

## The Inductive Effect and Ligand–Ligand Interactions in Mutual Influence of Ligands

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The inductive effect in series  $AF_5^{(n+1)-}$  and  $AF_5-Cl^{n-}$  ( $A = Si, P, S, Se$ ) has been calculated by an approximate non-empirical method. The effect is directed primarily along the *cis*-coordinate; with isoelectronic compounds of one period elements it is growing along the period from the left to the right. The role of ligand–ligand interactions in the mutual influence of ligands is examined.

The inductive effect and the non-valent ligand–ligand interactions affect the relative strength of  $A-X_{cis}$  and  $A-X_{trans}$  bonds in octahedral compounds of transition elements  $AX_5L$  in the same manner, but in compounds of non-transition elements they have opposite signs.

The inductive effect accounts for the weakening or strengthening of  $A-X$  bonds in  $AX_5L$  with respect to  $AX_6$  depending on the nature of the ligand  $L$ . The relative strength of  $A-X_{trans}$  and  $A-X_{cis}$  bonds in non-transition element compounds  $AX_5L$  depends on the balance between the inductive effect and the non-valent interactions.

### Introduction

Over the past few years much attention has been paid to specific manifestations of mutual influence of ligands in non-transition element compounds. Particularly, the bond characteristics in substituted complexes are changing mainly in *cis*-direction (in contrast to the well-known *trans*-influence in transition element compounds). Several theoretical models for the *cis*-influence were developed [1–6]. Later studies on mutual influence of ligands in non-transition element compounds have involved also MO LCAO calculations. A systematic investigation of tellurium hexafluoride derivatives ( $TeF_5X$ ) was carried out by Armstrong *et al.* [7], whose CNDO calculations of  $TeF_6$  and  $TeF_5X$  electronic structure (for 10 different substitutes) have indicated that upon substitution the  $B(Te-F_{cis})$  bond indices display greater decrease than the  $B(Te-F_{trans})$  indices, and electronic density on the  $F_{cis}$  atom becomes greater than on the  $F_{trans}$  atom ( $|q(F_{cis})| > |q(F_{trans})|$ ). These results have led to a conclusion about *cis*-influence in

$TeF_5X$ . We should also mention the calculation of  $SF_6$  and  $SF_5Cl$  by CNDO/2 method [8]: where the fact of *cis*-influence is supported by all the calculated characteristics, *i.e.* charges  $q(F)$ , bond indices  $B(S-F)$  and the total electron energy components  $E(S-F)$ . *Cis*-influence was also found in  $SiF_6^{2-}$  and  $SiF_5OH^{2-}$  calculations by the CNDO/2 method with geometry optimization [9], where it appeared from the calculated equilibrium distances, ligand charges and strength constants of Si–F bonds.

### Calculation of Mutual Influence of Ligands in Octahedral Compounds of Non-transition Elements

Our investigations of mutual influence of ligands in non-transition element compounds with the help of MO calculations were aimed at clearing the following questions: the direction of the inductive effect (*cis*- or *trans*-), its dependence on the central atom position in the periodic system, and correlation with the results of model approach [1, 2]. We shall consider the effects resulting from substitution of an F atom in silicon, phosphorus, sulphur and selenium hexafluorides ( $AF_6^{n-}$ ) by Cl, *i.e.* a less electronegative ligand with similar properties ( $AF_5Cl^{n-}$ ) and by a lone electron pair which may be regarded as a limiting case of a ligand with zero electronegativity ( $AF_5^{(n+1)-}$ ). MO calculations in the series  $AF_6^{n-}-AF_5Cl^{n-}-AF_5^{(n+1)-}$ , where  $A = Si, P, S, Se$ , were carried out within the framework of a non-empirical variant of NDDO valence approximation. The details of the calculation, as well as the MO energies and LCAO coefficients of the compounds listed were given elsewhere [10, 11].

As a criterion for the direction of mutual influence of ligands in substituted compounds  $AF_5X$  one may use the difference between effective charges  $\delta q = q(F_{cis}) - q(F_{trans})$ . There is considerable experimental evidence that accumulation of negative charge on the ligands correlates with the decrease in strength of the bond between the ligand and the central atom. These correlations are illustrated by Table I [12–16]. As seen from the Table, the increase in the central atom–ligand distance (bond weakening) upon

TABLE I. Interatomic Distances (Å) and Bond Energies (eV).

Compound	R(C-F)	$\Delta\epsilon_{F1s}$	Compound	R(Sn-Cl)	$\epsilon_{Cl2p_{3/2}}$
CF <sub>4</sub>	1.320	2.6	SnCl <sub>4</sub>	2.281	206.19
CF <sub>3</sub> H	1.334	1.7	MeSnCl <sub>3</sub>	2.306	205.52
CF <sub>2</sub> H <sub>2</sub>	1.357	0.73	MeSnCl <sub>2</sub>	2.327	204.95
CFH <sub>3</sub>	1.382	0.00	Me <sub>3</sub> SnCl	2.354	204.49

TABLE II. Effective Atomic Charges (distances in at. units).

