Structure of Bis(acetylacetonato)-dihalogenotin(IV) Complexes

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RECENT work[1] has shown that some β-diketone complexes of the dimethyltin(IV) cation of the general formula $Me_2Sn(R'COCHCOR'')_2$ adopt the trans-configuration. It has been suggested

[1] M. M. McGrady and R. S. Tobias, J. Amer. Chem. Soc., 1965, 85, 1909.

that the tin bonds strongly to the two methyl groups by means of nearly pure sp-hybridized orbitals, leaving the β-diketone groups less strongly bound.

This behaviour is by no means general for tin(IV) β-diketone complexes as normally prepared. For example, in the case of the dihalogenotin(IV) complexes, as prepared by the method of Morgan and Drew,[2] the high-resolution proton magnetic resonance spectra strongly suggest that the *cis*-configuration is the stable one in solution. In the table, we list the chemical shifts (τ-values relative to SiMe$_4$ as 10·00) and spin–spin splitting constants (in c./sec.) of the hydrogen atoms in the β-diketone ring for the three complexes SnX$_2$-(MeCOCHCOMe)$_2$ in which X = Cl, Br, I, in saturated solutions (usually less than 5%) in CDCl$_3$ and C$_6$H$_6$. Rather similar spectra have been obtained for a sample believed to be SnF$_2$-(acac)$_2$, but a pure compound has not yet been isolated. A symmetrical doublet (with ^{117}Sn–^{1}H and ^{119}Sn–^{1}H spin–spin splitting) appears in the methyl region, the position and separation of which show a strong solvent-dependence. Except in nitrobenzene solutions, where the separation is too small to be resolved, the two peaks are of equal intensity in all the complexes: furthermore, only *one* CH peak (with spin–spin splitting to ^{117}Sn and ^{119}Sn) is ever resolved. We believe that this is strong evidence in favour of the *cis*-configuration (point symmetry C_2).

In Me$_2$Sn(acac)$_2$, neither the methyl groups nor the CH group of the β-diketone ring show resolvable spin–spin splitting due to the Sn nucleus, whereas in the SnX$_2$(acac)$_2$ complexes there is generally a well-resolved splitting which increases as X goes from I to Cl. We have also observed[3] a splitting of 2·5 c./sec. between ^{195}Pt and the CH group of the β-diketone ring in Me$_3$Pt-(acac) (quinoline), but no splitting from ^{203}Tl or ^{205}Tl to CH has been resolved in Me$_2$Tl(acac). Part of the reason for its detection in the halogeno-tin(IV) complexes may be the undoubtedly large positive charge on the tin(IV) atom, but this would not explain directly why the *cis*-configuration seems to be preferred.

It appears that when tin(IV) is six-co-ordinated, $5s$, $5p$, and $5d$ orbitals are used in bonding in a way which depends on the effective positive charge on the tin(IV) atom. With two Sn–C bonds of low polarity, the d-orbitals are too high in energy to be used extensively in the bonding. The tin atom prefers to use sp_z hybrid orbitals (presumably with an admixture of sd_{z^2}), giving two strong *trans*-bonds, and allowing the $d_{x^2-y^2}$ orbital to form weaker hybridized orbitals with little s-character in the perpendicular plane. When the six ligands are more nearly equal in electronegativity (or in their position in the spectrochemical series) d^2sp^3 hybridization is possible and in the absence of strong steric effects the molecule adopts that configuration which causes the smaller splitting between the d_{z^2} and $d_{x^2-y^2}$ orbitals, namely the *cis*.[4] The s-character of the Sn bond increases considerably, thereby enhancing the spin–spin splitting to the methyl and CH groups of the β-diketone ring.

TABLE

Chemical shifts (τ-values) and spin–spin splitting constants (J *in c./sec.*) *in SnX$_2$(acac)$_2$ complexes*

Compound	Solvent	τ(CH$_3$)	τ(CH)	J(Sn–CH$_3$)	J(Sn–CH)
SnCl$_2$(acac)$_2$	CDCl$_3$	7·79, 7·88	4·29	7·2, 5·8	6·0
	C$_6$H$_6$	8·41, 8·43	4·93	6·8, 5·4	5·6
SnBr$_2$(acac)$_2$	CDCl$_3$	7·79, 7·90	4·28	6·2, 5·8	4·9
	C$_6$H$_6$	8·41, 8·44	4·91	6·6, n.r.	5·0
SnI$_2$(acac)$_2$	CDCl$_3$	7·83, 7·93	4·24	4·2, 4·0	2·8
	C$_6$H$_6$	8·45, 8·47	4·88	4·4, 4·2	2·8

(n.r. = not resolved)

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[2] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 1924, 372.
[3] K. Kite, J. A. S. Smith, and E. J. Wilkins, to be published.
[4] C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, 1962, pp. 106—107.