Perturbation Theory and the Effects of Substitution in Square and Bipyramidal σ-Bonded Compounds

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Abstract: The effects of substitution of L by L′ in square EL_4 and bipyramidal [trigonal (TB) EL_5, tetragonal (octahedral) EL_6, and pentagonal (PB) EL_7] σ-bonded complexes, for E a transition metal M or main group element A, have been considered in the framework of the perturbation theory of canonical MOs. The difference in ligand σ orbital energies, $\delta\alpha' = \alpha(L') - \alpha(L)$, where $\delta\alpha' > 0$ (<0) correspond to a better donor (acceptor) substituent L′, was taken as a perturbation and all changes in overlap populations of different E–L bonds, $\delta N(\text{E-L})/\delta\alpha'$, were obtained in terms of the ns, np, and $(n-1)$d contributions. It was found that in all transition metal complexes ML_n, the s and d contributions to $\delta N(\text{M-L}_{\text{trans}})/\delta\alpha'$ are always negative and bigger in absolute value than the p one, which is always positive. The s and d contributions to $\delta N(\text{M-L}_{\text{cis}})/\delta\alpha'$ are always of opposite sign, typically the s one positive and the d one negative, so that $\delta N(\text{M-L}_{\text{cis}})$ will be smaller in absolute value than $\delta N(\text{M-L}_{\text{tr}})$ and may be of any sign. The effects of substitution in main group element complexes AL_n strongly depend on the oxidation state of the central atom. The role of π-bonding effects was also briefly discussed. The results obtained agree with experiment and permit the fundamental regularities of substitution, particularly the trans and cis influence, in $EL_{n-k}L_k'$ complexes, to be explained and predicted.

Introduction

Recently we have developed the general analytical LCAO MO approach[2,3] for treating the effects of substitution of L by L′ in *any* chemical compound EL_n; E is a transition metal M or main group element A. In the preceding paper[2] we have considered these effects in linear EL_2 $D_{\infty h}$, trigonal AL_3 D_{3h}, and tetrahedral AL_4 T_d compounds where all the ligands L are geometrically equivalent with respect to the substituent L′ in the $EL_{n-1}L'$ complex. The purpose of the present work is to consider the effects of substitution in complexes where not all the ligands L are equivalent with respect to L′, namely, in square EL_4 D_{4h}, octahedral EL_6 O_h, trigonal EL_5 D_{3h}, and pentagonal EL_7 D_{5h} bipyramidal compounds. As earlier,[2,3] we choose the overlap population N(E–L) as a criterion of the E–L bond strength. Further, we adopt the difference in ligand σ orbital energies, i.e., diagonal matrix elements (Coulomb integrals)

$$\langle \sigma_{L'}|H|\sigma_{L'}\rangle - \langle \sigma_L|H|\sigma_L\rangle = \delta\alpha' \tag{1}$$

as a perturbation, so that, to first order, all changes in N(E–L) for a given ligand L will be (the closed-shell case)

$$\frac{\delta N(\text{E-L})}{\delta\alpha'} = \sum_{\chi}^{\text{s,p,d}} \sum_{i}^{\text{occ}} \sum_{j}^{\text{unocc}} \frac{c_{iL'}c_{jL'}(c_{i\chi}c_{jL} + c_{j\chi}c_{iL})S_{\chi L}}{\epsilon_i - \epsilon_j} \tag{2}$$

Here the LCAO MO coefficients c and energies ϵ are designated by the indexes where χ refers to AOs of the central atom E (χ = s, p, d), i and j to the occupied and vacant canonical MOs, respectively, and $S_{\chi L} = \langle\chi|\sigma_L\rangle$. Finally, for every bonding canonical MO

$$\psi = c_E\chi_E + c_L\theta_L \tag{3}$$

we shall use as its antibonding counterpart

$$\psi^* = c_L\chi_E - c_E\theta_L \tag{4}$$

where χ_E is an AO of the central atom E and θ_L is a symmetry-adapted group orbital formed from the σ_L orbitals, $c_E^2 + c_L^2 = 1$. All the interrelations between the coefficients c_E, c_L, the energies $\epsilon(\psi)$, $\epsilon(\psi^*)$, and other necessary formulas may be found in ref 2 and 3.

