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Trans Influence and Mutual Influence of Ligands Coordinated to a Central Atom

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The consequences of sharing a central-atom orbital by two or more ligand orbitals is examined in general by using a simple perturbation approach. If only the ML bonding partner of this interaction is occupied, then sharing of the central-atom orbital is not favored. If only the ML antibonding partner is occupied, then the reverse is true. The results are applied to an analysis of *trans*-L(MX_n)L systems where L is a single-faced π donor or acceptor (e.g., Mo(diphos)$_2$(C_2H_4)$_2$). When applied to an octahedrally based series of low-spin d^6 M(CO)$_x$ species, the ML π-bond stabilization energy, $\sum(\pi)$, fits a simple equation: $\sum(\pi) = A - [n_{\text{cis}} + 2n_{\text{trans}}]B$. Here n_{cis} and n_{trans} are the number of CO ligands cis and trans, respectively, to the one being considered (A and B are constants). This equation shows why CO-stretching force constants increase on increasing substitution and that trans ligands are more effective than cis ligands. Timney's equation, an experimentally derived relationship between CO force constants and structure, is of the same form. When applied to two different ligands, trans to each other in a metal complex, it quantifies previous ideas concerning the trans influence of ligands. It is shown that this need not be the only mechanism operating in these systems. Another effect is discussed wherein unoccupied orbitals of nonequivalent symmetry are allowed to mix into the occupied ones as the symmetry of the complex is lowered. This creates a bond weakening or strengthening in the M–L bond trans to the site of perturbation.

Of great interest to inorganic, especially transition-metal, chemists for many years has been the effect on a molecular property when one coordinated ligand is replaced by another. In some cases the result is dramatic if the molecular symmetry is reduced and spectroscopic transitions (e.g., IR or UV–vis absorptions) become allowed or vibrations, degenerate in the parent, split apart in energy. Equally obvious, however, are the observations that MX bond properties (length, vibrational force constant, and magnetic resonance parameters of X) are often very sensitive to the nature and number of other ligands coordinated to the metal.[2] For example, the ligand lying trans to X often exerts a large effect in square-planar d^8 and octahedral d^6 complexes (trans influence), usually much larger than any influence of the cis ligands.[2-4] As the number of ligands L coordinated to a central metal atom increases, the M–L vibrational force constants tend to become smaller.[5] In transition-metal carbonyls a similar effect shows up in the f_{CO} constants as the number of coordinated carbonyls increases. Here, trans CO groups contribute a much larger effect than cis CO groups.[6] In the carbonyl case there is a larger amount of experimental data relevant to this problem, and a recent study shows the effect to be additive to a remarkable degree.[7] In hypervalent molecules[8] such as ClF_3 and ClF_5 the bonds trans to each other are longer than those trans to a vacancy. In PF_5 the axial bonds are longer than the equatorial ones. Some of these observations have been rationalized over the years in qualitative terms which contain certain recurring themes. We have recast these ideas as three related points. (i) It is energetically unfavorable for two or more ligands to share the same central-atom orbital for π or σ bonding. If it is possible for the geometry to adjust in some manner to share two different orbitals, then this alternative is lower in energy. (ii) If some of the ligands must share the same orbital, then the strongest M–L bonds are for the symmetry-equivalent set of linkages for which the ratio, number of central-atom orbitals shared by these ligands/number of ligands, is largest. (iii) If two different ligands must share the same orbital, then an ill-defined (theoretically) differential bond-weaking process occurs. In this paper, using the angular overlap method, we shall show in simple molecular orbital terms how each of these points may be understood. Our model specifically excludes mixing of central-atom orbitals but concentrates on the consequences of central-atom orbital sharing. In the second part of the paper we relax this restriction and show from first-order perturbation theory how mixing of unoccupied orbitals can serve to increase or decrease trans M–L bond lengths.

Perturbation Approach to Orbital Interactions

Consider two interacting orbitals (or symmetry-adapted orbital sets) ϕ_i and ϕ_j whose energies before interaction are $\epsilon_i^{(0)}$ and $\epsilon_j^{(0)}$, respectively. The interaction energy of the two (eq 1) is simply given by the even powers of perturbation

$$\epsilon_k - \epsilon_k^{(0)} = \epsilon^{(2)} + \epsilon^{(4)} + \ldots = \frac{V_{ij}}{\Delta\epsilon_{ij}^{(0)}} - \frac{V_{ij}^4}{(\Delta\epsilon_{ij}^{(0)})^3} + \ldots \qquad (1)$$

theory where $V_{ij} = H_{ij} - S_{ij}\epsilon_k^{(0)}$ and $k = i$ or j. In the extended Hückel formalism if $\epsilon_i^{(0)}$ is identified with H_{ii} and H_{ij} is estimated by using the arithmetic mean Wolfsberg–Helmholz relationship $H_{ij} = {}^1/_2 KS_{ij}(H_{ii} + H_{jj})$ with $K = 2$, then the stabilization energy, ϵ, of the lower component is given by eq 2 where $k = H_{jj}$ and $\Delta\epsilon_{ij} = H_{ii} - H_{jj}$. The use of the first term

$$\begin{aligned}\epsilon = \epsilon_i - \epsilon_i^{(0)} &= \frac{k^2 S_{ij}^2}{\Delta\epsilon_{ij}} - \frac{k^4 S_{ij}^4}{(\Delta\epsilon_{ij})^3} + \ldots \\ &\simeq \beta S_{ij}^2 - \gamma S_{ij}^4\end{aligned} \qquad (2)$$

in this expression to describe many of the salient features of the transition metal–ligand interaction has been called the angular-overlap model[9] (ϕ_j = d orbital, ϕ_i = ligand σ or π orbital). It has been used mainly to describe magnetic and spectral properties of complexes but in our hands has been applied to many structural and kinetic problems in both main-group and transition-metal chemistry. The first term may be calculated either by evaluation of the overlap integral between the central-atom orbital and a symmetry-adapted ligand combination (S_{ij}') involving the n ligands such that $\epsilon^{(2)} = K^2 S_{ij}'^2/\Delta\epsilon_{ij}$ or by use of the ligand additivity scheme. Here (eq 3) S_{ij} is the overlap integral between a ligand σ orbital

$$\epsilon^{(2)} = \sum_{i=1}^{n} S_{ij}^2 \frac{k^2}{\Delta\epsilon_{ij}} \qquad (3)$$

located on a single-atom and a central-atom orbital. For the case where all of the ligands are identical, these two approaches are equivalent. For the quartic term with equivalent ligands we may not sum the S_{ij}^4 terms. Here we need to evaluate $(S_{ij}')^4$ or $(\sum_{i=1}^{n} S_{ij}^2)^2$. Of tremendous value has been the ability to write S_{ij} as a simple function (eq 4) of the molecular geometry (θ,ϕ) where S_λ ($\lambda = \sigma, \pi, \delta$) depends only on the nature of M, L, and the M–L distance. We then have a simple method to evaluate orbital-interaction energies, and these can

$$S_{ij} = S_\lambda[f_{ij}(\theta,\varphi)] \qquad (4)$$

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be expressed in the parameterized form of eq 5. The two

$$\epsilon = p\beta_\lambda S_\lambda^2 - p^2\gamma_\lambda S_\lambda^4 \qquad (5)$$

parameters of the model are the products $\beta_\lambda S_\lambda^2$ and $\gamma_\lambda S_\lambda^4$. p is a readily calculable number which is geometry dependent.

