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Qualitative Discussion of Alternative Coordination Modes of Diatomic Ligands in Transition Metal Complexes

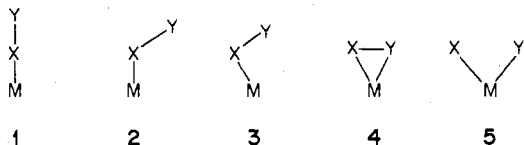
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Diatomic molecules coordinate to transition metal centers in a range of geometries that forms a kind of reaction coordinate, moving from M-X-Y linear to bent, through a kinked conformation, to a side-on, η^2 , or symmetrically bonded structure, and culminating in the oxidative addition process with the X-Y bond broken. We examine this deformation for L_nMXY ($n = 4, 5$) in square-pyramidal, trigonal-bipyramidal, and octahedral structures. A single Walsh diagram appears to hold for all diatomics and metals. Using the $\{MXY\}^n$ notation, where n is the number of electrons on the metal and in the π^* orbital of the diatomic, one finds a primary minimum for a side-on bonded $\{MXY\}^4$, with a possible secondary minimum for a linear structure, a linear $\{MXY\}^6$, a linear or bent $\{MXY\}^8$, a $\eta^2\{MXY\}^{10}$, and an oxidative addition for $\{MXY\}^{12}$. The molecular orbital picture leads to a qualitative understanding of how the specific nature of X, Y, and L and the d-electron configuration affect distortion. A strategy for bending the usually linear MCO and linearizing the usually bent MOO is discussed.

We present a qualitative molecular orbital picture of the bonding of a diatomic molecule XY to a transition metal fragment ML_n , a picture that spans the range of geometrical possibilities from the common linear coordination 1, through



bent and kinked geometries 2 and 3, to side-on or η^2 coordination 4, and finally to the oxidative addition product 5. Our intent is to understand how the specific diatomic XY, the d-electron configuration of the metal, and the electronic character of the other ligands on the metal influence progress along this "deformation coordinate".

The argument will be based on Walsh diagrams for the distortion sequence, constructed with the aid of extended Huckel calculations (see Appendix for computational details) and interpreted through a formalism which partitions the composite L_nMXY molecule into ML_n and XY fragments. The applications by Mingos,¹ Enemark and Feltham,² Eisenberg,³ Wayland,⁴ and their co-workers of Walsh diagram arguments for nitrosyl bending are related to our approach. Indeed, our interest in the problem of bending a general diatomic ligand was stimulated by the same nitrosyl problem which motivated these workers.^{5a,b,6}

At first sight it might seem foolhardy to venture that a single Walsh diagram would serve over a range of metals, of electronic counts, and of diatomic ligands. The magnitude of the problem is hinted at in Figure 1, which plots the computed energy levels of the first-row homonuclear diatomics side by side with the estimated energies of the 3d orbitals of the first transition series. A similar diagram was used by us in a study of dissociative chemisorption of diatomics on modeled W and Ni surfaces.^{5c} Obviously there is a wide range of relative

energies of ligand and metal orbitals which will make each case unique. Nevertheless, there exist significant symmetry-imposed restrictions on the possible interactions, and on these we will focus to construct our generalized Walsh diagram.

Before we embark on this course, we might note that Figure 1 points to a problem of electron assignment that plagues discussions of these molecules. The π^* orbitals of the diatomics are similar in energy to d orbitals on the metal. Their mutual overlap is sizable. Interaction between these orbitals thus will be strong, and any assignment of electrons in the molecule to one or the other piece, problematical. Sometimes one can turn to a structural or spectroscopic criterion for aid, but we think it is fair to say that such assignments have led to more heat than light. The situation is especially acute for the nitrosyl and dioxygen ligands, NO^2 and O_2 .⁷ Thus in $Ir(PPh_3)_2Cl_2(NO)$ one can argue whether one has Ir(I) and NO^+ or Ir(III) and NO^- . Similarly in $Ir(PPh_3)_2Cl(CO)(O_2)$ one could discuss whether the oxidation state of Ir is I, II, or III, with correspondingly neutral dioxygen, superoxide, or peroxide, respectively. The debate is avoided, which will not satisfy some, by adopting a very useful convention introduced by Enemark and Feltham.² For a given L_nMXY we specify the electronic configuration by $\{MXY\}^n$, in which the d electrons on the metal are counted together with only those electrons on the XY ligand which occupy the π^* or σ^* levels. Thus the cases above are $\{IrNO\}^8$ and $\{IrO_2\}^{10}$. Our studies will span a nine-electron series in which n in $\{MXY\}^n$ ranges from 4 to 12.

