A Tin-119 Mössbauer Study of Some Disulphoxide Complexes of Triphenyltin(IV) Chloride

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The tin-199 Mössbauer spectra of some disulphoxide complexes of triphenyltin(IV) chloride are reported. The Mössbauer parameters are discussed in terms of the bonding and structural properties of these complexes and are associated with the changes induced in the electronic and ligand environment of tin in triphenyltin(IV) chloride by complex formation.

Introduction

The preparation and characterisation by chemical analysis, infrared spectroscopy and NMR of previously unknown complexes between triphenyltin(IV) chloride and various disulphoxide ligands has recently been reported [1]. Although the structure of one of these complexes has been determined by X-ray crystallography [2], their general solid state properties have yet to be extensively investigated. Tin-119 Mössbauer spectroscopy is a very sensitive means by which the electronic and ligand environment of tin may be investigated and the technique is a potentially powerful means by which the nature of chemical bonding and structure in such solid complexes may be evaluated. We have therefore conducted some Mössbauer investigations of several disulphoxide complexes with triphenyltin(IV) chloride and have interpreted the data in terms of fundamental bonding and structural properties.

Experimental

Complexes between triphenyltin(IV) chloride and the disulphoxide ligands *rac*-$(PrSOCH_2)_2$, *meso*-$(PhSO)_2CH_2$, *rac*-$(PhSO)_2CH_2$, *meso*-$(PhSOCH_2)_2$, *rac*-$(PhSOCH_2)_2$ in which Ph = C_6H_5 and Pr = n-C_3H_7 were prepared according to methods previously described [1].

Tin-119 Mössbauer spectra were recorded at 298 K with a Microprocessor controlled Mössbauer spectrometer using a $Ca^{119}SnO_3$ source and samples containing *ca.* 10 mgSn/cm^2. The drive velocity was calibrated with a ^{57}Co/Rh source and iron foil. All the Mössbauer spectra were computer fitted.

Results and Discussion

The Mössbauer spectra were characterised by well resolved quadrupole split absorptions (Fig. 1). The ^{119}Sn Mössbauer parameters are tabulated in Table I.

TABLE I. Tin-119 Mössbauer Parameters.

Compound	$\delta^a \pm 0.03$ /mms^{-1}	$\Delta \pm 0.06$ /mms^{-1}
$(Ph_3SnCl)_2$ *rac*-$(PrSOCH_2)_2$	1.22	3.06
Ph_3SnCl *meso*-$(PhSO)_2CH_2$	1.46	3.36
Ph_3SnCl *rac*-$(PhSO)_2CH_2$	1.38	3.06
Ph_3SnCl *meso*-$(PhSOCH_2)_2$	1.37	3.15
Ph_3SnCl *rac*-$(PhSOCH_2)_2$	1.44	3.24
Ph_3SnCl	1.37	2.74

$^a\delta$ relative to tin(IV) oxide.

The Mössbauer data for triphenyltin(IV) chloride agree, within the limits of experimental accuracy, with those recorded during a number of other investigations [3–5]. The chemical isomer shifts of the complexes between triphenyltin(IV) chloride and the disulphoxides confirm the retention by tin of an oxidation state of -(IV). However, in contrast to the isomer shift data recorded from some triphenyltin(IV) chloride complexes of sulphoxides which are similar

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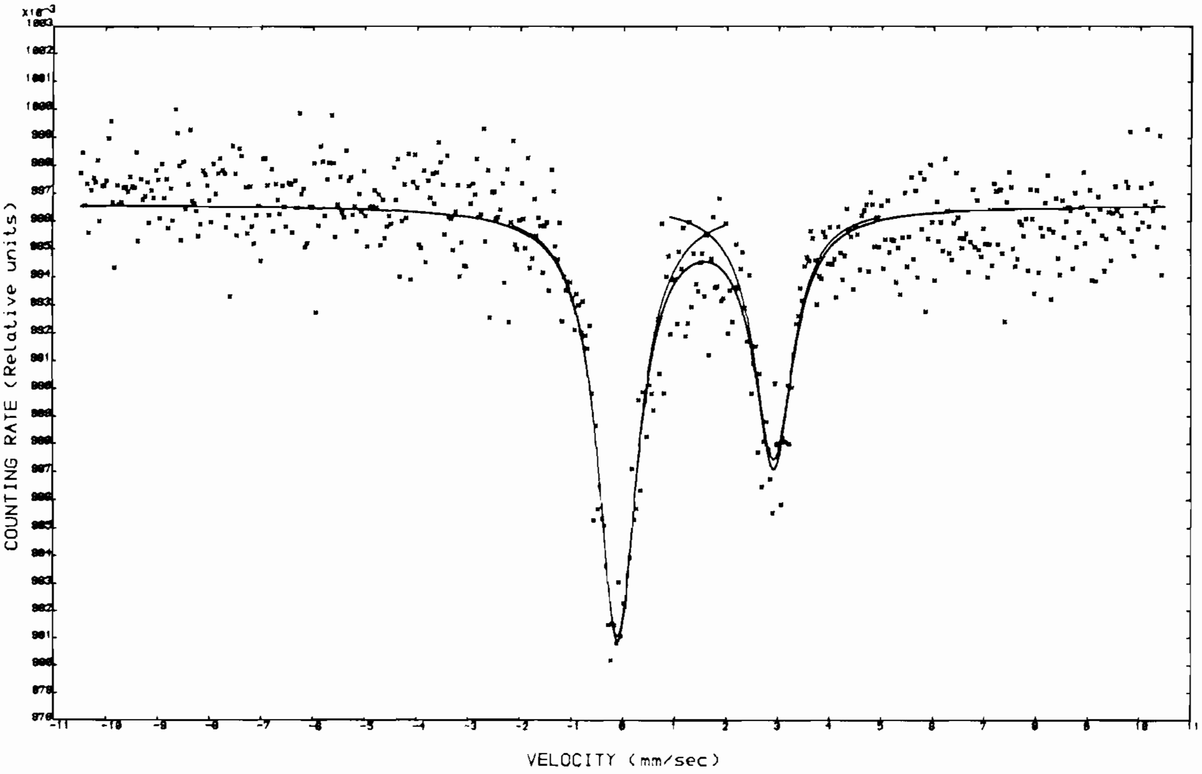

