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Relative Strengths of Axial and Equatorial Bonds and Site Preferences for Ligand Substitution in σ-Bonded Trigonal- and Pentagonal-Bipyramidal Complexes

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For bipyramidal trigonal (TB) EL_5 D_{3h} and pentagonal (PB) EL_7 D_{5h} complexes (E is a transition metal M or main-group element A) two problems have been considered: (1) the relative strengths of axial (ax) and equatorial (eq) bonds and (2) the site preferences (SP) of stronger donor (or acceptor) substituents L′. An analytical approach has been developed in the framework of canonical LCAO MO theory. Ratios of overlap populations $T = N_{eq}/N_{ax}$ were estimated for *n*s, *n*p, and $(n-1)$d contributions producing values of $1 < T^{(s)}$, $1 < T^{(p)} < 1.15$, $T^{(d^0-d^4)} \approx 1.5$, and $T^{(d^8)} \approx 0.3$ for TB complexes and $T^{(s)} < 1$, $0.9 < T^{(p)} < 1$, and $T^{(d^0-d^4)} \approx 1.2$ for PB complexes. The contributions all reinforce to make equatorial bonds relatively stronger than axial bonds, eq > ax, in AL_5 and ML_5 (d^0–d^4) complexes while the $T^{(d^8)}$ contribution dominates in ML_5 (d^8) complexes to make ax ≥ eq. The perturbing influence of $(n-1)d^{10}$ shells in AL_5 complexes was also examined and found capable of making ax > eq under certain conditions. The opposing contributions of s, p, and d in ML_7 (d^0–d^4) complexes equalize axial and equatorial bonds while s and p contributions predominate in AL_7 complexes resulting in ax > eq. SP for substituents were examined using perturbation theory with the finding that a stronger donor ligand will substitute equatorially in AL_5 and ML_5 (d^0–d^4) complexes and axially in ML_5 (d^8) and AL_7 complexes. Quantitative details must be considered in ML_5 (d^{10}) and ML_7 (d^0–d^4) cases. The relationship between bond energy and bond polarity criteria for SP (equivalent in some instances) was examined for all cases. The results obtained agree with the available experimental and computational data and permit a number of predictions to be made.

Introduction

By tradition most studies on the electronic and geometric structures of coordination compounds are devoted to the square or tetrahedral EL_4 and octahedral EL_6 complexes (E is a transition metal M or a main-group element atom A). In these polyhedra with very high symmetry all the ligands are geometrically equivalent, permitting symmetry arguments to be used most effectively. That, in turn, makes reliable many results obtained from a variety of approximate models. In particular, the theory of the mutual influence of ligands (MIL) has been developed only for square and octahedral complexes where all valence angles are equal to 90 or 180° reducing the MIL to the trans–cis influence.[2-5]

In recent years one can observe the sharply increasing interest in EL_5 and EL_7 polyhedra where all ligand positions can not be equivalent. Most effort has been directed to the problem of the relative stability of different possible polyhedra for a given composition EL_m and the barriers to their interconversion.[6-18] The present work will not address this problem but consider only bipyramidal structures, trigonal (TB) EL_5 and pentagonal (PB) EL_7. The difference between axial, $E-L_{ax}$, and equatorial, $E-L_{eq}$, bonds generates three specific problems of structure for these compounds (as compared with square and octahedral ones): (1) the relative strengths of the $E-L_{ax}$ and $E-L_{eq}$ bonds in unsubstituted complexes EL_m; (2) the site preference of a given substituent L′ for an axial or equatorial position under substitution $EL_m \rightarrow EL_{m-1}L'$; (3) differences in the influence of the ligand L′, in a substituted $EL_{m-1}L'$ complex, on the strength of the initial axial and equatorial bonds.

Sufficient experimental data exist for a discussion of some fundamental regularities in the structure of these complexes, especially EL_5. Moreover, quantitative quantum chemical calculations have been performed on specific EL_5[8,9,15-18] and

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Table I. Orbital Basis Functions Forming σ Bonds in Bipyramidal EL_m Complexes

complex	irreducible representation	AO's of E	group ligand orbitals
EL_5 D_{3h} TB $r = 3$	A_1'	s	$\sigma_{ax} = (1/2^{1/2})(\sigma_1 + \sigma_2)$
		d_{z^2}	$\sigma_{eq} = (1/3^{1/2})(\sigma_3 + \sigma_4 + \sigma_5)$
	A_2''	p_z	$(1/2^{1/2})(\sigma_1 - \sigma_2)$
	E'	p_x, $d_{x^2-y^2}$	$(1/6^{1/2})(2\sigma_3 - \sigma_4 - \sigma_5)^{a,b}$
		p_y, d_{xy}	$(1/2^{1/2})(\sigma_4 - \sigma_5)^{a,c}$
EL_6 O_h $r = 4$	A_{1g}	s	$(1/6^{1/2})(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)^{a,d}$
	E_g	d_{z^2}	$(1/3^{1/2})(\sigma_1 + \sigma_2) - [1/(2)(3^{1/2})](\sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)^{a,e}$
		$d_{x^2-y^2}$	$1/2(\sigma_3 - \sigma_4 + \sigma_5 - \sigma_6)^{a,f}$
	T_{1u}	p_z	$(1/2^{1/2})(\sigma_1 - \sigma_2)$
		p_x	$(1/2^{1/2})(\sigma_3 - \sigma_5)^{a,g}$
		p_y	$(1/2^{1/2})(\sigma_4 - \sigma_6)$
EL_7 D_{5h} PB $r = 5$	A_1'	s	$\sigma_{ax} = (1/2^{1/2})(\sigma_1 + \sigma_2)$
		d_{z^2}	$\sigma_{eq} = (1/5^{1/2})(\sigma_3 + \sigma_4 + \sigma_5 + \sigma_6 + \sigma_7)$
	A_2''	p_z	$(1/2^{1/2})(\sigma_1 - \sigma_2)$
	E_1'	p_x	$(2/5)^{1/2}\left(\sigma_3 + \sigma_4 \cos\frac{2\pi}{5} + \sigma_5 \cos\frac{4\pi}{5} + \sigma_6 \cos\frac{6\pi}{5} + \sigma_7 \cos\frac{8\pi}{5}\right)$
		p_y	$(2/5)^{1/2}\left(\sigma_4 \sin\frac{2\pi}{5} + \sigma_5 \sin\frac{4\pi}{5} + \sigma_6 \sin\frac{6\pi}{5} + \sigma_7 \sin\frac{8\pi}{5}\right)$
	E_2'	$d_{x^2-y^2}$	$(2/5)^{1/2}\left(\sigma_3 + \sigma_4 \cos\frac{4\pi}{5} + \sigma_5 \cos\frac{8\pi}{5} + \sigma_6 \cos\frac{12\pi}{5} + \sigma_7 \cos\frac{16\pi}{5}\right)$
		d_{xy}	$(2/5)^{1/2}\left(\sigma_4 \sin\frac{4\pi}{5} + \sigma_5 \sin\frac{8\pi}{5} + \sigma_6 \sin\frac{12\pi}{5} + \sigma_7 \sin\frac{16\pi}{5}\right)$

[a] These explicit expressions can be obtained from the relevant general relationships: [b] (17) for $r = 3$.[h] [c] (18) for $r = 3$.[h] [d] (11) or (14) for $r = 4$.[h] [e] (12) or (15) for $r = 4$.[h] [f] (16) for $r = 4$.[h] [g] (16) for $r = 2$ (the equatorial axis in a square).[h] [h] See explanations in the text.

EL_7[10,19] complexes which permit explanation of regularities, such as the site preferences for donor (acceptor) substituents in TB AL_5[20] or the influence of the metal d^x configuration on relative bond strengths of axial and equatorial bonds in TB ML_5.[9] Some regularities have been rationalized in the frameworks of other approaches, in particular the VSEPR models,[6] Bartell's "primary–secondary effects" approach,[11] the angular overlap model,[12] and the MO Walsh-type approach.[13,14] But, to our knowledge, there is no formalism embracing all of these problems explicitly in the framework of the LCAO MO theory, the most general language for describing electronic effects in chemical compounds.

Formulation of the Objective

The purpose of the present work is to develop such a general MO approach. Most of the problems of axial and equatorial nonequivalency will be considered as manifestations of the MIL in bipyramidal polyhedra EL_m for $m = 5$ (TB, D_{3h}) and $m = 7$ (PB, D_{5h}) with the octahedron, $m = 6$ (O_h), entering as the particular case when axial and equatorial positions are equivalent. In this sense we continue our earlier work on the MIL in square EL_4 and octahedral EL_6 complexes[21,22] where we found that some regularities for main-group element AL_m complexes may be both similar to and different from those for transition-metal ML_m complexes.[5,22,23] Needless to say, any model is formulated in relatively simple terms and one must accept some drastic approximations to obtain explicit interrelations among the parameters. At the same time quantitative computations may be based on a quite different, often much more sophisticated mathematical formalism taking into account many factors which have been neglected in the model or introduced in a nonexplicit form. Therefore, comparison of computational results with those from the model is usually not a trivial procedure and rather often these two groups of results should be compared with experimental data quite independently.

Due to computational difficulties, most calculations have been on simple systems such as PH_5 or PF_5 which have been calculated many times and by many methods including the ab initio (PH_5,[15] PF_5[18]), CNDO/2 (PF_5[17a]), GIVNAP and ARCANA (PH_5,[17b] PF_5[17b]), and EHM (PH_5,[8] PF_5[16]) methods. Calculations on other complexes are rare and have been usually performed by means of simple semiempirical methods, especially of the EHM type (for example, PCl_5,[16a] AsF_5,[17] or IF_7[19]), so that the ab initio calculations like those on VF_5 and VF_5^-[43a] are really unique.

The most interesting thing for a chemist is to predict regularities along the series EL_m when we replace either E or L, for instance, in the horizontal series from $CdCl_5^{3-}$ to $SbCl_5$, in the vertical series from PF_5 to BiF_5, or along the series PF_5, $P(OPh)_5$, PCl_5, PPh_5, etc. At present reliable calculations on entire series like these are impossible, so that any prediction, based on even very accurate calculations on the simplest compounds of the PH_5 or PF_5 type, is an extrapolation without well boundary conditions. In a situation like this the model predictions may not only be more "digestible" for a chemist but more informative as well. The model has advantages in that it can focus on the essential features and probe their importance one by one.