The Generalized Walsh Diagram

We wish to consider the interaction of a general diatomic in a range of geometries with a transition metal center that bears several ligands. For simplicity the discussion will be restricted to five- and six-coordinate complexes in which the ML_n fragment assumes the geometries 6-8.

The starting point for our discussion will be the interaction of a homonuclear diatomic in linear and η^2 coordination modes

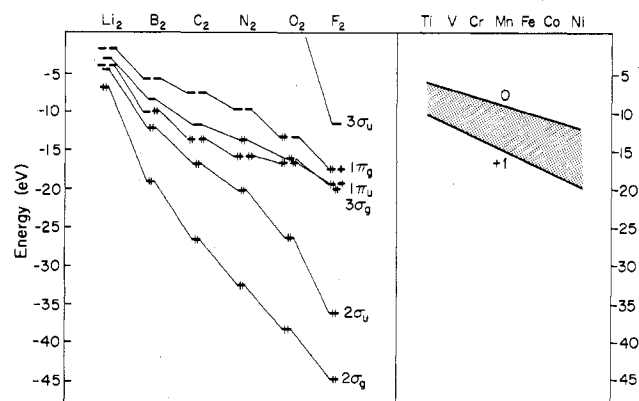


Figure 1. Approximate position of the energy levels of homonuclear diatomics (left) and the first transition series (right). The diatomic levels are taken from extended Hückel calculations with parameters specified in the Appendix. The metal levels will vary with the ligand set. The charge on the metal is likely to fall between 0 and $1+$, and accordingly we have plotted a band between the valence-state ionization potentials for those limits taken from C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory", W. A. Benjamin, New York, N.Y., 1964, p 120.

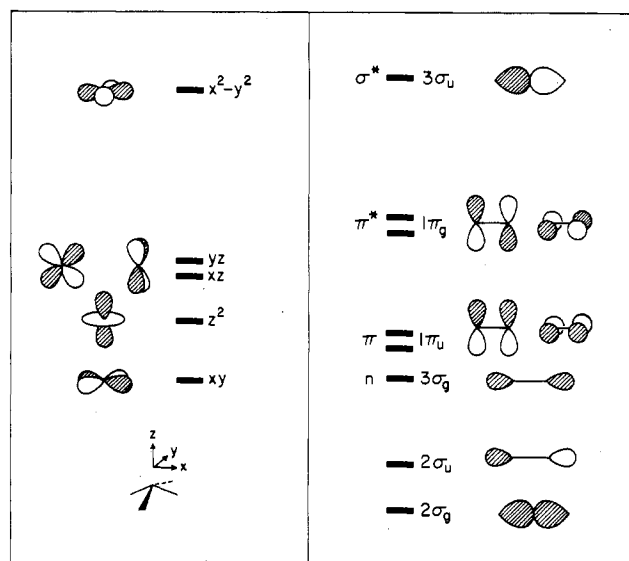


Figure 2. Schematic drawing of the valence orbitals of an ML_4 fragment (left) and a homonuclear diatomic (right). The ligand contribution in the ML_4 orbitals is omitted.

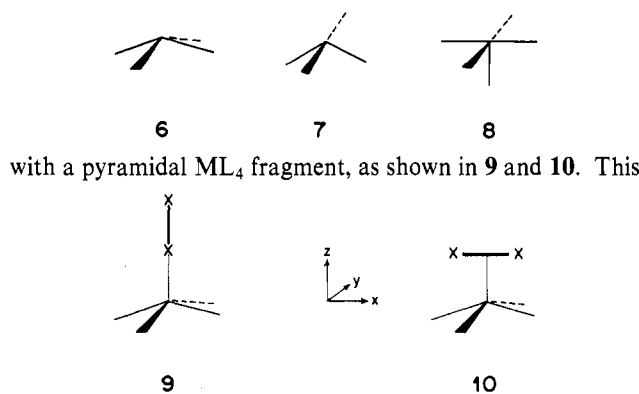


Figure 3. Some group overlaps between ML_4 and diatomic fragment orbitals. The specific numbers come from a calculation on TiL_4 and N_2 .