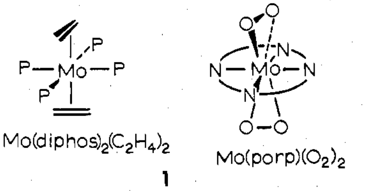
For n identical ligands containing $m\lambda$ orbitals a very useful sum rule[9a] applies (eq 6) to the first term in eq 2. The sum

$$\sum_j \sum_n \frac{k^2}{\Delta\epsilon_{ij}^{(0)}} S_{ij}^2 = \sum_j \frac{k^2}{\Delta\epsilon_{ij}} S_{ij}'^2 = m\beta_\lambda S_\lambda^2 \qquad (6)$$

of all interaction energies of ligand λ orbitals with a central-atom orbital, over all orbitals of that type (e.g., with all three 2p or all five 3d orbitals), is a constant. A similar rule does not hold for the second term in eq 2, and it is here where most of our discussion will lie.

Tendency of Two Ligands to Avoid Sharing the Same Orbital

In complexes of the type indicated in **1** where there are two



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trans ligands bearing a single π-type orbital (relative to the central atom), the staggered arrangement of these ligands is found.[11,12] Although the geometry is rather (Jahn–Teller) distorted, the trigonal-bipyramidal structure of $Cr^{III}Ph_5^{2-}$ contains[13] staggered trans axial phenyl groups. Ab initio calculations[14] on the molecules in **1** show that the staggered arrangement is most stable (by about 15 kcal/mol for **1a**). Extended Hückel calculations[15] on bis(ethylene)nickel also show that the D_{2h}, eclipsed geometry, **2**, is less stable than the D_{2d}, staggered conformation, **3**. The geometries of the matrix-synthesized molecules $M(C_2H_4)_2$ (M = Cu[16], Ni[17]) are unknown. The general conclusion[14,15] is that the stabilization of metal d orbitals with ethylene π* orbitals produced by the two interactions in **4** is greater than that associated with **5**; i.e., the ligand π* systems avoid sharing the same central-atom orbital. Another series of calculations[18] on *trans*-bis(carbene) $Cr^{(0)}$ molecules also show a preference for the staggered arrangement. A related example from organic chemistry is the D_{2d} geometry of the allene molecule **6**, where the two planes of the CH_2 groups attached to the central carbon atom are perpendicular. The $Si_2NBeNSi_2$ skeleton of the isoelectric $(Me_3Si)_2NBeN(SiMe_3)_2$ molecule has the same structure.[19] Although there are, in principle, steric reasons for favoring the staggered geometry, the trans ligand–ligand distances are large enough in these systems to clearly point to an electronic stabilization force of the sort described in **4** and **5** above. By way of contrast, these structural results must be compared with those for the diphenylmercury(II) species, related perhalo derivatives, and complexes containing these units. Here the eclipsed form, **7**, is almost universally found.[21,22] An exception is the $(C_6F_5)_2Hg$ molecule[23] where the two phenyl groups are twisted by about 55°, supposedly to relieve F···F replusions.

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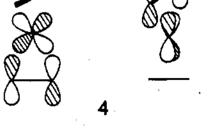

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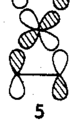

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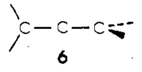

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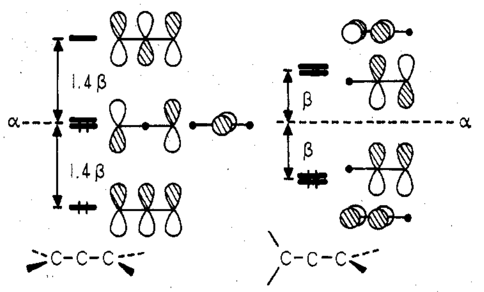


Figure 1. Hückel orbitals for eclipsed (D_{2h}) and staggered (D_{2d}) allene.

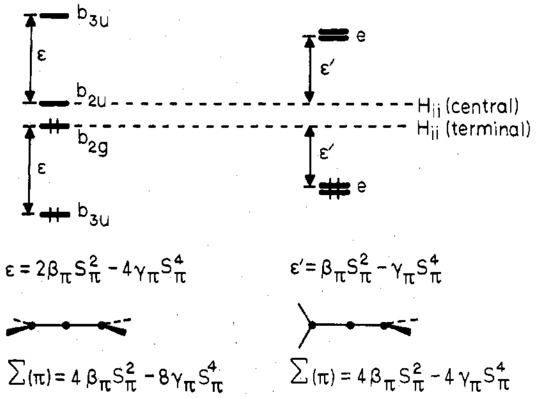
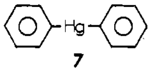


Figure 2. Molecular orbitals of eclipsed and staggered allene-type molecules using the angular overlap method (see ref. 24).



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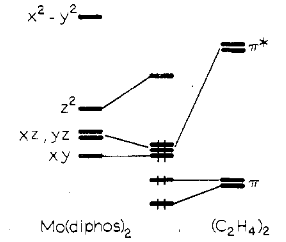
We will illustrate the molecular-orbital origin of these structural effects by applying two different approaches to the allene molecule: the well-known classical one which uses simple Hückel theory for the π-type orbitals and a more widely applicable method which uses the perturbation approach we described above.

Figure 1 gives the energies of planar (D_{2h}) and twisted (D_{2d}) allene species in terms of the Hückel α,β parameters (not to be confused with β_λ of eq 5). Figure 2 shows the energies of the orbitals by using the perturbation formalism. We arrive at these results in the following way. For the planar geometry the central atom p_π orbitals transform as $b_{2u} + b_{3u}$ and the "ligand" p_π orbitals as $b_{2g} + b_{3u}$. There are, therefore, two nonbonding orbitals (we have disregarded the methylene σ orbitals of π symmetry). The ligand b_{3u} combination is of the form of eq 7, and its overlap integral with the central carbon

$$\psi_{b_{3u}} = (1/2^{1/2})(p_{x1} + p_{x2}) \qquad (7)$$

atom p_x orbital is just $2^{1/2}S_\pi$, where S_π is the overlap integral of the central-atom p_x orbital with a single ligand p_x orbital. The second-order perturbation term is $2\beta_\pi S_\pi^2$, and the fourth order term is $4\gamma_\pi S_\pi^4$. Similar algebra allows derivation of the orbital energies for the D_{2d} conformation.[24] This method neatly shows then in a general way why the two ligands avoid sharing the same orbital. Since all the bonding orbitals are doubly occupied and the antibonding ones are empty, the sum rule of eq 6 holds for the quadratic contribution to the total stabilization energy of the system, and it is independent of angular geometry. However, the fourth-order term (quartic in S_π) included with a negative sign (representing a destabilizing effect) is geometry dependent. The greater the second-order stabilization energy of an orbital, the larger the corresponding quartic correction (see eq 5). The overall effect is that the ligands prefer to use the maximum number of central-atom orbitals of a given type since this will give rise to the smallest quartic destabilization. This result is a perfectly general one and may be shown[25] by using a well-known mathematical inequality.

The analysis of the staggered arrangement in transition-metal systems, where all of the M–L π-bonding orbitals are occupied and the antibonding ones empty, follows along similar lines. For the case where there are two ethylene molecules as in **1a**, the ML π-bonding orbitals which are filled are mainly the metal d orbitals (**8**). In this particular case, d^6, all three "octahedral" d_π orbitals are doubly occupied.



