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Ligand Site Preferences and Intramolecular Photochemical Rearrangements in Some Transition Metal Complexes. Simple Molecular Orbital Considerations

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The angular overlap model is used to determine the relative stability of the following systems as a function of d orbital configuration; cis and trans octahedral MA_2B_4, isomers of MA_3B_3, axially and equatorially substituted square-pyramidal and trigonal-bipyramidal MAB_4, and square-planar MA_2B_4. The most stable isomer is determined in each case. These ligand site preferences as a function of d orbital occupation numbers are used to provide a ready explanation of some cis–trans photochemical isomerization processes in some d^6 and d^8 systems.

Introduction

Recently, we have shown that the angular overlap model of transition metal–ligand interaction is a very powerful tool with which to view the shapes of a variety of transition metal complexes as a function of d electron configuration and the number of coordinated orthaxial ligands.[1,2] We have also shown that it may be used to view relative bond strengths in some four-, five-, and six-coordinate complexes.[3] In particular, we have suggested that the so-called Jahn-Teller distortions of octahedral d^9 complexes and the square planar–octahedral isomerization of similar d^8 systems are probably two manifestations of the same effect within the d manifold of orbitals. We have also demonstrated[1] that simple Wolfsberg–Helmholz or extended Hückel molecular orbital calculations quite faithfully reproduce these minimum energy angular structures, and that simple plotting of d orbital energies as a function of distortion coordinate led to energy diagrams which could be used qualitatively to rationalize the observed molecular shapes. Hoffmann and coworkers using essentially the same computational method have recently arrived at similar conclusions.[4] In this paper we shall extend these angular overlap ideas to those situations, where the ligands coordinated to the central atom are not all identical, and inquire which of the positional ligand permutations gives rise to the most stable structure. While some of the arguments for specific systems will be qualitatively familiar we describe a quantitative unifying method with which to view these observations. We shall use these ideas to rationalize some cis–trans photochemical isomerization processes which occur in octahedral d^6 and square-planar d^8 complexes.

The Angular Overlap Method

We have previously shown[1,2] that the total orbital electronic stabilization energy due to d orbital–ligand σ interaction of a metal–ligand system is approximately given by the expression

$$\Sigma(\sigma) = \beta_\sigma \Sigma h_j S^2\,[\Gamma_j(\mathrm{M});\ \sigma(\Gamma_j)] \qquad (1)$$

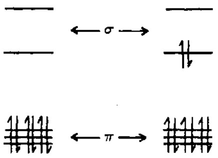
where h_j is the number of one-electron holes in the (predominantly d) metal ligand antibonding orbital of the jth representation. S is the overlap integral between the group of ligand σ orbitals transforming as Γ_j and the metal d orbital of the same symmetry species. β_σ is a parameter which measures the "strength" of the d orbital–ligand σ interaction. In the case of lower symmetry environments the following expression is simpler to handle

$$\Sigma(\sigma) = \sum_{\substack{\text{all d}\\ \text{orbitals}}} h_i \sum_{\substack{\text{all ligand}\\ \text{orbitals}}} S^2(\mathrm{X}_\sigma,\mathrm{d}_i)\beta_\sigma(\mathrm{X}) \qquad (2)$$

where we include the sum of the squared overlap integrals between the σ orbitals on each ligand X and the ith d orbital. The origin of these hole equations is readily seen in Figure 1 where the stabilization energy of the occupied bonding orbitals a, b, and c is canceled by occupation of their antibonding counterparts (a', b', c'). The total stabilization energy is given by $2D + 2E$, i.e., the destabilization energy times the number of holes in the unoccupied d orbitals. Similar equations to these hold when π interactions are considered. We will consider such interactions first since they are readily dismissed as being unimportant in determining site preferences of coordinated ligands in the geometries we have chosen to study.

π Bonding Effects within the d Orbital Manifold

In the spy and octahedral situation the lowest three d orbitals only are involved in π bonding and the highest two d orbitals exclusively in σ bonding. For the low-spin d^6 and d^8 configurations therefore all the d orbitals involved in π bonding are occupied. Thus, if the ligands are π donors then the total



π stabilization is zero ($\sum(\pi) = 0$) since the stabilization afforded by occupancy of the π bonding orbitals is completely

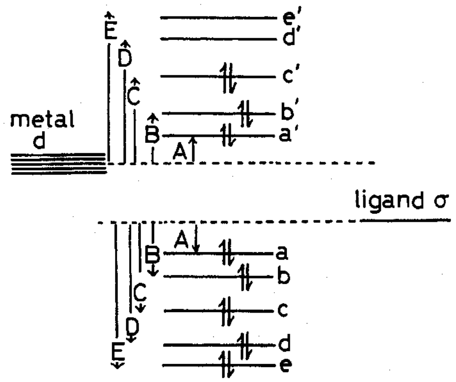


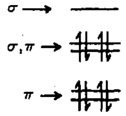
Figure 1. The origin of eq 1, showing that since the stablization energy afforded by the electrons in the bonding orbitals a, b, and c is offset by occupation of their antibonding counterparts, the total stabilization energy of the system = sum of number of holes in d orbitals times the destabilization energy of that d orbital.

offset by complete occupancy of the M–L π antibonding (mainly metal d) orbitals. For the case where the ligands are π acceptors these filled d orbitals are now M–L bonding and the corresponding M–L π antibonding orbitals are empty. The angular overlap model thus leads to

$$\Sigma(\pi) = 2\sum_x m\beta(X)S_\pi^2(X) \tag{3}$$

where m is the number of π orbitals used by each ligand X. (Each ligand thus contributes $2m\beta_\pi(X)S_\pi^2(X)$ in these orthogonal geometries to the total stabilization energy where S_π is the overlap integral of a ligand π orbital with d_{xz} (or d_{yz}) when the ligand lies along the z axis.) This function is independent of any isomeric arrangements in the spy or octahedral geometry simply because the three π type d orbitals lie in three mutually perpendicular planes. Similarly for intermediate spin d^6 systems where there is a hole in the d_π orbitals any difference from eq 3 above is independent of ligand position since in the orthogonal octahedron based structure all metal d_π orbitals are equivalent.

Thus π effects within the d orbital manifold are not of primary importance in altering the relative stabilities of isomers in these systems. In d^8 tbp structures similar arguments apply.



