Journal of Organometallic Chemistry, 273 (1984) 283–294
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

BIS(TRIORGANOMETAL) AND DIORGANOMETAL 1,3-DITHIOLATES $(R_3M)_2(C_6H_3XS_2)$ AND $R_2M(C_6H_3XS_2)$ (M = Sn, Pb; X = H, Cl)

KARIN GRATZ, F. HUBER,
Lehrstuhl für Anorganische Chemie II, Universität Dortmund, D-4600 Dortmund 50 (B.R.D.)

A. SILVESTRI and R. BARBIERI
Gruppo di Chimica dei Composti Organometallici, Istituto di Chimica Generale, Università di Palermo, I-90123 Palermo (Italy)

(Received April 24th, 1984)

Summary

Bis(triorganometal) and diorganometal 1,3-dithiolates $(R_3M)_2(C_6H_3XS_2)$ ($C_6H_5XS_2$ 1,3-dithiobenzene (for X = H) or 1,3-dithio-4-chlorobenzene (for X = Cl); M = Sn, X = Cl, R = CH_3, C_6H_5; M = Pb, X = H, Cl, R = CH_3, C_2H_5, C_6H_5) and $R_2M(C_6H_3XS_2)$ (R = CH_3, C_2H_5, C_6H_5; M = Sn, X = Cl; M = Pb, X = H, Cl) have been prepared as the first organometal IVB derivatives of 1,3-dithiols, and investigated by vibrational, ^{1}H NMR, and (in the case of organotin compounds) Mössbauer spectroscopy. The triorganometal derivatives are monomeric and the diorganometal derivatives dimeric in solution (37 °C). For the latter a twelve-membered ring structure is proposed for both solution and the solid state.

Introduction

There are many organotin and organolead derivatives of aliphatic dithiols [1–13] but knowledge on appropriate aromatic derivatives is limited to some toluene-3,4-dithiolates [8,12,13]. As part of our investigations of organometal derivatives of oligofunctional compounds we have now obtained the first organotin and organolead 1,3-dithiolates, and describe below their preparation and characterization.

Results and discussion

Various methods seemed feasible for the preparation of organotin and organolead dithiolates. Of these, acidolysis proved not to be practicable. The alkali metal chloride method and the neutralization were especially advantageous for preparing organotin 1,3-dithiolates in high yields and high purity. The alkali metal chloride

(Continued on p. 286)

0022-328X/84/$03.00

TABLE 1

PREPARATIVE METHODS, MELTING POINTS AND ANALYTICAL DATA FOR ORGANOMETAL 1,3-DITHIOLATES

Compound	M p (°C)	Method	Yield (%)	Analysis (Found (calcd)(%))			Molecular weight [a] (Found (calcd))	Solvent [b]
				C	H	Pb		
$Me_2Sn(C_6H_3ClS_2)$, $C_8H_9ClS_2Sn$	127–133	1	93	29.51	2.91	–	609	$CHCl_3$
				(29.70)	(2.78)		(323.4)	
$(Me_3Sn)_2(C_6H_3ClS_2)$, $C_{12}H_{21}ClS_2Sn_2$	72	2	87	28.52	4.20	–	488	$CHCl_3$
				(28.70)	(4.21)		(502)	
$Et_2Sn(C_6H_3ClS_2)$, $C_{10}H_{13}ClS_2Sn$	103–104	1	90	33.76	3.78	–	708.5	$CHCl_3$
				(34.16)	(3.70)		(351.5)	
$Ph_2Sn(C_6H_3ClS_2)$, $C_{18}H_{13}ClS_2Sn$	138	1	91	48.36	2.99	–	906,900,490	$CHCl_3$, CH_2Cl_2, DMSO
				(48.30)	(2.93)		(447.6)	
$(Ph_3Sn)_2(C_6H_3ClS_2)$, $C_{42}H_{33}ClS_2Sn_2$	118	2	93	57.80	3.58	-	860	$CHCl_3$
				(57.67)	(3.80)		(875)	
$Me_2Pb(C_6H_3ClS_2)$, $C_8H_9ClPbS_2$	285	2/3	81	23.44	2.27	50.4	404	DMSO
	(dec)			(23.33)	(2.20)	(50.30)	(411.9)	
$Me_2Pb(C_6H_4S_2)$, $C_8H_{10}PbS_2$	170	2/3	91	25.75	2.81	54.7	–	
	(dec)			(25.45)	(2.67)	(54.89)		
$(Me_3Pb)_2(C_6H_3ClS_2)$, $C_{12}H_{21}ClPbS_2$	110	3	89	20.94	3.19	60.8	653,685	acetone, $CHCl_3$
	(dec)			(21.22)	(3.12)	(61.00)	(679.3)	

