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Variable-temperature tin-119m Mössbauer spectroscopic and X-ray crystallographic study of triphenyltin(IV) chloroacetate, $[(C_6H_5)_3SnOC(O)CH_2Cl]$, and a redetermination of $d[\ln f(T)]/dT$ for triphenyltin(IV) acetate

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Abstract

Five-coordinate triphenyltin chloroacetate was assigned a rigid, carboxylate-bridged *trans*-C_3SnO_2 chain structure on the basis of variable-temperature tin-119m Mössbauer ($d[\ln f(T)]/dT$ -0.0105 K^{-1} for $80 \text{ K} \leq T \leq 130$ K) data, and the assignment has been confirmed by X-ray diffraction. Its structure is determined from 5372 $[(F_o)^2 > 3\sigma(F_o)^2]$ Mo-K_α reflections and refined to an R factor of 0.042; the compound crystallizes in the $P2_1/c$ space group with a 9.022(3), b 10.217(3), c 19.780(5) Å, β 92.46(2)°; $Z = 4$. Triphenyltin chloroacetate is isostructural with triphenyltin acetate, whose $d[\ln f(T)]/dT$ value has been redetermined to be -0.0143 K^{-1}.

Introduction

Triorganotin alkanoates are generally carboxylate-bridged, five-coordinate polymers [1] whose Sn–O–C=O : atoms comprise the repeat units. The polymer chain is zig-zag in trimethyltin acetate [2] and distorted helical in triphenyltin acetate [3], but is intermediate between the flat and helical conformations in the mixed compound dimethylphenyltin acetate [4]. Variable-temperature tin-119m Mössbauer spectroscopy [5,6] has been used to probe such structural variations since the temperature dependence of the Mössbauer recoil-free fraction f ($d[\ln f(T)]/dT = -a$) provides a spectroscopic means of distinguishing between rigid and flexible structures for organotin polymers. There is some overlap of the $-a$ values among the four (rod, zig-zag, stretched S and helical [7]) classes, but for phenyltin compounds in general the rigid polymers give rise to $-a$ values of the order of 0.011 K^{-1}, whereas for more flexible polymers, the $-a$ values approach those of non-interacting molecules (0.014–0.028 K^{-1}) [7].

Triphenyltin chloroacetate has in its ester unit an electron-withdrawing halogen, which could be expected to enhance the Lewis acidity of tin, but diminish the Lewis basicity of the carbonyl oxygen that participates in bridging [4]. Which of these two opposing effects will predominate can be assessed by comparing structural data for triphenyltin acetate and triphenyltin chloroacetate. The crystal structure and variable-temperature Mössbauer data have been previously reported [3] for triphenyltin acetate and the results of a similar study of the chloroacetate are described below.

Experimental

Crystals of triphenyltin chloroacetate were obtained by slow evaporation of a methanol solution containing equimolar amounts of $[2\text{-}HOC_5H_4NCH_2C(O)OH]Cl$ [8] and $(C_6H_5)_3SnOH$; m.p. 155–156 °C (Lit. 154–156 °C [9]). Anal. Found: C, 54.28; H, 3.86. $C_{20}H_{17}ClO_2Sn$ calcd.: C, 54.16; H, 3.86%. Mössbauer (80 K): isomer shift (IS) 1.31, quadrupole splitting (QS) 3.70, Γ_1 1.11, Γ_2 1.15 mm s^{-1}; slope of the variable-temperature (80 K $\leq T \leq$ 130 K; 6 points, corr. coeff. -0.999) Mössbauer plot a -0.0105 K^{-1}. For triphenyltin acetate, the Mössbauer data are: IS 1.28, QS 3.48, Γ_1 1.05, Γ_2 1.12 mm s^{-1}, a -0.0143 K^{-1} for 80 K $\leq T \leq$ 130 K; 6 points, corr. coeff. -0.0999.

Structure determination

Standard centering and auto-indexing procedures on the crystal of triphenyltin chloroacetate were performed with a Nicolet P3m automatic diffractometer (Mo-K_α radiation, λ 0.71073 Å). Although the α and γ angles were very nearly 90°, the axial photographs pointed to a triclinic cell, whose accurate dimensions, determined from a least-squares fit of 15 reflections ($44° < 2\theta < 45°$) scattered evenly throughout reciprocal space, were a 9.022(3), b 10.217(3), c 19.780(5) Å; α 89.96(3), β 92.46(2), γ 90.07(3)°. Procedures for data collection were as previously described [10]. The intensities of 4 standard reflections ($\bar{1}11$, 004, 020, 200) measured after every 96 data showed no significant crystal decay during the collection of 16407 independent ($-14 \leq h \leq 13$, $-16 \leq k \leq 16$, $0 \leq l \leq 32$) reflections. Redundant and equivalent reflections were averaged and converted to unscaled $|F_o|$ values, following corrections for Lorentz and polarization factors. The structure was solved by direct methods using the MULTAN-82 program. Full-matrix least-squares refinement followed by difference Fourier synthesis revealed the position of all atoms. The non-H atoms were refined anisotropically. The H-atoms were assigned isotropic temperature factors equal to 1.2 of their respective parent carbon atoms. The computations were performed on a PDP11/73 minicomputer with the TEXRAY structure determination package [11]. The atomic scattering factors were taken from the International Tables for X-ray Crystallography [12,13]; the effects of anomalous dispersion for the non-H atoms were included in F_c [14]. The initial refinement in the $P\bar{1}$ space group converged to $R = 0.046$, $R_w = 0.059$ for the 11080 observed