with a pyramidal ML_4 fragment, as shown in 9 and 10. This is a convenient beginning, since departures from these points are easily studied by perturbation theory. Among such perturbations are the conversion of a homonuclear into a heteronuclear diatomic, the modification of the ML_4 geometry from D_{4h} to C_{4v} to C_{2v} , or the addition of an extra ligand to give a six-coordinate structure. In a further simplification we consider the ligands L in ML_4 to bear σ orbitals alone, leaving an analysis of π effects until later.

The orbitals of a pyramidal ML_4 fragment⁸ are almost as well-known as those of a homonuclear diatomic.⁹ Both are illustrated schematically in Figure 2. These are not the only orbitals of these fragments, for we have omitted the core levels of the diatomic and the core levels and M-L bonding orbitals of ML_4 . In an attempt to strip the problem to its essentials we will make the following assumptions, in decreasing order of assurance that they are reasonable ones: (a) Omit the core and M-L bonding levels of the ML_4 fragment, as well as the high-lying $x^2 - y^2$. (b) Omit the s- and p-based orbitals in ML_4 . It turns out that these may contribute significantly to L_4M-XY bonding but do not provide a differential between the various structures. (c) Omit the $2\sigma_g$ and $2\sigma_u$ orbitals of the diatomic. In fact these have sizable overlaps with z^2 of ML_4 , but their net interaction with metal 3d orbitals is small as a consequence of the large energy gap separating these levels. (d) Omit $3\sigma_u$ or σ^* of the diatomic. Figure 1 shows that except for the dihalogen ligand the diatomic σ^* is too high in energy to interact strongly. We will have to bring this orbital back in when we discuss oxidative addition. (e) Omit $1\pi_u$, the bonding π levels of the diatomic. Even in the case of O_2 , where these levels are at low energy, we will find that their influence is indirectly felt. In N_2 or CO the d levels will

be between the π and π^* levels of the diatomic, and we will be obliged to consider them.

If we adopt as a trial these restrictions, we remain with four orbitals of ML_4 , the lower d-block levels, and three orbitals of the diatomic: $1\pi_g$ and $3\sigma_g$. To give the latter a mnemonic character we will refer to them in the subsequent discussion as π^* and n, respectively.

The strong constraints on interaction that are imposed by symmetry are analyzed next. Among these sets of four and three orbitals there are only two nonvanishing overlaps in the η^1 geometry 9 and three in the η^2 geometry 10. These are illustrated in Figure 3. Along each diagram is the corresponding group overlap in a model calculation described in the Appendix. These numbers will vary with metal, ligands, diatomic, and separation.¹⁰ Thus they are to be taken merely as indicative of the magnitude of the interaction.

The utility of the overlaps comes into play when one constructs the seven molecular orbitals of ML_4XX from the component fragment orbitals—four from ML_4 , three from X_2 . This is done in Figure 4. Let us look first at the η^1 case at the left. ML_4 xz , yz and ligand π^* interact to give bonding and antibonding combinations. No attempt is made in this figure to indicate the extent of localization of the molecular orbitals. Thus $xz + \pi^*$ indicates only that the combination is a bonding one, not the relative weight of the ML_4 and X_2 components. The latter will vary, depending on the relative energy of the interacting orbitals. Metal z^2 and diatomic n

