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Antimonium Pentachloride Electron Density Redistribution on Complexation

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ABSTRACT: *Electron structure changes of $SbCl_5$ on its complexation have been investigated by X-ray fluorescence spectroscopy and compared with corresponding earlier data for $SnCl_4L_2$ and $TiCl_4L_2$ complexes. X-ray spectral data analysis against the data of the heat of formation of the complexes, Mössbauer effect parameters, derivatographic data, and the valence vibration frequences have permitted an assessment of the complex stability against different factors and have proved donor electron density transfer from the donor to the acceptor to be small. It has been shown that the donor charge effect consists mainly of the acceptor bond polarization.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:543–548, 1998

INTRODUCTION

Our earlier investigations of the $SnCl_4L_2$ and $TiCl_4L_2$ electron structures revealed the significant difference between chlorine atom electron density changes in transition element complexes and nontransition ones [1–5]. Moreover, analysis of the chlorine atom Kα line shifts (ΔClKα) has proved that the electron density on the Cl atoms did not increase in nontransition element complexes with respect to that in a free acceptor. In contrast, in transition element complexes, the negative charge on chlorine atoms increased on complexation. One of the possible reasons for such differences could be a different acceptor reaction on acceptor geometry changes upon complexation.

In this article, the analysis of X-ray ClKα fluorescent spectra of $SbCl_5L$ complexes is presented against these complex parameters obtained by some other physical and chemical methods. These complexes are particularly interesting for the investigation because $SbCl_5$ is a standard acceptor used for complex formation enthalpy evaluation (Gutmann donor numbers DN [6]).

METHODS

Antimonium pentachloride complexes were obtained from appropriate solutions in CCl_4 under a neutral atmosphere. The elemental analysis proved the stoichiometric ratio of 1:1. IR spectra were recorded on a UR-20 spectrometer in the range 400–4000 cm^{-1} in KBr tablets. Derivatograms were obtained by use of the Paulik–Erdey derivatograph in a He atmosphere. The samples were heated to 500°C at the rate 10 deg/min.

X-ray fluorescence spectra were obtained by use of the X-ray spectrometer "Stearate." The spectra were excited by AgL radiation (X-ray tube operated at 0.4 Å and 4–10 kV), analyzed by a quartz crystal (plane of rhombohedron, bend radius 500 mm) and

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recorded by a proportional counter filled with an argon–methane mixture (P-10). Samples of solids were prepared by rubbing them on checkered nickel or copper plates. The $SbCl_5$ sample was prepared by its evaporation at 10^{-5} Torr on a nickel plate maintained at 77 K. The time of a single exposure for a Kα line was about 0.5 minutes. ClKα spectra determinations were repeated 16–20 times and averaged by the technique described in Ref. [7].

RESULTS AND DISCUSSION

Table 1 presents the experimental values of ClKα line shifts with respect to Cl_2 (ΔClKα) that are proportional to the effective charge on the chlorine atoms [2,5,7], the effective charges on Cl atoms (q_{Cl}) in nonempirical 4–31G** charge scale [5], ligand donor numbers (DN), the frequencies of valence vibrations of the donor–acceptor bonds and temperatures of the sample decomposition.

As follows from Table 1, $-\Delta$ClKα and $-q_{Cl}$ values increase with the ligand DN growth. These dependencies are linear for $SbCl_5L$ and $SnCl_4L_2$ complexes and practically absent for $TiCl_4L_2$ complexes (Figure 1). This is the effect of the difference in the properties of transition and nontransition elements.

The analysis of q_{Cl} value changes upon the antimonium pentachloride complexation has proved that the negative effective charge on the chlorine atoms does not increase in all complexes with respect to that for the initial acceptor Sb_2Cl_{10}*. Because, upon complex formation, the electron density on the central acceptor atom can only decrease, this effect can be explained by the influence of the acceptor geometry change, occurring upon complex formation, on the effective charge of the acceptor atoms.

