STUDY OF THE STRUCTURE AND COMPLEXATION OF ORGANIC AND INORGANIC DERIVATIVES OF METALS BY MEANS OF N.M.R. SPECTROSCOPY OF HEAVY NUCLEI

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ABSTRACT

Data are considered about the structure and complexation of many compounds of tin and mercury, obtained by the present authors and other investigators by means of n.m.r. spectroscopy of ^{119}Sn and ^{199}Hg. In the case of tin compounds important information can be derived from the values of chemical shifts $\delta(^{119}$Sn$)$ and spin–spin coupling constants $J(^{119}$Sn–C–^{1}H$)$, $J(^{119}$Sn–C–^{19}F$)$ and $J(^{119}$Sn–^{13}C$)$. Conclusions about the structure and complexation of mercury compounds are derived mainly from the spin–spin coupling constants $J(^{199}$Hg–C–^{1}H$)$, $J(^{199}$Hg–C–^{19}F$)$ and $J(^{199}$Hg–^{13}C$)$, though data about the $\delta(^{199}$Hg$)$ are also available.

The application of n.m.r. spectroscopy to the study of organic and inorganic derivatives of metals, the isotopes of which have necessary magnetic properties, was shown to be very productive from the viewpoint of information about the behaviour of these compounds in solution. This information is very important for solving the many problems of inorganic and organometallic chemistry. One such problem is the question about the effect of solvents upon the rates and mechanisms of inorganic and organometallic compounds[1].

A review about the p.m.r. spectra of different compounds of metals was published recently[2]. In the present work we are illustrating the possibilities of applying n.m.r. spectroscopy of heavy nuclei to the study of the structure and complexation of organic and inorganic derivatives of metals, using the data about the chemical shifts of ^{119}Sn and ^{199}Hg nuclei and their spin–spin coupling constants with ^{1}H, ^{13}C and ^{19}F for different compounds of tin and mercury.

TIN COMPOUNDS

In 1961 Burke and Lauterbur[3] studied ^{119}Sn n.m.r. spectra of eighteen organic and inorganic derivatives of tin and showed that $\delta(^{119}$Sn$)$ varied by 1850 ppm depending upon the structure of the molecules. It was assumed that such a large range of $\delta(^{119}$Sn$)$ values cannot be rationalized by changes in the diamagnetic term of the ^{119}Sn screening constant, but that it merely reflects

great sensitivity to changes in the structure of the paramagnetic term in the Ramsay equation. The unusual large solvent effect on $\delta(^{119}Sn)$, observed at the same time, was rationalized by the authors in terms of coordination between the solute and solvent molecules.

The list of tin compounds for which the values of $\delta(^{119}Sn)$ were reported[4–17] was then greatly increased. A review on the chemical shifts of ^{119}Sn has been submitted for publication[18] and therefore here we will only consider some of the data; but sufficient to show that in some cases there is a good correlation between the $\delta(^{119}Sn)$ value and the electron-withdrawing power of substituents (*Table 1*), but that in other cases the changes of $\delta(^{119}Sn)$ cannot be rationalized in a simple way.

Table 1. $\delta(^{119}Sn)$ values for Me_3SnX compounds[6,7]

X	Solvent	$\delta(^{119}Sn)$ (ppm)
Cl	CH_2Cl_2	−166
Br	Benzene	−128
CCl_3	Benzene	−85
CCl_2H	Benzene	−33
$CClH_2$	Benzene	−4
Me	CH_2Cl_2	0
Bu	Benzene	+2
Ph	−	+30
$CH=CH_2$	−	+35
Me_3Sn	Benzene	+113

The examples in *Table 2* show that in going from Me_4Sn to Me_3SnBr the expected deshielding of ^{119}Sn is observed. Further progressive substitution of Me on Br leads to a strong shift of resonance to a high field. This fact can be rationalized only if we assume an increasing contribution of the (d–p) π interactions with the increasing number of Br atoms.

