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## Investigation of the electronic structure of $\text{SnCl}_4\text{L}_2$ , $\text{TiCl}_4\text{L}_2$ and $\text{SbCl}_5\text{L}$ complexes by X-ray fluorescence spectroscopy

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### Abstract

The electronic structure of  $\text{SbCl}_5\text{L}$  complexes has been analyzed on the basis of the fluorescence spectra of the sulfur and chlorine atoms as well as quantum chemical  $X\alpha$ -DV and PM3 calculations. The results have been compared with the corresponding data for  $\text{SnCl}_4\text{L}_2$  and  $\text{TiCl}_4\text{L}_2$  complexes. An increase in electron density on the chlorine atoms accompanied by a decrease on the central metal atom has been observed for the complexes arranged according to their stability. The arrangement of Sn, Sb, and Ti complexes with dimethyl sulfide according to their increasing stability is in disagreement with the order of the complexes with respect to electron density on the sulfur atom.

### 1. Introduction

In our previous work [1,2] we measured  $\text{ClK}\alpha$  ( $\Delta(\text{ClK}\alpha)$ ) shifts, which appeared to be proportional to the effective charge on the chlorine atom ( $q_{\text{Cl}}$ ) [3] in  $\text{SnCl}_4\text{L}_2$  and  $\text{TiCl}_4\text{L}_2$  complexes. We have shown that the mean electron density on the chlorine atoms in  $\text{SnCl}_4\text{L}_2$  complexes neither changes when compared to  $\text{SnCl}_4$  in strong complexes nor significantly decreases in weak complexes, whereas in  $\text{TiCl}_4\text{L}_2$  complexes the electron density on the chlorine atoms increases considerably when compared to  $\text{TiCl}_4$ .

One reason for this difference in behavior of the  $\text{SnCl}_4\text{L}_2$  and  $\text{TiCl}_4\text{L}_2$  complexes may be the different response of the ionic character of the Sn–Cl and Ti–Cl bonds to changes in the acceptor geometry upon complex formation. Indeed, the results of the  $X\alpha$ -DV calculations, presented in Table 1, show that on changing the  $\text{SnCl}_4$  symmetry from tetrahedral to square planar and increasing the length of the Sn–Cl bond, which takes place during complex formation, the ionic character of the Sn–Cl bond decreases. However, the analogous changes for  $\text{TiCl}_4$  do not induce charge redistribution. Therefore, in the  $\text{TiCl}_4\text{L}_2$  complexes, contrary to the case of the  $\text{SnCl}_4\text{L}_2$  complexes, the changes in  $q_{\text{Cl}}$  upon complex formation are only a consequence of electron density transfer from the ligands.

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Table 1  
Net charges on the chlorine and metal (Me) atoms calculated with the  $X\alpha$ -DV method for different geometries of  $\text{SnCl}_4$  and  $\text{TiCl}_4$

Molecule	Symmetry	Distance Me–Cl (Å)	Net charge (e)	
			Cl	Me
$\text{SnCl}_4$	$T_d$	2.28	–0.32	1.28
	$D_{4h}$	2.28	–0.29	1.17
	$D_{4h}$	2.35	–0.28	1.12
$\text{TiCl}_4$	$T_d$	2.17	–0.998	3.997
	$D_{4h}$	2.17	–0.998	3.997
	$D_{4h}$	2.35	–0.999	3.998

## 2. Experimental

The complexes were obtained in their crystalline form by dissolving the anhydrous bases in a small volume of carbon tetrachloride and adding antimony pentachloride. The resulting precipitates were filtered off and dried in vacuum. The structures and purity of the complexes obtained were checked by IR and elemental analysis.

X-ray fluorescence spectra of chlorine and sulfur atoms were obtained with a STEARATE X-ray spectrometer. The spectra were excited by  $\text{AgL}$ -radiation and recorded with the help of a proportional counter filled with a mixture of argon and methane. The working regime of the X-ray tube was 6–10 kV, 0.4 A. The solid samples were prepared by depositing the compound by friction into the riffled copper or nickel plates. The  $\text{SbCl}_5$  sample was prepared by freezing it in vacuum into the nickel plate.

