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Figure 1: Structures I, II, and III: bipyramidal and octahedral complexes with Cl, Sn, and SR_2 vertices.

Abstract

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CHEMISTRY

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POLARITY AND STRENGTH OF INTERMOLECULAR BONDS IN COMPLEXES OF TIN TETRACHLORIDE WITH ORGANIC SULFIDES

To solve the question of the nature of intermolecular bonds in donor–acceptor-type complexes, it is necessary to know the character of the dependence between the polarity of the corresponding bonds and their strength. In the present work, the heats of formation and dipole moments of complexes of tin tetrachloride with sulfur-containing compounds have been measured. The dipole moments were determined by the method of dielectric titration ([1]), and the heats of formation by the method of calorimetric titration ([2]).

Tin tetrachloride gives, with sulfur compounds as well as with oxygen compounds, complexes of two types: of composition $SnCl_4 \cdot R_2S$ ([3,4]) with coordination number of tin 5, and of composition $SnCl_4 \cdot 2R_2S$ ([3,4]) with coordination number of tin 6. For complexes of composition $1:1$, the most probable conformation appears to be the (sp^3d) bipyramid I. Evidence in favor of this may be provided by the bipyramidal structure of the complex of trimethyltin chloride with pyridine, established by X-ray structural analysis ([5]), as well as by data on the dipole moments of $SnCl_4 \cdot R_2S$ (see below). Compounds of composition $1:2$ have an octahedral conformation ([6]); here the formation is possible of two isomers with cis-II and trans-III arrangement of the donor molecules.

Fig. 1. Curves of dielectrometric and calorimetric titration of a solution of $SnCl_4$ with sulfides $C_4H_9S(CH_2)_{nSC}4H_9$ and dioctyl sulfide

Figure 2: Fig. 1. Curves of dielectrometric and calorimetric titration of a solution of $SnCl_4$ with sulfides $C_4H_9S(CH_2)_{nSC}4H_9$ and dioctyl sulfide

With the aim of obtaining complexes of composition 1 : 2 of definitely cis structure, we turned to compounds of the type R—S—$(CH_2)_n$—S—R, which were synthesized by us from the corresponding 1,*n*-dichloro- or dibromoalkanes and sodium ethyl- or butyl mercaptides in alcohol ($n = 1, 2, 3, 4, 5, 6$ or 10 and R = C_2H_5 or C_4H_9). In the last two columns of Table 1 are given the boiling points t_{bp} and the values of the dipole moments of the substances studied. Depending on the size of the polymethylene chain n, such compounds can give with tin tetrachloride both complexes of composition 1 : 1 and more complex associates $(1 : 1)_p$. By the method of cryoscopic titration of solutions of tin tetrachloride in benzene with the compounds studied, and also by determining the molecular weight of the isolated complexes by cryoscopy and ebullioscopy, we established that at low concentrations (0.03 g-mol/l) the compounds $SnCl_4 \cdot$ R—S—$(CH_2)_n$—S—R, where $n = 1, 2$, or 3, are monomeric. Compounds with $n > 3$ are associated. The degree of association, for example, at $n = 6$, is 6–8. Judging from the magnitude of the dipole moment, such associates have a cyclic structure.

Figure 1 shows the experimental results for a series of systems. Here C_{SnCl_4} is the concentration of the initial solution of $SnCl_4$ in benzene (0.05–0.08 g-mol/liter), C is the sulfide concentration, $\Delta\varepsilon$ is the change in the dielectric constant of the tin tetrachloride solution upon addition of the corresponding sulfide, and Q/m_{SnCl_4} is the heat referred to 1 g-mol of $SnCl_4$ in the initial solution. The results of determining the dipole moments μ (in debyes) and heats of formation $-\Delta H$ (kcal/g-mol) of the complexes are given in Table 1. The melting points t_{m} of a series of isolated complexes, and the values of the molar polarization P_∞ and molar refraction R_D, are also indicated there.

