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(30) For the d^{10} systems $CdCl_5^{3-}$ and more strikingly $HgCl_5^{3-}$, the axial bond lengths are shorter than the equatorial. Shustorovich[15] has rationalized this nicely on the basis of sd mixing (rather than the sp mixing we treat here) by use of his perturbation theory approach.[15]

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Perturbation Approach to the Substitution Effects in σ-Bonded Coordination Compounds

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An analytical approach, in the framework of the perturbation theory of canonical LCAO MO's, to the effects of substitution of L by L′ in various σ-bonded coordination compounds, EL_m (E is a transition metal M or main group element A, m = 4-7), has been developed. The compounds in question include the square EL_4, octahedral EL_6, trigonal EL_5, and pentagonal EL_7 bipyramidal complexes. The difference in 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 changes in overlap population of all the nonequivalent E–L bonds, $\delta N(E\text{–}L)/\delta\alpha'$, were obtained in terms of the ns, np, and (n − 1)d contributions. It was found that in all transition-metal complexes, ML_m, the s and d contributions to $\delta N(M\text{–}L_{tr})/\delta\alpha'$ (tr = trans) are always negative and bigger in absolute value than the p one which is always positive. The s and d contributions to $\delta N(M\text{–}L_{cis})/\delta\alpha'$ are always of opposite sign, typically the s one positive and the d one negative, so that $\delta N(M\text{–}L_{cis})$ will be smaller in absolute value than $\delta N(M\text{–}L_{tr})$ and may be of any sign. The effects of substitution in the main-group element complexes AL_m, for which the hypervalent structure (with only ns and np valence orbitals) has been assumed, strongly depend on the oxidation state of the central atom. If A is of the highest oxidation state, under axial substitution the s and p contributions to $\delta N(A\text{–}L_{tr})/\delta\alpha'$ are typically of opposite sign, the s one positive and the p one negative. The relative values of these contributions and the resulting sign of $\delta N(A\text{–}L_{tr})/\delta\alpha'$ can depend not only on the nature of A and L but also on the type of polyhedra, AL_m. At the same time, for all AL_m polyhedra, the only contribution to $\delta N(A\text{–}L_{cis})/\delta\alpha'$, the s one, is always negative. If A is not of the highest oxidation state, both the s and p contributions to $\delta N(A\text{–}L_{tr})/\delta\alpha'$ are always negative, but $\delta N(A\text{–}L_{cis})/\delta\alpha' \equiv 0$. Under equatorial substitution, specifically for EL_5 and EL_7 complexes, the regularities for $\delta N(E\text{–}L_{cis})/\delta\alpha'$ remain the same as those under axial substitution, but the regularities for $\delta N(E\text{–}L_{eq})/\delta\alpha'$ prove to be even more varied than those for $\delta N(E\text{–}L_{tr})/\delta\alpha'$. In particular, in pentagonal-bipyramidal EL_7 complexes, the values of $\delta N(E\text{–}L_\theta)/\delta\alpha'$ for two nonequivalent equatorial ligands L_θ (forming valence angles $\theta = 2\pi/5$ and $4\pi/5$ with L′) may be of opposite sign. The role of π-bonding effects is also briefly discussed. The results obtained explain the nature and peculiarities of the fundamental substitution effects, particularly the trans and cis influence, and permit a number of predictions for scarcely studied compounds, specifically $AL_{m-k}L'_k$, to be made.

Introduction

All the possible polyhedra EL_m can be divided into two groups depending on the existence, or lack, of the geometrical equivalence of the $m - 1$ ligands L with respect to the substituent L′ in the $EL_{m-1}L'$ complex. The first group where all ligands L are equivalent include linear ELL′, planar-trigonal EL_2L' and tetrahedral EL_3L' compounds. The second group where not all the ligands L are equivalent include square EL_3L', octahedral EL_5L', trigonal-bipyramidal (TB) EL_4L' and pentagonal-bipyramidal (PB) EL_6L' complexes. The effects of substitution in complexes of the first group are the same for each L, and we have already considered this problem in another paper.[1] The purpose of the present work is to consider the effects of substitution in complexes of the second group.[2] The different geometrical positions in the polyhedra in question are shown in Figure 1. As earlier,[1-3] we choose the overlap population N(E–L) as a criterion of the E–L bond strength. Further, we adopt the difference in diagonal matrix elements (ligand σ-orbital energies)

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

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)

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

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

$$\psi = c_E\chi_E + c_L\theta_L \qquad (3)$$

we shall use as its antiboding counterpart

$$\psi^* = c_L\chi_E - c_E\theta_L \qquad (4)$$

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 and c_L, the energies $\epsilon(\psi)$ and $\epsilon(\psi^*)$, and other necessary formulas may be found in ref 1 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 shall consider

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Table I. Assignment of Orbitals in Some O_h and D_{4h} Complexes[a]

pt grp of symmetry	comp	irreducible representn	orbitals[b] E	L	L′
O_h	EL_6	A_{1g}	s	$(1/6^{1/2})(\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6)$	
		E_g	d_{z^2}	$(1/3^{1/2})(\sigma_1+\sigma_2)-(1/2(3^{1/2}))(\sigma_3+\sigma_4+\sigma_5+\sigma_6)$	
		T_{1u}	p_z	$(1/2^{1/2})(\sigma_1-\sigma_2)$	
D_{4h}	$EL_4L'_2$ EL_4	A_{1g}	s d_{z^2}	$^1/_2(\sigma_3+\sigma_4+\sigma_5+\sigma_6)$	$(1/2^{1/2})(\sigma_1+\sigma_2)$
		B_{1g}	$d_{x^2-y^2}$	$^1/_2(\sigma_3-\sigma_4+\sigma_5-\sigma_6)$	
		E_{1u}	p_x	$(1/2^{1/2})(\sigma_3-\sigma_4)$	

[a] Enumeration and designation of ligands are shown in Figures 1 and 2. [b] Only the group ligand orbitals including the perturbing orbital σ'_i are given (see the text).

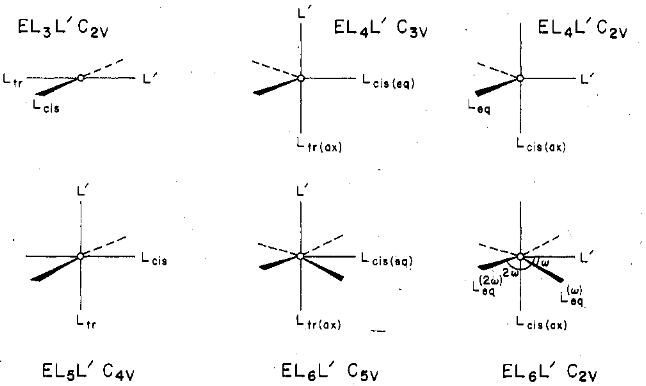

Figure 1. Different geometrical positions in monosubstituted $EL_{m-1}L'$ complexes.

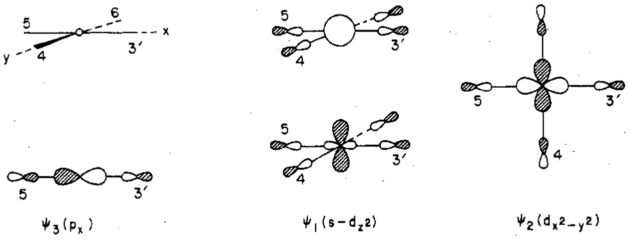

Figure 2. Substitution in square d^8 ML_4 complexes (L′ enters the L(3) position). The metal–ligand interactions for the occupied bonding MO's ψ_1, ψ_2, and ψ_3 are shown (see explanations in the text).