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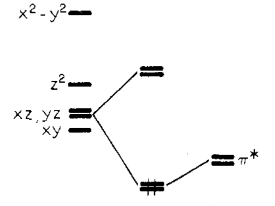
In the dioxygen complex, **1b**, (d^0) the ML π-bonding orbitals are ligand located (**9**). In the $CrPh_5^{3-}$ molecule the ML π-bonding orbitals similarly are ligand located, but the ML π-antibonding orbitals are half occupied (high-spin d^3).



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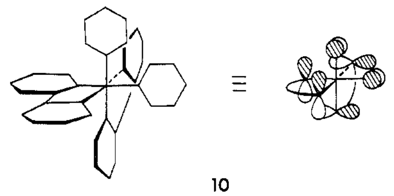
This is also the case for $Ph_2Cr(bpy)_2{}^+I^-$ which contains three mutually orthogonal pairs of π-type interactions (**10**). We emphasize that the results hold only for systems where the quadratic term is angularly independent, and we need to resort to quartic terms to find differential angular effects.



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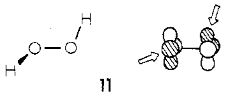
There are some other rather interesting cases where our theory applies. We can easily show the preference for the tetrahedral rather than square-planar geometry for saturated carbon atoms or isoelectronic species (e.g., $AlCl_4^-$). In the tetrahedral configuration three p orbitals are shared by the four ligand σ orbitals, but in the energetically unfavorable square-planar geometry two p orbitals are shared by the four ligand σ orbitals. In the latter case the out-of-plane p_z orbital cannot take part in the ML σ interaction.

The H_2O_2 and O_2F_2 molecules adopt a twisted nonplanar geometry, **11**, where each H or F atom is able to interact with a different component of the π_u orbital derived from the O_2 unit.



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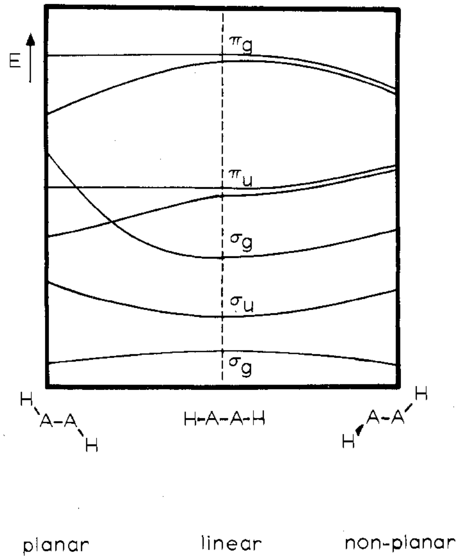

Figure 3. Qualitative molecular orbital scheme for bending linear A_2X_2 molecules. Adapted from ref 47.

By way of contrast, N_2F_2 with two less electrons exists in a planar geometry (cis and trans) where each F atom interacts with the same π_u component, **12**. N_2H_2 probably has a similar structure.

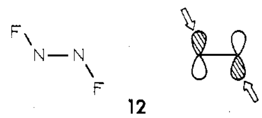

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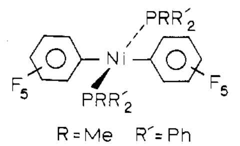
Figure 3 shows a qualitative orbital diagram for such A_2X_2 species as a function of bending. For N_2X_2 with the configuration $...(1\pi_u)^2$ the planar geometry is clearly favored. For O_2X_2 with the configuration $...(1\pi_u)^4$, from the structural observation that the skewed form is found, we again see that the preferred geometry is the one where two orbitals are stabilized rather than one, i.e., the X ligands avoid sharing the same A_2 orbitals.

Similar arguments may be used to rationalize the eclipsed conformation in $HgPh_2$ systems. Here in this d^{10} species both M–L π-bonding (mainly ligand) and M–L π-antibonding (mainly metal d) orbitals are occupied. In our previous discussions[10] of systems containing π donors we have found it convenient to allow the stabilization energy of the occupied M–L π-bonding set to cancel the destabilization of the M–L π^* set when viewing the more energetic σ interactions. Here, where the angular geometry is controlled by π bonding, we focus on the destabilization energy of these π^* orbitals, since energetically this is strictly larger than the corresponding stabilization energy of their bonding counterparts. From both the Hückel scheme of Figure 1 and the perturbation analysis in Figure 2 we can readily see that the eclipsed form is more stable for this electronic configuration. The same factor that gave the smallest stabilization energy now gives this geometry the smallest destabilization energy with the antibonding orbitals occupied. Thus, in cases where both M–L π-bonding and -antibonding orbitals are occupied, sharing of orbitals is a favorable situation. A similar orbital-sharing arrangement is found in low-spin, d^8, square-planar systems typified by **13**.[26]



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In addition to electronic effects there is, of course, a steric reason for the 90° dihedral angle between the plane defined by the X–Ni–X atoms and the planes of the phenyl rings.

In all of these examples the system has the capability of adjusting from an unfavorable angular geometry. But what about those systems where the angular disposition of ligands is fixed? We may divide them into two types: those species where there are two different types of ligands (e.g., axial and equatorial in the trigonal bipyramid; A and B sites in the dodecahedron) and those molecules where two chemically different ligands share the same central-atom orbital. Examples of this will be discussed in the next sections.

Systems with Two Different Ligand Sets

We have looked at this situation before when rationalizing computed bond-overlap populations and observed relative bond lengths in d^0 five-, seven-, and eight-coordinate geometries.[27] In general, the quartic stabilization energy term of eq 2 for each bonding orbital contains (n_1,n_2) from the two different sets of symmetry-unrelated ligands (eq 8). Here n_1 and n_2

$$\beta_\lambda S_{ij}'^2 = \beta_\lambda(n_1 S_\lambda^2 + n_2 S_\lambda^2) \qquad (8)$$

are numbers, not necessarily integers, which are calculable from the explicit form of the $f(\theta,\phi)$ of eq 4. Thus, the quartic term may be written as eq 9. We may then split up this term

$$\gamma_\lambda S_{ij}'^4 = \gamma_\lambda(n_1^2 + 2n_1n_2 + n_2^2)S_\lambda^4 \qquad (9)$$

into a contribution $(n_1^2 + n_1n_2)\gamma_\lambda S_\lambda^4$ associated with the ligand set 1 and $(n_2^2 + n_1n_2)\gamma_\lambda S_\lambda^4$ with set 2. Division of each term by the number of ligands in each set leads to the quartic destabilization energy per M–L bond. Therefore, the stabilization energy associated with the axial ligands in a D_{nh} complex of the above type depends in general upon the number of equatorial ligands present (and vice versa) in a very simple fashion via the cross term, n_1n_2 above. In these molecules this is true for metal d–ligand σ interactions, but the corresponding energies for interaction with the metal p orbitals show that since axial and equatorial interactions are separable (axial → p_z only, equatorial → p_x, p_y only) the axial bond stabilization energies from this source remain constant throughout the series: trigonal bipyramid (TB), octahedron (OCT), pentagonal bipyramid (PB), and hexagonal bipyramid (HB). In contrast, however, the equatorial bonds become progressively weakened such that, as a general rule, $r_{ax}/r_{eq} > 1$ for TB but $r_{ax}/r_{eq} < 1$ for PB and HB. We have rationalized along similar lines[28] the relative bond lengths in simple main-group systems (e.g., ClF_3, SF_4, BrF_5, PF_5, and IF_7) by dividing up the quartic destabilization term in the obvious way between two different ligand sets.