Compound	R(A-F <sub>cis</sub> )/R(A-F <sub>tr</sub> )	R(A-Cl)	q(F <sub>cis</sub> )	q(F <sub>trans</sub> )
SiF <sub>5</sub> <sup>3-</sup>	3.25/3.25	—	-0.579	-0.551
	3.45/3.25	—	-0.644	-0.567
PF <sub>5</sub> <sup>2-</sup>	3.25/3.25	—	-0.522	-0.471
	3.45/3.25	—	-0.560	-0.459
SF <sub>5</sub> <sup>-</sup>	2.95/2.95	—	-0.343	-0.289
	3.13/2.95	—	-0.385	-0.283
	3.25/3.06	—	-0.406	-0.281
	3.25/3.25	—	-0.406	-0.305
SeF <sub>5</sub> <sup>-</sup>	3.18/3.18	—	-0.485	-0.406
	3.37/3.18	—	-0.506	-0.385
SiF <sub>5</sub> Cl <sup>2-</sup>	3.17/3.17	4.09	-0.315	-0.320
PF <sub>5</sub> Cl <sup>-</sup>	3.06/3.06	3.91	-0.164	-0.161
SF <sub>5</sub> Cl	2.98/2.98	3.84	-0.048	-0.037
SeF <sub>5</sub> Cl	3.18/3.18	4.04	-0.195	-0.187

substitution is accompanied by the decrease in binding energies of the ligand inner electrons (negative charge accumulation). Such correlations are discussed at greater length in the monograph [17]. Calculations show [7-9] that the use of  $\delta q$  criterion leads to the same conclusions on the direction of the mutual influence of ligands as the other computed criteria (bond indices and bond energies).

Table II contains results of our calculations of effective charges on F<sub>cis</sub> and F<sub>trans</sub> atoms obtained from the Mulliken population analysis.

Let us now analyze the inductive effect upon substitution. We begin with the AF<sub>5</sub><sup>(n+1)-</sup> compounds, which must display maximum changes with respect to AF<sub>6</sub><sup>n-</sup>. All these compounds may be regarded as resulting from substitution of the A-F bond in the AF<sub>6</sub><sup>n-</sup> octahedron by a lone electron pair of atom A. In other words, the lone pair may be considered as a bond with zero electronegativity ligand X<sub>6</sub>, which is situated at an infinite distance from the central atom A, so that the A-X<sub>6</sub> bond is equivalent to atom A possessing a lone electron pair. Since the model ligand does not draw away any electronic density from atom A, but even supplies it with its own density, the differences in electronic density on the remaining five F atoms in AF<sub>5</sub><sup>(n+1)-</sup>

will be maximum, as well as the difference between F<sub>cis</sub> and F<sub>trans</sub>.

Table II shows that for all the compounds investigated the electron density associated with F<sub>cis</sub> atoms is greater than that on F<sub>trans</sub> atoms. We can therefore assume the A-F<sub>cis</sub> bond to weaken in comparison with the A-F<sub>trans</sub> bond, i.e. speak about *cis*-influence in the compounds considered. Of importance, the inequality  $|q(F_{cis})| > |q(F_{trans})|$  holds true even when the distances A-F<sub>cis</sub> and A-F<sub>trans</sub> are set equal in the calculation. As one would expect from general considerations, the increase in R(A-F<sub>cis</sub>) with respect to R(A-F<sub>trans</sub>) enhances the difference between q<sub>cis</sub> and q<sub>trans</sub> (primarily due to growing q<sub>cis</sub>). Accumulation of negative charge on equatorial F<sub>cis</sub> atoms owing to *cis*-influence does not therefore arise exclusively from distance changes, being only enhanced by them.

Let us now consider the case when one fluorine atom in AF<sub>6</sub> is substituted by a rather similar ligand, i.e. chlorine atom. The data given in Table II indicate that except in SiF<sub>5</sub>Cl<sup>2-</sup> the F<sub>cis</sub> atoms carry a higher charge (in absolute value) than the F<sub>trans</sub> atoms. Incidentally, these differences are very small, as should have been expected for substitution by Cl (cf. results for the series AF<sub>5</sub><sup>(n+1)-</sup>). Other calculations

also give small differences in charges for substituted chlorides:  $\delta q = -0.018$  for  $\text{SF}_5\text{Cl}$  [8] and  $-0.01$  for  $\text{TeF}_5\text{Cl}$  [7]. Below the conclusion about *cis*-influence will be compared to experimental data.

Let us now turn to the question how the degree of *cis*-influence depends on the central atom position in the periodic table. As a measure of *cis*-influence valid for different compounds one may use  $\delta q = q_{cis} - q_{trans}$  or  $\delta q/\bar{q}$ , where  $\bar{q}$  is the average between  $q_{cis}$  and  $q_{trans}$ . Applying either of these criteria to the data in Table II, we see that both in  $\text{AF}_5^{(n+1)-}$  and in  $\text{AF}_5\text{-Cl}^{n-}$  series the *cis*-influence grows in a sequence  $\text{Si} \rightarrow \text{P} \rightarrow \text{S}$ . Using reported data [18] on the  $\text{ClF}_5$  molecule calculation in the same approximation ( $q_{cis} = -0.22$ ,  $q_{trans} = -0.01$ ), we can extend this series to  $\text{Si} \rightarrow \text{P} \rightarrow \text{S} \rightarrow \text{Cl}$ . The  $\delta q$  criterion therefore suggests that in isoelectronic compounds *cis*-influence in the periodic system period grows from the left to the right.

