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UDC 543.422.25:547.1'13

The work reported here was carried out within the framework of a systematic quantitative investigation of the transmission capability (TC) of binuclear bridge groupings (BBG) containing a metal atom (M) [1-3]; in the present work, we used ¹⁹F-¹H NMR to investigate the comparative efficiency of transfer of electronic effects of substituents (EES) through the BBG M-S, and the influence of the solvent type on the transfer of these effects.

To this end, we synthesized a series of model compounds containing the BBGs Hg-S, Sn-S, and CH₂-S, of the types ArHgSC₆H₄F-4 (Ia-c and e-k), Ar₃SnSC₆H₄F-4 (IIc-j, l, m), ArSHgC₆H₄F-4 (IIIa-c, e-k), ArHgSC₆H₂Me₂-2,6-F-4 (IVa, e, h), and ArSCH₂C₆H₄F-4 (Va-c, d-h, j, k), where Ar is 4-Me₂NC₆H₄ (a), 4-MeOC₆H₄ (b), 4-MeC₆H₄ (c), 3-MeC₆H₄ (d), Ph (e), 4-ClC₆H₄ (f), 3-ClC₆H₄ (g), 4-FC₆H₄ (h), 3-FC₆H₄ (i), 3,4-Cl₂C₆H₃ (j), 3-CF₃C₆H₄ (k), 3,5-Cl₂C₆H₃ (l), and 3,4,5-Cl₃C₆H₂ (m), for which the chemical shifts of fluorine (δF) were determined in various solvents (Table 1). The positive sign corresponds to an upfield shift.

For a quantitative evaluation of the relative TC of the BBGs Hg-S and Sn-S in solvents that are comparatively inert with respect to specific solvation of M atoms (CHCl₃ and PhCl), we performed a statistical workup of the data for δF on compounds (I)-(III) and (V) (Table 2). Upon correlating δF for (I) and (II) relative to the previously obtained values of δF for the corresponding mononuclear analogs ArHgC₆H₄F-4 (VO) and Ar₃. For SnC₆H₄F-4 (VII) [4, 5], we obtained straight lines (see Table 2, equations 1 and 2), with slopes close to unity. This means that the efficiency of EES transfer in aryl rings with Hg and Sn atoms on the indicator fluorine atom is practically unchanged by the introduction of an additional bridge unit, a sulfur atom, into the systems (VI) and (VII). Thus, the property of exaltation of TC that was observed previously in the example of M-C [3] and M-N [1], this effect consisting of a slight change in the electronic conductance when the change is made from mononuclear to binuclear bridge systems, is also characteristic for the BBG M-S. From a comparison of all of the data that we have obtained, it follows that for the BBG M-X, where X is a heteroatom, this effect is manifested to a greater degree than for the BBG M-C.

In order to determine the reason for exaltation of TC of the BBG M-S in the example of Hg-S, we investigated the mechanism of transfer of EES in the system (I). By correlation of δF with the Taft inductive constants of the aromatic substituents σ_p° [4] and the Hammett polar constants σ_p [4] (equations 3 and 4), it was established that in the first case the quality of the linear relationship (r and s) is substantially better than in the second case. This fact indicates that in the compounds (I) there is no direct polar conjugation between the p-substituents in the aromatic ring and the indicator fluorine atom. On the basis of previously obtained data on the inductive character of interactions through Hg-C_{ar} bonds [5], and also the significant negative value of the resonance constant of the PhHgS grouping ($\sigma_R^\circ = 0.15$ [6]), we can conclude that the absence of any decrease in electronic conductance of the system when the change is made from (VI) to (I), which should take place through the action of a π -inductive effect [7] of EES transfer or a field effect [8], does not occur in view of the effective resonance interaction of the Hg-S fragment in (I) with the π -electrons of the fluoroaryl group.

This may be due to both σ, π -conjugation of the Hg-S σ -bond with the π -electron system and $p_\pi-p_\pi$ -conjugation of the unshared electron pair of the S atom with the π -electrons; therefore, in order to evaluate the contributions of each of these, we investigated compounds (IV) containing 2,6-dimethyl-4-fluorothiophenol substituents. Whereas the $p_\pi-p_\pi$ -conjugation effect is dominant in (I), the introduction of o-Me groups, disrupting the co-

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 4, pp. 803-809, April, 1983. Original article submitted May 27, 1982.