$(Me_3Pb)_2(C_6H_4S_2)$, $C_{12}H_{22}Pb_2S_2$	84	3	84	22.38	3.64	64.3	631,649	acetone, $CHCl_3$
	(dec)			(22.35)	(3.44)	(64.26)	(644.8)	
$Et_2Pb(C_6H_3ClS_2)$, $C_{10}H_{13}ClPbS_2$	275	3	87	27.25	2.87	47.1	887	DMSO
				(27.30)	(2.98)	(47.09)	(440)	
$Et_2Pb(C_6H_4S_2)$, $C_{10}H_{14}PbS_2$	220	3	84	29.53	3.31	51.2	–	
				(29.62)	(3.48)	(51.09)		
$(Et_3Pb)_2(C_6H_3ClS_2)$, $C_{18}H_{33}ClPb_2S_2$	101–103	3	91	28.23	4.30	54.3	779,745	DMSO,$CHCl_3$
				(28.32)	(4.36)	(54.28)	(763.4)	
$(Et_3Pb)_2(C_6H_4S_2)$, $C_{18}H_{34}Pb_2S_2$	83	3	83	29.59	4.87	56.8	711,732	acetone,$CHCl_3$
				(29.66)	(4.70)	(56.84)	(729)	
$Ph_2Pb(C_6H_3ClS_2)$, $C_{18}H_{13}ClPbS_2$	155	3	86	40.36	2.52	38.6	1045,507	$CHCl_3$,DMSO
	(dec)			(40.33)	(2.44)	(38.65)	(536)	
$Ph_2Pb(C_6H_4S_2)$, $C_{18}H_{14}PbS_2$	122	3	93	43.14	3.02	41.3	1001,998	$CHCl_3$,acetone
	(dec)			(43.10)	(2.81)	(41.31)	(501.6)	
$(Ph_3Pb)_2(C_6H_3ClS_2)$, $C_{42}H_{33}ClPb_2S_2$	116–117	2/3	93.5	47.67	3.34	39.4	1026,1094	CCl_4,acetone
				(47.98)	(3.16)	(39.40)	(1051.7)	
$(Ph_3Pb)_2(C_6H_4S_2)$, $C_{42}H_{34}Pb_2S_2$	121	2/3	88	49.11	3.53	40.6	1011	$CHCl_3$
				(49.59)	(3.37)	(40.74)	(1017.2)	

---

[a] Determined osmometrically in $CHCl_3$, CH_2Cl_2, CCl_4 or in acetone at 37 °C, determination in DMSO at 90 °C. [b] Solvent for molecular weight measurements.
[c] Decomposition before melting

method failed for organolead 1,3-dithiolates due to their thermal sensitivity, but the neutralization method was successful. Ligand exchange, used in the reaction of organolead acetates with 1,3-dithiols was also satisfactory. In the preparations of organolead 1,3-dithiolates light had to be excluded, and temperatures below 0 °C were advisable and the sensitivity of the dithiols to oxygen has always to be taken into account. The newly prepared 1,3-dithiolates with the methods used for their preparation are listed in Table 1, together with melting points, yields and analytical data. Details of the preparations are given in the Experimental.

The organotin, and the bis(triorganolead) 1,3-dithiolates are colourless. On exposure to light the lead compounds turn yellow within a few minutes. The diorganolead 1,3-dithiolates are yellow. All the organolead derivatives have to be stored at low temperature.

DTA/TG studies of the thermal decomposition of the compounds in no case showed distinguishable steps. Comparison of observed weights of the residue and of the weights, which were calculated by assuming radical decomposition or redistribution [14] indicated that in the case of bis(triorganometal) 1,3-dithiolates decomposition proceeds by a redistribution process. This was confirmed by the identification of Ph_4Pb, as the product of the first step of the redistribution of triphenyllead compounds in the solid state [15].

The bis(triorganolead) 1,3-dithiolates are soluble in acetone, and chloroform. The dialkyllead derivatives dissolve only in DMSO at about 90 °C, but decomposition is observed at this temperature. The tin compounds are very soluble in chloroform and methylene chloride, and less soluble in other organic solvents. All the compounds are insoluble in water and under normal conditions no hydrolysis occurs.

According to molecular weight measurements the bis(triorganometal) 1,3-dithiolates are monomeric in solution (see Table 1) and the diphenylmetal and the dialkyltin 1,3-dithiolates are dimeric. However, in DMSO, $Ph_2M(C_6H_3ClS_2)$ and $Me_2Pb(C_6H_3ClS_2)$ at 90 °C showed molecular weights corresponding to those of the monomers, but the possibility that decomposition products were responsible for the low value could not be ruled out. Such an explanation seems plausible, since the molecular weight of $Et_2Pb(C_6H_3ClS_2)$ in DMSO at 90 °C immediately after dissolution corresponded to that of a dimeric species but soon started to decrease, and decomposition products separated from the solution.