The present work will consider the first two problems mentioned above for EL_5 and EL_7 complexes, namely, the relative strength of axial and equatorial bonds and the site preferences for a more donor (acceptor) substituent. The third problem, the MIL in substituted complexes $EL_{m-k}L'_k$, will be considered in a subsequent paper.[24]

Results and Discussion

1. Composition and Energies of the Group Ligand Orbitals. Let us consider polyhedra EL_m where there are two axial ligands (1 and 2) on the z axis and r equatorial ligands (3, 4, ... $r + 2$) occupy vertices of a regular r polygon in the xy plane, the ligand 3 being on the x axis (Figure 1). Now compare the orbital basis sets forming σ bonds in these bipyramidal complexes (Table I). In the EL_6 O_h case s, p, and d orbitals belong to different irreducible representations. Only then is there no mixing of the central atom orbitals in the relevant canonical MO's of the EL_m complexes making the s, p, and d contributions to the relative strength of axial and equatorial bonds independent of each other, each axial contribution being equal to the corresponding equatorial one. In

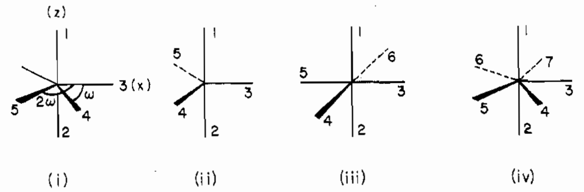

Figure 1. General scheme for bipyramidal complexes EL_m (i) and enumeration of ligands in TB EL_5 (ii), O_h EL_6 (iii), and PB EL_7 (iv). In the case (i) the coordinate axes and the valence angles are shown as well.

the D_{3h} EL_5 and D_{5h} EL_7 cases the s, p, and d contributions to the axial bond strength are unequal to the equatorial ones and must be considered separately. It is necessary also to take into account sd_{z^2} mixing in both ML_5 D_{3h} and ML_7 D_{5h} as well as $p_xd_{x^2-y^2}$ (p_yd_{xy}) mixing in ML_5 D_{3h} complexes, though certainly we can neglect these mixings in main group element complexes AL_m for which the hypervalent structure[25] without vacant *n*d orbitals is usually a rather good approximation.[26]

Let us begin with sd_{z^2} mixing. Table I lists four orbitals (s, d_{z^2}, σ_{ax}, and σ_{eq}) within the totally symmetric irreducible representation A_1 where

$$\sigma_{ax} = \frac{1}{(2(1 + S_{12}))^{1/2}}(\sigma_1 + \sigma_2) \tag{1}$$

and

$$\sigma_{eq} = \frac{1}{(r(1 + 2S_{34} + ...))^{1/2}}(\sigma_3 + \sigma_4 + ... + \sigma_{r+2}) \tag{2}$$

are reduced to the usual forms (see Table I)

$$\sigma_{ax} = \frac{1}{2^{1/2}}(\sigma_1 + \sigma_2) \tag{3}$$

and

$$\sigma_{eq} = \frac{1}{r^{1/2}}(\sigma_3 + \sigma_4 + ... + \sigma_{r+2}) \tag{4}$$

if we neglect all the overlap integrals $S_{ij} = \langle \sigma_i | \sigma_j \rangle$, $i \neq j$.

The fourth-order secular equation can be reduced by using linear combinations of σ_{ax} and σ_{eq} (eq 5 and 6), where φ_1 and

$$\varphi_1 = c_{11}\sigma_{ax} + c_{12}\sigma_{eq} \tag{5}$$

$$\varphi_2 = c_{21}\sigma_{ax} - c_{22}\sigma_{eq} \tag{6}$$

φ_2 are orthogonal to each other, φ_1 is orthogonal to d_{z^2}, and φ_2 is orthogonal to s, i.e.

$$\langle \varphi_1 | \varphi_2 \rangle = 0 \tag{7}$$

$$\langle \varphi_1 | d_{z^2} \rangle = 0 \tag{8}$$

$$\langle \varphi_2 | s \rangle = 0 \tag{9}$$

$$c_{11} = c_{22},\ c_{12} = c_{21},\ c_{11}^2 + c_{12}^2 = 1 \text{ for } S_{ij} = 0\ (i \neq j) \tag{10}$$

Though strict fulfillment of both conditions 8 and 9 is possible only in the EL_6 O_h case (where s and d_{z^2} belong to different irreducible representations), for the EL_5 and EL_7 cases these two orthogonalization schemes give us a possibility of estimating separately the s and d_{z^2} contributions to the relative bond strength (see below).

The s contribution will be entirely isotropic if we neglect interligand interactions. In fact, neglecting all the overlap integrals S_{ij} ($i \neq j$), we have for condition 9 the mutually orthogonal group orbitals (11) and (12). Because of the form

$$\varphi_1 = \left(\frac{1}{r + 2}\right)^{1/2}(\sigma_1 + \sigma_2 + ... + \sigma_{r+2}) \tag{11}$$

$$\varphi_2 = \left(\frac{r}{2(r + 2)}\right)^{1/2}(\sigma_1 + \sigma_2) - \left(\frac{2}{r(r + 2)}\right)^{1/2}(\sigma_3 + \sigma_4 + ... + \sigma_{r+2}) \tag{12}$$

of (11) the s contribution to the strength of all the bonds—both axial and equatorial—is the same. So the only way to take into account the real anisotropy of the s contribution is to include somehow interligand interactions (see below).

If we use the second orthogonalization scheme (8) and take into account [cf. (100)]

$$\frac{\langle \sigma_1 | d_{z^2} \rangle}{\langle \sigma_3 | d_{z^2} \rangle} = -2 \tag{13}$$

we obtain mutually orthogonal group orbitals (14) and (15).

$$\varphi_1' = \left(\frac{r}{2(r + 8)}\right)^{1/2}(\sigma_1 + \sigma_2) + \left(\frac{8}{r(r + 8)}\right)^{1/2}(\sigma_3 + \sigma_4 + ... + \sigma_{r+2}) \tag{14}$$

$$\varphi_2' = \left(\frac{4}{r + 8}\right)^{1/2}(\sigma_1 + \sigma_2) - \left(\frac{1}{r + 8}\right)^{1/2}(\sigma_3 + \sigma_4 + ... + \sigma_{r+2}) \tag{15}$$

It is obvious that φ_1 (11) coincides with φ_1' (14) and φ_2 (12) with φ_2' (15) only in the EL_6 O_h case where $r = 4$ (see Table I).

The forms of relevant equatorial ligand MO's φ_k depend upon whether or not there is a ligand trans to ligand 3. Letting $\theta = \omega, 2\omega, ...$, where $\omega = 2\pi/r$ stands for the valence angle between ligands 3 and 4 (see Figure 1 and Table I), we have the following:

(a) For a nondegenerate level when there exists a trans position

$$\varphi_k = (1/r)^{1/2}(\sigma_3 + \sigma_4 e^{i\theta} + \sigma_5 e^{2i\theta} + ... + \sigma_{r+2}e^{(r-1)i\theta}) \tag{16}$$

(b) For a doubly degenerate level where there is no trans position, but there are pairs of equivalent "quasi-cis" ligands

$$\varphi_k^{(1)} = (2/r)^{1/2}(\sigma_3 + \sigma_4 \cos\theta + \sigma_5 \cos 2\theta + ... + \sigma_{r+2}\cos(r - 1)\theta) \tag{17}$$

The second MO $\varphi_k^{(2)}$ will be, obviously,

$$\varphi_k^{(2)} = (2/r)^{1/2}(\sigma_4 \sin\theta + \sigma_5 \sin 2\theta + ... + \sigma_{r+2}\sin(r - 1)\theta) \tag{18}$$

There is a clear analogy in the forms of MO's (16)–(18) and the Hückel π MO's of cyclic polyenes C_rH_r where the forms of π MO's depend on whether the number *r* is even or odd.[27a] Further, one should emphasize that by symmetry the equatorial p_x,p_y orbitals interact with the group ligand orbitals corresponding to $\theta = \omega$ while the equatorial $d_{x^2-y^2}$,d_{xy} orbitals interact with the group ligand orbitals corresponding to $\theta = 2\omega$. Only in D_{3h} (TB), where $\omega = 2\pi - 2\omega$, $\cos\omega = \cos 2\omega = \cos 4\omega$, and $\sin\omega = -\sin 2\omega = \sin 4\omega$, do the two sets of orbitals belong to the same irreducible representation, e′.

Though neglecting S_{ij} ($i \neq j$), we shall not neglect resonance integrals $\beta_{ij} = \langle \sigma_i | H | \sigma_j \rangle$, $i \neq \theta$, so that the energies of the different group ligand orbitals (11)–(12) and (14)–(18) will be different. The significance of such energy splittings is demonstrated in the photoelectron spectrum of SF_6 where the energy splittings a_{1g}–t_{1u} and a_{1g}–e_g between the relevant group F 2s orbitals have been found to be equal to 2.7 and 4.9 eV, respectively.[28]

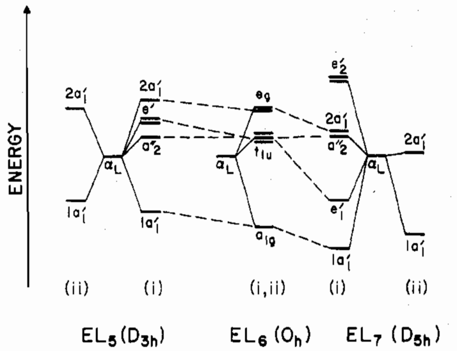

Figure 2. Relative energies of the group ligand σ orbitals in EL_5 (D_{3h}), EL_6 (O_h), and EL_7 (D_{5h}) complexes. For the a_1 MO's two cases are shown: (i) for the s orthogonalization and (ii) for the d_{z^2} orthogonalization. In the EL_7 complexes for the case (i) the energies of the MO's a_2'' and $2a_1'$ may be interchangeable; for the case (ii) the energy of $2a_1'$ may be higher or lower than α_L. The dotted lines connect orbitals of the same type. See the text for designations of the MO's.

The energies of the MO's (11)–(12) and (14)–(18) are as follows ($\alpha_L = \alpha$):

EL_5 D_{3h}

$$\alpha(1a_1') = \alpha + \tfrac{1}{5}(12\beta_{cis} + 6\beta_{eq} + 2\beta_{tr}) \quad \text{[the (11) type]} \tag{19}$$

$$\alpha(1a_1') = \alpha + \tfrac{1}{11}(24\beta_{cis} + 16\beta_{eq} + 3\beta_{tr}) \quad \text{[the (14) type]} \tag{20}$$

$$\alpha(2a_1') = \alpha - \tfrac{1}{5}(12\beta_{cis} - 4\beta_{eq} - 3\beta_{tr}) \quad \text{[the (12) type]} \tag{21}$$

$$\alpha(2a_1') = \alpha - \tfrac{1}{11}(24\beta_{cis} - 6\beta_{eq} - 8\beta_{tr}) \quad \text{[the (15) type]} \tag{22}$$

$$\alpha(a_2'') = \alpha - \beta_{tr} \tag{23}$$

$$\alpha(e') = \alpha - \beta_{eq} \tag{24}$$

EL_6 D_h

$$\alpha(a_{1g}) = \alpha + 4\beta_{cis} + \beta_{tr} \tag{25}$$

$$\alpha(t_{1u}) = \alpha - \beta_{tr} \tag{26}$$

$$\alpha(e_g) = \alpha - 2\beta_{cis} + \beta_{tr} \tag{27}$$

EL_7 D_{5h}

$$\alpha(1a_1') = \alpha + \tfrac{1}{7}(10\beta_{eq}^{(\omega)} + 10\beta_{eq}^{(2\omega)} + 20\beta_{cis} + 2\beta_{tr}) \quad \text{[the (11) type]} \tag{28}$$

$$\alpha(1a_1') = \alpha + \tfrac{1}{13}(16\beta_{eq}^{(\omega)} + 16\beta_{eq}^{(2\omega)} + 40\beta_{cis} + 5\beta_{tr}) \quad \text{[the (14) type]} \tag{29}$$

$$\alpha(2a_1') = \alpha + \tfrac{1}{7}(4\beta_{eq}^{(\omega)} + 4\beta_{eq}^{(2\omega)} - 20\beta_{cis} + 5\beta_{tr}) \quad \text{[the (12) type]} \tag{30}$$

$$\alpha(2a_1') = \alpha + \tfrac{1}{13}(10\beta_{eq}^{(\omega)} + 10\beta_{eq}^{(2\omega)} - 40\beta_{cis} + 8\beta_{tr}) \quad \text{[the (15) type]} \tag{31}$$

$$\alpha(a_2'') = \alpha - \beta_{tr} \tag{32}$$

$$\alpha(e_1') = \alpha + 0.618\beta_{eq}^{(\omega)} - 1.618\beta_{eq}^{(2\omega)} \tag{33}$$

$$\alpha(e_2') = \alpha - 1.618\beta_{eq}^{(\omega)} + 0.618\beta_{eq}^{(2\omega)} \tag{34}$$

Here $\beta_{ax} = \beta_{tr} = \beta_{12}$, $\beta_{cis} = \beta_{13}$, $\beta_{eq}^{(\omega)} = \beta_{34}$, and $\beta_{eq}^{(2\omega)} = \beta_{35}$ for the relevant internuclear distances $R_{12} = 2R$, $R_{13} = 1.41R$, $R_{34} = 1.73R$ (EL_5) or $1.17R$ (EL_7), and $R_{35} = 1.90R$ (EL_7) if all the bond lengths E–L are equal to R (see Figure 1).