Results and Discussion

Square Complexes EL_4 D_{4h}. 16e d^8 ML_4. Let us begin with transition metal complexes d^8 ML_4 where we will consider the effects of substitution of the ligand $L_{(1)}$ on the x axis. The relevant orbitals of the metal M and ligands L may be found in any textbook on quantum chemistry.[4] If we use the proper orthogonalized sd_{z^2} hybrids, namely

$$\phi_1 = \mu s + \nu d_{z^2} \tag{5}$$

$$\phi_2 = \nu s - \mu d_{z^2} \tag{6}$$

$$\left\langle \phi_1 \middle| \frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)\right\rangle = 0 \tag{7}$$

the relevant occupied MOs of ML_4 will be

$$\psi_1 = a(\nu s - \mu d_{z^2}) + b\frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \tag{8}$$

$$\psi_2 = g d_{x^2-y^2} + h\frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) \tag{9}$$

$$\psi_3 = e p_x + f\frac{1}{\sqrt{2}}(\sigma_1 - \sigma_3) \tag{10}$$

The vacant MOs obtained according to (3) and (4) correspond to $\psi_1^* = \psi_5$, $\psi_2^* = \psi_4$, and $\psi_3^* = \psi_6$ with the typical energy order[5]

$$\epsilon(\psi_1) < \epsilon(\psi_2) < \epsilon(\psi_3) < \epsilon(\psi_4) < \epsilon(\psi_5) < \epsilon(\psi_6) \tag{11}$$

Further, we can write

$$f^2 - e^2 > b^2 - a^2 \geq h^2 - g^2 > 0 \tag{12}$$

$$ef < ab \leq gh \tag{13}$$

$$E_{1j} > E_{2j} > E_{3j}, \quad j = 4, 5, 6 \tag{14}$$

To the first order, changes in the M-L_{tr} overlap population will be

$$\begin{aligned}\frac{\delta N(\text{M-L}_{\text{tr}})}{\delta\alpha'} = &-\frac{ab\nu}{4}\left[\left(\frac{f^2}{E_{35}} - \frac{e^2}{E_{16}}\right) + \frac{1}{2}\left(\frac{g^2}{E_{14}} - \frac{h^2}{E_{25}}\right)\right.\\ &\left. + \frac{a^2 - b^2}{2E_{15}}\right] S_s + \frac{ef}{2\sqrt{2}}\left[\frac{f^2 - e^2}{E_{36}} + \frac{1}{2}\left(\frac{g^2}{E_{34}} - \frac{h^2}{E_{26}}\right)\right.\\ &\left. + \frac{1}{2}\left(\frac{a^2}{E_{35}} - \frac{b^2}{E_{16}}\right)\right] S_{p\sigma} - \frac{\sqrt{3}gh}{8}\left[\left(\frac{f^2}{E_{34}} - \frac{e^2}{E_{26}}\right)\right.\\ &\left. + \frac{g^2 - h^2}{2E_{24}} + \frac{1}{2}\left(\frac{a^2}{E_{25}} - \frac{b^2}{E_{14}}\right)\right] S_{d\sigma} - \frac{ab\mu}{8}\left[\left(\frac{f^2}{E_{35}} - \frac{e^2}{E_{16}}\right)\right.\\ &\left. + \frac{1}{2}\left(\frac{g^2}{E_{14}} - \frac{h^2}{E_{25}}\right) + \frac{a^2 - b^2}{2E_{15}}\right] S_{d\sigma}\end{aligned} \tag{15}$$

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Taking into account (12) and (14), we obtain

$$\frac{f^2}{E_{35}} - \frac{e^2}{E_{16}} > \frac{f^2 - e^2}{E_{35}} > \frac{(h^2 - g^2) + (b^2 - a^2)}{2E_{35}} > \frac{h^2 - g^2}{2E_{25}} + \frac{b^2 - a^2}{2E_{15}} > \frac{1}{2}\left(\frac{h^2}{E_{25}} - \frac{g^2}{E_{14}}\right) + \frac{1}{2}\frac{b^2 - a^2}{E_{15}} \quad (16)$$

In the very last step of this chain of inequalities we also used $E_{14} \simeq E_{25}$. From (16) we immediately conclude that the s contribution to $\delta N(\mathrm{M{-}L_{tr}})/\delta\alpha'$ (15) is always negative. Quite similarly we find that the d_σ contributions are also negative but the p_σ one is positive. If we add the relationship

$$\frac{f^2}{E_{35}} - \frac{e^2}{E_{16}} \simeq \frac{f^2}{E_{34}} - \frac{e^2}{E_{26}} > \frac{f^2 - e^2}{E_{36}} \quad (17)$$

we come to the strict conclusion that the negative s and dσ contributions are always bigger in absolute value than the positive pσ contribution. Thus, for a better donor substituent L′ (when $\delta\alpha' > 0$) we can predict a trans weakening.

