

PREPARATION AND STRUCTURE OF TRIORGANOTIN AND TRIORGANOLEAD METHYLOXALATES

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Summary

Triorganotin and triorganolead methyloxalates $R_3MO_2CCO_2Me$ ($M = Sn, Pb$; $R = Me, Ph$) have been prepared by neutralization of HO_2CCO_2Me with the appropriate hydroxides. The crystal structure of $Ph_3PbO_2CCO_2Me$ has been determined by single crystal X-ray diffraction. In the chain-like structure the lead atom is in a slightly distorted trigonal bipyramidal environment, with C(phenyl) in the equatorial plane and the O atoms of bridging carboxylate groups in apical positions (Pb-O(1') 256.5(4), Pb-O(2) 238.4(4) pm; O(1')-Pb-O(2) 169.8(1)°. The distance Pb-O(1) of 342.6(4) pm is taken to indicate a weak chelating interaction. There is no inter-chain coordination. From vibrational spectral data analogous molecular structures are inferred for the other triorganometal methyloxalates.

Introduction

In triorganotin and triorganolead carboxylates R_3MO_2CR' ($M = Sn, Pb$) the carboxylate ligand has usually bridges, to produce chains, as in $Me_3PbO_2CCH_3$ [1] or in $Me_3SnO_2CCH_3$ [2], but chelating carboxylate groups are also known, e.g. in $Ph_3SnO_2CC_6H_4-2-OMe$ [3]. Donor substituents in the organic group R' may compete with the carboxylate group for the coordination site at M , e.g. the amino group in $Me_3SnO_2CCH_2NH_2$, in which the carboxylate group is monodentate and NH_2 is coordinated to Sn [4]. Steric and electronic effects operate to determine the resulting solid state structure, and often rather subtle differences seem to favour alternative bonding types; e.g. in $R_3MO_2CCH_2NHCOCH_3$ monodentate carboxylate and $M...OC(acetyl)$ coordination is observed [5], whereas in most $R_3MO_2CCH_2NHCOR'$ ($R' = H, Ph$) compounds "normal" bridging by bidentate carboxylate is found [6]. The differing coordination behaviour of substituted (and unsubstituted) carboxylates is not well understood, and it should be revealing to study other types of organotin and organolead carboxylates. Interesting compounds in this context are R_3M derivatives of the monoesters of oxalic acid $R_3MO_2CCO_2R'$

(M = Sn, Pb) formally containing an α -keto group. Only one example, $\text{Et}_3\text{PbO}_2\text{CCO}_2\text{Et}$, has been described [7], and this was not structurally characterized.

Experimental

Oxalic acid monomethyl ester was obtained by ion exchange (Amberlite 120, Fluka) from $\text{KO}_2\text{CCO}_2\text{CH}_3$ (prepared as described in ref. 8) in methanolic solution and used in situ. The compounds R_3MOH were prepared by literature procedures: M = Pb, R = Ph [9], R = Me [9]; M = Sn, R = Ph [10], R = Me [11]. Methanol was purified and dried by standard methods.

The IR spectra of Nujol mulls were recorded with a Perkin-Elmer PE 580B Spectrophotometer using CsBr windows. C and H were determined microanalytically, Sn was estimated gravimetrically as SnO_2 , and Pb was titrated against Titriplex III (2.5×10^{-2} molar) after digestion with concentrated H_2SO_4 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

The triorganometal compounds listed in Table 1 were precipitated at room temperature from equimolar amounts of R_3MOH and $\text{HO}_2\text{CCO}_2\text{Me}$ in methanol. They were purified by warming their suspensions in methanol and subsequently reducing volume of solvent. For yields and analytical data see Table 1.