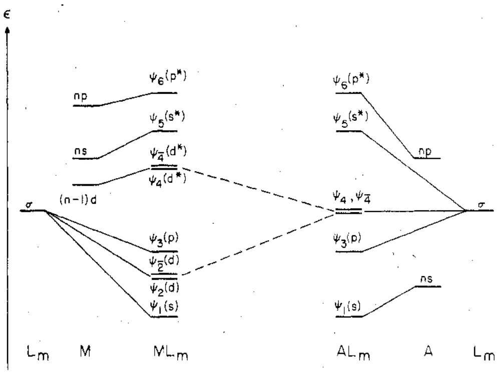

Figure 3. Molecular orbital energy level scheme for EL_m complexes (see explanations in the text).

the effects of substitution of the ligand L(3) (Figure 2). The relevant orbitals of the metal M and ligand L are given in Table I. We can reduce the 3 × 3 determinant of the A_1 representation to 2 × 2 and 1 × 1 ones if we use the proper orthogonalized sd_{z^2} hybrids (eq 5–7). Thus, the relevant

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

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

$$\langle \phi_1 | {}^1\!/_2(\sigma_3+\sigma_4+\sigma_5+\sigma_6)\rangle = 0 \tag{7}$$

occupied MO's of ML_4 will be given by eq 8–10. The vacant

$$\psi_1 = a(\nu s - \mu d_{z^2}) + b(1/2)(\sigma_3+\sigma_4+\sigma_5+\sigma_6) \tag{8}$$

$$\psi_2 = g d_{x^2-y^2} + h(1/2)(\sigma_3-\sigma_4+\sigma_5-\sigma_6) \tag{9}$$

$$\psi_3 = e p_x + f(1/2^{1/2})(\sigma_3-\sigma_5) \tag{10}$$

MO's 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[4,5]

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

as shown in Figure 3. The coefficients μ and ν ($\mu^2 + \nu_2 = 1$) in ψ_1 and ψ_5 may be found from (7), namely

$$\frac{\mu}{\nu} = -\frac{\langle d_{z^2}|\sigma_3\rangle}{\langle s|\sigma_3\rangle} \equiv \frac{S_{d\sigma}}{2S_s} \tag{12}$$

Thus, typically $\mu < \nu$ though μ and ν are substantially of the same order. Further, we can write eq 13–15 which reflect the

$$f^2 - e^2 > b^2 - a^2 \geq h^2 - g^2 > 0 \tag{13}$$

$$ef < ab \leq gh \tag{14}$$

$$E_{1j} > E_{2j} > E_{3j} \qquad j = 4, 5, 6 \tag{15}$$

relative energies of the *n*s, *n*p, $(n-1)$d orbitals, group ligand σ orbitals, and the resulting MO's of the complex ML_4.[6]

To the first order, changes in the $M\text{–}L_{tr}$ overlap population (tr = trans) will be as in eq 16. Here the main terms are

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

f^2/E_{34} and f^2/E_{35} as f is the biggest coefficient and E_{34} and E_{35} are the smallest excitation energies. Taking into account (13), we obtain (17). In the very last step of this chain of

$$\frac{f^2}{E_{35}} - \frac{e^2}{E_{16}} > \frac{f^2-e^2}{E_{35}} > \frac{(h^2-g^2)+(b^2-a^2)}{2E_{35}} > \frac{h^2-g^2}{2E_{25}} + \frac{b^2-a^2}{2E_{15}} > \frac{1}{2}\left(\frac{h^2}{E_{25}} - \frac{g^2}{E_{14}}\right) + \frac{1}{2}\,\frac{b^2-a^2}{E_{15}} \tag{17}$$

inequalities we also used $E_{14} \simeq E_{25}$. From (17) we immediately conclude that the s contribution to $\delta N(\mathrm{M-L_{tr}})/\delta\alpha'$ (eq 16) 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 of eq 18, we come to the strict conclusion that the negative s and dσ contributions are always bigger in absolute value than the positive pσ contribution.

$$\frac{f^2}{E_{35}} - \frac{e^2}{E_{16}} \simeq \frac{f^2}{E_{34}} - \frac{e^2}{E_{26}} > \frac{f^2 - e^2}{E_{36}} \qquad (18)$$

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 eq 19. The principal difference of (16) from (19)

$$\frac{\delta N(\mathrm{M-L_{cis}})}{\delta\alpha'} = \frac{ab\nu}{8}\left[\frac{b^2 - a^2}{E_{15}} - \left(\frac{h^2}{E_{25}} - \frac{g^2}{E_{14}}\right)\right]S_{\mathrm{s}} - \frac{(3^{1/2})gh}{16}\left[\left(\frac{b^2}{E_{14}} - \frac{a^2}{E_{25}}\right) - \frac{h^2 - g^2}{E_{24}}\right]S_{\mathrm{d}\sigma} + \frac{ab\mu}{16}\left[\frac{b^2 - a^2}{E_{15}} - \left(\frac{h^2}{E_{25}} - \frac{g^2}{E_{14}}\right)\right]S_{\mathrm{d}\sigma} \qquad (19)$$

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 (13)–(15) we can anticipate that the s and d contributions will be of opposite sign, the s one typically positive and the d one negative. Please note that in (16) both d contributions are negative but in (19) the d contribution from $d_{x^2-y^2}$ is major and negative but the d one from d_{z^2} is minor and positive, exactly as the positive s contribution. 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.

All these predictions from our model are confirmed by the extended Hückel method (EHM) calculations on the hypothetical model complexes NiH_4^{2-} and NiH_3X^{2-}[7] (Table II).

The experimental data also agree with our model conclusions. It is well-known that such strong ligands as H, CH_2R, or 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.[8-10] True, the mentioned lengthening typically takes place in complexes of Ni^{II}, Pd^{II}, and Pt^{II} like MD_2LL' where D = PR_3 or other neutral donor ligands.[8-10] However, one can show that our conclusion about δN(M–L) in ML_4 D_{4h} remains the same for $ML_2L'_2$ D_{2h}.[11] Referring the reader to the relevant reviews,[8-10] we shall discuss only a few examples (Table III).

In *trans*-$PtCl_2(PR_3)_2$[14] the Pt–Cl distance is shorter by 0.03 Å than the "standard" one.[12] It is tempting to consider this shortening as the cis strengthening for $\delta\alpha' > 0$ by such a strong donor ligand as PR_3 which usually causes a rather distinct trans lengthening, for instance, by 0.06 Å in *cis*-$PtCl_2(PR_3)_2$.[15] A similar conclusion appears from comparison with *trans*-$Pt(H)Cl(PR_3)_2$[16] where the H ligand causes a very large trans lengthening of the Pt–Cl bond by 0.11 Å, and the Pt–P bond lengths are shorter by 0.03 Å than those in *trans*-$PtCl_2(PR_3)_2$.[14] One should be very cautious here, however, because these cis shortenings may be mainly caused by steric factors due to distinct angular deformations.[14-17] Actually, in *trans*-$Pt(CH_2R)Cl(PR_3)_2$,[18] where the CH_2R ligand is much closer in size to Cl and P than H, the trans lengthening of the Pt–Cl bond proves to be the same (0.11 Å), but there is practically no cis shortening of the Pt–P bond.

These examples clearly show that in d^8 ML_4 complexes, the main changes under substitution 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 ML_6 complexes.

