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An ^{19}F NMR STUDY OF THE TRANSMITTING ABILITY OF METAL-CONTAINING BINUCLEAR BRIDGING GROUPS *

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Summary

Nine series of model compounds of the Ar_n–Q–Z–C_6H_4F-4 type have been studied by the ^{19}F NMR technique to determine the relative efficiency of the transmission of substituent effects through metal-containing binuclear bridging groups (BBG) of the –Q–Z– (Q = Hg, Sn; Z = CH_2, S, N) type. On the basis of the results obtained it was concluded that the increase of the transmitting ability (*TA*) of a metal-containing BBG is close to that of mononuclear metal bridges. It is assumed that this effect is caused by the σ,π-conjugation of the Q–Z σ-bonds with the π-electrons of the aromatic ring and/or by the conjugation of the lone electron pairs of Z with the π-electron system. The *TA* of metal-containing BBG depends substantially on the participation of the metal atom in inter- and intra-molecular coordination and decreases with increasing intensity of the coordination interaction.

Introduction

The problem of the transmission of substituent electron effects (*SEE*) through bridging groups containing heavy non-transition metal atoms is interesting for the theoretical chemistry of organometallic compounds.

Previously the transmission of SEE in mononuclear bridge systems of the $ArQC_6H_4F$-4 (Q = Hg, Sn, Bi, Si, P, N, CH) type [1–5] has been studied by ^{19}F NMR.

This work investigates the relative efficiency of the transmission of *SEE* through metal-containing binuclear bridging groups (BBG) of the –Q–Z– (Q = Hg, Sn; Z = CH_2, S, $N(SO_2Ph)$) type and the influence exerted on it by inter- and intramolecular coordination. We used the ^{19}F NMR technique as the investigation method.

(Continued on p. 84)

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* Dedicated to Prof. O.A. Reutov on the occasion of his 65th birthday.

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TABLE 1

^{19}F NMR CHEMICAL SHIFTS RELATIVE TO INTERNAL FLUOROBENZENE (ppm)

