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MÖSSBAUER SPECTRA OF ORGANOTIN COMPOUNDS
VI*. DITHIOLATOTIN COMPOUNDS

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SUMMARY

The Mössbauer spectra of a wide range of organo(dithiolato)tin compounds $R_2Sn(SR')_2$ have been measured. A comparison of calculated quadrupole splittings with the observed values has enabled structures to be assigned. Tetrahedral configurations occur in most of the compounds, the thioacetates (and probably the mercaptoacetates) being exceptional in having octahedral structures.

INTRODUCTION

Interpretation of the quadrupole interaction and, to a lesser extent, the chemical isomer shift obtained from the Mössbauer spectra has reached a degree of sophistication such that structural assignments may be made with some confidence for most of the organotin(IV) compounds studied[1–5].

Considering compounds containing tin–sulphur bonds the stereochemistry of a series of tetrathiolatotin adducts has been determined[1] and the predominant coordination at the tin atom in compounds of the type R_3SnSR' shown to be tetrahedral[1]. The presence of *cis* and *trans* forms among organotin bis(dithiocarbamates) has been demonstrated[6] and, in earlier work, the Mössbauer parameters of some dithiolatotin compounds and their adducts were interpreted[7].

In the present work, a systematic study is made of some organo(dithiolato)tin compounds, and calculations based on a recently developed molecular orbital approach[8] have been used to assist in structure determination.

RESULTS AND DISCUSSION

In the first experiment a series of bis(phenylthiolato)tin compounds with the general formula $R_2Sn(SPh)_2$ were prepared and examined. The Mössbauer spectral data are given in Table 1. As is usually found[9,10], in an isostructural series of this type, there are only minor variations in the quadrupole splitting, with the largest difference being shown by the methyl and phenyl compounds. It remains to be decided which structural type is present.

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* For Part V see ref. 12.

TABLE 1

MÖSSBAUER PARAMETERS OF BIS(PHENYLTHIOLATO)TIN COMPOUNDS

Compound	*Isomer shift*	*Quadrupole splitting*
$Me_2Sn(SPh)_2$	1.43	2.20
$Et_2Sn(SPh)_2$	1.50	1.98
$Pr_2Sn(SPh)_2$	1.50	2.01
$Bu_2Sn(SPh)_2$	1.50	1.96
$(C_8H_{17})_2Sn(SPh)_2$	1.48	1.92
$Ph_2Sn(SPh)_2$	1.40	1.71

TABLE 2

USE OF PARTIAL FIELD GRADIENT PARAMETERS TO ESTIMATE QUADRUPOLE SPLITTINGS (e^2Qq)

CALCULATION OF PARTIAL FIELD GRADIENT PARAMETERS

Compound	*Observed*[b] e^2Qq	*Ligand*[g]	*PFGP value*
Ph_3SnSPh	1.41[c]	SPh (tet)	−0.55
$(Bu_3SnSCH_2)_2$	1.75[d]	½(SCH_2CH_2S)(tet)	−0.50
Et_3SnSBu	1.80[e]	SBu (tet)	−0.48
$(Ph_3Sn)_2S$	1.46[f]	½S (tet)	−0.53
$Ph_3SnSCOMe$	1.65[c]	SCOMe (tet)	−0.44
$Ph_2Sn(SCOMe)_2$	2.28[c]	SCOMe (oct,t)	−0.38

CALCULATION OF QUADRUPOLE SPLITTINGS AND COMPARISON WITH OBSERVED VALUES[a]

Compound	*Calculated* e^2Qq *for the given geometry*[g]	*Observed* e^2Qq[c]
$R_2Sn(SPh)_2$	+1.88 (tet)	1.92–2.20
$Ph_2Sn(SPh)_2$	+1.63 (tet)	1.71
$Bu_2\overline{SnSCH_2CH_2S}$	+2.00 (tet) +1.88 (oct,t)[h]	2.36
$Ph_2\overline{SnSCH_2CH_2S}$	+1.75 (tet)	1.69
$R_2Sn(SR')_2$	+2.04 (tet)	1.58–2.11
Bu_2SnS	+1.93 (tet)	2.18
Ph_2SnS	+1.68 (tet)	1.60
$R_2Sn(SCOMe)_2$	+2.14 (tet) +2.60 (oct,t)	2.67–2.91
$Ph_2Sn(SCOMe)_2$	+1.89 (tet)	2.28

[a] Partial field gradient parameters are defined in ref. 8; methods of calculation are given in refs. 4 and 8. [b] All these values are assumed to be negative. [c] This work. [d] Ref. 1. [e] Ref. 11. [f] Ref. 12. [g] Abbreviations, tet = tetrahedral, oct = octahedral, c = *cis*, t = *trans*. [h] Using the *PFGP* value ½(SCH_2CH_2S) (oct) = −0.56 given in ref. 8.