TABLE 1. Chemical Shifts of Ffor (I)-(V) in Various Solvents in Relation to PhF (δ , ppm)

Compound	CHCl ₃	PhCl	C ₆ H ₆ N	Me ₂ SO	Compound	CHCl ₃	PhCl	C ₆ H ₆ N	Me ₂ SO
(Ia)	4,21	4,71	6,43	6,23	(IIIc)	-2,04	-1,43	0,31	-
(Ib)	-	4,55	-	-	(IIIe)	-2,24	-1,65	0,31	0,23
(Ic)	-	4,45	-	-	(III f)	-2,70	-1,99	0,24	-
(Ie)	-	4,28	6,46	6,26	(III g)	-2,70	-1,98	0,27	-
(If)	-	3,96	-	-	(III h)	-2,71	-	0,27	0,24
(I g)	-	3,90	-	-	(III i)	-3,01	-1,97	0,28	-
(I h)	3,45	4,04	6,30	7,23	(III j)	-2,94	-2,21	0,20	-
(I i)	-	3,81	-	-	(III k)	-2,83	-2,10	0,30	0,27
(I j)	-	3,71	6,31	6,25	(IV a)	-	4,26	-	-
(I k)	3,14	3,68	6,32	6,25	(IV e)	-	3,94	-	-
(II c)	3,41	-	3,70	4,81	(IV b)	-	3,71	-	-
(II d)	3,41	-	-	-	(Va)	-	3,06	3,00	2,90
(II e)	2,94	-	3,50	5,10	(Vb)	-	2,62	2,69	2,67
(II f)	1,81	-	3,16	5,37	(Ve)	-	2,54	2,58	2,57
(II g)	1,68	-	3,38	4,98	(Ve)	-	2,38	-	2,47
(II h)	2,18	-	3,37	5,23	(Vf)	-	2,00	2,19	2,30
(II i)	1,90	-	3,52	4,74	(Vg)	-	1,90	2,08	2,21
(II j)	0,73	-	2,66	4,67	(Vh)	-	1,79	2,08	2,21
(II l)	0,20	-	2,37	4,23	(Vj)	-	1,62	1,88	2,04
(II m)	-0,35	-	2,34	4,13	(Vk)	-	1,79	2,03	2,21
(III a)	-1,80	-1,14	0,39	0,24					
(III b)	-2,18	-1,47	0,28	-					

TABLE 2. Parameters of Correlation Equations $y = \rho x + c$

Equation	y	x	n*	$\rho \pm \Delta\rho$	s	r	c
1	$\delta F(I)$	$\delta F(VI)$	10	$1,05 \pm 0,16$	0,081	0,978	4,52
2	$\delta F(II)$	$\delta F(VII)$	10	$0,91 \pm 0,05$	0,102	0,997	4,35
3	$\delta F(I)$	σ_n	6	$-0,66 \pm 0,40$	0,144	0,883	4,30
4	$\delta F(I)$	σ_n	6	$-1,04 \pm 0,3$	0,074	0,971	4,35
5	$\delta F(I)$	$\delta F(III)$	9	$1,09 \pm 0,23$	0,096	0,971	6,11
6	$\delta F(III)$	$\delta F(V)$	8	$0,77 \pm 0,07$	0,046	0,993	-3,46
7	$\delta F(II)$	$\delta F(I)$	6	$1,18 \pm 0,17^\dagger$	0,129	0,993	12,23
8	$\delta F(VII)$	$\delta F(VI)$	9	$1,28 \pm 0,004^\dagger$	0,05	0,999	0,93

*n is the number of compounds in the series.

†Slope of correlation line was calculated from principle of EES additivity.

planarity of the system, should lead to a considerable decrease of the TC of the Hg-S BBG in (IV) in comparison with (I).

