

# Study of charges on heteroatoms in organic compounds of the second-row elements by X-ray fluorescence spectroscopy

## 12.\* Complexes of antimony pentachloride

G. N. Dolenko,<sup>a\*</sup> O. Kh. Poleshchuk,<sup>b</sup> B. P. Elin,<sup>a</sup> N. A. Koptseva,<sup>b</sup> and Ya. Kopur<sup>b</sup>

<sup>a</sup>*Irkutsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,  
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.*

*Fax: +7 (395 2) 46 6434*

<sup>b</sup>*Tomsk State Pedagogical Institute,  
75 Komsomol'sky prosp., 634041 Tomsk, Russian Federation*

The characteristic features of the electronic structure of  $\text{SbCl}_5\text{L}$  complexes has been studied in comparison with those of the  $\text{SnCl}_4\text{L}_2$  and  $\text{TiCl}_4\text{L}_2$  complexes. The results of X-ray structural analysis were correlated with the heats of complexation, the data of Mössbauer spectroscopy, derivatography, quantum-chemical PM3 calculations, and stretching frequencies of the donor-acceptor bonds. Based on these data, the contributions of different effects to the stabilities of complexes were determined, complexation enthalpies previously unknown were calculated, and a conclusion was drawn that the electron density transfer from the donor to the acceptor is small. The charge effect of the donor consists primarily in polarization of the acceptor bonds; this polarization decreases as a result of the change in the geometry of the acceptor upon complexation. The relative stabilities of the complexes with dimethyl sulfide were determined using a unique internal standard technique.

**Key words:** complexes of antimony pentachloride; redistribution of the electron density; stability of complexes, X-ray fluorescence spectroscopy,  $K\alpha$  shift.

Previously, using the  $\text{SnCl}_4\text{L}_2$  and  $\text{TiCl}_4\text{L}_2$  complexes as an example,<sup>2,3</sup> we found differences in the changes in the electron density on chlorine atoms upon complexation of transition and main-group elements with the L ligands. The data on the shifts of the  $K\alpha$  line of the Cl atom ( $\Delta\text{Cl-K}\alpha$ ) indicate that the electron density on chlorine atoms does not increase in complexes of the main-group elements as compared to that of a free acceptor. In complexes of transition metals, the negative charge on chlorine atoms increases upon complexation. The change in the geometry of acceptors upon complexation may be one of the causes of the differences observed.

In this work, we studied the  $\text{Cl-K}\alpha$ ,  $\text{S-K}\alpha$ , and  $\text{S-K}\beta$  X-ray fluorescence spectra of the antimony pentachloride complexes. The results obtained were compared with the data of different physicochemical methods and PM3 calculations. The complexes studied are of particular interest because  $\text{SbCl}_5$  is a standard acceptor for estimating the complexation enthalpy (Gutmann's donor numbers,  $DN^4$ ).

### Experimental

The complexes of antimony pentachloride were obtained in  $\text{CCl}_4$  solution under an inert atmosphere. The results of elemental analysis corresponded to the complexes of 1 : 1 composition. IR spectra were recorded on a UR-20 instrument using KBr pellets in the region 400–4000  $\text{cm}^{-1}$ . Derivatograms were recorded on a Paulik–Erdey derivatograph under a helium atmosphere. The resistance in the differential thermocouple and in DTG circuits was 1/2 and 1/20, respectively. The samples were heated to 500 °C at the rate of 10 °C  $\text{min}^{-1}$ .

X-ray fluorescence spectra were recorded on a STEARAT X-ray spectrometer. The operating conditions of an X-ray tube were 8 kV and 0.4 A. The spectra were excited with the braking radiation of a copper anode, analyzed with a quartz crystal (a rhombohedron plane), and recorded with a flow-type proportional counter filled with argon and methane. Samples were applied to grooved nickel supports. During exposure, the temperature of the sample was 100 K. The time of a single exposure was 20 s for  $K\alpha$  spectra and 4–5 min for  $K\beta$  spectra.  $K\alpha$  and  $K\beta$  spectra were recorded 16–20 and 3–4 times, respectively, and then they were averaged.

### Results and Discussion

Table 1 presents the experimental values of  $\Delta\text{Cl-K}\alpha$ , which are proportional to the effective charge on the

\* For Part 11, see Ref. 1.

