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Mössbauer and Related Studies of Tin(IV) Dithiolate Complexes.

Part I. The Preparation and Spectra of Complexes Containing 1,1- and 1,2-Dithiolato Ligands

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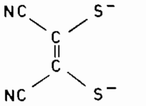
Anionic diorgano- and triorganotin complexes containing the potentially bidentate sulphur ligands $(CN)_2C_2S_2^{2-}$ *and* $CN(COOC_2H_5)C_2S_2^-$ *have been prepared and characterised. Mössbauer spectra have been measured at liquid nitrogen temperature and in some cases at 4.2K in an externally applied magnetic field. Structures are assigned to the complexes on the basis of their quadrupole splittings.*

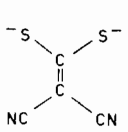
Introduction

Although a number of structural studies of tin(IV) complexes with sulphur ligands have been reported,[1–3] little is known about dithiolato complexes. In particular, there are no reports of systematic studies of complexes involving maleonitrile 1,2-dithiolate, I, or the related ligands, maleonitrile 1,1-dithiolate, II, 1-cyano-1-carbethoxy ethylene 2,2-dithiolate, III, and 1,1-dicarbethoxy ethylene 2,2-dithiolate (DED) IV:



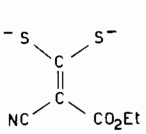
(I)

1,2-Maleonitrile dithiolate (1,2-MNT)



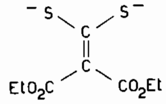
(II)

1,1-Maleonitrile dithiolate (1,1-MNT)



(III)

1-cyano 1-carbethoxy ethylene 2,2-dithiolate (CED)



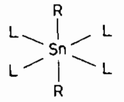
(IV)

1,1-Dicarbethoxy ethylene 2,2-dithiolate (DED)

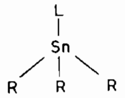
In beginning such a study, we have prepared and characterised a range of di- and triorganotin complexes with these ligands. We have measured their Mössbauer spectra and have assigned structures to a number of them. Measurement of the spectra of some selected compounds in an externally applied magnetic field facilitated the interpretation of the data. The application of ^{119}Sn Mössbauer spectroscopy to structural studies of organotin complexes has been outlined in a comprehensive review.[4] The quadrupole splitting, ΔE, is the most useful parameter that can be correlated with structure. It is given by:

$$\Delta E = {}^1/_2\, e^2Qq(1+\eta^2/_3)^{1/2}$$

Here, eq (= V_{zz}) is the principal component of the electric field gradient tensor and η is the asymmetry parameter given by $(V_{xx} - V_{yy})/V_{zz}$. The quadrupole moment of the I = $^3/_2$ state of the ^{119}Sn nucleus, Q, is known[2] to be negative. The sign of e^2Qq and hence of V_{zz}, together with an estimate of the magnitude of η can often be extracted from the Mössbauer spectrum run in an external field.[5] If the Z axis of an axially symmetric e.f.g. contains alkyl or aryl groups and electronegative ligands lie in the perpendicular plane, then V_{zz} is found to be negative whilst it is positive if the reverse is true. Examples of this are provided by *trans* octahedral R_2SnL_4 and tetrahedral R_3SnL tin compounds:



V_{zz} negative



V_{zz} positive

The crystal structures of a range of organotin compounds are now known from X-ray diffraction studies. In some cases, these structures are distorted from the higher stereochemistry of the point group and the interpretation of quadrupole splitting in advance of crystal structure determination is a risky exercise. It is the purpose of this paper to collect together some of what is already known about structure–quadrupole splitting correlations and to use this in drawing inferences about the new compounds described here.