Fig. 1. Curves of dielectrometric and calorimetric titration of a solution of $SnCl_4$ with sulfides $C_4H_9S(CH_2)_{nSC}4H_9$ and dioctyl sulfide

As can be seen (Fig. 1), the curves ε—C, Q—C, and also d—C (not shown here), referring to the systems $SnCl_4$—R—S—$(CH_2)_n$—S—R, have sharp inflections at a component ratio of 1 : 1. At this point the complex-formation process is completed. Since the final products of the $SnCl_4$—R_2S interaction are complexes of composition 1 : 2 (^{3}), it may be concluded that both sulfur atoms in the compounds R—S—$(CH_2)_n$—S—R participate in complex formation.

The character of the curves (Fig. 1) depends to a considerable extent on the value of n. The most stable complex, practically undissociated in solution, is formed in the case $n = 2$. The relatively large magnitude of the thermal effect, −27.4 kcal, also attests to the strength of the complex formed.

An equally stable complex with t_m = 180–181° is formed with the analogous compound containing ethyl radicals (17, Table 1). However, because of its poor solubility, we could not study its properties in greater detail.

In work (^{7}), the heat of formation of the complex $SnCl_4 \cdot CH_3S(CH_2)_2SCH_3$ was determined to be 28 kcal/g-mol. This value agrees well with those obtained by us. The greatest stability of the complexes at $n = 2$ is apparently explained by steric factors: the distance between the sulfur atoms in these compounds is close to the optimum distance for the cis conformation of complex (IV).

As regards the influence of the structure of sulfide molecules on their complex-forming ability with tin tetrachloride, the data of Table 1 show that the sulfur atoms in sulfides with n-aliphatic radicals C_3H_7, C_4H_9, C_8H_{17}, and also C_9H_{19} (^{3,4}) and $C_{16}H_{33}$ (^{3,4}) possess approximately the same

···with identical donor properties. The heats of formation and dipole moments of these complexes are close (1, 3, 5 and 2, 4, 6, Table 1).

Branching of the hydrocarbon radical adjacent to the sulfur atom leads, because of steric factors, to weakening of the donor-acceptor bonds (5 and 7, Table 1). A considerable decrease in the donor properties of the sulfur atom is also observed when alkyl radicals are replaced by aromatic (9, Table 1) or fatty-aromatic radicals (8, Table 1).

Table 1

No.	Complex	m.p., °C	P_∞	R_D	μ	ψSn ···S	$-\Delta H$	Sulfide b.p., °C/mm	Sulfide μ
1	$SnCl_4 \cdot (C_3H_7)_2S$	–	952.6	81.3	6.49*	3.3	12.9	142–143	1.55
2	$SnCl_4 \cdot 2(C_3H_7)_2S$	50–55	422.1	119.3	3.83*	–	24.7	142–143	1.55
3	$SnCl_4 \cdot (C_4H_9)_2S$	–	1021.5	90.5	6.71*	3.5	12.6	183–184	1.51
4	$SnCl_4 \cdot 2(C_4H_9)_2S$	42	484.6	137.6	4.10*	–	24.2	183–184	1.51
5	$SnCl_4 \cdot (C_8H_{17})_2S$	–	1079.9	127.5	6.79*	3.6	11.9	308–309	1.63
6	$SnCl_4 \cdot 2(C_8H_{17})_2S$	liquid	558.1	203.6	4.10*	–	22.9	308–309	1.63
7	$SnCl_4 \cdot (iso\text{–}C_6H_{13})_2S$	–	449.7	127.5	3.76	0.4	0.4	135–136/3	1.64
8	$SnCl_4 \cdot (C_6H_5CH_2)_2S$	–	580.6	110.8	4.77	1.5	3.8	m.p. 48–49	1.38
9	$SnCl_4 \cdot C_6H_5S \cdot C_2H_5$	–	451.6	86.8	4.20	0.9	2.0	78–79/8	1.48