The quadrupole splitting of $Bu_2Sn(SPh)_2$ is not as large as that observed for Bu_2SnI_2, ($e^2Qq=2.9$ mm/s)[10], implying that the polarity of the tin–iodine bond is greater than that of the tin–sulphur bond, since it is unlikely that angular distortion alone could account for the large difference in e^2Qq. It would be useful to calculate the magnitude of e^2Qq for tetrahedral bis(phenylthiolato)tin compounds. This can be done with the aid of the partial field gradient parameters (*PFGP*), obtained by Clark *et al.*[8]. The value of the *PFGP* of the SPh group is calculated from the quadrupole splitting of Ph_3SnSPh for which a tetrahedral structure has been assigned[1]. The close agreement between the calculated and observed quadrupole splittings (Table 2) for the $R_2Sn(SPh)_2$ compounds suggests that the tin atom is tetrahedrally bonded. The isomer shift hardly varies throughout the series but is somewhat lower than that found for the organotin diiodides[10].

Having observed that changing R in compounds of the type $R_2Sn(SR')_2$ results in only a slight modification of the field gradient at the tin nucleus, it is logical to examine next the effect of varying the organic group, R′, bound to the sulphur atom. The Mössbauer spectra for several dibutyl- and diphenyldithiolatotin compounds are recorded in Tables 3 and 4. For the diphenyltin compounds the value of e^2Qq for the tetrahedral $Ph_2Sn(SPh)_2$ may be used as a guide to structure assignment. Comparison with the other quadrupole splittings in Table 4 suggests that all these

TABLE 3

MÖSSBAUER PARAMETERS OF DITHIOLATODIBUTYLTIN COMPOUNDS

Compound	*Isomer shift*	*Quadrupole splitting*
$Bu_2Sn(SMe)_2$	1.48	2.11
$Bu_2Sn(SEt)_2$	1.45	1.66
$Bu_2Sn(SC_{12}H_{25})$	1.44	1.58
$Bu_2SnSCH_2CH_2S$	1.54	2.36
$Bu_2SnSCH_2CH_2CH_2S$	1.51	2.22
$Bu_2Sn(SPh)_2$	1.50	1.96
$(Bu_2SnS)_3$	1.46	2.18

TABLE 4

MÖSSBAUER PARAMETERS OF DITHIOLATODIPHENYLTIN COMPOUNDS

Compound	*Isomer shift*	*Quadrupole splitting*
$Ph_2SnSCH_2CH_2S$	1.37	1.69
$Ph_2SnSCH_2CH_2CH_2S$	1.39	1.72
Ph_2SnTdt[a]	1.36	1.99
$Ph_2Sn(SPh)_2$	1.40	1.71
$(Ph_2SnS)_3$	1.32	1.60

[a] Tdt = toluene-3,4-dithiolato.

diphenyltin compounds contain tetrahedrally coordinated tin atoms. The invariant isomer shift reinforces this conclusion of only one structural type. The lower value of the isomer shift when compared with the corresponding dialkyltin compounds (Table 3), is expected, the greater electron withdrawing effect of the phenyl group resulting in a reduction of the *s*-electron density at the tin nucleus. The dibutyltin compounds (Table 3), show a much wider range of e^2Qq values, and the question arises, is this due to distortions of a single structural type, or to variations in the co-ordination number at tin in the different compounds? Dibutylbis(phenylthiolato)tin shows a quadrupole splitting of 1.96 close to that calculated on the basis of a tetrahedral structure (Table 2) and calculations of this nature are a useful aid to structure assignment. (Ethane-1,2-dithiolato)diphenyltin exhibits a quadrupole splitting close to the calculated value whereas the agreement shown by the corresponding dibutyl compound is less good. This may be a function of the dithiolate ring, constraining the sulphur–tin–sulphur bond, though it could also indicate weak intermolecular S–Sn interaction. However, a simple octahedral structure may be ruled out since the calculated value of e^2Qq for such a species shows a greater discrepancy (Table 2). The dialkyl(ethane-1,2-dithiolato)tin compounds are therefore regarded as distorted tetrahedral molecules.