To estimate the relative energies of these MO's we should take into account the short-range character of β_{ij} interactions (cf. Appendix, Table VI), namely

$$\text{for } EL_5 \text{ and } EL_6 \quad |\beta_{cis}| \gg |\beta_{eq}| > |\beta_{tr}| \tag{35}$$

and

$$\text{for } EL_7 \quad |\beta_{eq}^{(\omega)}| \gg |\beta_{cis}| \gg |\beta_{eq}^{(2\omega)}| > |\beta_{tr}| \tag{36}$$

For example, estimating β_{cis} and β_{tr} for group ligand F 2s orbitals of the type (25)–(27) from the experimental data for SF_6[28] we obtain $\beta_{cis} \approx -1.0$ eV and $\beta_{tr} \approx 0$.

All this easily defines the relative order of the MO's $\alpha(1a_1')$, $\alpha(2a_1')$, $\alpha(a_2'')$, $\alpha(e_1')$, and $\alpha(e_2')$ which is shown in Figure 2.

The fine point is the relative order of the a_1' MO's obtained by the s and d_{z^2} orthogonalizations, i.e., (19) vs. (20) and (28) vs. (29). As the dominant β_{ij} value is β_{cis} for EL_5 and $\beta_{eq}^{(\omega)}$ for EL_7, we have to compare the magnitudes of the coefficients [see (11), (12) and (14), (15)] in (37) and (38), which is

$$\frac{2}{r+8} < \frac{1}{r+2} \quad \text{for } EL_5\ (r = 3) \tag{37}$$

$$\frac{2}{r(r+8)} < \frac{1}{r+8} \quad \text{for } EL_7\ (r = 5) \tag{38}$$

reflected in the coefficients in the MO's (19)–(20) and (28)–(31). We can see that, in both the EL_5 and EL_7 cases, the orthogonalization to d_{z^2} (8) increases the $1a_1'$ energy and decreases the $2a_1'$ energy, thus decreasing the energy splitting $\alpha(2a_1')$–$\alpha(1a_1')$ [see Figure 2].

2. Structure of σ MO's of EL_m Complexes. The MO energies (19)–(34) are necessary to estimate the strengths of the relevant E–L bonds. Remember that if we have any bonding MO

$$\psi = C_a\chi_a + C_b\chi_b \tag{39}$$

and its antibonding counterpart ($S_{ab} = 0$, $C_a^2 + C_b^2 = 1$)

$$\psi^* = C_b\chi_a - C_a\chi_b \tag{40}$$

there exist the following relations between the energy $\epsilon(\psi)$ and the coefficients C_a and C_b[29]

$$\epsilon(\psi) = \alpha_b - \frac{\beta_{ab}^2}{\alpha_a - \alpha_b} + \frac{\beta_{ab}^4}{(\alpha_a - \alpha_b)^3} - \ldots \tag{41}$$

$$C_a/C_b = ((\zeta^2 + 4)^{1/2} - \zeta)/2 \tag{42}$$

$$C_aC_b = 1/(\zeta^2 + 4)^{1/2} \tag{43}$$

where

$$\alpha_b < \alpha_a < 0, \quad \beta_{ab} < 0, \quad C_b > C_a > 0 \tag{44}$$

and

$$\zeta = (\alpha_b - \alpha_a)/\beta_{ab} > 0 \tag{45}$$

So, the product C_aC_b (43) [the bond order] monotonically decreases as the parameter ζ (45) increases, i.e., as the energy difference between interacting levels increases and the resonance (overlap) integral between them decreases (in absolute value).

We shall now consider interactions among the central atom s, p, and d orbitals and the group ligand orbitals for the following bonding σ MO's of bipyramidal complexes EL_{r+2}.

$$\psi(s) = as + \frac{b}{(r+2)^{1/2}}(\sigma_1 + \sigma_2 + \ldots + \sigma_{r+2}) \tag{46}$$

or

$$\psi(\mathrm{s}) = as + b\left[\left(\frac{r}{2(r+8)}\right)^{1/2}(\sigma_1 + \sigma_2) + \left(\frac{8}{r(r+8)}\right)^{1/2}(\sigma_3 + \sigma_4 + \ldots + \sigma_{r+2})\right] \quad (46')$$

$$\psi(\mathrm{p}_z) = c\mathrm{p}_z + \frac{d}{2^{1/2}}(\sigma_1 - \sigma_2) \quad (47)$$

$$\psi(\mathrm{p}_x) = e\mathrm{p}_x + f\left(\frac{2}{r}\right)^{1/2}[\sigma_3 + \sigma_4 \cos \omega + \ldots + \sigma_{r+2} \cos (r-1)\omega] \quad (48)$$

$$\psi(\mathrm{d}_{z^2}) = g\mathrm{d}_{z^2} + h\left[\left(\frac{r}{2(r+2)}\right)^{1/2}(\sigma_1 + \sigma_2) - \left(\frac{2}{r(r+2)}\right)^{1/2}(\sigma_3 + \sigma_4 + \ldots + \sigma_{r+2})\right] \quad (49)$$

or

$$\psi(\mathrm{d}_{z^2}) = g\mathrm{d}_{z^2} + h\left[\left(\frac{4}{r+8}\right)^{1/2}(\sigma_1 + \sigma_2) - \left(\frac{1}{r+8}\right)^{1/2}(\sigma_3 + \sigma_4 + \ldots + \sigma_{r+2})\right] \quad (49')$$

$$\psi(\mathrm{d}_{x^2-y^2}) = l\mathrm{d}_{x^2-y^2} + m\left(\frac{2}{r}\right)^{1/2}[\sigma_3 + \sigma_4 \cos 2\omega + \ldots + \sigma_{r+2} \cos 2(r-1)\omega] \quad (50)$$

Here (46), (46′) and (49), (49′) refer to (11), (14) and (12), (15), respectively; for (48) and (50) there exist the relevant counterparts of these doubly degenerate sets [$\psi(\mathrm{p}_y)$ and $\psi(\mathrm{d}_{xy})$, respectively]; and for all these MO's (46)–(50) we accept the relations (39)–(45). As the AO's d_{xz} and d_{yz} are not involved in the formation of σ bonds in any bipyramidal complex EL_m, the results obtained below will be the same for d^0–d^4 ML_m cases.

The only serious deviation from this MO scheme (46)–(50) arises in the TB D_{3h} ML_5 case where some distinct $\mathrm{p}_x\mathrm{d}_{x^2-y^2}$ ($\mathrm{p}_y\mathrm{d}_{xy}$) mixing can exist. So, instead of *four* MO's $\psi(\mathrm{p}_x)$, $\psi^*(\mathrm{p}_x)$, $\psi(\mathrm{d}_{x^2-y^2})$, $\psi^*(\mathrm{d}_{x^2-y^2})$ [(48) and (50) and their antibonding counterparts], we have *three* MO's of the type

$$\psi_i(\mathrm{p}_x,\mathrm{d}_{x^2-y^2}) = c_i'\mathrm{p}_x + g_i'\mathrm{d}_{x^2-y^2} + h_i'\left(\frac{2}{3}\right)^{1/2}(\sigma_3 - \tfrac{1}{2}\sigma_4 - \tfrac{1}{2}\sigma_5) \quad (51.i)$$

where the coefficients c_i', g_i', h_i' (i = 1, 2, 3) are defined by some variation procedure. For the d^0–d^4 ML_5 or AL_5 cases, only MO $\psi_1(\mathrm{p}_x, \mathrm{d}_{x^2-y^2})$ (51.1) will be filled. Because the major contribution to bonding is provided by the (n − 1)d orbitals in transition-metal complexes or the np orbitals in main-group complexes, we can replace $\psi_1(\mathrm{p}_x, \mathrm{d}_{x^2-y^2})$ (51.1) by $\psi(\mathrm{d}_{x^2-y^2})$ (50) in ML_5 and by $\psi(\mathrm{p}_x)$ (48) in AL_5 (see below). In the d^8–d^{10} ML_5 cases we have to fill $\psi_2(\mathrm{p}_x, \mathrm{d}_{x^2-y^2})$ (51.2) also, so the population η^2 of the ligand group orbital e′

$$\eta^2 = h_1'^2 + h_2'^2 = 1 - h_3'^2 \quad (52)$$

will be less than 1 and the magnitude of $h_3'^2 = 1 - \eta^2 > 0$ may be of importance for a number of consequences (see below).

The TB EL_5 D_{3h} complexes are very common for both main-group elements A and transition-metal atoms M. The D_{3h} d^0–d^1 ML_5 complexes exist only in the gas phase.[30] In the solid state the d^0–d^1 ML_5 complexes dimerize or polymerize to reach hexa (or higher) coordination around the central atom, so TB d^x ML_5 D_{3h} complexes are more common for $7 \leq x \leq 10$ (see references in ref 9).

The PB EL_7 D_{5h} complexes are most typical of (n − 1) d^0–d^4 transition metals[10] and only one nontransition complex of this type, IF_7, has been reliably identified.[31] The latter is easily understood, as the hypervalent central atom A using only ns and np orbitals can hardly hold seven ligands.[25]

3. Relative Strengths of Axial and Equatorial Bonds. As a criterion of the E–L bond strength, we choose the overlap population[32]

$$N'(\mathrm{E{-}L}) = 4\sum_i^{\mathrm{occ}}\sum_m c_{im}c_{i\mathrm{L}}S_{m\mathrm{L}} \quad (53)$$

or

$$N(\mathrm{E{-}L}) = \tfrac{1}{4}N'(\mathrm{E{-}L}) = \sum_i^{\mathrm{occ}}\sum_m c_{im}c_{i\mathrm{L}}S_{m\mathrm{L}} \quad (54)$$

Here c_{im} and $c_{i\mathrm{L}}$ stand for coefficients in the canonical σ MO ψ_i

$$\psi_i = \sum_m c_{im}\chi_m + \sum_{\mathrm{L}} c_{i\mathrm{L}}\sigma_{\mathrm{L}} \quad (55)$$

referring to a given irreducible representation, the χ_m are AO's on the central atom E, and $S_{m\mathrm{L}} = \langle\chi_m|\sigma_{\mathrm{L}}\rangle$.

In cases when, within a given irreducible representation, the number of unoccupied MO's ψ_j is less than that of occupied MO's ψ_i, it is more convenient to use the right part of the identity (see below)

$$\sum_i^{\mathrm{occ}} c_{im}c_{i\mathrm{L}} = -\sum_j^{\mathrm{unocc}} c_{jm}c_{j\mathrm{L}} \quad (56)$$

We shall consider separately the s, p, and d contributions to the strengths of $\mathrm{E{-}L_{ax}}$ and $\mathrm{E{-}L_{eq}}$ bonds. We shall begin with the p contribution because it is of greatest importance in hypervalent complexes AL_m and ties in directly with the previous discussion of the energy splitting of the ligand group orbitals.

(a) The p Contribution. In all the complexes EL_m the p orbital contribution to the overlap populations are [cf. (48)]

$$N_{\mathrm{eq}}^{(\mathrm{p})} = ef(2/r)^{1/2}S_{\mathrm{p}\sigma} \quad (57)$$

and [cf. (47)]

$$N_{\mathrm{ax}}^{(\mathrm{p})} = cd(\tfrac{1}{2})^{1/2}S_{\mathrm{p}\sigma} \quad (58)$$

In the O_h case $2/r = {}^1/_2$, so axial and equatorial bonds are equivalent and the MO's e′(x), e′(y), and a_2''(z) are degenerate. The ratio $T^{(\mathrm{p})}$ of these overlap populations may be written as in (59), which identically equals 1 in the EL_6 O_h

$$T^{(\mathrm{p})} = \frac{N_{\mathrm{eq}}^{(\mathrm{p})}}{N_{\mathrm{ax}}^{(\mathrm{p})}} = \frac{ef}{cd}\left(\frac{4}{r}\right)^{1/2} \quad (59)$$

case ($ef \equiv cd$, r = 4) but requires some analysis for the EL_5 and EL_7 cases.