Let us consider to what extent is this conclusion consistent with the experiments. As long as no data complete enough is available for the series we investigated, let us turn to experimental results on interatomic distances in the series  $\text{SbF}_5^{2-} - \text{TeF}_5^- - \text{IF}_5 - \text{XeF}_5^+$  (Table III).\* It appears from these data that inter-

atomic distances obey an inequality  $R(\text{A-F}_{cis}) > R(\text{A-F}_{trans})$ , which confirms the *cis*-influence of lone pair. However, the difference  $R(\text{A-F}_{cis}) - R(\text{A-F}_{trans})$  does not change monotonously in this series, even if we consider only mean values of  $R(\text{A-F}_{cis})$ , disregarding noticeable scatter in  $R(\text{A-F}_{cis})$  values. Moreover, it is necessary to take into account that the interaction of the  $\text{AF}_5^{(n+1)-}$  group with the surrounding atoms of the crystal distorts the symmetry of the group with respect to the point group  $C_{4v}$  (see, for example, [23] for  $\text{TeF}_5^-$ ). The same is true about  $\text{XeF}_5^+$ , where the lone pair of the Xe atom to a certain extent interacts with F anion atoms, so that the distance of these atoms from the central atom of the anion increases (see, for example, [28]). We suppose therefore that the experimental data available fail to permit an unambiguous conclusion about the dependence of *cis*-effect on the position of the central atom in the main period of the periodic table.

Let us consider the relevance of the model approaches [1-4] to the above calculations.

The best developed model theory of mutual influence of ligands [1-4] employs non-diagonal matrix elements between completely localized orbitals of  $\text{A-X}_i$  bonds as a measure of mutual influence of ligands in electronic density redistribution. The greater this element (in its absolute value), the greater the electronic density passing to the  $\text{X}_i$  atom upon substitution of the  $\text{A-X}_i$  bond by a more covalent bond (all other conditions being equal).

\*One must, of course, take into account that the data for compounds of the 5th period elements may differ from those for the 3rd period element compounds.

TABLE III. Interatomic Distances (Å) in the Groups  $\text{AF}_5^{(n+1)-}$  (standard deviations are given in parentheses, limiting values in square brackets).

Group	$R(\text{A-F}_{cis})$	$R(\text{A-F}_{trans})$	Compound	Reference
$\text{SbF}_5^{2-}$	2.04 (9)	2.00 (9)	$\text{K}_2\text{SbF}_5$ (cryst)	19, 20
	2.075 (3)	1.916 (4)	$(\text{NH}_4)_2\text{SbF}_5$ (cryst)	19
	2.07 (3)	2.01 (2)	$\text{Na}_2\text{SbF}_5$ (cryst)	21
	[2.05-2.10]			
$\text{TeF}_5^-$	1.96 (2)	1.84 (2)	$\text{KTeF}_5$ (cryst)	22
	1.952 (4)	1.862 (4)	$\text{KTeF}_5$ (cryst)	23
	[1.952-1.953]			
	1.93 (1)	1.81 (2)	$\text{CsTeF}_5$ (cryst)	24
	[1.91-1.95]			
$\text{IF}_5$	1.892 (5)	1.862 (10)	$\text{IF}_5 \cdot \text{XeF}_2$ (cryst)	25
	1.869 (5)	1.844 (25)	$\text{IF}_5$ (gas)	26
	1.87 (3)	1.75 (3)	$\text{IF}_5$ (cryst)	27
	[1.82-1.92]	[1.69-1.77]		
$\text{XeF}_5^+$	1.88 (8)	1.81 (8)	$[\text{XeF}_5^+][\text{PtF}_6^-]$ (cryst)	28
	[1.87-1.88]			
	1.845 (9)	1.793 (8)	$[\text{XeF}_5^+][\text{RuF}_6^-]$ (cryst)	29
	[1.841-1.848]			
	1.84 (1)	1.81 (1)	$[\text{XeF}_5^+]_2[\text{PdF}_6^{2-}]$ (cryst)	30
	[1.835-1.855]	[1.806-1.820]		
	1.76 (2)	$[\text{XeF}_5^+][\text{AsF}_6^-]$ (cryst)	31	
	[1.80-1.86]			
	2.88 (2)	1.75 (3)	$[\text{XeF}_5^+]\text{F}^-$ (cryst)	32

TABLE IV. Localized Orbitals of  $\sigma$ -Bonds in  $SF_5Cl^a$ .

LO type	AO of the Central Atom						Ligand AO (bond)		
	s	p	$d_{z^2}$	$d_{x^2-y^2}$	$P\pi$	$d\pi$	s	$\sigma$	$\pi$
equ.	0.33	0.47	-0.22	0.41	0.02	0.01	-0.38	0.58	-0.02
ax.	0.30	0.48	0.47				-0.35	0.58	
Cl	0.47	0.45	0.28				-0.26	0.54	

Ligand AO ( <i>trans</i> )			Ligand AO ( <i>cis</i> )			
s	$\sigma$	$\pi$	s	$\sigma$	$\pi$	$\bar{\pi}$
-0.07	-0.03	-0.02	0.06(-1,2)	-0.03(-4,7)	-0.02(-8, -5)	-0.08
-0.08	-0.01		0.02	-0.05	-0.11	
-0.05	-0.06		-0.05	-0.08	0.10	

<sup>a</sup>The indices equ., ax. and Cl refer to the bonds  $S-F_{cis}$ ,  $S-F_{trans}$  and  $S-Cl$ . The indices *cis* and *trans* refer to the ligands in the corresponding position to the bond under consideration. The  $z$  axis is directed as  $Cl-S-F_{trans}$ . The figures in parentheses refer respectively to  $F_{tr}$  and Cl, i.e. (-1,2) means -0.01, 0.02 for the functions  $F_{trans}$  and Cl respectively.

