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Mutual Influence of Ligands in Main Group Element Coordination Compounds

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The mutual influence of ligands (MIL) in main group element coordination compounds AL_n has been analyzed on the basis of the orbitally deficient scheme of the structure of these compounds. It is shown that the directing influence of ligand X in quasi-octahedral and quasi-square complexes AXL_m depends on the oxidation state of the central atom A. If A is not of the highest oxidation state (formally preserving ns^2 "lone pair"), in complexes AXL_m the trans influence must always take place. If A is of the highest oxidation state, the MIL regularities are of more complicated character. In particular, contrary to transition metal complexes MXL_m, a strong σ donor X (of the H or CH_3 type) can cause the strengthening of the A–L_{trans} bond at the expense of the weakening of the A–L_{cis} bonds, a multiply bonded ligand X (of the terminal oxygen type) can cause the relative cis weakening, a decrease of the A–F bond strength can be accompanied by an increase of spin–spin coupling constant $|J(A-F)|$, etc. The results obtained agree with the experimental data and permit a number of predictions to be made. The reasons for both similarity and difference in the displays of the MIL in transition metal MXL_m and main group AXL_m complexes are discussed.

Trans and Cis Influence. The mutual influence of ligands (MIL) in complexes is considered to be a fundamental problem in coordination chemistry. Here we shall be interested only in the directing influence of ligands, the most important display of which is the trans influence. As the term "trans influence" is used to describe rather heterogeneous things (see, for example, the latest relevant reviews[1–4]) it is useful to clarify the terminology.

Generally speaking, the substitution of ligand X in complexes EXL_m (E is a transition metal atom M or a main group element atom A) influences the properties of *all* E–L bonds. In this sense one can speak about both the trans and the cis influence in any coordination compound EXL_m containing trans and cis ligands.[1–3] However, if we want to find out the peculiarities of the directing influence of ligands (first of all, the differences between the MIL in complexes of transition and main group elements), it is much better to consider the trans or cis influence as a relative characteristic. That is, we deal with the trans influence in a EXL_m complex (where positions of formally identical ligands L are nonequivalent) if the influence of the ligand X on equilibrium properties of the E–L_{trans} bond is stronger than that on properties of the E–L_{cis} bond. Similarly, in the case of the cis influence the properties of the E–L_{cis} bond are more sensitive to the influence of the X ligand. It is of importance that in the framework of such a definition the trans (or cis) influence can result in both weakening and strengthening of the E–L_{trans} (E–L_{cis}) bond; the only thing that would matter is that the corresponding changes of the E–L_{cis} (E–L_{trans}) bond are less significant.

Really, the seeming chaotic displays of the MIL in transition metal complexes can be described as the trans influence only in the framework of the definition above when the trans influence is considered as a relative characteristic.[4,5]

Now we comment on the determination of the trans influence by means of quantum chemical computations of concrete complexes. The trans influence itself has various manifestations for each compound (depending on what property of the E–L bond is under consideration) and there exist hundreds of such compounds. Even if one takes only the geometric manifestations of trans influence, there should be performed enough accurate calculations with the variation of all internuclear distances and valence angles. At present such calculations on coordination compounds are beyond our possibilities (they become possible only for molecules containing light atoms in the framework of the MINDO/3 method[6]). In any case, all attempts that had been made to solve the MIL problem by quantitative calculations had rather limited success.[1,4]

All this makes it necessary to look for general qualitative models of the MIL. Recently we have developed such a model[4,7] based upon such fundamental properties of molecular orbitals as their nodal structure and symmetry (which determines bonding or antibonding character of MO's). In addition, the differences between covalent (due to unpaired electrons), donor–acceptor, and back-donation interactions are taken into account. On this basis we could obtain the trans-weakening series in complexes MXL_m (depending on X, M, and L) which permits the x-ray data for a great number of compounds to be explained, especially in those cases with multiple M–X bonds, where the trans influence is displayed most distinctly.[4]

The usefulness of this consideration prompted us to use a similar approach (based on the nodal structure and symmetry of LCAO MO's) for the analysis of the MIL in the main group element complexes.

