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# Preparation and structure of triorganotin, triorganolead and tetraphenylantimony derivatives of acetylenedicarboxylic acid, terephthalic acid and dithioterephthalic acid #

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Abstract. Triorganotin, triorganolead and tetraphenylantimony derivatives of acetylenedicarboxylic acid (H<sub>2</sub>ADC), terephthalic acid (H<sub>2</sub>TER) and dithioterephthalic acid (H<sub>2</sub>DTT) ( $R_3M$ ),X (M = Sn, Pb; R = Me, Ph; X = ADC, TER, DTT) and  $(Ph_4Sb)_2X (X = ADC, TER)$  were prepared by neutralization of  $R_3MOH$  or  $Ph_4SbOH$  with the appropriate acid (X = ADC, DTT) or by reaction of R<sub>3</sub>MCl or Ph<sub>4</sub>SbCl with K<sub>2</sub>TER. The crystal structures of (Me<sub>3</sub>Sn)<sub>2</sub>ADC and (Me<sub>3</sub>Sn)<sub>2</sub>TER were determined by X-ray diffraction. The Sn atoms are in slightly distorted trigonal-bipyramidal environments, with C(Me) in the equatorial plane and O(carboxyl) in apical positions. The carboxylate groups are bridging, leading to the formation of a two-dimensional polymer of puckered 22-membered [(Me<sub>3</sub>Sn)<sub>2</sub>ADC] and 26-membered [(Me<sub>3</sub>Sn)<sub>2</sub>TER] rings. From vibrational spectra, analogous structures are inferred for solid  $(Ph_3Sn)_2ADC$ ,  $(R_3Pb)_2ADC$  (R = Me, Ph), and (Me<sub>3</sub>Pb)<sub>2</sub>TER, but structures with unidentate - COO and - COS groups and tetracoordinated Sn or Pb and pentacoordinated Sb are proposed for the other compounds. The DTT ligands are linked by S bonds to M. According to IR and <sup>1</sup>H NMR studies the polymeric species dissociate on dissolution so that generally species with unidentate carboxylate groups are present. Sn and Pb in  $(R_3M)_2X$  (X = ADC, TER) are apparently tetracoordinated in CHCl<sub>3</sub>, but pentacoordinated in DMSO by addition of a solvent molecule.

### Introduction

The carboxylate group has different possibilities for bonding and therefore offers in a specific molecular unit great adaptability to electronic and/or steric effects of other substituents and allows intermolecular coordination. In organotin(IV) and organolead(IV) carboxylates, bridging and intermolecular chain formation are quite common<sup>1</sup>, though unidentate<sup>2</sup> and chelating bonding<sup>3</sup> as well as various intermediate types of bonding by the carboxylate group have also been observed. In tetraorganoantimony carboxylates essentially only unidentate bonding of the carboxylate group occurs, though additionally more or less weak intramolecular chelation may exist<sup>4</sup>. During our studies on organometal carboxylates we became interested in structural features of derivatives of such dicarboxylic acids, which are distinguished by a virtually rigid link to the two carboxylic groups. We therefore synthesized organotin, organolead and organoantimony derivatives of acetylenedicarboxylic acid (H<sub>2</sub>ADC), terephthalic acid (H<sub>2</sub>TER), and dithioterephthalic acid  $(H_2DTT)$ , and studied the structure

of these compounds, of which bis(triorganotin)acetylene dicarboxylates were prepared for the first time by *Luijten* and *van der Kerk*<sup>5</sup>.

#### Experimental

The organometallic educts were prepared according to standard procedures to be found in the literature:  $Me_3SnOH^6$ ,  $Me_3PbOH^7$ ,  $Ph_3SnOH$ ,  $Ph_3PbOH^8$ ,  $Ph_4SbOH^9$ ,  $Me_3SnCl^{10}$ ,  $Me_3PbCl$ ,  $Ph_3PbCl^{11}$ ,  $Ph_3SnCl^{12}$ .  $Ph_4SbCl$  was obtained from  $Ph_4SbOH$  and HCl.  $H_2ADC$ ,  $H_2TER$  (from EGA) and  $H_2DTT$  (from Fluka) were used as purchased.  $K_2TER$  was prepared by neutralizing  $H_2TER$  with KOH in water.  $CH_3OH$  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  $SnO_2$ . Pb was titrated against Titriplex III ( $2.5 \times 10^{-2}$  molar) after digestion with concentrated  $H_2SO_4$  and  $(NH_4)_2S_2O_8$ , and Sb was estimated iodometrically after analogous digestion followed by reduction of Sb(V).