Table 2. $\delta(^{119}Sn)$ values for Me_nSnBr_{4-n} ($n = 0 - 4$) compounds[3,6,7]

Compound	Solvent	$\delta(^{119}Sn)$ (ppm)
Me_3SnBr	Benzene	−128
Me_2SnBr_2	$CHCl_3$	−74
Me_4Sn	CH_2Cl_2	0
$MeSnBr_3$	CH_2Cl_2	+170
$SnBr_4$	−	+638

We will consider most carefully the spin–spin coupling constants of ^{119}Sn with ^1H, ^{13}C and ^{19}F nuclei, which are widely used for the structure analysis of different Δt inorganic compounds. First of all we will consider the influence of the nature of X in Me_3SnX on the $J(^{119}Sn–C–^1H)$ spin–spin coupling constants (*Table 3*).

Table 3. $J(^{119}Sn-C-^{1}H)$ values for solutions of Me_3SnX in CCl_4 [19–22]

X	$J(^{119}Sn-C-^{1}H)$ (Hz)
Me_3Sn	48.5
Me	54.0
C_6H_5	54.6
C_6Cl_5	56.8
I	57.2
Br	57.8
Cl	58.1
C_6F_5	58.4
CF_3	58.7
F	69.0

It is evident from the data of *Table 3* that $J(^{119}Sn-C-^{1}H)$ increases with an increase of the electron-withdrawing power of the group X. The up-to-date explanation of this fact is that there is a corresponding increase in the s character of the sp^3-hybrid orbitals of tin in the tin–carbon bonds[23–25]. This conclusion was first made by Holmes and Kaesz[26], who supposed that the main contribution to the observed coupling constants is made by the Fermi contact term and that these coupling constants do not depend upon the s electron density on coupled protons and the geminal angle Sn–C–H. Nevertheless, Verdonck and Van der Kelen[27–30] have shown the importance of such contributions as the spin-orbital term and the s electron density on coupled protons. On the other hand, it was shown recently that diastereotopic methyl groups[31] and anisochronic methylene protons[32], bonded with tin atoms in several types of the molecules, have different spin–spin coupling constants with ^{119}Sn nuclei. These facts were considered to be direct evidence for the angle dependence of $J(^{119}Sn-C-^{1}H)$[32].

Thus, in the course of the study of $J(^{119}Sn-C-^{1}H)$ values it is necessary to consider their dependence, not on the s-character of sp^n-hybrid orbitals of tin in Sn–C bonds, but on the relative content of s electrons in the whole fragment Sn–C–H, in which coupling occurs, and on the geminal angle between the Sn–C and C–H bonds. As regards the spin-orbital term, it is not so important for $J(^{119}Sn-C-^{1}H)$, but is more important in the cases of $J(^{119}Sn-C-^{19}F)$ and $J(^{119}Sn-^{13}C)$[28]. Unfortunately the number of literature values of $J(^{119}Sn-C-^{19}F)$ is small and most of them are given in *Table 4*.

Table 4. $J(^{119}Sn-C-^{19}F)$ for several organotin compounds[21, 33, 34]

Compound	$J(^{119}Sn-C-^{19}F)$ (Hz)	$J(^{119}Sn-C-^{1}H)$ (Hz)
Me_3SnCF_3	293.0	58.7
$Me_3SnCF_2CF_2H$	249.5	57.8
$Me_3SnCF_2CFHCF_3$	222.0	58.6
$Me_2SnH(CF_2CF_2H)$	251.0	62.8
$Me_2Sn(CF_2CF_2H)_2$	274.0	64.5

It is dangerous to draw any conclusions from these constants about their correlation with the structure of the molecules, especially since their changes do not correlate with the changes of $J(^{119}Sn-C-^{1}H)$ for these compounds.

$J(^{119}Sn-^{13}C)$ spin–spin coupling constants have been studied in the last few years for several types of organotin compounds (*Table 5*) and in recent work by Schaeffer and Zuckermann[40] they have been measured for thirteen *meta*- and *para*-substituted aryltrimethyltin compounds.