The time of a single exposition for the  $\text{ClK}\alpha$  line was 0.5 min. The experiment was repeated 16–20 times and the results were averaged. The recorded spectra of the samples studied were referred to the spectrum of  $\text{C}_6\text{Cl}_6$  used as a standard. The  $\text{SK}\beta$  spectra were recorded 3–4 times and the results were averaged.

To determine the charge distribution in the molecules, molecular orbital calculations were carried out with the PM3 method of the AMPAC program [4]. The  $X\alpha$ -DV method was used as in Ref. 2, and the INDO method as in Ref. 5.

## 3. Results and discussion

For the  $\text{SnCl}_4\text{L}_2$  and  $\text{TiCl}_4\text{L}_2$  complexes, we

observed different dependences of the complex stability, usually assumed to be proportional to the ligand-donating power (DN, defined as the enthalpy of  $\text{SbCl}_5\text{L}$  complex formation) on the charge on the chlorine atoms (see Fig. 1) [6]. For the  $\text{SnCl}_4\text{L}_2$  complexes, the value of  $\Delta(\text{ClK}\alpha)$  was found to increase linearly with increasing DN, whereas for the  $\text{TiCl}_4\text{L}_2$  complexes this dependence was much more complex.

For the  $\text{SbCl}_5\text{L}$  complexes, the dependence of electron distribution on the complex stability was similar to that observed for  $\text{SnCl}_4\text{L}_2$  and differed only by a smaller slope. For the  $\text{SbCl}_5\text{L}$  and  $\text{SnCl}_4\text{L}_2$  complexes, the  $^{35}\text{Cl}$  NQR frequencies decrease with increasing stability of the complexes which, within the Townes and Dailey approximation [7], is consistent with the increasing electron density at the chlorine atoms for complexes arranged according to their stability (deduced from  $\text{ClK}\alpha$  shift measurements).

Table 2 presents the values of  $\Delta(\text{ClK}\alpha)$ , the net charges on the chlorine atoms,  $q_{\text{Cl}}$ , calculated from  $\Delta(\text{ClK}\alpha)$  by the procedure described in ref. 3, and the values of DN and  $^{35}\text{Cl}$  NQR frequencies. According to the data of Table 2 and Fig. 1, the value of  $q_{\text{Cl}}$  increases with increasing DN and reaches a maximum for the  $\text{Sb}_2\text{Cl}_{10}$  dimer. (It should be pointed out that at a temperature of about 100 K, at which the X-ray fluorescence spectra of  $\text{SbCl}_5$  were taken,  $\text{SbCl}_5$  forms a dimer [8].)

For  $\text{SbCl}_5\text{L}$  and  $\text{SnCl}_4\text{L}_2$ , the observed changes in the charge on the chlorine atoms of the acceptor molecule upon complex formation [1,2] can be assumed to result from changes in the acceptor