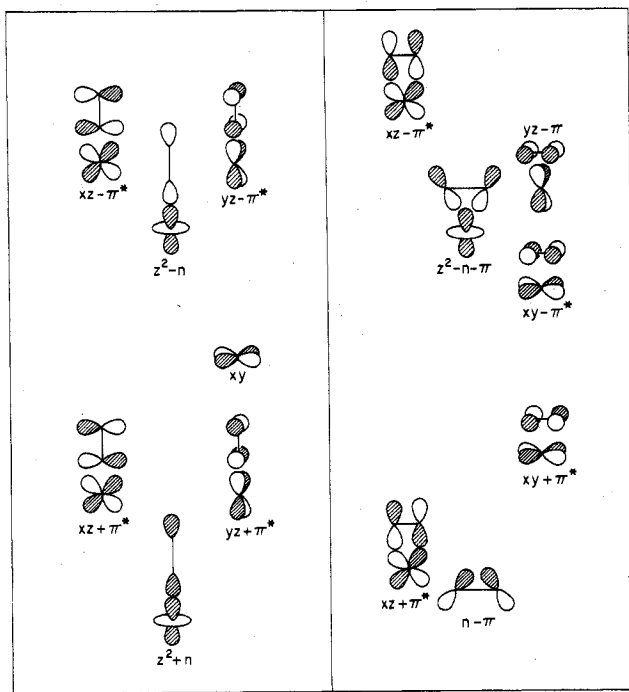
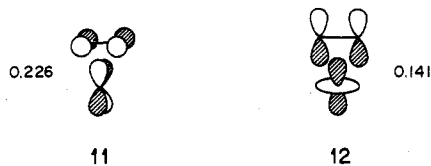


Figure 4. Schematic drawing of seven valence orbitals of the composite L_4MX_2 molecule in η^1 (left) and η^2 (right) geometries.

also interact strongly. Metal xy finds no diatomic orbital with which to interact. The exact ordering of the seven levels depends strongly on the metal and diatomic, except that there is no question that in a pair of interacting levels the bonding combination is the lower one. Especially sensitive to the specific metal, ligands, and diatomic is the relative energy of the $z^2 - n$ and $xz, yz - \pi^*$ levels.

The η^2 case on the right-hand side of Figure 4 is more complicated. Four of the levels are simple, the combinations of π_z^* with xz and π_y^* with xy . Notice the bonding-antibonding pair of the latter is split by less than that of the former, which in fact we have split more than $\pi^* + xz, yz$ in η^1 . This is based on the interaction overlap ordering of Figure 3. The other three orbitals are more complicated. They are derived from n, yz and z^2 . Among the three X_2 basis functions yz finds no match. But it has a large overlap with diatomic π_y , a basis function we chose to omit in approximation (e). The overlap is shown in 11. We have to include it, for it significantly



destabilizes yz . The other two orbitals, n and z^2 , might be thought to interact to give bonding and antibonding pairs. But note that their mutual overlap, as shown in Figure 3, is small. Instead z^2 has a larger overlap with π_z , as shown in 12. In fact z^2, n , and π are strongly mixed in the η^2 geometry. A second-order perturbation theoretical argument¹¹ could be given to rationalize the orbital shapes that result, but perhaps it is easier to begin by premixing n and π to give combinations 13 and 14 which interact well and poorly, respectively, with

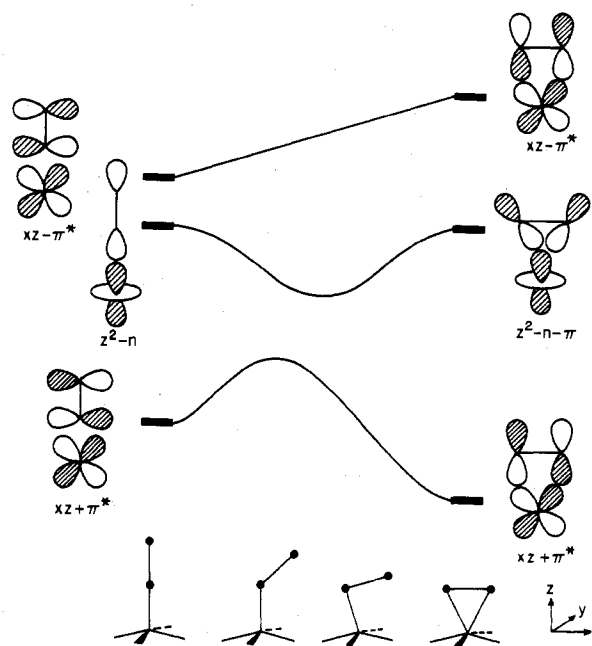
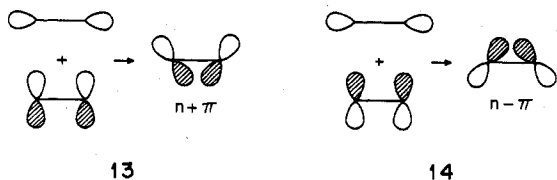
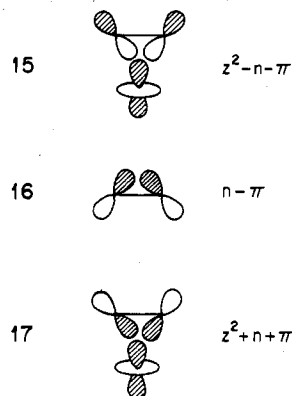