Table 5. $J(^{119}Sn-^{13}C)$ values for several organotin compounds[35][39]

Compound	Solvent	$J(^{119}Sn-^{13}C)$ (Hz)
Me$_4$Sn	+ 10 % dioxane[35]	340[35]
	+ 10 % benzene[36,37]	336[36]
		330[37]
Et$_4$Sn		321.5
(CH$_2$=CHCH$_2$)$_4$Sn		250
(Me$_3$Sn)$_2$C$_5$H$_4$		340
Me$_3$SnBr	+ 10 % benzene	380
Me$_2$SnCl$_2$	Acetone	556
MeSnBr$_3$	Benzene	640

It was shown that substituents with negative σ constants are in general associated with lower $J(^{119}Sn-^{13}C)$ values than those with positive σ constants, though the increase in the $J(^{119}Sn-^{13}C)$ value with increasing σ constant is not monotonic. At the same time $J(^{119}Sn-^{13}C_1)$ values decrease with increasing σ constants. These facts were rationalized[40] using Bent's isovalent hybridization model[41], according to which the redistribution of electrons in molecules occurs in such a way that s electrons of sp^n-hybrid orbitals of the central atom concentrate in the bonds with the most electropositive substituents; and p electrons concentrate in the bonds with the most electro-negative substituents.

The conclusions about the linear dependence of $J(^{119}Sn-C-^{1}H)$ on the s character of sp^n-hybrid orbitals of tin in Sn–C bonds, drawn by Holmes and Kaesz[26], in spite of the serious objections discussed above, have become very popular among scientists who have studied the complexation of organotin compounds[20,25,42-50]. We want to illustrate the applications of ^{119}Sn n.m.r. spectroscopy with the example of the Me$_3$SnX–D complexes, where X = Cl, Br, CF$_3$ and D = monodentate organic solvents, such as acetone, pyridine, dimethylformamide (DMFA), dimethylsulphoxide (DMSO) and hexa-methylphosphortriamide (HMPTA). Complexes of this type were isolated as molecular crystals[21,51] and according to the data of x-ray spectroscopy[52,53] they are likely to have a trigonal bipyramid structure. The electron distribution in these complexes depends upon the electron-donating ability of D and the electron-withdrawing power of X[54,55].

In solution there is an equilibrium between the free and complexed molecules of Me$_3$SnX. Therefore the observed $J(^{119}Sn-C-^{1}H)$ spin–spin coupling constants are:

$$J_{obs} = p_A J_A + p_{AD} J_{AD} \qquad (1)$$

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where p_A and p_{AD} are the molar fractions of a free acceptor and complex, and J_A and J_{AD} are the $J(^{119}Sn-C-^1H)$ constants for the same molecules. The study of the concentration and temperature dependences of $J(^{119}Sn-C-^1H)$, carried out[55] for several systems, enabled the J_{AD} and K_{eq} values to be obtained for these systems (Table 6).

Table 6. J_{AD} and K_{eq} values for Me_3SnX-D complexes[55]

D	X	J_{AD} (Hz)	K_{eq}† (mol^{-1})
Acetone	Cl	66.0	0.8 ± 0.1
	Br	65.5	0.6 ± 0.1
Pyridine	Cl	68.0	36 ± 3
	Br	67.6	28 ± 3
DMFA	Cl	70.0	3.0 ± 0.5
	Br	69.6	3.1 ± 0.3
DMSO	Cl	70.1	2.3 ± 0.4
	Br	69.6	3.1 ± 0.5
HMPTA	Cl	71.8	231 ± 9
	Br	71.3	232 ± 9

†K_{eq} values were obtained at -30 C, except for the DMSO complexes when they were measured at -10 C.

The results of Table 6 correlate well with the data from the study of the solvent effect upon the $\delta(^{119}Sn)$[6, 13] and $J(^{119}Sn-C-^1H)$ constants[45,46,49] in related systems. These results indicate the increase of the relative content of s electrons in the Sn–C–H fragment on passing from the free acceptor to the complex. In this case there is a good correlation between the increase of the relative content of s electrons in the Sn–C–H fragment and the growth of the relative content of p electrons in the Sn–Hal bonds (from n.q.r. data[54]).

Of special interest from this viewpoint are our recent results[21] concerning the effect of solvents upon $J(^{119}Sn-C-^1H)$ and $J(^{119}Sn-C-^{19}F)$ in Me_3SnCF_3 (Table 7).