It is interesting to investigate to what extent the model approach conclusions hold for actual localized orbitals in the compounds considered, and how the *cis*-influence criterion introduced [1-4] agrees with the above-discussed criterion  $\delta q$ . We suggested a fairly simple localization method [33] and used it to calculate localized MO corresponding to  $\sigma$ -bonds  $A-F_{eq}$ ,  $A-F_{ax}$ ,  $A-Cl$  and to lone pair of the A atom in all the systems studied [33, 34]. The degree of localization can be visualized from Table IV.

We have calculated matrix elements of a one-electron Hamiltonian,  $h_{ij}$ , in the basis of localized orbitals. In all the systems considered it was obtained that  $|h_{cis}| > |h_{trans}|$  and  $\Delta = h_{cis} - h_{trans} < 0$ . According to the model [1, 2] these results suggest *cis*-influence for the inductive effect; they are consistent with the above considered charge variations. The  $\Delta$  value, as well as the charge difference  $\delta q$ , grows as the central atom changes its position in the period from the left to the right. Accordingly, the results obtained in terms of localized orbitals are practically the same as those in terms of atom charges.

A graphical correlation between  $\delta q$  (for the  $AF_5X$  compounds) and  $\Delta$  (for  $AF_6$  octahedrons) is given in Fig. 1a. The transfer of electronic density on  $F_{cis}$  and  $F_{trans}$  atoms upon substitution is evidently proportional to the change of  $h_{cis}$  and  $h_{trans}$  matrix elements in the substituted compound with respect to similar matrix elements in the initial octahedron. One may therefore expect the values  $\delta q$  and  $\delta\Delta = \Delta(AF_5X) - \Delta(AF_6)$  to change synbatically. The calculated values of  $\delta q$  and  $\delta\Delta$  (Fig. 1b) support this conclusion.

Concluding this section, let us dwell in more detail upon the possible use of calculated charges on F atoms as a bond strength criterion in spite of their dependence on the method of calculation, basis, etc.

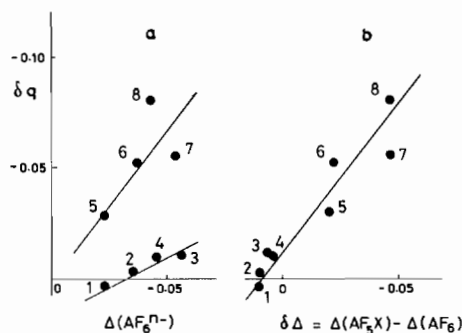


Figure 1. Correlation between difference in charges  $\delta q$  with the values  $\Delta$ (a) and  $\Delta\delta$ (b). 1,  $SiF_5Cl^{2-}$ ; 2,  $PF_5Cl^-$ ; 3,  $SF_5Cl$ ; 4,  $SeF_5Cl$ ; 5,  $SiF_5^{3-}$ ; 6,  $PF_5^{2-}$ ; 7,  $SF_5^-$ ; 8,  $SeF_5^-$ .

The drawbacks of Mulliken population analysis have been repeatedly cited in the literature [35, 36]. Specifically, participation of diffuse vacant AO of the central atom in the calculation basis results in far too high a Mulliken population of this atom. In fact, the electronic density corresponding to these diffuse orbitals is situated in the ligand region, as pointed out by Fenske *et al.* [36] in approximate calculation of transition element compounds including vacant np-AO. The same situation is reported [37] in case of approximate calculations of non-transition element compounds considering vacant nd-orbitals of the central atom. Particularly, in our case Mulliken population analysis for  $SF_5Cl$  results in the negative charge on the sulphur atom. In order to simply reduce the results to a form familiar to a chemist, one should ascribe to the central atom only a part of Mulliken's nd-AO population, while the rest is distributed between the ligands [10, 37]. With  $SF_5Cl$ , this modified estimation gives a  $q_s$  of about +1.

However, we are interested in the difference ( $\delta q$ ) between charges on structurally unequivalent F atoms ( $F_{cis}$  and  $F_{trans}$ ) rather than in the absolute values of effective charges. Consideration of these differences obtained according to Mulliken would hopefully yield qualitatively correct results. Incidentally, the above considered tendencies of mutual influence of ligands are retained in the modified estimation of charges. Specifically, the signs of  $\delta q$  are the same as for charges in Table II for all the members of the series  $AF_5^{(n+1)-}$  and  $AF_5Cl^{n-}$  (with the exception of  $PF_5Cl^-$ , where the difference in the effects was especially low). The conclusion about the growing *cis*-influence in isoelectronic compounds from the left to the right of the period is also completely valid.

### Ligand-Ligand Interactions

It appears thus from the above calculations, as well as from models and calculations by other workers, that the inductive effect in octahedral compounds of non-transition elements is directed mainly along the *cis*-coordinate when a substituent is introduced, in contrast to the *trans*-direction displayed by compounds of transition elements [17].

Such inversion of the inductive effect principal direction arising from the nature of the central atom is typical not only for acidoligands introduction,  $AX_6 \rightarrow AX_5L$ , but for a number of other substitutions in the  $AX_6$  octahedron. For instance, the inductive effect upon transitions  $AX_6 \rightarrow AX_5L$  (L is an acidoligand forming a more covalent bond A-L than A-X),  $AX_6 \rightarrow AX_5L$  (where L forms multiple bonds A=L),  $AX_6 \rightarrow AX_5L^s$ , where  $L^s$  is a strong donor, and  $AX_6 \rightarrow AX_5L^w$ , where  $L^w$  is a weak donor, is discussed in terms of perturbation theory [2]. Table V contains relevant results for the direction of the inductive effect.