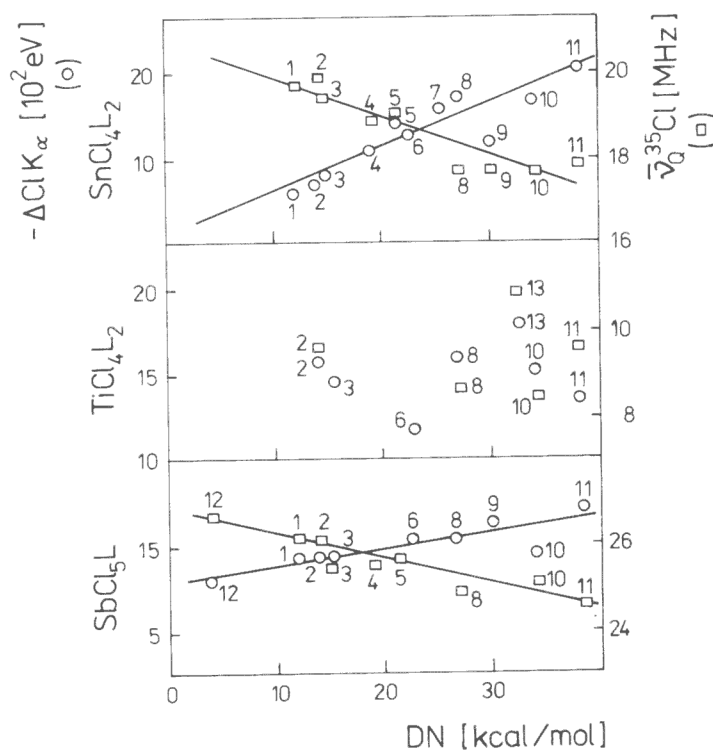


Fig. 1. The  $^{35}\text{Cl}$  NQR frequencies and  $\text{ClK}\alpha$  shifts vs. the ligand strength of the complexes  $\text{SnCl}_4\text{L}_2$ ,  $\text{TiCl}_4\text{L}_2$  and  $\text{SbCl}_5\text{L}$  with the ligands: (1)  $\text{PhCN}$ ; (2)  $\text{CH}_3\text{CN}$ ; (3) dioxane; (4)  $\text{CH}_3\text{OH}$ ; (5)  $\text{O}(\text{CH}_2)_4$ ; (6)  $(\text{CH}_3)_2\text{S}$ ; (7)  $\text{PPh}_3$ ; (8)  $(\text{CH}_3)_2\text{NCOH}$ ; (9)  $(\text{CH}_3)_2\text{SO}$ ; (10) pyridine; (11)  $[(\text{CH}_3)_2\text{N}_3\text{PO}]$ ; (12)  $\text{PhNO}_2$ ; (13)  $\text{Ph}_3\text{PO}$ .

Table 2

Parameters determined from the X-ray fluorescence spectra and the  $^{35}\text{Cl}$  NQR frequencies of the  $\text{SbCl}_5\text{L}$  complexes

Ligand (L)	$-\Delta(\text{ClK}\alpha)^a$ ( $10^2$ eV)	$-q_{\text{Cl}}^a$ ( $10^2 e$ )	$\nu_Q^{35}\text{Cl}^b$ (MHz)	$\text{DN}^c$ ( $\text{kcal mol}^{-1}$ )
—	18.9(17)	42(5)	28.04	
$[(\text{CH}_3)_2\text{N}]_3\text{PO}$	18.9(11)	42(4)	24.58	38.6
Pyridine	14.8(11)	31(4)	25.24	33.1
$(\text{CH}_3)_2\text{SO}$	17.9(17)	40(5)		29.8
$\text{Ph}_3\text{PS}$	16.7(8)	37(4)		
$(\text{CH}_3)_2\text{NCOH}$	15.6(13)	33(5)	24.90	26.5
$(\text{CH}_3)_2\text{S}$	15.2(6)	33(2)		23.5
Dioxane	13.3(21)	29(5)	25.65	14.8
$\text{CH}_3\text{CN}$	14.0(23)	31(6)	25.93	14.1
$\text{PhCN}$	13.6(21)	30(5)	26.21	11.9
Pyridine <i>N</i> -oxide	11.4(12)	25(4)		
$\text{PhNO}_2$	11.0(12)	24(4)	26.68	4.4

<sup>a</sup> The figures given in parentheses are the mean-square errors in units of the last digit quoted for the parameter.

<sup>b</sup> From Refs. 15 and 16.

<sup>c</sup> From Ref. 6.