Peculiarities of Chemical Bonding in Complexes of Transition and Main Group Elements. Any realistic MIL model must take into account the main differences in chemical bonding in transition metal coordination compounds MXL_m compared to main group element compounds AXL_m. In complexes ML_n the ligand valence σ orbitals are usually of lower energy than all metal valence ($(n-1)$d, ns, and np) orbitals. In complexes AL_n the typical picture is that the ligand valence σ orbital lies

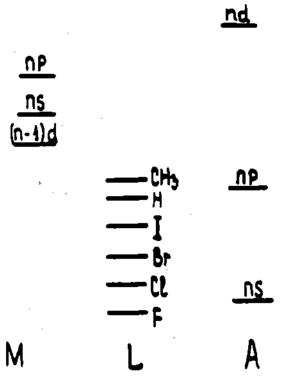

Figure 1. Mutual position of valence orbitals of the central atom and the ligands in typical complexes of transition and main group elements.

lower than the valence *n*d and *n*p orbitals of the atom A but higher than the *n*s orbital of the atom A (Figure 1). Moreover, for such ligands as H and CH_3, their σ orbitals may prove to be higher than *n*p orbitals of the atom A, especially if the latter is coordinated with strongly electronegative ligands of the halogen type.

If we consider a covalent σ bond E–L as a result of interaction of the ligand σ orbital with any hybrid sp^qd^r orbital of the central atom E, then for transition metals the contributions of *all* valence metal ($n - 1$)d, *n*s, and *n*p orbitals in polarity of the M–L σ bond will be of the same sign. Because of this, in complexes ML_n the different criteria of the covalent M–L bond strength (maximum overlap population, minimum polarity of the bond and maximum donor ability of the ligand X) lead, in principle, to the same results. At the same time, in main group element complexes the contribution of an *n*s orbital of the atom A to the polarity of the A–L σ bond must, as a rule, be opposite to the contributions of its *n*p and *n*d orbitals. So, in complexes MXL_m, all other conditions being equal, the strengthening of the M–X bond and the weakening of the M–L_{trans} bond occurs monotonically with an increase in the donor ability of an acido ligand X, while the most influencing ligands are the strongest donors (such as H and CH_3).[1,4] Meanwhile in complexes AXL_m the mentioned monotonic variation may be broken, and the influence of strong donors (of the H or CH_3 type) may result in both the trans weakening or trans strengthening, depending on the oxidation state of the central atom (see below).

Further, in the case of transition metals their valence ($n - 1$)d, *n*s, and *n*p orbitals are close enough in energy. As a result, all of them, in principle, can contribute significantly to the formation of metal–ligand bonds.[4,7d] In main group element compounds AL_n the picture changes greatly. Due to significant differences in energy between *n*s, *n*p, and *n*d orbitals of a central atom, the contribution of *n*d orbitals in the formation of A–L bonds is usually so small that the model of orbitally deficient hypervalent bonds (HVB) becomes the best initial approximation.[8] This HVB model, where only *n*s and *n*p orbitals of a central atom are taken into account, is the generalization of the known three-orbital three-center model.[9]

According to Musher,[8] in orbitally deficient compounds AL_n chemical bonds of three types can arise: (1) usual covalent (two-electron, two-center) A–L bonds; (2) three-center bonds of linear fragments L–A–L with the participation of only one *n*p orbital of the central atom; (3) bonds of the previous (second) type, but strengthened by the additional contribution of an *n*s orbital of the central atom. Bonds of the two latter types are called hypervalent I and II, respectively. It is obvious that for the given partners (A and L) the bond strength increases in the series

$$\text{hypervalent I} < \text{hypervalent II} < \text{covalent} \qquad (1)$$

Formulation of the Objective. The MIL in main group element complexes AXL_m has been studied (both experimentally and theoretically) considerably less than that in transition metal complexes MXL_m. In particular, only recently models[10,11] have been suggested in which attempts were made to find out the specificity of the MIL in main group element complexes. The first of them[10] is based of the equivalent MO theory; the second[11] on the perturbation theory for canonical MO's. These models lead to rather different conclusions; in addition, they can be formally applied only to complexes AXL_m where σ-bonded ligands X and L are close in their properties (see discussion in ref 12).

Therefore it seems more promising to consider primarily the "extreme" cases when the ligand X differs greatly from other ligands L. In these cases, first, the experimental evidence for the MIL is especially distinct and, second, one can hope to obtain a number of meaningful conclusions on the basis of purely qualitative arguments which do not depend on the choice of the quantitative approximation (the latter is of special importance due to the limited possibilities of computing approaches to the MIL problem). As we shall undertake a qualitative approach in the framework of the HVB scheme,[8] we shall further refer to it as the MIL–HVB model.[7e] Some preliminary results have been published elsewhere.[12] Here we shall extend and clarify our arguments and illustrate the main conclusions by some calculations. Besides, we shall discuss the relevant experimental data.