Table 7. $J(^{119}Sn-C-^1H)$ and $J(^{119}Sn-C-^{19}F)$ for Me_3SnCF_3 in different solvents[21]

Solvent	$J(^{119}Sn-C-^1H)$ (Hz)	$J(^{119}Sn-C-^{19}F)$ (Hz)
Cyclohexane	58.4	300
CCl$_4$	58.7	293
Et$_2$O	59.4	283
THF	61.9	235
Pyridine	62.7	188
DMFA	65.1	173
DMSO	66.4	144
HMPTA	68.6	115

A comparison with the data of Table 3 shows that the CF_3 group is very close to the halogens in its features, but that it is somewhat more electron-withdrawing. This allowed us to consider Me_3SnCF_3 as a more powerful acceptor of the electrons in complexation. But a comparison of the results in Tables 3, 6 and 7 shows that the variation of $J(^{119}Sn-C-^1H)$ values on

going from the solutions in CCl_4 to those in strong electron-donating solvents is far less in Me_3SnCF_3 (7–10 Hz) than in Me_3SnHal (12–14 Hz). In our opinion, these facts are convincing evidence that it is more difficult to form complexes of electron-donating solvents with Me_3SnCF_3 than with Me_3SnHal. Additional evidence for this conclusion is the fact that Me_3SnHal easily forms solid molecular complexes of the type $Me_3SnHal–D$[51], while in the case of Me_3SnCF_3 an analogous complex was isolated only with the most powerful electron-donating solvent HMPTA[21].

In complexes such as $Me_3SnX–D$ the tin atom is bonded to three electropositive (CH_3) and two electronegative [Hal (or CF_3) and D] substituents. Therefore on going from Me_3SnX to $Me_3SnX–D$ the relative content of s electrons in the Sn–C–H fragment increases as well as the relative content of p electrons in the Sn–X bonds. For complexes such as $Me_3SnHal–D$ the above-mentioned model is confirmed by n.m.r. (*Table 6*) and n.q.r.[54] data: for complexes of the type $Me_3SnCF_3–D$ this is borne out by the results of the $J(^{119}Sn–C–^1H)$ and $J(^{119}Sn–C–^{19}F)$ study (*Table 7*).

In completing the discussion about the structure and complexation of organotin compounds it is essential to emphasize that the changes of the relative content of s and p electrons in bonds of tin to carbon and other substituents occur simultaneously with the changes in the Sn–C–H and Sn–C–F angles. Consequently, the changes in spectral parameters on going from one molecule to another reflect the changes both in electron and spatial parameters of the molecules, i.e. these parameters cannot be considered separately.

MERCURY COMPOUNDS

The study of ^{199}Hg chemical shifts of organic and inorganic compounds has not been very intensive[56–61]. The latest data available are given in *Table 8*.

The limited data and the strong dependence of $\delta(^{199}Hg)$ on the solvent[61] make the correlation of these data with the electron structure of the compounds difficult. Nevertheless, it is evident[58,60] that the electronegative groups make a significant paramagnetic contribution to the observed screening constants.

Table 8. $\delta(^{199}Hg)$ values for some mercury compounds[61]

Compound	Solvent	$\delta(^{199}Hg)$ (ppm)
Me_2Hg		0
Bu_2Hg	CCl_4	205
$n-Pr_2Hg$	CCl_4	210
Et_2Hg	CCl_4	304
$i-Pr_2Hg$	CCl_4	597
$(CH_2=CH)_2Hg$	CH_2Cl_2	648
$(PhCH_2)_2Hg$	CH_2Cl_2	700
Ph_2Hg	CH_2Cl_2	742
$(CH_3COOCH_2)_2Hg$	CH_2Cl_2	769
$(CH_2=CCl)_2Hg$	CH_2Cl_2	1149

We will further concentrate our attention on the $J(^{199}Hg-C-^1H)$, $J(^{199}Hg-C-^{19}F)$ and $J(^{199}Hg-^{13}C)$ spin–spin coupling constants, and on their correlations with the structure of organomercury compounds and their complexes. First of all, let us consider the question about the influence of R and X in RHgX on the $J(^{199}Hg-C-^1H)$ constants. Some typical data are given in Table 9.