Compound	Solvent			
	CHCl_3	$\text{C}_6\text{H}_5\text{Cl}$	$\text{C}_5\text{H}_5\text{N}$	Me_2SO
Series I				
$(4\text{-MeOC}_6\text{H}_4)_3\text{SnCH}_2\text{C}_6\text{H}_4\text{F-4}$	6.93	–	7.01	7.43
$(4\text{-MeC}_6\text{H}_4)_3\text{SnCH}_2\text{C}_6\text{H}_4\text{F-4}$	6.91	–	6.98	7.09
$(3\text{-MeC}_6\text{H}_4)_3\text{SnCH}_2\text{C}_6\text{H}_4\text{F-4}$	7.04	–	–	–
$(\text{C}_6\text{H}_5)_3\text{SnCH}_2\text{C}_6\text{H}_4\text{F-4}$	6.71	–	6.63	6.72
$(4\text{-ClC}_6\text{H}_4)_3\text{SnCH}_2\text{C}_6\text{H}_4\text{F-4}$	5.64	–	5.85	6.21
$(3\text{-ClC}_6\text{H}_4)_3\text{SnCH}_2\text{C}_6\text{H}_4\text{F-4}$	5.59	–	5.68	6.24
$(4\text{-FC}_6\text{H}_4)_3\text{SnCH}_2\text{C}_6\text{H}_4\text{F-4}$	6.05	–	6.17	6.42
$(3\text{-FC}_6\text{H}_4)_3\text{SnCH}_2\text{C}_6\text{H}_4\text{F-4}$	5.74	–	5.95	6.24
$(3,5\text{-Cl}_2\text{C}_6\text{H}_3)_3\text{SnCH}_2\text{C}_6\text{H}_4\text{F-4}$	4.39	–	4.99	6.09
$(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_3\text{SnCH}_2\text{C}_6\text{H}_4\text{F-4}$	4.77	–	5.49	6.17
Series II				
$(4\text{-MeC}_6\text{H}_4)_3\text{SnSC}_6\text{H}_4\text{F-4}$	3.41	–	3.70	4.81
$(3\text{-MeC}_6\text{H}_4)_3\text{SnSC}_6\text{H}_4\text{F-4}$	3.41	–	–	–
$(\text{C}_6\text{H}_5)_3\text{SnSC}_6\text{H}_4\text{F-4}$	2.94	–	3.50	5.10
$(4\text{-ClC}_6\text{H}_4)_3\text{SnSC}_6\text{H}_4\text{F-4}$	1.81	–	3.10	5.37
$(3\text{-ClC}_6\text{H}_4)_3\text{SnSC}_6\text{H}_4\text{F-4}$	1.68	–	3.38	4.98
$(4\text{-FC}_6\text{H}_4)_3\text{SnSC}_6\text{H}_4\text{F-4}$	2.18	–	3.37	5.23
$(3\text{-FC}_6\text{H}_4)_3\text{SnSC}_6\text{H}_4\text{F-4}$	1.90	–	3.52	4.74
$(3,4\text{-Cl}_2\text{C}_6\text{H}_3)_3\text{SnSC}_6\text{H}_4\text{F-4}$	0.73	–	2.66	4.67
$(3,5\text{-Cl}_2\text{C}_6\text{H}_3)_3\text{SnSC}_6\text{H}_4\text{F-4}$	0.20	–	2.37	4.23
$(3,4,5\text{-Cl}_3\text{C}_6\text{H}_2)_3\text{SnSC}_6\text{H}_4\text{F-4}$	0.35	–	2.34	4.13
Series III				
$4\text{-Me}_2\text{NC}_6\text{H}_4\text{HgSC}_6\text{H}_4\text{F-4}$	4.21	4.71	6.43	6.23
$4\text{-MeOC}_6\text{H}_4\text{HgSC}_6\text{H}_4\text{F-4}$	–	4.55	–	–
$4\text{-MeC}_6\text{H}_4\text{HgSC}_6\text{H}_4\text{F-4}$	–	4.45	–	–
$\text{C}_6\text{H}_5\text{HgSC}_6\text{H}_4\text{F-4}$	–	4.28	6.46	6.26
$4\text{-ClC}_6\text{H}_4\text{HgSC}_6\text{H}_4\text{F-4}$	–	3.96	–	–
$3\text{-ClC}_6\text{H}_4\text{HgSC}_6\text{H}_4\text{F-4}$	–	3.90	–	–
$4\text{-FC}_6\text{H}_4\text{HgSC}_6\text{H}_4\text{F-4}$	3.45	4.04	6.30	7.23
$3\text{-FC}_6\text{H}_4\text{HgSC}_6\text{H}_4\text{F-4}$	–	3.81	–	–
$3,4\text{-Cl}_2\text{C}_6\text{H}_3\text{HgSC}_6\text{H}_4\text{F-4}$	–	3.71	6.31	6.25
$3\text{-CF}_3\text{C}_6\text{H}_4\text{HgSC}_6\text{H}_4\text{F-4}$	3.14	3.68	6.32	6.25
Series IV				
$4\text{-Me}_2\text{NC}_6\text{H}_4\text{SHgC}_6\text{H}_4\text{F-4}$	−1.80	−1.14	0.39	0.24
$4\text{-MeOC}_6\text{H}_4\text{SHgC}_6\text{H}_4\text{F-4}$	−2.18	−1.47	0.28	–
$4\text{-MeC}_6\text{H}_4\text{SHgC}_6\text{H}_4\text{F-4}$	−2.04	−1.43	0.31	–
$\text{C}_6\text{H}_5\text{SHgC}_6\text{H}_4\text{F-4}$	−2.24	−1.65	0.31	0.23
$4\text{-ClC}_6\text{H}_4\text{SHgC}_6\text{H}_4\text{F-4}$	−2.70	−1.99	0.24	–
$3\text{-ClC}_6\text{H}_4\text{SHgC}_6\text{H}_4\text{F-4}$	−2.70	−1.98	0.27	–
$4\text{-FC}_6\text{H}_4\text{SHgC}_6\text{H}_4\text{F-4}$	−2.71	–	0.27	0.24
$3\text{-FC}_6\text{H}_4\text{SHgC}_6\text{H}_4\text{F-4}$	−3.01	−1.97	0.28	–
$3,4\text{-Cl}_2\text{C}_6\text{H}_3\text{SHgC}_6\text{H}_4\text{F-4}$	−2.94	−2.21	0.20	–
$3\text{-CF}_3\text{C}_6\text{H}_4\text{SHgC}_6\text{H}_4\text{F-4}$	−2.83	−2.10	0.30	0.27
Series V				
$4\text{-Me}_2\text{NC}_6\text{H}_4\text{SCH}_2\text{C}_6\text{H}_4\text{F-4}$	–	3.06	3.00	2.90
$4\text{-MeOC}_6\text{H}_4\text{SCH}_2\text{C}_6\text{H}_4\text{F-4}$	–	2.62	2.69	2.67
$4\text{-MeC}_6\text{H}_4\text{SCH}_2\text{C}_6\text{H}_4\text{F-4}$	–	2.54	2.58	2.57