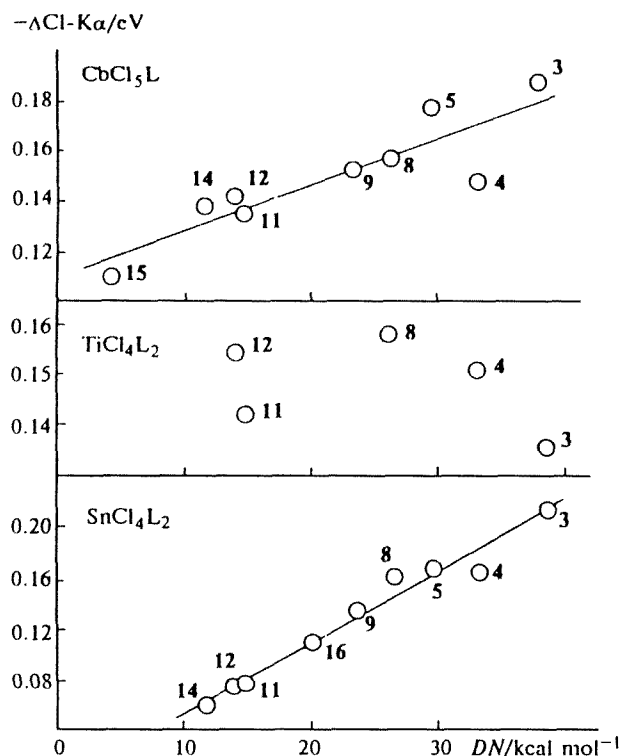


Fig. 1. Dependences of the Cl-K $\alpha$  shifts on the donor power of ligands in the  $\text{SnCl}_4\text{L}_2$ ,  $\text{TiCl}_4\text{L}_2$ , and  $\text{SbCl}_5\text{L}$  complexes. The numbers of the points correspond to the data in Table 1 (MeOH — 16).

chlorine atom ( $q_{\text{Cl}}$ ),<sup>5</sup> the values of  $q_{\text{Cl}}$  calculated by the PM3 method with full geometry optimization, the donor

numbers of the ligands, the temperatures of decomposition of the complexes, and stretching frequencies of the donor-acceptor bond ( $\nu_{\text{DA}}$ ).

From Table 1, it follows that  $-\Delta\text{Cl-K}\alpha$  and  $-q_{\text{Cl}}$  increase as the donor numbers of ligands increase. As is seen from Fig. 1, these dependences are linear for the  $\text{SbCl}_5\text{L}$  and  $\text{SnCl}_4\text{L}_2$  complexes, and they are virtually absent for the  $\text{TiCl}_4\text{L}_2$  complexes. Apparently, this fact is a manifestation of the specific features of transition- and main-group elements.

Analysis of changes in  $q_{\text{Cl}}$  upon complexation of antimony pentachloride demonstrated that in almost all complexes, except for 2 and 3 (see Table 1), the negative value of  $q_{\text{Cl}}$  with respect to the initial acceptor  $\text{Sb}_2\text{Cl}_{10}^*$  decreases, as is the case with the  $\text{SnCl}_4\text{L}_2$  complexes. Taking into account that the electron density on the central atom of the acceptor can only decrease upon complexation,<sup>2-4</sup> it is reasonable to attribute the observed effect to the influence of the changes in the geometry of the acceptor, which occur upon complexation, on the effective charges on the atoms of this acceptor.

This assumption is confirmed by the PM3 calculations carried out in this work. Table 2 presents the results of the calculations of the antimony pentachloride monomer and the corresponding dimer. The observed increase in the negative charge on chlorine atoms in the dimer relative to the monomer is about 12 %; this suggests that the Cl-K $\alpha$  shift for the monomeric form is  $-17$  eV.

\* In the measurements of the Cl-K $\alpha$  spectra at 100 K,  $\text{SbCl}_5$  is the dimer.<sup>6</sup>