<sup>#</sup> Dedicated to Prof. Dr. G. J. M. van der Kerk on the occasion of his 75th birthday.

The organometal compounds listed in Table I with yields and analytical data were synthesized by one of the following procedures under dry  $N_2$  at room temperature.

Table I	Preparation and	analytical d	lata of (R <sub>3</sub> )	$M)_2 X \ (M = S)_2 X$	n, Pb; R	= Me, Ph;	X = ADC, TER	, DTT) and (Ph	$(A_4Sb)_2X (X = A_4Sb)_2X$	ADC, TER).
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Compound	Procedure of	Yield	Mp.	Analysis [found (calcd.) %]			
Compound	preparation	(%)	(°C)	С	Н	М	
$(Me_{3}Sn)_{2}ADC (1)$ $C_{10}H_{18}O_{4}Sn_{2} (439.63)$	A	74	178	27.1 (27.32)	4.2 (4.13)	52.7 (54.00)	
$(Ph_3Sn)_2ADC (2) C_{40}H_{30}O_4Sn_2 (812.06)$	A	73	185 <sup>a,b</sup>	58.9 (59.16)	3.7 (3.72)	28.3 (29.23)	
(Me <sub>3</sub> Pb) <sub>2</sub> ADC (3) C <sub>10</sub> H <sub>18</sub> O <sub>4</sub> Pb <sub>2</sub> (616.65)	Α	85	90ª	19.6 (19.48)	3.0 (2.94)	67.0 (67.20)	
(Ph <sub>3</sub> Pb) <sub>2</sub> ADC (4) C <sub>40</sub> H <sub>30</sub> O <sub>4</sub> Pb <sub>2</sub> (989.08)	A	91	120ª	48.3 (48.58)	3.2 (3.06)	41.5 (41.90)	
$(Ph_4Sb)_2ADC (5) C_{52}H_{40}O_4Sb_2 (972.39)$	A	60	175ª	64.4 (64.23)	4.0 (4.15)	25.0 (25.04)	
$(Me_2Sn)_2TER$ (6) $C_{14}H_{22}O_4Sn_2$ (491.71)	В	79	212	34.4 (34.20)	4.6 (4.51)	47.1 (48.28)	
(Ph <sub>3</sub> Sn) <sub>2</sub> TER (7) C <sub>44</sub> H <sub>34</sub> O <sub>4</sub> Sn <sub>2</sub> (864.13)	В	81	164ª	61.2 (61.16)	3.7 (3.97)	26.9 (27.47)	
$(Me_{3}Pb)_{2}TER (8)$ $C_{14}H_{22}O_{4}Pb_{2} (668.73)$	В	76	148ª	25.2 (25.15)	3.1 (3.32)	62.1 (61.97)	
(Ph <sub>3</sub> Pb) <sub>2</sub> TER (9) C <sub>44</sub> H <sub>34</sub> O <sub>4</sub> Pb <sub>2</sub> (1041.15)	В	87	176ª	50.6 (50.76)	3.3 (3.29)	39.8 (39.80)	
(Ph <sub>4</sub> Sb) <sub>2</sub> TER (10) C <sub>56</sub> H <sub>44</sub> O <sub>4</sub> Sb <sub>2</sub> (1024.46)	В	83	218ª	65.7 (65.66)	4.0 (4.33)	23.5 (23.77)	
(Me <sub>3</sub> Sn) <sub>2</sub> DTT (11) C <sub>14</sub> H <sub>22</sub> O <sub>2</sub> S <sub>2</sub> Sn <sub>2</sub> (523.83)	A	91	155ª	31.9 (32.10)	4.3 (4.23)	44.8 (45.32)	
(Ph <sub>3</sub> Sn) <sub>2</sub> DTT (12) C <sub>44</sub> H <sub>34</sub> O <sub>2</sub> S <sub>2</sub> Sn <sub>2</sub> (896.25)	A	68	196	58.7 (58.96)	3.9 (3.82)	25.8 (26.49)	
$(Me_{3}Pb)_{2}DTT (13)$ $C_{14}H_{22}O_{2}Pb_{2}S_{2} (700.85)$	Α	87	136ª	24.1 (23.99)	3.3 (3.16)	59.2 (59.13)	
$(Ph_3Pb)_2DTT (14) C_{44}H_{34}O_2Pb_2S_2 (1073.27)$	Α	82	191ª	49.4 (49.24)	3.0 (3.19)	38.6 (38.61)	

<sup>a</sup> Decomposition. <sup>b</sup> Lit.<sup>5</sup> 185°C.

