Journal of Organometallic Chemistry, 290 (1985) 41–51
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

INVESTIGATIONS ON ORGANOTIN, ORGANOLEAD, LEAD(IV), AND LEAD(II) DITHIOLATES

KARIN GRÄTZ, FRIEDO HUBER,

Lehrstuhl für Anorganische Chemie II, Universität Dortmund, Postfach 500 500, D-4600 Dortmund 50 (F.R.G.)

ARTURO SILVESTRI, GIUSEPPE ALONZO and RENATO BARBIERI

Gruppo di Chimica dei Composti Organometallici, Istituto di Chimica Generale, Università di Palermo, 26-28, Via Archirafi, I-90123 Palermo (Italy)

(Received January 29th, 1985)

Summary

Bis(triorganometal) 1,2-dithiolates $(R_3M)_2S_2R'$ [$(HS)_2R' = C_7H_8S_2$ for toluene-dithiol-3,4 (H_2TDT); M = Sn, Pb; R = Ph; or $(HS)_2R' = C_{10}H_{14}S_2$ for 1,2-dimethyl-4,5-bis(mercaptomethyl)benzene (H_2DBB); M = Sn, R = CH_3, C_6H_5; M = Pb, R = C_6H_5], diorganometal 1,2-dithiolates R_2MS_2R' [$(HS)_2R' = C_6H_6S_2$ for 1,2-dimercaptobenzene (H_2DMB); M = Pb, R = CH_3, C_2H_5, C_6H_5; or $(HS)_2R' = H_2TDT$; M = Sn, R = CH_3, C_6H_5; M = Pb, R = C_6H_5; or $(HS)_2R' = H_2DBB$; M = Sn, R = CH_3, C_6H_5; M = Pb, R = CH_3, C_2H_5, C_6H_5; or $(HS)_2R' = C_8H_6N_2S_2$ for 2,3-dimercaptoquinoxaline (H_2QDT); M = Pb, R = C_6H_5] and some lead(IV) and lead(II) dithiolates $Pb(S_2R')_n$ [$(HS)_2R' = H_2DMB$, $n = 2$; $(HS)_2R' = H_2TDT$, $n = 2$; $(HS)_2R' = H_2DBB$, $n = 1$ or 2] have been prepared. Vibrational, ^1H NMR, and Mössbauer spectroscopic data are consistent with pentacoordination of tin in R_2SnTDT and with tetracoordination of tin in R_2SnS_2R' and $(R_3Sn)_2S_2R'$ in the solid state. The soluble compounds are monomeric in solution. Coupling constants for the methyltin compounds indicate tetracoordination in solution.

Introduction

Knowledge of organotin and organolead derivatives of aromatic dithiols is limited to some derivatives of 3,4-toluenedithiol (H_2TDT): R_2MTDT (M = Sn, Pb; R = Me, Ph) [1–5], and various N-donor [2] adducts and halide complexes of R_2SnTDT [6]. We were only recently able to prepare and characterize the first 1,3-dithiolates $(R_3M)_2(C_6H_3XS_2)$ and $R_2M(C_6H_3XS_2)$ (M = Sn, Pb; X = H, Cl) [7,8]. As a continuation of this work, and as part of our investigations of organometal derivatives of oligofunctional compounds, we synthesized triorganotin and triorganolead

0022-328X/85/$03.30

TABLE 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR ORGANOMETAL, LEAD(IV), AND LEAD(II) DITHIOLATES

[$C_7H_8S_2$ = toluenedithiol-3,4 (H_2TDT); $C_6H_6S_2$ = 1,2-dimercaptobenzene (H_2DMB); $C_{10}H_{14}S_2$ = 1,2-dimethyl-4,5-bis(mercaptomethyl)benzene (H_2DBB); $C_8H_6N_2S_2$ = 2,3-dimercaptoquinoxaline (H_2QDT)]