Results and Discussion

Complexes with the Central Atom of Low Oxidation States. In symmetric molecules AL_2 ($D_{\infty h}$), AL_4 (D_{4h}), and AL_6 (O_h) there are two MO's of the irreducible representation A_{1g} (to which belongs the s orbital of the atom A), one bonding a_{1g} and one antibonding a_{1g}^*. Therefore if the central atom is not of the highest oxidation state, formally preserving the ns^2 "lone pair", the antibonding a_{1g}^* MO will be occupied. Hence, in such complexes s bonding must be completely eliminated and all A–L bonds will be pure hypervalent I bonds.[8b,12] In substituted complexes AXL_m a lowering of symmetry results, strictly speaking, in some mixing of s and p orbitals. However, due to significant differences in their energies, the s contribution in the relevant occupied antibonding a_1^* MO will be much greater than the p contribution, and the s orbital population will be close to 2. Hence, the A–L bonds remain practically hypervalent I bonds and the influence of the σ-bonded ligand X will be transmitted through the np_σ orbital of the atom A in the linear X–A–L_{trans} fragment. This can result in the trans influence only because a p_σ orbital does not touch cis positions.

Thus, one can obtain the first conclusion: in complexes AXL_m where the central atom preserves the ns^2 "lone pair", the influence of the σ-bonded ligand X is a trans influence.

The regularities of this influence can be easily established from the general scheme of the three-center three-orbital interaction (which has been developed[4] for π bonding in transition metal complexes MXL_m as an example). In particular, the closer the energies of the ligand X σ orbital to the atom A *n*p orbital, the more the weakening of the A–L_{trans} bond. Here the covalent A–X bond's influence is stronger than that of the donor–acceptor A←X bond.[13] Further, the trans influence in complexes AXL_m in question must be, as a rule, displayed more strongly than that in complexes MXL_m. The fact is that in MXL_m the contributions of different components of the metal orbital basis (*n*s, (n – 1)d, *n*p) in the trans influence may be of opposite signs[11,14] (see also arguments on pp 10 and 21 in ref 4).

These conclusions are confirmed by x-ray data, for example, for the quasi-octahedral complexes of Sn(II), Sb(III), Te(IV), I(V), and Xe(VI)[15] or for the quasi-square complexes of

Table I. Assignments of Orbitals in D_{4h} Complexes AX_2L_4[a]

Irreducible representation	Orbitals: A	Orbitals: X and L[b]
A_{1g}	s	$\sigma_{ax}^{(X)}$: $\sigma_1 + \sigma_6$
		$\sigma_{eq}^{(L)}$: $\sigma_2 + \sigma_3 + \sigma_4 + \sigma_5$
A_{2u}	p_z	$\sigma_1 - \sigma_6$
B_{1g}		$\sigma_2 - \sigma_3 + \sigma_4 - \sigma_5$
E_u	p_x	$\sigma_2 - \sigma_4$
	p_y	$\sigma_3 - \sigma_5$

[a] Enumeration of ligands is given in Figure 2a. [b] Normalizing coefficients are omitted.

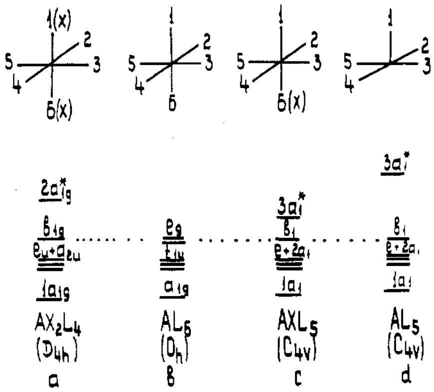

Figure 2. Arrangement of ligands and the scheme of the occupied σ MO's in 12e complexes: (a) AX_2L_4 (D_{4h}), (b) AL_6 (O_h), (c) AXL_5 (C_{4v}), (d) AL_5 (C_{4v}). Assignments of orbitals are shown in Tables I and II. See additional explanations in the text.

Te(II)[16] (ns^2 and ns^2np^2 electronic configurations of the central atom, respectively). In all of these cases the strong (shortened) A–X bond and the weak (lengthened) A–L bond are always located trans to one another, while the trans weakening is stronger than that in transition metal complexes.[1,4] For example, in complexes of Te(II) such a neutral donor as thiourea (tu) causes the trans lengthening of the Te–Br bond by 0.27 Å (in *cis*-$Te(tu)_2Br_2$ compared to *trans*-$Te(tu)_2Br_2$) and such an acido donor as C_6H_5 causes the trans lengthening of the Te–Cl bond by 0.7 Å (in *trans*-$Te(tu)_2(C_6H_5)Cl$ compared to *cis*-$Te(tu)_2Cl_2$).[16]

Complexes with the Central Atom of the Highest Oxidation State. As stated above, we are interested in the case when the ligand X differs greatly from ligands L. The donor ability of monovalent σ-bonded acido ligands X usually increases in the series[17]

$$F < Cl < Br < I < \ldots < H, CH_3, \ldots \tag{2}$$

As halogens usually play the role of ligands L, let us take an H atom or a CH_3 group as the ligand X. In other words, we consider the case when the σ orbital of the ligand X is close in energy to the np orbital of the atom A, while at the same time the σ orbitals of ligands L are close in energy to the ns orbital of the atom A.