#### Procedure A

A solution of  $R_3MOH$  or  $Ph_4SbOH$  in dry  $CH_3OH$  was added to a methanolic solution of  $H_2ADC$  or  $H_2DTT$  (mole ratio 2:1) over a period of 15 min. After stirring for 1 h the reaction mixture was dried *in vacuo*. The residue was suspended in  $CH_3OH$  while warming it (only slightly in the case of organolead compounds), then separated by filtration, dried in a vacuum desiccator over silica gel and stored in total darkness at 0°C.

### Procedure B

A solution of  $R_3MCl$  or  $Ph_4SbCl$  in  $CH_3OH$  was added over a period of 20 min to  $K_2TER$  (mole ratio 2:1) dissolved in a mixture of  $CH_3OH/H_2O$  (60:25 by vol.). The resulting precipitate was filtered off, washed with aqueous methanol and dried and stored according to Procedure A.

Suitable single crystals of  $(Me_3Sn)_2ADC(1)$  and  $(Me_3Sn)_2TER(6)$  for X-ray diffraction were obtained by slowly cooling the filtrate of hot suspensions of 1 and 6, respectively, in CH<sub>3</sub>OH, in the case of 1 after addition of Bu<sub>2</sub>O. Crystal data are listed in Table II.

The intensities were measured on a Nonius CAD-4 diffractometer employing graphite monochromated Ag-K $\alpha$  radiation. A *Lorentz*polarization correction and absorption correction via  $\psi$  scans was applied. The structure of 1 was solved by means of direct methods using the MULTAN80<sup>13</sup> program, that of 6 by applying the *Patterson* function and  $\Delta F$  syntheses. Refinement proceeded by means of full-matrix least-squares calculations, anisotropic for all non-H atoms, isotropic for all H atoms, which were placed in geometrically calculated positions (C-H 0.95 Å). Complex neutral-atom scattering factors were taken from Ref. 14. The following programs were used: Enraf-Nonius Structure Determination Package<sup>15</sup>, PARST<sup>16</sup> and SHELXTL PLUS<sup>17</sup>.

# **Results and discussion**

The compounds  $(R_3M)_2ADC$ ,  $(R_3M)_2DTT$  (M = Sn, Pb; R = Me, Ph) and  $(Ph_4Sb)_2ADC$  (Table I) can be easily prepared in ca. 60-90% yield by neutralizing the appropriate hydroxides R<sub>3</sub>MOH or Ph<sub>4</sub>SbOH with H<sub>2</sub>ADC or H<sub>2</sub>DTT, respectively, in methanol. Compounds 1 and 2 had already been obtained by Luijten and van der Kerk<sup>5</sup> by mixing  $R_3$ SnOH and  $H_2$ ADC and distilling the mixture with benzene to remove water formed in the reaction azeotropically. Yields were 68 and 59% respectively. To prepare  $(R_3M)_2TER$  (M = Sn, Pb; R = Me, Ph) and  $(Ph_4Sb)_2TER$ it was found that higher yields are obtained by reacting  $R_3MCl$  or  $Ph_4SbCl$  dissolved in methanol with  $K_2TER$ , the potassium salt of terephthalic acid, in a methanol/water mixture than by neutralization. All compounds are colorless. The antimony derivatives 5 and 10 are soluble in methanol, CHCl<sub>3</sub> or DMSO, the types (R<sub>3</sub>M)<sub>2</sub>DTT are appreciably soluble in CHCl<sub>3</sub>, less in methanol and poorly in DMSO. All other compounds prepared are only slightly soluble, the solubility decreasing in the series DMSO > methanol >  $CHCl_3$ .

The solid-state structures of 1 and 6 were determined by X-ray structure determination. The crystal data are listed in Table II, atomic coordinates and equivalent isotropic

Table II Crystal data of 1 and 6.