However, from a comparison of the ranges of variation of δF ($\Delta\delta F$) of the corresponding compounds (I) and (IV) (respective values of $\Delta\delta F$ are 0.67 and 0.55 ppm), it is evident that the change from (I) to (IV) is actually accompanied by an extremely small decrease of the TC of the Hg-S BBG ($\sim 20\%$). But this fact can be interpreted in two ways. On the one hand, the lack of a decrease of the TC in (IV) can be explained on the basis that even in the system (I), as a result of nonvalence interactions of the Hg atom with the o-H atoms, the angle between the HgSC_{ar} plane and that of the fluorothiophenol ring is already quite large, and hence the contribution of $p_\pi-p_\pi$ -conjugation is small. Therefore, the introduction of o-Me groups does not have any substantial effect on the conformation of the molecules and hence does not lead to a change in the intensities of $p_\pi-p_\pi$ -interaction. On the other hand, we can assume that the decrease in $p_\pi-p_\pi$ -conjugation upon introducing o-Me groups because of disruption of coplanarity of the orbitals of the S p-electrons and the ring π -electrons is compensated by an increase of conjugation of the Hg-S σ -bond of the σ, π -type, for which the molecular geometry becomes more favorable. Therefore, it is impossible to give a clear answer to the question of relative contributions of the σ, π - and $p_\pi-p_\pi$ -conjugation effects to the exaltation of TC of the Hg-S BBG until reliable data are obtained on the conformation of the compounds of the type of (I) and (IV) in solution.

With the aim of determining the influence of the order of arrangement of atoms in the Hg-S BBG in relation to the indicator group on the EES transfer efficiency, we compared the PC of series (I) and (II) compounds (see Table 2, equation 5). We found that for these arylmercuraryl sulfides, the order of arrangement of the units in the BBG has practically no ef-

TABLE 3. Ranges of Chemical Shifts for (I), (II), (III), and (V) in Different Solvents ($\Delta\delta F$, ppm)

Compound series	CHCl ₃	PhCl	Py	Me ₂ SO	PhNO ₂	MeCN
(I)	1,07	1,03	0,11	0,02	-	-
(II)	3,75	-	1,26	0,67	-	-
(III)	1,03	0,96	0,09	0,03	0,45	0,31
(V)	-	1,44	1,12	0,86	0,80	0,84

fect on the TC of the system ($\rho = 1.09$). In connection with data we had obtained previously on the substantial dependence of the indicator center sensitivity to EES on the direction of their transfer in the case of the Hg-N BBG [2], it next appeared advisable to study this question for the BBGs Hg-O and Hg-CH₂, so that we could determine which of the observed effects is the more characteristic for Hg-containing bridge systems.

For a quantitative evaluation of the relative TC of the BBGs Sn-S, Hg-S, and CH₂-S, we carried out a correlation of the values of δF of (II) relative to the corresponding (I), (III) relative to (V), and (VII) relative to (VI) (equations 6-8). Here we took into account the fact that the tin-containing bridge groups, in contrast to their Hg analogs, transfer the effect of not one but three variable substituents. Therefore, in order to reduce these bridge systems to identical conditions, in accordance with the principle of additivity of EES, we applied a factor of $1/3$ to the actually obtained values of ρ in equations 7 and 8; and in analysis of the relationships, we examined the calculated values ρ^* . The data indicate that both the mononuclear and binuclear tin-containing bridge groupings have a greater TC than do the Hg analogs. Here, when account is taken of the error in determining ρ ($\Delta\rho$) for a 95% level of confidence probability, the differences in TC between the BBGs Sn-S and Hg-S, and also between Sn and Hg, are practically identical. The replacement of the M atom in the Hg-S BBG by a C atom leads to an increase in the TC of the system; this is consistent with the previously obtained data on the greater efficiency of EES transfer through a CH₂ group in comparison with an Hg bridge atom [9].