Consider diorganotin bis(sulphur chelate) systems. These compounds have been described in the past as *cis* octahedral, *trans* octahedral, or tetrahedral with monodentate chelate rings. Bidentate chelates are implicit in the first two descriptions. It is necessary to consider what is implied by the words cis, trans, and tetrahedral and we shall argue that these terms are inappropriate for highly distorted systems. Examples of such distorted systems are provided by organotin–sulphur ligand complexes, in contrast to those involving oxygen donors, which are often quite regular, *e.g.*, *trans* octahedral $Me_2Sn(CH_3COCHCOCH_3)_2$.[6] The factors affecting the precise stereochemistry of these complexes have yet to be unravelled.

An example of a diorganotin bis(sulphur chelate) complex of known structure[7] is provided by bis(N,N-diethyldithiocarbamato)diphenylstannane, $Ph_2Sn(S_2CNEt_2)_2$. This is a six coordinate complex with symmetrical bidentate chelate rings and a C–Sn–C bond angle of 101°. Some authors[8, 9] have described this as "*cis* octahedral" although it and some related complexes were predicted[10] to have distorted structures as the signs of the quadrupole splitting were found to be opposite to what was expected on the basis of the additive model of electric field gradients. A dimethyl compound, $Me_2Sn(S_2CNMe_2)_2$ would be described as *trans* octahedral on the basis of its quadrupole splitting of 2.9 mm s^{-1}. Details of its molecular structure are now available and are given in Table I. It is one of the many cases where it has been established that the dithiocarbamato group is neither quite bidentate nor quite unidentate. Following de Vries and Herber, this bonding situation will be termed anisobidentate. The main difference between so-called *cis* and *trans* bis(N,N-dithiocarbamato)diorganostannanes involves this change in binding of the chelate, together with an increase in C–Sn–C bond angle from 101° to 136.5°. The angle increase, the change from aryl to alkyl groups, and the change in the binding of the chelates, combine to bring about a change in quadrupole splitting by a factor of approximately two. This factor of two is the basis of the original proposal that these two complexes were *cis* and *trans* octahedral complexes. It is now clear that this description is, at best, misleading, if not actually incorrect.

Anisobidentate dithiocarbamato groups are also present in $Me_2Sn[S_2CN(CH_2)_4]_2$, in two crystalline modifications of $Me_3SnS_2CNMe_2$, and in $Ph_3SnS_2CNEt_2$. It is quite impossible to estimate the effect of the longer Sn–S distance on the magnitude of the quadrupole

TABLE I.*

Compound	Bond Angle ° C–Sn–C	Sn–S Bond Length (A)		ΔE (mm s^{-1})	Sign of V_{zz}
$Ph_2Sn(S_2CNEt_2)_2$[a]	101.4	Sn–S_1 2.62 Sn–S_2 2.64	Sn–S_3 2.55 Sn–S_4 2.55	1.76[b]	negative[c]
$Me_2Sn(S_2CNMe_2)_2$[c]	136.0	Sn–S_1 2.50 Sn–S_2 2.95	Sn–S_3 2.51 Sn–S_4 3.06	3.14[e]	–
$Me_2Sn[S_2CN(CH_2)_4]_2$[f]	130	Sn–S_1 2.50 Sn–S_2 2.95	Sn–S_3 2.51 Sn–S_4 3.06	2.85[g]	–
$Me_3SnS_2CNMe_2$[h]	115 (C_2–Sn–C_3) 119 (C_4–Sn–C_3) 100 (C_2–Sn–C_4)	Sn–S_1 2.47 Sn–S_2 3.16		2.25[i]	–
$Ph_3SnS_2CNEt_2$[f]	127 C_{11}–Sn–C_{21} 107 C_{11}–Sn–C_{31} 105 C_{21}–Sn–C_{31}	Sn–S_1 2.53 Sn–S_2 3.06		1.85[i]	positive[e]