	1 (Me <sub>3</sub> Sn) <sub>2</sub> ADC	<b>6</b> (Me <sub>3</sub> Sn) <sub>2</sub> TER
Crystal system	monoclinic	monoclinic
Space group	P21	C2/c
Z	2	4
a (Å)	6.738(7)	13.220(9)
b (Å)	9.960(9)	10.084(7)
c (Å)	11.454(9)	14.125(9)
$\beta$ (degrees)	92.01(6)	97.49(6)
Unit cell volume (Å <sup>3</sup> )	768(1)	1867(2)
$D_{\text{calc.}} (g \cdot \text{cm}^{-3})$	1.901	1.749
Radiation (graphite monochromated)	AgKa	AgKα
$\lambda$ (A)	0.56087	0.56087
$\mu (mm^{-1})$	1.70	1.40
Crystal dimensions (mm)	$0.10 \times 0.26 \times 0.30$	$0.18 \times 0.18 \times 0.19$
<i>T</i> (°K)	291(1)	291(1)
<i>F</i> (000)	420	952
$\omega/2\theta$ Scan. Scan speed (deg min <sup>-1</sup> )	4	2.5
Lattice parameters from least-squares fit with 25 reflections up to $2\theta =$	37.5°	38°
$\theta$ range (deg)	$1^{\circ} \leq \theta \leq 22^{\circ}$	$1^{\circ} \leq \theta \leq 20^{\circ}$
N° of standard intensity reflections measured at $2\frac{1}{2}$ h intervals (only random deviations)	5	5
Least-squares refinement based on	F	5 F
N° of measured reflections	4077	3770
Part of reciprocal space measured	-9 < h < 9	-16 < h < 16
Ture of toopfood, space measured	$0 \le k \le 13$	$0 \le k \le 12$
	-15 5</td <td>-17 &lt; l &lt; 17</td>	-17 < l < 17
N° of unique reflections after averaging	2013	1751
Refined parameters	145	92
N° reflections with $I \ge 3\sigma(I)$	1710	1360
R	0.016	0.018
max./min. transmission	1.00/0.82	1 00/0 94
Systematic absences	(0k0) k = 2n + 1	(hkl) h + k = 2n + 1
-,		(h0l) l = 2n + 1
Weighting scheme $(w^{-1})$	$[\sigma^2(I) + (0.04 \cdot F_0^2)^2]^{1/2}$	$[\sigma^2(I) + (0.075 \cdot F_0^2)^2]^{1/2}$
S	0.81	0.70
Max. $\Delta/\sigma$	< 0.005	< 0.005
Largest peak in final $\Delta F$ map $(e \cdot Å^{-3})$	0.4(2)	0.4(2)
R R	0.020	0.023
<i>R</i>	0.025	0.031
<del>.</del>		



Fig. 1.  $(Me_3Sn)_2ADC$  (1): General view of a molecule, showing the atom numbering scheme. The symmetry code is given in Table IV.

Table III Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses of 1 and 6  $[U_{\rm eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})].$ 

	x	y	Z	$U_{eq}/U$
			<u>├</u> ──── <sup>─</sup> ────	
1				}
Sn(1)	0.61914(5)	0.47580(0)	01968(3)	34
Sn(2)	10010(5)	0.30809(4)	0.53342(3)	38
O(11)	0.4749(6)	0.2809(4)	0.0685(3)	48
O(12)	0.2427(5)	0.1397(4)	0.1231(3)	48
O(21)	0.0030(6)	0.5015(4)	0.4260(3)	50
O(22)	0.2003(6)	0.6503(4)	0.3452(4) = 0.1127(5)	56
C(12)	0.3407(8)	0.4874(8)	0.1435(5)	63
C(12)	0.8327(9)	0.3355(7)	-0.0713(6)	62
C(14)	0.3294(8)	0.2514(5)	0.1259(4)	38
C(15)	0.2496(9)	0.3519(6)	0.2061(5)	46
C(21)	-0.283(1)	0.4494(7)	0.6184(6)	71
C(22)	0.2020(9)	0.2922(7)	0.5845(5)	61
C(23)	-0.21/(1)	0.2182(7)	0.3/80(6)	08
C(24)	0.1230(9)	0.3343(0) 0.4341(5)	0.3340(4) 0.2710(5)	45
H(111)	0.34751(0)	0.56252(0)	16377(0)	110
H(112)	0.32637(0)	0.40764(0)	15697(0)	110
H(113)	0.24266(0)	0.49731(0)	05949(0)	110
H(121)	0.73791(0)	0.65304(0)	0.13204(0)	110
H(122)	0.55536(0)	0.58078(0)	0.18191(0)	110
H(123)	0.76268(0)	0.51300(0)	0.19003(0)	
H(131)	0.93060(0)	0.3/981(0)	11491(0) 00396(0)	110
H(132)	0.89390(0)	0.29329(0)	-11825(0)	110
H(133) H(211)	35765(0)	0.40460(0)	0.67547(0)	110
H(212)	20192(0)	0.51618(0)	0.65526(0)	110
H(213)	37087(0)	0.49045(0)	0.56245(0)	110
H(221)	0.22072(0)	0.21679(0)	0.63444(0)	110
H(222)	0.27900(0)	0.28135(0)	0.51724(0)	110
H(223)	0.242/6(0)	0.3/141(0)	0.62492(0)	
H(232)	-31694(0)	0.13317(0) 0.27430(0)	0.39371(0) 0.34400(0)	110
H(233)	11318(0)	0.20690(0)	0.32454(0)	110
()				
6				
Sn(1)	0.70996(2)	0.07460(2)	0.21133(2)	35
O(1)	0.6236(2)	0.2169(2)	0.1220(2)	46
O(2)	0.7009(2)	0.3920(3)	0.1905(2)	52
C(1)	0.6387(5)	-0.0/9/(4)	0.1251(4)	60
C(2)	0.0442(3)	0.1228(0)	0.3334(3) 0.1834(3)	67
C(3)	0.6361(3)	0.3417(3)	0.1308(3)	37
C(5)	0.5655(3)	0.4249(3)	0.0633(2)	31
C(6)	0.4828(3)	0.3656(4)	0.0092(3)	36
C(7)	0.5825(3)	0.5583(3)	0.0535(3)	37
H(11)	0.66387(0)	16311(0)	0.14925(0)	164
H(12)	0.56690(0)	07604(0)	0.1259/(0)	164
H(13) H(21)	0.05322(0) 0.67321(0)	00920(0)	0.00134(0) 0.38684(0)	164
H(22)	0.65731(0)	0.21347(0)	0.35114(0)	164
H(23)	0.57258(0)	0.10835(0)	0.32405(0)	164
H(31)	0.90632(0)	0.07507(0)	0.21872(0)	164
H(32)	0.86108(0)	0.12100(0)	0.11704(0)	164
H(33)	0.86914(0)	0.22032(0)	0.20173(0)	164
H(61)	0.47091(0)	0.27303(0)	0.01510(0)	164
н(/1)	0.63969(0)	0.29886(0)	0.09004(0)	164