TABLE 1 (continued)

Compound	Solvent			
	CHCl$_3$	C$_6$H$_5$Cl	C$_5$H$_5$N	Me$_2$SO
Series V				
PhSCH$_2$C$_6$H$_4$F-4	–	2.38	–	2.47
4-ClC$_6$H$_4$SCH$_2$C$_6$H$_4$F-4	–	2.00	2.19	2.30
3-ClC$_6$H$_4$SCH$_2$C$_6$H$_4$F-4	–	1.90	2.08	2.21
4-FC$_6$H$_4$SCH$_2$C$_6$H$_4$F-4	–	1.79	2.08	2.21
3,4-Cl$_2$C$_6$H$_3$SCH$_2$C$_6$H$_4$F-4	–	1.62	1.88	2.04
3-CF$_3$C$_6$H$_4$SCH$_2$C$_6$H$_4$F-4	–	1.79	2.03	2.21
Series VI				
4-Me$_2$NC$_6$H$_4$HgN(SO$_2$Ph)C$_6$H$_4$F-4	3.88	4.79	6.16	6.64
4-MeOC$_6$H$_4$HgN(SO$_2$Ph)C$_6$H$_4$F-4	3.63	4.41	–	–
4-MeC$_6$H$_4$HgN(SO$_2$Ph)C$_6$H$_4$F-4	3.58	4.50	5.99	6.74
PhHgN(SO$_2$Ph)C$_6$H$_4$F-4	3.44	4.36	5.89	6.67
4-FC$_6$H$_4$HgN(SO$_2$Ph)C$_6$H$_4$F-4	3.25	4.16	–	–
4-ClC$_6$H$_4$HgN(SO$_2$Ph)C$_6$H$_4$F-4	3.18	3.97	5.69	6.48
3-ClC$_6$H$_4$HgN(SO$_2$Ph)C$_6$H$_4$F-4	3.13	3.87	–	–
3-FC$_6$H$_4$HgN(SO$_2$Ph)C$_6$H$_4$F-4	3.12	3.96	–	–
3-CF$_3$C$_6$H$_4$HgN(SO$_2$Ph)C$_6$H$_4$F-4	3.00	3.69	5.50	6.38
3,4-Cl$_2$C$_6$H$_3$HgN(SO$_2$Ph)C$_6$H$_4$F-4	2.88	3.59	5.40	6.27
3,5-Cl$_2$C$_6$H$_3$HgN(SO$_2$Ph)C$_6$H$_4$F-4	2.80	3.37	–	–
3,4,5-Cl$_3$C$_6$H$_2$HgN(SO$_2$Ph)C$_6$H$_4$F-4	2.60	3.12	5.23	6.30
Series VII				
4-Me$_2$NC$_6$H$_4$CH$_2$N(SO$_2$Ph)C$_6$H$_4$F-4	0.25	0.51	0.71	0.91
4-MeOC$_6$H$_4$CH$_2$N(SO$_2$Ph)C$_6$H$_4$F-4	−0.06	0.21	0.44	0.78
4-MeC$_6$H$_4$CH$_2$N(SO$_2$Ph)C$_6$H$_4$F-4	0.01	0.24	0.47	0.76
PhCH$_2$N(SO$_2$Ph)C$_6$H$_4$F-4	−0.18	0.13	0.39	0.65
4-FC$_6$H$_4$CH$_2$N(SO$_2$Ph)C$_6$H$_4$F-4	−0.45	−0.17	0.19	0.54
4-ClC$_6$H$_4$CH$_2$N(SO$_2$Ph)C$_6$H$_4$F-4	−0.53	−0.27	0.11	0.50
3-ClC$_6$H$_4$CH$_2$N(SO$_2$Ph)C$_6$H$_4$F-4	−0.53	−0.28	0.06	0.44