* The numbering of the atoms follows that given in the crystallographic papers both already published and prepared for publication. [a] Ref. 5. [b] Ref. 6. [c] Ref. 8. [d] T. Kimura, N. Yasueka, N. Kasai, and M. Kakudo, *Bull. Chem. Soc. Jap.*, 1972, *45,* 1649. [e] B.W.F., unpublished results. [f] P.F. Lindley, personal communication. [g] Ref. 6. [h] G.M. Sheldrick and W.S. Sheldrick, *J. Chem. Soc. (A),* 1970, 490; G.M. Sheldrick, W.S. Sheldrick, R.F. Dalton, and K. Jones, *J. Chem. Soc. (A),* 1970, 493. [i] J. Ensling, P. Gütlich, K.M. Hasselbach and B.W. Fitzsimmons, *J. Chem. Soc. (A),* 1971, 1940.

splitting. In some cases, the effect seems to be small. We have measured the Mössbauer spectrum of the triphenyl compound $Ph_3SnS_2CNEt_2$, in an applied magnetic field. V_{zz} is positive and the asymmetry parameter, η, is small. Significant $Sn–S_2$ interaction would be expected to raise η. However, an η value of 0.3–0.4 would go undetected by this technique.

To summarise, two structural types have so far been observed for complexes $R_2Sn[S_2CNR'_2]_2$. The quadrupole splittings range from 1.7 to 3.1 mm s^{-1} and it is very clear that it is difficult to assign structure on the basis of the magnitude of quadrupole splitting alone.

Results and Discussion

Anionic complexes of formulae $[R_2Sn(1,2\text{-MNT})_2]^{2-}$, $[R_3Sn(1,1\text{-MNT}]^-$, $[R_2Sn(1,1\text{-MNT})_2]^{2-}$, $[R_3Sn(1,2\text{-MNT})]^-$, and $[R_2Sn(CED)_2]^{2-}$ were prepared. Three *tris* complexes of dithiolato ligands were also prepared and studied. The compounds together with their elemental analyses and Mössbauer spectral parameters, are listed in Table II.

We consider first the diorganotin compounds, 1–3, 6, 7, 9 and 10. Compounds 1–3 involve the common ligand, 1,1-MNT. The diaryl compound has a lower quadrupole splitting than the dialkyl compounds, as has been noted previously for related sets of compounds. Taking this into account, it is reasonable to assume that all three compounds possess essentially the same basic structure. The magnetically perturbed Mössbauer spectrum was measured for one of these compounds, $(Me_4N)_2[Bu_2Sn(1,1\text{-MNT})_2]$. V_{zz} is negative and the asymmetry parameter is low. This result is similar to what has been observed for a number of diorganotin bis(chelates) and it would appear that compounds 1–3 have distorted structures involving octahedral co-ordination, bidentate sulphur chelates, and C–Sn–C angles in the region of 130°. As indicated in Table II, a magnetic spectrum was also obtained for compound 6. Once again, V_{zz} is negative, so that this compound must be similar in all respects to compounds 1–3. The small increase in ΔE may be associated with a modest increase in the C–Sn–C bond angle. With

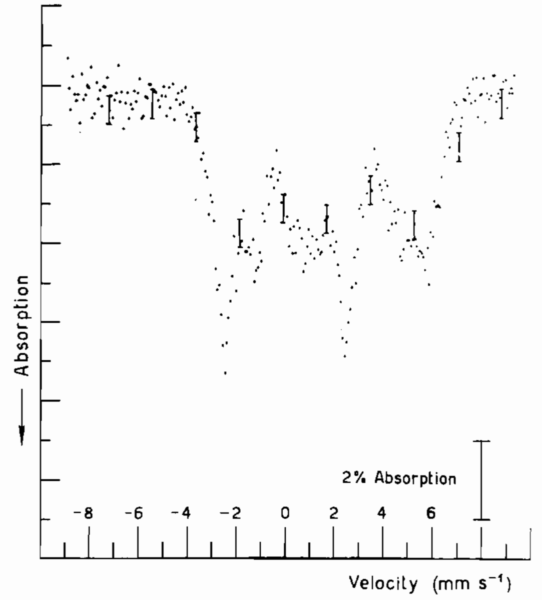


Figure 1. The Mössbauer spectrum of $(Me_4N)_2[Bu_2Sn(1,2\text{-MNT})_2]$ at 4.2K in a transverse magnetic field of 6.0 T.