$\text{Ph}_3\text{PbO}_2\text{CCO}_2\text{Me}$ was recrystallized from boiling methanol to give suitable single crystals. Crystal data for $\text{Ph}_3\text{PbO}_2\text{CCO}_2\text{Me}$: $\text{C}_{21}\text{H}_{18}\text{O}_4\text{Pb}$, $M = 541.57$, monoclinic, space group $P2_1/c$, a 936.9(4), b 1127.6(8), c 1811.0(8) pm, β 90.45(5)°, V 1913×10^6 pm³, $Z = 4$, D_c 1.880 Mg m⁻³, $\mu(\text{Mo-K}\alpha)$ 8.9 mm⁻¹, graphite monochromated Mo- $K\alpha$ radiation λ 71.069 pm, crystal size 0.11 \times 0.23 \times 0.32 mm; temperature 291(1) K, lattice parameter from least-squares fit with 25 reflexions in the range $18^\circ \leq 2\theta \leq 35.2^\circ$, CAD4 diffractometer, ω - 2θ scans, scan speed 2.5° min⁻¹, four standard reflexions recorded every 2 h showed an intensity decrease up to 12%; 3763 reflexions measured in the range $1^\circ \leq \theta \leq 25^\circ$, max. $(\sin \theta)/\lambda$ 0.59 pm⁻¹, $+11 \geq h \geq -11$, $0 \leq k \leq 13$, $0 \leq l \leq 21$; the following corrections were applied: Lorentz-polarization correction, absorption correction via ψ -scans, max/min. transmission 1.0/0.48, and intensity decay correction; systematic absences $(h0l)$ $l = 2n + 1$, $(0k0)$ $k = 2n + 1$; the structure was solved via Patterson function, ΔF

TABLE 1

ORGANOTIN AND ORGANOLEAD COMPOUNDS OF OXALIC ACID MONOMETHYL ESTER; YIELDS OF PREPARATION, ANALYTICAL DATA

Compounds	Yield (%)	M.p. (Decomp.) (°C)	Analysis (Found(calcd.)(%))		
			C	H	M
$(\text{CH}_3)_3\text{SnO}_2\text{CCO}_2\text{CH}_3$	56	128	28.5 (27.01)	4.6 (4.53)	43.7 (44.48)
$(\text{CH}_3)_3\text{PbO}_2\text{CCO}_2\text{CH}_3$	70	86	19.8 (20.28)	3.1 (3.40)	58.5 (58.31)
$(\text{C}_6\text{H}_5)_3\text{SnO}_2\text{CCO}_2\text{CH}_3$	65	143	55.9 (55.67)	4.1 (4.00)	25.6 (26.20)
$(\text{C}_6\text{H}_5)_3\text{PbO}_2\text{CCO}_2\text{CH}_3$	74	197	46.5 (46.57)	3.1 (3.35)	38.0 (38.26)

syntheses and full-matrix least-squares refinement with 2537 observed ($I > 3 \sigma(I)$) F_0 values and 236 refined parameters; all non-H atoms were refined anisotropically and a common isotropic temperature factor was refined for the H atoms, which were placed in geometrically calculated positions (C–H 95 pm); weighting scheme $w^{-1} = [\sigma^2(I) + (0.035 F_0^2)]^{1/2}$, $S = 1.19$, $R = 0.026$, $R_w = 0.030$, max. shift over error in the final refinement cycle 0.03, largest peak in the final ΔF -map $\pm 1.4(3) \times 10^{-6} \text{ e pm}^{-3}$ near the Pb position (Fourier ripples); complex neutral atom scattering factors from ref. 12; Programs: Enraf–Nonius structure determination package [13], ORTEP [14]. The least-squares plane through the positions C(11), C(21), C(31), Pb(1) (I): $-0.506x - 0.830y - 0.233z = 313.8 \text{ pm}$ with the distances from this plane C(11) 2.3(6), C(21) 2.4(6), C(31) 2.0(6), Pb(1) $-6.6(1) \text{ pm}$, through the positions O(1), C(1), O(2), C(2) (II): $0.573x + 0.149y - 0.806z = 263.6 \text{ pm}$ with the distances from the plane O(1) $-0.3(4)$, C(1) 0.7(6), O(2) $-0.3(4)$, C(2) $-0.2(6) \text{ pm}$ and through the positions O(3), C(2), O(4), C(1) (III): $-0.107x + 0.649y - 0.754z = 82.7 \text{ pm}$ with the distances from the plane O(3) 0.6(6), O(4) 0.5(6), C(2) $-1.4(6)$, C(1) 0.4(6) pm (x, y, z are orthogonalized coordinates). The dihedral angles are (I, II) $103.1(2)^\circ$, (I, III) $108.0(2)^\circ$ and (II, III) $50.0(2)^\circ$.

A complete list of bond lengths and angles and lists of thermal parameters and structure factors are available from the authors.