The highest lying d orbital (d_{z^2}) is involved purely in σ interaction and thus there are no holes in metal d orbitals involving π interactions. For the tbp d^6 system, however (whether intermediate or low spin), holes are present in the e' (in-plane π bonding) orbitals. Thus π donors will prefer to make use of the in-plane π bonding facilities (fewer M–L π antibonding electrons) while π acceptors will prefer interaction in the axial position, where the M–axial ligand π bonding orbitals (e'') are all filled. These arguments, concerning the often negligible importance of π effects within the d orbital manifold, are based on the assumption that the stabilization energy of a M–L π bonding orbital is exactly equal to the destabilization energy of its antibonding counterpart. This is only exactly true in the zero-overlap approximation. However, typical π overlap integrals between metal and ligand are around 0.1 and the error involved in this assumption is approximately $(1 - (1 + S^2)/(1 - S^2)) \simeq 0.02$ of the π stabilization energy. This is a negligible correction.

Neglect of s,p Orbitals on the Metal

We have ignored the presence of s and p orbitals on the metal center in this simple molecular orbital approach. That mixing of metal s,p orbitals into the ground state wave function does occur is certainly true but it is very difficult to say how extensive it will be. In extended Hückel molecular orbital language it will depend upon the size of the s,p orbital exponents relative to that chosen for the d orbitals and also on values chosen for the diagonal matrix elements. It is a problem very much akin to the assessment of the amount of d orbital involvement in second-row main-group systems, in S–O bonds for example. We have chosen to ignore s and p orbitals in our angular overlap treatment, partly because of the indeterminate nature of the degree of their involvement and partly because of the increase in algebraic complexity of the system represented basically by eq 1. We have previously concluded[2] that ligand π–metal d orbital interactions were of secondary importance, compared to σ effects, in determining the angular geometries of complexes. Similarly, we might expect metal–ligand π interactions arising through d–p mixing to be small compared to the metal d–ligand σ interactions which will be considered in this paper. Hoffmann[4,5] on the other hand in a wide-ranging series of recent papers on structural aspects of transition metal chemistry makes extensive use of d–p mixing to amplify several points. In our discussion below we shall not find it necessary to include metal s,p–ligand interactions.

Octahedral Complexes

In these examples we wish to know how the cis and trans isomers MA_2B_4 vary in stability as a function of d orbital configuration, depending upon the relative σ donor properties of the ligands A,B. In the angular overlap model the ligand of larger σ donor power is the one with the larger value of the product $\beta_\sigma S_\sigma^2$, i.e., the size of the "unit" of stabilization energy employed in our model. Initially, we shall examine the low-spin d^8 system with d orbital occupancy numbers 22220. The results will also be applicable to d^9 systems (22221) where quantitatively $\sum(\sigma)$ of eq 2 will be half as large reflecting one-half the number of one-electron holes in the highest energy d orbital. For the low-spin d^8 structure we need first of all to determine the relative destabilizations of the two highest energy d orbitals since depending upon the nature of the A and B ligands, sometimes d_{z^2} will be highest in energy within the d orbital manifold and sometimes $d_{x^2-y^2}$. Remembering that if we write the overlap integral for overlap of a ligand σ orbital located along the z axis with d_{z^2} as S_σ, then the overlap of a similar ligand along the x or y axis will have an overlap integral of $-{}^1/_2\, S_\sigma$ with the collar of d_{z^2} and $(3^{1/2}/2)S_\sigma$ with $d_{x^2-y^2}$.

We may now use eq 2 to derive the total d orbital stabilization energy of the complex. For the cis structure using the coordinate system of Figure 2 the destabilization energy of $d_{x^2-y^2}$ is

$$2\left(\frac{3^{1/2}}{2}\right)^2 \beta_\sigma(A)S_\sigma^2(A) + 2\left(\frac{3^{1/2}}{2}\right)^2 \beta_\sigma(B)S_\sigma^2(B) \tag{4}$$

$$= 1.5\beta_\sigma(A)S_\sigma^2(A) + 1.5\beta_\sigma(B)S_\sigma^2(B) \tag{5}$$

and that of d_{z^2} is similarly

$$2\beta_\sigma(B)S_\sigma^2(B) + 2\beta_\sigma(B)({}^1/_2)^2S_\sigma^2(B) + 2\beta_\sigma(A)({}^1/_2)^2S_\sigma^2(A) \tag{6}$$

$$= 2.5\beta_\sigma(B)S_\sigma^2(B) + 0.5\beta_\sigma(A)S_\sigma^2(A) \tag{7}$$

Thus if A is a better σ donor than B (implying that $\beta_\sigma(A)S_\sigma^2(A) > \beta_\sigma(B)S_\sigma^2(B)$) the highest energy d orbital is $d_{x^2-y^2}$ and the total value of $\sum(\sigma)$ is

$$\Sigma(\sigma) = 3\beta_\sigma(B)S_\sigma^2(B) + 3\beta_\sigma(A)S_\sigma^2(A) \tag{8}$$

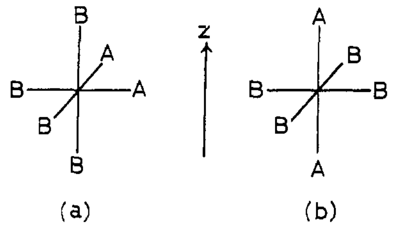


Figure 2. Definition of axis system for cis (a) and trans (b) octahedral MA_2B_4 isomers.