Table II. Changes in Overlap Populations of the E–H Bonds[a,b]

			bond	
comp	symmetry	X	$\mathrm{E-H_{ax(tr)}}$	$\mathrm{E-H_{eq(cis)}}$
NiH_3X^{2-}	C_{2v}	s	0.0047	−0.0047
		p	−0.0052	0.0
		d	0.0059	0.0036
		tot	0.0053	−0.0011
CrH_5X^{6-}	C_{4v}	s	0.0012	−0.0017
		p	−0.0032	0.0
		d	0.0053	0.0013
		tot	0.0033	−0.0004
FeH_4X^{5-}	C_{3v}	s	0.0026	−0.0028
		p	−0.0058	0.0
		d	0.0082	0.0017
		tot	0.0049	−0.0011
SH_5X	C_{4v}	s	−0.0059	0.0048
		p	0.0002	0.0
		tot	−0.0057	0.0048
PH_4X	C_{3v}	s	−0.0065	0.0039
		p	0.0080	0.0
		tot	0.0015	0.0039

[a] Table contains the values of ΔN(E–H), the difference in N(E–H) for the axially substituted $EH_{m-1}X$ and the parent EH_m compounds. [b] In these EHM calculations[7] the perturbation consisted of lowering the H_{ii} of one of the hydrogens (X) from −13.6 to −14.6 eV. This perturbation corresponds in our model to the $\delta\alpha' < 0$ case. This should be borne in mind while comparing these results with model predictions.

Table III. Bond Distances in Some Square Complexes

	dist, Å		
comp[a]	E–L	E–L′	ref
$[PtCl_4]^{2-}$	2.32 (Cl)		*b*
trans-$PtCl_2(NH_3)_2$	2.32 (Cl)	2.05 (N)	*c*
cis-$PtCl_2(NH_3)_2$	2.33 (Cl)	2.01 (N)	*c*
trans-$PtCl_2(PR_3)_2$	2.29 (Cl)	2.30 (P)	*d*
cis-$PtCl_2(PR_3)_2$	2.37 (Cl)	2.25 (P)	*e*
trans-$Pt(H)Cl(PR_3)_2$	2.42 (Cl)	2.27 (P)	*f*
trans-$Pt(CH_2R)Cl(PR_3)_2$	2.42 (Cl)	2.29 (P)	*g*
$[Te(tu)_4]^{2+}$	2.69 (S)		*h*
trans-$Te(etu)_2Br_2$	2.69 (S)	2.78 (Br)	*i*
trans-$Te(etu)_2I_2$	2.69 (S)	2.97 (I)	*i*
trans-$Te(etu)_2(SeCN)_2$	2.68 (S)	2.81 (Se)	*j*
trans-$Te(tu)_2(S_2O_2CH_3)_2$	2.67 (S)[l]	2.68 (S)	*k*
trans-$Te(etu)_2(S_2O_2CH_3)_2$	2.66 (S)[l,m]	2.69 (S)	*j*
	2.69 (S)[l,n]	2.69 (S)	*j*
trans-$Te(tu)_2(C_6H_5)Cl$[p]	2.68 (S)[q]	3.61 (Cl)	*o*

[a] tu = thiourea; etu = ethylenethiourea. [b] R. H. B. Mais, P. G. Owston, and A. M. Wood, *Acta Crystallogr., Sect. B*, **28**, 393 (1972). [c] G. H. W. Milburn and M. R. Truter, *J. Chem. Soc. A*, 1609 (1966). [d] Reference 14. [e] Reference 15. [f] Reference 16. [g] Reference 18. [h] K. Fosheim, O. Foss, A. Scheie, and S. Solheimsnes, *Acta. Chem. Scand.*, 19, 2336 (1965). [i] O. Foss, H. M. Kjöge, and K. Maröy, *ibid.*, 19, 2349 (1965). [j] Reference 20. [k] O. Foss, K. Maröy, and S. Husebye, *Acta Chem. Scand.*, 19, 2361 (1965). [l] Te–tu or Tu–etu bonds. [m] Triclinic dimorph. [n] Monoclinic dimorph. [o] O. Foss and K. Maröy, *Acta Chem. Scand.*, **20**, 123 (1966). [p] The phenyl group causes the exceptionally large trans (Cl) lengthening but in averaging only slightly influences the cis ligands. [q] The average from 2.61 and 2.74 Å.

AL_4. Main-group element complexes AL_4, where A is of the highest oxidation state, contain eight valence electrons and therefore have tetrahedral geometry.[19] The effects of substitution in tetrahedral $AL_{4-k}L'_k$ compounds have been considered earlier.[1] The square geometry of AL_4 can be realized *only if* there exist two neutral donor ligands, D, attached along the z axis resulting in a hexacoordinated complex, AL_4D_2 D_{4h}. We shall consider this case in the next section along with other octahedral complexes of the form AL_6.

Main-group element complexes of the form AL_4 can have square geometry, however, if A is not of the highest oxidation state, namely, in 12e complexes of the $Xe^{IV}F_4$ or $[Te^{II}Cl_4]^{2-}$ type.[19,20] If we adopt the hypervalent scheme for their structure[21] i.e., neglect the *n*d orbitals, we have eq 20–23. As

$$\mu = 0, \nu = 1 \tag{20}$$

$$g = 0, h = 1 \tag{21}$$

$$\psi_2 = \psi_2^* \tag{22}$$

$$\psi_2 = \psi_2^* = \psi_4 = \tfrac{1}{2}(\sigma_3 - \sigma_4 + \sigma_5 - \sigma_6) \tag{23}$$

there is no MO ψ_2 and the MO's ψ_4 and ψ_5 are occupied, only the E_{i6} transitions remain. Finally, we have to drop all the $S_{d\sigma}$ terms. Thus, we obtain eq 24 and 25 from (16) and (19).

$$\frac{\delta N(\mathrm{A{-}L_{tr}})}{\delta\alpha'} = -\frac{abe^2}{4}\left[\frac{1}{E_{56}} - \frac{1}{E_{16}}\right]S_s - \frac{ef}{2(2^{1/2})}\left[\frac{1}{2}\left(\frac{a^2}{E_{56}} + \frac{b^2}{E_{16}}\right) + \frac{1}{2E_{46}} - \frac{f^2 - e^2}{E_{36}}\right]S_{p\sigma} \tag{24}$$

$$\delta N(\mathrm{A{-}L_{cis}})/\delta\alpha' \equiv 0 \tag{25}$$

In main-group element complexes, AL_m, the difference $f^2 - e^2 \ll 1$ will be distinctily smaller than in transition-metal complexes, ML_m[22] (cf. (13)). Thus, taking into account (15), we find 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. (16)) where there are terms of opposite signs.

Again, the relevant experimental data on square AL_4 complexes have been obtained mainly for the $AL_2L'_2$ D_{2h} and $ALL''L'_2$ C_{2v} ones,[20] but our model conclusions for AL_4 D_{4h} remain valid for them[11] and, moreover, cannot be obscured by steric factors. The fact is that the hypervalent structure of the $AL_{4-k}L'_k$ complexes makes them very resistant to angular deformations[23] so that the valence angles L–A–L′, for instance, in different complexes of Te^{II}, have practically the "ideal" values of 90 and 180°[20] (unlike the distinct deviations from these values in complexes of Ni^{II}, Pd^{II}, and Pt^{II}[8-11,14-18]).

This result represents an explicit proof of the general statement made earlier[25] for the $AL_{m-k}L'_k$ complexes with the three orbital–four electron bonding, a result confirmed by all the available experimental data.[20,26] Some examples of *trans*-TeL_2D_2 complexes are given in Table III. They show that the cis bond lengths are strikingly insensitive to substitution. As for the trans changes, one need mention only one example. Though divalent, tellurium most often forms four-coordinated square-planar complexes; when a phenyl group is one of the ligands, the position opposite to the phenyl group is virtually vacant.[20,26] This situation is similar to the trans influence of the most strongly (multiply) bonded ligands, $O\overset{\rightarrow}{=}$ and $N\equiv$, in some transition-metal compounds, for instance, the tetragonal-pyramidal complexes $VO(acac)_2^+$[27] and $OsNCl_4^-$.[28]

Bipyramidal Complexes, EL_m. Considering octahedral complexes of the form EL_6 as the special case of tetragonal-bipyramidal ones, one can treat all the bipyramidal complexes, EL_5 D_{3h} (TB), EL_6 O_h, and 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. Thus, we shall consider one by one the axial and equatorial substitutions in these bipyramidal complexes.