This supposition has been confirmed by carried out PM3 calculations. Table 2 presents the results of PM3 calculations (by AMPAC program [9]) for different geometries of $SbCl_5$ monomer and the corresponding dimer. The obtained increase of negative q_{Cl} in dimer 1.6 with respect to that of monomer 1.2 of the geometry optimized is about 12%. This allows us to support an assumption of proportionality of ΔClKα and q_{Cl} (PM3) values that indicates the ClKα shift for the monomer form to be equal to -0.17 eV.

Upon the transition from the free monomer, $SbCl_5$, with the experimental geometry (**1.1**) to that in complexes (the square pyramid with increased Sb–Cl distance) (**1.5**), the negative effective charge on the chlorine atoms decreases by 16%. Therefore, the decrease of chlorine atom electron density in most complexes relative to that in the free $SbCl_5$

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*ClKα spectra were recorded at ~100 K at which $SbCl_5$ is a dimer [8].

TABLE 1 Parameters of SBCl$_5$Cl Complexes

N	*Ligand*	$-\Delta$*ClK*α^a*, eV, with Respect to* Cl_2	$-q_{Cl}$*, e*	ν_{DA}*,* cm^{-1}	t_d*°C*	*DN [6] kcal/mol*
1.1^b	—	$(0.18)^c$	0.26	—	—	—
1.2^b	—	$(0.17)^c$	0.24	—	—	—
1.3^b	—	$(0.18)^c$	0.26	—	—	—
1.4^b	—	$(0.16)^c$	0.23	—	—	—
1.5^b	—	$(0.15)^c$	0.22	—	—	—
1.6^b	—	0.189(17)	0.27(6)	—	—	—
2	1,10-phenantroline	0.206(5)	0.30(6)	700	310	(47^d; 50^e)
3	$(Me_2N)_3PO$	0.189(11)	0.27(6)	625	292	38.6
4	Py	0.148(11)	0.21(5)	—	—	33.1
5	Me_2SO	0.179(17)	0.26(6)	—	—	29.8
6	Bz_3N	0.160(5)	0.23(5)	508	289	(26^d; 32^e)
7	NOPy	0.159(8)	0.23(5)	495	260	(25^d; 31^e)
8	$Me_2NC(O)H$	0.156(13)	0.22(5)	440	240	26.6
9	Me_2S	0.152(6)	0.22(5)	—	—	23.5
10	α-Pic	0.149(8)	0.21(5)	477	230	(21^d; 29^e)
11	$O(CH_2)_4O$	0.133(21)	0.19(5)	350	160	14.8
12	MeCN	0.140(23)	0.20(5)	—	—	14.1
13	Bz_2S	0.131(6)	0.19(4)	390	173	(13^d; 21^e)
14	PhCN	0.136(21)	0.19(5)	—	—	11.9
15	$PhNO_2$	0.110(12)	0.15(4)	—	—	4.4

[a] In parentheses are given the mean square errors in the last significant digit, taken for the 95% confidence interval by Student's criterion.
[b] The designations correspond to those in Table 2.
[c] In assumption of proportionality between ΔClKα and q_{Cl} (PM3) values presented in Table 2.
[d] By Equation 5.
[e] By Equation 2.

TABLE 2 The Effective Atomic Charges Calculated by the PM3 Method for Different Forms of $SbCl_5$