A partial field gradient parameter for sulphur obtained from the tetrahedral bis(triphenyltin) sulphide gives a calculated quadrupole splitting value for diphenyltin sulphide which is in excellent agreement with the observed value and reasonable concurrence is observed between calculated and observed values for dibutyltin sulphide.

The third type of compound studied, the organotin bis(thioacetates) and bis(mercaptoacetates) contain a carbonyl group in the R′ moiety of $R_2Sn(SR')_2$. The Mössbauer spectra of these compounds are listed in Table 5. Once again the close similarity of the isomer shifts and quadrupole splittings within the thioacetate series suggests that the same structure is present. It remains to decide whether there is any evidence of tin–oxygen bonding. The infrared spectra of the thioacetate compounds were recorded for the region 4000–250 cm^{-1}. The spectrum of the free thioacetic acid in the region 1700–1600 cm^{-1} is complex with five intense bands at 1740, 1720, 1705, 1685, and 1672 cm^{-1}. The spectra of the organotin bis(thioacetates) in this region are simpler, with the bands shifting to a lower frequency, being observed at ca. 1665 m,

TABLE 5

MÖSSBAUER PARAMETERS OF ORGANOTIN DERIVATIVES OF MERCAPTOACETIC ACID AND THIOACETIC ACID

Compound	*Isomer shift*	*Quadrupole splitting*
$Et_2Sn(SCOMe)_2$	1.54	2.91
$Pr_2Sn(SCOMe)_2$	1.51	2.91
$Bu_2Sn(SCOMe)_2$	1.52	2.71
$(C_8H_{17})_2Sn(SCOMe)_2$	1.51	2.67
$Ph_2Sn(SCOMe)_2$	1.37	2.28
$Bu_2Sn(SCH_2CO_2C_9H_{19})_2$	1.43	2.42
$Bu_2Sn(SCH_2CO_2C_8H_{17}\text{-i})_2$	1.43	2.36
$(C_8H_{17})_2Sn(SCH_2CO_2H)_2$	1.42	2.40

1630 s, and 1618 (sh) s cm^{-1}, but the structural implications of this observation are not clear.

A comparison of the Mössbauer spectra of the thioacetates with those of the other dithiolatotin compounds is more useful. Firstly, the quadrupole splitting is noticeably increased, despite the earlier observation that varying R′, in $R_2Sn(SR')_2$ from methyl to phenyl, causes only marginal changes in e^2Qq. Secondly, using a *PFGP* value for the SCOMe group obtained by assuming that $Ph_3SnSCOMe$ is tetrahedral the quadrupole splittings which $R_2Sn(SCOMe)_2$ and $Ph_2Sn(SCOMe)_2$ would have if their configurations were tetrahedral were calculated. The large discrepancy between the calculated and observed values (Table 2), together with the earlier evidence leads us to favour an octahedral structure for these compounds, with oxygen–tin interaction. To test this the octahedral *PFGP* value for SCOMe obtained from the result for the diphenyltin compound was used to calculate e^2Qq for dibutyltin bis(thioacetate), and a better agreement between the observed and calculated values of e^2Qq is obtained (Table 2).

The enhanced values of the quadrupole splittings of the three mercaptoacetic acid derivatives in Table 5, compared with those for the simple thiolates $R_2Sn(SR')_2$, suggest that octahedral structures may be present here also.

EXPERIMENTAL

Details of the Mössbauer spectrometer have been described elsewhere[9]. Measurements were made with the samples cooled with liquid nitrogen, the spectra were calibrated using β-tin and tin(IV) oxide. The error associated with the isomer shift and quadrupole splitting measurements does not exceed ±0.05 mm/s. The Mössbauer results were computed on the University of London Atlas Computer using a programme kindly supplied by Dr. T. C. Gibb[13] which was modified to suit our requirements. The units for the isomer shift, and quadrupole splittings quoted in the Tables are mm/s, and the isomer shifts refer to tin(IV) oxide. The line widths observed were usually in the range 0.85–0.95 mm/s. For the frozen liquids studied, the liquid was injected into a polythene cell (containing thin aluminium strips to improve the thermal conductivity) which was then frozen in liquid nitrogen. The cell was then attached to the sample holder as described previously[9].