Let us begin with disubstituted complexes of the *trans*-AX_2F_4 type. As seen from Table I, the order of the six low MO's will be $1a_{1g} < e_u, a_{2u} < b_{1g} < 2a_{1g}^*$ (Figure 2a). Within the irreducible representation A_{1g} three MO's are formed. By definition, the first MO has no nodes and thus it is entirely bonding

$$1a_{1g}:\ s + \sigma_{ax}^{(X)} + \sigma_{eq}^{(L)} \tag{3}$$

while the third MO has two nodes and thus it is entirely antibonding

$$3a_{1g}^*:\ s - \sigma_{ax}^{(X)} - \sigma_{eq}^{(L)} \tag{4}$$

Table II. Assignments of Orbitals in C_{4v} Complexes AXL_5[a]

Irreducible representation	Orbitals: A	Orbitals: L[b]	Orbitals: X
A_1	s	$\sigma_{ax}^{(L)}$: σ_1	σ_6
	p_z	$\sigma_{eq}^{(L)}$: $\sigma_2 + \sigma_3 + \sigma_4 + \sigma_5$	
B_1		$\sigma_2 - \sigma_3 + \sigma_4 - \sigma_5$	
E	p_x	$\sigma_2 - \sigma_4$	
	p_y	$\sigma_3 - \sigma_5$	

[a] Enumeration of ligands is given in Figure 2c. [b] Normalizing coefficients are omitted.

The second MO must have only one node. If the A–X bond is strong enough, the nodal structure will be[13]

$$2a_{1g}^*:\ s + \sigma_{ax}^{(X)} - \sigma_{eq}^{(L)} \tag{5}$$

that is, bonding with respect to the axial ligands X and antibonding with respect to the equatorial ligands L (cf. Table VI in the Appendix).

However, in this case the axial A–X bonds in the linear X–A–X fragment strive to become normal covalent bonds with the participation of sp hybrid orbitals of the atom A (due to p bonding of the a_{2u} MO and s bonding of the $1a_{1g}$ and $2a_{1g}^*$ MO's). At the same time the equatorial A–L bonds in the linear L–A–L fragment approach hypervalent I bonds (due only to p bonding of the e_u MO as s bonding of the $1a_{1g}$ and s antibonding of the $2a_{1g}^*$ MO's will tend to balance); i.e., they get weaker compared to the equalized hypervalent II bonds in the parent complex AL_6. Analogous considerations are also valid for disubstituted complexes $AX_2L_2D_2$ where D is a neutral donor molecule.

The same result can be explained in other terms. The hypervalent I bonds are stable only if the ligands are of greater electronegativity than the central atom.[8,9] This is true for L = F, Cl, and Br but not for X = H or CH_3. Therefore the A–H or A–CH_3 bonds must be, as a rule, normal covalent bonds.[18]

Now let us turn to monosubstituted complexes AXL_5. As it follows from Table II, the order of the six low MO's will be $1a_1 < 2a_1, e < b_1 < 3a_1^*$ (Figure 2c). In AX_2L_4 and AXL_5 species the composition and the character of the e (bonding) and b_1 (nonbonding) MO's remain the same. One can think that in AXL_5 the $1a_1$, $2a_1$ and $3a_1^*$ MO's will be sufficient analogues of the $1a_{1g}$, a_{2u}, and $2a_{1g}^*$ MO's in AX_2L_4 (cf. Table VI). Therefore in complexes AXL_5 (as compared with AL_6) the A–$L_{cis(eq)}$ bonds will be weakened (though less than in AX_2L_4) but the A–$L_{trans(ax)}$ bond may be even strengthened. The structure of C_{4v} complexes AL_5 serves as an additional argument in favor this statement (see below).

So, we obtain the second conclusion: in complexes AXL_5 (AXL_3D_2) where the central atom is of the highest oxidation state (X = H, CH_3, etc., L = F, Cl, Br, etc.) one may expect lengthening of the A–L_{cis} bonds, with simultaneous shortening of the A–L_{trans} bonds as compared with the parent complex AL_{m+1} with equivalent A–L bonds.[19] This effect should get stronger in complexes AX_2L_4 ($AX_2L_2D_2$).

