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A PMR STUDY OF RELATIVE STRENGTH OF CHELATE RINGS IN THE C_6H_5Hg, $(C_6H_5)_3Sn$ AND $(C_6H_5)_3Pb$ DERIVATIVES OF SOME NITROGEN-CONTAINING THIOLS *

D.N. KRAVTSOV*, A.S. PEREGUDOV, E.M. ROKHLINA and E.I. FEDIN

Institute of Organo-Element Compounds, Academy of Sciences of the USSR, Vavilov Street 28, Moscow, 117334 (U.S.S.R.)

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Summary

The equilibrium constants for the exchange reactions involving the C_6H_5Hg, $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives of 2,6-dimethylthiophenol, 1-thionaphthol, 8-mercaptoquinoline, 2-mercaptopyridine and 2-dimethylaminothiophenol in chloroform have been determined by the PMR technique. The analysis of the data obtained allowed elucidation of the relative strength of chelate rings in the organometallic derivatives of the nitrogen-containing thiols studied.

Introduction

In a previous investigation of exchange equilibria of the metal—metal type involving organometallic derivatives of some substituted thiophenols [1] it was shown that in the case of organometallic derivatives of *o*-substituted thiophenols the ability of organometallic groups to participate in intramolecular coordination with the *o*-substituent increases in most cases in the order:

$$(C_6H_5)_3SnS < (C_6H_5)_3PbS < C_6H_5HgS$$

In general, the relative stability of chelate rings in the organometallic chelates can depend both on the nature of the organometallic group and on that of the donor atom, as well as on the size of chelate ring. In this connection it seemed of interest to elucidate the extent to which the relative strength of chelate rings formed by the above groups is influenced by the size of the chelate ring and by the type of hybridization of the donor atom. Model systems suitable for investigation of these problems appeared to involve the corresponding organometallic derivatives of thiols, in which the donor of the un-

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shared electron pair is represented by the nitrogen atom. It was hoped that the previously used method of exchange equilibria [1] would give the necessary information.

Results and discussion

In order to solve the above problems we used the PMR technique to study the equilibrium constants for the exchange reactions of organometallic derivatives of 2,6-dimethylthiophenol with those of 8-mercaptoquinoline, 2-mercaptopyridine, 2-dimethylaminothiophenol and 1-thionaphthol in chloroform:

$$(C_6H_5)_nMSC_6H_3(CH_3)_2\text{-}2,6 + (C_6H_5)_nM^*SR \rightleftharpoons (C_6H_5)_nM^*SC_6H_3(CH_3)_2\text{-}2,6 + (C_6H_5)_nMSR$$

$$(C_6H_5)_nM \neq (C_6H_5)_nM^* = C_6H_5Hg, (C_6H_5)_3Sn, (C_6H_5)_3Pb$$

R = 2-pyridyl (C_5H_4N-2), 8-quinolyl (C_9H_6N-8), 2-dimethylaminophenyl ($C_6H_4N(CH_3)_2$-2) or 1-naphthyl ($C_{10}H_7$-1).

This approach was based on the fact that the shielding of the methyl group protons in the organometallic derivatives of 2,6-dimethylthiophenol depends substantially on the nature of the organometallic group [1,2]. At the same time, the exchange reactions between the C_6H_5Hg, $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives of 2,6-dimethylthiophenol and the exchange reactions of the organometallic derivatives of 2,6-dimethylthiophenol with those of other substituted thiophenols are slow on the PMR time-scale, but proceed readily on the preparative timescale, especially for the systems involving the C_6H_5Hg derivatives [1—2].