No.	Complex	m.p., °C	P_∞	R_D	μ	ψSn···S	$-\Delta H$	Sulfide b.p., °C/mm	Sulfide μ
10	$SnCl_4 \cdot C_4H_9SCH_2SC_4H_9$	liquid	1578.3	103.2	8.42	2.7	14.5	117–120/9–10	1.34
11	$SnCl_4 \cdot C_4H_9S(CH_2)_2SC_4H_9$	90–91	2536.7	107.7	10.82	4.4	27.4	127–129/5	1.89
11	Same, isolated complex	90–91	2198	107.7	10.05	–	–	–	–
12	$SnCl_4 \cdot C_4H_9S(CH_2)_3SC_4H_9$	–	2157.4	112.3	9.96	3.9	25.3	194–196/47–50	2.02
13	$SnCl_4 \cdot C_4H_9S(CH_2)_4SC_4H_9$	130–131	–	–	–	–	20.5	143/2	2.10
14	$SnCl_4 \cdot C_4H_9S(CH_2)_5SC_4H_9$	123–125	–	–	–	–	25.1	132–135/1	2.14
15	$SnCl_4 \cdot C_4H_9S(CH_2)_6SC_4H_9$	135–136	(1101.6)	(126.1)	(6.86)**	–	27.4	172–176/5	2.15
16	$SnCl_4 \cdot C_4H_9S(CH_2)_{10}SC_4H_9$	–	–	–	–	–	24.0	206–208/1	2.24
17	$SnCl_4 \cdot C_2H_5S(CH_2)_2SC_2H_5$	180–181	–	–	–	–	–	80–81/6	1.89
18	$SnCl_4 \cdot CH_3S(CH_2)_2SCH_3$	–	–	–	–	–	28.0***	–	–

* D. M. measured previously (3, 4).
** The complex is associated.
*** Literature data (7).

Judging from the close values of the heats of formation of the complexes (2, 4, 6 and 11–16, Table 1), the sulfur atoms in the compounds R—S—$(CH_2)_n$—S—R, where R denotes *n*-aliphatic radicals, possess approximately the same donor properties as in *n*-aliphatic sulfides.

The observed differences in the heats of formation of the complexes $SnCl_4 \cdot$ R—S—$(CH_2)_n$—S—R for different n (9–16, Table 1) are due mainly to steric factors. Dielectrometric measurements in systems where $n > 3$, with the exception of the system with $n = 6$ (15, Table 1), were not carried out because of association.

Attention is drawn to the fact of a large difference between the dipole moments of the complexes $SnCl_4 \cdot 2R_2S$, where R denotes *n*-aliphatic radicals (3.8–4.1 D), and $SnCl_4 \cdot$ R—S—$(CH_2)_n$—S—R (8.4–10.8 D). Judging by the fact that

Fig. 2. Dependence of the polarity of donor-acceptor bonds on the heat of their formation in complexes of SnCl4 with various sulfides.

Figure 3: Fig. 2. Dependence of the polarity of donor-acceptor bonds on the heat of their formation in complexes of SnCl4 with various sulfides.

the heats of formation of these complexes are close (2, 4, 6 and 11—16, Table 1), it may be assumed that the nature of the intermolecular bonds in them is the same. The matter here is apparently the difference in their structure. The dipole moments of the complex $SnCl_4 \cdot 2R_2S$ are too large for them to be assigned the symmetrical trans-structure III, and at the same time they are considerably lower than the dipole moments of the complexes $SnCl_4 \cdot R—S—(CH_2)_n—S—R$, which have the cis-conformation IV.

The totality of the data obtained makes it possible to draw, as the most probable conclusion, that in the case of the complexes $SnCl_4 \cdot 2R_2S$ in solution we are dealing with an equilibrium mixture of cis-II and trans-III isomers. It is possible that, during synthesis, an equiprobable cis-trans distribution of donor molecules in the octahedron takes place. This conclusion is consistent with the fact that the dipole moment decreases on going from the complexes $SnCl_4 \cdot R_2S$, 6.4—6.8 D, to the corresponding complexes $SnCl_4 \cdot 2R_2S$, 3.8—4.1 D.

