The Mössbauer Effect and Chemistry. Part VII.[1] Preparation and Spectral Properties of Some Chloro(*NN*-dialkyldithiocarbamato)diorganostannanes

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Twelve complexes, $R_2SnCl(S_2CNR_2)$, have been synthesised and characterised. Although i.r. and n.m.r. spectroscopies do not afford clear evidence, tetrahedral structures involving unidentate dithiocarbamate have been assigned to the solid state on the basis of quadrupole splitting energies as measured by Mössbauer spectroscopy.

THE Mössbauer spectra of organotin compounds containing the dithiocarbamato-group have been collected and discussed over the past few years.[2] A number of *X*-ray studies on some of these compounds have helped in the understanding of the Mössbauer data. It has certainly emerged that these compounds were a somewhat unfortunate choice for Mössbauer work because the dithiocarbamato-group can apparently function equally well as a unidentate or a bidentate ligand. It is unidentate in the following tetrahedral compounds: $Me_3SnS_2CNMe_2$,[3] $Ph_3SnS_2CNEt_2$,[4] and $Me_2Sn[S_2CN(CH_2)_4]$.[4] This last compound was originally assigned the correct structure by us,[5] although we later had good reasons to revise this, along with several other compounds, $R_2Sn[S_2CNR_2]_2$, to a *trans*-octahedral structure.[2a] We are currently examining a wide range of these compounds by a variety of techniques to see if there is substantial variation in stereochemistry among them. The dithiocarbamato-group is both uni- and bi-dentate [6] in $Sn(S_2CNEt_2)_4$. So far, no *X*-ray structure for a truly octahedral bis(dithiocarbamato)diorganotin complex has been published, although it is understood that several such studies are in progress. Different workers [2b,7] have noted that the major component of the electric field gradient (e.f.g.) is positive at the tin nuclei in $Ph_2Sn[S_2CNEt_2]_2$. Because it is determinate, it has been concluded that the asymmetry parameter, η, is small and a distorted *cis*-octahedral structure involving bidentate dithiocarbamate seems more likely † than the tetrahedral

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† *X*-Ray diffraction studies have confirmed this structure. The C–Sn–C angle is *ca.* 101° (P. F. Lindley, Dept. of Crystallography, Birkbeck College, personal communication).

[1] Part VI, M. Cox, B. W. Fitzsimmons, L. F. Larkworthy, K. A. Rogers, and A. W. Smith, *J. Chem. Soc.* (*A*), 1971, 2158.

[2] (*a*) B. W. Fitzsimmons, A. A. Owusu, N. J. Seeley, and A. W. Smith, *J. Chem. Soc.* (*A*), 1970, 935; (*b*), R. V. Parish and C. E. Johnson, *J. Chem. Soc.* (*A*), 1971, 1906; (*c*) E. O. Kazimir, Thesis, Fordham University, 1969.

[3] 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.

[4] P. F. Lindley, Department of Crystallography, Birkbeck College, personal communication.

[5] B. W. Fitzsimmons, *Chem. Comm.*, 1968, 1485.

[6] C. S. Harreld and E. O. Schlemper, *Acta Cryst.*, 1971, **B27**, 1964.

[7] B. W. Fitzsimmons, unpublished results.

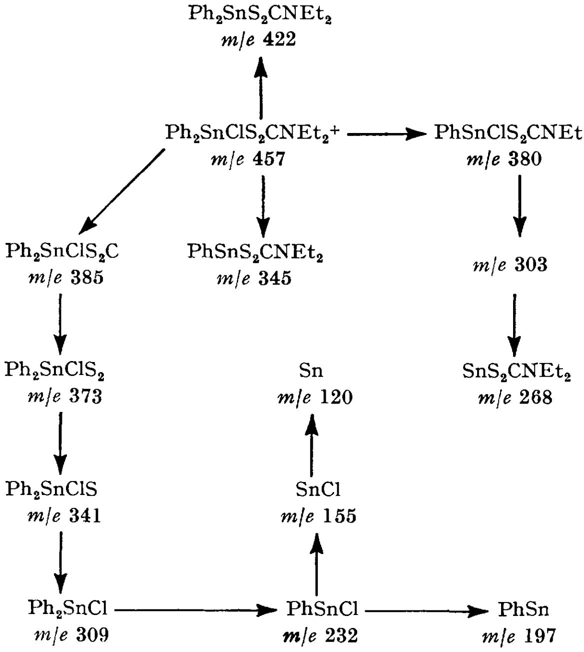
situation. However, the ambident nature of dithiocarbamate must be borne in mind when the stereochemistry of their complexes with organotin cations is under observation.