3-FC$_6$H$_4$CH$_2$N(SO$_2$Ph)C$_6$H$_4$F-4	−0.50	−0.23	0.13	0.50
3-CF$_3$C$_6$H$_4$CH$_2$N(SO$_2$Ph)C$_6$H$_4$F-4	−0.71	−0.45	−0.04	0.40
3,4-Cl$_2$C$_6$H$_3$CH$_2$N(SO$_2$Ph)C$_6$H$_4$F-4	−0.89	−0.59	−0.13	0.28
3,5-Cl$_2$C$_6$H$_3$CH$_2$N(SO$_2$Ph)C$_6$H$_4$F-4	−0.97	−0.67	−0.24	0.20
3,4,5-Cl$_3$C$_6$H$_2$CH$_2$N(SO$_2$Ph)C$_6$H$_4$F-4	−1.19	−0.89	−0.34	0.06
Series VIII				
4-Me$_2$NC$_6$H$_4$HgN(SO$_2$Ph)C$_6$H$_3$Br-2-F-4	–	1.82	–	–
4-MeC$_6$H$_4$HgN(SO$_2$Ph)C$_6$H$_3$Br-2-F-4	–	1.57	–	–
PhHgN(SO$_2$Ph)C$_6$H$_3$Br-2-F-4	–	1.56	–	–
4-ClC$_6$H$_4$HgN(SO$_2$Ph)C$_6$H$_3$Br-2-F-4	–	1.28	–	–
3,5-Cl$_2$C$_6$H$_3$HgN(SO$_2$Ph)C$_6$H$_3$Br-2-F-4	–	0.89	–	–
3-FC$_6$H$_4$HgN(SO$_2$Ph)C$_6$H$_3$Br-2-F-4	–	1.28	–	–
Series IX				
4-Me$_2$NC$_6$H$_4$CH$_2$N(SO$_2$Ph)C$_6$H$_3$Br-2-F-4	–	−2.29	–	–
4-MeC$_6$H$_4$CH$_2$N(SO$_2$Ph)C$_6$H$_3$Br-2-F-4	–	−2.66	–	–
PhCH$_2$N(SO$_2$Ph)C$_6$H$_3$Br-2-F-4	–	−2.89	–	–
4-ClC$_6$H$_4$CH$_2$N(SO$_2$Ph)C$_6$H$_3$Br-2-F-4	–	−3.29	–	–
3-FC$_6$H$_4$CH$_2$N(SO$_2$Ph)C$_6$H$_3$Br-2-F-4	–	−3.13	–	–
3,5-Cl$_2$C$_6$H$_3$CH$_2$N(SO$_2$Ph)C$_6$H$_3$Br-2-F-4	–	−3.67	–	–
3,4,5-Cl$_3$C$_6$H$_2$CH$_2$N(SO$_2$Ph)C$_6$H$_3$Br-2-F-4	–	−3.87	–	–
PhHgN(PhSO$_2$)C$_6$H$_4$F-3	−2.00	–	–	–
Ph$_3$SnCH$_2$C$_6$H$_4$F-3	0.62	–	–	–

Results and discussion

To solve the problem in question we have synthesized several series of model compounds $Ar_3SnCH_2C_6H_4F$-4 (I), $Ar_3SnSC_6H_4F$-4 (II), $ArHgSC_6H_4F$-4 (III), $ArSHgC_6H_4F$-4 (IV), $ArSCH_2C_6H_4F$-4 (V), $ArHgN(SO_2Ph)C_6H_4F$-4 (VI), $ArCH_2N(SO_2Ph)C_6H_4F$-4 (VII), $ArHgN(SO_2Ph)C_6H_3Br$-2-F-4 (VIII) and $ArCH_2N(SO_2Ph)C_6H_3Br$-2-F-4 (IX).