In the IR and Raman spectra of all 1,3-dithiolates the ν(SH) band was absent, and bands between 280 and 380 cm^{-1} were observed in the range in which ν(MS) are to be expected [11,16–18] (see Table 2). The Raman spectra of some organolead compounds could not be recorded, because of the deep colour or decomposition. The characteristic absorptions of the organo groups R (R = Me, Et, Ph) and of the dithiolate ligands (except ν(CS)) were practically unchanged when compared with those in the corresponding reactant. The ν(CS) band which appears in the 1,3-dithiolates at 680 cm^{-1}, was shifted to lower wavelengths; the shift was about 20–30 cm^{-1} for the phenylmetal and about 10 cm^{-1} for the alkylmetal derivatives (see Table 2). The ν_s(MC) and ν_{as}(MC) [19] bands in the IR and Raman spectra of the methylmetal compounds (see Table 2) were of about equal intensity. Since the exclusion principle is not obeyed, planarity of the MC_3 skeleton in the bis(triorganometal) derivatives and linearity of the MC_2 skeleton in the dimethylmetal derivatives is excluded.

The Mössbauer spectra of the organotin dithiolates consisted of well resolved

TABLE 2

VIBRATIONAL DATA FOR ORGANOTIN AND ORGANOLEAD 1,3-DITHIOLATES (cm^{-1}) (Raman data in brackets)

Compound	ν(C–S)	ν_{as}(M–Y) [a]	ν_s(M–Y) [a]	ν(M–S)		
1,3-$C_6H_5ClS_2$ [b]	680	–	–		–	
$Me_2Sn(C_6H_3ClS_2)$	670	550s	523m	361	330	
	(675)	(552)s	(525)vs	(360)	(330)	
$(Me_3Sn)_2(C_6H_3ClS_2)$	673	560m,540vs	512s	355	323	
	(675)	(560w,540s)	(515)vs	(355)	(325)	
$Et_2Sn(C_6H_3ClS_2)$	675	569	515	363	333	
	(670)	(565)	(515)	(365)	(340)	
$Ph_2Sn(C_6H_3ClS_2)$	670	265		360	340	320
	(653)	(265)	(240)		(349)	(320)
$(Ph_3Sn)_2(C_6H_3ClS_2)$	660	270	228	357	344	338
	(655)	(267)	(217)	(355)	(345)	
$Me_2Pb(C_6H_3ClS_2)$	675	490m	445m	341		297
	(673)	(490)m	(445)vvs	(340)		(302)
$(Me_3Pb)_2(C_6H_3ClS_2)$	670	485vvs	459vs	340	326	285
	(675)	(480)vs	(465)vvs	(343)	(333)	(290)
$Et_2Pb(C_6H_3ClS_2)$	670	470	433		338	293
	(670)	(470)	(430)		(333)	(295)
$(Et_3Pb)_2(C_6H_3ClS_2)$	680	461	439		325	271
	(675)	(463)	(438)		(335)	(275)
$Ph_2Pb(C_6H_3ClS_2)$	646			367		310
	(638)	(235)	(203)	(345)	(320)	(310)
$(Ph_3Pb)_2(C_6H_3ClS_2)$	665			343		307
	(645)	(225)	(200)	(340)		(305)
1,3-$C_6H_6S_2$ [b]	680	–	–		–	
$Me_2Pb(C_6H_4S_2)$	673	498m	460s			295
	(675)	(510)m	(465)vs		(310)	
$(Me_3Pb)_2(C_6H_4S_2)$	663	488s	460m	363		288
	(672)	(495)s	(467)vvs		(304)	(282)
$Et_2Pb(C_6H_4S_2)$	660	460	440			290
	(670)	(479)	(445)		(305)	
$(Et_3Pb)_2(C_6H_4S_2)$	675	465	438	350		
	(670)	(474)	(445)			(280)
$Ph_2Pb(C_6H_4S_2)$				367	310	
	(645)	(234)	(202)		(316)	(297)
$(Ph_3Pb)_2(C_6H_4S_2)$				379	315	282
	(648)	(228)	(200)		(320)	

[a] Y = CH_3, C_2H_5, C_6H_5. [b] 1,3-$C_6H_5ClS_2$ = 1,3-dithio-4-chlorobenzene; 1,3-$C_6H_6S_2$ = 1,3-dithiobenzene.

doublets with fairly narrow linewidths. The relevant parameters are reported in Table 3; the values of δ and ΔE are fully consistent with those of the analogous compounds listed in Table 4 (for environments of tin atoms Alk_2SnS_2, Alk_3SnS, Ph_2SnS_2 and Ph_3SnS, respectively), to which tetrahedral structures have been assigned from spectroscopic studies (see references in Table 4) and determined by X-ray diffractometry [25,26].