The data on equilibrium constants are presented in Table 1. Consideration of the results obtained shows that for the exchange reactions involving organometallic derivatives of 8-mercaptoquinoline, for which the possibility of formation of five-membered chelate rings exists [3], the position of the equilibrium deviates strongly from the statistical, especially for the systems containing the C_6H_5Hg derivatives. At the same time, the equilibrium constants for the reactions involving the organometallic derivatives of 1-thionaphthol, the molecular geometry of which is similar to that of the corresponding organometallic derivatives of 8-mercaptoquinoline, are close to unity. As was found earlier [1—2],

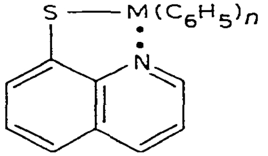
TABLE 1

EQUILIBRIUM CONSTANTS IN CHLOROFORM AT 25°C FOR THE REACTIONS OF $(C_6H_5)_nMSC_6H_3(CH_3)_2$-2,6 WITH $(C_6H_5)_nM^*SR$

$(C_6H_5)_nM$	$(C_6H_5)_nM^*$	R	*K*
C_6H_5Hg	$(C_6H_5)_3Sn$	8-quinolyl	105
C_6H_5Hg	$(C_6H_5)_3Pb$	8-quinolyl	>200
$(C_6H_5)_3Sn$	$(C_6H_5)_3Pb$	8-quinolyl	25
C_6H_5Hg	$(C_6H_5)_3Sn$	1-naphthyl	1.1
C_6H_5Hg	$(C_6H_5)_3Pb$	1-naphthyl	0.9
$(C_6H_5)_3Sn$	$(C_6H_5)_3Pb$	1-naphthyl	1.4
C_6H_5Hg	$(C_6H_5)_3Sn$	2-pyridyl	0.9
C_6H_5Hg	$(C_6H_5)_3Pb$	2-pyridyl	3.6
C_6H_5Hg	$(C_6H_5)_3Sn$	2-dimethylaminophenyl	>100
C_6H_5Hg	$(C_6H_5)_3Pb$	2-dimethylaminophenyl	>100
$(C_6H_5)_3Sn$	$(C_6H_5)_3Pb$	2-dimethylaminophenyl	1.3

the equilibrium constants for the exchange reactions of the C_6H_5Hg derivative of 2,6-dimethylthiophenol with the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives of thiophenol are also equal to unity. On the other hand, according to the literature data [4] the steric requirements of the *o*-fused benzene ring are greater than those of *o*-hydrogen atom. Thus it can be concluded that the C_6H_5Hg, $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives of 1-thionaphthol are destabilized to the same extent by the *o*-fused benzene ring. These results correspond to the previously obtained data [2] indicating that the steric requirements of the C_6H_5HgS, $(C_6H_5)_3SnS$ and $(C_6H_5)_3PbS$ groups are close to one another in non-bonded interactions of these groups with the *o*-methyl substituent.

At the same time, it has been shown earlier [1] that the polar effects of substituents in the thiophenol ring have practically no effect on the position of exchange equilibria involving the C_6H_5Hg, $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives of substituted thiophenols. These data indicate that the deviation of equilibrium constants from unity for the exchange reactions of the organometallic derivatives of 2,6-dimethylthiophenol with those of 8-mercaptoquinoline cannot be connected with the influence of steric factors or electronic substituent effects. Thus, it seems reasonable to conclude that the results obtained are due to the existence of intramolecular coordinative interactions in the organometallic derivatives of 8-mercaptoquinoline:



The strength of these interactions increases depending on the nature of organometallic group in the sequence: $(C_6H_5)_3Pb < (C_6H_5)_3Sn < C_6H_5Hg$. This indicates that, as in the case of the organometallic derivatives of *o*-substituted thiophenols [1], the C_6H_5HgS group forms the most stable chelate ring. In this connection it should be noted that our results are at variance with the conclusions reached by Sytsma and Kline [5], according to which the intramolecular coordination is absent in the CH_3Hg derivative of 8-mercaptoquinoline. The results obtained provide also evidence that the relative ability of the $(C_6H_5)_3$-SnS and $(C_6H_5)_3PbS$ groups for intramolecular coordination is reversed in the organometallic derivatives of 8-mercaptoquinoline, since in the case of the organometallic derivatives of *o*-substituted thiophenols the $(C_6H_5)_3PbS$ group forms in most cases more stable chelate rings than the $(C_6H_5)_3SnS$ group [1].