Table 3

The net charges calculated with the PM3 method for different geometries of  $\text{SbCl}_5$ 

Compound	Symmetry	Distance Sb–Cl (Å)	Atom	Net charge (e)	Average net charge (e)
$\text{SbCl}_5$	$C_{3v}$	2.277 <sup>a</sup>	Cl <sup>a</sup>	–0.171	–0.203
		2.338 <sup>b</sup>	Cl <sup>b</sup>	–0.252	
			Sb	1.016	
$\text{SbCl}_5$	$C_{4v}$	2.277 <sup>a</sup>	Cl <sup>a</sup>	–0.184	–0.200
		2.338 <sup>b</sup>	Cl <sup>b</sup>	–0.264	
			Sb	1.001	
$\text{SbCl}_5$	$C_{4v}$	2.40 <sup>a,b</sup>	Cl <sup>a</sup>	–0.154	–0.170
			Cl <sup>b</sup>	–0.236	
			Sb	0.851	
$\text{Sb}_2\text{Cl}_{10}$	$O_h$	2.35 <sup>a</sup>	Cl <sup>a</sup>	–0.206	–0.212
		2.37 <sup>b</sup>	Cl <sup>b</sup>	–0.072	
		2.55 <sup>c</sup>	Cl <sup>c</sup>	–0.507	
			Sb	1.061	

<sup>a</sup> Equatorial atom.<sup>b</sup> Axial atom.<sup>c</sup> Bridging atom.

geometry. The calculations with the PM3 method have confirmed the validity of this assumption. Table 3 includes the results of the PM3 calculations for  $\text{SbCl}_5$ , assuming its different geometry, and for the dimer  $\text{Sb}_2\text{Cl}_{10}$ .

The observed increase in the electron density on the chlorine atoms in the dimer  $\text{Sb}_2\text{Cl}_{10}$ , in comparison with that in the monomer  $\text{SbCl}_5$ , amounts to 12.5%, which allows an estimation of the  $\text{Cl K}\alpha$  shift of  $-0.166$  eV. On changing the geometry of the  $\text{SbCl}_5$  molecule from trigonal bipyramidal to square pyramidal, which takes place in  $\text{SbCl}_5\text{L}$  complexes, the negative charge on the chlorine atoms decreases by about 16%.

The decrease in the negative charge on the chlorine atoms (see Table 2), deduced from the  $\text{Cl K}\alpha$  shifts, must therefore be significant due to the change in the acceptor geometry. Thus, in strong complexes, the transferred electron density is greater than the change in charge due to the change in the acceptor geometry. In weak complexes, the change in the charge on the chlorine atoms induced by the change in the acceptor geometry is greater than the transferred electron density, which leads to a decrease in the  $\text{Cl K}\alpha$  shift.

It is interesting to analyze the changes in electron density on the central antimony atom upon complex formation on the basis of Mössbauer effect measurements and X-ray electron spectroscopy.

From analysis of the Mössbauer spectra [9] and  $\text{Sn K}\alpha$  shift data [10], the net charge on the tin atom in the  $\text{SnCl}_4\text{L}_2$  complexes is found to increase upon complex formation. To analyze the changes in the net charge on the antimony atom in the  $\text{SbCl}_5\text{L}$  complexes, we have performed the calculations with the INDO method for  $\text{SbCl}_5$  and the  $\text{SbCl}_5\text{L}$  complexes. Figure 2 presents the dependence of the Mössbauer isomeric shift on the calculated s (Sb) orbital electron population ( $N_s$ ), and Fig. 3 shows the dependence of the p (Sb) orbital electron population ( $N_p$ ) on  $N_s$  in  $\text{SbCl}_5\text{L}$  complexes.

For the  $\text{SbCl}_5\text{L}$  complexes, as for the  $\text{SnCl}_4\text{L}_2$  complexes, the net charge on the antimony atom  $q_{\text{Sb}}$  is greater than that for the  $\text{SbCl}_5$  molecule (Table 4). Figure 4 presents the dependences of the Mössbauer parameters and ionization potential  $\Delta E$  on  $\Delta(\text{Cl K}\alpha)$ . As can be seen from Fig. 4, the slope of the dependence  $\delta$  vs.  $\Delta(\text{Cl K}\alpha)$  is opposite to that observed for the  $\text{SnCl}_4\text{L}_2$  complexes [2]. This may be due to different signs of the  $\Delta R/R$  ratio for the Sn and Sb nuclei when