Tetrahedral environments for the tin atoms in our dithiolates are inferred also from quantitative, semiempirical rationalizations of the Mössbauer parameters ΔE and δ, as well as from the "fingerprint" criteria considered above. The calculated point-charge model values of ΔE, mm s^{-1}, for regular tetrahedral structures [10] are

TABLE 3

MÖSSBAUER DATA FOR ORGANOTIN 1,3-DITHIOLATES[a]

Compound	δ[b] (mm s^{-1})	ΔE[c] (mm s^{-1})	Γ_1[d] (mm s^{-1})	Γ_2[d] (mm s^{-1})
$Me_2Sn(C_6H_3ClS_2)$	1.44	2.00	0.89	0.94
$(Me_3Sn)_2(C_6H_3ClS_2)$	1.34	2.10	0.91	0.91
$Et_2Sn(C_6H_3ClS_2)$	1.55	2.34	0.97	0.96
$Ph_2Sn(C_6H_3ClS_2)$	1.38	1.54	0.96	0.96
$(Ph_3Sn)_2(C_6H_3ClS_2)$	1.32	1.58	0.90	0.91

[a] Determined at 77K Sample thicknesses were generally around 1 mg ^{119}Sn cm^{-2}. [b] Isomer shift with respect to $CaSnO_3$ at room temperature; standard error ±0.01 mm s^{-1}, see ref. 20 [c] Experimental nuclear quadrupole splitting; standard error ±0.01 mm s^{-1}. [d] Full widths at half-height of the resonance peaks

as follows: $Alk_2Sn(SPh)_2$, 1.88 [10]; Alk_3SnSPh, −1.64; $Ph_2Sn(SPh)_2$, 1.63 [10]; Ph_3SnSPh, −1.42. The experimental ΔE data for the dithiolates in Table 3 agree with those calculated for analogous environments of the tin atoms, although those of

TABLE 4

MOSSBAUER PARAMETERS FOR A SELECTION OF COMPOUNDS WITH C_2SnS_2 AND C_3SnS TETRAHEDRAL ENVIRONMENTS

Compound[a]	δ[b] (mm s^{-1})	ΔE[c] (mm s^{-1})	Ref
$Me_2Sn(SPh)_2$	1.43	2.20	10
$Me_2Sn(SC_{12}H_{25})_2$	1.44	1.59	21
$Me_2Sn(SCH_2C_6H_5)_2$	1.44	1.65	21
$Et_2Sn(SPh)_2$	1.50	1.98	10
$Pr^n_2Sn(SPh)_2$	1.50	2.01	10
$Bu^n_2Sn(SMe)_2$	1.48	2.11	10
$Bu^n_2Sn(SEt)_2$	1.45	1.66	10
$Bu^n_2Sn(SC_{12}H_{25})_2$	1.44	1.58	10,21
$Bu^n_2Sn(SPh)_2$	1.50	1.96	10
$Oct^n_2Sn(SPh)_2$	1.48	1.92	10
$Ph_2Sn(SPh)_2$	1.40	1.71	10
Et_3SnSBu^n	1.60	1.80	22
Et_3SnSPh	1.62	2.07	22
$Bu^n_3SnS(CH_2)_2SSnBu^n_3$	1.39	1.75	23
$Bu^n_3SnSC_{12}H_{25}$	1.50	1.44	21
$Bu^n_3SnSCH_2COONa$	1.45	1.59	21
Bu^n_3SnSPh	1.42	2.03	23
$Bu^n_3SnS(CH_2)_2CH(NH_2)COOH$	1.35	1.54	24
$Cy_3SnSCH_2CH(NH_2)COOH$	1.44	1.68	24
$Cy_3SnS(CH_2)_2CH(NH_2)COOH$	1.45	1.63	24
$Np_3SnSCH_2CH(NH_2)COOH$	1.36	1.79	24
$Np_3SnS(CH_2)_2CH(NH_2)COOH$	1.35	1.70	24
Ph_3SnSPh	1.40	1.16	22
Ph_3SnSPh	1.32	1.41	23
$Ph_3SnS(CH_2)_2SSnPh_3$	1.32	1.22	23
$Ph_3SnSCH_2CH(NH_2)COOH$	1.24	1.34	24
$Ph_3SnS(CH_2)_2CH(NH_2)COOH$	1.28	1.48	24

[a] Abbreviations: Cy = cyclohexyl, Np = neophyl. [b] Isomer shift with respect to SnO_2, $BaSnO_3$ or $CaSnO_3$, at liquid N_2 temperature. [c] Nuclear quadrupole splitting at liquid N_2 temperature.