Unfortunately, there are no experimental data on bond lengths in such AXL_5 complexes with six acido ligands. However, recently the complexes $Sn(CH_3)_mL_{4-m}D_2$, where L = Cl or Br, D = $PO[N(CH_3)_2]_3$, m = 0, 1, or 2, have been studied.[20] In these complexes two neutral donor molecules are located on the same coordinate axis and four acido ligands are located in quasi-square positions around atom Sn(IV). In complexes $Sn(CH_3)L_3D_2$ in both cases (L = Cl, Br) the Sn–L_{trans} bonds are shortened (by 0.05–0.14 Å) and the Sn–L_{cis} bonds are lengthened (by 0.06–0.09 Å) compared to the parent complexes SnL_4D_2. In complexes $Sn(CH_3)_2L_2D_2$, where all identical ligands are located in trans position one to another, the Sn–L_{cis} bonds are further lengthened (by ca. 0.2 Å) and the Sn–CH_3 bonds are shortened (by ca. 0.1 Å) as compared with $Sn(CH_3)L_3D_2$. The x-ray studies of similar octahedral Sn(IV) complexes[22] show also the substantial strength of H_3C–Sn–CH_3 bonds that is additionally confirmed by Mössbauer spectroscopic data.[23]

We have already noted that the cis weakening in AXL_5 and *trans*-AX_2L_4 complexes is mainly the result of occupation of some a_1^* MO which is antibonding with respect to equatorial ligands L_{cis}. This a_1^* level contains a remarkable contribution of the s orbital of atom A (cf. Table VI). Therefore in complexes AXL_5 and especially AX_2L_4 the s orbital population in A–L_{eq} bonds must increase compared to that of A–L bonds in the parent AL_6 complex. The fact is that the high unoccupied MO's of the relevant representation A_1 ($4a_1^*$, $5a_1^*$ in AXL_5 and $3a_{1g}^*$ in AX_2L_4) will contain mostly high-energy components of the initial orbital set, namely, p_z and $\sigma^{(X)}$.

As it follows from the theory of coupling constants J(A–L), in the case of L = F,[24] the bonding and antibonding valence LCAO MO's are distinguished by the signs between the orbital s_A and the group σ orbitals $[2p]_F$, but s_A and admixtures of the group orbital $[s]_F$ enter these valence MO's with the same (opposite) signs. This is obviously true not only for tetrahedra AF_4[24] but also for octahedra AF_6 as in both cases the A_1 representations (A_1 and A_{1g}, respectively) have the same structure. Therefore in AXF_5 and AX_2F_4 as compared with AF_6 the mentioned increase of s_A orbital population (as well as the decrease of the relevant exitation energies; see Figure 2 and Table V) must enlarge the absolute value of the Fermi contact term[24] in (negative) coupling constant J(A–F_{eq}).

Thus, one can formulate the third conclusion: in complexes AXF_5 (X = H, CH_3, etc.) a decrease of the A–F_{eq} bond strength may be accompanied by an increase of the (absolute) value of the coupling constant J(A–F_{eq}); this effect should get stronger in complexes AX_2F_4.

Really, on substituting atom F by X = H, CH_3, CF_3, or C_6H_5 in PF_6^- the predicted growth of coupling constants $|J(A–F_{eq})|$ takes place.[25] Such a dependence between the A–F bond strength and coupling constant J(A–F) is the peculiarity of main group element fluorides.[26]

As for the influence of a multiply bonded ligand X in complexes AXL_m, it may differ considerably from that in complexes MXL_m. For example, in C_{4v} complexes MXL_5 the M–X π bond arises at the expense of metal $(n-1)$d orbitals and does not practically involve metal *n*p orbitals which form equatorial M–L_{cis} σ bonds.[4] At the same time in similar complexes AXL_5 the central atom A has to use the same *n*p orbitals for the formation of both A–X π bonds and equatorial A–L_{cis} σ bonds.

Thus, a multiply bonded ligand X in complexes AXL_m (contrary to MXL_m) can hardly cause significant trans weakening. Moreover, in this case even the relative cis weakening can take place (A–L_{cis} bonds may be a bit longer than the A–L_{trans} bond).