Compound	M.p. (°C)	Method	Yield (%)	Analysis (Found (calcd.) (%))			Molecular weight [a] (Found (calcd.))	Solvent [b]
				C	H	Pb		
$Me_2Sn(C_7H_6S_2)$	110	1	46	35.66	3.86	–	310	CH_2Cl_2
$C_9H_{12}S_2Sn$				(35.66)	(3.96)		(303)	
$Ph_2Sn(C_7H_6S_2)$	153–154	1	44	53.24	3.89	–	424	CH_2Cl_2
$C_{19}H_{16}S_2Sn$				(53.42)	(3.75)		(427)	
$Me_2Sn(C_{10}H_{12}S_2)$	114	1	77	41.2	5.2	–	347	$CHCl_3$
$C_{12}H_{18}S_2Sn$				(41.77)	(5.26)		(345)	
$(Me_3Sn)_2(C_{10}H_{12}S_2)$	43–44	3	38	36.80	5.80	–	526	$CHCl_3$
$C_{16}H_{30}S_2Sn_2$				(36.68)	(5.77)		(523)	
$Ph_2Sn(C_{10}H_{12}S_2)$	178–183	1/2	79	56.35	4.85	–	465	acetone
$C_{22}H_{22}S_2Sn$				(56.31)	(4.73)		(469)	
$(Ph_3Sn)_2(C_7H_6S_2)$	111	3	79	60.40	4.40	–	835	$CHCl_3$
$C_{43}H_{36}S_2Sn_2$				(60.45)	(4.25)		(854)	
$(Ph_3Sn)_2(C_{10}H_{12}S_2)$	73	3	79	61.20	4.75	–	895	$CHCl_3$
$C_{46}H_{42}S_2Sn_2$				(61.64)	(4.72)		(896)	
$Me_2Pb(C_6H_4S_2)$	180–250 [c]	4	67	25.53	2.20	54.8	371	acetone
$C_8H_{10}PbS_2$				(25.45)	(2.67)	(54.89)	(377.5)	
$Me_2Pb(C_{10}H_{12}S_2)$	110–112 [d]	4	68	33.37	4.26	47.6	435	$CHCl_3$

$C_{12}H_{18}PbS_2$				(33.24)	(4.18)	(47.78)	(433.6)	
$Et_2Pb(C_6H_4S_2)$	180–250 [c]	4	70	29.67	3.36	51.0	401	acetone
$C_{10}H_{14}PbS_2$				(29.62)	(3.48)	(51.09)	(405.5)	
$Et_2Pb(C_{10}H_{12}S_2)$	92–94 [d]	4	67	36.24	4.68	44.6	491	$CHCl_3$
$C_{14}H_{22}PbS_2$				(36.42)	(4.80)	(44.88)	(461.7)	
$Ph_2Pb(C_6H_4S_2)$	151 [d]	4	82	43.14	3.08	41.3	526, 516	$CHCl_3$, acetone
$C_{18}H_{14}PbS_2$				(43.10)	(2.81)	(41.31)	(501.6)	
$Ph_2Pb(C_7H_6S_2)$	154–155 [e]	4	86	44.17	3.23	40.1	521, 524	$CHCl_3$, acetone
$C_{19}H_{16}PbS_2$				(44.26)	(3.13)	(40.18)	(515.7)	
$Ph_2Pb(C_{10}H_{12}S_2)$	110–112 [e]	4	81	47.23	3.92	37.2	559	$CHCl_3$
$C_{22}H_{22}PbS_2$				(47.38)	(3.98)	(37.14)	(558)	
$(Ph_3Pb)_2(C_7H_6S_2)$	142–144	4/3	90	50.44	3.84	40.1	968	acetone
$C_{43}H_{36}Pb_2S_2$				(50.08)	(3.52)	(40.18)	(1031.3)	
$(Ph_3Pb)_2(C_{10}H_{12}S_2)$	92	4/3	78	51.25	4.06	38.4	1073	$CHCl_3$
$C_{46}H_{42}Pb_2S_2$				(51.48)	(3.94)	(38.61)	(1073.4)	
$Ph_2Pb(C_8H_4N_2S_2)$ [f]	198 [d]	4	76	44.00	2.60	37.3	536	DMSO
$C_{20}H_{14}N_2PbS_2$				(43.39)	(2.55)	(37.42)	(557.7)	
$Pb(C_6H_4S_2)_2$	250 [c]	4	89	28.36	1.78	43.0	[g]	
$C_{12}H_8PbS_4$				(29.56)	(1.65)	(42.49)		
$Pb(C_7H_6S_2)_2$	250 [c]	4	80	33.00	2.28	40.1	[g]	
$C_{14}H_{12}PbS_4$				(32.61)	(2.35)	(40.18)		
$Pb(C_{10}H_{12}S_2)_2$	113–127 [d]	4	75	39.95	4.05	35.5	[g]	
$C_{20}H_{24}PbS_4$				(40.01)	(4.03)	(34.54)		
$Pb(C_{10}H_{12}S_2)$	141 [e]	4	65	29.71	3.22	51.3	[g]	
$C_{10}H_{12}PbS_2$				(29.76)	(3.00)	(51.35)		

[a] Determined osmometrically in $CHCl_3$, CH_2Cl_2, CCl_4, benzene, and acetone at 37°C, in DMSO at 90°C. [b] Solvent for molecular weight measurements. [c] Thermochromic effect. [d] Decomposition. [e] Decomposition prior to melting. [f] % N 5.10 (5.06). [g] Not measurable.