N	*Compound*	*Symmetry*	*Sb–Cl Distance, A*	*Atom*	*Effective Charge, e*	$\langle q_{Cl} \rangle$, *e*
				Cl^{eq}	−0.171	
			2.277^{eq}	Cl^{ax}	−0.252	
1.1	$SbCl_5$	C_{3V}	2.338^{ax}	Sb	1.016	−0.203
				Cl^{eq}	−0.155	
			2.350^{eq}	Cl^{ax}	−0.234	
1.2	$SbCl_5^a$	C_{3V}	2.373^{ax}	Sb	0.934	−0.187
				Cl^{eq}	−0.184	
			2.277^{eq}	Cl^{ax}	−0.264	
1.3	$SbCl_5$	C_{4V}	2.338^{ax}	Sb	1.602	−0.200
				Cl^{eq}	−0.161	
			2.347^{eq}	Cl^{ax}	−0.246	
1.4	$SbCl_5^a$	C_{4V}	2.376^{ax}	Sb	0.890	−0.178
				Cl^{eq}	−0.154	
			2.40^{eq}	Cl^{ax}	−0.236	
1.5	$SbCl_5$	C_{4V}	2.40^{ax}	Sb	0.851	−0.170
				Cl^{eq}	−0.206	
			2.35^{eq}	Cl^{ax}	−0.072	
			2.37^{ax}	Cl^{br}	−0.507	
1.6	$Sb_2Cl_{10}^a$	O_h	2.55^{br}	Sb	1.061	−0.212

[a] Optimized structure
[eq] Equatorial atom.
[ax] Axial atom.
[br] Bridging atom.

monomer **1.1** indicated by ClKα shifts (Table 1) is to a significant degree a consequence of the acceptor geometry change on complexation. In the strongest complexes **2**, **3**, and **5**, $-q_{Cl}$ values increase or do not change (in the range of accuracy achieved) with respect to that in **1.1**. This shows that, here, the increase of chlorine atom electron density is caused by the electron density transfer from the ligand dominates over the $-q_{Cl}$ decrease caused by the acceptor geometry change or is equal to that. In all of the remaining complexes, the chlorine electron density decreases, suggesting that the acceptor geometry change effect dominates over the effect of ligand electron density transfer. In Ref. [1], it had been shown that the geometry changes of free $SnCl_4$ that occurred in $SnCl_4L_2$ complexes led to analogous effects, whereas the geometry changes of $TiCl_4$ did not affect its charge distribution.

Table 1 also includes the frequences of the valency vibrations of the donor–acceptor bond ν_{DA} in $SbCl_5L$ complexes [10]. It is well known [11] that these frequencies should be related to the force constant f_{DA} according to the formula

$$\nu_{DA} \sim (f_{DA}/\mu)^{1/2} \tag{1}$$

where $\mu = m_D m_A/(m_D + m_A)$ is the reduced mass. If m_D and m_A values are similar, for serious consideration, the ν_{DA} values should vary in line with donor–acceptor bond stability and its force constant. Figure 2 presents plots of a dependence between ν_{DA} and DN of ligands considered, where DN values characterize the standard stabilities of the complexes. The least-square-method of analysis of this dependence leads to the correlation

$$\nu_{DA}\ (\mathrm{cm}^{-1}) = 10.9\ \mathrm{DN}\ (\mathrm{kcal/mol}) + 158$$
$$(r = 0.934, \quad s = 33, \quad n = 5) \tag{2}$$

The possibility of the complex stability, assumed with the help of ν_{DA} values, is also indicated by the dependencies of the latter on the temperature of complex decomposition, t_d°, which correspond in each case to the donor–acceptor bond cleavage. Fig-