Unfortunately, there are no experimental data on bond lengths in such compounds, but this conclusion is in agreement with some indirect data. For example, NMR ^{19}F spectra for complexes $ReOF_5$ and IOF_5 show that the mutual position of signals from axial and equatorial atoms F is opposite.[27] Further, in IOF_5 the force constant for the I–F_{trans} bond is a bit larger than that for the I–F_{cis} bonds (though in isoelectronic anions TeF_5O^- and SeF_5O^- the relative values of these constants are reverse).[28]

C_{4v} Complexes AL_5. The donor ability series (2) formally includes as the opposite extreme cases the "vacant orbital" and the "lone electron pair" (which correspond to the maximum acceptor and donor ability of the ligand X, respectively). Therefore C_{4v} complexes AL_5 with 10 and 12 valence σ electrons can be considered as derivatives of octahedral complexes AXL_5 for these two extreme cases.

Table III. Bond Lengths in Some C_{4v} Complexes AL_5

No. of valence σ electrons	Complex	Distance, Å			Ref
		R(A–L_{eq})$_{av}$	R(A–L_{ax})	ΔR	
10	$Sb(C_6H_5)_5$	2.22	2.12	0.10	*a*
	$InCl_5^{2-}$	2.46	2.42	0.04	*b*
		2.46	2.42	0.04	*c*
12	XeF_5^+	1.84	1.81	0.03	*d*
	IF_5	1.87	1.81	0.06	*d*
	TeF_5^-	1.95	1.86	0.09	*d*
	SbF_5^{2-}	2.08	1.92	0.16	*d*

[a] Reference 31. [b] Reference 32a. [c] Reference 32b. [d] Quoted in ref 33.

From the relevant MO scheme (see Table II and Figure 2d) it follows that the order of the six low MO's will be $1a_1 < e$, $2a_1 < b_1 < 3a_1^*$. In AXL_5 and AL_5 species the characters of e and b_1 MO's remain the same, so, only the changes within MO's of the representation A_1 should be taken into account. The formation of these MO's may be regarded as the following two-stage process: (1) the interactions of s with σ_{eq} and p_z with σ_{ax} resulting in the formation of the orbitals $\varphi_{1,3} \approx s \pm \sigma_{eq}$ and $\varphi_{2,4} \approx \sigma_{ax} \pm p_z$ (here the signs plus and minus correspond to bonding and antibonding interactions, respectively); (2) mixing of the orbitals φ_i.

As the p_z orbital lies higher than the orbital σ_{ax} (and σ_{eq}) and by symmetry does not mix with the orbital σ_{eq}, the relevant MO's will be

$$1a_1:\ \varphi_2 + \varphi_1 \approx s + (p_z) + \sigma_{ax} + \sigma_{eq} \tag{6}$$

$$2a_1:\ \varphi_2 - \varphi_1 \approx -(s) + p_z + \sigma_{ax} - (\sigma_{eq}) \tag{7}$$

$$3a_1^*:\ \varphi_3 + \varphi_4 \approx s - p_z + \sigma_{ax} - \sigma_{eq} \tag{8}$$

where the orbitals that play the role of admixtures are given in parentheses. Certainly, the real LCAO coefficients may vary significantly depending on the orbital parameters employed (cf. Table VI).

Similar to the AXL_5 case, the $3a_1^*$ MO (8) is antibonding with respect to the equatorial ligands, but with respect to the axial ligand it tends to be nonbonding (as the s and p contributions in the A–L_{ax} bond are opposite). In 12e complexes AL_5 the $3a_1^*$ MO is occupied; hence the bonding s contribution of the $1a_1$ MO will almost disappear and the A–L_{eq} bonds will be considered as hypervalent I bonds. At the same time the A–L_{ax} bond is an ordinary covalent bond (due to the $2a_1$ MO (7) that corresponds to the interaction of the p_z orbital of the atom A with the σ orbital of the axial ligand L_{ax}). So, the A–L_{ax} bond must be stronger (shorter) than the A–L_{eq} bonds (cf. ref 8a). In 10e complexes AL_5, where the $3a_1^*$ MO is unoccupied, the relative strength of the A–L_{ax} and A–L_{eq} bonds remains unchanged as the hypervalent II strengthening of all A–L bonds (due to the bonding s contribution of the $1a_1$ MO (6)) is approximately the same (cf. Table VI).

Thus, we come to the fourth conclusion: in C_{4v} complexes AL_5, not only with 12 but with 10 valence σ electrons, the axial bond must be shorter than the equatorial ones.[29]

It is known that in transition metal C_{4v} complexes ML_5 the relative strength of the M–L_{ax} and M–L_{eq} bonds depends on the electronic $(n-1)d^m$ configuration. The MO analysis shows[30] that the M–L_{ax} σ bond may be both stronger (in the case of d^0–d^6 and d^{10}) and weaker (in the case of d^8) than the M–L_{eq} bond. In reality, in the known C_{4v} complexes ML_5 one observes both possibilities (including the intermediate case of equal axial and equatorial bonds in $Pt(SnCl_3)_5^{3-}$).[30] It is obvious that main group element complexes can be included in this scheme as $(n-1)d^{10}$ complexes, as was done in ref 30.