Results and discussion

The title compounds $R_3MO_2CCO_2Me$ ($M = \text{Sn, Pb}$; $R = \text{Me, Ph}$; Table 1) can be easily prepared in ca. 60–80% yields by neutralizing the appropriate hydroxides R_3MOH with $HO_2CCO_2CH_3$ in methanol. The colorless compounds are insoluble in water. Except for $Me_3SnO_2CCO_2Me$, which is soluble in methanol, $CHCl_3$ and DMSO, they are only slightly soluble in DMSO but show some solubility in methanol. The molecular weight of freshly prepared $Ph_3PbO_2CCO_2Me$ was found by osmometry to be 545 at 45°C . Comparison with the calculated molecular weight of 541.6 shows that this compound is monomeric in solution.

In the IR spectra of all four compounds (Table 2), the $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ bands due to the methyl ester group are very similar, and appear at 1736 to 1750 cm^{-1} and 1215 to 1230 cm^{-1} , respectively. They correspond to the related bands of $KO_2CCO_2CH_3$ [15] and of dimethyl oxalate [16] (Table 2). In the latter compounds the methyl ester group is not involved in coordination, as shown by single crystal

TABLE 2

CHARACTERISTIC IR-FREQUENCIES FOR $R_3MO_2CCO_2Me$ ($M = \text{Sn, Pb}$; $R = \text{Me, Ph}$) AND KO_2CCO_2Me (in cm^{-1})

Compound	MeOC(O) group			MOC(O) group		
	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\Delta\nu$	$\nu_{as}(\text{CO})$	$\nu_s(\text{CO})$	$\Delta\nu$
KO_2CCO_2Me	1734vs	1211vs	523	1642vs	1380s	262
MeO_2CCO_2Me [16]	1764	1216/1189	548/575	–	–	–
$Me_3SnO_2CCO_2Me$	1750vs	1230vs	520	1632s/1612vs	1410m	222/202
$Me_3PbO_2CCO_2Me$	1737vs	1215vs	522	1611s/1595vs	1400s	211/195
$Ph_3SnO_2CCO_2Me$	1742vs	1221vs	521	1620s/1594vs	1415s	205/179
$Ph_3PbO_2CCO_2Me$	1736vs	1220vs	516	1618s/1592vs	1403s	215/189

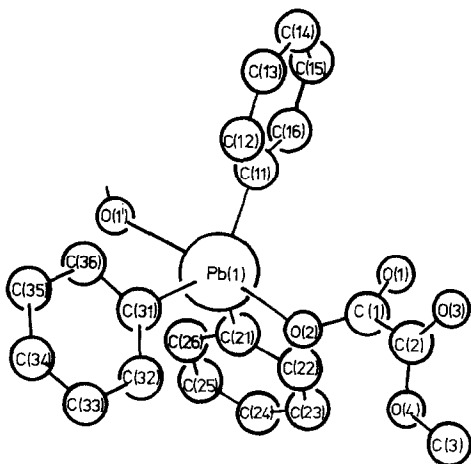


Fig. 1. Structure of $\text{Ph}_3\text{PbO}_2\text{CCO}_2\text{Me}$: one formula unit (plus $\text{O}(1')$), showing the atom numbering scheme. Symmetry code: $i = (\bar{x}, y - 1/2, 1/2 - z)$.

X-ray diffraction [17,18], and this is assumed to be the case also for $\text{R}_3\text{MO}_2\text{CCO}_2\text{Me}$ in view of the similarity of the IR band positions. A split band is observed in the compounds $\text{R}_3\text{MO}_2\text{CCO}_2\text{Me}$ in the ranges 1611 to 1632 and 1592 to 1612 cm^{-1} , and is assigned to $\nu_{\text{as}}(\text{CO})$. A band between 1400 to 1415 cm^{-1} is assigned to $\nu_{\text{s}}(\text{CO})$. From these band positions, which correspond to those found in other organometal carboxylates (see e.g. [19]), it is inferred that the carboxylate group is not unidentately bound to the R_3M group but is bridging. This leads to the formation of polymeric chains (vide infra). In the IR as well as in the Raman spectra of both of the $\text{Me}_3\text{MO}_2\text{CCO}_2\text{Me}$ compounds $\nu_{\text{as}}(\text{MC})$ and $\nu_{\text{s}}(\text{MC})$ are observed ($\nu_{\text{as}}/\nu_{\text{s}}$; IR(R); M = Pb: 500 m/460 w (500 m/460 s); M = Sn: 560 m/525 w (565 m/525 s) cm^{-1}). Therefore a regular trigonal planar arrangement of the MC_3 skeleton is excluded. We assume that the triphenylmetal compounds have the generally similar structures.