TABLE 5

DATA POINTS δ/Q_{Sn} FOR SOME SERIES OF DI- AND TRI-ORGANOTIN THIOLATES WITH TETRAHEDRAL TIN ENVIRONMENTS

(Calculations have been effected by the program CHELEQ, assuming tetrahedral valence bond structures of tin environments, with bond orders 1.00 and partial charges 0.00; further input parameters in the molecules have been attributed as usual [28,29]).

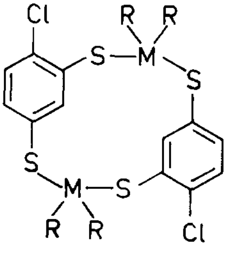
Homologous series [a]	δ [b]	Q_{Sn} [c]
$Alk_2Sn(SR)_2$	1.47 ± 0.01	0.118 ± 0.001
$Ph_2Sn(SR)_2$	1.39	0.166
Alk_3SnSR	1.44 ± 0.03	0.055 ± 0.001
Ph_3SnSR	1.30 ± 0.02	0.124

[a] Include the compounds listed in the Tables 3 and 4. [b,c] Mean values; standard errors are reported whenever applicable. [b] Mössbauer isomer shifts. [c] Partial atomic charges on tin, see text.

the Me_3Sn^{IV} and Et_2Sn^{IV} derivatives slightly exceed the usual maximum difference (± 0.4 mm s^{-1}) [27].

Rationalization of the δ values for the organotin dithiolates, (Table 3) has been effected by their correlation with partial atomic charges on tin, Q_{Sn}, obtained by valence state orbital electronegativity equalization upon bond formation [28,29]. The values in Table 5 clearly show that four distinct data points are obtained for any particular tetrahedral environment of tin atoms (where the individual values δ/Q_{Sn} of our compounds excellently insert), which could perhaps belong to two δ/Q_{Sn} correlations, i.e., $Alk_2Sn(SR)_2$-Alk_3SnSR and $Ph_2Sn(SR)_2$-Ph_3SnSR, concerning tetrahedral tin sites in R_2Sn^{IV} and R_3Sn^{IV} complexes.

An X-ray determination of 1,3-dithiolato-4-chlorobenzenediphenyltin(IV) showed that this compound is dimeric in the solide state [30]. A twelve-membered ring is formed by two molecules of $Ph_2Sn(C_6H_3ClS_2)$ according to (I):



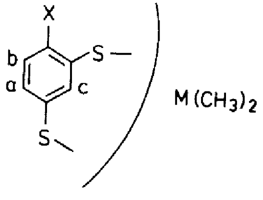
(I)

Neither intra- nor inter-molecular contacts increase the coordination of the central atom, which is tetrahedrally bonded by two C(phenyl) and two S atoms. This result confirms the tetrahedral coordination of Sn in $Ph_2Sn(C_6H_3ClS_2)$ inferred from Mössbauer measurements.

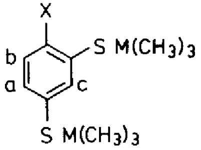
From the similarity of properties, the Mössbauer data for organotin 1,3-dithiolates, and the results of the X-ray structural study of 1,3-dithiolato-4-chlorobenzenediphenyltin(IV) [30], it is inferred that analogous MC_2 skeletons are present also in the other diorganometal 1,3-dithiolates. In this connection it should be recalled

TABLE 6

^{1}H NMR DATA FOR METHYLMETAL 1,3-DITHIOLATES. CHEMICAL SHIFTS δ(ppm) AND COUPLING CONSTANTS $^2J(^{119}Sn^1H)$ AND $^2J(^{207}Pb^1H)$ (Hz)