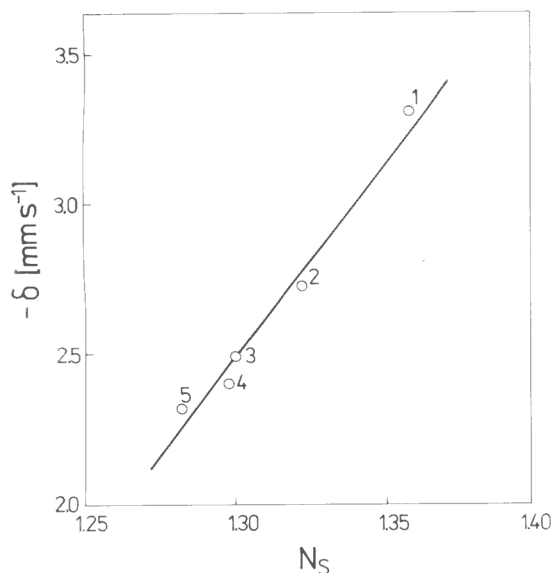


Fig. 2. The Mössbauer isomeric shift,  $\delta$ , vs. calculated s-orbital electron population,  $N_s$ , of the Sb atom in the compounds: (1)  $\text{SbCl}_5$ ; (2)  $\text{SbCl}_6^-$ ; (3)  $\text{SbCl}_5 \cdot \text{CH}_3\text{CN}$ ; (4)  $\text{SbCl}_5\text{PhCN}$ ; (5)  $\text{SbCl}_5\text{OSCl}_2$ .

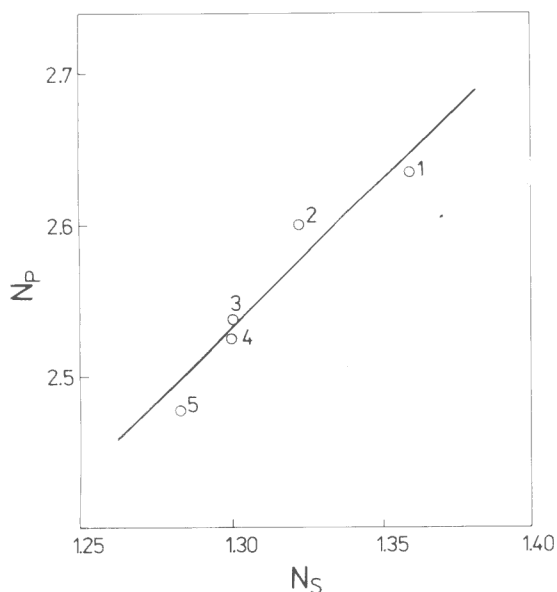


Fig. 3. The calculated p-orbital electron population,  $N_p$ , vs. s-orbital population,  $N_s$ , of the Sb atom in the compounds numbered as in Fig. 2.

the perturbation is proportional to the isomeric shift in the  $\text{SnCl}_4\text{L}_2$  and  $\text{SbCl}_5\text{L}$  complexes relative to  $\text{CaSnO}_3$  [11]. Analysis of the slopes of dependences of  $e^2Qq_{zz}$  and  $\Delta E\text{Sb}3d_{5/2}$  vs.  $\Delta(\text{ClK}\alpha)$  proves that  $q_{\text{Sb}}$  increases with increasing donor ability of the ligands. This, in the light of analogous data for the  $\text{SnCl}_4\text{L}_2$  complexes [12], seems to be characteristic of complexes of non-transition elements.