Change of Coordination Number

One of the most remarkable discoveries in the field of transition-metal carbonyls has been the formulation by Timney[7] of a simple master equation which predicts frequency-factored force field (F^4) "CO"-stretching force constants, f_{CO}, very accurately (eq 10). Here f_{MCO} is the F^4

$$f_{CO} = f_{MCO} + \sum n_\theta f_\theta(CO) + qf' \qquad (10)$$

force constant for the isoelectronic monocarbonyl (e.g., CrCO for $Cr(CO)_6$ and $Mn(CO)_5Br$), q is the formal charge on the complex, and n_θ is the number of CO groups at an angle θ to the one being considered. Thus for $Cr(CO)_6$ $f_{CO} = f_{CrCO} + f_{trans}(CO) + 4f_{cis}(CO)$. This expression can be extended to include $f_\theta(X)$ when other groups (X = PPh_3, PF_3, halide, NO, etc.) are also coordinated to the carbonyl (eq 11). Re-

$$f_{CO} = f_{MCO} + \sum n_\theta(CO)f_\theta(CO) + \sum n_\theta(X)f_\theta(X) + qf' \qquad (11)$$

markably, the $f_\theta(X)$ for a given value of θ and f' are independent of the metal, the charge, or the composition of the complex. For the CO ligand some values of $f_\theta(CO)$ are given in Table I. We may derive an equation very similar to eq 10 by using our approach. By looking at the σ or π manifold, we will obtain equations of the form of eq 12 (here shown

$$\sum_{CO}(\pi) = a - \sum n_\theta b_\theta(CO) \qquad (12)$$

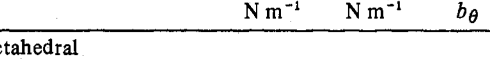
specifically for the π case) which describes the σ- or π-bond stabilization energy in a similar additive way in terms of angular constants, $b_\theta(CO)$.

Table I. Values of Timney f_θ Values[7] and the Corresponding Sensitivity Parameters (b_θ) Calculated by Using Our Simple Model

	$f_\theta(CO)$, N m^{-1}	$f_\theta(N_2)$, N m^{-1}	b_θ
octahedral			
cis	33.5	14.0	2
trans	126.1	52.0	4
tetrahedral[a]	37.3	5.7	1.43
trigonal bipyramidal[b,c]			
ax–ax	126.1		4
ax–eq	25.5		2
eq–eq	51.4		1

[a] For a d^{10} system. [b] For a low-spin d^8 system. [c] There is an ambiguity in the determination of these three values; the ax–ax parameter has been fixed at the value for the octahedral (trans) parameter. The other two then follow from the experimental data. The same comment applies to the b_θ values.

Let us look first at the π-stabilization energy afforded a low-spin d^6 $M(CO)_x$ system which has one of the geometries based on the octahedron shown in **14**. In this geometry σ and π interactions are separable because of the orthogonal arrangement of the ligands. In each case we see three π-type orbitals, derived from the t_{2g} trio at low energy. The π-stabilization energy of these orbitals after interaction with the ligand π* orbitals may be written in the form of eq 5 by using the simple approach we have shown previously for the allene system. S_π is now the overlap integral between one component of the π* orbital of a CO ligand lying along the z axis with d_{xz}. **15** shows the results for the octahedral case and **16** for a square pyramid where the axial/basal angle is set at 90° for simplicity. For the octahedron the total π-stabilization energy (low-spin, d^6) is $\sum(\pi) = 24\beta_\pi S_\pi^2 - 96\gamma_\pi S_\pi^4$, and, therefore, the π stabilization per M–CO linkage is $\sum_{CO}(\pi) = 4\beta_\pi S_\pi^2 - 16\gamma_\pi S_\pi^4$. For the square pyramid a similar analysis gives $\sum(\pi) = 20\beta_\pi S_\pi^2 - 68\gamma_\pi S_\pi^4$. In order to calculate $\sum_{CO}(\pi)$ we need to partition the quartic terms of **16** between the axial (set 1) and basal (set 2) ligands. This is readily done by following the prescription outlined in the previous section. The xy orbital is entirely involved in basal bonding ($n_1 = 0$, $n_2 = 4$), but xz and yz have a $2\beta_\pi S_\pi^2$ contribution from basal ($n_1 = 2$) and a $\beta_\pi S_\pi^2$ ($n_2 = 1$) contribution from axial ligands. This partitions the quartic term into $6\gamma_\pi S_\pi^4$ (from basal) and $3\gamma_\pi S_\pi^4$



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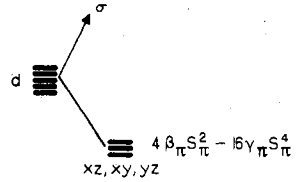

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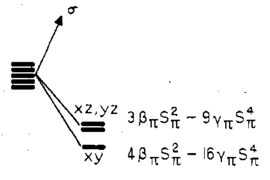

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(from axial) ligands ($9\gamma_\pi S_\pi^4$ total). Thus $\sum_{ax}(\pi) = 4\beta_\pi S_\pi^2 - 12\gamma_\pi S_\pi^4$ and $\sum_{ba}(\pi) = 4\beta_\pi S_\pi^4 - 14\gamma_\pi S_\pi^4$. We may calculate the relevant values for all of the bonds in the structures of **14**. They fit a simple equation given by eq 13. Here $A = 4\beta_\pi S_\pi^2$

$$\sum\nolimits_{CO}(\pi) = A - [n_{cis} + 2n_{trans}]B \qquad (13)$$

$- 4\gamma_\pi S_\pi^4$ and $B = 2\gamma_\pi S_\pi^4$. Thus, the sensitivity parameters of eq 12 are $b_{90°} = b_{cis} = 1$ and $b_{180°} = b_{trans} = 2$. There is good evidence that the CO-stretching force constant is dominated[29] by changes in π bonding between metal and CO, and this equation is then immediately comparable with eq 10 without the charge term. It represents a decreasing M–CO stabilization energy on increasing coordination number, which is reflected in a correspondingly higher CO-stretching force constant. Tetrahedral and trigonal-bipyramidal molecules may be included in the scheme[30] and the results are given in Table I. The results of the present analysis are in general qualitative agreement with the Timney f_θ values. From Smith's EHMO calculations[31] on octahedrally based $M(CO)_xX_{6-x}$ systems we may readily derive eq 14 which describes pretty well the M–C

$$\text{M–C } \pi \text{ bond order} = 2.000 - 0.1029n_{trans} - 0.05314n_{cis} \qquad (14)$$

π bond order in structures of this type. Interestingly, the ratio of the two sensitivity parameters here (1.94) is close to our value of 2 in eq 13. What, of course, our approach does not shed any light on is the rather remarkable fact that the f_θ values are independent of the nature of M (at least for the Cr–Ni series that have been most extensivly studied) or its oxidation state. A priori, one would have anticipated that the β_π, γ_π, and S_π parameters would have been sensitive to such changes.