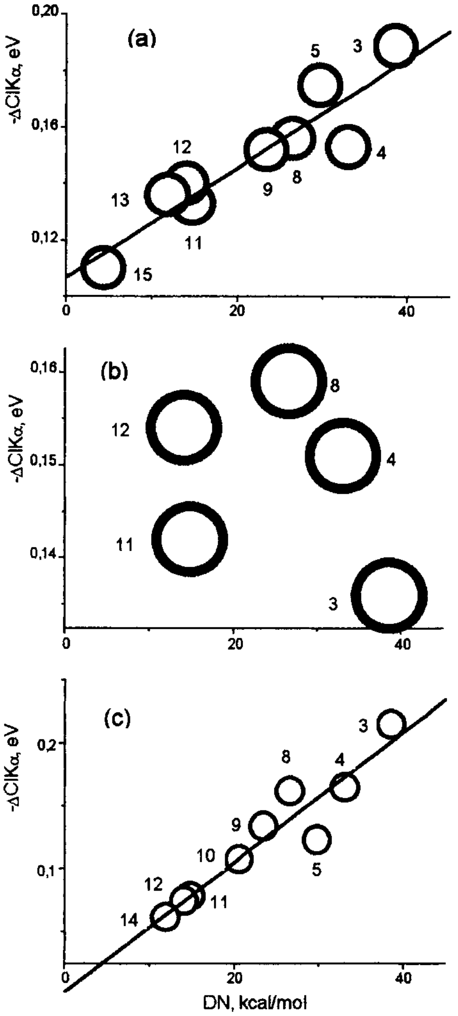

FIGURE 1 The ClKα shifts versus the ligand strength of the complexes (a) $SbCl_5L$, (b) $TiCl_4L_2$, and (c) $SnCl_4L_2$. Radius of circles corresponds to the errors of ΔClKα measurements. Numbering of points corresponds to that of the ligands in Table 1 (16 → L = MeOH).

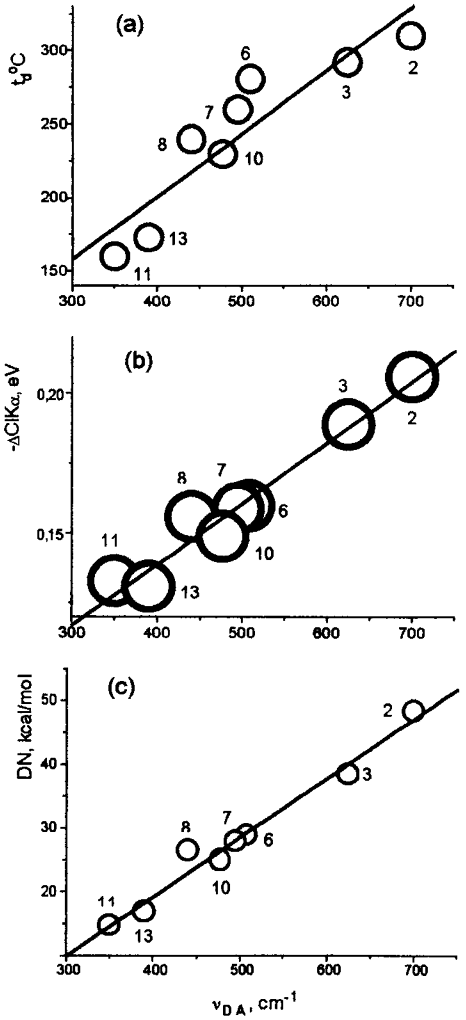

FIGURE 2 The frequencies of valence vibrations versus (a) the decomposition temperatures, (b) ClKα shifts, and (c) ligand strengths for the $SbCl_5L$ complexes. Numbering of points corresponds to that in Table 1.

ure 2 also presents a plot of the dependence between ν_{DA} and t_d° values (the latter being obtained by derivatographic investigation of the complexes considered) described by the correlation

$$\nu_{DA}\ (\text{cm}^{-1}) = 1.9t_d{}^\circ\text{C} + 33$$

$$(r = 0.90,\quad s = 46,\quad n = 8) \qquad (3)$$

One must remember that Equation 3 is approximate only because decomposition temperature may be connected with some other processes occurring simultaneously.