Table IV. Assignment of Orbitals in EL_5 D_{3h} and EL_7 D_{5h} Complexes[a]

comp	irreduc repre-sentn	orbitals[b] E	orbitals[b] L
EL_5	A'_1	s	$(1/5^{1/2})(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5)$
		d_{z^2}	$(3/10)^{1/2}(\sigma_1 + \sigma_2) - (2/15)^{1/2}\cdot(\sigma_3 + \sigma_4 + \sigma_5)$
	A''_2	p_z	$(1/2^{1/2})(\sigma_1 - \sigma_2)$
	E'	p_x $d_{x^2-y^2}$	$(1/6^{1/2})(2\sigma_3 - \sigma_4 - \sigma_5)$
EL_7	A'_1	s	$(1/7^{1/2})(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6 + \sigma_7)$
		d_{z^2}	$(5/14)^{1/2}(\sigma_1 + \sigma_2) - (2/35)^{1/2}\cdot(\sigma_3 + \sigma_4 + \sigma_5 + \sigma_6 + \sigma_7)$
	A''_2	p_z	$(1/2^{1/2})(\sigma_1 - \sigma_2)$
	E'_1	p_x	$(2/5)^{1/2}(\sigma_3 + \sigma_4(\cos 2\pi/5) + \ldots + \sigma_7(\cos 8\pi/5))$
	E'_2	$d_{x^2-y^2}$	$(2/5)^{1/2}(\sigma_3 + \sigma_4(\cos 4\pi/5) + \ldots + \sigma_7(\cos 16\pi/5))$

[a] Designation of ligands is shown in Figure 1. [b] Only the group ligand orbitals including the perturbing orbitals σ'_1 (axial substitution) or σ'_3 (equatorial substitution) are given.

In both ML_5 and ML_7 complexes there exists the problem of sd_{z^2} mixing within the A'_1 representation (see Table IV). Our previous analysis has shown[3] that the resulting bond strengths in ML_{r+2}, ML_5 and ML_7, are changed only slightly depending on which ortho-normalized linear combinations of $\sigma_{ax} = (1/(2^{1/2}))(\sigma_1 + \sigma_2)$ and $\sigma_{eq} = (1/(r^{1/2}))(\sigma_3 + \sigma_4 + \ldots + \sigma_{r+2})$, orthogonal to s or d_{z^2}, we use as the basis one. Therefore, for our further consideration we choose the linear combinations (26) and (27) where θ_2 (27) is orthogonal to s.

$$\theta_1 = (1/(r+2)^{1/2})(\sigma_1 + \sigma_2 + \ldots + \sigma_{r+2}) \tag{26}$$

$$\theta_2 = \left(\frac{r}{2(r+2)}\right)^{1/2}(\sigma_1 + \sigma_2) - \left(\frac{2}{r(r+2)}\right)^{1/2}(\sigma_3 + \sigma_4 + \ldots + \sigma_{r+2}) \tag{27}$$

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 due to the hypervalent structure we neglect the d-orbital contribution to bonding completely.

Axial Substitution. $(2r+4)$e–18e ML_{r+2}. We shall consider the effects of substitution of the ligand L(1). The relevant orbitals are given in Tables I and IV. Having taken into account (26)–(27), the occupied MO's of d^0 ML_{r+2} will be as shown in (28)–(30), and their vacant counterparts $\psi_1^* = \psi_5$,

$$\psi_1 = as + (b/(r+2)^{1/2})(\sigma_1 + \sigma_2 + \ldots + \sigma_{r+2}) \tag{28}$$

$$\psi_2 = gd_{z^2} + h\left[\left(\frac{r}{2(r+2)}\right)^{1/2}(\sigma_1 + \sigma_2) - \left(\frac{2}{r(r+2)}\right)^{1/2}(\sigma_3 + \sigma_4 + \ldots + \sigma_{r+2})\right] \tag{29}$$

$$\psi_3 = ep_z + f(1/2^{1/2})(\sigma_1 - \sigma_2) \tag{30}$$

$\psi_2^* = \psi_4$, and $\psi_3^* = \psi_6$ are obtained according to (3) and (4). The inequalities (13) and (14) which are typical for any transition-metal complex, ML_m, remain valid.[29] The MO energy level scheme is shown in Figure 3.

To first order, we obtain eq 31 for the M–L_{tr} bond. Thus, using the identity of eq 32 and writing out a chain of the

$$\frac{\delta N(\mathrm{M{-}L_{tr}})}{\delta\alpha'} = -\frac{ab}{(r+2)^{1/2}}\left[\frac{1}{2}\left(\frac{f^2}{E_{35}} - \frac{e^2}{E_{16}}\right) + \frac{r}{2(r+2)}\left(\frac{g^2}{E_{14}} - \frac{h^2}{E_{25}}\right) + \frac{a^2-b^2}{(r+2)E_{15}}\right]S_{\mathrm{s}} + \frac{ef}{2^{1/2}}\left[\frac{f^2-e^2}{2E_{36}} + \frac{r}{2(r+2)}\left(\frac{g^2}{E_{34}} - \frac{h^2}{E_{26}}\right) + \frac{1}{r+2}\left(\frac{a^2}{E_{35}} - \frac{b^2}{E_{16}}\right)\right]S_{\mathrm{p}\sigma} - gh\left(\frac{r}{2(r+2)}\right)^{1/2}\left[\frac{1}{2}\left(\frac{f^2}{E_{34}} - \frac{e^2}{E_{26}}\right) + \frac{r(g^2-h^2)}{2(r+2)E_{24}} + \frac{1}{r+2}\left(\frac{a^2}{E_{25}} - \frac{b^2}{E_{14}}\right)\right]S_{\mathrm{d}\sigma} \quad (31)$$

$$\frac{1}{2} \equiv \frac{r}{2(r+2)} + \frac{1}{r+2} \quad (32)$$

inequalities similar to those in (17), we obtain a strict conclusion that both the s and d_σ contributions to $\delta N(\mathrm{M{-}L_{tr}})/\delta\alpha'$ (31) are negative and bigger in absolute value than the p_σ one. The conclusion in question is only strengthened by relationship (33) [between the coefficients before the relevant square brackets in (31)]

$$\frac{ab}{(r+2)^{1/2}} + gh\left(\frac{r}{2(r+2)}\right)^{1/2} \gg \frac{ef}{2^{1/2}} \quad (33)$$

as

$$ab \simeq gh > ef \quad (14)$$

and

$$\frac{1}{(r+2)^{1/2}} + \left(\frac{r}{2(r+2)}\right)^{1/2} > \frac{1}{2^{1/2}} \quad (34)$$

Similarly, for the $\mathrm{M{-}L_{cis}}$ bond we have eq 35. As in the

$$\frac{\delta N(\mathrm{M{-}L_{cis}})}{\delta\alpha'} = \frac{ab}{(r+2)^{3/2}}\left[\frac{b^2-a^2}{E_{15}} - \left(\frac{h^2}{E_{25}} - \frac{g^2}{E_{14}}\right)\right]S_{\mathrm{s}} - \frac{gh(r)^{1/2}}{[2(r+2)]^{3/2}}\left[\left(\frac{b^2}{E_{14}} - \frac{a^2}{E_{25}}\right) - \frac{h^2-g^2}{E_{24}}\right]S_{\mathrm{d}\sigma} \quad (35)$$

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. Besides, comparison of (35) with (31) shows that we have not only smaller differences in the square brackets but the coefficients before them are also distinctly smaller, by $(r+2)^{-1}$ and $[2(r+2)]^{-1}$, respectively. Thus, $\delta N(\mathrm{M{-}L_{cis}})/\delta\alpha'$ has to be, as a rule, substantially smaller in absolute value than $\delta N(\mathrm{M{-}L_{tr}})/\delta\alpha'$.