$Me_2M(C_6H_3XS_2)$



$(Me_3M)_2(C_6H_3XS_2)$

Compound	X [b]	δ(CH$_3$)	δ [a]		δ [b]	δ [c]	^2J	
$C_6H_5ClS_2$	Cl	–	6.82–6.96		7.09	7.13–7.22	–	$CDCl_3$
$Me_2Sn(C_6H_3ClS_2)$	Cl	0.46		7.11–7.24		8.32	58	$CDCl_3$
		0.62		7.04–7.24		7.24–7.67	70	DMSO-d_6
$(Me_3Sn)_2(C_6H_3ClS_2)$	Cl	0.41		7.04–7.22		7.56	56	$CDCl_3$
		0.42		6.77–6.98 7.02–7.18		7.31	62	DMSO-d_6
$Me_2Pb(C_6H_3ClS_2)$	Cl	1.20	6.69–6.90		7.04–7.27	7.31–7.42	74	DMSO-d_6
		0.71 [a]					64 [a]	DMSO-d_6
$(Me_3Pb)_2(C_6H_3ClS_2)$	Cl	1.23	6.84–7.11		7.11–7.27	7.44–7.60	62	$CDCl_3$
							72	DMSO-d_6
$C_6H_6S_2$	H*	–	7.00		6.82	7.13	–	$CDCl_3$
$Me_2Pb(C_6H_4S_2)$	H*	1.16		6.68	to	7.36	76	DMSO-d_6
		0.71 [a]					64 [a]	DMSO-d_6
$(Me_3Pb)_2(C_6H_4S_2)$	H*	1.22		6.93–7.16		7.36–7.42	62	$CDCl_3$
							68	$(CD_3)_2CO$
		1.33		6.71		7.24	74	DMSO-d_6

[a] Due to Me_4Pb, see text [b] H*: equivalent to H_a

that non-linearity of the SnC_2 skeleton was indicated by the vibrational spectra of solid $Me_2Sn(C_6H_3ClS_2)$. It also seems reasonable to assume that non-planar MC_3 skeletons are present not only in the bis(trimethylmetal) derivatives but also in the other bis(triorganometal) 1,3-dithiolates.

Mass spectral data indicate a dimeric nature for the diorganotin derivatives. The mass spectra of the dialkyltin 1,3-dithiolates show peaks corresponding to the molecule ion M^+ of the dimeric unit:
M^+: $[Me_2Sn(C_6H_3ClS_2)]_2$ $m/e = 648$; $[Et_2Sn(C_6H_3ClS_2)]_2$ $m/e = 704$. The mass spectrum of the diphenyltin derivative did not show the M^+ ion but gave peaks corresponding to the monomer and also to ions with m/e values higher than calculated for the monomeric unit.

The observations that diorganotin 1,3-dithiolates are dimeric in the solid state and that diorganotin and diorganolead 1,3-dithiolates are dimeric in solution suggest that all the compounds in the solid state and in solution, have structures of the type shown in I.

The ^1H NMR spectra of all organometal 1,3-dithiolates showed no SH signals (δ(SH) of $C_6H_5ClS_2$ 3.40, 3.84 ppm; of $C_6H_6S_2$ 3.41 ppm). The chemical shifts and coupling constants for the methylmetal derivatives are listed in Table 6. In all cases the integration ratio corresponded to the calculated value: the ratio R_3M/dithiolate is 2/1 for the bis(triorganometal) derivatives, and R_2M/dithiolate = 1/1 for the diorganometal derivatives.

The proton H_c (see Table 6) shows a weak paramagnetic shift, which can be explained by inductive and anisotropic effects [31]. The values of the coupling constants (in $CDCl_3$) $^2J(^{119}Sn^1H)$ and $^2J(^{207}Pb^1H)$, respectively, correspond to values found in tetracoordinated organotin and organolead compounds: $^2J(^{119}Sn^1H)$ of Me_4Sn in CCl_4 54 Hz [32]; $^2J(^{207}Pb^1H)$ of Me_4Pb in CCl_4 60 Hz [8], in $CDCl_3$ 63 Hz [33,34]. In coordinating solvents the methylmetal 1,3-dithiolates show higher coupling constants as the coordination is increased [32,35,36].

The percentages *s*-character [32] of the Sn–C bond in $Me_2Sn(C_6H_3ClS_2)$ and $(Me_3Sn)_2(C_6H_3ClS_2)$ in $CDCl_3$ solution are calculated to be 27 and 26%, respectively, indicating tetracoordination, i.e. no additional coordination at Sn. Analogous calculation for $Me_2Sn(C_6H_3ClS_2)$ in DMSO-d_6 solution indicates 32% *s*-character, which corresponds quite well to pentacoordination and to trigonal bipyramidal geometry around Sn.

The value of 29% *s*-character calculated for $(Me_3Sn)_2(C_6H_3ClS_2)$ in DMSO-d_6 indicates that the hybridization at Sn is changed towards sp^2 by coordination of DMSO molecules. This observation is in accordance with the generally observed lower coordination tendency of triorganotin compounds compared with diorganotin compounds.