Table 1

Atomic coordinates and equivalent isotropic factors for triphenyltin chloroacetate

Atom	x	y	z	B_{iso} (Å^2) [a]
Sn	0.08857(3)	0.70106(2)	0.23687(1)	2.300(4)
Cl	0.3707(1)	1.0386(1)	0.10475(7)	4.75(3)
O(1)	0.2064(3)	0.8683(3)	0.1940(2)	3.00(5)
O(2)	0.0463(3)	1.0163(3)	0.2272(1)	2.97(5)
C(1)	0.1480(4)	0.9811(4)	0.1912(2)	2.66(6)
C(2)	0.1988(6)	1.0756(5)	0.1384(3)	4.5(1)
C(11)	0.1429(4)	0.7418(4)	0.3406(2)	2.68(6)
C(12)	0.1865(5)	0.6376(4)	0.3821(2)	3.67(9)
C(13)	0.2346(6)	0.6571(5)	0.4489(3)	4.3(1)
C(14)	0.2388(6)	0.7814(6)	0.4754(2)	4.4(1)
C(15)	0.1971(6)	0.8857(5)	0.4347(2)	4.5(1)
C(16)	0.1487(5)	0.8676(4)	0.3681(2)	3.60(9)
C(21)	0.2412(4)	0.5682(3)	0.1959(2)	2.47(6)
C(22)	0.2141(5)	0.5080(4)	0.1343(2)	3.49(8)
C(23)	0.3156(6)	0.4214(5)	0.1080(3)	4.5(1)
C(24)	0.4479(5)	0.3916(5)	0.1447(3)	4.7(1)
C(25)	0.4767(5)	0.4526(6)	0.2057(3)	5.2(1)
C(26)	0.3741(5)	0.5398(5)	0.2317(3)	4.03(9)
C(31)	−0.0963(4)	0.7403(4)	0.1696(2)	2.80(7)
C(32)	−0.0664(5)	0.7651(5)	0.1022(2)	3.51(8)
C(33)	−0.1797(7)	0.7858(5)	0.0541(3)	4.6(1)
C(34)	−0.3227(6)	0.7850(5)	0.0716(3)	5.2(1)
C(35)	−0.3576(6)	0.7608(7)	0.1376(4)	5.9(1)
C(36)	−0.2430(5)	0.7405(6)	0.1867(3)	4.6(1)

[a] $B_{iso} = \exp(-2\pi^2[h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2hkabU_{12} + 2hlacU_{13} + 2klbcU_{23}])$.

$[(F_o)^2 > 3\sigma(F_o)^2]$ reflections, but examination of equivalent reflections revealed that the intensities of the *hkl* and $h\bar{k}l$ reflections were equal within experimental error. The structure was thus re-refined in the monoclinic $P2_1/c$ space group; the final R and R_w factors are 0.042 and 0.063, respectively. The fractional coordinates and isotropic temperature factors for the non-H atoms for the final refinement cycle are

Table 2

Selected bond distances (Å) and angles (°) in triphenyltin chloroacetate

Bond distances			
Sn–O(1)	2.201(2)	Sn–O(2)′ [a]	2.372(2)
Sn–C(11)	2.130(2)	Sn–C(21)	2.119(2)
Sn–C(31)	2.127(2)	O(1)–C(1)	1.267(3)
O(2)–C(1)	1.239(3)	C(1)–C(2)	1.508(4)
C(2)–Cl	1.755(3)	$\langle$C–C$\rangle_{phenyl}$	1.385(4)
Bond angles			
O(1)–Sn–O(2)′	174.75(6)	O(1)–Sn–C(11)	97.16(8)
O(1)–Sn–C(21)	91.00(7)	O(1)–Sn–C(31)	89.50(8)
O(2)′–Sn–C(11)	88.07(8)	O(2)′–Sn–C(21)	87.41(7)
O(2)′–Sn–C(31)	86.51(8)	C(11)–Sn–C(21)	111.51(9)
C(11)–Sn–C(31)	135.08(9)	C(21)–Sn–C(31)	112.73(9)
Sn–O(2)′–C(1)′	143.7(2)	$\langle$C–C–C$\rangle_{phenyl}$	120.0(3)

[a] (′) transformation: $\bar{x}$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$.

listed in Table 1. Table 2 lists selected bond lengths and angles. Listings of anisotropic temperature factors and structure factors are available from the authors.