A similar analysis may be carried out for the σ manifold of the molecules in **14**. We find an exactly similar expression (eq 15). Here $A' = 2\beta_\sigma S_\sigma^2 - 2\gamma_\sigma S_\sigma^4$ and $B' = 2\gamma_\sigma S_\sigma^4$ for all

$$\sum\nolimits_{CO}(\sigma) = A' - [\tfrac{1}{4}n_{cis} + n_{trans}]B' \qquad (15)$$

molecules except the T-shaped one. In this case two d orbitals mix together and complicate the situation.

Both eq 13 and 15 indicate that for these systems the geometry with the maximum number of cis ligands is most stable. In each case addition of a cis ligand causes a smaller destabilization of the system than addition of a trans one. We have seen[32] this result in the σ manifold before, and for this particular electronic configuration (low-spin, d^6) $Cr(CO)_4$ prefers the octahedral cis divacant geometry rather than the square plane.[33] We now see that here σ and π effects work in the same direction. This equation also provides a neat rationale for observation that the M–L vibrational frequencies and force constants in general decrease as the coordination number of the metal increases. Adams' extensive listing[4] shows many examples.

Note again that these arguments based on the quartic term hold only for those cases where the larger quadratic term is independent of geometry. Although this is true for the low-spin d^6 systems under consideration, for low-spin d^8 molecules, square-planar (e.g., $Ni(CN)_4^{2-}$) and T-shaped ($Rh(PPh_3)_3^{+}$ [34]) geometries are found for three- and four-coordinate molecules. These structures are set by operation of the angular-dependent quadratic σ term.

Structural studies of transition-metal carbonyls and their derivatives suggest that in addition to the trend shown by the force constant data above, the M–CO bond shortens with increasing substitution by ligands, X, which are usually poorer π acceptors than CO. Importantly, M–CO bonds which are trans to a X substituent in an octahedrally based low-spin d^6 system are significantly shorter (Table II) than CO bonds which are trans to other CO ligands. This is in agreement with our scheme above and, of course, the Timney equation. In addition to $Cr(CO)_3$ and $Cr(CO)_4$ having C_{3v} and C_{2v} geometries, respectively, there is a much larger number of cis and *fac* di- and trisubstituted carbonyls than trans and *mer* species. Also in low-spin d^8 trigonal-bipyramidal molecules, carbonyl groups prefer equatorial positions where they receive a smaller quartic π destabilization term ($b_\theta = 1$ from Table I) than in the axial positions ($b_\theta = 4$). The overall energies of attachment of the extra ligand are, of course, a stabilization via the (angle-independent) quadratic term. This site preference is in contrast to the preference of σ donors for the axial positions. Both of these conclusions may also be reached by rather different molecular orbital arguments.[35]

Table II. M–C Bond Lengths in $M(CO)_xX_{6-x}$ Compounds

molecule	M–C dist, Å trans to CO	 cis to CO	ref
$Cr(CO)_6$	1.909 (3)		*a*
$Cr(CO)_5PPh_3$	1.867 (4)–1.894 (4)	1.845 (4)	*b*
$Cr(CO)_5P(OPh)_3$	1.892 (5)–1.904 (6)	1.861 (4)	*b*
$W(CO)_5tmt^{c,d}$	1.95 (2)	2.05 (3)	*e*
$Cr(CO)_4dppe^{f}$	1.884 (7)	1.831 (7)	*g*
$Mo(CO)_4dppe$	2.04	1.93	*h*
trans-$Cr(CO)_4[P(OPh)_3]_2$	1.88 (1)		*i*
fac-$Cr(CO)_3(PPh_3)_3$		1.838 (7)	*j*
cis-$Cr(CO)_2(Ph_3)_4$		1.817	*k*
$(CO)_5Cr(triphos)Mn(CO)_3Br$		1.61 (5)–1.70 (5)[l]	*o*
$(CO)_5Cr(triphos)Mn(CO)_3Br$	1.71 (5)–1.88 (5)[m,n]	1.96[m,n]	*o*

[a] A. Whitaker and J. W. Jeffrey, *Acta Crystallogr., Sect. B*, 23, 977 (1977). [b] H. J. Plastas, J. M. Stewart, and S. O. Grim, *J. Am. Chem. Soc.*, 91, 4326 (1969). [c] tmt = thiomorpholine-3-thione. [d] Similar results are found in a variety of related species: e.g., M. Cannas, G. Carta, D. De Fillipo, G. Marongiu, and E. F. Trogu, *Inorg. Chim. Acta*, 10, 145 (1977). [e] M. Cannas, G. Carta, A. Cristini, and G. Marongiu, *Acta Crystallogr. Sect. B*, 31, 2909 (1975). [f] dppe = 1,2-bis((diphenylphosphino)ethane). [g] M. J. Bennett, F. A. Cotton, and M. D. La Prade, *Acta Crystallogr. Sect. B*, 27, 1899 (1971). [h] K. K. Cheung, T. F. Lai, and K. S. Mok, *J. Chem. Soc. A*, 1644 (1971). [i] H. S. Preston, J. M. Stewart, H. J. Plastas, and S. O. Grim, *Inorg. Chem.*, 11, 161 (1972). [j] G. Huttner and S. Schelle, *J. Organomet. Chem.*, 47, 383 (1973). [k] G. Huttner and S. Schelle, *J. Cryst. Mol. Struct.*, 1, 69 (1971). [l] Mn–C. [m] Cr–C. [n] This structure is included to show that the M–C bond cis to CO is not always shorter than those trans to CO. [o] M. L. Schneider, N. J. Colville, and I. S. Butler, *J. Chem. Soc., Chem. Commun.*, 799 (1972).

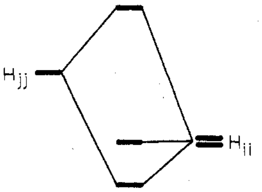
If other ligands are coordinated to the metal in addition to CO, then we may formally include them in our perturbation scheme (see later for exact details). The general result is in eq 16 where C is a product term containing both X and CO

$$\sum\nolimits_{CO}(\pi) = A - [n_{cis}{}^{(CO)} + 2n_{trans}{}^{(CO)}]B - [n_{cis}{}^{(X)} + 2n_{trans}{}^{(X)}]C \qquad (16)$$

AOM parameters. Table I shows that the three available values for N_2 are qualitatively in the same order as the b_θ values.

The Case of Different Ligands

We consider here a simple, linear, triatomic trans LML′ system where the central M atom contains a single orbital (d_{z^2}, p_z, or s) which may interact with the σ orbitals on the two ligands L and L′. Three cases may immediately be described within the language of the extended Hückel method. (i) The ligands L and L′ are identical, and the σ orbitals have equal values of H_{ii} and S_{ij} (orbital energy and overlap integral with the central-atom orbital, respectively). (ii) The ligands are different with different S_{ij} but have the same values of H_{ii}. (iii) Both H_{ii} and S_{ij} are different. Cases (i) and (ii) are easily solved by solution of the secular determinant. If $|H_{ij}| < |H_{ii}|$, then the three molecular orbitals that result are shown in **17**.



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The M–L,L′ bonding orbital lies to lower energy than H_{ii} and the antibonding orbital to higher energy than H_{jj}. A nonbonding orbital lies at H_{ii}. Case (iii) is more complex; the secular determinant reduces to a cubic. The nonbonding level lies somewhere between the H_{ii} values of L and L′.