These structural proposals were confirmed for $\text{Ph}_3\text{PbO}_2\text{CCO}_2\text{Me}$ by the results of the X-ray structure determination. The structure of this compound is shown in Fig. 1 and a stereoview of the unit cell in Fig. 2. Positional parameters and equivalent values U_{eq} of the anisotropic temperature factors β_{ik} are given in Table 3, and bond lengths and bond angles in Table 4. The unit cell contains four asymmetric molecules. The central atom Pb has a distorted trigonal bipyramidal surrounding, the atoms C(11), C(21) and C(31) forming the equatorial plane, from which Pb is shifted towards O(2); O(1') and O(2) are in apical positions, and show different Pb–O distances (Pb–O(2) 238.4(4) pm; Pb–O(1') 256.5(4) pm). The distortion is also demonstrated by the angle O(1')–Pb–O(2) 169.8(1)°. The arrangement and also the Pb–C and C–C bond lengths (Table 4) as well as the bond angles (Table 4) correspond to those in the comparable parts of analogous compounds, e.g. $\text{Ph}_3\text{PbO}_2\text{CCH}_3$ [20] or Ph_3PbOH [21]. The C–O distances in the bridging carboxylate group (C(1)–O(1) 124.0(7), C(1)–O(2) 123.8(7) pm) are not significantly different (Table 4), and correspond to the distance 124.0 pm for the two appropriate bonds in $\text{KO}_2\text{CCO}_2\text{Me}$ [17]. The distance Pb–O(1) (342.6(4) pm) is longer than the

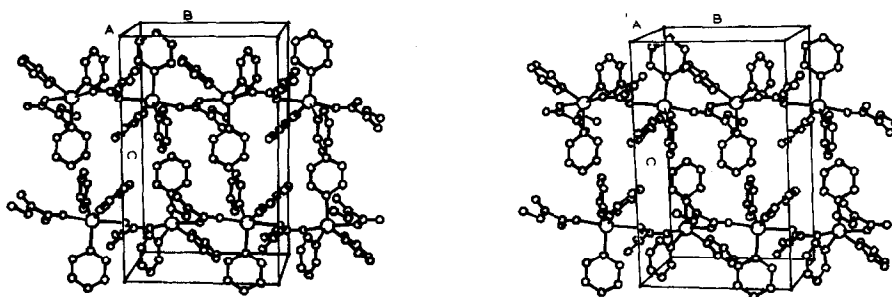


Fig. 2. Stereoscopic view of the unit cell of $\text{Ph}_3\text{PbO}_2\text{CCO}_2\text{Me}$.

sum of the covalent radii (220 pm), but is distinctly shorter than the sum of the Van der Waals radii (~ 372 pm, if Van der Waals radii of 220 and 152 pm are assumed for Pb and O, respectively [22]), indicating weak interaction. This implies that the carboxylate group $\text{O}(2)\text{C}(1)\text{O}(1)$ is weakly chelating to Pb, which accounts for the fact that the bridge between Pb and Pb' is not symmetric. Similar conclusions are

TABLE 3

FRACTIONAL ATOMIC COORDINATES AND TEMPERATURE FACTORS ($\text{\AA}^2 \times 10^3$) FOR $\text{Ph}_3\text{PbO}_2\text{CCO}_2\text{Me}$