thermal parameters  $U_{eq}$  are given in Table III\*, and bond lengths and bond angles in Table IV. The structures of these

\* Lists of the structure factors and anisotropic thermal parameters have been deposited with the editorial office of Recueil as Supplementary Publication No. Recl. 00. Copies may be obtained from editorial office Recueil, P.O. Box 90613, 2509 LP The Hague.

Table IV Bond distances (Å) and angles (°) with e.s.d.'s in parentheses.

 $a = 1 - x, \ 0.5 + y, \ -z$   $b = -x, \ -0.5 + y, \ 1 - z$ 

a = 1 - x, 1 - y, -zb = 1.5 - x, -0.5 + y, 0.5 - z

compounds are shown in Figures 1 and 2, and stereoviews (also demonstrating the unit cell) in Figures 3 and 4.

In both compounds each Sn atom has a distorted trigonal bipyramidal environment, three Me groups being only slightly shifted out of the equatorial plane (Table V). The apical positions are occupied by O atoms of asymmetrically bridging carboxylate groups. In this way each Me<sub>3</sub>Sn group links two dicarboxylate moieties, each of which in turn coordinates four Me<sub>3</sub>Sn units. The resulting two-dimensional polymer is composed of puckered rings, each containing four Me<sub>3</sub>Sn units, two 'internal' dicarboxylate moieties and two bridging carboxylate groups of 'external' dicarboxylate moieties. In the case of 1 the ring is 22-membered (Fig. 3), in the case of 6 26-membered (Fig. 4).

Some differences in the structures of 1 and 6 should be noted. The smaller size of ADC compared to that of TER allows a more dense packing in 1 (Table II). The molecular units of 1 are, in contrast to 6, unsymmetrical, the Sn atoms having slightly different environments. The C<sub>3</sub>Sn planes of 1



Fig. 2.  $(Me_3Sn)_2TER(6)$ : General view of a molecule, showing the atom numbering scheme. The symmetry code is given in Table IV.



Fig. 3. Stereoscopic view of a fragment of a layer in the crystal structure of 1, showing also the unit cell.

form an angle of  $8.3(6)^\circ$ , while in **6** these planes are coplanar. Also the angles formed by the planes of the C<sub>3</sub>Sn and CCOO units in **1** are different:  $67.7(5)^\circ$  and  $69.1(5)^\circ$ , respectively; the corresponding angles in **6** are identical and measure  $87.2(4)^\circ$  (Table V). Also a larger dihedral angle of the carboxylate groups is observed in **6** [23.2(4)°] than in **1** [10.1(5)°]. In **1** the distances between Sn(1) and O(11a) [3.150(4)Å] and between Sn(2) and O(21b) [3.154(4) Å] are appreciably shorter than the sum of the *van der Waals* radii (3.56Å<sup>18</sup>) suggesting a weak interaction. The corresponding distances in **6** are however a little larger [3.214(4) Å]; since the angle C(2)-Sn(1)-C(3) opposite to O(2) is enlarged, in 6 a weak interaction between Sn(1) and O(2) can not be excluded.