Similarly, for the $\mathrm{M{-}L_{cis}}$ bond we have

$$\frac{\delta N(\mathrm{M{-}L_{cis}})}{\delta\alpha'} = \frac{ab\nu}{8}\left[\frac{b^2 - a^2}{E_{15}} - \left(\frac{h^2}{E_{25}} - \frac{g^2}{E_{14}}\right)\right] S_\mathrm{s} - \frac{\sqrt{3}gh}{16}\left[\left(\frac{b^2}{E_{14}} - \frac{a^2}{E_{25}}\right) - \frac{h^2 - g^2}{E_{24}}\right] S_{\mathrm{d}\sigma} + \frac{ab\mu}{16}\left[\frac{b^2 - a^2}{E_{15}} - \left(\frac{h^2}{E_{25}} - \frac{g^2}{E_{14}}\right)\right] S_{\mathrm{d}\sigma} \quad (18)$$

The principal difference of (15) from (18) is that the latter does not contain the p contribution, i.e., not only the $S_{\mathrm{p}\sigma}$ terms but also the terms with the coefficients f and e. From (12)-(14) we can anticipate that the s and d contributions will be of opposite sign, the s one typically positive and the d one negative. Thus, $\delta N(\mathrm{M{-}L_{cis}})/\delta\alpha'$ will be smaller in absolute value than $\delta N(\mathrm{M{-}L_{tr}})/\delta\alpha'$ and may be, in principle, of any sign.

The experimental data agree perfectly with our model conclusions. It is well-known that such strong donor ligands as H, $\mathrm{CH_2R}$, or $\mathrm{SiR_3}$ cause a significant lengthening of the $\mathrm{M{-}L_{tr}}$ bonds, by 0.11-0.14 Å, though changing very slightly the $\mathrm{M{-}L_{cis}}$ bond lengths.[6-8] Referring the reader to the relevant reviews[6-8] we would like to stress that in d^8 $\mathrm{ML_4}$ complexes the main changes under substitution always occur along the linear L′-M-L fragment, the trans lengthening for a better donor substituent L′. The cis changes are relatively smaller so that the steric factors can play the decisive role. We shall see below that exactly the same picture is valid for octahedral $\mathrm{ML_6}$ complexes.

$\mathbf{AL_4}$. Main group element complexes $\mathrm{AL_4}$ can have square geometry only if A is not of the highest oxidation state, namely, in 12e complexes of the $\mathrm{Xe^{IV}F_4}$ or $[\mathrm{Te^{II}Cl_4}]^{2-}$ type.[9,10] If we adopt the hypervalent scheme for their structure,[11] i.e., neglect the *n*d orbitals, we reduce (15) and (18) to

$$\frac{\delta N(\mathrm{A{-}L_{tr}})}{\delta\alpha'} = -\frac{abe^2}{4}\left[\frac{1}{E_{56}} - \frac{1}{E_{16}}\right] S_\mathrm{s} - \frac{ef}{2\sqrt{2}}\left[\frac{1}{2}\left(\frac{a^2}{E_{56}} + \frac{b^2}{E_{16}}\right) + \frac{1}{2E_{46}} - \frac{f^2 - e^2}{E_{36}}\right] S_{\mathrm{p}\sigma} \quad (19)$$

$$\frac{\delta N(\mathrm{A{-}L_{cis}})}{\delta\alpha'} \equiv 0 \quad (20)$$

In main group element complexes AL_m the difference $f^2 - e^2 \ll 1$ will be distinctly smaller than in transition metal complexes ML_m[12] (cf. (12)). Thus, taking into account (14), we find that not only the s but also the p_σ contribution to $\delta N(\mathrm{A{-}L_{tr}})/\delta\alpha'$ will be negative. Therefore for a better donor substituent L′ we can foresee a trans weakening which must be relatively more significant than that in transition metal complexes (cf. (15)) where there are terms of opposite signs.

This result represents an explicit proof of the general statement made earlier[13] for the $\mathrm{AL}_{m-k}\mathrm{L}_k{}'$ complexes with the 3o-4e bonding, a result confirmed by all the available experimental data.[10,14] For instance, in the relevant square $\mathrm{Te^{II}}$ complexes, when a phenyl group is one of the ligands, the position opposite to the phenyl group is virtually vacant[10,14] but the cis bond lengths are strikingly insensitive to substitution.

Bipyramidal Complexes $\mathbf{EL}_m$. Considering octahedral complexes $\mathrm{EL_6}$ as the special case of tetragonal bipyramidal ones, one can treat all the bipyramidal complexes, $\mathrm{EL_5}$ D_{3h} (TB), $\mathrm{EL_6}$ O_h, and $\mathrm{EL_7}$ D_{5h} (PB), along similar lines. Such an approach proved to be rather fruitful in considering relative bond strengths in these polyhedra[3] and we shall follow it in the present work.