Table 9. $J(^{199}Hg-C-^1H)$ constants for RHgX compounds in $CDCl_3$[62-65]

R＼X	R	I	Br	Cl	OAc
Me_3CCH_2[62]	94.0	—	192.0	193.0	204.0
Me[25,63]	104.3	192.0	212.0	215.0	220.0
$CF_3CH_2CH_2$[64]	110.4	198.0	—	223.0	—
$PhCH_2$[65]	131.3	—	252.0	263.0	264.5

The data of Table 9 show an increase of $J(^{199}Hg-C-^1H)$ values with the growth of electron-withdrawing power of the groups R and X. For compounds of the type $(RR'CH)_2Hg$[66] and RCO_2HgCH_3[67] linear dependences of $J(^{199}Hg-C-^1H)$ with pK_a of $RR'CH_2$ and RCOOH, respectively, were observed. For phenyl[68] and benzyl[69,70] derivatives of mercury the regularities in changes of the $J(^{199}Hg-^1H)$ constants through the 3–7 carbon atoms were traced.

In 1963 Hatton, Schneider and Siebrand[71] analysed the dependences of $J(^{199}Hg-C-^1H)$ on the nature of X in methyl and ethyl derivatives of mercury and derived the conclusion that the main contribution in the observed constants is made by the Fermi contact coupling. The contribution of spin–orbital coupling was estimated as negligible, while the dipole–dipole term was shown to be important in some cases. Recently[72] an extended Hückel procedure for calculating $J(^{199}Hg-C-^1H)$ constants for a variety of methylmercury systems was outlined. This author[72] concluded that the orbital contraction of the 6s orbital of mercury with increasing electronegativity of the substituent X is an important contributing factor to the large range spanned by these coupling constants.

In connection with these conclusions[71,72] it is very interesting to analyse the results of the $J(^{199}Hg-C-^{19}F)$ and $J(^{199}Hg-^{13}C)$ study. Some of the $J(^{199}Hg-C-^{19}F)$ values are given in Table 10.

Table 10. $J(^{199}Hg-C-^{19}F)$ values for CF_3HgX compounds[73-75]

X	Solvent	$J(^{199}Hg-C-^{19}F)$ (Hz)
CH_3	CH_2Cl_2	932
C_6H_5	$CHCl_3$	1008
CF_3	$CHCl_3$	1250
I	CH_2Cl_2	1710
Br	$CHCl_3$	1800
Cl	$CHCl_3$	1920
CF_3CO_2	$CHCl_3$	2208

It is evident from the data of *Table 10* that in this case the $J(^{199}Hg-C-^{19}F)$ values also increase very sharply with the growth of the electron-withdrawing power of the group X, i.e. they manifest the same features as the $J(^{199}Hg-C-^{1}H)$ values in relative compounds of the type CH_3HgX. Using the viewpoint already stated in the discussion of $J(^{119}Sn-C-^{1}H)$, we can conclude that in the case of compounds such as RHgX the growth of electron-withdrawing power of X results in a redistribution of electrons, so that the relative content of s electrons increases in the C–Hg bonds and the relative content of p electrons increases in the Hg–X bonds. In this case the contraction of the valence 6s orbital of mercury is bound to change the valence angles Hg–C–H and Hg–C–F. Recently $J(^{199}Hg-C-^{19}F)$ values were obtained for the wide range of fluoroalkyl[76-78], and earlier for fluorovinyl[79], and fluorophenyl[60] derivatives of mercury.

$J(^{199}Hg-^{13}C)$ spin–spin coupling constants became available recently[37,38,62,80-82] owing to the development of the new technique in n.m.r. spectroscopy. $J(^{199}Hg-^{13}C)$ values for compounds of the type $(RCH_2)_2Hg$ are given in *Table 11*.

Table 11. $J(^{199}Hg-^{13}C)$ values for $(RCH_2)_2Hg$ compounds[37,38,62,82]

R	Solvent	$J(^{199}Hg-^{13}C)$ (Hz)
C_6H_5	$CHCl_3$	631
CH_3	$CHCl_3$	648
$CH_3CH_2CH_2$	—	656
$(CH_3)_3C$	—	684
H	—	690
CH_3OCO	$CHCl_3$	753
CF_3	$CHCl_3$	896

It is evident from the data of *Table 11* that $J(^{199}Hg-^{13}C)$ increases with the growth of the electron-withdrawing power of the group R. An exception in this series is dibenzylmercury: in the opinion of these authors[82] this can be rationalized by $\sigma-\pi$ conjugation in the $C_6H_5-CH_2-Hg$ fragment, which was postulated earlier in our laboratory[83]. It is interesting that $J(^{199}Hg-^{13}C)$ also increases with increasing electron-withdrawing power of X in compounds of the type $(CH_3)_3CCH_2HgX$[62]; the data in *Table 12* show this.