The coupling constants $^2J(^{207}Pb^1H)$ of $(Me_3Pb)_2(C_6H_3ClS_2)$ and of $(Me_3Pb)_2(C_6H_4S_2)$ also increase on going from $CDCl_3$ to DMSO-d_6 as solvent (see Table 6), indicating increase of the coordination number. The same trend was observed in some dimethyllead complexes [37].

The coupling constants $^2J(^{207}Pb^1H)$ of $Me_2Pb(C_6H_3ClS_2)$ and $Me_2Pb(C_6H_4S_2)$ in DMSO-d_6 solution are comparable to those of the appropriate bis(trimethyllead) derivatives (values of $^2J(^{207}Pb^1H)$ for the dimethyllead compounds in $CDCl_3$ could not be determined, due to lacking solubility). We assume that the dimethyllead derivatives also coordinate DMSO molecules, like the dimethyltin compounds.

In the ^1H NMR spectra of solutions of the dimethyllead compounds signals at δ 0.71 ppm, $^2J(^{207}Pb^1H)$ couplings of 64 Hz were observed. These can be assigned to Me_4Pb, which was produced by decomposition during dissolution of the compounds in DMSO-d_6 (solid decomposition products separated from the solution, see above). Changes in the ^1H NMR spectra of $Et_2Pb(C_6H_3ClS_2)$ and $Et_2Pb(C_6H_4S_2)$ in DMSO-d_6 can be interpreted similarly in terms of formation of Et_4Pb.

Experimental

The lead derivatives had to be prepared in anhydrous solvents under argon with exclusion of light. The dithiols were treated with the appropriate diorganometal compounds in the molar ratio 1/1 and with the triorganometal compounds in the molar ratio 1/2. Lead was determined complexometrically, and C and H by the usual method. IR spectra (CsBr, Nujol) were recorded with Perkin–Elmer grating spectrometers PE 457 and PE 580B, Raman spectra with a Coderg laser Raman spectrometer PHO (λ 488 nm; 647.1 nm), and ^1H NMR spectra with a Perkin–Elmer 90 MHz spectrometer R32 at 37 °C.

The Mössbauer spectra were obtained as usual [38]. 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 each prepared by one or more of the following procedures.

Procedure 1

A mixture of 1.1 g KOH in 15 ml methanol and 1.35 g 1,3-dithio-4-chlorobenzene in 10 ml methanol was homogenized by shaking, and the pH value was adjusted to 7 by addition of 2 *N* hydrochloric acid if necessary. Solutions or suspensions of 7.6 mmol R_2SnCl_2 (R = Me, Et, Ph) in 10 ml water were added during 0.5 h with vigorous stirring. After 2 h the white, crystalline 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.

Procedure 2

A solution of 3 mmol dithiol in 20 ml methanol was added during 0.5 h to a suspension of 6 mmol R_3SnOH (R = Me, Ph) in 20 ml methanol. After 2 h the precipitate which had separated was recrystallized from $CHCl_3$. Ph_3PbOH and $Me_2Pb(OH)_2$ were treated analogously with the dithiols at -10 to -70 °C. Because of their insolubility the dimethyllead derivatives could not be recrystallized. 1,3-Dithiolato-4-chlorobenzenediphenyltin(IV) could also be prepared by the neutralization method if the starting compound Ph_2SnO was used immediately after its preparation.

Procedure 3

A solution of 2.5 mmol dithiol in 20 ml absolute methanol (or acetone) was added to a suspension of 2.5 mmol $R_2Pb(OAc)_2$ (R = Me, Et, Ph) or 5 mmol R_3PbOAc (R = Me, Et, Ph) in 20 ml absolute methanol (or acetone). In the case of the reactions with $R_2Pb(OAc)_2$ a yellow product separated, and was filtered off after 1 h. It was washed with methanol or acetone and dried in vacuo. To avoid redistribution the suspensions of $R_2Pb(OAc)_2$ (R = Me, Et), were prepared with ice cooling.

In the case of the reactions of R_3PbOAc only small amounts of a yellow product separated and this was filtered off and discarded. The slightly yellow filtrates were concentrated in vacuo at −10 °C, and during this operation a slightly yellowish white product separated, which quickly turned yellow on exposure to light.