In low-spin d^1–d^8 (11–18e) ML_5, d^1–d^6 (13–18e) ML_6, and d^1–d^4 (15–18e) ML_7 complexes the extra electrons occupy the MO's 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.

The above conclusions are entirely confirmed, for instance, by the EHM calculations on the model 18e complexes, CrH_6^{6-}, CrH_5X^{6-}, and FeH_5^{5-}, FeH_4X^{5-} [7] (see Table II). Here, as for the 16e square complexes NiH_4^{2-} and NiH_3X^{2-}, for a better acceptor substituent, X ($\delta\alpha' < 0$), there has been found a trans strengthening but a cis weakening, the former several times larger than the latter. Again, the s and d contributions to $\delta N(\mathrm{M{-}L_{tr}})$ are of the same sign (positive), but the p one is of the opposite sign (negative). The s and d contributions to $\delta N(\mathrm{M{-}L_{cis}})$ are of opposite sign, however, the s one negative and the d one positive.

As for the relevant experimental structural data, the various ML_5L' complexes have been studied most systematically,[8,9,13] the data on ML_4L' complexes are significantly poorer,[31] and ML_6L' complexes are entirely unknown.[32] Among the known ML_4L' compounds, perhaps, the most suitable examples are the series of the 18e, d^8, $MH(PR_3)_4$, C_{3v} complexes, $CoH(PF_3)_4$,[34] $CoH[PPh(OEt)_2]_4$,[35] and $RhH(PPh_3)_4$.[36] In all the cases there exist serious angular deformations resulting in the almost tetrahedral group MP_4, so there is little sense in comparing with the "ideal" TB geometry. It is worthwhile to mention, however, that in $CoH[PPh(OEt)_2]_4$,[35] the only complex among the three where the position of H has been found and where the valence angles P_{ax}–Co–P_{eq} are the smallest on average, the axial Co–P bond is longer than any of the equatorial Co–P bonds (2.128 and 2.103, 2.115, 2.126 Å, respectively). As in the "ideal" d^8, ML_5, TB complexes, the axial bonds must be shorter or at least equal to the equatorial ones,[3,37] such a trans lengthening can be considered a consequence of substitution.

As for the 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,[8,9,13,38] we shall give only a few expressive examples (see Table V). Here, as in the above case of square complexes ML_4–$MLL'L''_2$, we shall use the data on the various substituted complexes ML_5L'–$ML_kL'L''_{5-k}$.[11] Further, we include the data on the multiply bonded ligands L′ ($N\equiv$, $O\overset{\rightarrow}{=}$, $M\overset{4}{-}$) because the multiple $M\overset{\cdot\cdot}{-}L'$ bonds have short lengths and therefore strong σ components. The values of $N(\mathrm{M{-}L})$, however, depend on α_L and β_{ML} in a similar way.[13]

As a measure of the trans and cis changes, one usually uses two parameters, $\Delta = R(\mathrm{M{-}L_{tr}}) - R(\mathrm{M{-}L_{cis}})$ and $\Delta' = R(\mathrm{M{-}L_{tr}}) - R(\mathrm{M{-}L})_{std}$.[12] Thus, $\Delta > \Delta'$ corresponds to cis shortening but $\Delta < \Delta'$ to cis lengthening. We see from Table V that both σ and multiply bonded ligands, L′, usually cause a large trans lengthening the value of which strongly depends on the nature of M, L, and L′. These regularities are well-known and have been qualitatively explained earlier.[13,39] One can show that these regularities also follow from our model,[40,41] but here we are mostly interested in the cis changes. As seen from Table V, typically $\Delta \leq \Delta'$ and $\Delta - \Delta' \ll \Delta$ or Δ'. Thus, in the octahedral complexes in question the cis changes are typically much smaller than the trans ones and have the same sign. Remember that the calculated values of $\Delta N(\mathrm{Cr{-}H_{tr}})$ and $\Delta N(\mathrm{Cr{-}H_{cis}})$ in CrH_5X^{6-} (see Table II) are of opposite sign. So, our model predictions that $\delta N(\mathrm{M{-}L_{tr}})/\delta\alpha'$ will be negative and typically larger in absolute value than $\delta N(\mathrm{M{-}L_{cis}})/\delta\alpha'$ which may be of any sign (cf. also ref 30b) perfectly agree with these experimental and computational findings. 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 Mo^{IV} [42] and Re^{V} [43] 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 ($g = 0$, $h = 1$, $\psi_2 = \psi_4$ is occupied, ψ_5 and ψ_6 are vacant), we reduce (31) and (35) to (36) and (37). The value of δN-

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

$$\frac{\delta N(\mathrm{A{-}L_{cis}})}{\delta\alpha'} = -\frac{ab}{(r+2)^{3/2}}\left[\frac{1}{E_{45}} - \frac{b^2-a^2}{E_{15}}\right]S_{\mathrm{s}} \tag{37}$$

$(\mathrm{A{-}L_{cis}})/\delta\alpha'$ is always negative, so for the 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[11] 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 $\mathrm{AL}_{m-1}\mathrm{L}'$ 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[44] which will be discussed in detail below.

Our model conclusions are confirmed by the EHM calculations on different $\mathrm{AL}_{m-1}\mathrm{L}'$ complexes. There is some tendency for $\delta N(\mathrm{A{-}L_{tr}})$ and $\delta N(\mathrm{A{-}L_{cis}})$ to be of the same sign for strongly electronegative ligands, L, like F and of opposite sign for weakly electronegative ligands like H.[11]

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, and (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 complexes, the regularities of substitution are simple and less varied than those in AL_m[25] complexes where they drastically depend on the oxidation state of A and fine details of the relative orbital energies.

The experimental check of the above conclusions in TB $\mathrm{AL_4L'}$ and PB $\mathrm{AL_6L'}$ complexes may be obscured by the nonequivalence of axial and equatorial bonds. Besides, at present there are no experimental data on PB $\mathrm{AL_6L'}$ complexes at all.[32] As for TB $\mathrm{AL_5}$ complexes, they are stable only for strongly electronegative ligands, L (for instance, F or Cl), and the axial bonds are more polar and weaker than the equatorial ones.[3,37,45] So, axial substitution in $\mathrm{AL_4L'}$ is preferable for a stronger acceptor ligand, L′ ($\delta\alpha' < 0$),[3,37,45] which is difficult to realize. Most of the known TB $\mathrm{AL}_{5-k}\mathrm{L'}_k$ complexes correspond to the equatorial substitution by a stronger donor ligand ($\delta\alpha' > 0$), and we shall consider them below.