1,2-dithiolates, which had not previously been mentioned in the literature. These along with the first examples of some other unknown types of compounds, namely organolead and organotin derivatives of 1,2-dimethyl-4,5-bis(mercaptomethyl)benzene (H_2DBB) and diphenyllead quinoxaline-2,3-dithiolate (Ph_2PbQDT) [2,3-dimercaptoquinoxaline: H_2QDT] are described below, as well as some other new diorganolead 1,2-dithiolates. We have also made some lead(IV) and lead(II) dithiolates. The 3,4-toluenedithiolates $M(TDT)_2$ and related compounds (M = Sn, Pb) [2,3,6,9,10] and PbTDT [11] have been studied before.

Results and discussion

The compounds studied are listed in Table 1 along with the methods of preparation, yields, analytical data, molecular weights, and melting points. The lead compounds are conveniently obtained by ligand exchange starting from the appropriate organolead acetate, lead(IV) acetate, or lead(II) acetate and the dithiols. The acetate R_3PbOAc (R = Me, Et) reacted with H_2DBB at −10 to 30°C in acetone, but only decomposition products could be isolated. Reaction of R_3PbOAc and H_2DMB (H_2DMB = 1,2-dimercaptobenzene) under the same conditions occurred only to a minor extent. The yellow reaction product decomposed upon attempted isolation. Ph_2SnDBB was obtained when freshly prepared diphenyltin oxide was treated immediately with H_2DBB. The alkali chloride method was used to prepare R_2SnTDT (R = Me, Ph) [2] and Me_2SnDBB. During all the procedures in the preparation of organolead dithiolates light had to be excluded and reactions had to be performed at or below 0°C. The sensitivity of dithiols to oxidants must always be borne in mind. All organotin dithiolates prepared in this work are colorless. The lead(IV) and lead(II) dithiolates are yellow to orange, and the organolead dithiolates are yellow, except for $(Ph_3Pb)_2$DBB which separates after its preparation as white crystals, which turn yellow on exposure to light. The organolead derivatives must be stored at low temperature. Most of them decompose on or before melting. No conclusions regarding definite steps of thermal decomposition could be drawn from DTA/TG measurements.

The organotin dithiolates, the dialkyllead derivatives of H_2DBB and H_2DMB, and the phenyllead dithiolates with the exception of Ph_2PbQDT are soluble in $CHCl_3$ and/or acetone. In such solutions they are monomeric (see Table 1). R_2PbDMB (R = Me, Et) undergoes aging, and after some days it dissolves completely in DMSO only at about 90°C. Ph_2PbQDT also is soluble in DMSO, and is monomeric in this solvent. The dialkyllead derivatives of H_2TDT requires a temperature of 90°C for dissolution in DMSO, and decomposition occurs at this temperature. The lead(II) and the lead(IV) dithiolates are insoluble in common organic solvents, but the lead(IV) dithiolates show some solubility in pyridine. All the compounds are insoluble in water and under normal conditions no hydrolysis occurs.

The IR and Raman data are listed in Table 2. The Raman spectra of some lead and organolead dithiolates could not be measured because of the deep color or decomposition. The ν(SH) band was missing in all the spectra. Frequencies in the range 280–380 cm^{-1} can be assigned to ν(MS) [12–15]. Except for ν(CS) the characteristic absorptions of the organic groups at M and of the dithiolate ligands were practically unchanged in the products compared with those of the appropriate

TABLE 2

VIBRATION SPECTRAL DATA FOR ORGANOMETAL, LEAD(IV), AND LEAD(II) DITHIOLATES (cm^{-1})

[Raman data in parentheses; formula abbreviations see Table 1]