Some relevant x-ray data are given in Table III. Let us remember that 10e complexes AL_5 usually have trigonal-bipyramidal configuration and only two complexes of such a composition, $Sb(C_6H_5)_5$[31] and $InCl_5^{2-}$,[32] are found to have tetragonal-pyramidal configuration. Though they are probably of C_{2v} rather than of C_{4v} symmetry,[31,32b] the axial A–L bond is shorter than any equatorial A–L bond; this is the only thing that would matter for our discussion.

The increased strength of the axial bond as compared with the equatorial bonds has been found in the quantitative calculations on 10e C_{4v} configurations of PL_5 (L = H, F)[34] and SiH_5^-.[35] As this result is obtained both with and without *n*d orbitals of the central atom, it is an additional argument in favor of the hypervalent structure of main group element complexes. In general, the up-to-date calculations on complexes of Si, P, S, and Cl[36] convincingly demonstrate that the characteristic features of these complexes can be obtained regardless of 3d orbitals of the central atom. The same conclusion may be reached experimentally, e.g., from the x-ray photoelectron data.[37]

As there exist many 12e complexes AL_5 and all of them have the same C_{4v} geometry, we give in Table III only the isoelectronic series

$$\mathrm{XeF_5^+,\ IF_5,\ TeF_5^-,\ SbF_5^{2-}} \qquad (9)$$

The MIL–HVB model leads[12] to the rather paradoxical conclusion that along the series (9) the difference in charges of ligands L_{ax} and L_{eq} must decrease, but the differences of the bond lengths $\Delta R = R(A-L_{eq}) - R(A-L_{ax})$ will increase in general.

As the A–L bond lengths, especially in molecular ions, depend on the crystal environment, the values of ΔR, as a rule, form certain ranges (for example, for XeF_5^+ ΔR = 0.03–0.07 Å[33]). However, the average ΔR values increase along the series (9). This is shown in Table III, where (according to ref 33) we accept ΔR = 0.03, 0.06, 0.09, and 0.16 Å, respectively (though, certainly, such an ideal monotonic sequence is not necessary, only the trend is of importance—the increase of ΔR values from XeF_5^+ up to SbF_5^{2-}).[38]

The major difference in geometry between 10e and 12e complexes AL_5 is the magnitude of the valence angle $L_{ax}AL_{eq}$ which in the first case is larger than 90° but in the second case smaller than 90°. These angular deformations can be naturally explained in the framework of the VSEPR (Nyholm–Gillespie) theory,[39] but this theory is not suitable to explain the picture of bond lengths.

Conclusion

We see that in main group element complexes the MIL has more various manifestations as compared with transition metal complexes. Moreover, here the MIL has a number of substantial peculiarities to describe which the usual terminology of trans–cis influence is sometimes insufficiently expressive.[21] As A–L bond properties may change in a nonmonotonic way while substituting the ligand X and may prove to be sensitive to fine details of the structure of the complex AXL_m as a whole (first of all, to the relative energies of orbitals of A, X, and L), differences in the MIL may prove to be rather remarkable even within series of the most similar compounds.

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Appendix

In order to illustrate some MIL–HVB model conclusions we have performed a number of calculations on complexes AF_6, AHF_5, AH_2F_4, and AF_5 in the framework of the extended Hückel method[40] using the computing program[41] (without the charge iteration). The parameters employed are given in Table IV; some results are collected in Tables V–VII.

Table IV. Parameters Employed in Extended Hückel Calculations

Atom	Orbital	$-H_{ii}$, eV	Slater exponent
A′	3s	20.0	1.83
	3p	11.0	1.83
A″	3s	30.0	2.03
	3p	15.0	2.03
F	2s	40.0	2.425
	2p	18.1	2.425
H	1s	13.6	1.30

Table V. MO's and Their Energies ($-E$, eV)[a]