First, we compare cases (i) and (ii) using the perturbation formalism described above. The stabilization energy of the bonding orbital in case (ii) is given by eq 17. For case (i)

$$\epsilon = \frac{k^2(S_\sigma^2 + S_\sigma'^2)}{\Delta\epsilon} - \frac{k^4(S_\sigma^2 + S_\sigma'^2)^2}{\Delta\epsilon^3} \tag{17}$$

$S_\sigma = S_\sigma'$. If the stabilization energy is now distributed between the M–L and M–L′ bonds, by dividing the cross terms in the quartic portion equally, then in our shorthand notation (since both ligand σ orbitals have the same value of H_{ii}) with two electrons in the bonding orbital the stabilization energies of each ML bond may be written as in eq 18. Note that the

$$\begin{aligned} \Sigma_{\mathrm{ML}}(\sigma) &= 2\beta_\sigma S_\sigma^2 - 2\gamma_\sigma(S_\sigma^4 + S_\sigma^2 S_\sigma'^2) \\ \Sigma_{\mathrm{ML'}}(\sigma) &= 2\beta_\sigma S_\sigma'^2 - 2\gamma_\sigma(S_\sigma'^4 + S_\sigma'^2 S_\sigma^2) \end{aligned} \tag{18}$$

nonbonding orbital which may also be occupied receives no stabilization energy and does not figure in these expressions.[36] These equations immediately give us a trans influence. The stabilization energy of the ML bond depends upon the properties of the ligand sharing the same orbital. In the symmetric ML_2 complex the stabilization energy of each ML bond is $2\beta_\sigma S_\sigma^2 - 4\gamma_\sigma S_\sigma^4$. Thus the difference in ML stabilization energy on changing the nature of the other ligands is given by eq 19. If the ligand L′ has a larger overlap with the central atom than does L ($S_\sigma' > S_\sigma$), then the ML bond is weakened. If $S_\sigma' < S_\sigma$, then the ML bond is strengthened. A plot of $S_\sigma^2(S_\sigma^2 - S_\sigma'^2)$ against the relevant change in ML bond-overlap population from an EHMO calculation on a test MH_2 molecule in which S_σ and S_σ' were varied by changing the ML and ML′ distances gave a smooth curve which encourages our qualitative use of this simple function.

$$\Delta_{\mathrm{ML}} = 2\gamma_\sigma S_\sigma^2(S_\sigma^2 - S_\sigma'^2) \tag{19}$$

Case (iii), in general, gives rather complex expressions for the orbital energies on direct solution of the secular determinant, but here let us use the concept of ligand additivity (eq 3) which seems to be valid in the limited number of cases where it can be tested. This puts the second-order stabilization energy of the bonding orbital in MLL′ equal to the sum of that due to ML and ML′ (eq 20). In this case the quartic term is simply given by eq 21. The analogous equation to eq 19 representing the bond weakening/strengthening compared to that in ML_2 is then eq 22.[37] This is tremendously important in understanding the trans influence in octahedral and square-planar complexes.

$$\epsilon^{(2)} = k^2\left(\frac{S_\sigma^2}{\Delta\epsilon} + \frac{S_\sigma'^2}{\Delta\epsilon'}\right) \tag{20}$$

$$\begin{aligned} \epsilon^{(4)} &= \epsilon^{(2)}\left(\frac{kS_\sigma^2}{(\Delta\epsilon)^2} + \frac{kS_\sigma'^2}{(\Delta\epsilon')^2}\right) \\ &= k^4\left(\frac{S_\sigma^2}{\Delta\epsilon} + \frac{S_\sigma'^2}{\Delta\epsilon'}\right)\left(\frac{S_\sigma^2}{(\Delta\epsilon)^2} + \frac{S_\sigma'^2}{(\Delta\epsilon')^2}\right) \end{aligned} \tag{21}$$

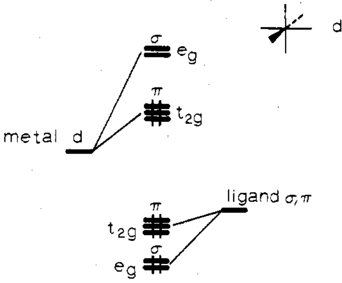
$$\Delta_{\mathrm{ML}} = 2k^4\frac{S_\sigma^2}{(\Delta\epsilon)^2}\left[\frac{S_\sigma^2}{\Delta\epsilon} - \frac{S_\sigma'^2}{\Delta\epsilon'}\right] \tag{22}$$

McWeeney, Mason, and Towl[38] decided that a good function with which to view the trans influence of ligands in square-planar complexes was the function $S^2/\Delta\epsilon$ since from perturbation theory this represented the size of the ML interaction. S was the ligand σ–metal 5p overlap integral and $\Delta\epsilon$ their orbital energy separation. This, of course, is exactly the parameter occurring in the brackets of eq 22. Increasing Pt–Cl bond length in trans $PtClX_2R$ complexes was well correlated experimentally with decreasing orbital electronegativity of the R group.[2,38] This is precisely what we find from eq 22 also. The ML stabilization energy decreases (and thus we expect the ML bond length to increase) with increasing $1/\Delta\epsilon'$ or decreasing $\Delta\epsilon'$. Since the H_{jj} value remains fixed, decreasing $\Delta\epsilon'$ represents decreasing orbital electronegativity. Langford and Gray[4] based their theory of the trans influence on the magnitude of M–L and M–L′ overlap integrals only. If the σ orbital of the ligand L has a greater overlap with the metal pσ orbital than does that of L′, then the ML bond is strengthened at the expense of the ML′ bond. This is clearly a restatement of eq 19. The overlap calculations of Gray and Langford have been extended[38] to a series of metals and a number of ligands. For example, in Pt(II) complexes these σ-overlap integrals have the same qualitative trends as the bond lengths in the $PtClX_2R$ series.

Pearson[39] introduced the concept of antisymbiosis by his conclusion that the ligands which produced the largest effect in the bonds trans to themselves were also the ones which were most susceptible to bond-length variations by changes in the nature of the trans ligand. Equation 22 describes this effect perfectly (it is also observed in the relative overlap populations in our hypothetical MH_2 molecule). A large change in ML stabilization energy is to be expected if $S_\sigma'^2/\Delta\epsilon$ for the trans ligand L′ is very different from $S_\sigma^2/\Delta\epsilon$ for L. In addition, a large effect is to be seen in the ML bond if $S_\sigma^2/\Delta\epsilon$, the term outside the parentheses, is large itself.

π Donors

The systems which have generally been studied in relationship to the trans influence have been low-spin d^6 and d^8 complexes containing π-donor ligands where all ML σ- and π-bonding orbitals are filled, **18**, and all ML π-antibonding ones as well. As before, when considering the angular geometry of two planar ligands around a central metal atom where the antibonding orbitals are filled (e.g., $HgPh_2$), we need to focus on the destabilization energy of the ML antibonding π orbitals. The energetics are described by eq 23 and 24 which are exactly analogous to eq 18 and 19. The difference in stabilization energy for MLL′ is given in eq 24 and implies



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$$\text{M–L destabilization} = 2\beta_\pi S_\pi^2 - 2\gamma_\pi(S_\pi^4 + S_\pi^2 S_\pi'^2) \tag{23}$$

$$\Delta_{\mathrm{ML}} = 2\gamma_\pi S_\pi^2(S_\pi'^2 - S_\pi^2) \tag{24}$$

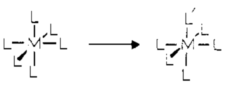
that the stronger the ML′ π interaction becomes the *stronger* the ML bond becomes. Since we are concerned here with occupied ML antibonding orbitals, the weakening/strengthening process is opposite to that for the π-acceptor or σ-donor cases we described above. It is unfortunately difficult to find data which either support or oppose the implications of eq 24.