Figure 5 presents the  $\text{SK}\beta$  fluorescence spectra of the complexes of  $(\text{CH}_3)_2\text{S}$  with  $\text{SnCl}_4$ ,  $\text{TiCl}_4$  and  $\text{SbCl}_5$  and, for the sake of comparison, the spectrum of  $(\text{CH}_3)_2\text{S}$ . In Ref. 13, we have introduced the concept of an energy level of a hypothetical electron lone-pair of a sulfur atom, ( $hn_s$ ), whose energy depends only on the charge on the sulfur atom. The position of this level in the  $\text{SK}\beta$  spectrum was related to the value of the  $\text{SK}\alpha$  shift, proportional to the net charge on the sulfur atom [3]. The following relationship was obtained by comparing the short-wave maxima in the  $\text{SK}\beta$  spectra of saturated sulfides with the corresponding values of  $\Delta(\text{SK}\alpha)$ :

$$\begin{aligned} hn_s(\text{K}\beta)(\text{eV}) &= E(n_s \rightarrow 1S_s) \\ &= 0.0056(3)\Delta\text{SK}\alpha(\text{eV} \times 10^3) \\ &\quad + 2468.37 \end{aligned} \quad (1)$$

where  $r = 0.973$ ,  $s = 0.06$ ,  $n = 26$

In fact, this level can be treated as a reference level in the analysis of the changes in the spectral structure occurring upon complexation and caused only by orbital interactions devoid of the effect of charge changes on the sulfur atom. It follows from Fig. 5 that the intensity of the short-wave maximum A, which in the  $\text{SK}\beta$  spectra of sulfides corresponds to the transition from the  $n_s$  level to the vacancy K of the sulfur atom, significantly decreases and is considerably shifted towards longer wavelengths with respect to the  $hn_s$  level ( $\text{K}\beta$ ).

This shift,  $\Delta n_s$ , characterizes quantitatively the bonding nature of the highest occupied molecular orbital. The observed shift towards longer wavelengths indicates that the  $n_s$  level interacts with the vacant levels of the acceptor, being mainly of the d type. The differences in shapes of the  $\text{SK}\beta$

Table 4

Parameters determined from the Mössbauer spectra and X-ray electron data for the  $\text{SbCl}_5\text{L}$  complexes

Ligand (L)	$-\delta_{\text{Sb}}^{121\text{a}}$ (mm s <sup>-1</sup> )	$-e^2Qq_{zz}^b$ (mm s <sup>-1</sup> )	$N_s^{\text{Sb}}$	$N_p^{\text{Sb}}$	$q_{\text{Sb}}$ (e)	$\Delta E_{\text{Sb}3d_{5/2}^c}$ (eV)
—	3.20	2.80	1.357	2.649	0.994	
$[(\text{CH}_3)_2\text{N}]_3\text{PO}$	2.18	4.42	1.277	2.493	1.230	323.25
$(\text{CH}_3)_2\text{SO}$	2.56	5.30	1.307	2.551	1.142	322.95
$(\text{CH}_3)_2\text{NCOH}$	2.36	5.21	1.291	2.520	1.189	322.80
$\text{CH}_3\text{CN}$	2.50	6.90	1.302	2.542	1.156	322.45
$\text{PhCN}$	2.39	5.80	1.296	2.527	1.177	
$\text{PhNO}_2$	2.77	6.31	1.323	2.583	1.094	

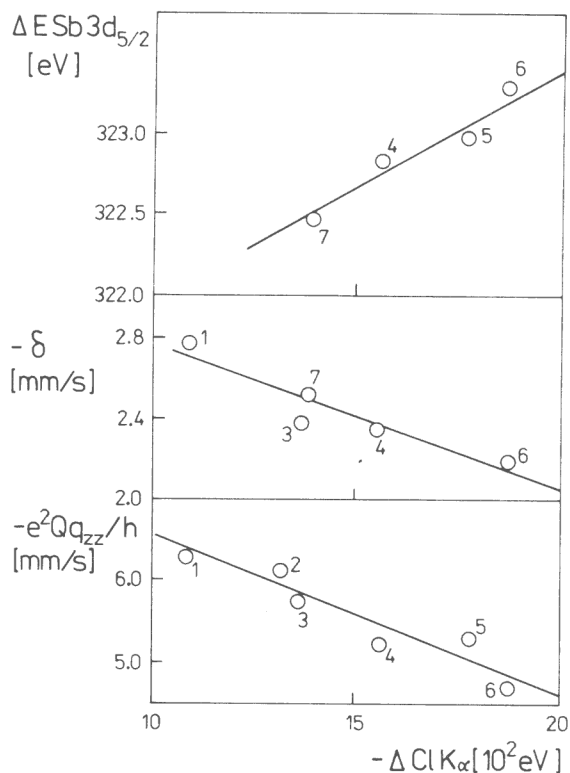
<sup>a</sup> With respect to  $\text{CaSnO}_3$ ; from Ref. 18.<sup>b</sup> From Ref. 18.<sup>c</sup> From Ref. 17.