Compound	ν(C–S)	ν_{as}(M–Y) [a]	ν_s(M–Y) [a]		ν(M–S)	
$C_6H_6S_2$ (H_2DMB)	660	–	–		–	
Me_2PbDMB [b]	656	–[c]	463w	355	345	
Et_2PbDMB [b]	–[d]	473	460, 430	355	340	298
Ph_2PbDMB	650	–[e]	–[e]		350	
	(642)	(235)	(205)		(351)	
$Pb(DMB)_2$	658	–	–		356	
	(657)	–	–			(276)
$C_7H_8S_2$ (H_2TDT)	687	–	–		–	
	(690)	–	–		–	
Me_2SnTDT	637	555s	524vs	376	335	310
	(635)	(548)m	(523)vvs	(369)	(330)	(310)
Ph_2SnTDT	678	287	–[e]	358	338	311
	(661)	(270)	(222)	(370)	(342)	(322)
$(Ph_3Sn)_2$TDT	660	265	–[e]	375	363	335
	(658)	(267)	(222)	(375)	(363)	(338)
Ph_2PbTDT	631	–[e]	–[e]	352		312
	(640)	(235)	(205)	(350)		(315)
$(Ph_3Pb)_2$TDT	617	–[e]	–[e]	350		
	(640)	(225)	(200)	(350)		(305)
$Pb(TDT)_2$	635	–	–		369	
						(320)
$C_{10}H_{14}S$ (H_2DBB)	678	–	–		–	
Me_2SnDBB	688	548s	527s		345	
	(688)	(544)m	(525)vs		(333)	
$(Me_3Sn)_2$DBB	653	538vs	513s	363	344sh	
	(675)	(538)vvs	(513)m	(363)	(345)	(332)
Ph_2SnDBB	630	265	–[e]	365	345	
	(660)	(263)	(225)	(360)	(345)	
$(Ph_3Sn)_2$DBB	662	268	–[e]		340	
	(658)	(265)	(217)		(345)	(310)
Me_2PbDBB [b]	628	499s	462s	365	333	298
Et_2PbDBB	665	478	448		339	298
	–[d]	(480)	(450)			(297)
Ph_2PbDBB	677	–[e]	–[e]	355	322	290
	(645)	(224)	(207)		(315)	(292)
$(Ph_3Pb)_2$DBB	675	225	210		310	
	(645)	(224)	(210)		(309)	(298)
$Pb(DBB)_2$	678	–	–		355	
	(680)					(300)
PbDBB [b]	682	–	–		390	
$C_8H_6N_2S_2$ (H_2QDT) [f]	658	–	–		–	
Ph_2PbQDT [g]	644	–[e]	–[e]		–[d]	
	(642)	(235)	(208)	(324–300) br		

[a] Y = CH_3, C_6H_5. [b] Decomposed in laser beam during Raman measurements. [c] Superimposed by ligand vibrations. [d] No assignment made due to low intensity in the appropriate range. [e] Not observable. [f] ν(C–N) 1259 cm^{-1}. [g] ν(C–N) 1270 (1267) cm^{-1}.

dithiolate educt. Modes ν(CS) were more or less shifted to lower wave numbers (see Table 2). From these observations complete reaction of the SH groups of the dithiol substrates and formation of M–S bonds (M = Sn, Pb) could be inferred.

The IR and Raman bands of solid H_2QDT at 3110 and 3090 cm^{-1}, and at 1630 and 1610 cm^{-1}, respectively, can be assigned, following ref. 16, to ν(NH) and δ(NH). These absorptions are missing in the spectra of solid Ph_2PbQDT, but there is a broad Raman band at 300–325 cm^{-1}, which can be assigned to ν(Pb–S) [14,15]. From these observations it can be concluded that QDT^{2-} is bonded in its enol-form [16] to the diphenyllead moiety through the S atoms. Further evidence for this comes from the shift of ν(CN) to higher and of ν(CS) to lower wave numbers. This type of bonding is consistent with the high affinity of sulfur to lead.

The values of the nuclear quadrupole splitting parameters ΔE_{exp}, shown in Table 3, strongly suggest that our organotin(IV) dithiolates fall into two structurally distinct classes: (i) R_2SnTDT; (ii) R_2SnDBB, $(R_3Sn)_2DBB$ and $(Ph_3Sn)_2TDT$.

A solid state trigonal bipyramidal polymeric structure with bridging sulfur atoms, such as I in Fig. 1, has, in fact, been previously assigned [17] to R_2SnTDT (R = Me, Ph) on the basis of the X-ray crystal and molecular structure of the homologous compound Me_2Sn-ethane-1,2-dithiolate [21,22] as well as of the calculated point-charge model values of ΔE for a series of R_2Sn^{IV} dithiolates [17]. In the latter context, tetrahedral type structures II, Fig. 1, can be excluded in view of the values of ΔE_{calcd} shown in Table 3.