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 W.E. Davidson, K. Hills and M.C. Henry, J. Organomet. Chem., 3 (1965) 285.
2 E.S. Bretschneider and C.W. Allen, J. Organomet. Chem., 38 (1972) 43.
3 E.S. Bretschneider and C.W. Allen, Inorg. Chem., 12 (1973) 623.
4 R.H. Cragg and A. Taylor, J. Organomet. Chem., 99 (1975) 391.
5 M. Wieber and M. Schmidt, Z. Naturforsch. B, 18 (1963) 849.
6 M. Wieber and M. Schmidt, Angew. Chem., 75 (1963) 1116.
7 M. Wieber and M. Schmidt, Z. Naturforsch. B, 18 (1963) 846.
8 L.M. Epstein and D.K. Straub, Inorg. Chem., 4 (1965) 1551.
9 M. Dräger, Z. Anorg. Allg. Chem., 477 (1981) 154.
10 R.C. Poller and J.N.R. Ruddick, J. Organomet. Chem., 60 (1973) 87; and refs. therein.
11 G. Domazetis, R.J. Magee, B.D. James and J.D. Cashion, J. Inorg. Nucl. Chem., 43 (1981) 1351.
12 M. Wieber and U. Baudis, J. Organomet. Chem., 125 (1977) 199.
13 M. Wieber and M. Schmidt, J. Organomet. Chem., 2 (1964) 129.
14 G. Calingaert, Chem. Rev., 43 (1925) 2.
15 R. Leibold and F. Huber, Third Int. Conf. Organometal. Coord. Chem. Ge, Sn, Pb, Dortmund, 1980, 87.
16 H. Schumann, Z. Anorg. Allg. Chem., 354 (1967) 192.
17 H. Schumann and P. Reich, Z. Anorg. Allg. Chem., 375 (1970) 72.
18 R.C. Poller and J.A. Spillman, J. Chem. Soc. A, (1966) 1024.
19 T. Tanaka, Organomet. Chem. Rev. A, 5 (1970) 1.
20 R. Barbieri, A. Silvestri, G. van Koten and J.G. Noltes, Inorg. Chim. Acta, 40 (1980) 267.
21 C.H. Stapfer and R.H. Herber, J. Organomet. Chem., 66 (1974) 425.
22 A.N. Nesmeyanov, V.I. Gol'danskii, V.V. Khrapov, V.Ya. Rochev, D.N. Kravtsov and E.L. Rokhlina, Izv. Akad. Nauk. SSSR, Ser. Khim., (1968) 793; English transl. p. 763.
23 R.C. Poller and J.N.R. Ruddick, J. Chem. Soc. Dalton Trans., (1972) 555.
24 P.J. Smith, R.L. Hyams, J.S. Brooks and R.W. Clarkson J. Organomet. Chem., 171 (1979) C29.
25 (a) N.G. Bokii, Yu.T. Struchkov, D.N. Kravtsov and E.M. Rokhlina, Z. Strukt. Khim., 14 (1973) 291; Engl. transl. p. 258; (b) 15 (1974) 497; Engl. transl. p. 424.
26 P.L. Clarke, M.E. Cradwick and J.L. Wardell, J. Organomet. Chem., 63 (1973) 279.
27 M.G. Clark, A.G. Maddock and R.H. Platt, J. Chem. Soc., Dalton Trans., (1972) 281.
28 (a) W.L. Jolly and W.B. Perry, J. Am. Chem. Soc., 95 (1973) 5442; (b) Inorg. Chem., 11 (1974) 2686; and refs. therein.
29 (a) E. Rivarola, A. Silvestri and R. Barbieri, Inorg. Chim. Acta, 28 (1978) 233; (b) R. Barbieri and A. Silvestri, ibid., 47 (1981) 201; (c) J. Chem. Soc. Dalton Trans. (1984) 1090; (d) R. Barbieri, E. Rivarola, A. Silvestri, F. Huber and W.N. Aldridge, Int. Conf. on the Applications of Mössbauer Effect, Alma Ata, USSR, Sept. 26th–Oct. 1st, 1983, Abstr., paper B7; p. 80 and refs. therein.
30 H. Preut, K. Grätz and F. Huber, Acta Cryst. 40C (1984) 941.
31 D.H. Williams and I. Flemming, Spektroskopische Methoden zur Strukturaufklärung, G. Thieme, Stuttgart, 1975.
32 J.R. Holmes and H.D. Kaesz, J. Am. Chem. Soc., 83 (1961) 3903.

33 G.D. Shier and R.S. Drago, J. Organomet. Chem., 6 (1966) 359.
34 H.P. Fritz and K.E. Schwarzhans, J. Organomet. Chem., 1 (1964) 297.
35 P.B. Simons and W.A.G. Graham, J. Organomet. Chem., 8 (1967) 479.
36 M.L. Maddox, N. Flitcraft and H D. Kaesz, J. Organomet. Chem., 4 (1965) 50.
37 T. Majima and Y Kawasaki, Bull. Chem. Soc. Jpn., 51 (1978) 2924
38 A. Silvestri, E. Rivarola and R Barbieri, Inorg. Chim. Acta, 23 (1977) 149; and refs. therein.