Using (44), (47), and (48), we find

$$cd = \frac{1}{(\zeta_{\mathrm{ax}}^2 + 4)^{1/2}} = \frac{1}{\left(\left(\dfrac{\alpha_{\mathrm{p}} - \alpha_{\mathrm{ax}}^{(\mathrm{p})}}{\beta_{\mathrm{ax}}^{(\mathrm{p})}}\right)^2 + 4\right)^{1/2}} \quad (60)$$

$$ef = \frac{1}{(\zeta_{\mathrm{eq}}^2 + 4)^{1/2}} = \frac{1}{\left(\left(\dfrac{\alpha_{\mathrm{p}} - \alpha_{\mathrm{eq}}^{(\mathrm{p})}}{\beta_{\mathrm{eq}}^{(\mathrm{p})}}\right)^2 + 4\right)^{1/2}} \quad (61)$$

$$\beta_{\mathrm{ax}}^{(\mathrm{p})} = (\tfrac{4}{2})^{1/2}\beta_{\mathrm{p}\sigma} \quad (62)$$

$$\beta_{\mathrm{eq}}^{(\mathrm{p})} = (r/2)^{1/2}\beta_{\mathrm{p}\sigma} \quad (63)$$

$$\frac{\beta_{\mathrm{ax}}^{(\mathrm{p})}}{\beta_{\mathrm{eq}}^{(\mathrm{p})}} = \left(\frac{4}{r}\right)^{1/2} > 1 \quad \text{for TB } (r = 3) \quad (64)$$

$$\equiv 1 \quad \text{for } O_h \ (r = 4) \tag{65}$$

$$< 1 \quad \text{for PB } (r = 5) \tag{66}$$

where $\beta_{p\sigma} = \langle p_z|H|\sigma_1\rangle = \langle p_x|H|\sigma_3\rangle$. Letting $\alpha_p - \alpha_i^{(p)} = \Delta\alpha_i^{(p)}$ and introducing the parameter

$$\gamma_i = \Delta\alpha_i^{(p)}/\beta_{p\sigma} \tag{67}$$

we have

$$\frac{ef}{cd} = \left(\frac{r(\gamma_{ax}^2 + 8)}{4(\gamma_{eq}^2 + 2r)}\right)^{1/2} \tag{68}$$

or

$$T^{(p)} = \frac{N_{eq}^{(p)}}{N_{ax}^{(p)}} = \left(\frac{\gamma_{ax}^2 + 8}{\gamma_{eq}^2 + 2r}\right)^{1/2} \tag{69}$$

From the energies (20), (24) and (32), (33) and the relations (64), (66) we have

$$\text{for TB} \quad |\alpha_{ax}^{(p)}| > |\alpha_{eq}^{(p)}|, \quad \alpha_p - \alpha_{ax}^{(p)} > \alpha_p - \alpha_{eq}^{(p)} \tag{70}$$

$$|\beta_{ax}^{(p)}| > |\beta_{eq}^{(p)}| \tag{71}$$

$$\text{for PB} \quad |\alpha_{ax}^{(p)}| < |\alpha_{eq}^{(p)}|, \quad \alpha_p - \alpha_{ax}^{(p)} < \alpha_p - \alpha_{eq}^{(p)} \tag{72}$$

$$|\beta_{ax}^{(p)}| < |\beta_{eq}^{(p)}| \tag{73}$$

So there is a tendency for ζ_{ax} and ζ_{eq} to be approximately equal to each other, and therefore for qualitative estimates (see Section 4 and especially the subsequent paper[24]) we shall use the relations

$$c \approx e, \quad d \approx f, \quad cd \approx ef \tag{74}$$

But in principle $\zeta_{ax} \neq \zeta_{eq}$ and as we usually have

$$|\alpha_{ax}^{(p)} - \alpha_{eq}^{(p)}| \ll |\alpha_p - \alpha_L| \tag{75}$$

the typical relations will be

$$\zeta_{ax} < \zeta_{eq} \quad \text{for TB} \tag{76}$$

$$\zeta_{ax} > \zeta_{eq} \quad \text{for PB} \tag{77}$$

By the way, using the expressions (41) and (42) and (62) and (63), we can predict that in AL_5 and AL_7 complexes the bonding (filled) MO's a_2'' and e' must be very close in energy and even interchangeable. Actually, in the ab initio calculations on PH_5[15a,b] the MO e' lies slightly lower than the MO a_2'', but the two are inverted in the EHM calculations on PH_5,[8] the energy difference being 0.4–0.7 eV. The same inversion with the same energy difference takes place for the ab initio[18] and EHM[17] calculations on PF_5. Moreover, in the same multi-STO-Hückel calculations on PF_5 and PCl_5[33] e' lies 0.1 eV lower than a_2'' in PF_5 but 0.6 eV higher in PCl_5. According to the EHM calculations, e_1' lies 0.5 eV lower than a_2'' in IF_7.[19] In the PE spectra of PF_5 and PCl_5,[33] the only experimental results available, the energies of a_2'' and e' are not distinguishable.

If we neglect the difference $\alpha_{ax}^{(p)} - \alpha_{eq}^{(p)}$ as compared with $\alpha_p - \alpha_L$, i.e., we accept[34]

$$\Delta\alpha_{ax}^{(p)} = \Delta\alpha_{eq}^{(p)} = \Delta\alpha^{(p)} = |\alpha_p - \alpha_L| \tag{75$'$}$$

$$\gamma_{ax} = \gamma_{eq} = \gamma \tag{78}$$

we immediately obtain

$$cd = \left(\frac{1}{2\gamma^2/4 + 4}\right)^{1/2} \tag{79}$$

$$ef = \left(\frac{1}{2\gamma^2/r + 4}\right)^{1/2} \tag{80}$$

$$cd > ef, \quad c > e, \quad d < f \quad \text{for TB} \tag{81}$$

$$cd < ef, \quad c < e, \quad d > f \quad \text{for PB} \tag{82}$$

$$T^{(p)} = \left(\frac{\gamma^2 + 8}{\gamma^2 + 2r}\right)^{1/2} = \left(1 + \frac{1}{3 + \frac{1}{2}\gamma^2}\right)^{1/2} \quad \text{for TB } (r = 3) \tag{83}$$

$$= 1 \quad \text{for } O_h \ (r = 4) \tag{84}$$

$$= \left(1 - \frac{1}{5 + \frac{1}{2}\gamma^2}\right)^{1/2} \quad \text{for PB } (r = 5) \tag{85}$$

As $\gamma^2 > 0$, we have [cf. (81), (82), and (59)] the following main inequalities:

$$1 < T^{(p)} < (4/3)^{1/2} = 1.15 \quad \text{for TB} \tag{86}$$

$$0.89 = (4/5)^{1/2} < T^{(p)} < 1 \quad \text{for PB} \tag{87}$$

Thus, the p-orbital contribution will cause the relative strengthening of equatorial bonds in the TB case and axial bonds in the PB case in the ranges defined by the inequalities (86) and (87).[34]

It is obvious from the structure of γ (67) and the relations (83) and (85) that this inequivalence of axial and equatorial bonds will rapidly disappear with an increase in $\Delta\alpha^{(p)}$ (75′), i.e., an increase in the electronegativity difference of the central atom and ligand. We can expect the equalization of all E–L bonds, i.e., the decrease of the relevant ratios $\Delta R/R$, along the series $SbCl_5 > SnCl_5^- > (InCl_5^{2-}) > CdCl_5^{3-}$ or $PPh_5 > PCl_5 > P(OPh)_5 > PF_5$ in agreement with experiment (Table II). We shall discuss them in more detail after consideration of the s contribution to relative bond strengths.

(b) The s Contribution. In order to estimate the s contribution we can first neglect sd_{z^2} mixing, especially for hypervalent AL_m complexes. An accurate solution of the relevant secular equation for the A_1 representation would produce the MO's in (88), where k = 1, 2, and 3 and the normalizing

$$\psi_k(ka_1') = a_k's + \frac{b_k'}{N_b}(\sigma_1 + \sigma_2 + \ldots + \sigma_{r+2}) + c_k'\left[\frac{1}{N_{c,ax}}(\sigma_1 + \sigma_2) - \frac{1}{N_{c,eq}}(\sigma_3 + \sigma_4 + \ldots + \sigma_{r+2})\right] \tag{88}$$

coefficients a_k', b_k', c_k', N_b, $N_{c,ax}$, and $N_{c,eq}$ are defined by some variational procedure. Depending on the sign of the sum P [cf. (56)]

$$P = a_1'c_1' + a_2'c_2' = -a_3'c_3' \tag{89}$$

the axial bonds will be stabilized if $P > 0$ or destabilized if $P < 0$ (all the products $a_k'b_k'$ give an isotropic contribution).

We shall simulate the structure of $\psi_k(ka_1')$ [88] by perturbing the initial set

$$\psi_1(1a_1') = as + \frac{b}{(r + 2)^{1/2}}(\sigma_1 + \sigma_2 + \ldots + \sigma_{r+2}) \tag{46}$$

$$\psi_2(2a_1') = \left(\frac{r}{2(r + 2)}\right)^{1/2}(\sigma_1 + \sigma_2) - \left(\frac{2}{r(r + 2)}\right)^{1/2}(\sigma_3 + \sigma_4 + \ldots + \sigma_{r+2}) \tag{10}$$

$$\psi_3(3a_1') = bs - \frac{a}{(r + 2)^{1/2}}(\sigma_1 + \sigma_2 + \ldots + \sigma_{r+2}) \tag{90}$$

the set corresponding to the isotropic s contribution which was obtained by neglecting all the overlap integrals $S_i = \langle\sigma_i|\sigma_j\rangle$, $i \neq j$, in the interaction of the s orbital with the ligand group orbitals φ_1 (11) and φ_2 (12). The relevant determinant will be

$$\begin{vmatrix} \alpha_s - \epsilon & (r+2)^{1/2}\beta_s & 0 \\ (r+2)^{1/2}\beta_s & \alpha_{(1)} - \epsilon & H_{12}(\beta_{ij}) \\ 0 & H_{12}(\beta_{ij}) & \alpha_{(2)} - \epsilon \end{vmatrix} = 0$$

where all the designations are quite obvious. If we neglect $H_{12}(\beta_{ij}) = \langle \varphi_1 | H | \varphi_2 \rangle$, we obtain the simplest set (46), (10), and (90) but, if we consider $H_{12}(\beta_{ij})$ as a perturbation (taking into account resonance integrals $\beta_{ij} = \langle \sigma_i | H | \sigma_j \rangle$), we can improve our results.

To first order, the sum P (89) for EL_{r+2} will be

$$P = \frac{ab}{E_{23}} H_{12}(\beta_{ij}) \tag{91}$$

where a and b are taken from (46) and (90), E_{23} is the exciting energy from the MO ψ_2 (12) to ψ_3 (90), and

$$\frac{r+2}{(2r)^{1/2}} H_{12} = \beta_{cis} + \beta_{tr} - 2\beta_{eq} \quad \text{for } EL_5\ D_{3h} \tag{92}$$

$$= 2\beta_{cis} + \beta_{tr} - \beta_{tr} - 2\beta_{cis} \quad \text{for } EL_6\ O_h \tag{93}$$

$$= 3\beta_{cis} + \beta_{tr} - 2\beta_{eq}^{(\omega)} - 2\beta_{eq}^{(2\omega)} \quad \text{for } EL_7\ D_{5h} \tag{94}$$

In the EL_6 O_h case we obtain the trivial result $H_{12} \equiv 0$. In other cases the sign of H_{12} depends, in principle, on the magnitudes of β_{ij}. But, as we have already said, β_{cis} dominates in EL_5 while $\beta_{eq}^{(\omega)}$ does in EL_7. Thus $H_{12} < 0$ in the TB complexes, but $H_{12} > 0$ in the PB ones. This conclusion is confirmed by numerical estimations of H_{12} if we approximate β_{ij} as $\beta_{ij} = -|\text{const}| R_{ij}^{-n}$ (see Appendix, Table VI). As r, ab, and E_{23} are positive, the sign of P coincides with the sign of H_{12}. We are led to the conclusion that the s contribution will cause the axial bonds to be relatively weakened in the EL_5 case but strengthened in the EL_7 case. Therefore the ratios $T^{(s)}$ will be

$$T^{(s)} = \frac{N_{eq}^{(s)}}{N_{ax}^{(s)}} > 1 \quad \text{for TB } EL_5 \tag{92'}$$

$$\equiv 1 \quad \text{for } O_h\ EL_6 \tag{93'}$$

$$< 1 \quad \text{for PB } EL_7 \tag{94'}$$

which qualitatively are the same as for the p contribution [cf. (83)–(87)].