The situation changes drastically in going to the exchange equilibria involving the organometallic derivatives of 2-mercaptopyridine, because in this case the position of the equilibrium is either statistical or very close to statistical. According to the literature X-ray data [6] a four-membered chelate ring exists in the CH_3Hg derivative of 2-mercaptopyrimidine in the crystalline state. On the basis of the similarity in geometry of virtual intramolecular coordinative interactions for the above compound and the C_6H_5Hg derivative of 2-mercaptopyridine one may also expect the formation of a four-membered chelate ring in the latter case. Accordingly, the values of the equilibrium constants for the exchange reactions indicate that in the organometallic derivatives of 2-mercaptopyridine the relative strength of the chelate rings increases depending on the nature of the organometallic group in the order: $(C_6H_5)_3PbS < (C_6H_5)_3SnS \approx C_6H_5HgS$. Thus, the decrease in the size of the chelate ring along with the retention of the nature of the donor atom leads for nitrogen-containing chelate rings to the disappearance of the difference in the strength of intramolecular coordination for the C_6H_5HgS and $(C_6H_5)_3SnS$ groups and to the decrease in this difference for the $(C_6H_5)_3SnS$ and $(C_6H_5)_3PbS$ groups.

The data of Table 1 show that for the exchange reactions involving the organometallic derivatives of 2-dimethylaminothiophenol the position of equilibrium is practically statistical for the exchanging group pair $(C_6H_5)_3Sn$/-$(C_6H_5)_3Pb$, but differs strongly form statistical for the systems containing the C_6H_5Hg derivatives. The shift of the equilibrium in favour of the C_6H_5Hg derivative of 2-dimethylaminothiophenol demonstrates the greater stability of the chelate ring in this compound in comparison to the corresponding $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives. At the same time, the strength of virtual chelate rings in the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives of 2-dimethylaminothiophenol should be comparable.

In considering the results obtained it should be pointed out that in general, for a given donor atom and chelate ring size, the relative stability of chelate rings formed by organometallic groups must depend on the overall coordinating ability of the central metal atom and on the conformity of the geometry of the chelate ring to the optimal geometry of coordinative interactions for the corresponding organometallic group. In the organometallic derivatives of thiophenols the C_6H_5Hg group has a greater tendency to coordinate with the nitrogen atom of pyridine type than the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ groups. This is evidenced by the greater change in fluorine chemical shift on transfer from chlorobenzene to pyridine for the C_6H_5Hg-derivative of *p*-fluorothiophenol than for the corresponding $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives [2]. On the other hand, the optimal orbital geometry of the tri-coordinated mercury atom is favourable for the formation of chelate rings by the C_6H_5Hg group [2]. In contrast, the preferred geometry of the penta-coordinated sp^3d-hybridized state does not favour the formation of chelate rings by the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ groups [2]. The above factors readily explain the greater stability of the chelate ring in the C_6H_5Hg derivative of 8-mercaptoquinoline as compared to the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives.

According to the data on the metal—sulphur distances and the values of the C_{Ar}—S—M angle in the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives of some thiophenols [7,8], the geometry of intramolecular coordinative interactions in the corresponding derivatives of 8-mercaptoquinoline should be quite similar. The slight differences may be caused only by the small difference in the lengths of the Sn—S and Pb—S bonds (about 0.08 Å). In this connection the greater stability of the chelate ring for the $(C_6H_5)_3Sn$ derivative may result from the fact that tin is a "harder" Lewis acid than lead [9]. Another possible cause may be the better conformity of the chelate ring geometry to the requirements of orbital overlap in the case of the $(C_6H_5)_3Sn$ derivative.