Table 1. Parameters of the  $\text{SbCl}_5\text{L}$  complexes

Compound	Ligand	$-\Delta\text{Cl-K}\alpha_{\text{Cl}_2}/\text{eV}^a$	$-q_{\text{Cl}}/e$	$DN^d/\text{kcal mol}^{-1}$	$\nu_{\text{DA}}/\text{cm}^{-1}$	$T/^\circ\text{C}$
1a <sup>b</sup>	—	0.189(17)	0.21	—	—	—
1b <sup>b</sup>	—	(0.18)	0.20	—	—	—
1c <sup>b</sup>	—	(0.18)	0.20	—	—	—
1d <sup>b</sup>	—	(0.15)	0.17	—	—	—
1e <sup>b</sup>	—	(0.17)	0.19	—	—	—
2	Phen	0.206(5)	—	(47 <sup>c</sup> , 50 <sup>d</sup> )	700	310
3	(Me <sub>2</sub> N) <sub>3</sub> PO	0.189(11)	0.31	38.6	625	292
4	Py	0.148(11)	0.28	33.1	—	—
5	Me <sub>2</sub> SO	0.179(17)	0.30	29.8	—	—
6	Bz <sub>3</sub> N	0.160(5)	—	(26 <sup>c</sup> , 32 <sup>d</sup> )	508	289
7	NOPy	0.159(8)	—	(25 <sup>c</sup> , 31 <sup>d</sup> )	495	260
8	Me <sub>2</sub> NC(O)H	0.156(13)	0.29	26.5	440	240
9	Me <sub>2</sub> S	0.152(6)	0.25	23.5	—	—
10	$\alpha$ -Pic	0.149(8)	—	(21 <sup>c</sup> , 29 <sup>d</sup> )	477	230
11	O(CH <sub>2</sub> ) <sub>4</sub> O	0.133(21)	0.21	14.8	350	160
12	MeCN	0.140(23)	0.27	14.1	—	—
13	Bz <sub>2</sub> S	0.131(6)	—	(13 <sup>c</sup> , 21 <sup>d</sup> )	390	173
14	PhCN	0.136(21)	0.27	11.9	—	—
15	PhNO <sub>2</sub>	0.110(12)	—	4.4	—	—

<sup>a</sup> Calculated relative to  $\text{Cl}_2$ ; the r.m.s. error in the last significant figure is given in parentheses. <sup>b</sup> For the description of compounds, see Table 2. The values of  $\Delta\text{Cl-K}\alpha$  given in parentheses were obtained under the assumption that the values of  $q_{\text{Cl}}(\text{PM3})$  and  $\Delta\text{Cl-K}\alpha$  are proportional. <sup>c</sup> The estimation was made according to Eq. (4). <sup>d</sup> The estimation was made according to Eq. (1). Phen is 1,10-phenanthroline.

**Table 2.** Charges on atoms in the molecules of antimony pentachloride with different geometry calculated by the PM3 method

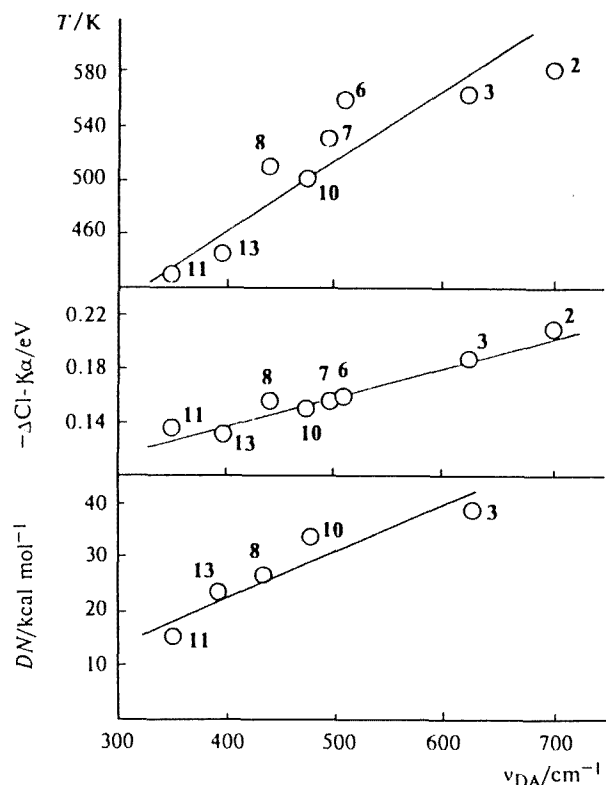
Com- pound	Dis- tance/Å	Sym- metry	Atom	Charge, $q_{i,e}/e$	$\bar{q}_{Cl}/e$
Sb <sub>2</sub> Cl <sub>10</sub> <sup>a</sup> ( <b>1a</b> )	2.35 <sup>b</sup>	~O <sub>h</sub>	Cl <sup>b</sup>	−0.206	−0.213
	2.37 <sup>c</sup>		Cl <sup>c</sup>	−0.072	
	2.55 <sup>d</sup>		Cl <sup>d</sup>	−0.507	
			Sb	1.061	
SbCl <sub>5</sub> ( <b>1b</b> )	2.277 <sup>b</sup>	~C <sub>3v</sub>	Cl <sup>b</sup>	−0.171	−0.203
	2.338 <sup>c</sup>		Cl <sup>c</sup>	−0.252	
	13.0 <sup>b</sup>		Sb	1.016	
SbCl <sub>5</sub> ( <b>1c</b> )	2.277 <sup>d</sup>	~C <sub>4v</sub>	Cl <sup>b</sup>	−0.184	−0.200
	2.338 <sup>c</sup>		Cl <sup>c</sup>	−0.264	
	13.0		Sb	1.001	
SbCl <sub>5</sub> ( <b>1d</b> )	2.40	~C <sub>4v</sub>	Cl <sup>b</sup>	−0.154	−0.170
	13.0 <sup>c</sup>		Cl <sup>c</sup>	−0.236	
			Sb	−0.851	
SbCl <sub>5</sub> <sup>a</sup> ( <b>1e</b> )	2.349 <sup>b</sup>	~C <sub>3v</sub>	Cl <sup>b</sup>	−0.155	−0.187
	2.373 <sup>c</sup>		Cl <sup>c</sup>	−0.234	
			Sb	0.935	