Important as it is, the inductive effect is not the only constituent of mutual influence of ligands. An essential role is played by direct ligand-ligand interaction.

The role of ligand-ligand, or, more precisely, non-valent interactions in the  $A-X_{cis}$  and  $A-X_{trans}$  bond

strength in compounds like  $AX_5L$  was often discussed in the literature (see, for instance [2, 38, 39] and refs. in Table IX, X). The current theories fail to describe the influence of ligand-ligand interactions on the relative strength of  $A-X_{cis}$  and  $A-X_{trans}$  bonds. However, this influence is usually assumed to be associated with variations of the L-A- $X_{cis}$  angle. For instance, according to Gillespi's model the introduction of a covalent bond A-L, multiple bond A=L or a strong donor  $L^s$  ( $A-L^s$ ) results in deviation of equatorial X atoms of the  $AX_5L$  molecule towards  $A-X_{trans}$  (Fig. 2a), whereas introduction of a weak donor  $L^w$  ( $A-L^w$ ) leads to the deviation towards this weakened bond  $A-L^w$  (Fig. 2b). In principle,

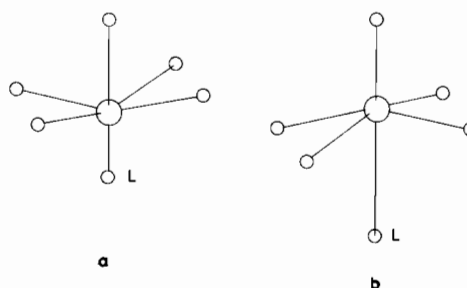


Figure 2. Different cases of deformation in  $AX_5L$  octahedral compounds.

both cases *a* and *b* can exhibit a greater weakening or strengthening of *cis*-bonds, as well as *trans*-bonds, if only ligand-ligand interactions are taken into account. However, to our mind it is more reasonable (see, for instance [2, 38, 39], and refs. in Tables IX and X), that in the *a* case (Fig. 2) the  $A-X_{trans}$  bond is weakened more than the  $A-X_{cis}$  bond under the influence of  $X...X$  and  $X...L$  interactions. On the contrary, in the case *b* the  $A-X_{trans}$  bond is strengthened more than the  $A-X_{cis}$  bond with respect to A-X bond in  $AX_6$  (if we confine ourselves to ligand-ligand interactions only). This conclusion seems especially reasonable if large angular distortions are involved. Let us emphasize that, unlike the inductive effect, the ligand-ligand interactions are believed to be independent of the central atom A.

TABLE V. Weakening of the A-X Bond in  $AX_5L$  vs. Inductive Effect  $I(X-A-L)$  and Non-valent Interactions  $X...X^a$ .

A	Interaction	A-L	A=L	A-L <sup>s</sup>	A-L <sup>w</sup>
Non-transition	$I(X-A-L)$	<i>cis</i> > <i>tr.</i>	<i>cis</i> > <i>tr.</i>	<i>cis</i> > <i>tr.</i>	<i>cis</i> > <i>tr.</i> <sup>b</sup>
	$X...X$	<i>tr.</i> > <i>cis</i>	<i>tr.</i> > <i>cis</i>	<i>tr.</i> > <i>cis</i>	<i>tr.</i> > <i>cis</i>
Transition	$I(X-A-L)$	<i>tr.</i> > <i>cis</i>	<i>tr.</i> > <i>cis</i>	<i>tr.</i> > <i>cis</i>	<i>tr.</i> > <i>cis</i>
	$X...X$	<i>tr.</i> > <i>cis</i>	<i>tr.</i> > <i>cis</i>	<i>tr.</i> > <i>cis</i>	<i>tr.</i> > <i>cis</i>

<sup>a</sup>The A-L  $\sigma$ -bond is more covalent than A-X,  $L^s$  is a strong donor,  $L^w$  is a weak donor. <sup>b</sup>The results refer to strengthening of the A-X bond in case of inductive effect and to lower weakening of the A-X bond in case of ligand-ligand interactions.

The effect of ligand–ligand interactions on the relative strength of  $A-X_{cis}$  and  $A-X_{trans}$  bonds is illustrated by Table V. The overall influence of the  $A-X$  bond substitution by the  $A-L$  bond in the octahedron consists of the inductive effect across the central atom and direct ligand–ligand interactions. As appears from Table V, in transition element compounds the direction of the inductive effect coincides with the influence of ligand–ligand interactions on relative strength of  $A-X_{cis}$  and  $A-X_{trans}$  bonds, whereas in non-transition element compounds these directions are opposite.

Below we shall examine only octahedral compounds of non-transition elements.\* The importance of ligand–ligand interactions in relative strengths of  $A-X_{cis}$  and  $A-X_{trans}$  bonds in non-transition element compounds has already been considered in [2, 38, 39]. As evident from Table V, the relationship between the inductive effect and ligand–ligand interactions may result in either *trans*- or *cis*-effects. The experimental evidence available suffices for revealing the relative role of these factors in mutual influence of ligands in non-transition element compounds.

Below we shall consider experimental data for compounds of  $AF_5L$  type or related compounds. In accordance with Table V we shall examine 3 kinds of  $A-L$  bonds, paying attention not only to the relative strength of  $A-X_{cis}$  and  $A-X_{trans}$  bonds, but also to their variation with respect to the initial compound  $AX_6$ .