For I–XI the ^{19}F NMR chemical shifts with respect to PhF were determined in different solvents (Table 1). The positive sign corresponds to highfield shifts.

By correlation analysis of the data obtained the relative transmitting ability (*TA*) of the investigated BBG were quantitatively assessed (Table 2).

When we correlated the ^{19}F NMR shifts for the binuclear bridging systems I, II, III and VI with those for corresponding mononuclear compounds $Ar_3SnC_6H_4F$-4 (X) [2] and $ArHgC_6H_4F$-4 (XI) [1] we got straight lines with slopes (ρ) close to unity (Table 2, nos. 1–4). This means that for 95% confidence level the efficiency of transmission of *SEE* to the indicator F atom practically does not change or even somewhat increases in going from mono- to bi-nuclear bridge compounds.

In contrast, a similar transition from $ArCH_2C_6H_4F$-4 (XII) to $ArCH_2CH_2C_6H_4$-F-4 (XIII) [6] (Table 2, no. 5) is accompanied by a considerable decrease in *TA*, which is understandable for the transition from a less extended, to a more extended system.

We investigated the transmission mechanism of *SEE* in binuclear bridging systems to determine the cause of increase of *TA* for metal–carbon or metal–heteroatom bridging groups.

On correlation of the ^{19}F NMR shifts for I, III and VI with σ_p^0 and σ_p constants of aryl groups [7] (Table 2, nos. 6–11) it was established that in the first case the quality (r, S) of linear dependences obtained is markedly better than in the latter.

TABLE 2

PARAMETERS OF THE CORRELATION EQUATION $y = \rho x + c$ (n = number of points; S = estimated standard error; r = correlation coefficient; $\Delta\rho$ = absolute error of the coefficient ρ for 95% confidence level)

	y = ^{19}F NMR chemical shifts for	x = ^{19}F NMR chemical shifts for	n	$\rho \pm \Delta\rho$	S	r	c
1	I	X	10	0.79 ± 0.04	0.100	0.997	7.90
2	II	X	10	0.91 ± 0.05	0.102	0.997	4.35
3	III	XI	10	1.05 ± 0.16	0.081	0.978	4.52
4	IV	XI	12	1.18 ± 0.09	0.050	0.995	4.51
5	XIII	XII	5	0.30 ± 0.03	0.010	0.999	0.01
6	I	σ_p^0	5	-2.99 ± 1.05	0.125	0.982	6.53
7	I	σ_p	5	-2.12 ± 2.00	0.150	0.926	6.36
8	III	σ_p^0	6	-1.04 ± 0.30	0.074	0.971	4.35
9	III	σ_p	6	-0.66 ± 0.40	0.144	0.883	4.30
10	VI	σ_p^0	6	1.05 ± 0.23	0.060	0.985	1.31
11	VI	σ_p	6	0.72 ± 0.33	0.110	0.939	4.25
12	X	VII	6	0.64 ± 0.07	0.030	0.996	-1.27
13	XI	IX	7	1.10 ± 0.11	0.071	0.993	-2.92

TABLE 3

INDUCTIVE AND RESONANCE PARAMETERS OF Ph_nQZ AND Ph_nQ SUBSTITUENTS

Ph_nQZ	σ_I	σ_r^0	Ph_nQ	σ_I	σ_r^0
Ph_3SnCH_2	0.01	−0.21	Ph_3Sn	0.18	0.03
Ph_3SnS	0.10	−0.14			
PhHgS	0.23	−0.15	PhHg	0.12	0.02
$PhHgN(SO_2Ph)$	0.37	−0.19			

This indicates that there is no direct polar conjugation between the *p*-substituents in the aromatic rings and the indicator fluorine atom in the compounds investigated.

