4$) and subsequent analysis has confirmed the non-centrosymmetric space group as being correct, with occupation of the four general positions. The x and y coordinates of the tin atom were readily located using the Patterson function and the remaining atoms were located from successive electron density syntheses. The methyl hydrogens were located, but given ideal geometry (C—H 1.08 Å) and a common isotropic temperature factor. Scattering factors were calculated using an analytical approximation [9] and the weighting scheme adopted was $w = 1.000/(\sigma^2(F_0) + 0.0075\,(F_0)^2)$. Full matrix refinement with anisotropic temperature factors applied to all non-hydrogen atoms gave the final $R = 0.040$ and $R' = 0.044$. The final positional parameters are given in Table 2, bond distances and angles in Table 3. Lists of structure factors, thermal parameters and mean planes data are available on request from the authors (I.W.N.).

Discussion

The Mössbauer parameters for dimethylchlorotin acetate are given in Table 1. The R_{80} value of 0.032 is significant, indicating a polymeric structure [4], and the quadrupole splitting ($\Delta E_Q = 3.56$ mm s^{-1}) suggests that the tin atom is five or six coordinate. Similar organotin carboxylates of known six coordinate structures have quadrupole splittings in the range $\Delta E_Q = 3.6$—3.9 mm s^{-1} [10].

The X-ray analysis confirms the polymeric nature of dimethylchlorotin acetate (Fig. 1) and Me_2ClSn units are found to be linked together via acetate bridges to give chains running along the a direction. The acetate ligands are effectively planar and orientated such that the O(1), O(2), C(1), C(2) mean plane is almost coincident with the tin and chlorine atoms, and bisects the C(3)—Sn—C(4) angle. (Sn, Cl, C(3), C(4)) lie −0.56, −0.030, −1.982, 1.951 Å, respectively, out of the mean plane). The resulting coordination about tin is best described as distorted trigonal bipyramidal with the chlorine and two methyl carbon atoms forming a trigonal arrangement about the metal. O(2) and O(1′) occupy the axial positions such that the O(2)—Sn—O(1′) bond angle is 170.1(2)° and the Sn—O(2), O(1′) distances are 2.165(6) and 2.392(7) Å, respectively. While these tin—oxygen distances fall within the range of reported values [11—14], they are significantly different and it is of note that the longer distance is associated with the oxygen atom involved in an additional tin—oxygen interaction. Although the Sn—O(1) distance of 2.782(7) Å is considerably larger than the sum of the covalent radii (2.13 Å), it is well within the sum of the Van der Waals' radii (3.70 Å) and distortions about the tin can be attributed to a weak yet significant Sn—O(1) interaction. Thus the metal atom is found to be 0.173 Å out of the Cl, C(3), C(4) plane and in a direction away from O(1′) and toward O(1) and O(2). In addition, the angular distortions about tin, viz. C(3)—Sn—C(4) 140.9(6)°, O(1′)—Sn—O(2) 170.1(2)°, are such as to facilitate a Sn—O(1) interaction. Thus, while O(2) is monodentate with respect to tin, O(1) interacts with both Sn and Sn″, thereby increasing the overall coordination number for tin to six.

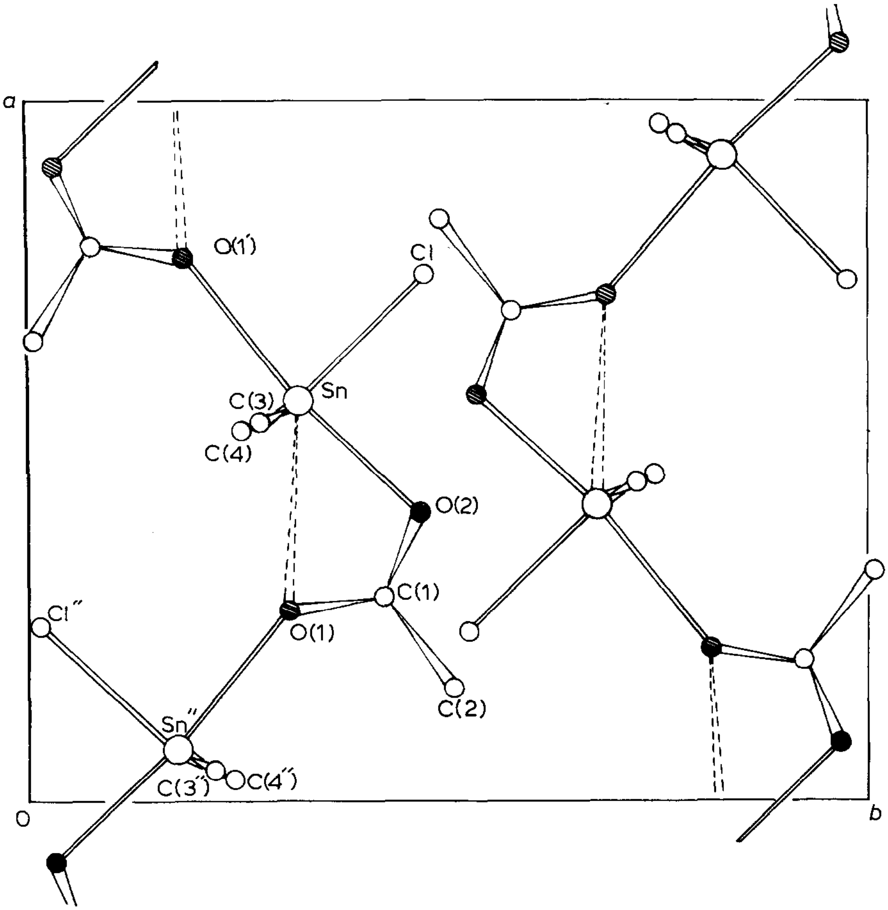

Fig. 1. Projection down the *c* axis showing the polymeric nature of dimethylchlorotin acetate.

The crystallographic results are in accord with the Mössbauer data and in this instance lend weight to the use of a room temperature Mössbauer resonance as evidence for a polymeric structure.

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