Thus, practically the only objects for an experimental check of our model results might be the octahedral complexes $\mathrm{AL_5L'}$. Unfortunately, there are too little reliable experimental data to check our prediction.[46] One of the best examples is the recent redetermination of the structure of $\mathrm{SF_5Cl}$[47] where microwave and electron diffraction data have been combined. The S–F$_{\mathrm{tr}}$ and S–F$_{\mathrm{cis}}$ bonds were found to be lengthened as compared with $\mathrm{SF_6}$ (1.588, 1.566, 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 which agrees with the EHM calculations on $\mathrm{SF_5Cl}$.[47]

The X-ray determinations of $\mathrm{Xe(OSeF_5)_2}$[48] and $\mathrm{U(OTeF_5)_6}$[49] where the $\mathrm{AF_5(OR)}$ entities are of approximately C_{4v} symmetry show no definite regularities of the A–L$_{\mathrm{tr}}$ and A–L$_{\mathrm{cis}}$ bond lengths. Thus, there is an urgent need for new experimental and computational data on $\mathrm{AL}_{m-1}\mathrm{L}'$ complexes for wide ranges of A, L, and L′ to check our model conclusions.[50]

Comparing $\mathrm{AL_6}$ O_h with $\mathrm{AL_4L'_2}$ D_{4h} (Table I), we find that all the changes are determined by changes in the s bonding. Namely, we have the three-orbital interaction between s, $(1/2^{1/2})(\sigma'_1 + \sigma'_2)$, and $^1/_2(\sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$ in $\mathrm{AL_4L'_2}$ instead of the two-orbital interaction between s and $(1/6^{1/2})(\sigma_1 + \sigma_2 + \ldots + \sigma_6)$ in $\mathrm{AL_6}$. As follows from the general properties of three orbital–four center bonding,[1] for a better donor L′ this must result in a weakening of the A–L bonds in $\mathrm{AL_4L'_2}$ as compared with $\mathrm{AL_6}$, i.e., a weakening of the A–L$_{\mathrm{cis}}$ bonds. Similar arguments are valid while going from $\mathrm{AL_4L'_2}$ D_{4h} to $\mathrm{AL_2L'_2L''_2}$ D_{2h}.

Thus, we can predict that along the series *trans*-$\mathrm{AL_4L''_2} \to$ *trans*-$\mathrm{AL_3L'L''_2} \to$ *trans*-$\mathrm{AL_2L'_2L''_2}$ for a better donor, L′, all the cis bonds, A–L and A–L″, must be monotonically lengthened,[52] but in $\mathrm{AL_3L'L''_2}$ the A–L$_{\mathrm{tr}}$ bond can be shortened as compared with $\mathrm{AL_4L''_2}$. The complexes $\mathrm{SnX}_{4-k}(\mathrm{CH_3})_k\mathrm{D_2}$, X = Cl, Br and k = 0–2, D = $[(\mathrm{CH_3})_2\mathrm{N}]_3\mathrm{PO}$,[44] provide just such a case (see Table VI). It is worth mentioning that this trans shortening takes place for moderately electronegative ligands like Cl and Br (but not for F!), in agreement with our model conclusions and the results of the calculations on $\mathrm{SH_5X}$ (see Table II).

14e $\mathrm{AL_6}$. There are a few known examples of such octahedral complexes [$\mathrm{SbBr_6^{3-}}$, $\mathrm{AX_6^{2-}}$ (A = Se, Te and X = Cl, Br)[19]] where the central atom A is not in the highest oxidation state. This case is quite similar to the 12e $\mathrm{AL_4}$ one. The relevant relationships are given in eq 38 and 39. The con-

$$\frac{\delta N(\mathrm{A{-}L_{tr}})}{\delta\alpha'} = -\frac{abe^2}{2(6^{1/2})}\left[\frac{1}{E_{56}} - \frac{1}{E_{15}}\right]S_{\mathrm{s}} - \frac{ef}{2^{1/2}}\left[\frac{1}{6}\left(\frac{a^2}{E_{56}} + \frac{b^2}{E_{16}}\right) + \frac{1}{3E_{46}} - \frac{f^2-e^2}{2E_{36}}\right]S_{\mathrm{p}\sigma} \tag{38}$$

$$\delta N(\mathrm{A{-}L_{cis}})/\delta\alpha' \equiv 0 \tag{39}$$

clusion from (38) is obviously the same as the one from (24): both the s and pσ contributions are negative, so that for a better donor, L′, we can foresee a strong trans weakening. Because of a lack of experimental data on substituted $\mathrm{AL}_{6-k}\mathrm{L'}_k$ complexes, this conclusion may be considered as a prediction for checking. We shall not consider the similar complexes of the 12e $\mathrm{AL_5}$ and 16e $\mathrm{AL_7}$ type as they do not have the TB and PB forms, respectively.[19]

Equatorial Substitution. We shall now consider the effects of substitution of the equatorial ligand L(3) on the x axis. The relevant orbitals are given in Table IV. As the orbitals σ_1 and σ_3 enter only the MO's ψ_1 and ψ_2 which are the same in our model for both axial and equatorial substitution, the relationships (35) and (37) 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 $\mathrm{EL_6}$ O_h equatorial substitution is equivalent to axial for all ligands,[56] only the $\mathrm{EL_5}$ D_{3h} and $\mathrm{EL_7}$ D_{5h} cases are left to discuss.

10–18e $\mathrm{ML_5}$ and 14–18e $\mathrm{ML_7}$. The relevant expressions for $\delta N(\mathrm{M{-}L})/\delta\alpha'$ are very cumbersome and include many terms depending on the sign of cos θ, $\theta = \omega$ or 2ω (see Figure 1). Nevertheless, one can show[11] 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 foresee, however, one result which is specific to the $\mathrm{ML_7}$ case: for the two equatorial ligands, L(4) and L(5), which

Table V. Bond Distances in Some Octahedral Complexes

comp	d^n	dist, Å M–L_{tr}	 M–$L_{cis(av)}$	Δ[a]	Δ'[b]	ref
trans-$Pt(CH_2R)Br_3(AsR_3)_2$	d^6	2.57 (Br)	2.46 (Br)	0.11	0.12	*c*
$Rh(CH_2R)Cl_2D_3$	d^6	2.53 (Cl)	2.34 (Cl)	0.19	0.19	*d*
$[Rh(C_2H_5)(NH_3)_5]^{2+}$	d^6	2.26 (N)	2.07 (N)	0.19	0.21	*e*
$[Rh(H)(NH_3)_5]^{2+}$	d^6	2.24 (N)	2.07 (N)	0.17	0.21	*f*
trans-$Cr(p\text{-}C_6H_4CH_3)(THF)_3Cl_2$	d^3	2.21 (O)	2.04 (O)	0.17	~0.2	*g*
$[Re_2Cl_4(HCOO)_2Cl_2]^{2+}$	d^4	2.71 (Cl)	2.32 (Cl)	0.39	0.32	*h*
$[OsNCl_5]^{2-}$	d^2	2.60 (Cl)	2.36 (Cl)	0.24	0.24	*i, j*
$[ReOCl_5]^{2-}$	d^2	2.47 (Cl)	2.39 (Cl)	0.08	0.08	*k*
$ReNCl_2(PR_3)_3$	d^2	2.56 (Cl)	2.45 (Cl)	0.11	0.17	*l*
$ReOCl_3(PR_3)_2$	d^2	2.47 (Cl)	2.42 (Cl)	0.05	0.08	*m*
$MoOCl_2(PR_3)_3$(blue)	d^2	2.55 (Cl)	2.46 (Cl)	0.09	0.15	*n*
$MoOCl_2(PR_3)_3$(green)	d^2	2.43 (Cl)	2.48 (Cl)	−0.05	0.03	*o*
$[NbOF_5]^{2-}$	d^0	2.06 (F)	1.84 (F)	0.22	0.23	*p*
$[MoOF_5]^{2-}$	d^1	2.03 (F)	1.86 (F)	0.17	0.20	*q*

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Table VI. Bond Distances (Å) in $SnX_{4-k}(CH_3)_kD_2$ Complexes[a,b]

comp	Sn–C	Sn–X_{tr}	Sn–X_{cis}	Sn–O
trans-$SnCl_4D_2$		2.36[c]	2.40[c]	2.13
trans-$SnCl_3(CH_3)D_2$	*d*	2.31	2.46	2.18
trans-$SnCl_2(CH_3)_2D_2$	2.14		2.57	2.26
trans-$SnBr_4D_2$		2.54[c]	2.56[c]	2.09
trans-$SnBr_3(CH_3)D_2$	*d*	2.40	2.65	2.16
trans-$SnBr_2(CH_3)_2D_2$	2.14		2.74	2.23

[a] X = Cl, Br; k = 0–2; D = $[(CH_3)_2N]_3PO$. [b] Reference 44. [c] Sn–X distance in the relevant linear X–Sn–X fragment. [d] Not determined.