<sup>a</sup> Optimized geometry. <sup>b</sup> Equatorial atoms. <sup>c</sup> Axial atoms. <sup>d</sup> Bridging atoms.

In going from the free SbCl<sub>5</sub> monomer in the form of a trigonal pyramid to a square pyramid with elongated Sb—Cl distances that are typical of SbCl<sub>5</sub> in complexes, the negative charge on chlorine atoms decreases by 16 %. As is seen from the Cl—K $\alpha$  shifts, the electron density on chlorine atoms decreases in complexes relative to the free SbCl<sub>5</sub> monomer (see Table 1); this is, apparently, largely due to a change in the geometry of the acceptor. In the most stable complexes (2, 3, and 5), the values of  $-q_{Cl}$  increase because the electron density transfer from the ligand dominates over a decrease in the electron density on chlorine atoms caused by the change in the geometry of the acceptor. In less stable complexes, a change in  $-q_{Cl}$  associated with the change in the geometry of the acceptor dominates over the effect of the electron density transfer or is comparable with this effect; as a result, the Cl—K $\alpha$  shifts either remain virtually unchanged (complexes 6–9) or decrease (complexes 4 and 10–15) as compared to the free acceptor.\*

Table 1 presents also the stretching frequencies of the donor-acceptor bond ( $\nu_{DA}$ ) in the SbCl<sub>5</sub>L complexes. It is known<sup>8</sup> that in most cases, these frequencies vary in parallel with the force constant  $f_{DA}$ .

Figure 2 presents the dependence of  $\nu_{DA}$  on the donor numbers of ligands, which characterize the "stan-

**Fig. 2.** Dependences of the stretching frequencies of the donor-acceptor bond on the donor power of ligands, Cl—K $\alpha$  shifts, and decomposition temperatures of the SbCl<sub>5</sub>L complexes. The numbers of the points correspond to the data in Table 1.

dard" stability of the SbCl<sub>5</sub>L complexes. Processing of this dependence by the least-squares method yields the correlation relation

$$\nu_{DA}/\text{cm}^{-1} = 10.9 DN (\text{kcal mol}^{-1}) + 158 \quad (r = 0.934, s = 33, n = 5). \quad (1)$$

The dependence of  $\nu_{DA}$  on the decomposition temperature of the complexes ( $t_d$ ), which somehow characterizes the strength of the donor-acceptor bond, is also evidence that the stability of complexes may be determined from the values of  $\nu_{DA}$ . Figure 2 shows the dependence of  $\nu_{DA}$  on  $t_d$  (the values of  $t_d$  were determined by derivatographic decomposition of a number of SbCl<sub>5</sub>L complexes); this dependence has the following form:\*

$$\nu_{DA}/\text{cm}^{-1} = 1.9 t_d + 33 \quad (r = 0.90, s = 46, n = 8). \quad (2)$$

\* Previously,<sup>2</sup> we demonstrated that the change in the geometry of the free SnCl<sub>4</sub> when it forms the SnCl<sub>4</sub>L<sub>2</sub> complexes gives the same result. A change in the geometry of TiCl<sub>4</sub> has no effect on  $q_{Cl}$ .

\* Dependence (2) is only qualitative because the temperature of decomposition may also be associated with other process, which occur in parallel.

From the previous works<sup>2,3,5</sup> it follows that for the  $\text{SnCl}_4\text{L}_2$  complexes, the negative  $\text{Cl-K}\alpha$  shifts increase as the complexes become more stable. For the  $\text{SbCl}_5\text{L}$  complexes, the situation must be similar. In particular, this is evidenced by the linear dependence of  $\Delta\text{Cl-K}\alpha$  on  $\nu_{\text{DA}}$ , which is shown in Fig. 2 and is described by the equation

$$\nu_{\text{DA}}/\text{cm}^{-1} = 4400(-\Delta\text{Cl-K}\alpha) (\text{eV}) - 209$$

$$(r = 0.980, s = 21, n = 8), \quad (3)$$

as well as by the dependence shown in Fig. 1:

$$\Delta\text{Cl-K}\alpha/\text{eV} = 0.0022 \Delta N (\text{kcal mol}^{-1}) + 0.103$$

$$(r = 0.974, s = 0.005, n = 8). \quad (4)$$

It is possible to determine previously unknown enthalpies of complexation for some complexes of antimony pentachloride from Eqs. (1) and (4). The corresponding values are given in Table 1. It should be noted that according to the values of  $\text{Cl-K}\alpha$ ,  $\nu_{\text{DA}}$ , and  $t_d$ , complex 2 is the most stable of all known  $\text{SbCl}_5\text{L}$  complexes. It is not inconceivable that the coordination number of the Sb atom in this complex is 7 because of the formation of a cycle that has the form of a pentagonal pyramid.

It is appropriate to use the data of Mössbauer and X-ray photoelectron spectroscopy for analysis of the changes in the electron density at the central antimony atom upon complexation. Note that in the  $\text{SnCl}_4\text{L}_2$  complexes, the positive charge  $q_{\text{Sn}}$  increases upon complexation as follows from the data of Mössbauer spectroscopy<sup>8</sup> and from the  $\text{Sn-K}\alpha$  shifts.<sup>9</sup> With the aim of analyzing the changes in the electron density at the antimony atom in the  $\text{SbCl}_5\text{L}$  complexes, we carried out calculations of the free acceptor and its complexes with HMPA, DMF,  $\text{OPCl}_3$ , MeCN, and  $\text{Me}_2\text{SO}$  by the PM3 method with full geometry optimization. The following correlation relations were established between the chemical shifts in the Mössbauer spectrum ( $\delta$ ) and the populations of the valence *s* and *p* orbitals of the antimony atom:

$$-\delta/\text{mm s}^{-1} = 2.43 N_p - 2.18$$

$$(r = 0.934, s = 0.07, n = 6). \quad (5)$$

$$N_p = 14.2 N_s - 24.0 (r = 0.990, s = 0.03, n = 6). \quad (6)$$

Table 3 presents the experimental Mössbauer shifts, quadrupole coupling constants  $e^2Qq_{zz}$ ,  $^{121}\text{Sb}$ , populations of valence *s* and *p* orbitals of the antimony atom (determined with the use of Eqs. (5) and (6)), and the energies of the  $\text{Sb}3d_{5/2}$  level for a number of  $\text{SbCl}_5\text{L}$  complexes. As in the case of complexes of tin chloride, in the complexes of antimony pentachloride an increase in the positive charge at the central atom of the acceptor compared to the free acceptor occurs. Figure 3 shows the dependence of the frequencies of  $^{35}\text{Cl}$  NQR, Mössbauer parameters, and  $E_{\text{Sb}3d_{5/2}}$  on the  $\text{Cl-K}\alpha$  shifts. In all cases, the dependences observed are approximately linear.\* All these dependences are indicative of an increase in the positive  $q_{\text{Sb}}$  as the negative  $q_{\text{Cl}}$  increases and, hence, as the donating power of the ligand increases. Taking into account analogous data that we obtained for the complexes of tin chloride, this fact is, apparently, typical of all complexes of main-group metals.

Different signs of the changes in the electron density upon complexation for the central and other atoms of the acceptor indicate that the ligand polarizes the acceptor bonds rather than transfers its electron density on the unoccupied orbitals of the acceptor; this fact may account for the observed dependence of the  $\Delta\text{Cl-K}\alpha$  values on the enthalpy of complexation.

According to the Klopman's theory,<sup>10</sup> the interaction between the donor and the acceptor in complex compounds may be either charge- or orbital-controlled. However, it is seen from Eq. (4) that in the complexes of antimony pentachloride, the enthalpy of complexation correlates with the charges on chlorine atoms. This fact, coupled with the fact that the transfer of the electron density from the donor to the acceptor is small,

\* The reverse slope of the dependence of  $\delta$  on  $\Delta\text{Cl-K}\alpha$  occurs as compared to that observed previously<sup>3</sup> for the  $\text{SnCl}_4\text{L}_2$  complexes. This is associated with the difference in signs of the  $\Delta R/R$  ratios for the Sn and Sb nuclei upon excitation, which is proportional to the Mössbauer shifts in the complexes of tin chloride and antimony pentachloride relative to the source  $\text{CaSnO}_3$ .<sup>11</sup>

Table 3. NQR and Mössbauer parameters for the  $\text{SbCl}_5\text{L}$  complexes

