Structure of Five-co-ordinate Sn^{IV} Isomers from Mössbauer Quadrupole Splittings

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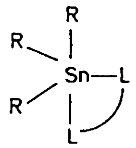
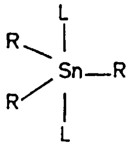
Summary The three isomers of trigonal bipyramidal R_3SnL_2 have been distinguished by linear regression analysis of new ^{119}Sn quadrupole splitting data for five-co-ordinate R_3SnL_2 and six-co-ordinate R_2SnL_4 species, showing that the five-co-ordinate systems have splittings ranging from *ca.* 1·7—2·3 mm s^{-1} for *cis*-R_3SnL_2, *ca.* 3·0—3·9 mm s^{-1} for *equatorial*-R_3SnL_2, and *ca.* 3·5—4·1 mm s^{-1} for *mer*-R_3SnL_2.

Mössbauer quadrupole splittings of six-co-ordinate and four-co-ordinate Sn^{IV} compounds are now well understood in terms of the additivity model.[1] Five-co-ordinate Sn^{IV} quadrupole splittings have not yet been satisfactorily interpreted,[1a] although they have been used to predict a large number of five-co-ordinate Sn^{IV} structures.[2] However, as Clark *et al.*[1a] have pointed out, the five-co-ordinate problem is greatly complicated by having to assign different partial quadrupole splittings to axial and equatorial groups. Until this is done, structural predictions cannot be made with confidence. In addition, the structural data necessary for an analysis of quadrupole splittings are largely lacking.[3] Until the recent publication of a *cis*-R_3SnL_2 structure (I) of triphenyltin *N*-benzoyl-*N*-phenylhydroxamate[4] all other known structures had equatorial R groups (II). No definite examples of isomer (III) are known, although Ho and Zuckerman[2d] have recently suggested that tricyclohexyltin acetate has this structure rather than the four-co-ordinate structure given by the X-ray study[5] or the associated structure suggested by Platt.[6]

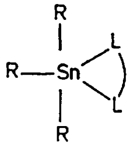
We now report quadrupole splittings for a large number of novel neutral and cationic species of the three different isomers of R_3SnL_2 (R = Me, Ph; L = neutral monodentate ligand or L_2 = bidentate ligand). All new compounds gave good analyses and sharp melting points.[7] We have correlated the five-co-ordinate quadrupole splittings with the quadrupole splittings for the corresponding six-co-ordinate *trans*-R_2SnL_4 compounds, or twice the quadrupole splitting of the *cis*- Ph_2SnL_4 [L_2 = anions of benzoylacetone (bzac), dibenzoylmethane (bzbz), and 8-hydroxyquinoline (oxin)]. It is apparent that three distinct correlations are obtained, and the isomers have been assigned in the Figure. The partial quadrupole splitting treatment strongly suggests that the three Ph_3SnL_2 compounds with small quadrupole splittings have structure (I), and a single crystal X-ray study of $Ph_3Sn(bzbz)$ confirms this structure.[7b] The crystal structure data[3] on Me_3SnL_2 (L = monodentate) compounds show that such compounds have structure (II). The largest five-co-ordinate quadrupole splittings are assigned to isomer (III). There is still a slight possibility that the bidentate ligands bridge rather than chelate [structure (IV)], but few examples of bridging acetylacetonate ligands are known. In any case, the co-ordination environment of Sn in structures (III) and (IV) will be very similar. Linear polymeric structures with equatorial R groups (as found in R_3Sn acetates[8]) can be ruled out due to the multiple infrared Sn–C bands in the 550 cm^{-1} region.[7]



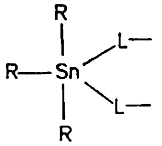
(I)



(II)



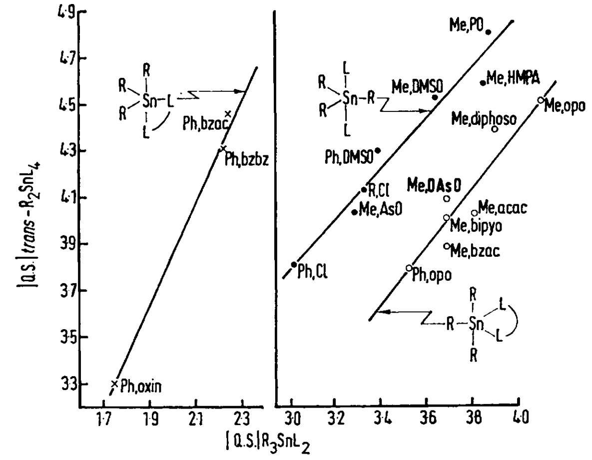
(III)



(IV)

Our results show that five-co-ordinate R_3SnL_2 quadrupole splittings span almost the entire range of quadrupole splittings from four-co-ordinate R_3SnL values to *trans*-R_2SnL_4 values. Thus many of the structural conclusions reported previously are not well-founded; in particular, it should be noted that isomer (III) gives a larger "normalized' quadrupole splitting than isomer (II) in contrast to that previously calculated.[2b,d] This clearly emphasizes that a given ligand must be assigned different partial splitting parameters in the axial and equatorial positions.

The correlations shown in the Figure are all statistically acceptable, and the relative slopes of the three lines (I > III > II) are in agreement with the predictions of the additivity model. The intercept obtained from a linear regression of the Me compounds with structure (II) implies that the predicted quadrupole splitting of the unknown Me_5Sn^- species is $+0{\cdot}56$ mm s^{-1}. The regression lines shown for isomers (I) and (III) apply only in the region where (in notation of Ref. 1a) $|\sigma_R^{tbe} - \sigma_R^{tba}|$ and $|\sigma_L^{tbe} - \sigma_L^{tba}|$ are both much less than $|\sigma_R - \sigma_L|$. Analysis of the intercepts is more complicated in these cases.



FIGURE

Plot of the magnitude of the quadrupole splittings for *trans*-R_2SnL_4 species (or twice *cis*-R_2SnL_4) versus the magnitude of the quadrupole splitting for R_3SnL_2 species. The lines are least-squares fits to the data. Units are mm s^{-1}; PO = triphenylphosphine oxide; DMSO = dimethyl sulphoxide; AsO = triphenylarsine oxide; HMPA = hexamethylphosphoramide; R = alkyl groups (average of quadrupole splittings taken by Clark *et al.*[1a]); bipyo = 2,2'-bipyridine *NN'* dioxide; opo = methylenebis(diphenylphosphine oxide); diphoso = ethylenebis(diphenylphosphine oxide); OAsO = methylenebis(diphenylarsine oxide).

The regression analysis used in the present paper forms the basis of a method for constructing a scale of relative partial quadrupole splitting parameters, similar to those given previously for four- and six-co-ordinate species.[1a] Further, the calculated error of the least-squares fits can be used to obtain tolerance levels providing a quantitative guide to the probable correctness of predictions based on the additivity model. These developments will be fully reported in a subsequent paper.

(*Received*, 17*th December* 1973; *Com.* 1702.)

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