TABLE II. Mössbauer Parameters and Elemental Analysis for Compounds.[a]

	Calc. (%)			Found (%)							Magnetic
	C	H	N	C	H	N	δ	ΔE	Γ_1	Γ_2	Perturbation
1. $(Me_4N)_2[Me_2Sn(1,1\text{-MNT})_2]$	37.43	5.20	14.55	36.6	6.38	14.23	1.44	2.75	0.96	0.90	–
2. $(Me_4N)_2[Bu_2Sn(1,1\text{-MNT})_2]$	43.57	6.35	12.70	43.35	6.54	12.59	1.55	2.87	1.10	0.88	V_{zz} negative, η small
3. $(Me_4N)_2[Ph_2Sn(1,1\text{-MNT})_2]$	47.95	4.85	11.97	48.22	4.95	12.85	1.36	2.32	0.80	0.76	–
4. $(Me_4N)[Me_3Sn(1,1\text{-MNT})]$	34.95	5.6	11.11	33.85	5.3	10.86	1.33	2.07	0.86	0.90	–
5. $(Me_4M)[Ph_3Sn(1,1\text{-MNT})]$	55.36	4.78	7.44	55.85	5.43	7.78	1.26	1.53	0.86	0.84	V_{zz} positive, η small
6. $(Me_4N)_2[Bu_2Sn(1,2\text{-MNT})]$	43.57	6.35	12.70	42.84	6.67	12.45	1.60	3.13	1.02	1.08	V_{zz} negative, η small
7. $(Me_4N)_2[Ph_2Sn(1,2\text{-MNT})]$	47.95	4.85	11.97	47.31	4.70	11.52	1.15	1.54	0.88	0.98	symmetric spectrum, $\eta \rightarrow 1$
8. $(Me_4N)[Ph_3Sn(1,2\text{-MNT})]$	55.36	4.78	7.44	55.57	4.87	7.45	1.25	1.48	0.82	0.88	–
9. $(Et_4N)_2[Bu_2Sn(CED)_2]$	49.85	7.84	6.45	50.92	7.82	6.81	1.50	2.50	0.88	0.90	–
10. $(Et_4N)_2[Ph_2Sn(CED)_2]$	52.95	6.60	6.17	52.64	6.50	6.00	1.10	1.35	0.80	0.86	–
11. $(Me_4N)_2[Sn(1,1\text{-MNT})_3]$	34.93	3.52	16.29	34.68	3.76	16.07	1.08	0.00	1.10	–	–
12. $(Me_4N)_2[Sn(1,2\text{-MNT})_3]$	34.93	3.52	16.29	35.17	3.70	16.10	1.04	0.00	1.84	–	–
13. $(Me_2N)_2Sn(DED)_3$	39.63	5.62	2.88	39.15	5.48	2.8	1.03	0.00	1.14	–	–

[a] δ, ΔE, Γ_1, and Γ_2, are in mm s^{-1}; δ is with respect to a room temperature source of $BaSnO_3$. [b] ± 0.04 mm s^{-1}.
[c] Line width (full width at half maximum).

compound 7 however, a substantial lowering in ΔE is evident. The magnetic spectrum (Figure 2) indicates that the asymmetry parameter is close to unity. This observation, together with the fall in ΔE from the value obtained for compound 3, leads to the conclusion that this is a four co-ordinate compound with essentially unidentate chelate ligands. Compound 9 has parameters sufficiently similar to those of compounds 1 and 2 for us to propose that it also has a six co-ordinate structure involving bidentate ligands. Compound 10 would appear to be similar in all respects to compound 7.