It is easy to show that the MO's $\psi_2'(2a_1')$ obtained from the MO set (46), (10), and (90) will be

$$\psi'(2a_1') = a_2's + |c_{ax}|(\sigma_1 + \sigma_2) - |c_{eq}|(\sigma_3 + \sigma_4 + \ldots + \sigma_{r+2}) \tag{95}$$

where

$$a_2' = ab\left(\frac{1}{E_{12}} + \frac{1}{E_{23}}\right) H_{12} \tag{96}$$

[here $E_{12} > 0$ is the excitation energy from the MO (46) to the MO (12)]. Thus the nodal structures of $\psi(2a_1')$ will be

$$\psi(2a_1') = s - \sigma_{ax} + \sigma_{eq} \quad \text{for TB } EL_5 \tag{97}$$

but

$$\psi(2a_1') = s + \sigma_{ax} - \sigma_{eq} \quad \text{for PB } EL_7 \tag{98}$$

which is confirmed by the results of quantitative calculations on AL_5[8,15,18] and IF_7.[19]

The perturbation approach may be applied to *any* three-orbital, four-electron case,[23] in particular, to the analysis of the MO's in any three-atom molecules or fragments L′–E–L where every atom has one valence orbital (of σ or π type). By definition the first MO has no nodes and thus is entirely bonding

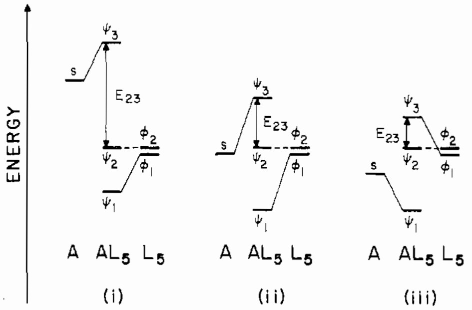

Figure 3. Energy splitting of the a_1' MO's in the TB AL_5 complexes. It is shown why E_{23} decreases as the difference in energy $\alpha_s - \alpha_L$ decreases. The cases (i), (ii), and (iii) correspond to typical situations in $HgCl_5^{3-}$, PF_5, and PCl_5, respectively. See the text for designations of the MO's.

$$\psi_1 = \chi_E + \chi_{L'} + \chi_L$$

while the second MO must have one node. However, the problem is where this node is located, in the E–L′ or E–L region, which correspond respectively to the MO's

$$\psi_2^{(1)} = \chi_E - \chi_{L'} + \chi_L \tag{97'}$$

$$\psi_2^{(2)} = \chi_E + \chi_{L'} - \chi_L \tag{98'}$$

This nodal distribution determines the relative strength of the E–L′ and E–L bonds and is one of the decisive factors in the theory of the mutual influence of ligands.[21,22] The perturbation approach permits the nodal distribution (97′) and (98′) to be found quite reliably.[23] It is of importance because until now the relationships like (97) and (98) have not been explained qualitatively in an unequivocal way. For example, it is tempting to explain the energetic preference of the nodal structure (97) over (98) in TB AL_5 complexes by the fact that (97) corresponds to *three* bonding (equatorial) vs. *two* antibonding (axial) interactions. However, from (12)

$$\left| \frac{c_{ax}}{c_{eq}} \right| = \frac{r}{2} \tag{99}$$

so that in the AL_5 case $|c_{ax}/c_{eq}| = {}^3/_2$ [cf. Appendix, (142)] which exactly compensates the above ratio of the numbers of bonding and antibonding interactions. The main weakness of the above argument is that it would lead to the incorrect conclusion that the same nodal structure (97) occurs in the PB AL_7 case.

The usefulness of the relation (91) is that it permits the relative changes in the s overlap populations and s characters of A–L_{ax} and A–L_{eq} bonds to be predicted. The numerical value of the parameter ab/E_{23} in (91) will increase as ab increases and the energy gap E_{23} decreases. As seen from Figure 3, this gap will be less the lower the energy of the s orbital relative to the group ligand orbitals. Though the product ab may be changed in a nonmonotonical way while the s orbital energy decreased along the series (i)–(ii)–(iii) in Figure 3, these changes in ab are insignificant compared with changes in E_{23}.

This consequence of (91) is confirmed by the EHM calculations on PF_5 and PCl_5.[16] The employed parameters ($\alpha_{P3s} = -20.20$, $\alpha_{F2p} = -20.86$, $\alpha_{Cl3p} = -15.3$ eV) correspond to the cases (ii) and (iii) in Figure 3, and the s characters of P–L_{ax} and P–L_{eq} bonds have been found to be 19.4 and 20.4% for PF_5 and 11.7 and 25.5% for PCl_5. The drastic increase in the P 3s character in equatorial as compared with axial bonds is

Table II. Bond Lengths (Å) of Some TB AL_5 and ML_5 $(n-1)d^{10}$ Complexes

complex	phys state	$R(\text{E–L}_{ax})_{av}$	$R(\text{E–L}_{eq})_{av}$	ΔR(ax–eq)	$\Delta R/R_{av}$	ref
PF_5	g	1.58	1.53	0.04	0.03	*a*
$P(OPh)_5$	c	1.66	1.60	0.06	0.04	*b*
PCl_5	g	2.12	2.02	0.10	0.05	*c*
PPh_5	c	1.99	1.85	0.14	0.07	*d*
AsF_5	g	1.71	1.65	0.06	0.03	*e*
$SbCl_5$	c	2.34	2.29	0.05	0.02	*f*
$SnCl_5^-$	c	2.38	2.36	0.02	0.01	*g*
$CdCl_5^{3-}$	c	2.53	2.56	−0.03	−0.01	*h*
$HgCl_5^{3-}$	c	2.52	2.64	−0.12	−0.05	*i*

[a] K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, 4, 1775 (1965). [b] R. Sarma, F. Ramirez, B. McKeever, J. F. Marecek, and S. Lee, *J. Am. Chem. Soc.*, 98, 581 (1976). [c] W. J. Adams and L. S. Bartell, *J. Mol. Struct.*, 8, 23 (1971). [d] P. J. Wheatley, *J. Chem. Soc.*, 2206 (1964). [e] F. B. Clippard, Jr., and L. S. Bartell, *Inorg. Chem.*, 9, 805 (1970). [f] S. M. Ohlberg, *J. Am. Chem. Soc.*, 81, 811 (1959). [g] Reference 35. [h] Reference 36. [i] Reference 37.

the main reason for the increase of the total ratio N_{eq}/N_{ax} which (without 3d orbitals of the P atom) has been found to be 1.08 for PF_5 and 1.55 for PCl_5.

Finally, the relationship (91) permits the influence of steric effects to be included. As P is a function of β_{ij} which rapidly decreases (in absolute value) with increasing interligand distances, one can expect that, other conditions being equal, the relative equatorial strengthening will be larger the smaller the bond length R(A–L).

Qualitative similarity of the s and p contributions permits the $\Delta R/R_{av}$ regularities in AL_m complexes to be explained. The simplest regularity concerns AL_5 complexes when we fix an atom A, its s orbital being at the same energy as the σ orbital of some initial ligand L. In the AL_5' series where donor ability of the ligand L′ increases (and bond lengths do not change greatly) both s and p contributions to the relative equatorial strengthening will increase monotonically, increasing $\Delta R/R_{av}$. The series PL_5 where L = F, OPh, Cl, and Ph is just such a case (see Table II).

If L is fixed as A varies along a group of the periodic table, values of $\Delta R/R$ should decrease (by the inverse of the previous argument), but possible nonmonotonic changes in the s and p contributions may complicate the trend in question. Two pairs of complexes PF_5 and AsF_5 and PCl_5 and $SbCl_5$ (see Table II) are good illustrations. In the former case the values of $\Delta R/R$ are practically the same; in the latter case the decrease of $\Delta R/R$ is quite obvious.

However complicated the regularities of $\Delta R/R$ prove to be, the s and p contributions can result only in a relative weakening of axial bonds, though for strong donor central atoms this weakening must be very small as, for example, in $SnCl_5^-$.[35] Two TB AL_5 complexes, $CdCl_5^{3-}$[36] and $HgCl_5^{3-}$,[37] are known at present where axial bonds are shorter than equatorial ones, so we have to look for the source of this reversal.

In PB AL_7 complexes we can predict the relative strengthening of axial bonds with similar regularities to the TB AL_5 case (but of opposite sign). Unfortunately, reliable structural data are known only for IF_7 where indeed the I–F_{ax} length is much shorter than the I–F_{eq} one (ΔR = −0.072 Å[31]).

(c) The d Contribution. (i) The $(n-1)d^{10}$ Case. On the basis of EHM calculations Hoffmann, Muetterties, et al.[9,10] have done an excellent analysis of relative bond strengths and site preferences in transition-metal complexes ML_5[9] and ML_7[10] as a function of d^x electronic configuration of the central atom. We shall show that our model leads to the same qualitative results, but first we want to examine a special subclass of complexes, $(n-1)d^{10}$ ML_5, which previously[9] has been considered exactly the same as the AL_5 case. As in the formally isoelectronic AL_5 case, to a first approximation, the hypervalent scheme[25] can be adopted for $(n-1)d^{10}$ ML_5 complexes with *n*s and *n*p orbitals responsible for bonding. In contrast to AL_5, however, the axial bonds are shorter, e.g., ΔR = −0.03 Å in $CdCl_5^{3-}$[36] and −0.12 Å in $HgCl_5^{3-}$.[37] To our knowledge, no theoretical model or calculation has explained this shortening.[38] As shown above, the s and p contributions can lead only to relative strengthening of axial bonds in any TB complex, though in the cases of the $CdCl_5^{3-}$ and $HgCl_5^{3-}$ this strengthening must be minimal.

Let us try to estimate the influence of filled $(n-1)d^{10}$ shells. In neutral AL_5 complexes with A belonging to the end groups of the periodic table, the central atom has either no $(n-1)$d orbitals at all (Si, P, S, etc.) or very deeply lying $(n-1)d^{10}$ orbitals (As, Sb, Sn, Sb, etc.).[39] It is another story for the beginning group elements, especially for such 2B elements as Cd or Hg. For example, the energy difference between 6s and 5d atomic orbitals in gaseous Hg equals only ca. 5 eV.[40] Certainly this difference will be smaller in anionic complexes like $HgCl_5^{3-}$.