TABLE 3

EXPERIMENTAL AND CALCULATED MÖSSBAUER PARAMETERS FOR ORGANOTIN(IV) DITHIOLATES [a]

Compound [b]	δ [c] ($mm\ s^{-1}$)	ΔE_{exp} [d] ($mm\ s^{-1}$)	Ref.	ΔE_{calcd} [e] ($mm\ s^{-1}$)	Structure (see Fig. 1)	Ref.
Me_2Sn TDT	1.39	2.62	2	−2.33	I	17
				(±)1.88	II	4
Ph_2Sn TDT	1.36	1.93	2	−1.95	I	17
	1.36	1.99	4	(±)1.63	II	4
Me_2Sn DBB	1.37	1.68	this work	−2.33	I	17
				(±)2.04	II	4
$(Me_3Sn)_2$ DBB	1.32	1.69	this work	1.75; 1.80 [f]	III	4
				−2.67	IV	this work
Ph_2Sn DBB	1.30	1.27	this work	−1.95	I	17
				(±)1.75	II	4
$(Ph_3Sn)_2$ TDT	1.31	1.49	this work	−1.42	III	7
				−2.22	IV	this work
$(Ph_3Sn)_2$ DBB	1.33	1.34	this work	−1.54	III	this work
				−2.22	IV	this work

[a] The experimental parameters were determined at 77 K. The absorber sample thickness was in the range 0.4–0.9 mg $^{119}Sn\ cm^{-2}$. Full widths at half-height of the resonance peaks are about 0.9 $mm\ s^{-1}$. [b] $C_7H_6S_2 = TDT^{2-}$; $C_{10}H_{12}S_2 = DBB^{2-}$. [c] Isomer shift with respect to room temperature SnO_2 or $CaSnO_3$. [d] Experimental nuclear quadrupole splitting. [e] Calculated point-charge model values [19]. The following partial quadrupole splitting parameters, pqs, $mm\ s^{-1}$, have been employed [4,17–20]: Structures I and IV (Fig. 1): $\{Alk\}^{tbe} = -1.13$; $\{Ph\}^{tbe} = -0.98$; $\{S\}^{tba}_{bridging} = -0.18$; $\{S\}^{tbe} = -0.60$ (tba = trigonal bipyramidal apical; tbe = trigonal bipyramidal equatorial). Structures II and III: $([Alk]\text{-}[hal])^{tet} = -1.37$; $([Ph]\text{-}[hal])^{tet} = -1.26$; $([S\text{-}Alk]\text{-}[hal])^{tet} = -0.49$; $([S\text{-}Ph]\text{-}[hal])^{tet} = -0.55$. [f] Experimental data used in the estimation of pqs values $([S\text{-}Alk]\text{-}[hal])^{tet}$ [4].

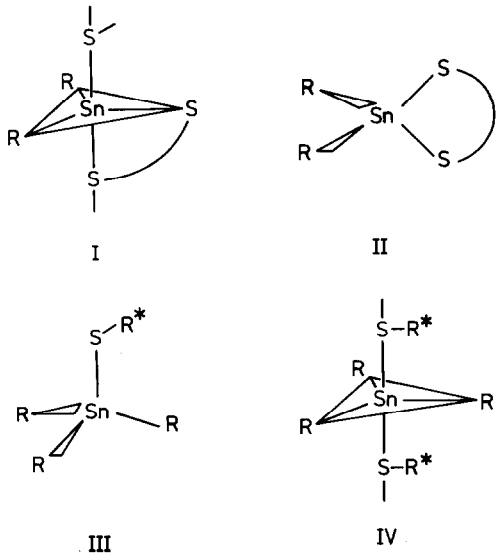


Fig. 1. Regular structures of tin sites in organotin(IV) complexes of dithiolates assumed in point-charge model calculations of the nuclear quadrupole splittings ΔE_{calcd} (Tab. 3).

The ΔE_{exp} data for Me_2SnDBB, $(R_3Sn)_2DBB$ (R = Me, Ph) and $(Ph_3Sn)_2TDT$ agree well with the corresponding values [7] of a series of tetrahedral $Alk_2Sn(SAlk)_2$, $R_3SnSAlk$ and Ph_3SnSPh compounds. In comparison with these values, ΔE_{exp} for Ph_2SnDBB would appear to be particularly low, but it is clearly consistent with a tetrahedral type C_2SnS_2 configuration.