Systems where a π donor (L) and a π acceptor (L′) share the same central-atom orbital constitute an interesting variation. For the case where this ML π-antibonding–ML′ π-bonding orbital is filled, reworking the above arithmetic (but with a sign change for $\Delta\epsilon'$, converting it from a π donor to an acceptor) shows that the σ acceptor will weaken the ML bond but the π donor strengthens the ML′ bond. At face value this prediction does not seem to hold. CO and C_2H_4 are not particularily good trans-influence ligands, even though they are good π acceptors. Recall, however, that the size of the effect also relies on how good a π donor the trans ligand is ($2\gamma_\pi S_\pi^2$ term in eq 24) via the antisymbiotic effect. Unless L is a good π donor, it will not be significantly affected by the π-acceptor properties, however good they are, of the L′ ligand.

Polarization by Virtual Orbitals and the Trans Influence

Although our scheme gives results which are in good accord with experiment and quantifies the three points noted in the Introduction, there is another factor which in some cases may be of equal or perhaps greater importance. This mechanism involves two orbitals on the central atom (each of different parity), whereas in the method previously developed only one orbital on the central atom was considered. The mixing of these two orbital types as the symmetry of the molecule is lowered gives rise to a trans- or mutual-ligand influence. We shall show how this mechanism operates in some detail for octahedral ML_6, square-planar ML_4, and trigonal-bipyramidal ML_5 complexes where L is a σ donor.

On the left side of Figure 4 are the well-known valence orbitals of an octahedral ML_6 molecule. The ligand orbitals are illustrated here as s orbitals for convenience; sp-hybridized donor functions could equally well be utilized with the same result. The perturbation to be initially considered consists of increasing the electronegativity of one of the ligands, L′, as illustrated in **19** → **20**. The orbitals of **19**, shown on the left of Figure 4, will respond by mixing together to produce a new set orbitals which describe the perturbed system. It is not, however, necessary to trace the evolution of all of the orbitals in **20** from **19**. There are three factors which simplify the analysis for our purposes. (i) Only those orbitals which transmit the perturbation need to be considered. In other words, all crucial orbitals in **19** must have atomic coefficients on what will become the perturbed ligand and the trans one. (ii) Only mixing of virtual orbitals into occupied ones will produce a M–L overlap population differential between the cis and trans ligands. The intermixing of occupied sets will serve to redistribute electron density within each molecular orbital; however, the overlap population between each atom is a sum over all occupied orbitals. Therefore, the effect of this intermixing on the overlap population cancels. (iii) The mixing coefficient of orbital *j* into orbital *i* is given by eq 25



19 20

$$c_{ji} = \frac{H_{ii} - S_{ij}\epsilon_i^{(0)}}{\Delta\epsilon_{ij}^{(0)}} \qquad (25)$$

(to first order). Equation 25 indicates that the most important mixings will occur between orbitals with the smallest energy gap (HOMO–LUMO interactions) and/or the largest numerator in the above expression. With these simplifications in mind let us return to the **19** → **20** transformation. From inspection of Figure 4 it is clear that one component of the t_{1u} set, **21** and one component of e_g, **22**, are the occupied and unoccupied orbitals, respectively, which form the dominant contribution to the trans influence. Recall that L′ is more electronegative than L; thus, **22** mixes into **21** with the phase shown, increasing the electron density on the more electronegative ligand. The shape of the resultant orbital, **23**, illustrates the increase in overlap population for the trans M–L bond and also points to a small weakening of the cis M–L bonds. We contend that this increase in overlap population will be reflected in a shorter M–L bond. The concept of mixing an antibonding level into the ground state to produce a stronger bond may seem a little unsettling at first. The overlap population in **23** can be derived from contributions from **21** and **22** (which will lead to only a small difference between the cis and trans overlap populations at reasonable values of the mixing coefficient) plus a "cross term", **24**. This cross term which contains the largest atomic coefficients in **21** and **22** dominates the overlap-population differential. An EHMO calculation on a model d^6 MH_6 molecule[40] showed a direct relationship between the cis and trans M–H overlap-population difference and the first-order mixing coefficient of **22** into **21** as a function of changing the H_{ii} on one of the hydride ligands. A similar effect is obtained if the overlap integral of the σ orbital on L′ with the metal p orbital on M

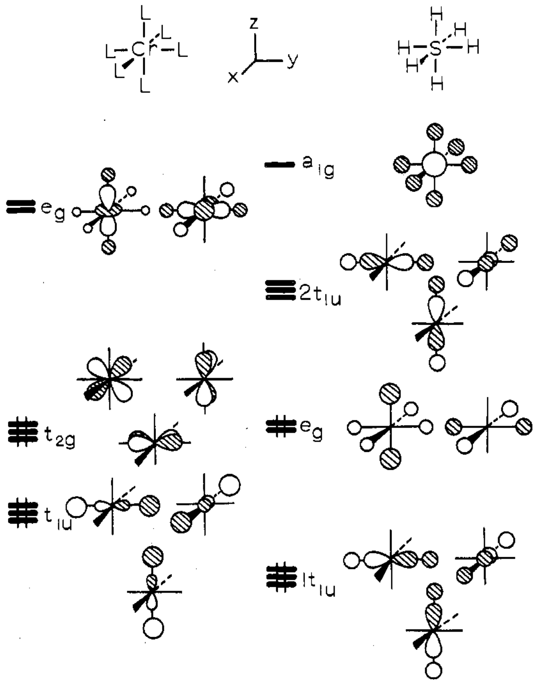
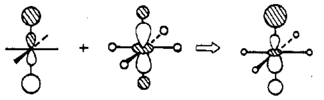


Figure 4. The important valence orbitals and approximate ordering of energies for ML_6 (on the left side of this figure) and SH_6 (on the right side) molecules.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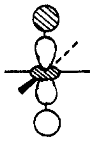
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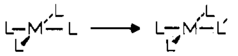
decreases by changing the orbital exponent on L′. An analysis of d^8 square-planar ML_4 perturbations, **25**, and d^8 trigonal-bipyramidal ones, **26**, can readily be deduced. The dominant mixing, shown by **27** and **28**, is a natural extension to the ML_6 case. Thus in each system this model predicts that the substitution of a more electronegative ligand will strengthen the trans M–L bond which is in accord with experimental data.[2]



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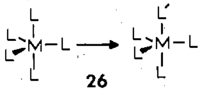

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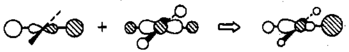

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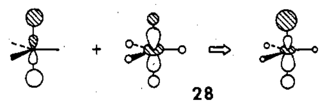