Figure 5. Evolution along the deformation coordinate of the three levels symmetric with respect to the xz plane.

n . Three orbitals result, 15 → 17, of which the top two are



included in Figure 4.

We now wish to correlate the levels of the η^1 and η^2 geometries. Before we proceed to do this, there is one further simplification that is convenient. This is to remove from consideration the lowest orbital on either side in Figure 4, $z^2 + n$ or $n - \pi$. The reason for doing this is in part that this orbital is not important in setting a geometrical preference and in part that it is mainly a diatomic donor orbital whose electrons are not counted in the $\{MXY\}^n$ notation. The six levels that remain in fact are to be occupied by just those n electrons which were associated with the metal d block and the diatomic π^* .

Along the deformation coordinate $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$ only a mirror plane of symmetry is retained. Three of the six levels under discussion are symmetric with respect to this plane; three are antisymmetric. Let us consider these symmetry-partitioned blocks one by one. To determine the initial slope of each orbital we will apply standard perturbation theory arguments:¹² (1) if a motion decreases an overlap, then bonding orbitals will be destabilized and antibonding orbitals stabilized; (2) if the lower symmetry allows two orbitals to interact, they will repel each other.

The set of our symmetric levels is shown in Figure 5. The lower level is $M-X_2$ bonding; the upper two levels are $M-X_2$ antibonding. The initial slopes are determined by this factor, superimposed on which is the interaction caused by sym-

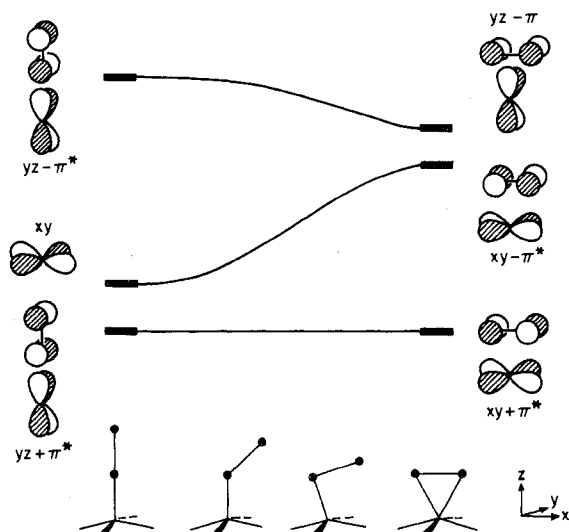
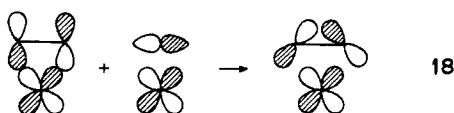


Figure 6. Evolution along the deformation coordinate of the three levels antisymmetric with respect to the xz plane.

metry-lowering. This is especially important for the pair $xz - \pi^*$ and $z^2 - n$ which in most of the cases that we have studied lie close to each other in energy. The $xz - \pi^*$ level should have been stabilized on the basis of decreased antibonding with bending, but in fact interaction with $z^2 - n$ overrides this trend.

The set of three levels antisymmetric with respect to the plane of bending is shown in Figure 6. There is only one bonding level: $yz + \pi^*$ on the left, $xy + \pi^*$ on the right. These correlate across, a strong xy - yz mixing occurring in the process. The nonbonding xy orbital in η^1 becomes a metal- X_2 antibonding $xy - \pi^*$ combination in η^2 . The antibonding $yz - \pi^*$ correlates with the slightly less antibonding $yz - \pi$.