The structural data of the phenyl ring in **6** correspond fully to those reported for  $H_2 TER^{19}$  and  $Et_2 TER^{20}$ . However, the dihedral angle of the phenyl skeleton and the carboxylate group in **6** [11.6(3)°] is remarkably larger than in  $H_2 TER$ [5.2(5)°<sup>19</sup>] or in  $Et_2 TER$  (coplanar<sup>20</sup>). The distance C(15)-C(25) in **1** of 1.167(8) Å corresponds to the bond lengths of 1.168(2) Å and 1.174(2) Å observed in the free acid<sup>21,22</sup>.

Table V Equations of best planes, deviations from these planes (Å  $10^3$ ) and dihedral angles (°) of 1 and 6; e.s.d.'s in parentheses.

Equation of plane	Plane No	Atoms of plane and deviations	Dihedral angle
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	I II III IV	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	I/II 8.3(5) I/III 67.7(5) II/IV 69.1(5) III/IV 10.1(5)
$ \begin{array}{rcl} 6 & - 0.398x + 0.733y - 0.552z = & 4.790 \text{ \AA} \\ 0.751x - 0.022y - 0.660z = & -4.848 \text{ \AA} \\ 0.666x - 0.194y - 0.720z = & -3.430 \text{ \AA} \end{array} $	I II III	$\begin{array}{llllllllllllllllllllllllllllllllllll$	I/II 87.2(4) II/III 11.6(4)



Fig. 4. Stereoscopic view of fragments of layers in the crystal structure of 6, showing also the unit cell. The methyl groups bound to tin are omitted for clarity.

In the IR spectra of the title compounds the carboxylate bands are observed in the characteristic regions<sup>23</sup>:  $v_{as}(CO_2)$ between 1631 and 1555 cm<sup>-2</sup> and  $v_s(CO_2)$  between 1369 and 1298 cm<sup>-1</sup> (Table VI). On the basis of the difference  $\Delta v$  $[v_{as}(CO_2) - v_s(CO)_2]^{23}$  the compounds can be divided in two classes: the bis(triphenylmetal) terephthalates 7 and 9 and the bis(tetraphenylantimony) dicarboxylates 5 and 10 show high  $\Delta v$  values (between 283 and 333 cm<sup>-1</sup>), while all other compounds, including 1 and 6 show  $\Delta v$  values between 207 and 229 cm<sup>-1</sup> (Table VI). We therefore assume that the carboxylate bonding pattern in the compounds 2, 3, 4, and 8 is analogous to that in 1 and 6, in which according to the X-ray structure determination (see above) the carboxylate groups are bridging. In this context it should be noted that  $v_{as}(MC)$  and  $v_{s}(MC)$  are observed both in the IR and in the Raman spectra of the trimethyllead compound 8 (3 decomposes during Raman measurements) as well as in the spectra of both trimethyltin compounds 1 and 6, but  $v_{as}(MC)$  shows a higher intensity in the IR and  $v_s(MC)$  a higher intensity in the Raman spectrum (Table VI). This excludes a regular trigonal planar arrangement of the MC<sub>3</sub> skeleton and therefore also unidentate carboxylate bonding.

The strikingly higher  $\Delta v$  values for 5, 7, 9 and 10 are an indication of a carboxylate bonding different from that in the compounds 1 to 4, 6 and 8. Since in acetates unidentate carboxylate groups show distinctly higher  $\Delta v$  values than bidentate carboxylate groups<sup>23</sup> we propose that in 5, 7, 9 and 10 unidentate carboxylate groups are present. This would imply that the central atom Sb in 5 and 10 is pentacoordinated, in agreement with previous findings that hexacoordination of Sb in tetraorganoantimony carboxylates is unusual<sup>4,24</sup>. The structural differences between the triphenylmetal derivatives 2 and 4 (bridging COO groups) and 7 and 9 (unidentate COO groups) in the solid state might be correlated with the assumption<sup>25</sup> that  $\alpha$ -substitution in carboxylate ligands is to a large extent responsible for the preference of unidentate bonding of the COO group in such cases.