Let us consider the perturbation interaction of filled $(n-1)$d orbitals of $a_1'(d^2_{z^2})$ and $e'(d^2_{x^2-y^2},d^2_{xy})$ symmetries with the relevant MO's $\psi(s)$, $\psi^*(s)$ and $\psi(p_x)$, $\psi^*(p_x)$ [see (39), (40), (46), and (48)]; $\Delta E_{ax} \leq \Delta E_{eq}$ corresponds to the excitation energies from $(n-1)d^2_{z^2}$ to $\psi^*(s)$ and from $(n-1)d^2_{x^2-y^2}$ to $\psi^*(p_x)$, respectively. As we consider only σ bonds A–L, all the relevant matrix elements should be expressed in terms of $\beta_{d\sigma} = -|\text{const}|S_{d\sigma}$. This can be performed by using the expansions[41] (omitting non-σ components) of (100) and (101),

$$d_{z^2} = d_{z'^2}(\cos^2\omega - \tfrac{1}{2}\sin^2\omega) + \ldots \qquad (100)$$

$$d_{x^2-y^2} = d_{z'^2}\frac{3^{1/2}}{2}\sin^2\omega + \ldots \qquad (101)$$

where ω is the angle between axis z and z' (in the xz plane) and the z' axis is the axis of the A–L σ bond.

After the relevant transformations, we obtain, as a first-order perturbation, the $(n-1)d^{10}$ orbital contribution to $N(\text{A–L}_{ax})$ and $N(\text{A–L}_{eq})$

$$\Delta N(\text{A–L}_{ax}) = |\text{const}|\frac{S^2{}_{d\sigma}}{10}\frac{a^2}{\Delta E_{ax}} \qquad (102)$$

$$\Delta N(\text{A–L}_{eq}) = |\text{const}|\frac{S^2{}_{d\sigma}}{20}\left(\frac{15c^2}{\Delta E_{eq}} - \frac{a^2}{\Delta E_{ax}}\right) \qquad (103)$$

The first (positive) term in (103) is defined by the $d^2_{x^2-y^2}$ contribution and the second (negative) term by the $d^2_{z^2}$ contribution. a and $c \approx e$ (74) are the coefficients from the MO's (46) and (48). Since $\Delta E_{ax} \leq \Delta E_{eq}$ (see above), we find, as a condition for relative axial strengthening, $\Delta N(\text{A–L}_{ax}) > \Delta N(\text{A–L}_{eq})$, that

$$a > 5^{1/2}c \qquad (104)$$

Let us emphasize that the inequality (104) reflects the $(n-1)d^{10}$ contribution to the bond strength via the algebraic coefficients of s and p orbitals in the relevant MO of an AL_5 complex. For strongly donor atoms like Cd and Hg where valence p orbitals lie rather high (they are even vacant in the neutral atom ground state), the condition (104) looks reasonable.[42] For the usual electronegative atoms A, where ΔE_{ax} and ΔE_{eq} are large, the relative axial strengthening due to the $(n-1)d^{10}$ contribution must be extremely small [cf. (102) and (103)] and can not overcome the relative equatorial strengthening due to the *n*s and *n*p contributions.

So it is worthwhile to distinguish the $(n-1)d^{10}$ ML_m cases from the nd^0 AL_m cases. We shall include in the former class atoms M of the beginning groups of the periodic table (Cu^I, Hg^{II}, Cd^{II}, etc.) and in the latter class atoms A of the middle and end groups ($\mathrm{Sn^V}$ ($\mathrm{Sn^-}$), $\mathrm{P^V}$, $\mathrm{I^{VII}}$, etc.).

In the $\mathrm{AL_7}$ D_{5h} PB case the contribution of $(n-1)\mathrm{d}^{10}$ shells includes only the $(n-1)\mathrm{d}^2{}_{z^2}$ contribution because $(n-1)$ $\mathrm{d}^2{}_{x^2-y^2}\mathrm{d}^2{}_{xy}$ interact with the filled ligand group orbitals within the irreducible representation $\mathrm{e_2'}$ (remember that the influence of $(n-1)\mathrm{d}^2{}_{x^2-y^2}\mathrm{d}^2{}_{xy}$ orbitals in the $\mathrm{AL_5}$ D_{3h} TB case is defined by the presence of vacant antibonding orbitals within the e′ representation to which p_x, $\mathrm{d}_{x^2-y^2}$, p_y, and d_{xy} belong). After the relevant transformations we obtain

$$\Delta N_{\mathrm{ax}} = -|\mathrm{const}|\frac{S^2{}_{\mathrm{d}\sigma}}{14}\,\frac{a^2}{\Delta E_{\mathrm{ax}}} \qquad (105)$$

$$\Delta N_{\mathrm{eq}} = |\mathrm{const}|\frac{S^2{}_{\mathrm{d}\sigma}}{28}\,\frac{a^2}{\Delta E_{\mathrm{ax}}} \qquad (106)$$

i.e., contrary to the $\mathrm{AL_5}$ D_{3h} TB case, $(n-1)\mathrm{d}^2{}_{z^2}$ will destabilize axial bonds and stabilize equatorial ones. Thus the *n*s, *n*p, and $(n-1)\mathrm{d}^{10}$ contributions are always of opposite sign. Again, for atoms in the last groups of the periodic table, ΔE_{ax} is very large, so it is not surprising that in $\mathrm{IF_7}$ axial bonds prove to be distinctly shorter than equatorial ones (as discussed above). At the same time we might predict that in anionic complexes of the $\mathrm{AL_7}^{n-}$ type (if such can be made) the $(n-1)\mathrm{d}^{10}$ contribution may become remarkable and ΔR will be smaller in absolute value, perhaps changing sign as compared with ΔR in $\mathrm{IF_7}$ (cf. $\mathrm{SnCl_5^-}$ and $\mathrm{HgCl_5^{3-}}$).

(ii) The $(n-1)\mathrm{d}^x$ Case. Now we turn to the $(n-1)$d contribution in transition-metal complexes $\mathrm{ML_5}$ and $\mathrm{ML_7}$. Our arguments will be rather similar to those used earlier to estimate the p contribution. The only substantial complication is that the d_{z^2} orbital contributes to both axial and equatorial bonds [a fact already used to obtain the relations (102) and (103) and (105) and (106)]. Further, we can use two forms of MO's including the d_{z^2} orbitals, namely (49) or (49′), the latter being preferable. Taking into account (16), (49′), (50), (100), and (101) and introducing the obvious designations, we obtain

$$N_{\mathrm{ax}}{}^{(\mathrm{d})} = gh\left(\frac{4}{r+8}\right)^{1/2} S_{\mathrm{d}\sigma} \qquad (107)$$

$$N_{\mathrm{eq}}{}^{(\mathrm{d})} = \left(gh\left(\frac{1}{4(r+8)}\right)^{1/2} + lm\left(\frac{3}{2r}\right)^{1/2}\right)S_{\mathrm{d}\sigma} \quad \text{for } \mathrm{ML_5} \text{ and } \mathrm{ML_7} \qquad (108)$$

$$= \left(gh\left(\frac{1}{4(r+8)}\right)^{1/2} + lm\left(\frac{3}{4r}\right)^{1/2}\right)S_{\mathrm{d}\sigma} \quad \text{for } \mathrm{ML_6}\ O_h \qquad (109)$$

$$T^{(\mathrm{d})} = \frac{N_{\mathrm{eq}}{}^{(\mathrm{d})}}{N_{\mathrm{ax}}{}^{(\mathrm{d})}} = {}^1\!/_4 + \frac{lm}{gh}\left(\frac{3(r+8)}{8r}\right)^{1/2} \quad \text{for } \mathrm{ML_5} \text{ and } \mathrm{ML_7} \qquad (110)$$

$$= {}^1\!/_4 + \frac{lm}{gh}\left(\frac{3(r+8)}{16r}\right)^{1/2} = 1 \quad \text{for } \mathrm{ML_6}\ O_h\ (r = 4) \qquad (111)$$

$$\beta_{\mathrm{ax}}(\mathrm{a_1'}) = \frac{(r+8)^{1/2}}{2}\beta_{\mathrm{d}\sigma} \qquad (112)$$

$$\beta_{\mathrm{eq}}(\mathrm{e_1'}) = \left(\frac{3r}{8}\right)^{1/2}\beta_{\mathrm{d}\sigma} \qquad (113)$$

Table III. Bond Lengths (Å) in Some PB $\mathrm{AL_7}$ and $\mathrm{ML_7}$ Complexes

complex	d^x	phys state	$R(\mathrm{E{-}L_{ax}})_{\mathrm{av}}$	$R(\mathrm{E{-}L_{eq}})_{\mathrm{av}}$	ΔR(ax−eq)	ref
$\mathrm{IF_7}$	$n\mathrm{d}^0$	g	1.78_6	1.85_8	−0.07	*a*
$\mathrm{ReF_7}$	$(n-1)\mathrm{d}^0$	g			-0.06^c	*b*
$\mathrm{ZrF_7}^{3-}$	$(n-1)\mathrm{d}^0$	c	2.00	2.03	−0.03	*d*
$\mathrm{V(CN)_7}^{4-}$	$(n-1)\mathrm{d}^2$	c	2.14_4	2.14_9	~0.0	*e*

[a] Reference 31. [b] Reference 45. [c] Only the mean Re–F distance is given (1.835 ± 0.001 Å). The uncertainty in the equatorial–axial difference is on the order of 0.02 Å. [d] H. J. Hurst and J. C. Taylor, *Acta Crystallogr., Sect. B*, **26**, 417, 2136 (1970). [e] R. A. Levenson and R. L. R. Towns, *Inorg. Chem.*, **13**, 105 (1974).

Table IV. χ Contribution to $T^{(\chi)}$ in Complexes EL_m

complex	$T^{(\mathrm{s})}$	$T^{(\mathrm{p})}$	$T^{(\mathrm{s+p})\,a}$	$T^{(\mathrm{d})}$	ref
TB $\mathrm{EL_5}$ D_{3h}	>1	1.0–1.15	>1	~1.5	this work
	1.14	1.13	1.13		*b*
	1.12	1.04			*c*
			1.06		*d*
			1.08		*e*
			1.16	1.79^m	*f*
			1.17		*g*
			1.22		*h*
			1.23		*i*
			1.25		*j*
			1.37^n		*k*
			1.55^n		*l*
PB $\mathrm{EL_7}$ D_{5h}	<1	0.9–1.0	<1	~1.2	this work
			0.73	1.19	*f*

[a] The total ratio $T^{(\mathrm{s+p})} = N_{\mathrm{eq}}{}^{(\mathrm{s+p})}/N_{\mathrm{ax}}{}^{(\mathrm{s+p})}$. [b] Our EHM calculations on some typical $\mathrm{AL_5}$ complex (see Appendix). [c] CNDO/2 calculation on $\mathrm{PF_5}$.[17a] [d] Ab initio calculation on $\mathrm{PF_5}$.[18a] [e] EHM calculation on $\mathrm{PF_5}$.[16a] [f] EHM calculation on some typical $\mathrm{ML_5}$ and $\mathrm{ML_7}$ $(n-1)\mathrm{d}^0$–d^4 complexes.[44] [g] Ab initio calculation on $\mathrm{PF_5}$.[18b] [h] GIVNAP + ARCANA calculation on $\mathrm{PH_5}$.[17b] [i] GIVNAP + ARCANA calculation on $\mathrm{PF_5}$.[17b] [j] Ab initio calculation on $\mathrm{PH_5}$.[15c] [k] Ab initio calculation on $\mathrm{PH_5}$.[15a] [l] EHM calculation on $\mathrm{PCl_5}$.[16a] [m] This value seems to be too large to be typical, not only by comparison with our model upper limit $T^{(\mathrm{d})} < 1.6$ (118′) but also by comparison with the ab initio calculations on $\mathrm{VF_5}$ ($3\mathrm{d}^0$) and $\mathrm{VF_5^-}$ ($3\mathrm{d}^1$) where the ratios $N(\mathrm{V{-}F_{eq}})/N(\mathrm{V{-}F_{ax}})$ were found to be 1.06 and 1.12, respectively.[43a] [n] This increased value of $T^{(\mathrm{s+p})}$ reflects an increase of the s contribution as compared with that in $\mathrm{PF_5}$ (see text).