As a continuation of earlier work, we have prepared and characterised a range of compounds, $R_2SnCl(S_2CNR'_2)$, (I), where R = alkyl, phenyl and R′ = various. These compounds are listed in the Table, together with analytical data and m.p.s. Mass spectra were obtained for these new compounds as an aid to characterisation and we unravelled the fragmentation pattern in several cases in order to see how the dithiocarbamato-group had broken down. We propose to study the influence of the metal on the fragmentation patterns of the more simple sulphur ligands such as dithiocarbamate and xanthate. The fragmentation pattern of compound 10, $Ph_2SnCl(S_2CNEt_2)$, is summarised in Scheme 1. Apart from tin, the most abundant peak in the mass spectrum is that of Ph_2SnClS_2C. It is of interest that the decomposition of this ion takes place in stages and that there are no tin-free species observed in the spectrum.

Analytical data, m.p.s and Mössbauer spectral parameters [a] for chloro(*NN*-dialkyldithiocarbamato)diorganostannanes

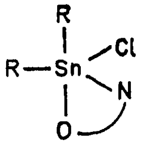
		Calculated				Found						
	Compound	C	H	N	Cl	C	H	N	Cl	m.p.	δ	ΔE
(1)	$Me_2SnClSCSNMe_2$	19·9	4·65	4·0		20·2	4·3	3·5		136—137	1·28	2·98
(2)	$Me_2SnClSCSNEt_2$	25·3	4·8	4·2	10·6	25·4	5·0	4·0	10·5	92—93	1·28	2·72
(3)	$Me_2SnClSCSN(CH_2Ph)_2$	44·75	4·4	3·05	7·8	45·0	4·5	3·4	7·3	164—166	1·35	2·80
(4)	$Me_2SnClSCSN(CH_2)_4$	25·4	4·25	4·25	10·75	26·0	4·1	4·5	11·0	98—100	1·34	2·90
(5)	$Bu_2SnClSCSNMe_2$	34·0	6·2	3·6	9·15	34·3	5·4	3·2	9·8	(54—55) [b]	1·45	3·14
(6)	$Bu_2SnClSCSNEt_2$	37·5	6·75	3·35	8·55	38·0	6·7	3·0	8·6	37—38	1·39	2·76
(7)	$Bu_2SnClSCSN(CH_2Ph)_2$	51·1	5·9	2·6	6·5	49·3	5·9	2·4	6·9	36—38	1·40	2·81
(8)	$Bu_2SnClSCSN(CH_2)_4$	37·65	6·3	3·4	8·55	38·3	6·9	2·9	8·2	(50—52) [b]	1·31	2·88
(9)	$Ph_2SnClSCSNMe_2$	42·05	3·75	3·25		42·0	3·9	3·3		140—141	1·23	2·19
(10)	$Ph_2SnClSCSNEt_2$	44·7	4·4	3·05		44·2	4·2	2·9		144—145	1·14	2·28
(11)	$Ph_2SnClSCSN(CH_2Ph)_2$[13]	55·85	4·15	2·4	6·1	56·5	4·1	2·7	6·9	136—138	1·08	2·34
(12)	$Ph_2SnClSCSN(CH_2)_4$[13]	44·2	3·95	3·1		44·4	3·7	2·6		138—139	1·23	2·31

[a] All spectra obtained at 80 K employing a room temperature source of Ba $^{119}SnO_3$. δ And ΔE are in mm s^{-1} with δ relative to SnO_2, and both are accurate to within ±0·05 mm s^{-1}. [b] B.p. at 760 mmHg.



SCHEME 1

Fragmentation pattern of $Ph_2SnCl(S_2CNEt_2)$



(II)

Some quinolin-8-olato-analogues of (I) have been prepared and their Mössbauer spectra measured and analysed.[8] There it was argued that the compounds were monomeric as in (II) and the Mössbauer spectra of some thiocyanates, $R_2Sn(NCS)$(quinolin-8-olato) have been interpreted in terms of *cis–trans* isomerism but details of this isomerism were not discussed.[9] The Mössbauer parameters of the compounds prepared for this study are summarised in the Table. Like all diorganotin(IV) complexes, they exhibit quadrupole splitting and have chemical isomeric shifts, relative to SnO_2, in the range 1—1·5 mm s^{-1}.[10] These chemical isomeric shifts do not vary greatly along this series of compounds and will not be discussed further. The quadrupole splittings arise from the interaction of the e.f.g. at the tin nuclei with the quadrupole moment of the $I = \frac{3}{2}$ state of ^{119}Sn. It is accepted practice to visualise the e.f.g. as arising from differences in σ-bonding about the tin.[11] We concentrate attention first on the alkyl derivatives, compounds 1—8. The average value for the quadrupole splitting is 2·90 mm s^{-1}. The values of 2·85 mm s^{-1} and 2·25 mm s^{-1} found for the known tetrahedral compounds, $Me_2Sn[S_2CN(CH_2)_4]_2$ and $Me_3SnS_2CNMe_2$, can be used in the calculation of a partial field gradient for the unidentate dithiocarbamato-group. We follow the convention of Clark *et al.*[12] in which the partial field gradient

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[8] R. C. Poller and J. N. R. Ruddick, *J. Chem. Soc.* (*A*), 1969, 2273.