In order to evaluate the influence of the solvent type on the TC of these BBGs, we calculated the range of variation of δF ($\Delta\delta F$) for each of the series of compounds (I), (II), (III), and (V) in inert solvents (CHCl₃, PhCl) and in coordinating aprotic polar solvents (Py, Me₂SO) (Table 3). An analysis of these data shows that for all of the series of compounds investigated, the change of Py and Me₂SO is accompanied by a successive decrease of $\Delta\delta F$, i.e., a decrease of the EES transfer efficiency. Along with this, the degree of this decrease is different for different systems. We can assume that the decrease of electronic conductance in coordination-saturated substituted benzyl aryl sulfides (V) in polar coordinating solvent media, the same as in the case of other bridge systems ArQC₆H₄F-4 [10], may take place because of dipole-dipole interaction. At the same time, the action of these factors alone cannot explain the decrease of the TC in the Hg and Sn analogs in series (I), (III), and (II), the degree of which is considerably greater than in the case of aryl benzyl sulfides. For these systems, probably, the observed effect is due to both dipole-dipole and coordination interaction with the solvent. It is known that in the case of bridge systems of the type ArQC₆H₄F-4, for which there is no possibility of coordination with the solvent, the degree of decrease of the phenomenological TC of the system when the change is made from nonpolar to polar solvents is proportional to the difference between the Dimroth parameters for these solvents. And indeed, the change from PhCl ($E_T = 37.5$ kcal/mole [11]) to PhNO₂ ($E_T = 42$ kcal/mole) and MeCN ($E_T = 46$ kcal/mole) brings about approximately the same decrease as the change to Py ($E_T = 40.2$ kcal/mole) and Me₂SO ($E_T = 45$ kcal/mole). In contrast, for compounds (III), $\Delta\delta F$ decreases less sharply when the change is made to PhNO₂ and MeCN than to Py and Me₂SO. These data confirm the conclusion that in the case of the compounds (III), specific solvation plays a significant role. On the basis that (V), (III), and (I) in the first approximation are structurally related systems, we can assume that the influence of dipole-dipole interactions on their TC is approximately identical. This has enabled us to estimate, in the first approximation, the relative contribution of coordination with the solvent to the overall effect of the TC decrease for (I) and (III), which accounts for approximately 68% in the Py and 57% in the Me₂SO.

From the data on $\Delta\delta F$ it also follows that coordinating solvents have substantially less influence on the TC of the Sn derivatives (II) in comparison with the Hg-containing systems

TABLE 4. Characteristics of Compounds Investigated

Compound	Yield, %	mp, °C (solvent), or bp, °C (P, mm Hg)	Found/calculated, %		
			C	H	S
(Ib)	60	99-100 (ethanol)	<u>35,71</u> 35,90	<u>2,50</u> 2,54	<u>-</u> 7,37
(Ic)	79	121-122 (ethanol)	<u>37,21</u> 37,27	<u>2,59</u> 2,64	<u>7,90</u> 7,65
(If)	80	159-160 (ethanol)	<u>32,84</u> 32,80	<u>1,86</u> 1,83	<u>7,43</u> 7,29
(Ig)	76	135-137 (ethanol)	<u>32,84</u> 32,80	<u>1,71</u> 1,83	<u>7,61</u> 7,29
(Ii)	58	123-124 (ethanol)	<u>33,80</u> 34,08	<u>1,86</u> 1,90	<u>8,05</u> 7,58
(Ij)	53	166-167 (ethanol)	<u>30,48</u> 30,42	<u>1,52</u> 1,48	<u>6,80</u> 6,76
(Ik)	64	95-96 (hexane)	<u>33,18</u> 33,01	<u>1,98</u> 1,70	<u>6,37</u> 6,78
(IId)	50	Oil	<u>62,47</u> 62,46	<u>4,95</u> 4,85	<u>-</u> -
(IIg)	99	»	<u>49,72</u> 49,65	<u>2,82</u> 2,78	<u>-</u> -
(IIi)	99	»	<u>54,94</u> 54,26	<u>3,20</u> 3,04	<u>-</u> -
(IIl)	40	107-108 (hexane)	<u>42,28</u> 42,14	<u>1,83</u> 1,92	<u>16,77*</u> 17,35
(IIIb)	45	102-103 (ethanol)	<u>35,81</u> 35,90	<u>2,09</u> 2,54	<u>7,84</u> 7,37
(IIIc)	40	120-121 (ethanol)	<u>37,03</u> 37,27	<u>2,54</u> 2,64	<u>7,79</u> 7,65
(IIIf)	80	191-192 (ethanol)	<u>32,24</u> 32,80	<u>1,85</u> 1,83	<u>7,61</u> 7,29
(IIIg)	80	143-144 (ethanol)	<u>32,29</u> 32,80	<u>1,99</u> 1,83	<u>7,63</u> 7,29
(IIIi)	65	109-110 (ethanol)	<u>33,82</u> 34,08	<u>2,08</u> 1,90	<u>7,72</u> 7,58
(IIIj)	50	198-199 (acetone)	<u>30,31</u> 30,42	<u>1,60</u> 1,48	<u>6,94</u> 6,76
(IIIk)	71	114-115 (ethanol)	<u>32,94</u> 33,01	<u>1,91</u> 1,70	<u>6,71</u> 6,78
(Vb)	43	50-52 (methanol)	<u>68,17</u> 67,71	<u>5,20</u> 5,27	<u>13,10</u> 12,91
(Vc)	58	55-57 (methanol)	<u>72,43</u> 72,38	<u>5,56</u> 5,64	<u>13,97</u> 13,80
(Vf)	20	47-48 (methanol)	<u>61,68</u> 61,77	<u>4,04</u> 3,98	<u>13,07</u> 12,68
(Vg)	20	195-200 (12)	<u>61,36</u> 61,77	<u>3,81</u> 3,98	<u>12,61</u> 12,68
(Vh)	56	41-42 (methanol)	<u>66,43</u> 66,08	<u>3,94</u> 4,26	<u>13,62</u> 13,56
(Vj)	65	36-37 (methanol)	<u>53,82</u> 53,32	<u>3,37</u> 3,15	<u>10,89</u> 11,16
(Vk)	42	142-145 (5)	<u>58,56</u> 58,76	<u>3,04</u> 3,52	<u>10,90</u> 11,19
(VIIIg)	96	108-110 (aq. ethanol)	<u>45,86</u> 45,95	<u>2,76</u> 2,78	<u>25,13*</u> 25,23
(VIIIi)	95	126-128 (ethanol)	<u>51,10</u> 51,35	<u>2,84</u> 3,18	<u>28,20*</u> 27,80