Crystal data: Triphenyltin chloroacetate, $C_{20}H_{17}ClO_2Sn$, M_r 443.50, monoclinic, $P2_1/c$, a 9.022(3), b 10.217(3), c 19.780(5) Å, β 92.46(2)°; V 1822(2) Å^3, $Z = 4$; D_x 1.616 g cm^{-3}, D_m 1.613 g cm^{-1} ($ZnBr_2/H_2O$), μ_{Mo} 15.66 cm^{-1}, $F(000)$ 880, $R = 0.042$, $R_w = 0.063$ for 5372 $[(F_o)^2 > 3\sigma(F_o)^2]$ reflections.

Discussion

The Mössbauer IS and QS values for triphenyltin acetate and triphenyltin chloroacetate are in good agreement with reported values [3,9]. The variable-temperature study yielded a $-a$ value of 0.0105 K^{-1} for the latter compound, a value indicative of a rigid polymeric conformation. The $-a$ value is slightly larger for triphenyltin formate (0.0115 K^{-1} [15]) and triphenyltin 3-benzoylpropionate (0.0126 K^{-1} [16]); both compounds are helical, carboxylate-bridged chains. An example of a helical, polymeric triorganotin carboxylate that is not carboxylate-bridged is triphenyltin 8-quinolyloxyacetate monohydrate (0.0199 K^{-1} [17]); the water is coordinated to tin and the molecules are held together by hydrogen bonds between the water and the heteroatoms of the quinolyloxy group. The $-a$ value of 0.0191 K^{-1} reported for triphenyltin acetate [3] therefore appeared to us to be too high for a typical carboxylate-bridged structure, and we redetermined it and found it to be 0.0143 K^{-1}, which although still large, is more in keeping with the rigid polymeric conformation.

The crystal structure of triphenyltin chloroacetate is illustrated in Fig. 1. The molecules are carboxylate-bridged into a distorted helical chain whose geometry at tin is trigonal bipyramidal, with the oxygen atoms in the axially-most-electronegative positions (O–Sn–O′ 174.75(6)°). The covalent and coordinate tin–oxygen bonds are somewhat unequal (2.201(2), 2.372(2) Å). The sum of angles in the equatorial plane is 359.3(3)°, and the angle is closest to the acyl oxygen (135.08(9)°) is opened up from the sp^2 angle of 120°. In the crystal structure of triphenyltin acetate [3], the covalent Sn–O bond is 2.185 Å and the dative Sn–O bond is 2.349

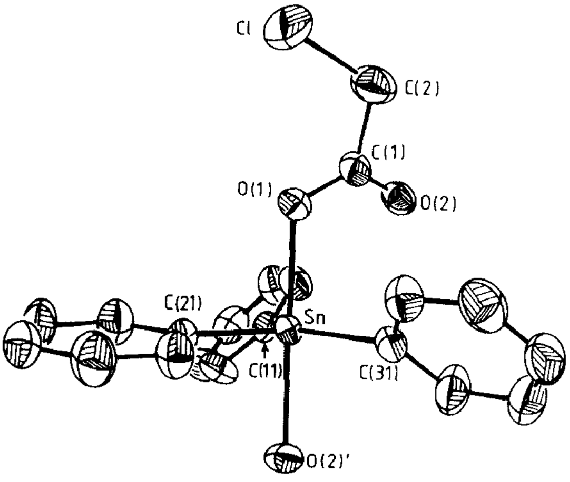

Fig. 1. Triphenyltin chloroacetate.

Å, the two axial bonds forming an angle of 173.6°. The effect of the chlorine substituent in the acetate group on bond lengths is therefore seen to be marginal *, and the fractional atomic coordinates of the non-H atoms of the triphenyltin chloroacetate molecule (Table 1) are, in fact, nearly identical to those reported [3] for triphenyltin acetate. The compounds are isostructural, as are triphenyltin saccharin-ethanol [18] and triphenyltin saccharin-glycolic acid [19]; however, trivinyltin acetate and trivinyltin chloroacetate [20] are not, although the geometries around the tin atoms are similar.

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* *Note added in proof*: Two more chlorine atoms disrupt the polymeric structure, and triphenyltin trichloroacetate is a four-coordinate molecule: S.M. Roe and N.W. Alcock, Sixth International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin and Lead, Brussels, Belgium, July 23–28 (1989), p. 23.