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Preliminary communication

The application of Mössbauer spectroscopy to the study of intermolecular association in organotin compounds

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Although considerable attention has been focused on the use of Mössbauer spectroscopy to study the structures of organotin compounds[1-7], the interpretation of observed quadrupole splittings has been hindered by the lack of a definitively tetrahedral compound, containing ligands for which data on five- and six-coordinate compounds are also available. In this communication we present data (Table 1) identifying the range of quadrupole splittings associated with tetrahedral structures, leading to a greater understanding of the relationship between quadrupole splitting and intermolecular association.

The crystal structure of $Ph_2SnI(CH_2)_4SnIPh_2$ has been shown[8] to have a slightly distorted tetrahedral coordination of the tin atoms with no short intermolecular Sn–I distances, and hence can be used as a standard tetrahedral compound. The measured quadrupole splitting (Table 1) of 2.37 mm/s is similar to those observed for the compounds Ph_3SnI and Neo_3SnI (Table 2) suggesting that these compounds also have tetrahedral structures; the small differences in the quadrupole splittings are probably due to the greater polarity of tin–phenyl compared with tin–alkyl bonds[1]. The quadrupole splittings of the compounds Neo_3SnX(X = F, Cl, Br) and Ph_3SnX(X = Cl, Br) (Table 2) are similar to those of the iodides and increase uniformly with decreasing atomic number of the halogen, consistent with tetrahedral coordination. Further the observed quadrupole

TABLE 1

MÖSSBAUER DATA

Compound	δ^a (mm · sec^{-1})	Δ (mm · sec^{-1})
$Ph_2SnI(CH_2)_4SnIPh_2$	1.44	2.37
(cyclo-$C_6H_{11})_3SnF$	1.56	3.96
(cyclo-$C_6H_{11})_3SnCl$	1.64	3.49
(cyclo-$C_6H_{11})_3SnBr$	1.63	2.90
(cyclo-$C_6H_{11})_3SnI$	1.64	2.77
(cyclo-$C_6H_{11})_3SnO\cdot COCH_3$	1.57	3.27

^{a}relative to SnO_2

TABLE 2

QUADRUPOLE SPLITTING DATA (mm · sec^{-1})

	X				
	F	Cl	Br	I	OCOR
Ph_3SnX	3.53[b]	2.56[b]	2.48[b]	2.25[b]	2.26[e,f]
Neo_3SnX[a]	2.79[c]	2.65[c]	2.645[c]	2.40[c]	2.45[c,g]
Me_3SnX	3.82[d]	3.44[d]	3.39[d]	3.10[d]	3.68[e,g]

[a] Neo = neophyl, 2-methyl-2-phenyl-1-propyl, $(CH_3)_2C(C_6H_5)CH_2$-. [b] Ref.2. [c] Ref.9. [d] Values are an average of those given in Ref.14 and Ref.15. [e] Ref.3. [f] R = CH(Et)Bu. [g] R = Me.

splittings of the compounds $Neo_3SnOCOCH_3$ and $Ph_3SnOCOCHEtBu$ (Table 2) which are postulated to have tetrahedral structures[3,9] are also close to that of $Ph_2SnI(CH_2)_4SnIPh_2$. Hence the quadrupole splittings of the compounds Neo_3SnX(X = F, Cl, Br, I, $OCOCH_3$) and Ph_3SnX(X = Cl, Br, I, OCOCEtBu) can be taken as representative of unassociated tetrahedral trialkyl- and triaryl-tin compounds and these data suggest that quadrupole splittings in tetrahedral tin compounds are generally less than 2.8 mm/s. The quadrupole splittings of the compounds Me_3SnX(X = F, Cl, Br, I, $OCOCH_3$) (Table 2) are typical of those found for compounds with associated five-coordinate structures[2,3]

It will be noted that these quadrupole splittings are much larger than those predicted by application of the point charge model[2], which gives a range 2.07—1.67 mm/s for the compounds Neo_3SnX(X = F, Cl, Br, I) and of 1.66—1.46 mm/s for the compounds Ph_3SnX(X = Cl, Br, I). This discrepancy was attributed to a residual association in these compounds but can now be seen to arise from inaccuracies in the point charge model. In fact it can be shown that this discrepancy is a reflection of a fundamental weakness in the point charge model when applied to compounds of differing coordination[10] numbers.

The data in Table 2 allows Mössbauer spectroscopy to be used to indicate the extent of intermolecular association in organotin compounds. An excellent example is found in the data for the tricyclohexyltin compounds (Table 1). Thus an X-ray diffraction study[11] has shown that the structure of tricyclohexyltin acetate consists of discrete four-coordinate tin molecules. The large intermolecular tin—oxygen distance of 3.48 Å seems to preclude any intermolecular interaction. However the observed quadrupole splitting of tricyclohexyltin acetate is much greater than that expected for a four-coordinate species and clearly indicates significant intermolecular association despite the large Sn—O distance.

In the case of the tricyclohexyltin halides, the fluoride and chloride give quadrupole splittings which are similar to those found for their trimethyltin analogues indicating polymeric five coördinate structures. In contrast, tricyclohexyltin bromide and iodide give quadrupole splittings which are midway between those found for trimethyl- and trineophyl-tin bromide and iodide. This is strong evidence for a weak but definite intermolecular association and these compounds probably have similar structures to tricyclohexyltin acetate.

The tetrahedral structures of the compounds Neo_3SnX(X = F, Cl, Br, I, $OCOCH_3$) and Ph_3SnX(X = Cl, Br, I) and the weakening of the intermolecular association in tricyclohexyltin derivatives are probably due to steric effects. From the data in Tables 1 and 2 it can be seen that the steric effects of these ligands have the approximate orderings Neo > Ph > cyclo-C_6H_{11} > Me and I > Br > Cl > $OCOCH_3$ > F.

Recent papers[12,13] have dealt with the theoretical interpretation of the quadrupole splittings of "tetrahedral" tin compounds. However using the data in Table 2, it can be seen that some of the compounds, which were used as examples of tetrahedral species, do in fact have essentially five-coordinate structures; for example the compounds R_3SnX(R = Et, Pr, Bu, iso-Bu; X = F, Cl, Br)[12] and $(PrF_3)_3SnCl$ and Et_3SnBr[13] are probably five-coordinate. As a result the conclusions reached should be treated with caution, and in particular the variations in α_{Cl} observed[13] between the compounds $(PrF_3)_nSnCl_{4-n}$ and Ph_nSnCl_{4-n} are more probably due to differences in structure rather than π-bonding effects as suggested.

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