*Content of Sn.

†As in the Russian original - Publisher.

(I) and (III), for which the change to Me₂S₀ leads to the virtual disappearance of sensitivity of the indicator group to EES. This effect is in all probability related to the greater acceptor capability of the vacant 6p-orbitals of the Hg atom in comparison with the acceptor capability of the 5d-orbitals of the Sn or its 5p-orbitals under conditions of formation of four-electron three-center bonds in coordination of compounds of the type of R₃SnX with the solvent [12]. Moreover, this effect may be due to greater steric hindrance in the Sn compounds, blocking the approach of the solvent molecules to the central metal atom.

EXPERIMENTAL

The ^{19}F - $\{^1\text{H}\}$ NMR spectra were taken in an RYa-2309 spectrometer (84.56 MHz) at $\sim 20^\circ$ and in a Tesla BS-497 spectrometer (94.075 MHz) at 25°C . All measurements were made on dilute solutions at concentrations of 0.2 or 0.05 M. The experimental error in determining δF was no greater than ± 0.01 ppm. The solvents were purified by standard techniques and were distilled in a stream of dry argon.

The arylmercury 4-fluorothiophenolates were obtained by the interaction of 4-fluorothiophenol with arylmercury acetates. The substituted 4-fluorophenylmercury thiophenolates were synthesized by reactions of 4-fluorophenylmercury acetate with substituted thiophenolates. The substituted 4-fluorophenyl benzyl sulfides were obtained by the action of substituted sodium thiophenolates on 4-fluorobenzyl chlorides. The triaryltin 4-fluorothiophenolates containing electron-donor or weak electron-acceptor substituents, such as 4- ClC_6H_4 or 4- FC_6H_4 , were synthesized by the action of sodium 4-fluorothiophenolate on triarylstannyl chlorides. We had established [13] that under these conditions, triarylstannyl chlorides containing strong electron-acceptor substituents are symmetrized with the quantitative formation of the corresponding tetraarylstannanes. Therefore, the above-indicated 4-fluorothiophenolates were obtained by the interaction of triaryltin hydroxide (VIIIg, i) with thiophenol or by reaction of triaryltin chlorides, or their complexes with DMFA, with thiophenol in the presence of pyridine. The triaryltin hydroxides were obtained by the action of excess caustic on the corresponding chlorides.

The purities of the compounds were checked by means of ^{19}F NMR spectra and thin-layer chromatography on Al_2O_3 . We established that the triaryltin 4-fluorothiophenolates containing strong electron-acceptor substituents are symmetrized when they are chromatographed on Al_2O_3 . Therefore, the oily compounds in this case were obtained from the analytically pure materials without any further chromatographic purification. The constants and analytical data for the new compounds are listed in Table 4. Also given are typical examples of the synthesis of the compounds.