For the trans structure of Figure 2 the destabilization energy of $d_{x^2-y^2}$ is

$$4\beta_\sigma(B)\left(\frac{3^{1/2}}{2}\right)^2 S_\sigma^2(B) = 3\beta_\sigma(B)S_\sigma^2(B) \tag{9}$$

and of d_{z^2} is

$$2\beta_\sigma(A)S_\sigma^2(A) + 4\beta_\sigma(B)(^1/_2)^2S_\sigma(B) \tag{10}$$

$$= 2\beta_\sigma(A)S_\sigma^2(A) + \beta_\sigma(B)S_\sigma^2(B) \tag{11}$$

If A is a better σ donor than B then d_{z^2} lies higher in energy than $d_{x^2-y^2}$ and the total contribution to $\sum(\sigma)$ is

$$\Sigma(\sigma) = 4\beta_\sigma(A)S_\sigma^2(A) + 2\beta_\sigma(B)S_\sigma^2(B) \tag{12}$$

This is a larger value than that of eq 7 and thus the stronger σ donors in the d^8 case prefer the trans configuration. We can use the same method to investigate the site preferences when in MA_2B_4 B is a better σ donor than A. In this case in the cis structure the highest energy d orbital is d_{z^2} and in the trans geometry it is $d_{x^2-y^2}$. The total stabilization energy of the cis structure is thus

$$\Sigma(\sigma) = 5\beta_\sigma(B)S_\sigma^2(B) + \beta_\sigma(A)S_\sigma^2(A) \tag{13}$$

and of the trans arrangement

$$\Sigma(\sigma) = 6\beta_\sigma(B)S_\sigma^2(B) \tag{14}$$

Surprisingly, perhaps, the trans geometry is still the more stable. Thus the most stable arrangement for MA_2B_4 for this particular configuration is independent of the nature of the ligands A and B. An explanation of this observation is readily available by remembering that the most stable geometry[2] of an MB_4 species with this electronic configuration is the square-planar one (e.g., $PtCl_4^{2-}$). Thus if the two weaker σ ligands are attached to the MB_4 plane to give the trans octahedral structure the square-planar arrangement containing the stronger σ donor ligands is preserved. (We may think of the square-planar (four coordinate) structure as being six coordinate in which two axial ligands have zero σ strength.) The cis arrangement which would destroy this stable square-planar unit is thus less attractive. For the case where the ligands A are better σ donors than B then the A ligands, by comparison of eq 8 and 10, prefer to overlap with d_{z^2} rather than $d_{x^2-y^2}$ (since here the overlap is better), also giving a stable trans arrangement of these two ligands.

Since the σ orbital stabilization energy of the metal–ligand system is determined by the orbital occupation numbers of the two highest orbitals in the octahedral geometry, the same conclusions reached for low-spin d^8 also apply to intermediate spin d^6 (22110), d^7 (22210), and all other systems where square-planar geometries are also predicted for the four-coordinate units. Calculation of the $\sum(\sigma)$ values by the above route leads to the same conclusions as for the d^8 system for these configurations. There are no octahedral low-spin d^8 complexes available since the high-spin configuration is always favored due to the proximity in energy of the two highest energy d orbitals. Fe(II) systems are either low spin (22200) or high spin (21111) and it is difficult to find any compounds with the 22110 configuration in the electronic ground state. This particular electronic configuration however will be vital to our photochemical discussion below.

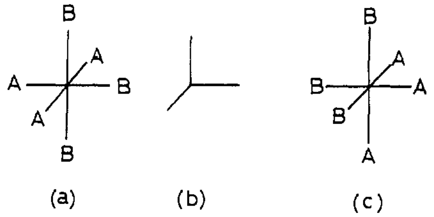


Figure 3. (a) MA_3B_3 isomer preserving a T of A and B ligands. (b) Geometry of three-coordinate low-spin d^6 systems. (c) MA_3B_3 isomer preserving the arrangement shown in (b) of both A and B ligands.

For the low-spin d^6 systems (22200) where both the d orbitals involved in σ interactions are completely empty the total stabilization energy using eq 2 becomes

$$\Sigma(\sigma) = 8\beta_\sigma(B)S_\sigma^2(B) + 4\beta_\sigma(A)S_\sigma^2(A) \tag{15}$$

for both cis and trans arrangements of ligands. Thus, the quadratic term in the overlap integral predicts equal stability for both isomers. In our qualitative discussion of the four-coordinate d^6 ML_4 systems with the cis divacant geometry we had to revert to considerations of quartic terms in the overlap integral to conclude that this was the most stable geometry (compared to square planar).[2] Such a procedure is not a very satisfying one when faced with ligands of more than one type coordinated to the metal and we shall rely on the method above based on the stabilities of the relevant four-coordinate units to decide upon the relative stabilities due to d orbital interaction of these six-coordinate isomeric complexes. The fact that we need to revert to a discussion of quartic terms to examine ligand site preferences implies that the energy differences between cis and trans structures are probably smaller for the d^6 low-spin species than they are for the corresponding low-spin d^8 systems. If we conclude that the octahedral cis divacant structure is the more stable[2] for four-coordinate low-spin d^6 systems as evidenced by the observation[6] of that structure for $Cr(CO)_4$ then we expect the cis isomer of MA_2B_4 to be the more stable when the A are poorer σ donors than B. This (by comparison with the square plane in the d^8 case) retains the cis divacant arrangement of strong σ donors. Experimentally,[7-9] the cis isomer of $Co(CN)_4(H_2O)_2^-$ (d^6) for example is found to be thermodynamically more stable than the trans in solution at room temperature although the two isomers are rapidly interconverting at 25°C. (At 2°C this interconversion may be frozen.) Similarly for d^6 $M(CO)_4I_2$ (M = Fe, Ru, Os) the more stable isomer[10,11] is the cis one, the trans isomer thermally isomerizing to the cis at room temperature. In a large number of FeL_4H_2 complexes (L = phosphine, phosphite) only the cis forms are found. For $Fe(CO)_4(SiCl_3)_2$ the cis isomer is more stable[12] but for $Os(CO)_4(SiCl_3)_2$ only the trans isomer has been made.[12]

By considering the equilibrium geometries of the corresponding three-coordinate complexes MB_3 we may predict the most stable isomers for the MA_3B_3 system. For the low-spin d^8 configuration the most stable angular geometry of an MB_3 unit is predicted to be a T shape. Thus the most stable isomer MA_3B_3 (irrespective of the relative ligand strengths of A and B) will be that of Figure 3a (mer) where the T arrangement of both stronger and weaker σ ligands is preserved. Similarly for low-spin d^6 the C_{3v} structure of Figure 3b is predicted for the MB_3 unit. $Cr(CO)_3$ has this geometry.[6] This leads to the fac structure of Figure 3c when three A ligands are additionally coordinated to the metal. Here also the fac structure

Table I. Most Stable Isomer in Octahedral Complexes as a Function of d Orbital Configuration