In both $\mathrm{ML_5}$ and $\mathrm{ML_7}$ complexes there exists the problem of sd_{z^2} mixing within the $\mathrm{A_1}'$ representation. Our previous analysis has shown[3] that the resulting bond strengths in ML_{r+2}, $\mathrm{ML_5}$ and $\mathrm{ML_7}$, are changed only slightly depending on which orthonormalized linear combinations of $\sigma_\mathrm{ax} = (1/\sqrt{2})(\sigma_1 + \sigma_2)$ and $\sigma_\mathrm{eq} = (1/\sqrt{r})(\sigma_3 + \sigma_4 + \ldots + \sigma_{r+2})$, orthogonal to s or d_{z^2}, we use as the basis one. Therefore for our further consideration we choose the linear combinations

$$\theta_1 = \frac{1}{\sqrt{r+2}}(\sigma_1 + \sigma_2 + \ldots + \sigma_{r+2}) \quad (21)$$

$$\theta_2 = \sqrt{\frac{r}{2(r+2)}}(\sigma_1 + \sigma_2) - \sqrt{\frac{2}{r(r+2)}}(\sigma_3 + \sigma_4 + \ldots + \sigma_{r+2}) \quad (22)$$

where θ_2 (22) is orthogonal to s. Such a choice makes all the relationships easier to obtain, in particular, by reducing the transition metal cases to the main group element ones where owing to the hypervalent structure we neglect the d orbital contribution to bonding completely.

Axial Substitution. $\mathbf{(2r + 4)}$e–18e $\mathbf{ML}_{r+2}$. We shall consider the effects of substitution of the ligand $\mathrm{L}_{(1)}$ on the *z* axis. The relevant orbitals can be found in ref 3 and 4.

The occupied MOs of d^0 ML_{r+2} will be

$$\psi_1 = a\mathrm{s} + \frac{b}{\sqrt{r+2}}(\sigma_1 + \sigma_2 + \ldots + \sigma_{r+2}) \quad (23)$$

$$\psi_2 = g\mathrm{d}_{z^2} + h\left[\sqrt{\frac{r}{2(r+2)}}(\sigma_1 + \sigma_2) - \sqrt{\frac{2}{r(r+2)}}(\sigma_3 + \sigma_4 + \ldots + \sigma_{r+2})\right] \quad (24)$$

$$\psi_3 = e\mathrm{p}_z + f\frac{1}{\sqrt{2}}(\sigma_1 - \sigma_2) \quad (25)$$

and their vacant counterparts $\psi_1{}^* = \psi_5$, $\psi_2{}^* = \psi_4$, and $\psi_3{}^* = \psi_6$ are obtained according to (3) and (4). The inequalities (12) and (13) which are typical for any transition metal complex ML_m remain valid.

To first order, we obtain for the $\mathrm{M{-}L_{tr}}$ bond

$$\frac{\delta N(\mathrm{M{-}L_{tr}})}{\delta\alpha'} = -\frac{ab}{\sqrt{r+2}}\left[\frac{1}{2}\left(\frac{f^2}{E_{35}} - \frac{e^2}{E_{16}}\right) + \frac{r}{2(r+2)} \times \left(\frac{g^2}{E_{14}} - \frac{h^2}{E_{25}}\right) + \frac{a^2 - b^2}{(r+2)E_{15}}\right] S_\mathrm{s} + \frac{ef}{\sqrt{2}}\left[\frac{f^2 - e^2}{2E_{36}} + \frac{r}{2(r+2)}\left(\frac{g^2}{E_{34}} - \frac{h^2}{E_{26}}\right) + \frac{1}{r+2}\left(\frac{a^2}{E_{35}} - \frac{b^2}{E_{16}}\right)\right] S_{\mathrm{p}\sigma} - gh\sqrt{\frac{r}{2(r+2)}}\left[\frac{1}{2}\left(\frac{f^2}{E_{34}} - \frac{e^2}{E_{26}}\right) + \frac{r(\mathrm{g}^2 - h^2)}{2(r+2)E_{24}} + \frac{1}{r+2}\left(\frac{a^2}{E_{25}} - \frac{b^2}{E_{14}}\right)\right] S_{\mathrm{d}\sigma} \quad (26)$$

Thus, using the identity

$$\frac{1}{2} \equiv \frac{r}{2(r+2)} + \frac{1}{r+2} \qquad (27)$$

and writing out a chain of the inequalities similar to those in (16) we obtain a strict conclusion that both the s and d_σ contributions to $\delta N(\mathrm{M{-}L_{tr}})/\delta\alpha'$ (26) are negative and bigger in absolute value than the positive p_σ one.