Fig. 4. Plots of  $-e^2Qq_{zz}$ ,  $-\delta$  and  $\Delta E_{\text{Sb}3d_{5/2}}$  vs.  $-\Delta \text{Cl K}\alpha$  for  $\text{SbCl}_5\text{L}$  complexes with the ligands (L): (1)  $\text{PhNO}_2$ ; (2) dioxane; (3)  $(\text{PhCN})$ ; (4)  $(\text{CH}_3)_2\text{NCOH}$ ; (5)  $(\text{CH}_3)_2\text{SO}$ ; (6)  $[(\text{CH}_3)_2\text{N}]_3\text{PO}$ ; (7)  $\text{CH}_3\text{CN}$ . The energies of the  $\text{Sb}3d_{5/2}$  level are determined relative to those of  $\text{Cl}2p_{3/2}$ .

spectra of the complexes studied (see Fig. 5) can be explained by the presence of partly populated valence d orbitals, apart from the vacant ones, in Ti, in contrast to Sn and Sb.

The enthalpy of complex formation of  $\text{SnCl}_4$ ,  $\text{TiCl}_4$  and  $\text{SbCl}_5$  with sulfides can be determined from change in the position of the center of gravity, CG, of the  $\text{SK}\beta$  spectrum, which in

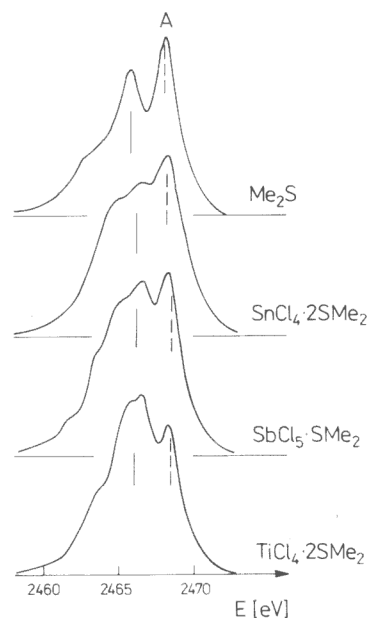


Fig. 5. The  $\text{SK}\beta$  spectra of the  $\text{SnCl}_4$ ,  $\text{TiCl}_4$  and  $\text{SbCl}_5$  complexes with dimethyl sulfide. The solid line denotes the center of gravity of the spectrum (CG), while the broken line denotes the position of the  $h\nu_s$  ( $\text{K}\beta$ ) level.

Table 5

Parameters determined from the X-ray spectra of the sulfur atoms for some of the complexes studied