Table VII. P–F Bond Distances (Å) in Some TB Complexes

comp	symmetry	P–F_{ax}	P–F_{eq}	ref
PF_5	D_{3h}	1.577	1.534	*a*
PF_4H	C_{2v}	1.594	1.550	*b*
PF_4CH_3	C_{2v}	1.612	1.543	*c*
$PF_3(CH_3)_2$	C_{2v}	1.643	1.619	*c*
$PF_2(CH_3)_3$	D_{3h}	1.685		*d*

[a] Reference 58a. [b] Reference 57. [c] Reference 58b. [d] Reference 58c.

are nonequivalent to equatorial substitution, the values of δN(M–L(4)) and δN(M–L(5)) will be, most probably, of opposite sign, the former positive and the latter negative for a better donor ligand, L′. As there are no relevant experimental data on ML_6L' complexes,[32] 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 (10–18e), ML_4L', C_{2v} complexes. Unfortunately, there are no relevant structural experimental data.[31]

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[19]). For all AL_{r+2} complexes

$$\frac{\delta N(\text{A–L}_{ax})}{\delta\alpha'} = -\frac{ab}{(r+2)^{3/2}}\left[\frac{1}{E_{45}} - \frac{b^2-a^2}{E_{15}}\right]S_s \quad (40)$$

which, of course, coincides with $\delta N(\text{A–L}_{cis})$ (37) 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, also.[11]

In AL_5 under equatorial substitution, which is typical for a better donor, L′ ($\delta\alpha' > 0$),[3,37,45] $\delta N(\text{A–L}_{ax})$ has only the negative s contribution, but $\delta N(\text{A–L}_{eq})$ has typically the negative s and positive p contributions.[11] 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_4L', L′ = H[57] or CH_3[58b] (Table VII), as well as the calculations on these and related molecules[11,59] agree with this prediction. From the general properties of three orbital–four electron bonding it follows[1] 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[58] (see Table VII). Here the arguments are quite similar to those which we used above to explain a weakening of the $\text{A–L}_{cis(eq)}$ bonds in the $AL_4L'_2$ D_{4h} as compared with AL_6 O_h complexes.

It should be stressed that the regularities of equatorial substitution in AL_5 D_{3h} compounds may be quite different from those in the planar trigonal AL_3 D_{3h} compounds.[1] The reason is the presence of the additional nonbonding a'_1 MO of d_{z^2} symmetry (see Table IV) whose contribution to the s part of $\delta N(\text{A–L}_{eq})/\delta\alpha'$ is always positive. So, although in planar AL_2L' the total s contribution to the A–L_{eq} bond strength for a better donor, L′, is always negative, it may be both negative and positive in AL_4L' C_{2v} compounds. This result is a consequence of the fact that the A–L_{eq} bonds correspond to the valence angle of 120° which is intermediate between 90° (for the $\text{A–L}_{cis(ax)}$ bond where the s contribution is always negative) and 180° (for the A–L_{tr} bond where the s contribution is typically positive).

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 δN(A–L(4)) will be the same as δN(A–L(1)) but opposite from δN(A–L(5)). The same is true for the signs of the s contributions to these δN(A–L(i)) values. Though there are no relevant experimental data, our conclusions are confirmed by the EHM calculations on some AL_7 complexes.[60,11] It is worth stressing two computational conclusions. First, the values of the s contributions to $\delta N(\text{A–L}_{cis})$ are practically the same for both axial and equatorial substitution which confirms the adopted identity of (37) and (40). Second, the p contributions to δN(A–

Table VIII. 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_3L' C_{2v}	$MLL'L''_2$ C_{2v}	s	–	$+^a$
d^0–d^8	ML_5 D_{3h}	ML_4L' C_{3v}		p	+	none
d^0–d^6	ML_6 O_h	ML_5L' C_{4v}	$ML_3L'L''_2$ C_{2v}	d	–	$-^a$
d^0–d^4	ML_7 D_{5h}	ML_6L' C_{5v}		tot	–	$\pm\delta^b$
d^0–d^8	ML_5 D_{3h}	ML_4L' C_{2v}		s	*c*	$+^a$
d^0–d^4	ML_7 D_{5h}	ML_6L' C_{2v}		p		none
				d		$-^a$
				tot		$\pm\delta^b$
12e	AL_4 D_{4h}	AL_3L' C_{2v}	$ALL'L''_2$ C_{2v}	s	–	none
14e	AL_6 O_h	AL_5L' C_{4v}	$AL_3L'L''_2$ C_{2v}	p	–	none
				tot	–	none
10e	AL_5 D_{3h}	AL_4L' C_{3v}	$AL_3L'_2$ $D_{3h}{}^d$	s	$+^a$	–
12e	AL_6 O_h	AL_5L' C_{4v}	$AL_3L'L''_2$ C_{2v}	p	$-^a$	none
14e	AL_7 D_{5h}	AL_6L' C_{5v}	$AL_5L'_2$ $D_{5h}{}^d$	tot	$\pm^e$	–
10e	AL_5 D_{3h}	AL_4L' C_{2v}	$AL_3L'_2$ C_{2v}	s	*c*	–
14e	AL_7 D_{5h}	AL_6L' C_{2v}		p		none
				tot		–

[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(ω), L(2ω), etc. depends on the value of the relevant valence angle $\theta = \omega, 2\omega$, etc. In particular, in EL_6L' C_{2v} complexes the values of $\delta N(\text{E–L}(\omega))$ and $\delta N(\text{E–L}(2\omega))$ may be of opposite sign. See details in the text. [d] In the $AL_3L'_2$ and $AL_2L'_3$ D_{3h} complexes there exist only the A–L_{cis} bonds, A–L_{eq} and A–L_{ax}, respectively. The same holds for the $AL_5L'_2$ and $AL_2L'_5$ D_{5h} complexes. [e] The effect may be of any sign and comparable and even bigger in absolute value than the cis effect (see, for instance, the SH_5X and PH_4X cases in Table II, SF_5Cl,[27] and $SnX_{4-k}(CH_3)_kD_2$,[44] Table VI).

$L_{ax})/\delta\alpha'$ and $\delta N(\text{A–L}_{eq})/\delta\alpha'$ prove to be of any sign, and their relative values vary over an exceptionally large range which illustrates the impossibility of making definite qualitative predictions about these bonds.

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 also. In principle, the result of the total $\sigma + \pi$ perturbation will depend on both the geometry of $ML_{m-k}L'_k$ and the nature of M, L, and L′. The problem is usually simplified, however, by the fact that the σ bonding is typically much stronger than the π bonding. In this case, especially for highly symmetric polyhedra like ML_6 O_h or ML_4 D_{4h} complexes, 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 three orbital–*n* electron bondings (where *n* depends on the occupation numbers of the interacting orbitals) considered in the preceding paper.[1] Such three-orbital bondings in ML_3L' or ML_5L' will involve the metal orbital, say, d_{xz}, the perturbing ligand orbital, π'_{3z} or π'_{1x}, respectively (see Figures 1 and 2), and the proper linear combination of other ligand π orbitals. 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.[61] So, in ML_5L' for π donors, L, and vacant d_π metal orbitals, we will have typical three orbital–four electron 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.[13] Here we will mention only transition-metal carbonyls whose structures can be understood if the σ donor–acceptor M←CO bond is weaker than the π back-donation M→CO ones.[13] For this reason, strong σ donors such as H or CH_3, which cause a significant weakening of usual σ bonds like M–Cl_{tr}, result in a *strengthening* of the M–CO_{tr} bonds compared with those in linear OC–M–CO fragments.[13] Further, π-bonding effects can play an important role in many substitution reactions of square transition-metal complexes, but the relevant kinetic regularities are determined mainly by the structure of pentacoordinated transition states rather than that of the initial reactant.[62]