The correlation of a bridging type of carboxylate bonding with a  $\Delta v$  value higher than 200 cm<sup>-1</sup> needs a short comment. A very thorough comparison of vibrational spectra of acetates of which X-ray structure determinations were available<sup>23</sup> demonstrated that compounds with bridging carboxylate groups exhibit  $\Delta v$  values below about 200 cm<sup>-1</sup>, while those with unidentate acetate ligands have

Table VI Characteristic IR frequencies for  $(R_3M)_2X$  (M = Sn, Pb; R = Me, Ph; X = ADC, TER, DTT),  $(Ph_4Sb)_2X$  (X = ADC, TER),  $K_2ADC$  and  $K_2TER$  (in  $cm^{-1}$ ).

Compound	$v_{as}(CO_2)$	v <sub>s</sub> (CO <sub>2</sub> )	$\Delta v(CO_2)$	v <sub>as</sub> (MC) <sup>a</sup>	v <sub>s</sub> (MC) <sup>a</sup>
1 <sup>b</sup>	1596s/1582s	1363s,br	226°	555m [555m]	519m [530w, 525vs]
2	1560vs	1350s	210		)
3 <sup>d</sup>	1586s/1570vs	1349s	229°	500s <sup>[e]</sup>	470vw <sup>[e]</sup>
4	1555s	1339s	216		<b>,</b>
5	1631vs	1298s	333		
K <sub>2</sub> ADC	1620vs	1368s	252		
6	1595vs/1582vs	1368vs	221°	<sup>f</sup> [550w]	f [518vs]
7	1630vs	1339s	291		
8	1582vs/1570vs	1369vs	207°	498m [495w]	470vw [470vs]
9	1620vs	1337vs	283		
10	1630vs	1310vs	320		
K,TER	1575vs	1395vs	180		
11	(1619vs) <sup>8</sup>	(898vs) <sup>h</sup>	-	540m [540m]	518w [520s]
12	(1618vs) <sup>8</sup>	(893vs) <sup>h</sup>	-		
13	(1595vs) <sup>8</sup>	(910vs) <sup>h</sup>	-	494m [495w]	468vw [470vs]
14	(1612vs) <sup>8</sup>	(892vs) <sup>h</sup>	-		

<sup>a</sup> Raman frequencies in []. <sup>b</sup>  $v(C \equiv C)$  2380 cm<sup>-1</sup>. <sup>c</sup> Mean value. <sup>d</sup>  $v(C \equiv C)$  2305 cm<sup>-1</sup>. <sup>e</sup> Decomposition during measurement. <sup>f</sup> Overlapping bands. <sup>g</sup> v(C=O). <sup>h</sup> v(CS).

higher  $\Delta v$  values. The study of the present compounds and similar observations on triorganotin and triorganolead methyl oxalates<sup>26</sup> show, however, that the limiting  $\Delta v$  value for bridging and unidentate COO groups in dicarboxylates is higher than in acetates, possibly at or slightly above 230 cm<sup>-1</sup>. It also should be emphasized that the structural classification of acetates on the basis of  $\Delta v$  values<sup>23</sup> cannot be generalized for predicting bonding types of carboxylate groups in derivatives of other carboxylic acids other than acetic acid.

The appearance of  $v(C\equiv C)$  in the IR spectra of 1 and 3 (Table VI) gives weight to the proposal that both compounds have analogous structures. Moreover, it indicates a lowering in symmetry of the ADC moiety. This is in accordance with the finding that two different carboxylate groups are present in 1 (see above). In the other H<sub>2</sub>ADC derivatives  $v(C\equiv C)$  was not observed, suggesting a higher symmetry of the ADC link of the phenylmetal groups. The fact that in the spectra of the compounds 2, 4 and 5 - in contrast to 1 and 3 -  $v_{as}(CO_2)$  and  $v_s(CO_2)$  are not split, points in the same direction. In the case of 5, in which unidentate carboxylate groups are assumed (see above), the absence of  $v(C\equiv C)$  might possibly indicate *anti* configuration of the two COOSbPh<sub>4</sub> ligands attached to the ethynyl group.