The symmetric and antisymmetric orbital sets are combined in Figure 7. A wealth of geometrical information is explicitly revealed by the Walsh diagram of this figure. $\{MXY\}^4$ systems are likely to be η^2 or side-on bonded, with a possible subsidiary minimum in the η^1 geometry. $\{MXY\}^6$ fills the third level which clearly favors a linear η^1 structure. $\{MXY\}^8$ moves the system to a bent or kinked structure; $\{MXY\}^{10}$ moves it to a η^2 structure again. The two further electrons in $\{MXY\}^{12}$ would push the system back toward linearity. But in a linear configuration occupation of three metal-ligand antibonding orbitals, $xz - \pi^*$, $yz - \pi^*$, and $z^2 - n$, would cancel all the factors bonding the diatomic to the metal. The diatomic would depart. In the case of $X_2 =$ dihalogen the σ^* orbital is at low energy. It saves the situation by mixing with xz in such a way as to cut down the metal-diatomic antibonding. This is shown in 18. Of course population of σ^* breaks the already long



bond between X and Y. We have here the oxidative addition process.

The general Walsh diagram of Figure 7 is supported by our previous extended Hückel calculations on $IrL_4(NO)$ and $MnL_4(NO)$ ^{5a} as well as calculations on $IrL_4(O_2)$ and TiL_4 and FeL_4 complexes with C_2 , N_2 , and O_2 . As noted earlier, there is substantial variation in the level ordering at the extremes of the diagram, as a consequence of the wide range of metals and diatomic energies. This is especially true for the $z^2 - n$ and xz , $yz - \pi^*$ levels on the η^1 side and the $z^2 - n - \pi$ and $xy - \pi^*$ and $yz - \pi$ levels on the η^2 side. Avoided crossings arising from level inversions complicate the picture. But when these are unscrambled, the striking feature of the various

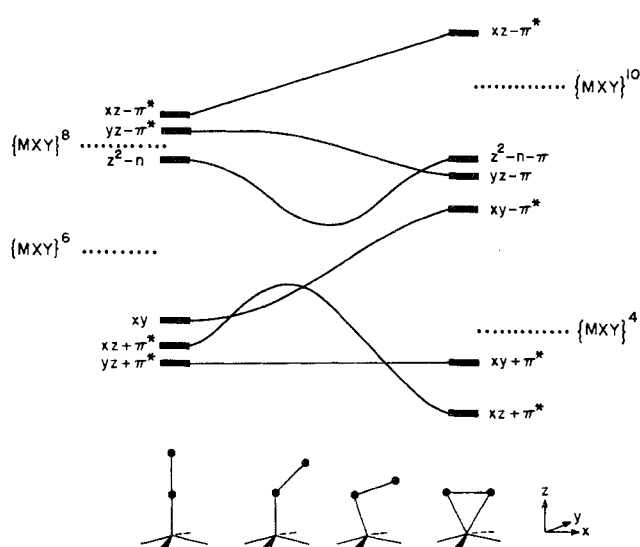


Figure 7. Walsh diagram for L_nMXY ($n = 4, 5$), for the deformation coordinate linking η^1 and η^2 geometries. Dotted lines and $\{MXY\}^n$ labels indicate the filled-unfilled level gap for various electron counts.

computed diagrams is how closely they resemble each other. The next section will discuss the effect of various perturbations on the basic model, but at this point it is appropriate to mention the extent to which available structural information supports this picture.

There are numerous O_2 complexes of the early transition metals. The Stomberg¹³ and Weiss¹⁴ groups have determined the structures of many of these. Most contain more than one dioxygen ligand, and in all cases the O_2 unit is side-on or η^2 bonded. Several structures containing a single dioxygen are known, all $\{MOO\}^4$ and η^2 . Among these are $MoOF_4(O_2)^{2-}$,^{15a} $[Ti(O_2)(dipic)O_2]O^{2-}$,^{15b} $TiF_2(dipic)(O_2)^{2-}$ and $Ti(H_2O)_2(dipic)(O_2)$,^{15c} $VO(H_2O)(dipic)(O_2)^{-}$,^{15d} and $Ti(octaethylporphyrin)O_2$.^{15e} An interesting conclusion that can be drawn from our correlation diagram is that for $\{MOO\}^4$ complexes there may exist the possibility of another local minimum, at higher energy, for an end-on bonded diatomic. Such a geometry would provide a way-point in some hypothetical process for interchanging the two ends of a side-on bonded O_2 . We do not know if this process has been looked for experimentally but consider it an interesting possibility. It should be noted that the three low-lying levels on the left side of the Walsh diagram are closely spaced. In the η^1 geometry an $\{MXY\}^4$ complex is likely to possess a high-spin ground state.