### Discussion of Experimental Data

#### *Substitution of a $\sigma$ -Bond $A-X$ by a more Covalent $\sigma$ -Bond $A-L$*

The experimental data are given in Tables VI–VIII. They are fairly consistent with theoretical expectations of the inductive effect in  $AF_5L$  compounds as compared to  $AF_6$ , and in parameters of  $A-X_{cis}$  bonds compared to  $A-X_{trans}$  bonds. Two facts attract special interest.

(1) The inductive effect is especially pronounced when a ligand is replaced by a lone electron pair (see Table VI). The inductive influence of the lone pair can also be readily traced for interatomic distances. For instance, the distance  $Te-F$  equals [50] 1.82 Å in  $TeF_6$ , but 1.86 Å for  $Te-F_{trans}$  and 1.95 Å for  $Te-F_{cis}$  in  $TeF_5^-$  (Table III); the distance  $Sb-Cl$  equals [51] 2.36 Å in  $SbCl_6^-$ , but 2.356 Å for  $Sb-Cl_{trans}$  and 2.582–2.690 Å for  $Sb-Cl_{cis}$  in  $SbCl_5^{2-}$  [52]. (The *cis*- and *trans*-indices are given with respect to the lone pair at the Te and Sb atoms, which acts as an electro-positive ligand).

\*Data for octahedral compounds of transition elements are examined in the monograph [17].

(2) Tin compounds display particularly striking example of *cis*-influence (Table VIII). When one Cl or Br atom in  $SnHal_4 2L$  is replaced by a Me group, which forms a  $Sn-Me$  bond more covalent than the  $Sn-Cl$  and  $Sn-Br$  bonds, the  $Sn-Cl_{cis}$ ,  $Sn-Br_{cis}$  and  $Sn-O_{cis}$  bonds become longer, whereas the  $Sn-Cl_{trans}$  and  $Sn-Br_{trans}$  bonds become even somewhat shorter. Introduction of a second Me group enhances the elongation of bonds in *cis*-position to the Me group, while the  $Sn-Me$  distance in *trans*-position decreases. Theories do predict [2, 3] such “non-classical” *trans*-effects in non-transition element compounds.

At the same time, when the difference in inductive effect in *cis*- and *trans*-direction is small, interactions between ligands may result in greater elongation of the  $A-X_{trans}$  bond with respect to the  $A-X_{cis}$  bond. Let us turn to the paper [38], where the molecular structure of  $SF_5Cl$  is investigated by gas phase electron diffraction. The results cited suggest that  $\Delta R = R(S-F_{cis}) - R(S-F_{trans}) = +0.003$  Å. However, mutual processing of microwave [53] and electron diffraction results, which provides for more reliable molecular structure determination, gives  $\Delta R = -0.022$  Å (all the bonds are longer than in  $SF_6$ ). The difference in force constants of  $S-F$  bonds in  $SF_5Cl$  is also small (see Table VI).

In addition to the papers cited in Table VI, the inequality  $K_{trans} > K_{cis}$  in  $AF_5Hal$  compounds was obtained also [54–56]. However, different force constants have been reported for the  $SF_5Cl$  molecule [38] ( $K_{trans} = 4.64$  mdyne/Å,  $K_{cis} = 4.65$  mdyne/Å), *i.e.* the possible predominance of *trans*-influence was stated.

#### *Substitution of $A-X$ Bond by the Multiple Bond $A=O$*

To begin with, the decrease in strength constants (Table VI) in  $AF_5O^{(n+1)-}$  compounds with respect to  $AX_6^{n-}$  suggests a strong inductive effect. However, it is difficult to determine the predominant direction of inductive effect combined with ligand–ligand interactions, hence the controversy in explanation of experimental results.

Dominating *cis*-direction ( $K_{trans} > K_{cis}$ ) was reported [44, 46] for  $SO_4^{2-}$  and  $IOF_5$  and dominating *trans*-direction ( $K_{trans} < K_{cis}$ ) for  $SeOF_5^-$  and  $TeOF_5^-$  [43]. An inequality  $K_{trans} < K_{cis}$  may also be obtained [39] for  $IOF_5$ ; it was found [39] from electronographic and microwave results that  $R(I-F_{cis}) < R(I-F_{trans})$ , the difference being 0.046 Å.

A rather intriguing circumstance is that in  $IF_5$  the distances equal [39]  $R(I-F_{cis}) = 1.87$  Å,  $R(I-F_{trans}) = 1.84$  Å, while in  $IOF_5$   $R(I-F_{cis}) = 1.817$  Å,  $R(I-F_{trans}) = 1.863$  Å, *i.e.* upon transition  $IF_5 \rightarrow IOF_5$  the  $I-F_{cis}$  bonds do become shorter due to the inductive effect, but at the same time the  $I-F_{trans}$  bond becomes longer. We believe the latter effect arises from the fact that the  $F...F$  ligand interaction in

TABLE VI. Force Constants of Different Bonds (mdyne/A).

A	AF <sub>6</sub> [40]	AF <sub>5</sub> Cl [40]		AF <sub>5</sub> Br [41]		AOF <sub>5</sub> <sup>-</sup>		AF <sub>5</sub> <sup>-</sup> [42]	
		<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
S	4.845	4.623	4.593	4.50	4.29	3.75	3.60	4.12	2.06
Se	4.946	4.836	4.514			2.98	3.59	3.82	2.41
Te	5.081	4.929	4.760			3.38	4.16	3.56	2.28
							[44]		
							[43]		
							[43]		

A	AF <sub>6</sub> <sup>+</sup> [45]	AOF <sub>5</sub> [46]		AF <sub>5</sub> [42]	
		<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
Cl				3.47	2.67
Br				4.03	3.30
I	5.60	4.60	4.42	4.82	3.81

TABLE VII. Force Constants for Different Bonds (mdyne/A) [47, 48].