Earlier [1], we had shown for $SnCl_4L_2$ complexes that the negative ClKα shifts linearly increase with the growth of complex stability. The same must be expected for $SbCl_5L$ complexes. In fact, there are two linear dependencies, one between ΔClKα and ν_{DA} values shown in Figure 2 and described by the correlation

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

$$(r = 0.980,\quad s = 21,\quad n = 8) \qquad (4)$$

and the other between ΔClKα and DN shown in Figure 1, described by the correlation

$$-\Delta\text{ClK}\alpha\ (\text{eV}) = 0.0022\ \text{DN (kcal/mol)} + 0.103$$

$$(r = 0.974,\ s = 0.005,\ n = 8) \qquad (5)$$

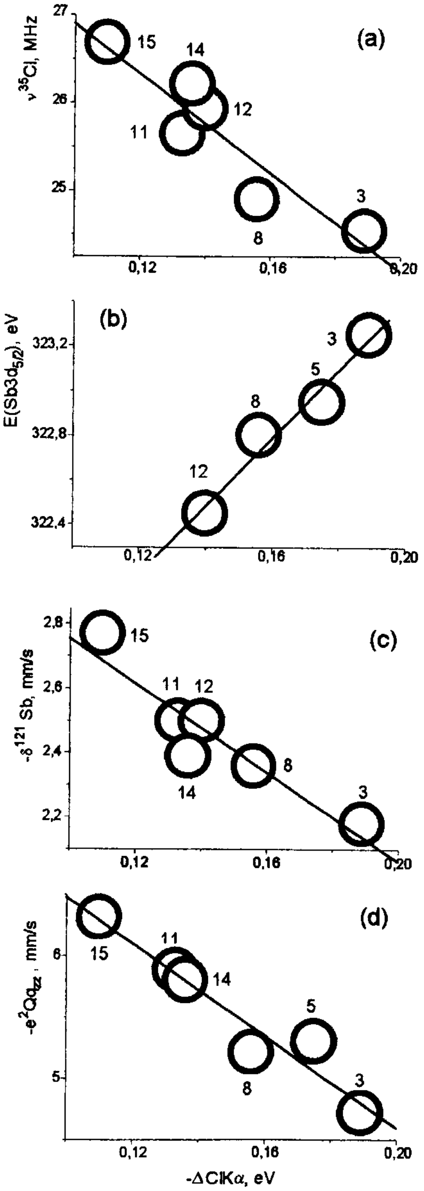

FIGURE 3 The (a) ^{35}Cl NQR frequencies, (b) energies of $Sb3d_{5/2}$ level, (c) ^{121}Sb chemical shifts, and (d) quadrupole coupling constants versus ClKα shifts for $SbCl_5L$ complexes. Circle radius corresponds to errors of ClKα shift measurements. Numbering of points corresponds to that in Table 1.

With the help of Equations 2 and 5, the enthalphies of complex formation unknown earlier for a number of $SbCl_5L$ complexes could be found. The corresponding calculated values are given in Table 1 in parentheses. As follows from the ΔClKα, ν_{DA}, and t_d° experimental values, complex **2** is the most stable among all known $SbCl_5L$ complexes. One may suppose that here the Sb atom coordination number is equal to 7 due to the bidentate ligand coordination.

For analysis of electron density changes on the central Sb atom, upon complex formation, it is relevant to use Mössbauer and X-ray electron spectroscopy data. As follows from the Mössbauer effect data [12] and SnKα shifts [13] for $SnCl_4L_2$ complexes and free $SnCl_4$, the positive charge on the Sn atom increases on complexation. To analyze the electron density changes on the Sb atom in $SbCl_5L$ complexes, we performed PM3 calculations for the free acceptor and its complexes with L = $(Me_2N)_3PO$, $Me_2NC(O)H$, $OPCl_3$, Me_2SO, and MeCN with full geometry optimization. The following are relations between Mössbauer spectra chemical shifts (δ) and the electron population of the valency Sb p-orbitals (N_p):

$$-\delta\ (\text{mm/s}) = 2.43\ N_p\ (e) - 48.2$$

$$(r = 0.934,\quad s = 0.07,\quad n = 6) \tag{6}$$

$$N_p\ (e) = 14.2\ N_s\ (e) - 24.0$$

$$(r = 0.990,\quad s = 0.03,\quad n = 6) \tag{7}$$

where N_s is the electron population of the valency Sb s-orbitals.

