Mössbauer Spectra of Hexaco-ordinate Complexes of Tin(IV) containing Two Tin–Carbon Bonds: a Correlation of Quadrupole Splitting with Stereochemistry

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THERE is much of interest in the stereochemistry of hexaco-ordinate complexes of Group IVB.[1] The structures of such complexes containing two alkyl or aryl groups have generally been taken to be based on a linear C–E–C unit (E is a Group IVB element).[2] Recently however, the structure of the compound $Me_2SnOxin_2$ (oxin = 8-hydroxy-quinolinolate$^-$) in the solid state has been investigated by *X*-ray diffraction and the methyl groups were found[4] to be essentially *cis* with respect to each other although the octahedron is somewhat distorted ($\angle$C–Sn–C$\sim$109°).

Here are reported the Mössbauer spectra of these and certain other hexaco-ordinate complexes of tin(IV) containing two tin–carbon bonds. The measurement of a Mössbauer spectrum permits the calculation of δ, the chemical isomeric shift, and ΔE, the quadrupole splitting. ΔE, our main concern here, is non-zero when there is an electric field gradient at the tin nucleus.[5] It is known that whilst ΔE is immeasurably small for hexaco-ordinate Sn(IV) complexes with ligands having as donor atoms any of the following: F, Cl, Br, I, O, S or N, it is appreciable in complexes of the type R_2SnX_4 where X_4 is made up from the above list.[6] It follows that the magnitudes of the electric field gradients at the Sn nuclei in compounds R_2SnX_4 are controlled by the geometrical arrangement of the C–Sn–C unit. Two important arrangements of this unit are with the carbon atoms mutually *cis* or *trans*. The electric field gradients will be axially symmetric in each case.

We have previously made a study of *cis–trans* complexes of Fe^{II} and found that the ΔE values

TABLE

Mössbauer parameters and stereochemical assignments for complexes R_2SnX_4[c,d]

	R_2SnX_4	ΔE(mm.sec.$^{-1}$)	δ(mm.sec.$^{-1}$)	Assignment from Mössbauer spectrum	Assignment from other techniques
1	$Me_2SnOxin_2$	1·98[a]	0·77[a]	*cis*	*cis*, *X*-ray[4]
2	$[PyH]_2[Me_2SnCl_4]$	4·32	1·59	*trans*	*trans*, i.r.[3]
3	$Me_2SnAcac_2$	3·93	1·18	*trans*	*trans*, i.r., Raman n.m.r.[2]
4	$Ph_2SnOxin_2$	1·78	0·83	*cis*	*cis*, dipole moment[10]
5	$Ph_2SnAcac_2$	2·14	0·74	*cis*	—
6	$[PyH]_2[Ph_2SnCl_4]$	3·80	1·44	*trans*	—
7	$Ph_2Sn[O_2P(OEt)_2]_2$	4·22	1·04	*trans*	—
8	Me_2SnCl_2bipy	4·09[a]	1·55[a]	*trans*	*trans*, i.r.[11]
9	Me_2SnCl_2phen	4·03[b]	1·32[a]	*trans*	—
10	$Bu^n{}_2SnCl_2$phen	4·07[b]	1·69[b]	*trans*	*trans*, dipole moment[9]
11	$Bu^n{}_2SnCl_2$bipy	3·83[b]	1·56[b]	*trans*	*trans*, dipole moment[9]

[a] Data from Ref. 8; [b] Data from Ref. 9; [c] Absorber temperatures $\sim$80°K in all cases; [d] δ and ΔE are accurate to at least $\pm 0\cdot2$ mm sec.$^{-1}$ and δ is expressed relative to tin(IV) oxide, with β-tin at 2·70 mm. sec.$^{-1}$. The data from Ref. 9 has been converted to this scale by adding 1·52 mm. sec.$^{-1}$ to the isomeric shifts.

were within experimental error as predicted[7] *via* a point-charge model, *viz.* $\Delta E_{trans} = 2\Delta E_{cis}$. We now report that this relationship also holds good for *cis*- and *trans*-R_2SnX_4, where R is alkyl or aryl and X_4 is made up from Cl, O, or N.

Our own data and some available from the literature[8,9] is collected together in the Table. Certain of these compounds have been studied by other techniques and where definite proposals regarding the stereochemistry have been made from these studies they are included.

Compounds 1—3 have been the most carefully examined and they serve as reference compounds. At once the 2 : 1 *trans* : *cis* ratio for ΔE is seen to hold good and it can therefore be stated that those compounds with $\Delta E \sim 2$ mm. sec.$^{-1}$ are *cis* and those with $\Delta E \sim 4$ mm. sec.$^{-1}$ are *trans*. With this information the stereochemistries of remaining compounds can be assigned. When available, the stereochemistries already assigned are in agreement. It is of interest that the *trans*-arrangement of alkyl or aryl groups is not quite so generally common as is sometimes supposed and also that Mössbauer spectroscopy now provides a convenient means whereby the structures of these compounds may be further investigated.

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