The following compounds were kindly supplied by Messrs. Albright and Wilson Ltd. and were used as received, *i.e.* without further purification: $Bu_2Sn(SC_{12}H_{25})_2$, $Bu_2Sn(SCH_2CO_2C_9H_{19})_2$, $Bu_2Sn(SCH_2CO_2C_8H_{17}\text{-i})_2$, $(C_8H_{17})_2SnS$ and $(C_8H_{17})_2Sn(SCH_2COOH)_2$. We are grateful to Dr. I. H. Siddiqui[14] for providing specimens of dibutylbis(methylthiolato)tin and dibutylbis(ethylthiolato)tin. The following compounds were made by published procedures: $R_2\overline{SnSCH_2CH_2S}$ (R = butyl and phenyl)[15], $R_2\overline{SnSCH_2CH_2CH_2S}$ (R = butyl and phenyl)[15], diphenyl(toluene-3,4-dithiolato)tin[15], dibutyltin sulphide[16], diphenyltin sulphide[17] and bis(phenylthiolato)dipropyltin[18].

Preparation of dimethylbis(phenylthiolato)tin

Dimethyltin dichloride (1.65 g, 0.0075 mole) was dissolved in dried benzene (50 ml) and the solution added to a second benzene solution containing sodium phenylthiolate (1.83 g, 0.015 mole). The resulting mixture was warmed with stirring for

2 h. The precipitate was filtered off and the benzene slowly removed to reduce the volume. On cooling the remaining solution, a white solid was formed. m.p. 37–38° (lit.[19] m.p. 38–39°). Yield 2.40 g (87%).

Preparation of bis(phenylthiolato)diphenyltin

Diphenyltin dichloride (1.71 g, 0.005 mole) was dissolved in dried benzene (200 ml), and sodium phenylthiolate (1.22 g, 0.010 mole) in ethanol (20 ml) was added. The solution was warmed and stirred for 4 h. After filtering off the white solid which formed the solvent was slowly removed under reduced pressure on a rotary evaporator, leaving an oil which solidified on cooling. It was recrystallised from absolute ethanol to give the product m.p. 65–66° (lit.[20] m.p. 65°), yield 2.1 g (84%). The other phenylthiolates were prepared in a similar way; Table 6 gives their elemental analyses.

Preparation of dibutyltin bis(thioacetate)[21]

Dibutyltin oxide (1.24 g, 0.005 mole) was suspended in dried benzene and thioacetic acid (0.76 g, 0.010 mole) was added. The mixture was stirred for 2 h at 20°, to form a clear solution. The water formed during the reaction was removed by azeotropic distillation. After filtering the solution the solvent and excess thioacetic acid were removed under reduced pressure on a rotary evaporator. The remaining liquid was distilled at low pressure to give the bis(thioacetate), b.p. 130–135°/1 mmHg. A similar procedure was used for diphenyltin bis(thioacetate) where the oil solidified and was recrystallised from benzene to produce a white solid, m.p. 64–65°. The other thioacetates were prepared in a similar way, and their elemental analyses are given in Table 6.

TABLE 6

SOME DETAILS OF THE COMPOUNDS PREPARED

Compound	*Analyses, found (calcd.) (%)*				*B.p. (°C/mmHg) [or m.p. (°C)]*
	C	*H*	*S*	*Sn*	
$Et_2Sn(SPh)_2$	49.1 (48.6)	5.3 (5.1)	16.1 (16.3)	30.5 (30.1)	[a]
$Bu_2Sn(SPh)_2$	43.9 (43.4)	3.5 (3.6)			247–250/1
$(C_8H_{17})_2Sn(SPh)_2$	60.4 (59.7)	7.9 (7.9)	11.3 (11.4)	21.2 (21.1)	[a]
$Ph_2Sn(SPh)_2$	58.3 (58.6)	4.4 (4.1)	13.1 (13.0)		[65–66]
$Et_2Sn(SCOMe)_2$	30.1 (29.4)	5.1 (4.9)	20.0 (19.6)	36.8 (36.3)	148–155/4
$Pr_2Sn(SCOMe)_2$	33.7 (33.8)	5.3 (5.6)	18.5 (18.1)	33.7 (33.4)	[a]
$(C_8H_{17})_2Sn(SCOMe)_2$	48.4 (48.5)	8.3 (8.1)		24.0 (23.9)	[a]
$Ph_2Sn(SCOMe)_2$	45.5 (45.4)	4.1 (3.8)	15.5 (15.2)		[64–65]

[a] Product was a liquid which was not distilled

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