Table V. Site Preference for a Stronger Donor Substituent L′ in TB $\mathrm{EL_5}$ and PB $\mathrm{EL_7}$ Complexes

complex	d^x	site preference
TB $\mathrm{EL_5}$ D_{3h}	$\mathrm{AL_5}$ $n\mathrm{d}^0$	equatorial[a]
	$\mathrm{ML_5}$ $(n-1)\mathrm{d}^0$–d^4	equatorial[a]
	$\mathrm{ML_5}$ $(n-1)\mathrm{d}^8$	axial[a]
	$\mathrm{ML_5}$ $(n-1)\mathrm{d}^{10}$	dependent upon parameter values[b]
PB $\mathrm{EL_7}$ D_{5h}	$\mathrm{AL_7}$ $n\mathrm{d}^0$	axial[b]
	$\mathrm{ML_7}$ $(n-1)\mathrm{d}^0$–d^4	dependent upon parameter values[b]

[a] The result agrees with the known experimental and computational data (see, for instance, ref 8, 9, 15, 16, 18, 20). [b] This result is specific to the present work (see text).

(In the O_h case (113) becomes $(3^{1/2}/2)\beta_{\mathrm{d}\sigma}$, so that $(r+8)^{1/2}/2 \equiv (3r)^{1/2}/2$ for $r = 4$ which must be by symmetry.) In the expression (114) the parameters γ_{ax} and γ_{eq} are the d analogues of the relation (67). Typically for transition-metal complexes

$$\frac{lm}{gh} = \left(\frac{1 + \dfrac{\gamma_{\mathrm{ax}}{}^2}{r+8}}{1 + \dfrac{2}{3r}\gamma_{\mathrm{eq}}{}^2}\right)^{1/2} \qquad (114)$$

$$\frac{\alpha_d - \alpha(2a_1')}{\alpha_d - \alpha(e_i')} = \frac{\gamma_{ax}}{\gamma_{eq}} < \left(\frac{2(r+8)}{3r}\right)^{1/2} = 1.56 \quad \text{for TB } (r = 3) \quad (115)$$

$$= 1.32 \quad \text{for PB } (r = 5) \quad (116)$$

so that

$$lm/gh < 1 \quad (117)$$

and, from (110),

$$T^{(d)} = \frac{N_{eq}{}^{(d)}}{N_{ax}{}^{(d)}} < 1.42 \quad \text{for TB } (r = 3) \quad (118)$$

$$< 1.24 \quad \text{for PB } (r = 5) \quad (119)$$

Using (49) instead of (49′) leads, in the same way, to

$$T^{(d)} = \frac{1}{r} + \frac{lm}{gh}\,\frac{(3(r+2))^{1/2}}{r} \quad (110')$$

$$\frac{lm}{gh} = \left(\frac{1 + \dfrac{\gamma_{ax}{}^2(r+2)}{18r}}{1 + \dfrac{\gamma_{eq}{}^2(2r)}{3}}\right)^{1/2} < 1 \quad (114')$$

and

$$T^{(d)} = \frac{N_{eq}{}^{(d)}}{N_{ax}{}^{(d)}} < 1.62 \quad \text{for TB } (r = 3) \quad (118')$$

$$< 1.16 \quad \text{for PB } (r = 5) \quad (119')$$

From Figure 2 and discussion above it appears that *lm* and *gh* will be close, especially in the ML_7 case, i.e.

$$g \approx l, \quad h \approx m, \quad lm \approx gh \quad (74')$$

which is similar to the relations (74) [see also ref 34b].

So, neglecting the complications connected with the sd_{z^2} mixing (in particular, the MO φ_1 (11) gives some additional contribution to $T^{(d)}$ of the opposite signs for ML_5 and ML_7), we obtain the following approximate ranges:

$$\text{for TB } ML_5 \ d^0\text{–}d^4 \quad T^{(d)} \approx 1.5 \quad (120)$$

$$\text{for PB } ML_7 \ d^0\text{–}d^4 \quad T^{(d)} \approx 1.2 \quad (121)$$

Thus, in the ML_5 d^0–d^4 complexes the d contribution is of the same sign as that of the s and p contribution, so axial bonds must be weaker than equatorial ones.

Unfortunately, the known structural (electron diffraction) data[30] are not accurate enough to determine the difference in axial and equatorial bonds, though this difference can reach 0.1 Å,[30] a rather large value even compared to the AL_5 D_{3h} complexes (cf. Table II). But our conclusion agrees with the results of quantitative calculations[9,43a,b,44] (cf. also Table IV).

In the ML_5 D_{3h} d^8 cases the vacant hybrid orbital (51.3) is entirely antibonding, the coefficient c_3' before the p_x orbital being much larger than g_3' before the $d_{x^2-y^2}$ orbital.[9] Thus the $d_{x^2-y^2}$ (d_{xy}) contribution to $T^{(d)}$ may be neglected, but $T^{(p)}$ changes insignificantly. So, taking into account only the $(n-1)d_{z^2}$ contribution to $T^{(d)}$, we obtain, from (110) and (110′), the approximate range

$$\text{for TB } ML_5 \ d^8 \quad T^{(d)} = 0.25\text{–}0.33 \quad (120')$$

This drastic decrease in $T^{(d)}$ can result in the relative strengthening of axial bonds.[52] Actually, in all of the known TB ML_5 d^8 complexes, axial bonds are either the same [e.g., $Pt(SnCl_3)_5{}^{3-}$] or shorter (see ref 9 and references therein).

On the contrary, in ML_7 D_{5h} PB complexes (the d^0–d^4 case) the d contribution is of the opposite sign as that of the s and p contribution, so we can expect, as a rule, substantial equalizing of all the bonds. Actually, in all known ML_7 D_{5h} complexes the differences in bond lengths are insignificant (Table III).

The opposing contributions are clearly reflected in calculations on a typical complex d^0–d^4 ML_7 D_{5h}[10] where overlap populations of the M–L_{ax} and M–L_{eq} bonds differ hardly at all (0.55 and 0.52, respectively). The small differences in total energies of different polyhedra ML_7[10] and a suggestion of the d-orbital contribution of Re atom as the main reason for a substantial difference in the hardness of D_{5h} polyhedra ReF_7 vs. IF_7[45] also agree with our results.

Our estimates for the $T^{(x)}$ ranges are summarized in Table IV and compared with published calculations. Agreement among them is quite satisfactory.[34b]

4. Relative Stability of Axial and Equatorial Isomers. Nonequivalency of axial and equatorial positions in EL_5 TB and EL_7 PB complexes raises the question of which positions should be preferable upon substitution of a ligand L by a given ligand L′. For clarity let us accept that L′ is a stronger donor ligand than L, i.e.

$$\langle \sigma_{L'}|H|\sigma_{L'}\rangle - \langle \sigma_L|H|\sigma_L\rangle = \delta\alpha' > 0 \quad (122)$$

and consider this change in the diagonal matrix element as a perturbation. To determine which isomer—axial or equatorial—should be more stable we have to find the difference in total energies of the two isomers

$$\Delta E'_{ax-eq} = E'_{ax} - E'_{eq} = 2\left(\sum_i^{occ}\epsilon'_{i,ax} - \sum_i^{occ}\epsilon'_{i,eq}\right) \quad (123)$$

Thus, $\Delta E'_{ax-eq} > 0$ (<0) means that the equatorial (axial) isomer is more stable which corresponds to a relatively stronger equatorial (axial) bond. If we take for all the MO's the form (55) and for their energies the form (41), we obtain to first order[46]

$$\delta\epsilon_i' = c^2_{iL'}\delta\alpha' \quad (124)$$

and the total perturbation energy of each isomer may be written as

$$\delta E' = 2\sum_i^{occ}\delta\epsilon_i' = 2\sum_i^{occ}c^2_{iL'}\delta\alpha' \quad (125)$$

Therefore the energy difference (123) may be rewritten as

$$E' = \frac{\Delta E'_{ax-eq}}{\delta\alpha'} = 2\left(\sum_i^{occ}c^2_{iL',ax} - \sum_i^{occ}c^2_{iL',eq}\right) \quad (126)$$

Since $\delta\alpha' > 0$ (122), $E' > 0$ (<0) again corresponds to the more stable equatorial (axial) isomer.

To obtain the energy (125) to first order we can use unperturbed MO's (46)–(50) of the EL_m complex. For our purpose we can accept $c = e$ and $d = f$ (74) and $g = l$ and $h = m$ (74′). In non-transition-element complexes the relations among the coefficients will be

$$h \gg f > b \quad (127)$$

and we can neglect small *n*d admixtures, simply assuming $h = 1$ and $g = 0$. In AL_m cases there is no sd_{z^2} mixing and the s contribution will be considered to be isotropic.

In transition-metal complexes the situation is more complicated. First, in the inequality

$$f \gg b > h \quad (128)$$

we can neglect no coefficients. Second, sd_{z^2} mixing forces us to check the results of both orthogonalization schemes for the a_1' group ligand orbitals. Thus, for ML_m complexes we shall give two values of E'(126), for MO's (11), (12) and (14), (15), which we shall name E'(s) and $E'(\mathrm{d}_{z^2})$, respectively. Third, in the ML_5 TB case we have to take into account $\mathrm{p}_x\mathrm{d}_{x^2-y^2}$ ($\mathrm{p}_y\mathrm{d}_{xy}$) mixing, i.e., to consider the MO's (51.1) and the relationship (52) where

$$h_1' < h \qquad (129)$$

but

$$h < f < \eta < 1 \qquad (130)$$

With all this we obtain the following expressions for E'.

(a) The TB EL_5 Case.

(1) AL_5 $n\mathrm{d}^0$

$$E' = \tfrac{1}{3}(1 - f^2) = e^2/3 > 0 \qquad (131)$$

This result illustrates the well-known Muetterties rule[20] concerning the preference for equatorial substitution by stronger donor ligands. Moreover, from (131) and (126) we can predict that this preference will increase as the difference in electronegativities of L and L′ increases ($\delta\alpha'$ increases) and the difference in electronegativities of A and L decreases (e increases); i.e., for a given L the donor ability of A decreases. Unfortunately, there is no relevant experimental data.

(2) ML_5 $(n - 1)\mathrm{d}^0$–d^4

$$E'(\mathrm{s}) = f^2 - h^2 > 0 \qquad (132)$$

$$E'(\mathrm{d}_{z^2}) = f^2 - \tfrac{7}{33}b_2 - \tfrac{26}{33}h^2 > 0 \qquad (132')$$

Equatorial substitution is always preferable which reflects the fact that all the $T^{(x)} > 1$.

(3) ML_5 $(n - 1)\mathrm{d}^8$

$$E'(\mathrm{s}) = f^2 + \tfrac{1}{3}h^2 - \tfrac{4}{3}\eta^2 < 0 \qquad (133)$$

$$E'(\mathrm{d}_{z^2}) = f^2 - \tfrac{7}{33}b^2 + \tfrac{6}{11}h^2 - \tfrac{4}{3}\eta^2 < 0 \qquad (133')$$

Axial substitution is always preferable.

(4) ML_5 $(n - 1)\mathrm{d}^{10}$

$$E'(\mathrm{s}) = f^2 + \tfrac{1}{3} - \tfrac{4}{3}\eta^2 < \text{or} > 0 \qquad (134)$$

$$E'(\mathrm{d}_{z^2}) = f^2 + \tfrac{6}{11} - \tfrac{4}{3}\eta^2 < \text{or} > 0 \qquad (134')$$

This uncertainty in the signs of E' reflects the fact that equatorial bonds may be stronger or weaker than axial bonds depending upon the values of the coefficients f and η [cf. the inequality (104)].

(b) The O_h EL_6 Case. For any d^x configuration and any central atom (A or M) we have the trivial identity

$$E'(\mathrm{s}) = E'(\mathrm{d}_{z^2}) = 0 \qquad (135)$$

For example, in the ML_6 d^0 case

$$E' = 2\left(\frac{b^2}{6} + \frac{f^2}{2} + \frac{h^2}{3} - \frac{b^2}{6} - \frac{f^2}{2} - \frac{h^2}{12} - \frac{h^2}{4}\right) \equiv 0 \qquad (135')$$

(c) The PB EL_7 Case.