The point-charge model treatment of ΔE parameters confirms the presence of tetrahedral tin environments of type III, Fig. 1, for $(R_3Sn)_2DBB$ and $(Ph_3Sn)_2TDT$ in view of the excellent agreement between the values of ΔE_{exp} and ΔE_{calcd} in Table 3, while excluding [18] the (in principle) possible trigonal bipyramidal structure IV. As far as the R_2SnDBB complexes are concerned the tetrahedral structure II can be definitely assigned to the dimethyltin complex for the same reasons [18], and must be preferred for the diphenyltin complex in view of the better agreement of its ΔE_{exp} value with the corresponding ΔE_{calcd} value; the tbp structure I is excluded in both cases (see Table 3).

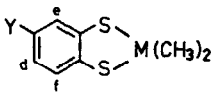
The isomer shift data, δ, for the compounds listed in Table 3 seem to be practically independent of whether the assigned structures are trigonal bipyramidal or tetrahedral (vide supra), and essentially correspond to the respective δ data for tetrahedral $R_2Sn(SR')_2$ and R_3SnSR' compounds [7]. This suggests that two bridging sulfur atoms (in R_2SnTDT, structure I) and one terminal sulfur (in $R_2Sn(SR')_2$, structure II) have comparable effects in determining the *s*-electron density at the tin nucleus.

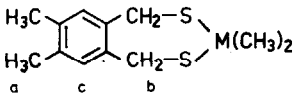
The ^1H NMR spectra of all the organometal compounds prepared in this investigation show no SH signals. Chemical shifts and coupling constants $^2J(^{119}Sn^1H)$ and $^2J(^{207}Pb^1H)$ of methylmetal derivatives are listed in Table 4. In all cases the integration ratio was as expected: the R_3M/dithiolate ratio is 2/1 for the bis(triorganometal) derivatives, and the R_2M/dithiolate ratio is 1/1 for the diorganometal derivatives.

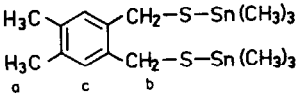
TABLE 4

^{1}H NMR DATA FOR METHYLMETAL DITHIOLATES; CHEMICAL SHIFTS δ(ppm) AND COUPLING CONSTANTS $^2J(^{119}Sn^1H)$ AND $^2J(^{207}Pb^1H)$ (Hz)

(Formula abbreviations see Table 1)







Compound	Y [a]	δ(Y)	δ(SH)	δ(MCH$_3$)	δ(a)	δ(b)	δ(c)	δ(d)*	δ(e)	δ(f)	^2J	Solvent
H_2TDT	CH_3	2.22	3.51	–	–	–	–	6.88	7.22	7.26	–	$CDCl_3$
			3.69									
Me_2Sn TDT	CH_3	2.20	–	0.96	–	–	–	6.57	7.11	7.20	60	$CDCl_3$
H_2DMB	H*	6.93–7.18	4.31	–	–	–	–	6.93–7.18	7.29–7.51		–	$CDCl_3$
Me_2Pb DMB	H*	6.64–6.80	–	0.98	–	–	–	6.64–6.80	7.22–7.38		94	DMSO-d_6
H_2DBB	–	–	1.84	–	2.23	3.79	7.04	–	–	–	–	$(CD_3)_2CO$
Me_2Sn DBB	–	–	–	0.22	2.14	3.92	6.93	–	–	–	66	DMSO-d_6
	–	–	–	0.24	2.20	3.96	7.06	–	–	–	61	$CDCl_3$
$(Me_3Sn)_2$ DBB	–	–	–	0.38	2.18	3.87	6.91	–	–	–	56	$CDCl_3$
				0.33	2.11	3.73	6.84				58	DMSO-d_6
Me_2Pb DBB	–	–	–	1.13	2.19	4.14	7.03	–	–	–	82	$(CD_3)_2CO$

[a] H* = Equivalent to H_d.