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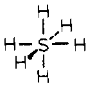
However, the reverse trend has often been found in main-group compounds, depending upon the oxidation state of the central metal and electronegativity of the ligands.[2] Let us consider the perturbation on going from SH_6 to SH_5X where X is more electronegative than H. This is diagramed in **29** → **30**. The important valence orbitals of SH_6 are sketched on the right side of Figure 4. It is found the the mixing of a_{1g}, **31**, into one component of e_g, **32**, forms the major contribution to the S–H overlap-population changes. The resultant orbital, **33**, indicates a weakening of the trans S–H bond and a strengthening of the cis ones. One might have thought, using energy-gap arguments, that one component of $2t_{1u}$, **34**, would mix into **31** more than **32**. This tends to strengthen the trans S–H bond and has no effect on the cis ones. However, the mixing coefficient of **32** into **31** is over twice as large as that for **34** into **31** from our extended Hückel calculations.[41] This is a consequence of a much larger numerator in eq 25 (via the H_{ij} term) for the former interaction compared with the latter. In actual fact, both interactions occur so that the trans S–H overlap population diminishes slightly while the cis ones increase.[42] An extension to other main-group compounds with alternative geometries (e.g., PH_5, etc.) leads to analogous results. This sort of mechanism which we have outlined in this section has been viewed, and similar results have been obtained by using an umbrella perturbation method by Shustorovich.[43] Another approach which leads to the same resultant orbitals as the procedure we have used considers the valence orbitals of a trans L′···L fragment and their interaction with the valence orbitals of the ML_{n-2} fragment. Thus SH_6 is constructed from SH_4^{2+} and $H \cdots H^{2-}$. The orbital-interaction diagram is then modified by perturbing the $H \cdots H^{2-}$ fragment to an $X \cdots H^{2-}$ one. A recent example of this method as applied to bond length variations has been given by Howell.[44] The rehybridization (as the nature of the trans ligand changes) model was suggested many years ago by Syrkin.[45]



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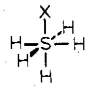

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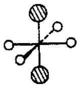

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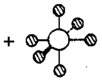

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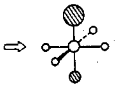

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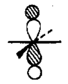

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Clearly then, there is more than one effect predicted to operate here. In some cases such as the underwriting of Timney's equation (eq 10) the orbital-sharing ideas are the only way to describe the problem. In other cases, notably the trans influence, both effects may be important. In none of our examples in this paper do we find any cases where the two approaches give opposite results. By way of contrast,[46] in our discussion of bond length/bond angle correlations in small molecules, we found one case where orbital-sharing ideas gave an answer in agreement with the observed structural trends and virtual orbital mixing gave the opposite and incorrect result. We also found cases where the reverse was true—virtual orbital mixing dominated. Thus, rather than proposing an alternative way to look at the structural features in these molecules we hope that we have drawn attention to *two* of the simple molecular orbital effects which may be important.

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(24) Our AOM treatment of allene includes different values of H_{ii} for the chemically inequivalent central and terminal carbon $p\pi$ orbitals so that β of eq 2 does not become infinite. This could be included in the Hückel approach by using different α values.
(25) If $\sum_{i=1}^{m} n_i = c$ (constant), then from the Cauchy–Schwartz inequality $c^2 \geq n_i^2 \geq c^2/m$. The minimum value of $\sum_{i=1}^{m} n_i^2$ is for $n_1 = n_2 = \ldots = n_m$ and the maximum for $n_1 = c$ and all other $n_i = 0$. In the present case we identify n_i with $S_{ij}'^2$ and c arises through the sum rule of eq 5. Then the maximum value of the quartic term appears at the planar geometry of allene where all the latent interaction is contained in one bonding orbital ($n_1 \neq 0$, $n_2 = 0$) and the minimum value at the twisted geometry where the interaction is shared between two orbitals ($n_1 = n_2$). A similar result, but with some qualifications concerning the phrase "sharing of orbitals", applies to central-atom d-ligand σ interactions. Here, although the sum rule applies as before, the ligand overlap integral, for example, along the x axis with $x^2 - y^2$ is only $3^{1/2}/2$ of the value for ligand overlap along the x axis with z^2, i.e., whereas, the three p orbitals are "equivalent", the five d orbitals are not.
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(37) This is reached by an obvious algebraical division of the cross terms in eq 22 between ML and ML′. If the cross terms are divided equally, then the relevant equation becomes

$$2\frac{S_\sigma^{\,2}}{(\Delta\epsilon)^2}\left[\frac{S_\sigma^{\,2}}{\Delta\epsilon} - \frac{S_\sigma'^{\,2}}{\Delta\epsilon'}\,\frac{\tfrac{1}{2}(\Delta\epsilon + \Delta\epsilon')}{\Delta\epsilon'}\right]$$

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Metalloporphyrin–Ligand Equilibria: A Ligand Field Rationale

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Equilibrium constants for the reaction PM–OH_2 ⇄ PM–OH (K_{OH}) are reported where P = tetraphenylporphyrinsulfonate or hematoporphyrin and M = Cr(III), Mn(III), Fe(III), Co(III), or Rh(III). The observed trends in the binding constants may be explained by a simple electrostatic (ligand field) model. For a tetragonal field, the calculated effective charge along the *z* axis is shown to correlate with the binding constant of axial OH^-. Similar trends are observed for imidazole binding to metalloporphyrins. It is found that the magnitude of the equilibrium constants is surprisingly independent of the nature of the porphyrin substituents. Finally, the relationship between these trends in axial bonding and heme protein conformational energy is briefly discussed.

Introduction

The reactions of ligands with metalloporphyrins have long been of active interest to both biochemists and coordination chemists.[1] However, this interest has not yet translated into a general understanding of the factors which control metalloporphyrin–ligand equilibria (and kinetics).[2]

To understand the general trends in such bonding, two limiting approaches might be taken. The first treats metalloporphyrins by using a tetragonally distorted ligand field model, so that some molecular orbitals may be designated as clearly metal centered. The occupancy of these orbitals would thereby influence the strength of metal–ligand interaction. In this approach, porphyrins are treated much the same as other ligands (e.g., simple amines) and constructs of formal metal oxidation states retain some significance (e.g., $[CoTPPS_4]^{3-27}$ may be treated as a "d^6 Co(III)" complex).

By contrast, it is often argued in the extensive porphyrin literature that metal–ligand orbital mixing is so extensive that the concept of metal centered MO's loses significance.[2–6] For example it has been noted that there is a "necessity to choose a strongly delocalized model of electronic configuration of the complex compared to the usual metal centered description".[6] Others have argued in a similar vein that orbital mixing is so complete in metalloporphyrins that assignment of electrons to metal-centered orbitals and concurrent assignment of formal oxidations states is invalid.[5,7] Previous investigations of ligand equilibria of metalloporphyrins have been limited to a single metal with a single type of porphyrin.[3–9] Thus cross comparisons could not apparently be made between, e.g., CoTPPS and FeHMP. In this case, trends in metalloporphyrin ligand equilibria would not be easily discerned.

In order to test these limiting models, we have determined ligation (hydrolysis) equilibria constants

$$\mathrm{MPOH_2} \xrightleftharpoons{K_{\mathrm{OH}}} \mathrm{MPOH} + \mathrm{H^+}$$

for a series of metalloporphyrins MP where M = Cr(III), Mn(III), Fe(III), Co(III), or Rh(III) and P = tetraphenylporphinesulfonate (TPPS) or hematoporphyrin (HMP). More limited data for metal–imidazole binding are also reported. The results are shown to be semiquantitatively explained by a simple electrostatic model. Finally, the implications of these results for heme protein chemistry are briefly discussed.

Experimental Section

Materials. Ligands. Hematoporphyrin free base was purchased from Sigma Chemicals. TPP and TPPS[27] were synthesized and purified by standard procedures.[1,16] All metal salts and metal carbonyls were reagent grade, purchased from Alfa. Water was doubly distilled and deionized.

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