Table 12. $J(^{199}Hg-^{13}C)$ values for $(CH_3)_3CCH_2HgX$ compounds in $CDCl_3$[62]

X	$J(^{199}Hg-^{13}C)$ (Hz)	$J(^{199}Hg-C-^{1}H)$ (Hz)	$J(^{13}C-^{1}H)$ (Hz)
$CH_2C(CH_3)_3$	684	94.0	126.0
CH_3	690	102.0	126.5
$CH_2=CH$	820	109.0	127.5
CN	1404	173.0	135.0
Cl	1514	193.0	138.0

It follows that $J(^{199}\text{Hg}-^{13}\text{C})$ spin–spin coupling constants are affected in compliance with the redistribution of electrons according to Bent, and depend mainly on the relative content of s electrons in the Hg–C bonds. It is interesting that changes in $J(^{199}\text{Hg}-^{13}\text{C})$ for compounds of the type $(\text{CH}_3)_3\text{CCH}_2\text{HgX}$ are proportional to changes in $J(^{199}\text{Hg}-\text{C}-^{1}\text{H})$ for the same compounds. In this case only chlorine gives a deviation from the linear dependence of these constants, and this can be rationalized by the (d–p) π conjugation of the methylene group and mercury atom[62]. At the same time $J(^{199}\text{Hg}-\text{C}-^{1}\text{H})$ constants depend linearly on $J(^{13}\text{C}-^{1}\text{H})$ for the CH_2 group. The authors[62] believe that these data provide evidence for the increase of the s character of the sp^3-hybrid orbitals of methylene carbon in C–C and C–H bonds, for its decrease in C–Hg bonds and for the decrease of the geminal angle H–C–Hg with the growth of the electron-withdrawing power of X.

Thus, $J(^{199}\text{Hg}-\text{C}-^{1}\text{H})$, $J(^{199}\text{Hg}-\text{C}-^{19}\text{F})$ and $J(^{199}\text{Hg}-^{13}\text{C})$ spin–spin coupling constants are extremely sensitive spectral parameters and they give very important information about the electron and spatial structure of organomercury compounds.

The application of n.m.r. spectroscopy of ^{199}Hg to the study of complexation of organomercury molecules in solutions has been successful. First of all, it should be noted that $J(^{199}\text{Hg}-\text{C}-^{1}\text{H})$, $J(^{199}\text{Hg}-\text{C}-^{19}\text{F})$ and $J(^{199}\text{Hg}-^{13}\text{C})$ constants are extremely dependent upon the nature of the solvent in which the given organomercury compound is studied (*Tables 13–16*).

Table 13. The effect of solvents on the $J(^{199}\text{Hg}-\text{C}-^{1}\text{H})$ in $(\text{RCH}_2)_2\text{Hg}$ compounds[20, 85–87]

R \ Solvent	CCl$_4$	CH$_2$Cl$_2$	Dioxane	Pyridine	DMFA	DMSO
CH$_3$[85]	98.0	98.0	101.0	102.0	102.5	104.5
H[20]	102.0	102.0	103.0	107.5	108.5	109.5
C$_6$H$_5$[86, 87]	132.0	137.0	138.0	141.5	142.0	146.0
CH$_2$=CH[87]	137.9	143.3	146.5	148.2	148.9	150.7

Table 14. The effect of solvents on the $J(^{199}\text{Hg}-^{13}\text{C})$ and $J(^{199}\text{Hg}-\text{C}-^{1}\text{H})$ constants in Et_2Hg[82, 85]

Solvent	$J(^{199}\text{Hg}-^{13}\text{C})$ (Hz)	$J(^{199}\text{Hg}-\text{C}-^{1}\text{H})$ (Hz)
CCl$_4$	642	98.0
CHCl$_3$	648	98.0
DME	663	101.0
Pyridine	679	102.0
DMSO	688	104.5