Similarly, for the M–L_{cis} bond we have

$$\frac{\delta N(\mathrm{M{-}L_{cis}})}{\delta\alpha'} = \frac{ab}{(r+2)^{3/2}}\left[\frac{b^2-a^2}{E_{15}} - \left(\frac{h^2}{E_{25}} - \frac{g^2}{E_{14}}\right)\right] S_{\mathrm{s}} - \frac{gh\sqrt{r}}{[2(r+2)]^{3/2}}\left[\left(\frac{b^2}{E_{14}} - \frac{a^2}{E_{25}}\right) - \frac{h^2-g^2}{E_{24}}\right] S_{\mathrm{d}\sigma} \qquad (28)$$

As in the d^8 ML_4 D_{4h} case, we come to the conclusion that the s and d_σ contributions to $\delta N(\mathrm{M{-}L_{cis}})/\delta\alpha'$ will be of opposite sign. Thus, $\delta N(\mathrm{M{-}L_{cis}})/\delta\alpha'$ has to be, as a rule, substantially smaller in absolute value than $\delta N(\mathrm{M{-}L_{tr}})/\delta\alpha'$ and may be of any sign.

In low-spin d^1-d^8 (11e-18e) ML_5, d^1-d^6 (13e-18e) ML_6, and d^1-d^4 (15e-18e) ML_7 complexes the extra electrons occupy the MOs which do not involve the perturbing σ_1' orbital. Thus, the results in question hold for all these complexes. In other words, for axial substitution the regularities of $\delta N(\mathrm{M{-}L_{tr}})$ and $\delta N(\mathrm{M{-}L_{cis}})$ have to be the same for all transition metal complexes.

As for the relevant experimental structural data, the various ML_5L' complexes have been studied most systematically,[6,7,15] the data on ML_4L' complexes are significantly poorer,[16] and ML_6L' complexes are entirely unknown.[17] For octahedral complexes ML_5L' all the available experimental results correspond to the trans influence with the main changes always within the linear fragment L′-M-L, in complete agreement with our model conclusions. Referring the reader to the recent reviews,[6,7,15] we would like to stress again that as $|\delta N(\mathrm{M{-}L_{cis}})/\delta\alpha'|$ must be small, the value and even the sign of $\delta N(\mathrm{M{-}L_{cis}})$ can depend strongly on steric factors, especially in less symmetric complexes. The d^2 $\mathrm{MO^{IV}}$ [19] and $\mathrm{Re^{V}}$ [20] complexes of the $ML_kL'L''_{5-k}$ type are good examples of steric influences.

($2r + 4$)e AL_{r+2}. In this case the central atom A is of the highest oxidation state. Adopting the hypervalent scheme we reduce (26) and (28) to

$$\frac{\delta N(\mathrm{A{-}L_{tr}})}{\delta\alpha'} = \frac{ab}{\sqrt{r+2}}\left[\frac{r}{2(r+2)E_{45}} - \frac{1}{2}\left(\frac{f^2}{E_{35}} - \frac{e^2}{E_{16}}\right) + \frac{b^2-a^2}{(r+2)E_{15}}\right] S_{\mathrm{s}} - \frac{ef}{\sqrt{2}}\left[\frac{r}{2(r+2)E_{46}} - \frac{f^2-e^2}{2E_{36}} + \frac{1}{r+2}\left(\frac{b^2}{E_{16}} - \frac{a^2}{E_{35}}\right)\right] S_{\mathrm{p}\sigma} \qquad (29)$$

$$\frac{\delta N(\mathrm{A{-}L_{cis}})}{\delta\alpha'} = -\frac{ab}{(r+2)^{3/2}}\left[\frac{1}{E_{45}} - \frac{b^2-a^2}{E_{15}}\right] S_{\mathrm{s}} \qquad (30)$$

The value of $\delta N(\mathrm{A{-}L_{cis}})/\delta\alpha'$ is always negative, so for a better donor substituent L′ ($\delta\alpha' > 0$) we can predict with certainty a cis weakening. The analysis of $\delta N(\mathrm{A{-}L_{tr}})/\delta\alpha'$ is more complicated. One can show[21] that the s and p contributions to $\delta N(\mathrm{A{-}L_{tr}})/\delta\alpha'$ will be typically of the opposite signs, the s one positive and the p one negative, but the relative values of each contribution may depend on all components of AL_m, i.e., A, L, and even m. We can foresee that in some $AL_{m-1}L'$ complexes, for $\delta\alpha' > 0$, one might observe a trans strengthening (in contrast to only a trans weakening in 12e AL_4 D_{4h} complexes where A is not of the highest oxidation state). Actually, this effect has been observed in some $\mathrm{Sn^{IV}}$ complexes.[22]

It should be stressed that some ambiguity of model conclusions for $\delta N(\mathrm{A{-}L_{tr}})$ in AL_m complexes where A is of the highest oxidation state only reflects the very complicated reality. Remember that in ML_m complexes the ligand orbitals σ_L usually lie lower than *all* the metal orbitals, ns, np, $(n-1)$d, but in AL_m complexes the ligand orbitals lie typically between the np and ns orbitals of A. Therefore in ML_m the regularities of substitution are simpler and less varied than those in AL_m[13] where they drastically depend on the oxidation state of A and fine details of the relative orbital energies.