	AH_2F_4 (D_{4h})		AF_6 (O_h)		AHF_5 (C_{4v})		AF_5 (C_{4v})	
A	MO	$-E$	MO	$-E$	MO	$-E$	MO	$-E$
A′	$2a_{1g}$*	13.76			$3a_1$*	14.33	$3a_1$*	5.32
	b_{1g}	17.64	e_g	17.64	b_1	17.64	b_1	17.64
	e_u	18.72	t_{1u}	18.87	e	18.82	$2a_1$	18.70
	a_{2u}	18.78			$2a_1$	18.83	e	18.82
	$1a_{1g}$	20.46	a_{1g}	20.16	$1a_1$	20.33	$1a_1$	20.20
A″	$2a_{1g}$*	14.52			$3a_1$*	15.28	$3a_1$*	9.38
	b_{1g}	17.64	e_g	17.64	b_1	17.64	b_1	17.64
	e_u	19.37	t_{1u}	19.51	e	19.45	$2a_1$	19.33
	a_{2u}	19.75			$2a_1$	19.58	e	19.45
	$1a_{1g}$	24.41	a_{1g}	23.04	$1a_1$	23.83	$1a_1$	23.47

[a] Assignments of orbitals are in Tables I and II and in Figure 2; parameters are from Table IV.

Table VI. Nodal Structures of Some Occupied MO's of the A_1 Type[a]

		Coeff in LCAO MO[b]				
Complex	MO	s	p_z	σ_1[c]	σ_6	$\sigma_{eq}^{(L)}$[c]
AH_2F_4	$2a_{1g}$*	0.220		0.571	0.571	−0.270
		0.211		0.495	0.495	−0.363
	$1a_{1g}$	0.330		0.127	0.127	0.379
		0.529		0.156	0.156	0.265
AHF_5[d]	$3a_1$*	0.155	−0.260	0.103	0.731	−0.213
		0.133	−0.294	0.211	0.598	−0.296
	$2a_1$	−0.018	0.172	0.089	−0.137	−0.047
		−0.002	0.325	0.152	−0.174	−0.012
	$1a_1$	0.299	−0.061	0.100	0.135	0.365
		0.489	−0.117	0.169	0.175	0.274
AF_5[d]	$3a_1$*	0.495	−0.942	0.214		−0.196
		0.394	−0.878	0.278		−0.264
	$2a_1$	−0.038	0.171	0.557		−0.104
		−0.032	0.320	0.616		−0.082
	$1a_1$	0.297	−0.049	0.349		0.378
		0.500	−0.111	0.262		0.303

[a] Assignments of orbitals are in Tables I and II and in Figure 2. [b] For each coefficient two entries are given, for A′ and A″, respectively (see Table IV). [c] The p_σ orbital of the relevant ligand L. [d] In C_{4v} complexes for the axial interactions L_{ax}–A–X the nodeless combinations correspond to $\sigma_1 + s + \sigma_6$ and $\sigma_1 + p_z - \sigma_6$.

Table VII. Total Overlap Populations of A–F Bonds[a]

Complex	$A-F_{eq}$	$A-F_{ax}$
AF_6 (O_h)	0.279	0.279
	0.356	0.356
AHF_5 (C_{4v})	0.247	0.264
	0.310	0.344
AH_2F_4 (D_{4h})	0.221	
	0.262	

[a] For each bond two entries are given, for A′ and A″, respectively (see Table IV).

The central atom A is considered to be a typical atom of the third period. Two sets of parameters were used (A′ and A″ which approximately simulate S and Cl, respectively). For ligands F and H (as L and X, respectively) the standard parameters have been taken.[30,40] The internuclear distances are R(A–F) = 1.60 Å and R(A–H) = 1.35 Å. For off-diagonal matrix elements the relationship $H_{ij} = 1.75S_{ij}(H_{ii} + H_{jj})$ has been used.

In principle, the σ orbital of any ligand (except H) is a hybrid, so the parameters of this σ orbital are rather ambiguous. Thus, all four fluorine valence orbitals ($2s2p_{xyz}$) have been taken into account and all MO's (both σ and π) have been calculated. The number of these MO's (28, 24, 25, and 22 for AF_6, AF_5, AHF_5, and AH_2F_4, respectively) exceeds greatly the number of σ MO's treated by the model (cf. Tables I and II, Figure 2, and the relevant portions of the text). Nevertheless the "model" σ MO's can be separated with sufficient accuracy (as we hope). MO energies given in Table V justify the MO diagrams shown in Figure 2. The coefficients in the most important LCAO MO's given in Table VI confirm the nodal structures of the MO's (3)–(8) and the relevant arguments in the text. The total overlap populations given in Table VII illustrate a weakening of the A–F_{eq} bonds in the sequence $AF_6 > AHF_5 > AH_2F_4$ (though a strengthening of the A–F_{trans} bond in AHF_5 as compared with AF_6 is not reproduced[19]). There is no illustration concerning the relationship between the A–F bond strength and coupling constant J(A–F) as the program[41] does not give us the separate s population on atoms.

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