$$U_{\text{eq}} = \frac{1}{24\pi^2} \sum_i \sum_j \beta_{ij} a_i \times a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Pb(1)	0.06756(2)	0.19234(2)	0.26157(1)	33.0(1)
O(1)	0.0647(4)	0.4962(4)	0.2603(2)	43(1)
O(2)	0.2129(4)	0.3558(4)	0.2984(3)	45(1)
O(3)	0.2084(6)	0.6212(5)	0.3782(3)	85(1)
O(4)	0.3934(5)	0.5440(5)	0.3232(3)	85(1)
C(1)	0.1713(6)	0.4598(5)	0.2945(3)	34(1)
C(2)	0.2595(7)	0.5501(5)	0.3377(3)	42(1)
C(3)	0.4872(9)	0.6272(9)	0.3641(6)	109(4)
C(11)	-0.1265(6)	0.2578(6)	0.3144(3)	37(1)
C(12)	-0.1325(8)	0.2537(7)	0.3905(4)	56(3)
C(13)	-0.2560(9)	0.2931(7)	0.4255(4)	75(3)
C(14)	-0.3713(8)	0.3318(7)	0.3840(5)	70(3)
C(15)	-0.3638(8)	0.3377(6)	0.3086(5)	63(3)
C(16)	-0.2397(7)	0.3002(6)	0.2736(4)	48(1)
C(21)	0.1326(6)	0.2005(5)	0.1467(3)	35(1)
C(22)	0.1904(8)	0.3044(6)	0.1180(4)	53(3)
C(23)	0.2362(9)	0.3066(7)	0.0442(4)	67(3)
C(24)	0.2243(8)	0.2057(8)	0.0014(4)	66(3)
C(25)	0.1690(8)	0.1035(8)	0.0291(4)	63(3)
C(26)	0.1241(7)	0.0992(7)	0.1027(4)	56(3)
C(31)	0.1993(7)	0.0838(5)	0.3352(3)	38(1)
C(32)	0.3451(7)	0.0947(7)	0.3370(4)	58(3)
C(33)	0.4306(8)	0.0209(8)	0.3818(5)	77(3)
C(34)	0.3640(9)	-0.0613(7)	0.4248(4)	80(3)
C(35)	0.2173(9)	-0.0755(7)	0.4245(4)	72(3)
C(36)	0.1351(8)	-0.0019(6)	0.3794(4)	54(3)

TABLE 4

BOND LENGTHS (pm) AND BOND ANGLES ($^{\circ}$) IN $\text{Ph}_3\text{PbO}_2\text{CCO}_2\text{Me}^a$

Pb(1)–C(11)	219.0(6)	C(1)–O(1)	124.0(7)
Pb(1)–C(21)	217.5(6)	C(1)–O(2)	123.8(7)
Pb(1)–C(31)	218.5(6)	C(1)–C(2)	152.4(8)
Pb(1)–O(1')	256.5(4)	C(2)–O(3)	119.0(8)
Pb(1)–O(2)	238.4(4)	C(2)–O(4)	128.6(8)
Pb(1)–O(1)	342.6(4)	C(3)–O(4)	148.1(11)
C(11)–Pb(1)–C(21)	130.1(2)	Pb(1)–O(1')–C(1')	138.4(4)
C(11)–Pb(1)–C(31)	112.9(2)	Pb(1)–O(2)–C(1)	122.5(4)
C(21)–Pb(1)–C(31)	116.5(2)	O(1)–C(1)–O(2)	126.4(5)
C(11)–Pb(1)–O(1')	87.5(2)	O(1)–C(1)–C(2)	117.9(5)
C(21)–Pb(1)–O(1')	91.6(2)	O(2)–C(1)–C(2)	115.7(5)
C(31)–Pb(1)–O(1')	83.2(2)	O(3)–C(2)–O(4)	124.1(6)
C(11)–Pb(1)–O(2)	95.2(2)	O(3)–C(2)–C(1)	123.2(6)
C(21)–Pb(1)–O(2)	94.1(2)	O(4)–C(2)–C(1)	112.7(5)
C(31)–Pb(1)–O(2)	86.8(2)	C(2)–O(4)–C(3)	116.1(6)
O(1')–Pb(1)–O(2)	169.8(1)		

^a Numbering of atoms according to Fig. 1.

indicated by the torsion of the oxalate skeleton. The C–O distances in the methyl ester group show the expected differences (Table 4) and compare well with those in $\text{KO}_2\text{CCO}_2\text{Me}$ [17] or oxalic dimethyl ester [18]. The planes through the two carboxylate groups form a dihedral angle of $50.0(2)^{\circ}$, what is in contrast to the equiplanar arrangement in $\text{KO}_2\text{CCO}_2\text{Me}$ [17] and $\text{MeO}_2\text{CCO}_2\text{Me}$ [18].

When heated $\text{R}_3\text{MO}_2\text{CCO}_2\text{Me}$ compounds decompose before melting. In all cases one of the decomposition products was the dimethyl ester of oxalic acid. Its formation leads to development of two phases. Formation of a colorless melt and a white precipitate was previously observed when $\text{Et}_3\text{PbO}_2\text{CCO}_2\text{Et}$ decomposed during attempts to determine its melting point [7].

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