Compound	$\Delta(S K\alpha)^a$ ( $10^3$ eV)	$q_s^b$ (e)	$h\nu_S(K\beta)$ (eV)	$E_A(K\beta)$ (eV)	$CG(K\beta)$ (eV)	$\Delta n_S$ (eV)	$\Delta CG$ (eV)	$\delta(\Delta CG)$ (eV)
$(CH_3)_2S$	-63(6)	-0.10(2)	8.02(4)	8.1(1)	6.1	-0.1(1)	1.9	0.0
$SnCl_4 \cdot 2S(CH_3)_2$	2(14)	0.00(2)	8.38(8)	8.2(1)	6.3	0.2(1)	2.1	0.2
$SbCl_5 \cdot S(CH_3)_2$	17(7)	0.03(2)	8.47(5)	8.3(1)	6.15	0.2(1)	2.3	0.4
$TiCl_4 \cdot 2S(CH_3)_2$	-3(10)	0.00(2)	8.35(6)	8.11(5)	6.0	0.24(8)	2.4	0.5
$Bz_2S^c$	-61(10)	-0.10(2)	8.03(6)	8.05(6)	6.05	-0.02(8)	2.0	0.0
$SnCl_4 \cdot 2Bz_2S$	-12(12)	-0.02(2)	8.30(7)	7.7(1)	5.8	0.6(1)	2.5	0.5

<sup>a</sup> Relative to  $S_8$ .<sup>b</sup> The  $q_S$  values were determined from the measured  $SK\alpha$  shifts ( $\Delta SK\alpha$ ) using the method described in detail in Ref. 3.<sup>c</sup> Bz, benzoyl substituent.

turn depends on  $3p_S$  electron distribution relative to the  $h\nu_S$  level ( $K\beta$ ). It follows from Fig. 5 and Table 5 that the values of  $\Delta CG$  of the  $S K\beta$  spectra of the complexes  $SnCl_4 \cdot 2SBz_2$ ,  $TiCl_4 \cdot 2S(CH_3)_2$  and  $SbCl_5 \cdot S(CH_3)_2$  decrease by 0.3–0.5 eV when compared to the values of the appropriate free ligands. In the  $SK\beta$  spectrum of the  $SnCl_4 \cdot S(CH_3)_2$  complex, the  $CG$  change is considerably less pronounced.

Using the data of Table 5 we could arrange the complexes of Sb, Sn and Ti chlorides with  $(CH_3)_2S$  according to their increasing stability as:



This ordering is consistent with the one according to increasing enthalpy of complex formation [6,14]. It should be emphasized, however, that the above ordering is different from the one according to decreasing electron density on the sulfur atom upon complex formation:



However, the changes in the electron density on the sulfur atom can be related to the changes in the  $^{35}Cl$  NQR frequencies of the ligand (e.g.  $POCl_3$ ). This relation turns out to be linear (see Fig. 6), which indicates the influence of the inductive effect on both the  $^{35}Cl$  NQR frequencies and  $SK\alpha$  shifts, upon complex formation.

#### 4. Conclusions

Differences in the ordering of Sn, Sb and Ti

complexes with  $(CH_3)_2S$ , according to their stability and decreasing electron density on the sulfur atom, as well as changes in positions of the centers of gravity of the  $SK\beta$  spectra, suggest that electron density transfer cannot be the main factor in determining complexation. The enthalpy of complex formation of  $(CH_3)_2S$  with  $SbCl_5$  proves that the complexes are of medium strength and changes in the geometry of their acceptor molecules induce considerable changes in the electron density on the sulfur atom.

#### 5. Acknowledgment

We are grateful to the State Committee for

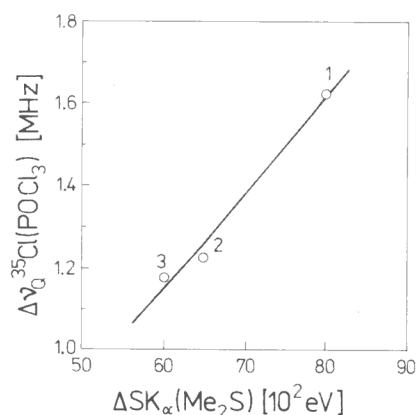


Fig. 6. The  $^{35}Cl$  NQR frequencies of  $POCl_3$  vs. the  $\Delta(SK\alpha)$  shifts of  $S(CH_3)_2$  in the complexes studied with the acceptors: (1)  $SbCl_5$ ; (2)  $SnCl_4$ ; (3)  $TiCl_4$ .



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