22200 22100	22210, 22211, 22221 22110, 22220
cis-MB_4A_2	*trans*-MB_4A_2
fac-MB_3A_3	*mer*-MB_3A_3

leaves the 3A ligands and 3B ligands in identical surroundings. This geometry will be the lower energy one irrespective of the relative σ strengths of A and B. Thus $Cr(CO)_3(PH_3)_3$ is found[14] as the cis complex as are[15] $M(CO)_4(P_4S_3)_2$ and $M(CO)_3(P_4S_3)_3$ (M = Cr, Mo). In the latter case, any steric considerations would favor trans arrangements for the cage ligands. Electronic factors seem to win here. In the mixed compound Ru-*trans*-$(PPh_3)_2$-*cis*-$(CO)_2$-*cis*-I_2 this isomer is the more stable[16] at room temperature. The form where all the ligands are trans to one another reverts to the other thermally at room temperature. The more stable form contains the strong σ ligands (CO, PPh_3) in the cis divacant structure. A summary of the predicted isomeric preferences as a function of d electron configuration is given in Table I.

Photochemical Cis to Trans Isomerization in d^6 Octahedral Complexes

It has been pointed[17,18] out that barriers to intramolecular rearrangements in four- and six-coordinate structures are generally expected to be high. The bond-breaking mechanism followed by facile five-coordinate rearrangement is generally regarded as being less energetic than the intramolecular six-coordinate rearrangements. Until recently, the only known examples of facile nondissociative rearrangement processes involving six-coordinate molecules were the FeL_4H_4 systems (L = phosphine, phosphite). However, there are now some other examples[9,13] also involving nonchelating ligands, and also evidence concerning photochemical cis–trans conversion.

For $Co(CN)_4(H_2O)_2^-$ the cis isomer is experimentally[7-9] the thermodynamically more stable isomer as discussed above and thermal cis–trans equilibration is prevented if the temperature is kept at 2°C. On photolysis in one of the d–d bands of the cis isomer at 2°C, however, the trans isomer is produced. Irradiation of the trans isomer leads to virtually no conversion to the cis arrangement. Experimental evidence supports a nondissociative intramolecular process. (Similarly, it has been shown[10] that d^6 cis $Fe(CO)_4I_2$ may be converted to the trans isomer by sunlight and the trans isomer reverts slowly to the cis structure by a thermal process in the dark. Here, however, there is strong evidence that the photochemical process proceeds via a dissociative pathway.[19]) Qualitatively we may understand these observations on the cobalt system in the light of our previous discussion concerning the stability preferences for the molecule as a function of d orbital occupation numbers and noting that the ground state isomers are connected via a low-energy (thermally accessible) barrier if the cis–trans exchange occurs in an intramolecular fashion. The preferred geometrical arrangement in the excited electronic state (22110) as we discussed above is the trans isomer (Table I), the geometry dominated by the four strong CN^- σ ligands (compared to H_2O). If the lifetime of the excited electronic state is long compared to the rate of passage over the barrier some sort of thermal distribution favoring the trans geometry may be built up. It is this distribution favoring the trans structure which is "frozen" on return to the electronic ground state. The experimentally observed quantum yield is very high[8] (0.4) and argues for a rearrangement process in the excited state determined by the relative stabilities of cis and trans isomers as we describe here, rather than a statistical distribution based on the number of cis and trans permutations. In this latter case, the maximum possible quantum yield would be $^1/_8$ (0.125). We expect similar observations to be made on the compound $Co(CN)_3(H_2O)_3$, for example, where by using the results of the previous section and the argument discussed here a photochemical rearrangement from fac to mer should be possible. This has recently also been observed experimentally.[7] The photoisomerization of Ru-*trans*-$(PPh_3)_2$-*cis*-$(CO)_2$-*cis*-I_2 (A) to the structure where all pairs of ligand are trans to one another[16] (B) may also be rationalized on similar lines (Figure 4). Structure B thermally reverses to A and the entire process is understood on the simple basis that CO and PPh_3 are better σ donors than I. They will therefore adopt the cis divacant and square-planar arrangements in ground and excited states, respectively.

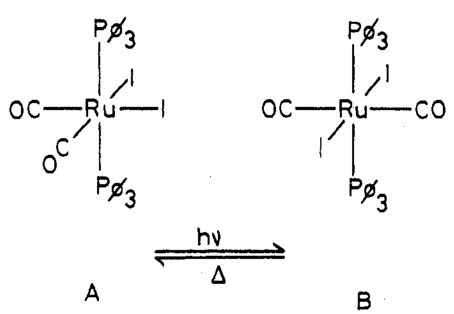


Figure 4. Photoisomerization of $Ru(CO)_2(PPh_3)_2I_2$.

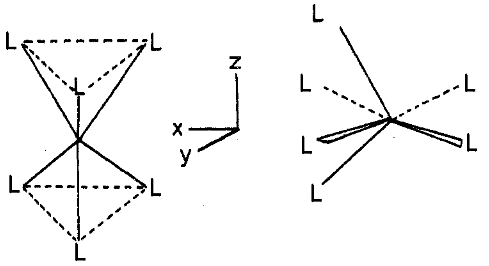
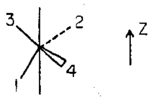


Figure 5. Axis system for the trigonal prism and bicapped tetrahedron.

We may envisage two intramolecular motions by which such a cis–trans rearrangement may occur, via the trigonal prism (Figure 5) and bicapped tetrahedron. We may use eq 1 to inquire which of the two processes will give rise to the lowest energy pathway relating the two isomers. First, we examine the case where all six ligands are the same. Initially, we consider the bicapped tetrahedral geometry. To simplify the algebra we shall initially modify the structure slightly by allowing the "capping" ligands to lie along a single axis and requiring that the bond angles within each pair of orthogonal pairs in the tetrahedron (atoms 1, 2 and 3, 4) are kept at 90° rather than the tetrahedral angle of 109.5°, viz.,