Inspection of molecular models shows that in the virtual chelate rings of the organometallic derivatives of 2-mercaptopyridine the conditions for orbital overlap are less favourable than in the corresponding derivatives of 8-mercaptoquinoline. Under these circumstances the shorter Hg—S distance (2.34 Å) [10] as compared to 2.43 Å for Sn—S [7] may be important in eliminating the difference in coordinating abilities of the $(C_6H_5)_3SnS$ and C_6H_5HgS groups. The similar difference in the Pb—S and Sn—S distances [7,8] may reduce the difference in stability of chelate rings in the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives of 2-mercaptopyridine. The further reduction of the difference in stabilities of chelate rings formed by the $(C_6H_5)_3SnS$ and $(C_6H_5)_3PbS$ groups on going to the corresponding derivatives of 2-dimethylaminothiophenol may be also caused by the fact that the greater length of the Pb—S bond as compared to the Sn—S bond [7,8] reduces the non-bonded interactions between the $(CH_3)_2N$ group and the C_6H_5 radicals on the metal atom. Finally, the still smaller range of the above non-bonded interactions in the C_6H_5Hg derivative of 2-dimethylaminothiophenol favours the greater stability of the chelate ring formed by the C_6H_5-HgS group in this case.

In conclusion it may be said that the results obtained in the present investigation show that for the same donor atom the variation in the size of chelate ring and type of orbital hybridization exerts a marked influence on the relative stability of chelate rings formed by the $(C_6H_5)_nMS$ groups containing mercury, tin and lead.

Experimental

The investigation of exchange equilibria was performed by using an RYA-2309 NMR spectrometer operating at 90 MHz. The equilibrium constants for the exchange reactions were calculated from equilibrium concentrations of the reactants and products, which were obtained by integrating the *o*-methyl group signals for one of the reactants and one of the products after attainment of equilibrium, the latter being approached by starting with both possible pairs of the reactants. The relative error in equilibrium constants did not in most cases exceed ±15%. Only for the equilibrium constant values of 25 and higher did it increase to ±30%. The exchange reactions were run in chloroform at 25°C, 0.2 *M* initial concentrations of the reactants being used. The chemical shifts of the *o*-methyl group protons for the organometallic derivatives of 2,6-dimethylthiophenol in chloroform had been determined previously [1]. The chemical shifts of the $(CH_3)_2N$ group protons for $(C_6H_5)_nMSC_6H_4N(CH_3)_2$-2 in chloroform relative to internal TMS are equal to 2.25, 2.46 and 2.84 ppm to lower field for $(C_6H_5)_nM = (C_6H_5)_3Sn$, $(C_6H_5)_3Pb$ and C_6H_5Hg, respectively, at 0.1 *M* concentration.

The organometallic derivatives of 2,6-dimethylthiophenol and the $(C_6H_5)_3Sn$ derivatives of 8-mercaptoquinoline and 2-mercaptopyridine have been described elsewhere [2,3,11]. The other organometallic derivatives investigated were prepared by the action of phenylmercury hydroxide on the thiols or by the interaction of phenylmercury acetate, triphenyltin and -lead chlorides with the sodium salts of thiols in ethanol. The compounds were purified by crystallization from appropriate solvents. The organometallic derivatives of 2-mercaptopyridine and 2-dimethylaminothiophenol were recrystallized from ethanol, the $(C_6H_5)_3Pb$ derivative of 8-mercaptoquinoline from methanol and the C_6H_5Hg and $(C_6H_5)_3Sn$ derivatives of 8-mercaptoquinoline from propanol. The