To determine the nature of the electron interactions across different bonds in the binuclear systems being considered we have used *FCS* for $Ph_nQZC_6H_4F$-4(3) (Table 1 and ref. 8) and Taft's equations [9] for calculation of the inductive (σ_I) and resonance constants of the groups Ph_nQZ, (Z = N, S or C) (Table 3). Data analysis showed that while the interactions along the metal–aromatic carbon bonds are mainly inductive (Table 3, Ph_nQ groups) a substantial contribution to the interactions along the heteroatom–aromatic carbon or aliphatic carbon–aromatic carbon bonds is made by resonance effects.

Thus, it can be concluded that the absence of decrease in *TA* in going from mono- to bi-nuclear organometallic systems, which should have taken place if electron effects were transmitted by the π-inductive mechanism or the field effect is, most probably, explained by the presence in binuclear systems of an effective σ,π-conjugation of the metal–heteroatom or metal–carbon σ-bond with π-electrons of the fluorophenyl ring, or a p_π–p_π conjugation of the heteroatom lone electron pair with the π-electron system.

To study the possible influence of specific solvation on the *TA* of metal-containing bridge systems they were investigated in inert and coordinating solvents. The existence of such interaction is indicated by an increase in fluorine screening in going from PhCl, inert to specific solvation of metal atoms to the coordinating DMSO (Table 1). Apparently, this results from the partial transfer of electron density of a solvent lone electron pair to the vacant orbitals of the metal atom, leading to increase in the electron-donating effect of Ph_nQZ groups. This conclusion is confirmed by very small changes in fluorine screening which occur with a similar transition for carbon-containing compounds (series V and VII).

To evaluate the possible influence of specific solvation on the *TA* of metal-containing BBG the ^{19}F NMR chemical shift ranges were calculated for each series of compounds in inert and solvating solvents (Table 4). Analysis of the data obtained shows that for all the investigated series the transfer to Py and DMSO is accompanied by successive decrease in *TA*. The extent of this decrease, for sulphur-containing compounds is different for carbon- and mercury-containing systems. According to the literature, the decrease of *TA* of systems with a coordinative saturated bridging group on transfer to polar coordinating solvents takes place mainly owing to dipole–dipole interactions [12]. However, the action of the above factor alone cannot explain the decrease in *TA* in the case of arylmercury 4-fluorothiophenoxides where this decrease is markedly greater. For these systems, the observed effect is evidently caused by dipole–dipole and coordination interactions with the solvent. It is known that in the case of bridge systems, for which the possibility of coordination

TABLE 4

^{19}F NMR CHEMICAL SHIFT RANGES FOR Ar$_n$QZC$_6$H$_4$F-4 IN CHCl$_3$ AND DMSO (ppm)

-QZ-	CHCl$_3$	Me$_2$SO
-Sn-CH$_2$-	2.16	1.26
-Sn-S-	2.91	1.00
-Hg-S-	1.00	0.04
-Hg-N-	1.28	0.40
-CH$_2$-S-	1.44	0.86
-CH$_2$-N-	1.46	0.85

with the solvent is excluded, the decrease of *TA* in going from a non-polar to a polar solvent is proportional to the difference in Dimroth's parameters E_T [13] for these solvents. The transfer from PhCl to PhNO$_2$ and MeCN causes approximately the same decrease in *TA* for carbon compounds as the transfer to Py and DMSO (Table 5). In contrast, for organomercury compounds, the range of the ^{19}F NMR shifts decreases less sharply in going to polar noncoordinating solvents than to Py and DMSO. These data confirm the conclusion that specific solvation plays a significant role in the decrease of TA of organomercury systems in coordinating solvents.