As we may readily calculate, the destabilization energy of d_{z^2} is then $3\beta_\sigma S_\sigma^2$, that of $d_{x^2-y^2}$ and d_{zx} zero, and that of d_{yz} and d_{xy} $1.5\beta_\sigma S_\sigma^2$. For the genuine bicapped tetrahedron where the two capping ligands are directed through the middle of the two faces of the four-coordinate geometry, we find that this simplified scheme needs to be slightly modified. The degenerate pair of σ d orbitals split apart in energy (to $1.333\beta_\sigma S_\sigma^2$ and $1.667\beta_\sigma S_\sigma^2$). The d orbital levels are shown in Figure 6. In this rather unsymmetrical environment the d orbitals are best given by the axis system employed by Hoffmann, Howell, and Rossi.[20] We may consider the trigonal prism to be constructed from two apically joined ML_3 units with a droop angle (from D_{3h}) of $\sin^{-1} (^1/_3)^{1/2}$. Putting d_{z^2} along the threefold axis leads to a zero destabilization energy for d_{z^2}, $\beta_\sigma S_\sigma^2$ for $d_{x^2-y^2}$ and d_{xy}, and $2\beta_\sigma S_\sigma^2$ for d_{xz} and d_{yz}

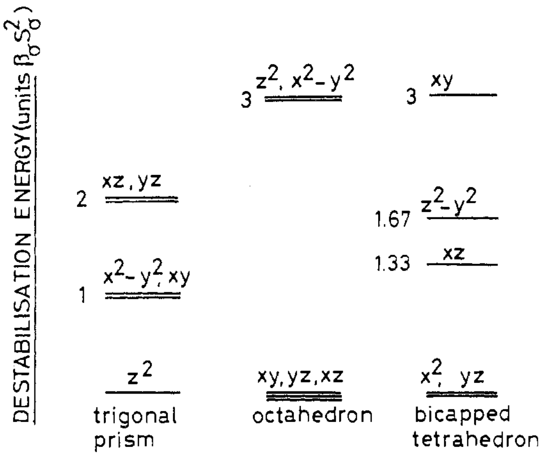


Figure 6. d orbital destabilization energies (in units of $\beta_\sigma S_\sigma^2$) for the trigonal prism, octahedron, and bicapped tetrahedron.

Table II. $\Sigma(\sigma)$ Values for Some Six-Coordinate Geometries (units of $\beta_\sigma S_\sigma^2$)

System	Octahedral	Bicapped tetrahedron	Trigonal prism
Low d^6	12	9.333	8
Int d^6	9	9	7
Low d^7	9	7.667	6
Low d^8	6	6	4
High d^8	6	4.667	4
d^9	3	3	2

(Figure 6). The calculated values of $\sum(\sigma)$ are shown in Table II for some d orbital configurations of interest. It is interesting to note that for these systems the trigonal prism is less stable than either of the other two geometries, but that the bicapped tetrahedron is often close in energy to the octahedron. Of special interest in our case is the intermediate d^6 configuration (22110) where both octahedron and bicapped tetrahedron are of equal energy. (The crystal field theory also shows[21] that for all d^n configurations the trigonal prism is either less stable or as equally stable as the octahedral geometry. The largest energy difference (in CFSE) is for the low-spin d^6 configuration, as also indicated by Table II.) We also note that the energy difference between octahedron and intermediate in the electronic ground state of the low-spin d^6 system is smaller for the bicapped tetrahedron structure ($2.667\beta_\sigma S_\sigma^2$) than for the trigonal prism ($4\beta_\sigma S_\sigma^2$). We should not rely too much on this conclusion since the neglect of nonbonded interactions in the crowded bicapped tetrahedron structure may mean that overall this mechanism is not the favored route. In the excited state (int spin d^6) the electronic contribution to the rotation barrier is seen to be zero for the bicapped tetrahedron and $2\beta_\sigma S_\sigma^2$ for the trigonal prism. The important conclusion is that in both cases smaller barriers are predicted in the excited state compared to the electronic ground state.

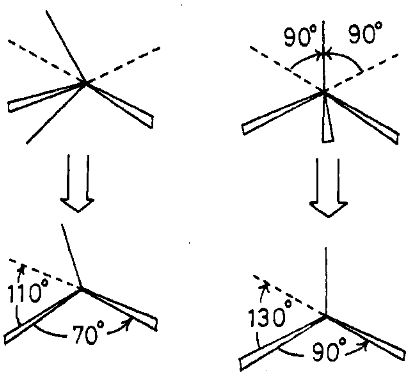


Figure 7. Figure showing similarity between the four-coordinate units MB_4 derived from the MB_4A_2 bicapped tetrahedron and trigonal prism.

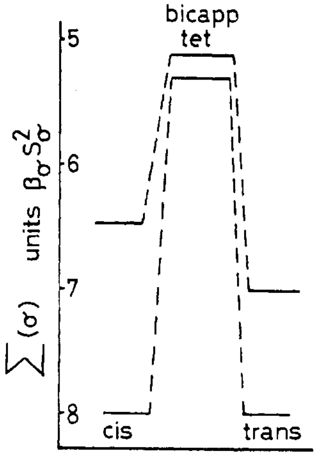


Figure 8. Energies of MB_4A_2 systems (σ strength of A ligands = 0) in ground and excited electronic states for cis and trans octahedral geometries and a bicapped tetrahedral intermediate.

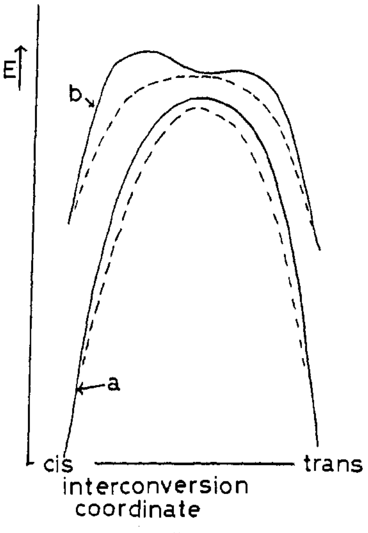


Figure 9. Results of extended Hückel calculations for a d^6 MB_4-A_2 system in ground (a) and excited (b) electronic states. Full curve via bicapped tetrahedral intermediate; dashed curve via trigonal prismatic intermediate.