Unfortunately, there are too little reliable experimental data to check our predictions. One of the best examples is the recent redetermination of the structure of SF_5Cl[23] where microwave and electron diffraction data have been combined. The S-F_{tr} and S-F_{cis} bonds were found to be lengthened as compared with SF_6 (1.588, 1.566 and 1.561 Å, respectively), the trans one longer than the cis one by 0.02 Å. This prevailing trans lengthening has been explained, however, by steric ("secondary relaxation") effects rather than the electronic ("primary") ones. Thus, there is an urgent need for new experimental and computational data on $AL_{m-1}L'$ complexes for wide ranges of A, L, and L′ to check our model conclusions.

14e AL_6. There are a few known examples of such octahedral complexes [$SbBr_6^{3-}$, AX_6^{2-} (A = Se, Te, X = Cl, Br)[9]] where the central atom A is not in the highest oxidation state. This case is quite similar to the 12e AL_4 one, namely, for a better donor L′ we can foresee a strong trans weakening and insignificant cis changes. Because of a lack of experimental data on substituted $AL_{6-k}L_k'$ complexes this conclusion may be considered as a prediction. We will not consider the similar complexes of the 12e AL_5 and 16e AL_7 type as they do not have the TB and PB forms, respectively.[9]

Equatorial Substitution. We will now consider the effects of substitution of the equatorial ligand $L_{(3)}$ on the x axis. The relevant orbitals are given in ref 3. As the orbitals σ_1 (along the z axis) and σ_3 enter only the MOs ψ_1 (23) and ψ_2 (24), which are the same in our model for both axial and equatorial substitution, the relationships (28) and (30) for $\delta N(\mathrm{E{-}L_{cis}})$ will be the same. In other words, in our model the influence of the ligand $L_{(1)}$ on $L_{(3)}$ will be the same as that of $L_{(3)}$ on $L_{(1)}$. Thus, we need to consider the effects of substitution of the ligand $L_{(3)}$ only on other equatorial ligands, $L_{(4)}$, $L_{(5)}$, etc. As in EL_6 O_h equatorial substitution is equivalent to axial for *all* ligands,[24] only the EL_5 D_{3h} and EL_7 D_{5h} cases are left to discuss.

10e-18e ML_5 and 14e-18e ML_7. The relevant expressions for $\delta N(\mathrm{M{-}L})/\delta\alpha'$ are very cumbersome and include many terms depending on the signs of cos θ where θ are the valence angles. Nevertheless, one can show[21] that for equatorial substitution the changes $\delta N(\mathrm{M{-}L})$ for the equatorial ligands will be larger in absolute value than those for the axial (cis) ligands. We can also foresee one result which is specific to the ML_7 case: for the two equatorial ligands, $L_{(4)}$, $\theta = 72°$, and $L_{(5)}$, $\theta = 144°$, which are nonequivalent to equatorial substitution, the values of $\delta N(\mathrm{M{-}L_{(4)}})$ and $\delta N(\mathrm{M{-}L_{(5)}})$ will be, most probably, of opposite sign, the former positive, the latter negative for a better donor ligand L′. As there are no relevant experimental data on ML_6L' complexes,[17] the above result is a prediction.

The general conclusion about the smaller changes for the axial compared with the equatorial position seems to be valid also for the d^0-d^8 (10e-18e) ML_4L' C_{2v} complexes. Unfortunately, there are no relevant structural experimental data.[16]

10e AL_5 and 14e AL_7. In these cases the central atom A is of the highest oxidation state (otherwise these complexes will not be of the regular bipyramidal forms[9]). For all Al_{r+2} complexes

$$\frac{\delta N(\mathrm{A{-}L_{ax}})}{\delta\alpha'} = -\frac{ab}{(r+2)^{3/2}}\left(\frac{1}{E_{45}} - \frac{b^2-a^2}{E_{15}}\right) S_{\mathrm{s}} \qquad (31)$$