Compound	Ligand	$E_{\text{Sb}3d_{5/2}}$ /eV <sup>a</sup>	$\nu^{35}\text{Cl}$ /MHz <sup>b</sup>	$-\delta^{121}\text{Sb}$ mm s <sup>-1</sup> <sup>c</sup>	$-e^2Qq_{zz}$	$N_s$	$N_p$	$q_{\text{Sb}}$
1	—	321.90	28.04	3.20	2.80	1.84	2.21	0.95
2	$[\text{Me}_2\text{N}]_3\text{PO}$	323.25	24.54	2.18 <sup>d</sup>	4.72 <sup>d</sup>	1.82	1.79	1.39
3	$\text{Me}_2\text{NC(O)H}$	322.80	24.90	2.36	5.21	1.82	1.87	1.31
4	$\text{O}(\text{CH}_2)_4\text{O}$	—	25.65	2.50	5.88	1.82	1.92	1.26
5	MeCN	322.45	25.93	2.50	6.90	1.82	1.92	1.26
6	PhCN	—	26.21	2.39	5.80	1.82	1.88	1.30
7	PhNO <sub>2</sub>	—	26.68	2.77	6.31	1.83	2.04	1.13

<sup>a</sup> According to the data in Ref. 17. <sup>b</sup> According to the data in Refs. 14, 15. <sup>c</sup> According to the data in Ref. 16. <sup>d</sup> The values for the  $\text{SbCl}_5 \cdot \text{OPMe}_3$  complex.

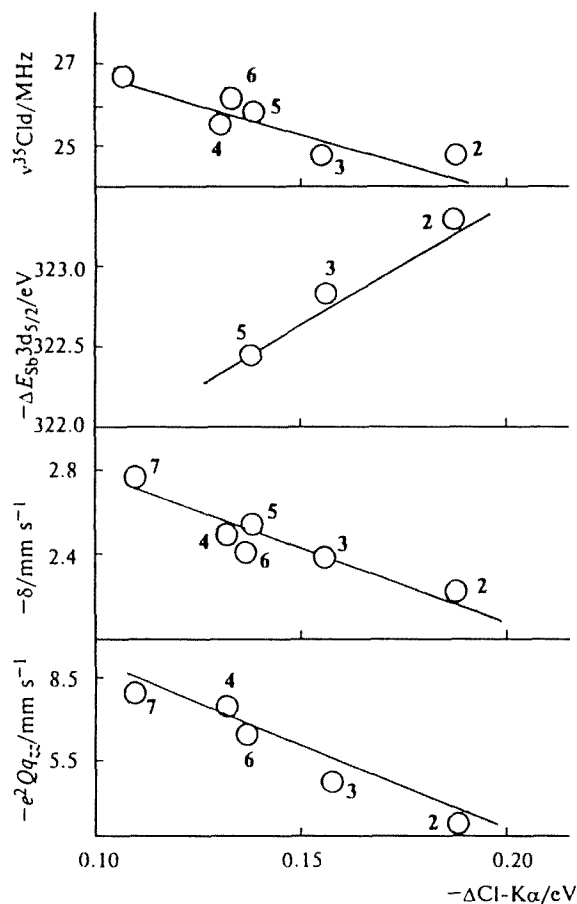


Fig. 3. Dependences of the isomeric  $^{121}\text{Sb}$  shift, the quadrupole coupling constants, frequencies of  $^{35}\text{Cl}$  NQR, and energies of the  $\text{Sb}3d_{5/2}$ -level on the values of  $\Delta\text{Cl-K}\alpha$  in the  $\text{SbCl}_5\text{L}$  complexes. The energies of the  $\text{Sb}3d_{5/2}$ -level are given relative to the  $\text{Cl}_2\text{P}_{3/2}$ -level. The numbers of the points correspond to the data in Table 3.

may indicate that the interaction of  $\text{SbCl}_5$  with ligands is predominantly charge-controlled.

Figure 4 shows the S-K $\beta$  fluorescence spectra of the  $\text{Me}_2\text{S}$  molecule and its complexes with  $\text{SbCl}_5$ ,  $\text{SnCl}_4$ , and  $\text{TiCl}_4$ . Previously,<sup>12</sup> we introduced the concept of the hypothetical level of the lone electron pair of the sulfur atom ( $\Gamma_{n_s}$ ), whose energy depends only on the charge on the sulfur atom. The position of this level in the S-K $\beta$  spectrum is related to the value of the S-K $\alpha$  shift by the correlation equation (obtained by comparing the energy of the short-wave peak in the S-K $\beta$  spectra of saturated sulfides, which have a virtually "pure"  $n_s$  level, with the values of  $\Delta\text{S-K}\alpha$ ):

$$\Gamma_{n_s}(\text{K}\beta)/\text{eV} = E(n_s \rightarrow l_s) = 5.6(3)\Delta\text{S-K}\alpha(\text{eV}) + 2468.37(1) \quad (r = 0.973, s = 0.06, n = 26). \quad (7)$$