We now examine the other extreme where in the MA_2B_4 complex the A are very much weaker σ donors than the B ligands and the angular energy changes are dominated by the B ligands. We now have a four-coordinate problem. One very interesting feature is the close geometrical resemblance between the two four-coordinate fragments derived from the two intermediate geometries under consideration. This is shown in Figure 7 but is very much easier to see on a model. For the four-coordinate structure based on the bicapped tetrahedron we calculate the set of d orbital energy levels $0.05\beta_\sigma S_\sigma^2$, $0.8333\beta_\sigma S_\sigma^2$, $\beta_\sigma S_\sigma^2$, and $1.665\beta_\sigma S_\sigma^2$ which leads to stabilization energies of $5.333\beta_\sigma S_\sigma^2$ (ls d^6) and $5.1633\beta_\sigma S_\sigma^2$ (int d^6). Remembering that the quadratic stabilization energies for the cis (octahedral cis divacant) and trans (square planar) four-coordinate MB_4 units are $8\beta_\sigma S_\sigma^2$ each for the 22200 configuration and $6.5\beta_\sigma S_\sigma^2$ and $7\beta_\sigma S_\sigma^2$ respectively for the 22110 configuration, we may construct the diagram of Figure 8. A diagram very similar to this should exist for the trigonal prismatic pathway due to the small difference in energy between the pseudo-four-coordinate structures derived from bicapped tetrahedron and trigonal prism. Therefore for systems where one type of σ ligand B is very much stronger

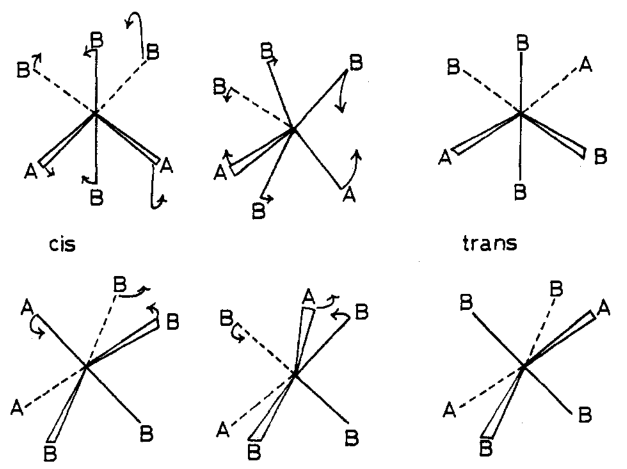


Figure 10. Cis–trans interconversion via bicapped tetrahedron and trigonal prism.

than the other A, the difference in energy between the two pathways may be very small and unresolvable.

We have carried out some extended Hückel molecular orbital calculations to see if these simple ideas are reproduced in a more rigorous regime. Figure 9 shows a sum of the total orbital energies for the two electronic configurations of d^6 MA_2B_4 calculated by modifying our molecular orbital approach of ref 1 to include two ligands of poorer σ donor qualities than the four already present. This was done in a purely qualitative way by changing the orbital exponent and diagonal matrix element of the σ orbital of two of the ligands such that their σ stabilization energy was less than that of the other four. Thus the energy scale and energy differences of Figure 9 are to be regarded only as representative of the trends expected when two of the ligands of the octahedral structure are replaced with weaker σ donors. Three points are apparent. First, the calculated difference in stability for the two low-spin d^6 isomers is smaller than that for the intermediate spin d^6 configuration, as we suggested earlier. Second, the barrier to isomer interconversion is smaller in the excited state than in the ground state also as we predicted using our model. Third, the energy curves for the bicapped tetrahedron and trigonal prism pathways are very similar.

The present calculations suggest then that it may be difficult to decide between the pathways via the trigonal prism and bicapped tetrahedral intermediates and that one route may not be overwhelmingly favored relative to all others. Figure 10 shows the geometrical distortions leading to cis–trans interconversion in the two cases. Probably the most important fact is that we predict and calculate a much smaller barrier in the electronic excited state than in the ground state thus making facile cis–trans interconversion in the former a likely proposition. However, if Franck–Condon factors are favorable it is quite possible that the cis → trans process in the excited electronic process may be a downhill one all the way, i.e., on excitation of the cis structure the excited state is created with already enough energy to surmount the barrier.

Square-Pyramidal Complexes

In this section we view the ligand site preferences in these five-coordinate complexes and reserve discussion on possible photochemical rearrangement processes in these five-coordinate systems for a further publication.

We investigate first the d^8 (22220) situation and inquire whether the stronger σ donor ligand prefers axial (apical) or equatorial (basal) sites. In this geometry the highest energy d orbital is $d_{x^2-y^2}$. For these five-coordinate systems there is no overlap of the axial ligand σ orbital with unoccupied d orbitals and thus no contribution to $\sum(\sigma)$ of eq 2. Overlap of the equatorial σ orbitals with the empty d orbital is possible, however, and gives a total stabilization for MAB_4 with A axial of

$$\Sigma(\sigma) = 6\beta_\sigma(B)S_\sigma^2(B) \qquad (16)$$

For the case where the A ligand occupies an equatorial position

$$\Sigma(\sigma) = 4.5\beta_\sigma(B)S_\sigma^2(B) + 1.5\beta_\sigma(A)S_\sigma^2(A) \qquad (17)$$

Thus it is obvious that the stronger σ donor (whether A or B) prefers the basal or equatorial position. We have previously decided for this 22220 configuration that the bond strength between the central metal and the axial ligand is zero[3] (if only d orbital–ligand σ interactions are included), whereas that between the central atom and the equatorial ligands is certainly nonzero. We have also noted[3] the particularly striking short equatorial bond lengths and very long axial bond lengths in a large number of low-spin d^8 and d^9 systems, which indicate equatorial σ preference. Thus, the stronger σ donor occupies the site with the largest latent bond strength, and we expect on similar grounds therefore the most stable square-pyramidal isomer with a mixture of ligands to be the one where the worst σ donor is relegated to an axial position. These structures leave the square-planar arrangement of strongest σ donors untouched. Similar conclusions can be drawn for the other configurations d^9 (22221), d^7 (22210), and for intermediate-spin d^6 (22110). Interestingly, the equatorial preference for the strong σ ligand should be replaced by an axial preference in an excited electronic state of the d^9 configuration (22212) for example and generally in any configuration where the highest lying d orbital contains more electrons than the second highest energy orbital. Here the electron hole of eq 2 lies in the d_{z^2} orbital. Such a prediction has yet to be conclusively demonstrated experimentally. However, the complex $Ir(MeNC)_4^+$ associates photochemically with a fifth ligand[22] and the product dissociates in the dark. This very unusual reaction (photochemical association) may be readily understood by simply considering the d orbital occupation numbers of the complex in ground and excited electronic states. In the electronic ground state (22220) the axial bond strength is zero (since there are two electrons in d_{z^2}). But in the excited state (22211) there is a hole in d_{z^2} leading to a nonzero stabilization energy associated with the axial ligand–metal bond. Axial σ preference in the d^8 system should occur also if the angle between axial and equatorial ligands is increased from 90° to a value such that the d_{z^2} orbital is now highest in energy. Using trigonometrical functions of the relevant overlap integrals in terms of the droop angle θ from the orthogonal structure, this crossover occurs at $\theta \sim 40°$. Thus for all chemically likely (with droop angles generally 20°) low-spin d^8 examples equatorial σ preference should be the rule. Shorter equatorial than axial bond lengths are thus universally found.[23]