Fig. 1. Tin-119 Mössbauer spectrum recorded from Ph_3SnCl *rac*-$(PhSO)_2CH_2$.

to those of pure triphenyltin(IV) chloride [4, 5], the isomer shifts for the disulphoxide complexes reported here are, with the exception of $(Ph_3SnCl)_2$ *rac*-$(PrSOCH_2)_2$, slightly more positive than that for triphenyltin(IV) chloride. It is also clear that the magnitude of the quadrupole splittings recorded from these complexes exceeds that recorded from pure triphenyltin(IV) chloride.

The reactions between triphenyltin(IV) chloride and the disulphoxide ligands have, with the exception of that producing $(Ph_3SnCl)_2$ *rac*-$(PrSOCH_2)_2$, been reported [1] to give 1:1 complexes in which the disulphoxide acts as a bidentate chelating agent around a central tin atom. In such compounds the six coordinate tin atom may be envisaged as a constituent of either a six- or seven-membered ring. Although other Mössbauer studies of six coordinate organotin(IV) compounds have associated the quadrupole splitting data with the configuration, for example *cis-trans* effects, about tin [6, 7] and which in our case could involve *fac-mer* effects, uncertainty remains as to whether the electric field gradient at the tin nuclei is largely determined by the disposition of the tin–carbon bonds [8] or whether it arises primarily from the electronegativity differences between attached groups or from $p\pi$–$d\pi$ interactions [9]. In these respects it is important to note that geometrical effects may also be reflected in the ^{119}Sn chemical isomer shifts [9, 10]. Whilst acknowledging that the nature of the substituents on organic groups attached to tin will effect its electronic environment [11], the Mössbauer parameters recorded here suggest that there is no significant difference in the electron and ligand distribution about tin when it is a constituent of either a six- or seven-membered ring. Despite the uncertainty which pervades the interpretation of Mössbauer parameters observed in organotin complexes the increased ^{119}Sn quadrupole splitting recorded from the triphenyltin(IV) chloride complexes with disulphoxide ligands may reasonably be associated with increased asymmetry at the nucleus. Indeed, similar effects have been observed [4, 12] when other organotin(IV) halides undergo complex formation. Given that compounds such as triphenyltin(IV) chloride form chain polymers through chlorine bridges such that pentacoordinate tin adopts a trigonal bipyramidal coordination [13] it is quite reasonable to envisage that the formation of a 1:1 monomeric complex would be accompanied by breaking of the intermolecular chlorine bridges and a concomitant decrease in molecular structure. It would seem that the symmetry conveyed by six coordination about tin in such complexes does not outweigh an enhanced distortion of the electronic environment resulting from complex formation.

The compound $(Ph_3SnCl)_2$ *rac*-$(PrSOCH_2)_2$, δ 1.22 mms^{-1}; Δ 3.06 mms^{-1}, is conspicuous by virtue of its chemical isomer shift which is smaller than that of triphenyltin(IV) chloride and its quadrupole splitting which, although larger than triphenyltin(IV) chloride, is smaller than any of the other disulphoxide complexes investigated. The structure of $(Ph_3SnCl)_2$ *rac*-$(PrSOCH_2)_2$ has been shown by X-ray crystallography [2] to be a 2:1 adduct in which the pentacoordinate tin atoms occupy trigonal bipyramidal sites. The smaller chemical isomer shift in the adduct reflects a diminuation of the *s*-electron density at the tin nucleus which presumably results from complex formation and reflects electron donation to the tin which increases the shielding of the *s*-electrons. Such donation to tin is clearly stronger in this complex than the other disulphoxide complexes. The smaller quadrupole splitting of the 2:1 adduct, as compared with the other disulphoxide complexes, may be associated with this effect and reflects a more symmetrical distribution of electron density around tin in a dimeric species with more molecular symmetry than the monomeric complexes.

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