[9] M. A. Mullins and C. Curran, *Inorg. Chem.*, 1968, **7**, 2584.

[10] P. J. Smith, *Organometallic Chem. Rev.*, 1970, **5**, *A*, 373.

[11] R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, 1970, **4**, 65.

[12] M. G. Clark, A. G. Maddock, and R. H. Platt, *J.C.S. Dalton*, 1972, 281.

of an alkyl group is taken as zero and calculate an average value of 1·17. We combine this number with a value for chloride of 1·33 to calculate a theoretical quadrupole splitting for $R_2SnCl(S_2CNR'_2)$ of 2·87 mm s^{-1}. This calculated value can be compared with an average value of 2·90 mm s^{-1} observed for compounds 1—8. This agreement between calculated and observed quadrupole splitting does not, of itself, prove that this range of compounds are all tetrahedral. However, even in the absence of reliable partial field gradient values for five-co-ordinate compounds, we can reasonably expect such structures containing bidentate dithiocarbamate to exhibit quadrupole splittings in the region of 3·4 mm s^{-1}. We therefore feel reasonably certain that tetrahedral structures can be assigned to compounds 1—8.

Compounds 9—12 are biphenyl compounds. If their structures are analogous to those of compounds 1—8, slightly lower quadrupole splitting than the alkyl analogues are expected, because a partial field gradient value of 0·13 has been assigned to these ligands relative to the zero of the alkyl group. After correcting for the asymmetry parameter, a value of 2·57 mm s^{-1} is calculated for such a compound. Once again, the agreement between the observed and calculated values is reasonable. These calculations are summarised in Scheme 2.

$Me_3SnS_2CNMe_2$	$Me_2Sn[S_2CN(CH_2)_4]_2$
$\Delta E_{obs} = 2{\cdot}25$ mm s^{-1}	$\Delta E_{obs} = 2{\cdot}85$ mm s^{-1}
$[S] = 2{\cdot}25/2 = 1{\cdot}12$	$Vpp = 2{\cdot}47$
	$[S] = 1{\cdot}23$

Average tetrahedral $[S] = 1{\cdot}17$

Calculation of quadrupole splitting expected for tetrahedral $R_2SnClS_2CNR'_2$ and tetrahedral $Ph_2SnClS_2CNR'_2$

ΔE calc. $= 1{\cdot}15(1{\cdot}17 + 1{\cdot}33) = 2{\cdot}87$ mm s^{-1}
ΔE calc. $= 1{\cdot}15(1{\cdot}17 + 1{\cdot}33 - 0{\cdot}26) = 2{\cdot}57$ mm s^{-1}

SCHEME 2

Calculations of partial field gradient for unidentate $R_2N-CS_2^-$

We conclude that compounds of formula (I) contain unidentate dithiocarbamato-groups in an essentially tetrahedral stereochemistry.

These conclusions imply that dithiocarbamate behaves as a unidentate ligand throughout this series of compounds. We looked for alternative evidence on this point by taking the proton magnetic resonance spectra of some of these compounds containing the *NN*-dimethyldithiocarbamato-group. O'Connor *et al.*, have established[13] a ^1H n.m.r. method for distinguishing between uni- and bi-dentate dithiocarbamate (unidentate $Me_2N-CS_2^-$, methyl resonance at τ 7·24. Bidentate, $Me_2N-CS_2^-$, methyl resonance at τ 6·72). This method is inapplicable to the organotin complexes of interest, presumably because higher co-ordination numbers can be adopted in solution. For instance, $Me_3SnS_2CNMe_2$, is known to involve a unidentate ligand in the solid state but in deuteriochloroform, a single resonance at τ 6·55 was observed. Similarly, compounds 1 and 9 showed single resonances at τ 6·60 and 6·65 respectively. We conclude that these compounds involve bidentate Me_2N-CS_2 in solution, irrespective of their structure in the solid state. It would be therefore of interest to study the Mössbauer spectra of frozen solutions. We also examined the i.r. spectra of compounds 1—12 quite carefully but were unable to utilize any of the published assignments[14] as our spectra were always too complex in the significant regions.

EXPERIMENTAL

The compounds were prepared by the room temperature reaction of stoicheiometric quantities of diphenyltin dichloride or dialkyltin dichloride with sodium *NN*-dialkyldithiocarbamate in butan-2-one as solvent. Sodium chloride was removed by filtration and the crude products recrystallised from butan-2-one or distilled under reduced pressure as appropriate. Mössbauer spectra were measured at 80 K using apparatus employed previously.

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[13] C. O'Connor, J. D. Gilbert, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 84.

[14] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Nature*, 1956, **177**, 1042.