Compound	K(Sn-Hal)
SnF <sub>6</sub> <sup>2-</sup>	2.8
<i>trans</i> -Me <sub>2</sub> SnF <sub>4</sub> <sup>2-</sup>	1.2
SnCl <sub>6</sub> <sup>2-</sup>	1.5
<i>trans</i> -Me <sub>2</sub> SnCl <sub>4</sub> <sup>2-</sup>	0.8
SnBr <sub>6</sub> <sup>2-</sup>	1.2
<i>trans</i> -Me <sub>2</sub> SnBr <sub>4</sub> <sup>2-</sup>	1.1

IOF<sub>5</sub> is stronger than in IF<sub>5</sub> because the I-F<sub>*cis*</sub> distance in IOF<sub>5</sub> is shorter, while the F<sub>*cis*</sub>-I-F<sub>*trans*</sub> angle remains the same.

#### Substitution of A-X Bond by A-L, where L is a Neutral σ-Donor

As indicated [2], the substitution AX<sub>6</sub><sup>n-</sup> → AX<sub>5</sub>-L<sup>(n-1)-</sup> presents two different cases. First, that of a strong donor L<sup>s</sup>, which weakens the A-X bonds in AX<sub>5</sub>L<sup>(n-1)-</sup> with respect to AX<sub>6</sub><sup>n-</sup> on account of the inductive effect.

For the group of compounds considered we have currently no reliable evidence of a strong donor L<sup>s</sup> increasing the electron density at the AX<sub>5</sub> fragment in octahedral complexes AX<sub>5</sub>L<sup>(n-1)-</sup>, thus making the A-X bonds weaker than in the initial octahedron AX<sub>6</sub><sup>n-</sup>. Presumably, S<sub>4</sub>N<sub>4</sub> is such a donor, (see Table IX), since in SbCl<sub>5</sub>S<sub>4</sub>N<sub>4</sub> the Sb-Cl bonds are in fact somewhat longer than they average in SbCl<sub>6</sub><sup>-</sup>, though the Sb-Cl<sub>*cis*</sub> bonds deviate towards the donor. With SbCl<sub>5</sub>S<sub>4</sub>N<sub>4</sub> the Sb-Cl<sub>*cis*</sub> bond is somewhat longer than Sb-Cl<sub>*trans*</sub>, as follows from consideration of the inductive effect for strong donors.

The principal body of evidence for the group of compounds under consideration concerns L<sup>w</sup> donors, which make the A-X bonds in AX<sub>5</sub>L<sup>(n-1)-</sup> compounds stronger than in initial octahedrons AX<sub>6</sub><sup>n-</sup> (Tables IX-XI). The data presented in the tables suggest the following conclusions.

(1) In agreement with the inductive effect the increase in the donor capacity of the ligand L weakens the A-X bonds. In particular, the Sb-Cl bonds in SbCl<sub>5</sub>L become longer, while the distance between the ligand L and the Sb atom becomes shorter.

TABLE VIII. Interatomic Distances (Å)<sup>a</sup> [49].

Compound	Sn-O	Sn-Hal	Sn-Me	Sn-Hal'	Sn-Me'
<i>trans</i> -Me <sub>2</sub> SnBr <sub>2</sub> ·2L	2.23	2.76	2.14		
<i>trans</i> -MeSnBr <sub>3</sub> ·2L	2.16	2.65		2.40	
<i>trans</i> -SnBr <sub>4</sub> ·2L	2.09	2.54		2.54	
<i>trans</i> -Me <sub>2</sub> SnCl <sub>2</sub> ·2L	2.26	2.57	2.14		
<i>trans</i> -MeSnCl <sub>3</sub> ·2L	2.18	2.46		2.31	2.24
<i>trans</i> -SnCl <sub>4</sub> ·2L	2.13	2.40		2.36	

<sup>a</sup>Error in R ± 0.1 Å. L = hexamethylphosphortriamide. The bond Sn-Hal' and Sn-Me' are in *trans*-position.

TABLE IX. Interatomic Distances (Å).

Compound	SbCl <sub>6</sub> <sup>-</sup>	SbCl <sub>5</sub> S <sub>4</sub> N <sub>4</sub>	SbCl <sub>5</sub> CH <sub>3</sub> CN	2SbCl <sub>5</sub> ·S <sub>2</sub> N <sub>2</sub>	
R(Sb-Cl <sub>trans</sub> )	2.36	2.37	2.35	2.310	2.313
R(Sb-Cl <sub>cis</sub> )		2.39	2.36	2.310	2.291
R(Sb-N)		2.17	2.23	2.281	2.285
<Cl-Sb-N		89.0	84.9	83.04	
References	51	57	58	59	

TABLE X. Interatomic Distances in SbCl<sub>5</sub>L, Å.

L	R(Sb-Cl <sub>trans</sub> )	R(Sb-Cl <sub>cis</sub> )	R(Sb-O)	Ref.
OP(CH <sub>3</sub> ) <sub>3</sub>	2.34	2.34	1.94	60
HCON(CH <sub>3</sub> ) <sub>2</sub>	2.33	2.34	2.05	61
SeOCl <sub>2</sub>	2.346	2.337	2.12	62
	2.318	2.338	2.04	
POCl <sub>3</sub>	2.32	2.33	2.17	60
CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> COCl	2.305	2.318	2.253	63
C <sub>6</sub> H <sub>5</sub> COCl	2.318	2.320	2.317	64
C <sub>2</sub> Cl <sub>4</sub> O <sub>2</sub> CO	2.28	2.31	2.40	65
(COCICH <sub>2</sub> ) <sub>2</sub>	2.298	2.326	2.428	51

TABLE XI. Force Constants of Bonds (mdyne/Å) [66–68].