Table 3 presents the measured Mössbauer chemical shifts, quadrupole coupling constants e^2Qq_{zz} for ^{121}Sb, electron populations of the Sb $s$and p orbitals (obtained by Equations 6 and 7) and Sb $3d_{5/2}$ level energies obtained by X-ray electron spectroscopy for a number of $SbCl_5L$ complexes and free acceptors [14]. Similar to observations for tin chloride complexes, in antimonium pentachloride complexes, the positive effective charge on the central acceptor atom increases with respect to that in the free acceptor. Figure 3 presents the dependencies, close to linearity,* between ^{35}Cl NQR frequencies, Mössbauer chemical shifts, quadrupole coupling constants e^2Qq_{zz} ^{121}Sb, $E(\text{Sb}3d_{5/2})$, and ClKα shifts in all complexes investigated.†

All these dependencies show that the positive q_{Sb} increases linearly with the negative q_{Cl} growth and thus (see Equation 5) with the ligand donor strength increase. In view of the similar results obtained for $SnCl_4L_2$ complexes, one can assume that this effect is characteristic for all nontransition element complexes.

According to the Klopman theory [11], in complex compounds, the donor–acceptor interaction can be either charge or orbital controlled. As follows from data obtained in nontransition element complexes, the complex formation enthalphy is correlated with the effective charges on each acceptor atom. This indicates that, in nontransition element complexes, the acceptor interaction with ligands is, to a significant degree, charge controlled.

The opposite signs of the electron density change on the central acceptor atom and on terminal acceptor atoms on complexation prove that there is no effective electron density transition from the ligand to the vacant acceptor orbitals. On complexation, the

TABLE 3 Parameters of NQR and Mössbauer Spectra for $SbCl_5L$ Complexes

Compound	$E(Sb3d_{5/2})$, [14],eV	$\nu^{35}Cl$, [15,16], MHz	$-\delta^{121}Sb$, [17], mm/s[a]	$-e^2Qq_{zz}$, [17], mm/s	N_s, e	N_p, e	q_{Sb}, e
1.1	312.9	28.04	3.20	2.80	1.84	2.21	0.95
3	323.25	24.54	2.18[b]	4.72[b]	1.82	1.79	1.39
5	322.95	—	2.56	5.30	1.83	2.202	1.15
8	322.80	24.90	2.36	5.21	1.82	1.87	1.31
11	—	25.65	2.50	5.88	1.82	1.92	1.26
12	322.45	25.93	2.50	6.90	1.82	1.92	1.26
14	—	26.21	2.39	5.80	1.82	1.88	1.30
15	—	26.68	2.77	6.31	1.83	2.04	1.13

[a] With respect to $CaSnO_3$.

[b] Data for $SbCl_5 \cdot OPMe_3$ complex.

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*The slope of the δ dependence on ΔClKα is opposite to that observed earlier for $SnCl_4L_2$ complexes [3]. This is a consequence of the opposite signs of the $\Delta R/R$ ratio for Sb and Sn nuclei on their excitation that is proportional to Mössbauer chemical shifts in tin chloride and antimonium pentachloride complexes with respect to $CaSnO_3$ [18].

†One can see that the meanings corresponding to the free acceptor do not satisfy any dependence presented in Figure 3. This indicates that all parameters presented in Figure 3 except ΔClKα are connected linearly with effective atomic charge only for compounds where the central atom has the alike symmetry of surroundings.

polarization of all acceptor bonds has occurred and is proportional to the complex formation enthalphy. These results are consistent with those calculated by Norokuma [19] for BF_3L and BH_3L complexes where the basic contribution of electrostatic interactions to the complex formation enthalphy had previously been established.

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