TABLE 2

MELTING POINTS AND ANALYTICAL DATA FOR THE ORGANOMETALLIC DERIVATIVES OF THIOLS

Compound	M.p. (°C)	Analyses (found (calcd.) (%))		
		C	H	M
$C_6H_5HgSC_5H_4N$-2	79—80	34.02	2.32	51.80
		(33.87)	(2.35)	(51.35)
$(C_6H_5)_3PbSC_5H_4N$-2	101—103	50.36	3.46	37.77
		(50.39)	(3.50)	(37.61)
$C_6H_5HgSC_9H_6N$-8	148—149	41.09	2.51	45.89
		(40.93)	(2.49)	(45.63)
$(C_6H_5)_3PbSC_9H_6N$-8	110—112	54.18	3.68	34.61
		(54.12)	(3.58)	(34.76)
$C_6H_5HgSC_{10}H_7$-1	150—151	43.98	2.77	45.91
		(43.93)	(2.67)	(45.70)
$(C_6H_5)_3SnSC_{10}H_7$-1	89—90	66.01	4.32	23.38
		(66.15)	(4.47)	(23.64)
$(C_6H_5)_3PbSC_{10}H_7$-1	100—101	56.09	3.55	35.20
		(56.28)	(3.69)	(34.67)
$C_6H_5HgSC_6H_4N(CH_3)_2$-2	93—95	39.00	3.65	46.14
		(39.07)	(3.49)	(46.74)
$(C_6H_5)_3SnSC_6H_4N(CH_3)_2$-2	116—117	62.72	5.03	23.73
		(62.15)	(4.98)	(23.71)
$(C_6H_5)_3PbSC_6H_4N(CH_3)_2$-2	96—98	52.65	4.26	34.98
		(52.88)	(4.22)	(35.08)

organometallic derivatives of 2-mercaptopyridine and 2-dimethylaminothiophenol were obtained as colourless crystals, those of 8-mercaptoquinoline as pale yellow crystalline substances.

The sodium salt of 8-mercaptoquinoline, phenylmercury acetate, triphenyltin and triphenyllead chlorides were available commercially and were used without further purification. The preparations of 2,6-dimethylthiophenol, 1-thionaphthol, 2-mercaptopyridine (2-thiopyridone), 2-dimethylaminothiophenol and phenylmercury hydroxide were carried out according to the procedures reported in the literature [2,12—15]. The purity of the thiols was checked by the PMR technique.

The melting points and analytical data for the new organometallic derivatives of thiols are presented in Table 2. The melting points are not corrected. The preparations of some compounds described below are illustrative of the experimental procedures used in the synthesis of the organometallic derivatives investigated.

Phenylmercury 2-dimethylaminothiophenoxide

To a hot solution of 1.08 (3.5 mmol) of phenylmercury hydroxide [15] in 50 ml of ethanol was added 0.51 g (3.5 mmol) of 2-dimethylaminothiophenol. After cooling to room temperature the resulting precipitate was filtered and recrystallized from ethanol, yielding 1.2 g (80%) of colourless crystals.

Phenylmercury 8-quinolylmercaptide

To a hot solution of 0.91 g (5 mmol) of the sodium salt of 8-mercaptoquinoline in 30 ml of ethanol was added a hot solution of 1.68 g (5 mmol) of phenylmercury acetate in 50 ml of the same solvent. After cooling the reaction mixture to room temperature the separated precipitate was filtered, washed with water, dried and recrystallized from propanol, yielding 1.5 g (69%) of pale yellow crystals.

Triphenyltin 1-thionaphthoxide

To a hot solution of 1.93 g (5 mmol) of triphenyltin chloride in 50 ml of methanol was added a hot solution of 0.12 g sodium and 0.8 g (5 mmol) of 1-thionaphthol in 20 ml of the same solvent. After evaporation of the solvent under reduced pressure the resulting solid was washed with water, dried and recrystallized from ethanol, affording 1.42 g (60%) of colourless crystals.

Triphenyllead 2-pyridylmercaptide

To a hot solution of 2.37 g (5 mmol) of triphenyllead chloride in 50 ml of ethanol was added a solution of sodium salt of 2-mercaptopyridine, prepared from 0.12 g of sodium and 0.5 g (5 mmol) of 2-mercaptopyridine in 30 ml of ethanol. After cooling to room temperature the precipitate formed was filtered, washed with water, dried and recrystallized from ethanol, yielding 2.0 g (75%) of colourless crystals.

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