Table I. Signs of the χ Contributions to $\delta N(\text{E–L})/\delta\alpha'$

complex			bond	
parent	substituted	χ	E–L$_{tr}$	E–L(L″)$_{cis}$
d^8 ML$_4$ D_{4h}	ML$_3$L′ C_{2v}, MLL′L″$_2$ C_{2v}	s	–	$+^{a}$
d^0–d^8 ML$_5$ D_{3h}	ML$_4$L′ C_{3v}	p	+	none
d^0–d^6 ML$_6$ O_h	ML$_5$L′ C_{4v}, ML$_3$L′L″$_2$ C_{2v}	d	–	$-^{a}$
d^0–d^4 ML$_7$ D_{5h}	ML$_6$L′ C_{5v}	total	–	$\pm\delta^{b}$
d^0–d^8 ML$_5$ D_{3h}	ML$_4$L′ C_{2v}	s	^{c}	$+^{a}$
d^0–d^4 ML$_7$ D_{5h}	ML$_6$L′ C_{2v}	p		none
		d		$-^{a}$
		total		$\pm\delta^{b}$
12e AL$_4$ D_{4h}	AL$_3$L′ C_{2v}, ALL′L″$_2$ C_{2v}	s	–	none
14e AL$_6$ O_h	AL$_5$L′ C_{4v}, AL$_3$L′L″$_2$ C_{2v}	p	–	none
		total	–	none
10e AL$_5$ D_{3h}	AL$_4$L′ C_{3v}, AL$_3$L′$_2$ $D_{3h}{}^{d}$	s	$+^{a}$	–
12e AL$_6$ O_h	AL$_5$L′ C_{4v}, AL$_3$L′L″$_2$ C_{2v}	p	$-^{a}$	none
14e AL$_7$ D_{5h}	AL$_6$L′ C_{5v}, AL$_5$L′$_2$ $D_{5h}{}^{d}$	total	±	–
10e AL$_5$ D_{3h}	AL$_4$L′ C_{2v}, AL$_3$L′$_2$ C_{2v}	s	^{c}	–
14e AL$_7$ D_{5h}	AL$_6$L′ C_{2v}	p		none
		total		–

[a] The opposite sign is not excluded. [b] The effect is relatively small in absolute value and may be of any sign. [c] The influence of the equatorial substituent L′ on other equatorial ligands L depends on the value of the relevant valence angle θ. See details in the text. [d] In the AL$_3$L$_2$′ and AL$_2$L$_3$′ D_{3h} complexes there exist only the A–L$_{cis}$ bonds, A–L$_{eq}$ and A–L$_{ax}$, respectively. The same holds for the AL$_5$L$_2$′ and AL$_2$L$_5$′ D_{5h} complexes.

which, of course, coincides with $\delta N(\text{A–L}_{cis})$ (30) for the axial substitution. Though the relevant expressions for $\delta N(\text{A–L}_{eq})/\delta\alpha'$ include many terms depending on the valence angles θ, they can be analyzed in explicit form, too.[21]

In AL$_5$ under equatorial substitution, which is typical for a better donor L′ ($\delta\alpha' > 0$),[3,25] $\delta N(\text{A–L}_{ax})$ has only the negative s contribution but $\delta N(\text{A–L}_{eq})$ has typically the negative s and positive p contributions.[21] So $\delta N(\text{A–L}_{ax})$ must always be negative and larger in absolute value than $\delta N(\text{A–L}_{eq})$ which for strongly electronegative ligands L will be negative as well. The experimental data on PF$_4$L′, L′ = H,[26] CH$_3$,[27b] agree with this prediction. From the general properties of 3o-4e bonding it follows[2] that this tendency to weaken the axial A–L bonds must be most distinct in trisubstituted complexes of the PF$_2$(CH$_3$)$_3$ D_{3h} type which again agrees with experiment.[27]

In AL$_7$ the A–L$_{(4)}$ bond corresponds to the valence angle of 72°, close to 90° (A–L$_{cis}$), but the A–L$_{(5)}$ bond corresponds to 144° closer to 180° (A–L$_{tr}$). So, we can foresee that for a given substituent L′, typically, the sign of $\delta N(\text{A–L}_{(4)})$ will be the same as $\delta N(\text{A–L}_{(1)})$ but opposite to $\delta N(\text{A–L}_{(5)})$. The same is true for the signs of the s contributions to these $\delta N(\text{A–L}_i)$ values.

The major conclusions of the present work are summarized in Table I. Certainly, these results can be extended easily to embrace other properties of the E–L bonds besides their strengths (lengths). These aspects have been discussed already for linear ELL′, planar trigonal AL$_{3-k}$L$_k$′, and tetrahedral AL$_{4-k}$L$_k$′ compounds.[2] For instance, a positive sign of the p contribution corresponds to an increase of the E–L bond polarity as the p orbitals are the highest of the valence orbitals. Further, the sign of the s contribution determines the change of the s character of the relevant E–L bond which is directly related to isomer shifts δ_E of the Mössbauer spectra or nuclear spin coupling constants $^1K(\text{E–L})$ of NMR spectra. Such relationships are not trivial, however, especially for $^1K(\text{E–L})$, where the theory[28] predicts, in agreement with experiment, quite different regularities of $^1K(\text{E–L})$ in various EL$_{m-k}$L$_k$′ compounds depending on E, L, L′, and even k.