In the organolead derivatives of H_2DBB there is a significant low field shift of the signals of the CH_2 protons in DBB^{2-}, the deshielding being largest in Ph_2PbDBB [$\delta(CH_2)$(in $CDCl_3$) 4.31 ppm; $\delta(CH_2)$ of H_2DBB 3.79 ppm], with respect to Alk_2PbDBB [Alk = Me, Et; $\delta(CH_2)$ (in acetone-d_6) 4.14, 4.24 ppm]. The relevant chemical shift value of $(Ph_3Pb)_2DBB$ was found to be δ 4.00 ppm (in $CDCl_3$). The diorganotin compounds R_2SnDBB [R = Me, Ph; $\delta(CH_2)$ (in $CDCl_3$) 3.96, 3.98 ppm] also show a low field shift, though markedly less than that for R_2PbDBB, and in contrast to the lead compounds there is practically no difference between Me_2SnDBB and Ph_2SnDBB. The complexity of the various factors determining the chemical shift $\delta(CH_2)$ is also demonstrated by the triorganotin species $(R_3Sn)_2DBB$ [R = Me, Ph; $\delta(CH_2)$ (in $CDCl_3$) 3.87, 3.78 ppm]: the methyl compound, like Me_2SnDBB, shows a distinct, though small low field shift with respect to H_2DBB, while $\delta(CH_2)$ for the diphenyltin derivative is practically the same as in H_2DBB.

Coupling constants $^2J(^{119}Sn^1H)$ for Me_2SnTDT, Me_2SnDBB and $(Me_3Sn)_2DBB$ in $CDCl_3$ solution are in the range 56 to 61 Hz (Table 4), and correspond to those for other tetracoordinated organotin dithiolates [7]. ^1H NMR spectra of the methyllead derivatives could not be measured in non-coordinating solvents because of insolubility. From a comparison of the coupling constants $^2J(^{207}Pb^1H)$ for dimethyllead 1,3-dithiolates [7] and Me_2PbTDT [5] with those for Me_2PbDMB in DMSO-d_6 and Me_2PbDBB in $(CD_3)_2CO$, it is inferred that coordination in all these compounds is greater than four.

Experimental

Because of their thermal instability the lead derivatives were prepared in anhydrous solvents under argon with exclusion of light at -10 to $-70°C$.

The dithiols were treated with the appropriate diorganometal compounds or lead(II) acetate in 1/1 molar ratio, with the triorganometal compounds in 1/2 molar ratio, and with lead(IV) acetate in 2/1 molar ratio. Lead was determined complexometrically, IR spectra (CsBr, Nujol) were recorded on Perkin–Elmer grating spectrometers PE 457 and PE 580B, Raman spectra on a Coderg laser Raman spectrometer PHO (λ 488 nm; 647.1 nm), and ^1H NMR spectra on a Perkin–Elmer 90 MHz spectrometer R 32 at 37°C. The Mössbauer spectra were obtained as previously described [23]. A $Ca^{119}SnO_3$ source from the Radiochemical Centre, Amersham (G.B.) was used, moving at room temperature with constant acceleration and triangular waveform. The compounds listed in Table 1 were prepared by one or more of the following procedures.

Procedure 1

A mixture of 0.3 g KOH in 10 ml methanol and 2.5 mmol dithiol in 10 ml methanol was homogenized by shaking at room temperature, and the pH value was adjusted to 7 if necessary by addition of 2 *N* hydrochloric acid. Solutions of suspensions of 2.5 mmol R_2SnCl_2 (R = Me, Ph) in 10 ml water were added during 0.5 h with vigorous stirring. A white crystalline precipitate separated immediately. After 1 h the precipitate was filtered off, washed with water, dried in vacuo and dissolved in CH_2Cl_2. The solution was dried over Na_2SO_4, and the product was precipitated by addition of n-hexane then recrystallized from $CHCl_3$.

Procedure 2

A solution of 2 mmol Ph_2SnCl_2 in 5 ml methanol was added to a mixture of 0.25 g KOH and 5 ml methanol. Ph_2SnO separated immediately. It was washed twice with methanol and added to a solution of 2 mmol dithiole in methanol or $CHCl_3$ within 5 min. After 1 h small amounts of unchanged Ph_2SnO were filtered off, and the clear colorless filtrate was concentrated in vacuo. During this operation a white product separated, and was recrystallized from acetone.

Procedure 3

A solution of 2 mmol dithiol in 15 ml acetone (or methanol or $CHCl_3$) was added during 0.5 h at room temperature with vigorous stirring to a suspension of 4 mmol R_3SnOH (R = Me, Ph) in 15 ml acetone (or methanol or $CHCl_3$). After 1 h the white precipitate was filtered off, dried in vacuo and dissolved in $CHCl_3$. The solution was dried over Na_2SO_4, concentrated in vacuo, and cooled, and the product was precipitated by addition of n-hexane.