For the low-spin d^6 system $\sum(\sigma)$ for all possible MAB_4 ligand arrangements is identical, a result analagous to the six-coordinate case in the previous section. However, by analogy with these systems we expect the cis divacant structure of the strong σ ligands to be preferred and thus the cis MAB_4 vacancy structure to be more stable than the trans arrangement. As with the corresponding octahedral complexes we expect the energy differences between the possible isomers in the ls d^6 case to be smaller than that for the d^8 systems above. Thus the poorer σ donor should preferentially reside in an equatorial position (in contrast to the low-spin d^8 case above). Similar arguments hold for d^0–d^5 systems where the two highest d orbitals are completely vacant and also for the high-spin d^8 (22211) system where two-electron holes have been replaced by one-electron holes. In the survey of a series of compounds with this configuration by Orioli we see[24] that the equatorial bond lengths are generally little different from the axial ones. This, as we have just suggested, implies smaller site preferences here than in those systems where large differences in $\sum(\sigma)$ are predicted. Rossi and Hoffmann[5] have rationalized the ligand site preferences for d^0–d^6 and d^{10} systems (weaker σ donor equatorial) on the basis of hybridization with s and p orbitals. Here we have suggested that similar conclusions may be drawn if d orbitals only are used in bonding.

Trigonal Bipyramidal Complexes

For the low-spin d^8 configuration only the d$_{z^2}$ orbital is vacant and $\sum(\sigma)$ for the MA$_4$B structure with B axial becomes

$$\Sigma(\sigma) = 2\beta_\sigma(\mathrm{B})S_\sigma^{\,2}(\mathrm{B}) + 3.5\beta_\sigma(\mathrm{A})S_\sigma^{\,2}(\mathrm{A}) \qquad (18)$$

and for MA$_4$B with an equatorial B ligand

$$\Sigma(\sigma) = 5\beta_\sigma(\mathrm{A})S_\sigma^{\,2}(\mathrm{A}) + 0.5\beta_\sigma(\mathrm{B})S_\sigma^{\,2}(\mathrm{B}) \qquad (19)$$

The stronger σ donor thus prefers the axial position, this being the arrangement of larger $\sum(\sigma)$.

For the d^8 system we have previously shown[3] that for bonding within the d orbital manifold the axial bond strength was greater than the equatorial. Thus by comparison with the spy case the stronger σ donor ligand is expected to preferentially reside in an axial position, being the one with largest latent metal–ligand strength, a conclusion confirmed by the evaluation of $\sum(\sigma)$ in (18) and (19) above.

For intermediate-spin d^6 systems where two unpaired electrons reside in the degenerate pair (in D_{3h}) of d$_{x^2-y^2}$, d$_{xy}$, we may calculate similar stabilization energies. For MA$_4$B with B axial

$$\Sigma(\sigma) = 2\beta_\sigma(\mathrm{B})S_\sigma^{\,2}(\mathrm{B}) + 5.75\beta_\sigma(\mathrm{A})S_\sigma^{\,2}(\mathrm{A}) \qquad (20)$$

with B equatorial

$$\Sigma(\sigma) = 1.25\beta_\sigma(\mathrm{B})S_\sigma^{\,2}(\mathrm{B}) + 6.5\beta_\sigma(\mathrm{A})S_\sigma^{\,2}(\mathrm{A}) \qquad (21)$$

Thus again the axial position is favored for the better donor but by a smaller amount than in the d^8 case. For the d^0–d^4 systems where the value of $\sum(\sigma)$ is independent of the isomer under consideration there is no differential stabilization arising from interaction within the d orbital manifold. For the d^8 tbp case it is now quite well established experimentally[25] that good σ donors prefer the axial site as we have suggested above. For example in d^8 Ir(CH$_3$)Phos)$_2$(COD), CH$_3$ a very strong donor occupies[26] the axial position in the tbp structure, and in Ru(NO)HL$_3$(d^7) complexes[27] the NO and H ligands are trans to each other in axial positions. For these systems, however, our simple scheme is not the whole story. In Mn(CO)$_4$NO,[28] NO (probably the better σ donor) occupies an equatorial site in opposition to our conclusions, based on σ effects alone (although some workers would claim that the σ strength of the CO ligand is seldom exceeded and would not be perturbed by this result). The equatorial preference of π acceptors is not predicted on this model.

Square-Planar Complexes

In the square-planar geometry, the highest lying orbital is d$_{x^2-y^2}$ (if the molecule lies in the xy plane). The total orbital stabilization is thus given by

$$\Sigma(\sigma) = 3\beta_\sigma(\mathrm{A})S_\sigma^{\,2}(\mathrm{A}) + 3\beta_\sigma(\mathrm{B})S_\sigma^{\,2}(\mathrm{B}) \qquad (22)$$

irrespective of whether the A and B ligands are situated cis or trans with respect to each other in the square plane. This equivalence arises simply through the identical location of the four ligands in both isomers with respect to the four lobes of the d$_{x^2-y^2}$ orbital. Any differential stabilization between the two structures must then arise through d–p mixing in the lower than D_{4h} symmetry environment of the isomeric complex (cf. explanation of the trans influence). In the distorted tetrahedral structure (C_{2v}) found for high-spin d^8 systems similar ligand equivalence with respect to the two highest energy d orbitals also suggests that any differential d orbital stabilization between the possible isomeric permutations will be small.