The important result of the present work (see Table I) is that signs of the s and total contributions to $\delta N(\text{E–L})$ will be the same for M–L$_{tr}$, A(HOS)–L$_{cis}$, and A(NHOS)–L$_{tr}$ but may be opposite for M–L$_{cis}$ and A(HOS)–L$_{tr}$ (HOS and NHOS designate the highest and not the highest oxidation state, respectively). This result removes some apparent contradictions among various correlations between the E–L bond strength and properties such as $^1K(\text{E–L})$, δ_E, etc.[28] As a whole, all such regularities represent the essence of the effects of substitution in any chemical compound which for coordination compounds are usually considered as manifestations of the mutual influence of ligands.[6,7,15]

Comparison with Other Approaches. Our model has been developed in the framework of the perturbation theory of canonical MOs. This theory is widespread in chemistry of organic π electron systems[29] where each atom has only one valence orbital. Attempts to apply this theory to σ-bonded compounds where the central atom uses the s, p, d valence set, to our knowledge, include only two studies.[30,31] First, Baranovsky and Sizova[30] have considered substitution in some square Pt^{II} complexes, changes in the effective charges of the ligands L having been chosen as the criterion of Pt–L bond strength. This criterion is less general than that of the overlap population;[32] in particular, it is especially poor for the A–L bonds in most AL$_m$ compounds.[13] Second, Popov[31] has considered substitution in octahedral complexes EL$_6$ and used the criterion of the overlap population. Popov's approach is rather similar to ours. One of the differences is that we express $\delta N(\text{E–L})/\delta\alpha'$ in terms of the overlap integrals $S_{\chi L} = \langle\chi|\sigma_L\rangle$, χ = s, p, d, for a given ligand L rather than of the group overlap integrals.[31] Besides, we accepted somewhat different approximations while considering the MO energy level scheme in EL$_m$ complexes. There is, however, one peculiarity of our approach which is most important. Popov has considered only the octahedral EL$_6$ case and it is not clear how to apply this approach to less symmetric complexes, for instance, to TB EL$_5$ and PB EL$_7$ ones. Our approach embraces all the polyhedra EL$_m$, with the octahedron EL$_6$ entering as the special case of a bipyramidal complex with equivalent axial and equatorial positions.[33]

On π Bonding Effects. If the M–L bond contains not only a σ but also a π component, the latter will contribute to the substitution effects, too. The problem is usually simplified, however, by the fact that the σ bonding is typically much stronger than the π one. In this case, especially for highly symmetric polyhedra like ML$_6$ O_h or ML$_4$ D_{4h}, where p and d orbitals belong to different irreducible representations, π

bonding involves mainly the d_π metal orbitals, so the π perturbations are eventually reduced to perturbations of the many-center 3o-*n*e bondings (where *n* depends on the occupation numbers of the interacting orbitals) considered in the preceding paper.[2] The L_{tr} contribution will always be larger than the L_{cis} ones because of the structure of the symmetry-adapted π orbitals in ML_m.[4,35] So in ML_5L' for π donors L and vacant d_π metal orbitals we will have typical 3o-4e bondings with a better π donor L′ weakening *all* the perturbed M–L π bonds but mainly the $M{-}L_{tr}$ one.

As the prevailing trans influence remains specific for both σ and π perturbations, something new can be expected *only if* the σ and π contributions are of opposite sign, the latter being larger in absolute value. General regularities of the mutual influence of ligands with multiple metal–ligand bonds have been considered elsewhere.[15]

Conclusion

The approach developed in the present and preceding[2] works represents an attempt to apply the perturbation theory of canonical MOs to the effects of substitution in main polyhedra EL_m. The value of the approach in question is, first of all, that it uses simple, justifiable initial assumptions and treats all complexes EL_m in the framework of substantially the same formalism. The effects are formulated in terms which can be computed directly (as the overlap population is) and can be easily compared with molecular orbital calculations and experiment. We saw that the agreement with the results is very encouraging. In particular, both similarities and differences in substitution in transition metal and main group element complexes as well as the dependences of the effects on the nature of E, L, and L′ can be understood. The understanding of the regularities permits, in turn, the far extrapolations to be made, which is especially important for unknown or scarcely studied compounds. In total, the approach in question, in spite of its simplicity, proves to be rather effective and can stimulate new researches.[36]

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