Compound	AsF <sub>5</sub> ·NCCH <sub>3</sub>	SbF <sub>5</sub> ·NCCH <sub>3</sub>	SbCl <sub>5</sub> ·NCCH <sub>3</sub>
K(A-Hal) in AHal <sub>6</sub> <sup>-</sup>	3.1	3.4	1.5
K(A-Hal <sub>trans</sub> )	4.34	4.20	1.78
K(A-Hal <sub>cis</sub> )	5.07	4.60	2.40

TABLE XII. Interatomic Distances, Å, in MF<sub>4</sub>Bipy<sup>a</sup> [69].

M	Si	Ge	Sn
R(M-F <sub>cis</sub> )	1.656	1.777	1.944
R(M-F <sub>trans</sub> )	1.630	1.759	1.924
R(M-N)	1.977	2.026	2.182
<N <sub>1</sub> MN <sub>2</sub>	79.7	79.3	75.1

<sup>a</sup>The index *trans* refers to the bonds lying in one plane with the M-N bonds.

(2) The distance Sb-Cl<sub>cis</sub> is approximately equal to the distance Sb-Cl<sub>trans</sub>. In most cases, however, especially when the Sb-L distance is long, the Sb-Cl<sub>cis</sub> distance is likely to be longer than Sb-Cl<sub>trans</sub>. This slight nonsystematic shrinking of the Sb-Cl<sub>trans</sub> bond must be due to non-valence ligand-ligand interaction (Table V).

(3) Likewise, the dominating ligand-ligand interactions appear to account for the inequality R(M-

F<sub>cis</sub>) > R(M-F<sub>trans</sub>) (see Table XII [69]) in compounds MF<sub>4</sub>Bipy, where the M-F<sub>cis</sub> bonds are deviated towards the M-N bonds in a similar way to the Sb-Cl<sub>cis</sub> bonds in SbCl<sub>5</sub>L.

The force constants of A-Hal bonds seem to be less affected by interactions of this kind, hence (K(A-Hal<sub>trans</sub>) < K(A-Hal<sub>cis</sub>), as would appear if only inductive interactions A-X and A-L through the atom A are considered (Table V). Thus the inequality *cis* > *trans* is observed (Table V). Incidentally, domination of the inductive effect may be displayed not only in force constants of the bonds, but also in interatomic distances. For instance [70], the distance In-Cl in InCl<sub>6</sub><sup>3-</sup> is 2.523 Å, while in *cis*-InCl<sub>4</sub>·(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> R(In-Cl<sub>cis</sub>) = 2.425 Å and R(In-Cl<sub>trans</sub>) = 2.485 Å (the *trans* index refers to the In-Cl bonds in a plane with the In-H<sub>2</sub>O bonds).

It is interesting to compare these results to bond lengths in K<sub>2</sub>[InCl<sub>5</sub>H<sub>2</sub>O] [71]. In this complex the distances In-Cl<sub>cis</sub> and In-Cl<sub>trans</sub> equal 2.480 and 2.474 Å, respectively, *i.e.* shortening of In-Cl bonds,



not unexpectedly, is less pronounced than in the couple  $\text{InCl}_6^{3-}$  and  $\text{InCl}_4(\text{H}_2\text{O})_2^-$ . It is also noteworthy that in the  $\text{InCl}_5\text{H}_2\text{O}^{2-}$  group the distances  $\text{In}-\text{Cl}_{\text{cis}}$  and  $\text{In}-\text{Cl}_{\text{trans}}$  practically coincide, which means that here the ligand-ligand interactions are of high importance.

Analysis of the above data suggests the following conclusions on the relative role of the inductive effect and ligand-ligand interactions in determining the direction of mutual influence of ligands in octahedral compounds of main group elements.

(1) The inductive effect accounts for weakening or strengthening of  $\text{A}-\text{X}_{\text{trans}}$  and  $\text{A}-\text{X}_{\text{cis}}$  bonds in substituted  $\text{AX}_5\text{L}$  octahedrons. In particular, introduction of a more covalent  $\text{A}-\text{L}$   $\sigma$ -bond weakens the  $\text{A}-\text{X}$  bonds (Tables VI-VIII), while that of a weak ligand  $\text{L}^{\text{w}}$  strengthens these bonds (Tables IX, X).

(2) Introduction of a ligand L into the  $\text{AX}_6$  octahedron produces influence, which consists of the inductive effect and the variation of ligand-ligand interactions. As these two components have opposite directions, either *cis*- or *trans*-influence can be dominating. *Cis*-influence occurring in many compounds indicates that the inductive effect is associated mainly with the *cis*-coordinate, in agreement with the available models and calculations.

(3) Different experimental characteristics display different sensitivity to the inductive effect and to ligand-ligand interactions. Force constants appear to be more sensitive to the inductive effect than interatomic distances (*cf.* results for  $\text{SbCl}_5\text{CH}_3\text{CN}$  in Tables IX and XI). It is also not impossible that the effect of non-valent interactions is more pronounced in interatomic distances than in force constants (see results for  $\text{AF}_5\text{Cl}$ ). This conclusion is preliminary and may be changed on accumulation of new experimental evidence.

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