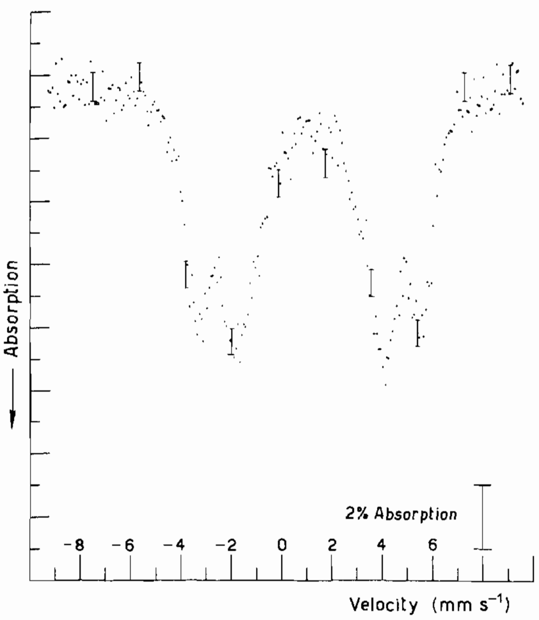


Figure 2. The Mössbauer spectrum of $(Me_4N)_2[Ph_2Sn(MNT)_2]$ at 4.2 in a transverse magnetic field of 6.0 T.

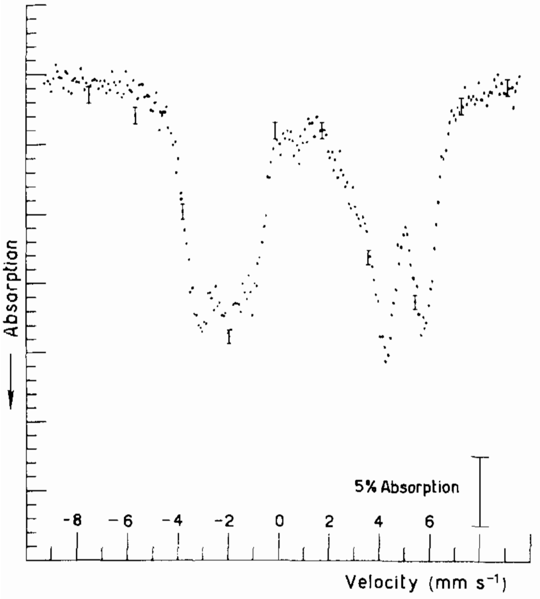


Figure 3. The Mössbauer spectrum of compound $(Me_4N)[Ph_3Sn(1,2\text{-}MNT)]$ at 4.2 in a transverse magnetic field of 6.0 T.

There are three triorganotin compounds in this series 4, 5 and 8. The difference between the alkyl and aryl compound is in the same sense as has been noted in an earlier study and we consider that the observed splittings are too low to bring five co-ordination into serious consideration. Indeed, five co-ordination has not yet been observed for any complex of the type R_3Sn(bidentate S-chelate). V_{zz} for compound 5 is positive in agreement with the suggested structure, although pentaco-ordination is not thereby eliminated. We therefore conclude that this series of triorganotin complexes is essentially four co-ordinate and that the fifth Sn–S interaction produces no detectable effect on the Mössbauer parameters.

Experimental

Zero-field Mössbauer spectra were measured on a constant acceleration spectrometer. Absorbers were maintained at 80 ± 2K and a source of Ba $^{119m}SnO_3$ was used at room temperature. Calibration of the spectrometer was achieved by using a ^{57}Co source and an iron foil absorber. The spectra in magnetic fields were determined by Dr. B. W. Dale and his staff at the Physico-Chemical Measurement Unit, Harwell, with the support of the Science Research Council. The samples were cooled to liquid helium temperature and a transverse magnetic field generated by a superconducting magnet was applied. The strengths of the magnetic fields were obtained from the manufacturer's current–field calibration curve. Zero field spectra were fitted, using a standard least-squares program, assuming Lorentzian line shapes.

The new organotin complexes listed in Table II were prepared by standard methods from organotin chlorides and alkali metal salts of the dithiolate ligands synthesised according to literature procedures.[11]

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