Considering that the investigated mercury- and carbon-containing compounds (series IV and V; VI and VII) are assumed to be structurally similar systems and, hence, the influence of the dipole–dipole ineractions on their *TA* should be approximately the same, we attempted to estimate the relative contribution (α) of coordination with the solvent to the overall decrease in *TA* for organo-mercury systems:

$$\alpha = \left\{ \left[\frac{\Delta\delta(^{19}\mathrm{F})_{(\mathrm{solv.})} - \Delta\delta(^{19}\mathrm{F})_{(\mathrm{PhCl})}}{\Delta\delta(^{19}\mathrm{F})_{(\mathrm{PhCl})}} \right]_{\mathrm{HgQ}} - \left[\frac{\Delta\delta(^{19}\mathrm{F})_{(\mathrm{solv.})} - \Delta\delta(^{19}\mathrm{F})_{(\mathrm{PhCl})}}{\Delta\delta(^{19}\mathrm{F})_{(\mathrm{PhCl})}} \right]_{\mathrm{CH_2Q}} \right\} \cdot 100\%$$

where $\Delta\delta(^{19}F)$ is the chemical shift range in the corresponding solvent and Q = S or N.

The contribution of specific solvation to the decrease in *TA* varies from 20 to 68% and is greater for arylmercury-4-fluorothiophenoxides than for *N*-arylmercury-4′-fluorobenzenesulphonanilides (Table 6). The smaller contribution of specific solvation for the latter system may be caused by steric hindrance by the PhSO$_2$ group to the approach of the coordinating solvent molecule to the Hg atom, or by the weak intramolecular coordination between the C$_6$H$_5$SO$_2$ oxygen and the Hg atom [14].

TABLE 5

RATIOS OF THE ^{19}F NMR CHEMICAL SHIFT RANGES IN A GIVEN SOLVENT TO THAT IN CHLOROBENZENE FOR ArSHgC$_6$H$_4$F-4 AND ArSCH$_2$C$_6$H$_4$F-4

System	Solvent			
	C$_6$H$_5$NO$_2$ (E_T 42 kcal mol^{-1})	MeCN (E_T 46 kcal mol^{-1})	C$_5$H$_5$N (E_T 40.2 kcal mol^{-1})	Me$_2$SO (E_T 45 kcal mol^{-1})
ArSHgC$_6$H$_4$F-4	0.32	0.47	0.09	0.03
ArSCH$_2$C$_6$H$_4$F-4	0.56	0.60	0.78	0.58

TABLE 6

α VALUES FOR Hg–Q (%)

Hg–Q	Solvent	
	C_5H_5N	Me_2SO
Hg–N	20	46
Hg–S	68	57

To investigate further the question of the possible influence of intramolecular coordination of the *TA* of binuclear organomercury systems we examined the series of *N*-arylmercury-2′-bromo-4′-fluorobenzenesulphonanilides (VIII) in which, according to literature data, there may be intramolecular coordination between the Hg and the Br *o*-atoms [15], and their carbon analogues (IX).

We carried out statistical analysis of the ^{19}F NMR data obtained for VI, VII, VIII and IX (Table 1) to obtain the relative *TA* of BBG Hg–N and CH_2–N in the *o*-bromo-substituted and unsubstituted systems. According to the results, (Table 2, nos. 12, 13) the introduction of the Br atom at the *o*-position to the $ArHgNSO_2Ph$ group results in a substantial decrease in *TA* of the corresponding system. A similar process for the C analogues has practically no effect on the *TA* of the CH_2–N group. These results indicate that the decrease in *TA* going from VI to VIII can be attributed to the influence of intramolecular coordination.

Thus, we may conclude that the *TA* of metal-containing BBG depends substantially on the participation of the metal atom in the inter- and intra-molecular coordination interactions, the *TA* of the systems decreases with increasing intensity of coordination interactions.

Experimental

The ^{19}F NMR spectra were recorded at 25°C on the RYA-2309 and Tesla BS-497 spectrometers operating respectively at 84.56 and 94.075 MHz. All measurements were done on solutions of 0.2 and 0.05 *M* concentrations. The experimental error in the estimation of chemical shifts was not greater than ± 0.01 ppm. All solvents used were purified by conventional methods and distilled under dry argon.

The compounds studied have been synthesized by conventional methods and their preparations has been described elsewhere [16–21].

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