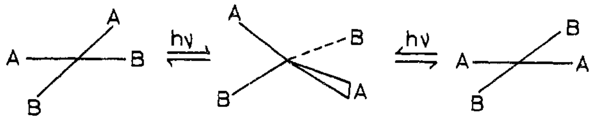


Figure 11. Suggested photochemical pathway for cis–trans isomerization of d^8 sp complexes.

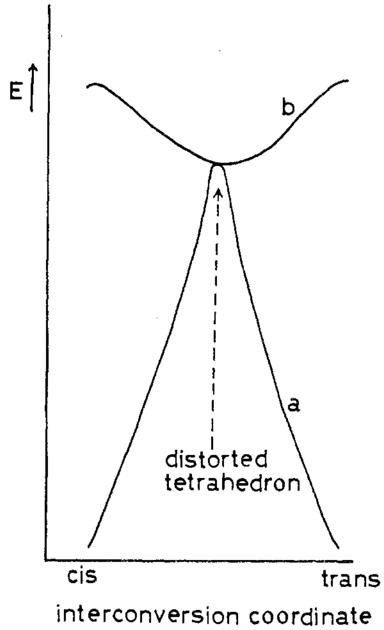


Figure 12. Results of extended Hückel calculations for interconversion of cis and trans d^8 MB$_2$A$_2$ system for (a) electronic ground state and (b) excited state.

Cis–Trans Isomerization in Square-Planar d^8 Complexes.

This process has been known for some time and was initially noticed since the photostationary equilibrium between cis and trans isomers of low-spin d^8 (22220) was different from the thermal one.[29] This behavior was rationalized on the basis of a distorted tetrahedral excited state intermediate[30] which could collapse to either cis or trans structure (Figure 11). Recent flash photolysis work has investigated this process in more detail.[31] The ground state interconversion is symmetry forbidden.[32] This equilibrium has several obvious similarities to the well-known cis–trans photosensitized isomerization of ethylenes, if we remember that the equilibrium geometry predicted[1] and observed for a large number of species with the 22211 electronic configuration (the lowest energy electronic configuration accessible by d–d excitation of the 22220 configuration) is indeed a distorted tetrahedron of the sort envisaged above. Our calculations using the molecular orbital method of ref 1 give results similar (Figure 12) to those obtained by Richardson et al.[33] who investigated these potential surfaces for the specific case of glycinate ligands using the EHMO method. As predicted above, the energy difference between cis and trans square-planar isomers in both ground and excited electronic states is found to be very small. A barrier to cis–trans interconversion in the electronic ground state (22220) exists and there is a definite minimum at the approximately tetrahedral (C_{2v}) geometry in the excited state. Excitation of either cis or trans d^8 MA$_2$B$_2$ thus leads to a distorted tetrahedral intermediate in the excited state which may decay back to either cis or trans ground state MA$_2$B$_2$ (Figure 12). This leads to a photostationary equilibrium dependent upon the details of the crossing point of the two curves which will certainly be different from any thermal or kinetic cis–trans equilibrium existing in the ground state. A significant difference to the six-coordinate case is that all four ligands are virtually equivalent in the excited state equilibrium geometry. We do not expect to see therefore any restriction of the scheme of Figure 11 when the σ donor characteristics of A and B are varied. For the six-coordinate case, the excited state minimum energy geometry was very sensitive to the nature of the ligands.

Gerlach and Holm have commented that from experimental results there is no evidence that for a given complex well defined minima exist corresponding to *both* planar and (distorted) tetrahedral isomers unless the two systems have different spin multiplicity. On these grounds there should be large barriers to intramolecular rearrangements in these systems. The orbital occupation numbers of the two spin systems are 22220 ($S = 0$) and 22211 ($S = 1$). The first excited singlet state has the same orbital occupation numbers as the $S = 1$ spin species, and if the *angular* geometry is determined predominantly by orbital energy changes of the system on distortion then these two systems should have the same geometry. The differences in electron correlation energy between first excited singlet and triplet states should not affect the geometry. Only small effects on the angular geometry might be anticipated via differences in configuration interaction effects. Thus, in the electronic ground state intramolecular rearrangement of the square-planar complex may only take place via a change in spin multiplicity, and photochemically via promotion of an electron from HOMO to LUMO. Both processes are identical when treated purely on an orbital occupancy basis.

Conclusion

The simple molecular orbital approach used here, based upon metal d orbital–ligand σ interactions only, is obviously a very useful way to view the site preferences of ligands in these transition metal complexes. Combined with the rules for predicting the molecular geometry of these MB_3 and MB_4 systems described earlier,[2] the assessment of the relative stabilities of two permutational isomers is a straightforward matter. Only for some trigonal bipyramidal complexes with strong π acids does the simple scheme give the wrong answer. It is not alone however in being unable to completely rationalize the relative bond strengths in trigonal bipyramidal systems.[35]

The two photochemical rearrangement processes discussed above have several ingredients in common. An excited state potential surface with respect to a particular molecular motion that is different to the one found for the electronic ground state is a necessary condition for such a photochemical process. However, only in the four-coordinate case does the distortion coordinate contain what may be termed an intermediate in the excited electronic state. In the six-coordinate system the process is probably best described as a thermal rearrangement within the excited state lifetime. The relative σ donor characteristics of the ligands concerned do not directly influence the course of the rearrangement in the square-planar system but are shown to be of prime importance in the nondissociative photochemistry of the six-coordinate systems.

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(35) Hoffmann and Rossi[5] have rationalized the equatorial preference for good π acids in the trigonal-bipyramidal geometry by allowing d–p mixing to occur on the central metal atom. One of the consequences of such an interaction is the predicted larger equatorial than axial bond strengths in d^{10} tbp systems. In $CdCl_5^{3-}$ (T. V. Long, A. W. Herlinger, E. F. Epstein, and I. Bernal, *Inorg. Chem.*, **9**, 459 (1970)), however, the observed bond lengths (2.53 Å (ax), 2.56 Å (eq)) are in opposition to such ideas. The difference (2.518 (4) Å (ax), 2.640 (4) Å (eq)) is even larger in $HgCl_5^{3-}$ (W. Clegg, D. A. Greenhalgh, and B. P. Straughan, *J. Chem. Soc., Dalton Trans.*, in press).