4-Methoxyphenylmercury 4-Fluorothiophenolate. To a hot solution of 1.8 g (5 mmoles) of mercury 4-methoxyphenylacetate in 50 ml of absolute ethanol, a solution of 0.64 g (5 mmoles) of 4-fluorothiophenol in 10 ml of the same solvent was added. The reaction mixture was cooled and then evaporated to dryness under vacuum. After recrystallization from ethanol we obtained 1.3 g (60%) of a colorless crystalline substance with mp $99\text{--}100^\circ\text{C}$.

4-Fluorobenzyl 4-Methoxyphenyl Sulfide. To a solution of 2.16 g (15 mmoles) of 4-fluorobenzyl chloride in 30 ml of absolute ethanol, a solution of sodium 4-methoxythiophenolate was added, this solution having been obtained from 0.33 g (15 mmoles) sodium and 2.2 g (15 mmoles) 4-methoxythiophenol in 50 ml of absolute alcohol. The reaction mixture was heated to boiling, cooled, and held 1 h, after which the solvent was taken off under vacuum, and the residue was washed with water and vacuum-dried over P_2O_5 . After recrystallization from methanol, we obtained 1.6 g (43%) of a colorless crystalline substance with mp $50\text{--}52^\circ\text{C}$.

Tris(3-tolyl)tin 4-Fluorothiophenolate. To a solution of 2.14 g (5 mmoles) of tris(3-tolyl)stannyl chloride in 25 ml of absolute ethanol, a solution of sodium 4-fluorothiophenolate was added, this solution having been obtained from 0.64 g (5 mmoles) 4-fluorothiophenol and 0.12 g (5 mmoles) sodium in 25 ml of absolute ethanol. The reaction mixture was heated to boiling, and the solvent was taken off under vacuum. The residue was washed with water, dissolved in ether, and dried, after which the ether was driven off and the residue was chromatographed on Al_2O_3 (petroleum ether/ethyl acetate 6/1, R_f 0.64). Obtained 1.3 g (50%) of a light-yellow oily substance.

Tris(3,5-dichlorophenyl)tin 4-Fluorothiophenolate. To a solution of 2 g (4 mmoles) of tris(3,5-dichlorophenyl)tin chloride in 25 ml of absolute ethanol, 0.39 g (5 mmoles) of absolute pyridine and 0.64 g (5 mmoles) of 4-fluorothiophenol were added. The reaction mixture was heated to boiling, the alcohol was taken off under vacuum, and the residue was washed with water, extracted with ether, and dried with Na_2SO_4 . The solvent was removed under vacuum. After recrystallization of the residue from hexane, obtained 1.3 g (40%) of a colorless crystalline substance with mp $107\text{--}108^\circ\text{C}$.

Tris(3-chlorophenyl)stannyl Hydroxide. A solution of 3 g (6 mmoles) of tris(3-chlorophenyl)stannyl chloride in 25 ml of ether was treated with excess 5% aqueous NaOH . The resulting precipitate was filtered off and washed with ether. Obtained 2.7 g (90%) of a colorless crystalline substance with mp $108\text{--}110^\circ\text{C}$.

Tris(3-chlorophenyl)tin 4-Fluorothiophenolate. To a solution of 0.2 g (4 mmoles) of tris(3-chlorophenyl)tin hydroxide in 10 ml of absolute methanol, a solution of 0.05 g (4 mmoles) of p-fluorothiophenol was added with stirring; the solvent was driven off, and the residue was held overnight in a vacuum desiccator over P₂O₅. Obtained 0.22 g (99%) of a colorless, transparent oil. Analogously, obtained tris(3-fluorophenyl)tin 4-fluorothiophenolate.

CONCLUSIONS

¹⁹F-¹H NMR has been used to investigate the comparative efficiency of transfer of electronic effects of substituents (EES) through metal-sulfur binuclear bridge groupings, in model systems Ar_nMSC₆H₄F-4 (M = Hg, Sn, CH₂; n = 1, 3). In transmission capability, Hg-S and Sn-S are very little different from the mononuclear analogs Hg and Sn. The order of arrangement of the units in the Hg-S bridge has no effect on the transmission capability. The CH₂-S bridge has a greater transmission capability than Hg-S. The EES transfer efficiency through the metal-sulfur bridge is much lower in coordinating polar solvents. An estimate has been made of the relative contributions of dipole-dipole and coordination interactions with the solvent to the overall effect in lowering the transmission capability.

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