Concluding Remarks

The major conclusions of the present work are summarized in Table VIII. Certainly, these results can be extended easily to embrace other properties of the E–L bonds besides their strengths (lengths).[1,2] For instance, the sign of the s contribution determines the change of the s character of the relevant E–L bond which is directly related to the isomer shifts δ_E of the Mössbauer spectra or the nuclear-spin coupling constants ${}^1K$(E–L) of NMR spectra. Such relationships are not trivial, however, especially for ${}^1K$(E–L) where the theory[63] predicts, in agreement with experiment, quite different regularities of ${}^1K$(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 VIII) is that the signs of the s and total contributions to δN(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[64] some apparent contradictions among various correlations between the E–L bond strength and properties such as ${}^1K$(E–L), δ_E, etc.[8-10,13,38]

At present, a huge volume of experimental data is available on various aspects of substitution in different polyhedra, EL_m, and certainly these data have been interpreted in this or that way. Especially many experimental data and various theoretical treatments have been devoted to the trans and cis influence (effect) in square and octahedral complexes.[8,9,13,38] The effects of substitution in TB EL_5 complexes have also been studied rather well both experimentally and computationally.[31,37,45,59] However, until now, a unified analytical approach to the effects of substitution embracing all the EL_m polyhedra has not existed.

Our model has been developed in the framework of the perturbation theory of canonical LCAO MO's. This theory is widespread in the chemistry of organic π-electron systems[65] where each atom has only one valence orbital. We have eventually developed "a three-dimensional Hückel MO model"[66] which can be applied to any σ-bonded coordination compound where the central atom uses the s, p, d valence set.[67] The value of the approach in question is, first of all, that it uses simple, justifiable initial assumptions and treats all EL_m complexes 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. We hope that our approach can stimulate new research.

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Perturbation Theory and Spin-Coupling Constants in Substituted Compounds. Ligands with Valence *ns* Orbitals

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An analytical perturbation extension of the Pople–Santry theory of the Fermi contact term in reduced spin-coupling constants ^1K(E–L) has been developed for the substituted compounds $EL_{m-k}L'_k$ (E is a transition metal, M, or main-group element, A) where the ligands L have a valence *ns* orbital. The difference in ligand σ-orbital energies, $\delta\alpha' = \alpha(L') - \alpha(L)$, was taken as a perturbation. It was found that changes in ^1K(E–L) under substitution should typically follow changes in the s contributions to the E–L bond-overlap population, the latter having been determined earlier for the various polyhedra $EL_{m-k}L'_k$. The obtained results agree with experiment and permit the known regularities of ^1K(E–L) to be explained and a number of predictions to be made.

Introduction

At present, NMR spectroscopy is one of the most widespread methods for studying different chemical problems.[1,2] As the efficiency and informativity of any experimental technique is eventually determined by the accuracy of its theory, much effort has been devoted to developing the theories of NMR chemical shifts and reduced spin-coupling constants, K(E–L).[1,2] As K(E–L) values are not very sensitive to external factors such as temperature, solvents, etc., they can be considered as intrinsic characteristics of the E–L interactions, especially for directly bonded atoms E and L in various EL_m compounds (E is a transition metal, M, or main-group element, A). The general theory of ^1K(E–L) is extremely complicated,[3] and, in fact, there exists only one analytical version of this theory which is of general chemical importance, namely, the Pople–Santry (P–S) theory,[4] which is based on the LCAO MO approximation. Although all three possible contributions to ^1K(E–L), namely, the Fermi contact (FC), orbital, and spin-dipolar terms, are included, the interpretation of ^1K(E–L) is usually reduced to a consideration of the FC term which is typically dominant[1,2] and analytically the simplest.[3,4] The major restriction of the P–S theory,[4] however, is that very elegant and simple expression (of the FC term only) applies just to unsubstituted EL_m compounds where all ligands must be geometrically equivalent. It is not quite obvious how to apply the P–S theory to ^1K(E–L) in various substituted $EL_{m-k}L'_k$ compounds with different geometries and different E, L, L′, and k.

As the FC term in ^1K(E–L) is eventually determined by the s-orbital interactions, it is reasonable to connect changes in ^1K(E–L) under substitution, $EL_m \rightarrow EL_{m-k}L'_k$ with changes in the s_E–s_L contributions to the σ E–L bond. One must, however, distinguish ligands L with valence *ns* orbitals (H, CH_3, PR_3, etc.) from L with a low lone ns^2 pair (F) because the FC mechanisms will be quite different for each case.[4] Recently we have developed a general perturbation approach to the effects of substitution in various σ-bonded $EL_{m-k}L'_k$ compounds permitting changes in the valence s (as well as p and d) contributions to the E–L bond-overlap populations to be obtained in explicit form.[5-7] Our perturbation approach may be used to modify the P–S theory to make it applicable to substituted $EL_{m-k}L'_k$ compounds. In the present paper we will develop the theory of ^1K(E–L) for ligands L with valence *ns* orbitals, a straightforward matter for our perturbation formalism.[5-7] The theory of spin-coupling constants in various fluorides, requiring some extension of our formalism, will be given elsewhere.[8]

Results and Discussion

General Relationships. In the framework of the P–S theory the FC term will be[4] given by eq 1. Here $\pi_{s_Es_L} = \pi_{\mu\nu}$ is a

$$^1K(E-L) = |\mathrm{const}|\cdot\pi_{s_Es_L} \tag{1}$$

mutual polarizability of the orbitals. $s_E = \mu$ and $s_L = \nu$ in eq

$$\pi_{\mu\nu} = 4 \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{unocc}} (\epsilon_i - \epsilon_j)^{-1} c_{i\mu} c_{i\nu} c_{j\mu} c_{j\nu} \tag{2}$$

2 where the indices i and j refer to the occupied and unoccupied canonical LCAO MO's of the compound in question. For ligands L with valence *ns* orbitals, the σ_L orbitals are either pure s ones (for instance, 1s for H) or some hybrids

$$\sigma_L = c_s s_L + c_p p_L \tag{3}$$

with valence s contributions.

Expressions 1 and 2 can be substantially simplified for the special case of EL_m compounds where, first, *all* ligands, L, are geometrically equivalent, and, second, *only one* central atom orbital, s_E, belongs to the totally symmetric (A_1) irreducible representation. In this case,[4] there will be only two MO's of A_1 symmetry which contribute to ^1K(E–L), namely, bonding ϕ_1 (4) and antibonding ϕ_1^* (5). Taking into account (3), $\pi_{\mu\nu}$

$$\phi_1 = as_E + b(1/m^{1/2})(\sigma_1 + \sigma_2 + ... + \sigma_m) \tag{4}$$

$$\phi_1^* = bs_E - a(1/m^{1/2})(\sigma_1 + \sigma_2 + ... + \sigma_m) \tag{5}$$

(2) is reduced to (6) so that for such EL_m compounds we have

$$\pi_{s_Es_L} = \frac{1}{\epsilon(\phi_1^*) - \epsilon(\phi_1)} \frac{4a^2b^2c_s^2}{m} > 0 \tag{6}$$

(7) which is always positive and proportional to the square of

$$^1K(E-L) = |\mathrm{const}'|\cdot P_{s_Es_L}^2 \tag{7}$$

the E–L s bond order, $P_{s_Es_L}$ (cf. ref 4).

If all ligands L are not geometrically equivalent (for instance, in trigonal-bipyramidal EL_5, D_{3h} complexes) or more than one central atom orbital belongs to the totally symmetric