The IR absorptions of the H<sub>2</sub>DTT derivatives 11 to 14 between 1619 and 1595 cm<sup>-1</sup> (Table VI) can be assigned to v(C=O) and those between 910 and 892 cm<sup>-1</sup> to  $v(C-S)^{27}$ . Since no absorptions appear in the ranges characteristic for v(C-O) or  $v(C=S)^{28}$ , bonding of  $R_3M$  to S and not to O of the thiocarboxylate group can be safely assumed. This would be consistent with findings for some trimethyltin thioxarboxylates  $Me_3SnSC(O)C_6H_4X^{27}$ . The slightly lower value of v(C=O) and the slightly higher value of v(C-S) in the spectrum of 13 compared to the values for 11, 12 and 14 should indicate differences in the structures of these compounds. Additionally, the intensities of v(MC) of 13 in the IR and Raman spectra are distinctly different from those of 11 (Table VI). These observations would be consistent with the assumption that in 11, 12 and 14 the central atoms have tetrahedral configuration and unidentate M-S bonding, while in 13 additional coordination of O(carboxyl) to Pb and appropriate adjustment of the Me<sub>3</sub>Pb moiety in the direction of a trigonal bipyramid occurs.

It was possible to prepare solutions of 5 and 10 to 14 in  $CHCl_3$  of a sufficiently high concentration for IR measurements. The spectra, except that of 13, were not significantly

different from the solid-state spectra, and therefore we assume 5, 10 to 12 and 14 to be present in solution as molecular species in which the organometal moiety is tetrahedral and ADC or DTT, respectively, bond unidentately. In the spectrum of 13, v(C=O) is shifted to 1615 cm<sup>-1</sup> and v(C-S) to 896 cm<sup>-1</sup>, corresponding to the appropriate band positions found for 11, 12 and 14. We therefore assume that 13 dissociates on dissolution in CHCl<sub>3</sub> to form species which are structured like those of 11, 12 and 14.

Results of <sup>1</sup>H NMR measurements in CDCl<sub>3</sub> are consistent with this interpretation. The coupling constants  ${}^{2}J(MH)$  of 11 and 13 (Table VII) are in the range of tetracoordinated species<sup>29,30</sup>. The same is true for 1. The data in Table VII demonstrate furthermore that the  $\delta$  values shift to a higher field and the  ${}^{2}J(SnH)$  values increase when CDCl<sub>3</sub> is substituted by  $CD_3OD$  or DMSO- $d_6$ , indicating an increase in the coordination number with increasing donor strength of the solvent. From the coupling constants  ${}^{2}J(SnH)$  of 1 obtained from solutions of 1 in the above solvents the scharacter of the Sn-C bonds is calculated<sup>30</sup> to be 27.7 in CDCl<sub>3</sub>, 30.9 in CD<sub>3</sub>OD and 32.0% in DMSO-d<sub>6</sub>, corresponding to transition from tetrahedral to trigonalbipyramidal coordination of Sn by increasing coordination of solvent molecules. The values of  ${}^{2}J(PbH)$  of 3 and 8 of 83.2 and 84.0 Hz, respectively, obtained in DMSO- $d_{6}$  also correspond to established values of solutes with pentacoordinated Pb<sup>29</sup>. Considering the lower value of  ${}^{2}J(PbH)$ of 8 in CD<sub>3</sub>OD (80.0 Hz) a relationship between solvent donor strength and coordination analogous to that in the Me<sub>3</sub>Sn derivatives is proposed.

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Table VII <sup>1</sup>H NMR chemical shift data (in ppm) of the title compounds in different solvents.

Compound	$\delta(CH_3 - M)$	$\delta(-C_6H_4-)$	$^{2}J(\mathrm{M}^{1}\mathrm{H})$	Solvent <sup>a</sup>	Compound	$\delta(C_6H_5)  \delta(-C_6H_4-)$	Solvent <sup>a</sup>
1	0.40 s	-	69.0	A	2	7.8–7.1 m –	Α
	0.54 s	-	67.6	B			
	0.60 s	-	63.6	C	4	7.9–7.0 m –	A
3	1.38 s	-	83.2	A	5	7.9–7.2 m –	A
6	0.46 s	7.96 s	69.3	A	10	7.9 – 7.0 m	A
	0.52 s	8.32 s	66.4	В			
8	1.34 s	7.55 s	84.0	A	12	8.6 – 7.6 m	С
	1.44 s	8.03 s	80.0	В	}		
11	0.91 s	8.40 s	68.0	Α	14	7.6 – 8.7 m	С
	0.54 s	8.00 s	62.0	В	]		
	1.02 s	8.55 s	58.0	С			
13	1.71 s	8.33 s	65.0	С			

<sup>a</sup> A = DMSO- $d_6$ , B = CD<sub>3</sub>OD, C = CDCl<sub>3</sub>.

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