Procedure 4

A solution of 2.5 mmol dithiol in 20 ml absolute methanol (or acetone) was added to solutions or suspensions of 2.5 mmol $R_2Pb(OAc)_2$ (R = Me, Et, Ph) or 5 mmol Ph_3PbOAc in 20 ml absolute methanol (or acetone) at temperatures between 0 and $-30°C$. In nearly all cases clear or slightly turbid mixtures were obtained. After 10 to 30 min stirring small amounts of yellow products were filtered off. The clear yellow filtrates were concentrated in vacuo at 0 to $-10°C$, and during this operation slightly yellowish white to bright yellow products separated. These were recrystallized from $CHCl_3$. Most of the products, especially the alkyl derivatives, quickly turned yellow or orange on exposure to light and lost their solubility.

A yellow precipitate was immediately formed from Ph_3PbOAc and toluene-dithiol-3,4. It was recrystallized from $CHCl_3$. Lead(IV) and lead(II) acetates were similarly treated with the dithiols. The reactions with H_2DBB had to be performed at about 0°C but other products could also be obtained at room temperature. In all cases yellow to orange finely divided products separated immediately, and were separated on the centrifuge. Because of their insolubility the lead(IV) and lead(II) dithiolates could not be recrystallized.

Acknowledgements

Financial assistance from Fonds der Chemischen Industrie, of the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, and of Consiglio Nazionale delle Ricerche, Roma, is gratefully acknowledged. We also thank Dr. M. Buschhoff, Schering AG, Bergkamen, for gifts of organotin compounds.

References

1 M. Wieber and M. Schmidt, J. Organomet. Chem., 2 (1964) 129.
2 L.M. Epstein and D.K. Straub, Inorg. Chem., 4 (1965) 1551.
3 R.C. Poller and J.A. Spillman, J. Chem. Soc. (A), (1966) 958.
4 R.C. Poller and J.N.R. Ruddick, J. Organomet. Chem., 60 (1973) 87.
5 M. Wieber and U. Baudis, J. Organomet. Chem., 125 (1977) 199.
6 A.C. Sau, R.O. Day and R.R. Holmes, Inorg. Chem., 20 (1981) 3076.

7 K. Grätz, F. Huber, A. Silvestri and R. Barbieri, J. Organomet. Chem., 273 (1984) 283.
8 H. Preut, K. Grätz and F. Huber, Acta Cryst., C40 (1984) 941.
9 F.H. Fink, J.A. Turner and D.A. Payne, J. Amer. Chem. Soc., 88 (1966) 1571.
10 A.C. Sau, R.R. Holmes, K.C. Molloy and J.J. Zuckerman, Inorg. Chem., 21 (1982) 1421.
11 T.B. Ktenas and M.D. Taylor, J. Therm. Anal., 25 (1982) 563.
12 G. Domazetis, R.J. Magee, B.D. James and J.D. Cashion, J. Inorg. Nucl. Chem., 43 (1981) 1351.
13 R.C. Poller and J.A. Spillmann, J. Chem. Soc. (A), (1966) 1024.
14 H. Schumann, Z. Anorg. Allg. Chem., 354 (1967) 192.
15 H. Schumann and P. Reich, Z. Anorg. Allg. Chem., 375 (1970) 72.
16 G. Peyronel, A. Pignedoli and W. Malavasi, Spectrochim. Acta, A32 (1976) 1015; and refs. therein.
17 R. Barbieri, A. Silvestri, F. Di Bianca, E. Rivarola and R. Cefalù, Mössbauer Effect Reference and Data Journal, 6 (1983) 69; and refs. therein.
18 M.G. Clark, A.G. Maddock and R.H. Platt, J. Chem. Soc., Dalton Trans., (1972) 281.
19 G.M. Bancroft and R.H. Platt, Adv. Inorg. Chem. Radiochem., 15 (1972) 59.
20 G.M. Bancroft, V.G. Kumar Das, T.K. Sham and M.G. Clark, J. Chem. Soc., Dalton Trans., (1976) 643.
21 M. Dräger, Z. Anorg. Allg. Chem., 477 (1981) 154.
22 A.S. Secco and J. Trotter, Acta Cryst., C39 (1983) 451.
23 A. Silvestri, E. Rivarola and R. Barbieri, Inorg. Chim. Acta, 23 (1977) 149; and refs. therein.