(1) AL_7 $n\mathrm{d}^0$

$$E' = \tfrac{1}{5}(f^2 - 1) = -e^2/5 < 0 \qquad (136)$$

This result is quite opposite to that in the AL_5 case (131). The relevant interpretation is analagous to that given for the AL_5 series (see above) if we replace the word "donor" by "acceptor".

(2) ML_7 $(n - 1)\mathrm{d}^0$–d^4

$$E'(\mathrm{s}) = f^2/5 - h^2/5 > 0 \qquad (137)$$

$$E'(\mathrm{d}_{z^2}) = f^2/5 + \tfrac{9}{130}b^2 - \tfrac{11}{65}h^2 < \text{or} > 0 \qquad (137')$$

This case is the only one where the site preference depends on the details of sd_{z^2} mixing because $T^{(\mathrm{s})} < 1$ and $0.9 < T^{(\mathrm{p})} < 1$ (87), but $T^{(\mathrm{d})} \approx 1.2$ (121).

All the above results are summarized in Table V.

The site preference expressed in terms of the bond or total energy differences E' (126) exactly corresponds to that in terms of bond polarities. In an unsubstituted complex EL_m the effective charges of the axial ligand L_1 (q_1) and equatorial ligand L_3 (q_3) will be

$$q_1 = 1 - 2\sum_i^{\mathrm{occ}} c^2_{i1} \qquad (138)$$

$$q_3 = 1 - 2\sum_i^{\mathrm{occ}} c^2_{i3} \qquad (139)$$

where c_{ik} stands for the coefficient of the σ_k orbital in the occupied LCAO MO ψ_1. Therefore the difference in effective charges of the axial L_1 and equatorial L_3 ligands will be equal to the negative of E' (126), namely

$$q = q_1 - q_3 = 2\left(\sum_i^{\mathrm{occ}} c^2_{i3} - \sum_i^{\mathrm{occ}} c^2_{i1}\right) = -E' \qquad (140)$$

Consequently, $q < 0$ (>0) means not only that the axial (equatorial) ligand is more electronegative but also that the equatorial (axial) bond is stronger. This relation easily explains why site preferences may be predicted in terms of bond polarity as is usually done.[47]

Caution must be exercised, however. It is obvious that the equation (140) can hold only as long as a bond strength is defined by its covalency. With significant Madelung corrections, as in the case of strongly polar hypervalent main-group complexes, the correspondence between bond polarity and bond strength may not be clear at all.[48] In addition, we want to stress that the two criteria only need coincide when the s, p, and d contributions to the relative bond strength are of the same sign, as in the TB AL_5, ML_5 d^0–d^4, or PB AL_7 cases. Otherwise the two criteria may lead to different conclusions.

A perfect example exists in the PB ML_7 d^0–d^4 complexes where $T^{(\mathrm{s})} < 1$, $T^{(\mathrm{p})} < 1$, but $T^{(\mathrm{d})} > 1$. Quantitative calculations have shown[10] that less polar equatorial bonds have smaller overlap population than more polar axial bonds. According to the bond strength criterion, a stronger donor ligand L′ should prefer the axial position, but, according to the bond polarity criterion, the equatorial position. In principle the first criterion is more general because it reflects the relative thermodynamic stability of the isomers. The second criterion may dominate in the kinetics of the substitution reaction but, if there are no serious obstacles to interligand exchange, i.e., the interconversion barrier is not very high, the more stable isomer must be formed. While in both known examples of substituted ML_7 complexes—$\mathrm{OsH_4(PR_3)_3}$[49] and $\mathrm{IrH_5(PR_3)_2}$[50]—the stronger donor ligand, hydrogen, occupies equatorial positions (in agreement with the bond polarity criterion[10]) this may just be a result of steric repulsion of the bulky PR_3 ligands. Future experimental and computational data should answer this new question: which of the two criteria is more general?

Conclusion

We see that our analytical LCAO MO approach allows the separate s, p, and d contributions to relative bond strengths to be obtained in explicit form. In particular, our approach is able to take into account the anisotropy of the s contribution and to estimate some effects of sd_{z^2} and $\mathrm{p}_x\mathrm{d}_{x^2-y^2}$ ($\mathrm{p}_y\mathrm{d}_{xy}$) mixing (which other qualitative models failed to do). The main results of our work are given in Tables IV and V. We see that the

Table VI. Values of H_{12}[a,b]

	n		
complex	1	2	3
EL_5	1.207	0.750	0.479
EL_7	−0.134	−0.254	−0.341

[a] See the expression (92) for EL_5 and (94) for EL_7. [b] All the values of H_{12} have to be multiplied by $[(r + 2)/(2r)^{1/2}]R^{-n}$, where *R* is the E–L bond length.

Table VII. Parameters Employed in EHM Calculations

atom	orbital	$-H_{ii}$, eV	Slater exponent
A	3s	20.0	1.83
	3p	11.0	1.83
H	1s	13.6	1.30
L	3s	15.0	1.30

Table VIII. Overlap Populations $N_{eq}^{(X)}$ and $N_{ax}^{(X)}$ in TB AL_5

X	3s	3p	3s + 3p (total)
$N_{eq}^{(X)}$	0.134	0.220	0.354
$N_{ax}^{(X)}$	0.117	0.195	0.312
$T^{(X)}$	1.14[a]	1.13[b]	1.13

[a] Cf. the inequality (92′). [b] Cf. the inequality (86).

*n*s and *n*p contributions in TB EL_5 complexes are always opposite to those in PB EL_7 complexes. Further, in the TB ML_5 case the $(n - 1)$d contribution can greatly strengthen those of *n*s and *n*p, but in the PB ML_7 case the $(n - 1)$d contribution always opposes those of *n*s and *n*p. Our results agree with the known experimental and computational trends. Moreover, a number of results have been obtained for the first time, for instance the explanation of axial strengthening in $CdCl_5^{3-}$ and $HgCl_5^{3-}$, the prediction of possible axial weakening in AL_7^{n-} complexes, and the prediction of the relative stability of isomers in the AL_m series depending on the nature of A and L.

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Appendix

Table VI illustrates different signs of the s contributions to the relative axial and equatorial bond strengths in EL_5 and EL_7 complexes.

In order to illustrate some model conclusions we performed EHM[49] calculations on TB complexes AL_5 and AL_4H. The parameters employed are given in Table VII.

The central atom A is considered to be a typical atom of the third period; the ligand L some 3s σ ligand of the Cl type; for ligand H the standard parameters have been taken.[9,51] The internuclear distances are $R(A{-}L_{ax}) = R(A{-}L_{eq}) = 2.05$ 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.

The overlap populations in AL_5 are given in Table VIII. The $1a_1'$ and $2a_1'$ MO's are found to be

$$\psi(1a_1') = 0.61s + 0.24_3(\sigma_1 + \sigma_2) + 0.23_5(\sigma_3 + \sigma_4 + \sigma_5) \tag{141}$$

$$\psi(2a_1') = 0.02s - 0.58(\sigma_1 + \sigma_2) + 0.38(\sigma_3 + \sigma_4 + \sigma_5) \tag{142}$$

i.e., in the $1a_1'$ all the coefficients before σ_k are approximately the same [cf. the relationship (11)], the nodal structure of the $2a_1'$ corresponds to $s - \sigma_{ax} + \sigma_{eq}$ [cf. the relationship (97)] and the ratio of the axial and equatorial coefficients −0.58:0.38 = −1.52 is almost equal to the "unperturbed" value −1.50 [cf. the relationship (99)]. Finally, the difference in total energy *E′* of axial (C_{3v}) and equatorial (C_{2v}) isomers AL_4H is positive and equal to 0.45 eV [cf. the relationship (131) from which $\Delta E' \approx 0.17$ eV]. Finally, the difference in total energy *E′* of axial (C_{3v}) and equatorial (C_{2v}) isomers AL_4H is positive and equal to 0.45 eV [cf. the relationship (131) from which $\Delta E' \approx 0.17$ eV].

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Synthesis and Electrochemical and Photoemission Properties of Mononuclear and Binuclear Ruthenium(II) Complexes Containing 2,2′-Bipyridine, 2,9-Dimethyl-1,10-phenanthroline, 2,2′-Bipyrimidine, 2,2′-Biimidazole, and 2-Pyridinecarboxaldimine Ligands

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Four new *mononuclear* ruthenium(II) complexes, $[Ru(PTPI)_3]^{2+}$ (PTPI = 2-*p*-tolylpyridinecarboxaldimine) and $[Ru(bpy)_2B]^{2+}$ [B = 2,9-dimethyl-1,10-phenanthroline (2,9-Me_2phen), 4,4′-dimethyl-2,2′-bipyrimidine (4,4′-Me_2bpyrm), and 2,2′-biimidazole (biimH_2)], have been prepared as PF_6^- salts and their electrochemical and photoemission properties investigated in solution. In addition, the ligand-bridged *binuclear* species $[Ru(bpy)_2(B)Ru(bpy)_2](PF_6)_4$ (B = bpyrm and 4,4′-Me_2bpyrm) have also been obtained as by-products in the synthesis of the mononuclear complexes and separated from their mononuclear analogues by Sephadex chromatography. The *mononuclear* compounds all exhibit polarograms in acetonitrile consistent with quasi-reversible, one-electron [Ru(II) → Ru(III)] oxidation processes with $E_{1/2}$ potentials (SCE) ranging from 0.93 to 1.29 V. The $E_{1/2}$ potentials suggest an ordering in the B ligand π-acceptor ability of biimH_2 ≪ 2,9-Me_2phen ∼ bpy < 4,4′-Me_2bpyrm < bpyrm. The *binuclear* [Ru(II),Ru(II)] complexes possess polarograms displaying two, one-electron oxidation processes ($\Delta E_{1/2} = 0.18$ V) corresponding to production of the mixed-valence [(Ru(II),Ru(III)] and fully oxidized [Ru(III),Ru(III)] species. At room temperature and in acetonitrile, the mononuclear B = 2,9-Me_2phen, bpyrm, 4,4′-Me_2bpyrm, and biimH_2 complexes have dπ^* absorption and luminescence spectra similar to that of $[Ru(bpy)_3]^{2+}$, with emission bands occurring between 588 and 600 nm in all cases. Under similar conditions, the bipyrimidine-bridged *binuclear* complexes do not exhibit emission spectra in the 350–800-nm region. The emission spectrum observed for the $[Ru(PTPI)_3]^{2+}$ complex is probably not of dπ^* origin, with the emission bands being blue shifted (at ∼345 and 400 nm) relative to the 496- and 552-nm dπ^* absorption bands.

Introduction

The synthesis of $[Ru(bpy)_3]X_2{\cdot}nH_2O$ by Burstall[2] (bpy = 2,2′-bipyridine) in 1936 led to little interest in the complex until 1959 when Paris and Brandt[3] discovered its visible-region luminescence at 77 K. After further inquiries mainly by Crosby and co-workers,[4–6] a large amount of evidence accumulated from luminescence lifetime studies of $[Ru(bpy)_3]^{2+}$ and related complexes that strongly supported a dπ^*[5,7,8] heavy-atom perturbed,[9] spin-forbidden process as the basis for the observed phenomenon. This suggests an analogy to the more familiar spin-forbidden organic phosphorescence phenomena where the electronic decay is from a triplet excited state to the singlet ground state. For the $[Ru(bpy)_3]^{2+}$ case, however, there exist four emitting states, and spin labels on these states have recently been abandoned because of the large spin–orbit coupling expected for the formally d^5 metal center of the dπ^* excited states.[10] Further, it has been proposed that (1) metal–ligand dπ^* charge transfer must be at lower energy than dd* ligand field or $\pi\pi^*$ ligand antibonding states,[11] (2) the ground-state complex must be diamagnetic,[11] and (3) the metal ion d electrons in the dπ^* excited state must also be as "paired" as possible.[12,13] These conditions apparently constitute

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