In the S-K $\beta$  spectrum, the  $\Gamma_{n_s}(\text{K}\beta)$  level serves as a label with the use of which it is possible to analyze the spectral changes caused only by orbital interactions, i.e.,

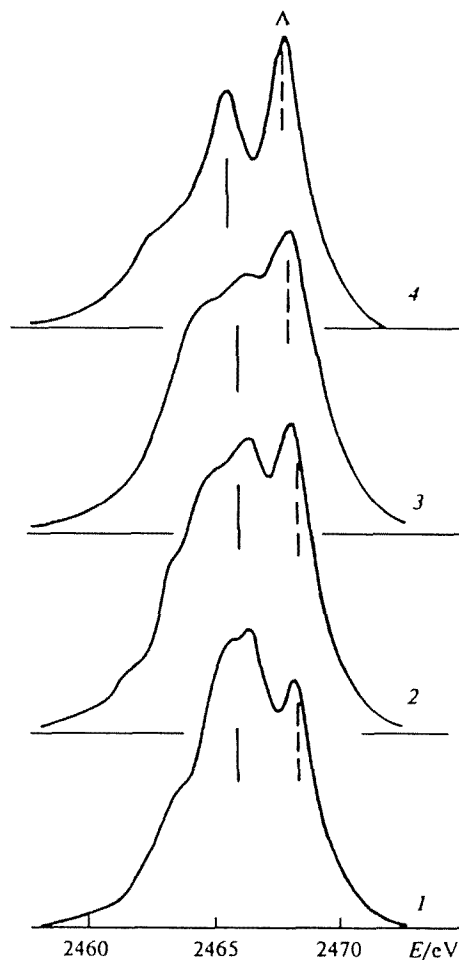


Fig. 4. S-K $\beta$  spectra of the  $\text{TiCl}_4 \cdot 2\text{SMc}_2$  (1),  $\text{SbCl}_5 \cdot \text{SMc}_2$  (2),  $\text{SnCl}_4 \cdot 2\text{SMc}_2$  (3), and  $\text{Me}_2\text{S}$  (4) complexes. The vertical solid line indicates the center of gravity; the dashed line indicates the  $\Gamma_{n_s}/\text{K}\beta$  level.

the spectral changes free of charge effects. It is seen from Fig. 4 that the intense short-wave peak A, which in the case of free  $\text{Me}_2\text{S}$  corresponds to the  $n_s \rightarrow l_s$  transition, decreases in intensity and is shifted to the long-wave region with respect to the  $\Gamma_{n_s}(\text{K}\beta)$  level. This shift ( $\Delta n_s$ ) quantitatively characterizes the degree of the binding character of HOMO and is indicative of its stabilization by the interaction of the  $n_s$  level with unoccupied orbitals of the acceptor. The difference in the profiles of the S-K $\beta$  spectra considered is attributable to the fact that the Ti atom, unlike Sn and Sb, has occupied valence d orbitals along with unoccupied orbitals.

The enthalpy of formation of the complexes with sulfides may be determined by the stabilization of the center of gravity (CG) of the S-K $\beta$  spectrum, which characterizes the  $3p_s$ -electron distribution. It would appear reasonable to determine the stabilization of the center of gravity upon complexation as a difference in positions of the centers of gravity of the S-K $\beta$  spectrum

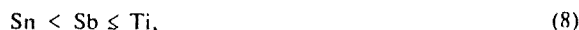
Table 4. X-Ray characteristics of the S atom in the series of complexes studied

Compound	$\Delta S\text{-K}\alpha \cdot 10^3/\text{eV}^a$	$q_S/\text{e}^b$	$\Gamma_{n_S}(\text{K}\beta)$	$E_A(\text{K}\beta)$	$\text{CG}(\text{K}\beta)$	$\Delta n_S$	$\Delta \text{CG}$	$\delta(\Delta \text{CG})$
			relative 2460.00 eV			eV		
$\text{Me}_2\text{S}$	-63(6)	-0.10(2)	8.02(4)	8.10(1)	6.10	-0.10(1)	1.9	0.0
$\text{SnCl}_4 \cdot 2\text{SMe}_2$	2(14)	0.00(2)	8.38(8)	8.20(1)	6.30	0.20(1)	2.1	0.2
$\text{SbCl}_5 \cdot 2\text{Me}_2$	17(7)	0.03(2)	8.47(5)	8.30(1)	6.15	0.20(1)	2.3	0.4
$\text{TiCl}_4 \cdot 2\text{SMe}_2$	-3(10)	0.00(2)	8.35(6)	8.11(5)	6.00	0.24(8)	2.4	0.5