The analysis of the data of *Tables 13* and *14* shows that the $J(^{199}\text{Hg}-\text{C}-^{1}\text{H})$ and $J(^{199}\text{Hg}-^{13}\text{C})$ constants increase with the growth of the electron-donating abilities of the solvents. In this case it is very important for the interpretation of these data that the $J(^{199}\text{Hg}-\text{C}-\text{C}-^{1}\text{H})$ and $J(^{199}\text{Hg}-\text{C}-^{13}\text{C})$ constants in Et_2Hg are solvent independent and equal to 127.5[85] and 25[82] Hz, respectively. We believe that it is this circumstance that gives rise to changes

in spin–spin coupling constants on complexation and determines the solvation mechanism of organomercury compounds. Taking into account that the main contribution in all the observed heteronuclear spin–spin coupling constants is made by the contact Fermi coupling, specified by the s electron density on the coupled nuclei[71], it can be suggested that s electron density in a mercury atom does not change on the solvation of organomercury compounds[85]. If this is not the case, the β constants of mercury will be affected as well as the corresponding α constants. Therefore, no matter what complex is formed, R_2Hg–D or R_2Hg–2D, solvation occurs on account of the interaction of the p electrons of the heteroatom in D and the low-energy vacant orbitals of mercury. As a result of this interaction an additional electron density is transferred to the organomercury molecule and in the complex formed the redistribution of electrons occurs according to Bent, so that the relative content of the s electron increases in the Hg–C bonds and the relative content of p electrons increases in the Hg–D bonds. As for β-carbon nuclei and more so for β-hydrogen nuclei, the redistribution seems to be unpropagated to them because of the deterioration of the inductive effect. It is possible that the alternative mechanisms of solvation and changes in spin–spin coupling constants of mercury with the carbon and hydrogen nuclei occur; the effect of solvents on the $J(^{199}Hg$–C–$^{19}F)$ is highly contradictory. Thus, with the growth of the electron-donating ability of the solvent these constants increase for CF_3HgX compounds (Table 16), but decrease for R_2Hg compounds (Table 15).

Table 15. The effect of solvents on $J(^{199}Hg$–C–$^{19}F)$ for R_2Hg compounds[77].

R \ Solvent	CCl$_4$	CH$_2$Cl$_2$	DME	Pyridine
CF$_3$CF$_2$	793	787	745	684
CF$_3$CFCl	689	680	585	533
(CF$_3$)$_2$CF	535	507	387	338
CF$_3$CFH	511	510	494	443

Table 16. The effect of solvents on $J(^{199}Hg$–C–$^{19}F)$ for CF_3HgX compounds[75]

X \ Solvent	Benzene	CH$_2$Cl$_2$	THF	Acetone	DMFA	DMSO
I	1708	1722	1752	1758	1766	1766
Cl	1906	1922	1914	1924	1934	1942
CF$_3$CO$_2$	2158	2189	2190	2194	2198	2198

It is interesting that there is an increase of $J(^{199}Hg$–C–C–$^{19}F)$ in all molecules under investigation and $J(^{199}Hg$–C–$^1H)$ in $(CF_3CFH)_2Hg$. The authors[77] believe that such an anomaly in the behaviour of $J(^{199}Hg$–C–$^{19}F)$ for R_2Hg is due to the interaction of α-fluorine p electrons with the vacant

orbitals of the mercury atom. Perhaps this question will be clarified after the study of the solvent effect on $J(^{199}\text{Hg-C}^{-19}\text{F})$ and $J(^{199}\text{Hg-C}^{-1}\text{H})$ in $C_6H_5CH_2HgCF_3$[88, 89], which is underway in our laboratory.

Thus, we conclude that n.m.r. spectroscopy of heavy nuclei is an extremely powerful method of investigation of the structure and complexation of different derivatives of metals. The solving of some important problems in this field, such as the detailed understanding of the contributions in heavy nuclei screening constants, the elucidation of spin–spin coupling constants of these nuclei with other nuclei, and the determination of the signs of $J(^{119}\text{Sn-C}^{-19}\text{F})$ and $J(^{199}\text{Hg C}^{-19}\text{F})$ constants will allow this method to be used even more productively for obtaining information about the structure and complexation of many inorganic and organometallic compounds.

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