Using the method of dielectrometric titration we showed (3, 4) that the formation of the complexes $SnCl_4 \cdot 2R_2S$ occurs stepwise. It was of interest to determine whether the donor-acceptor bonds are equivalent.

The heats of formation of $SnCl_4 \cdot 2R_2S$ are approximately twice as large as those of $SnCl_4 \cdot R_2S$ (Table 1). The difference in the heats of addition of the first and second sulfide molecules is small and amounts to ~ 1 kcal/mole: 12.9 and 11.8 in the system with $(C_3H_7)_2S$, 12.6 and 11.6 in the system with $(C_4H_9)_2S$, and 11.9 and 10.9 in the system with $(C_8H_{17})_2S$. It is possible that this difference is associated with a change in the spatial conformation of the molecules.

Fig. 2. Dependence of the polarity of donor-acceptor bonds on the heat of their formation in complexes of $SnCl_4$ with various sulfides.
1 —(iso-$C_8H_7)_2S$,
2 —$C_6H_5SC_2H_5$,
3 —$(C_6H_5CH_2)_2S$,
4 —$C_4H_9SCH_2SC_4H_9$,
5 —$(C_8H_{17})_2S$,
6 —$(C_4H_9)_2S$,
7 —$(C_3H_7)_2S$,
8 —$C_4H_9S(CH_2)_3SC_4H_9$,
9 —$C_4H_9S(CH_2)_2SC_4H_9$.

In analyzing the dipole moments of the complexes studied from the point of view of determining the polarity of intermolecular bonds, it is necessary to take into account the circumstance that the sulfur atom, apparently, forms donor-acceptor bonds by means of a $3p^2$ unshared electron pair. In this case the dipole moment of the sulfide will lie in a plane approximately perpendicular to the direction of the bond being formed. Such a position of the sulfide molecule was found by X-ray structural analysis in the complex of dibenzyl sulfide with iodine (^{8}). Taking this into account, and assuming a bipyramidal conformation I for the complexes $SnCl_4 \cdot R_2S$ and an octahedral *cis* conformation for the complexes $SnCl_4 \cdot R—S—(CH_2)_n—S—R$ $(n = 1, 2, 3)$, we attempted to estimate the magnitude of the dipole moment attributable to the intermolecular Sn ... S bond. The dipole moment of Sn—Cl was taken to be 3.0 D (see Table 1).

The experimental values of the heats of formation $-\Delta H$ (per one Sn ... S bond) and of the dipole moments $\mu_{Sn...S}$ lie well on the straight line $\mu_{Sn...S} - (\Delta H_{Sn...S})$, $(-\Delta H_{Sn...S})$.

Because of the poor solubility of the complexes in indifferent solvents (octane, hexane, cyclohexane), the calorimetric measurements were carried out in benzene. In doing so, the energy of dissociation of the $SnCl_4$ complex with benzene was not taken into account; for this type of complex it amounts to ~ 1 kcal/mole. If this correction is introduced into the values of $-\Delta H$ obtained by us, the experimental straight line will pass through the origin, i.e., one may speak of the existence of direct proportionality between $-\Delta H_{Sn...S}$ and $\mu_{Sn...S}$.

A similar dependence between the heat of formation and the polarity of intermolecular bonds has also been established in complexes of organic sulfides with iodine (^{9}).

Apparently, the observed regularity is general for n, σ-complexes of the donor-acceptor type. It testifies in favor of the existing point of view that bonds in such compounds are formed by the unshared electron pair of the donor molecule and the vacant valence orbitals of the acceptor molecule, and is, to a certain extent, a quantitative criterion of the validity of this concept, showing that the strength of such bonds is determined by the degree of charge transfer from donor to acceptor.

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