<sup>a</sup> Calculated relative to  $S_8$ . <sup>b</sup> The values of  $q_S$  were determined from the experimental S-K $\alpha$  shifts using the correlation equation previously obtained;<sup>5</sup> this equation relates  $\Delta S\text{-K}\alpha$  in a number of model compounds to the values of  $q_S$  calculated by the CNDO method.

of sulfide with respect to the  $\Gamma_{n_S}(\text{K}\beta)$  level ( $\Delta \text{CG}$ ) in the free state and in the complex. From Fig. 4 and Table 4 it follows that the values of the centers of gravity of the S-K $\beta$  spectra of the  $\text{TiCl}_4 \cdot 2\text{SMe}_2$  and  $\text{SbCl}_5 \cdot \text{SMe}_2$  complexes are stabilized by 0.3–0.5 eV as compared to the free ligand. In the  $\text{SnCl}_4 \cdot 2\text{SMe}_2$  complex, the stabilization of the center of gravity of the S-K $\beta$  spectrum is somewhat smaller.

Based on the data obtained, the following series of increasing stabilization of the 3p<sub>S</sub>-electron distribution in the complexes with  $\text{Me}_2\text{S}$  may be written:



which virtually coincides with the series of increasing enthalpies of complexation:<sup>4,7</sup>



It is interesting to note the difference between this series and the series of decreasing electron density at the sulfur atom upon complexation:



Apparently, the difference in series (8)–(10) indicates that the electron density transfer from the ligand to the acceptor is not the determining characteristic of the energy of complexation, which agrees well with the conclusions made previously.

## References

1. G. N. Dolenko, V. P. Elin, O. Kh. Poleshchuk, A. L. Litvin, and V. K. Voronov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 411 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, 40, 352 (Engl. Transl.)].
2. G. N. Dolenko, O. Kh. Poleshchuk, V. P. Elin, A. L. Litvin, I. V. Udachin, and A. L. Ivanovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2522 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, 38, 2314 (Engl. Transl.)].
3. O. Kh. Poleshchuk, B. Nogaj, G. N. Dolenko, and V. P. Elin, *J. Mol. Struct. (Theochem.)*, 1993, 297, 295.
4. V. Gutmann, *Coordination Chemistry in Non-Aqueous Solutions*, Springer-Verlag, Wien, New York, 1968.
5. G. N. Dolenko, A. L. Litvin, V. P. Elin, and O. Kh. Poleshchuk, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 403 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, 40, 345 (Engl. Transl.)].
6. O. Kh. Poleshchuk and Yu. K. Maksyutin, *Zh. Fiz. Khim.*, 1979, 53, 55 [*Russ. J. Phys. Chem.*, 1979, 53 (Engl. Transl.)].
7. E. N. Gur'yanova, I. P. Gol'dshtein, and I. P. Romm, *Donorno-akseptornaya svyaz' [Donor-Acceptor Bonds]*, Khimiya, Moscow, 1973 (in Russian).
8. V. A. Varnek, O. Kh. Poleshchuk, L. N. Mazalov, and D. M. Kizhner, *Zh. Strukt. Khim.*, 1982, 23(1), 98 [*J. Struct. Chem.*, 1982, 23 (Engl. Transl.)].
9. L. M. Dautov, E. R. Ishkenov, and E. K. Pichugina, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* [*Bull. Kaz. Acad. Sci., Ser. Chem.*], 1983, 56 (in Russian).
10. G. Klopman, *J. Am. Chem. Soc.*, 1968, 90, 233.
11. R. V. Parish, *Coor. Chem. Rev.*, 1982, 42, 1.
12. G. N. Dolenko, A. L. Litvin, and V. P. Elin, *Zh. Strukt. Khim.*, 1991, 32(6), 61 [*J. Struct. Chem.*, 1991, 32 (Engl. Transl.)].
13. A. F. Wells, *Structural Inorganic Chemistry*, Oxford Univ. Press, Fir Lawn, 1983.
14. O. Kh. Poleshchuk and Yu. K. Maksyutin, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1975, 2579 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, 39, No. 12 (Engl. Transl.)].
15. J. R. Bensadon and E. A. C. Lucken, *J. Chem. Soc., Dalton Trans.*, 1983, 19.
16. J. M. Friedt, G. K. Shenoy, and M. J. Burgard, *J. Chem. Phys.*, 1973, 59, 4468.
17. K. Burger and E. Fluck, *Inorg. Nucl. Chem. Lett.*, 1974, 10, 171.

Received July 13, 1995