Linearly coordinated $\{MXY\}^6$ complexes of CO, CN, and N_2 are legion. The challenge of constructing a bent carbonyl group will be taken up below. $\{MXY\}^8$ complexes of CO, CN, N_2 , NO, and O_2 are known. Some are linear, some are bent, and a few show signs of the kinking distortion. The structurally most diverse group among them is the nitrosyls, which exhibit the entire range of geometries $1 \rightarrow 3$.¹⁶

With two more electrons we reach the well-known class of side-on bonded or η^2 five-coordinate dioxygen complexes exemplified by $IrCl(CO)O_2(PPh_3)_2$ ¹⁷ and containing many other members.¹⁸ All are $\{MOO\}^{10}$ complexes. Excellent discussions of the transformation of η^1 into η^2 bonding, $1 \rightarrow 2 \rightarrow 4$, have been given by Veillard, Dedieu, and Rohmer⁶ⁱ and by Teo and Li.^{6o}

The chemistry of diatomic ligands coordinated to metal complexes of d^8 electronic configuration, often reversibly, leads very naturally to the problem of oxidative addition. Coordinative association between CO and Vaska's compound, $Ir(CO)Cl(PPh_3)_2$,¹⁹ progresses through the ligands NO and O_2 into dissociative addition with the halogens.²⁰ A hypothetical addition complex $Ir(CO)Cl(PPh_3)_2(Cl_2)$ would be

an $\{MXY\}^{12}$ system. The dissociation of the diatomic bond is consistent with the above discussion. A concerted cis addition of XY to a square-planar complex is a symmetry-allowed process.^{21,22}

It should be noted that the instability of $\{MXY\}^{12}$ complexes is limited to five- and six-coordinated structures. If the metal atom carries fewer ligands, then such complexes are perfectly reasonable. Examples are $(PPh_3)_2PtO_2$ ^{23a} and $(t-BuNC)_2NiO_2$.^{23b} Unrelated to this but interesting in the present context is the recent study of electrochemical reduction of $Ir(dppe)_2X_2$, X = O, S, Se. The reduced systems, formally $\{IrXX\}^{11}$, readily cleave off the X_2^- anion.²⁴ The implication is drawn that the orbital occupied by the extra electron is strongly metal- X_2 antibonding.

Before we leave this section we must warn the reader again how qualitative our conclusions are. The orbital set we study is highly restricted. The total energy changes we compute for various ligands and electron counts follow the implications drawn from the individual levels in the Walsh diagram discussed above. But the precise energies are sensitive to the parameters of the extended Hückel method, which in turn has well-known deficiencies. We feel more confident about the slopes of the levels and the general features of the diagram than about the energy gaps in Figure 7. The level positions vary widely with the character of the ML_n fragment and the diatomic.

Perturbations on the Basic Diagram

The first of these addresses the question of what is the effect of moving from a homonuclear to a heteronuclear diatomic, for instance, CO, NO, or CN^- . The perturbation is predictable. In any orbital pair localization on the more electronegative atom occurs in the lower energy combination and on the more electropositive atom in the higher energy combination.^{9,12} Thus in CO π has a greater coefficient on the oxygen, but π^* and n (the higher energy member of the $n_1 \pm n_2$ set) are more localized on the carbon. The net effect on the general correlation diagram is minor, but the effect on net bonding may be great. The localization of n and π^* on the near atom will make the molecule bond preferentially through that less electronegative atom. In this context an interesting potential ligand whose coordination chemistry has not been sufficiently explored is BF, isoelectronic with N_2 and CO. On the η^2 side electronic asymmetry between X and Y in the diatomic XY will naturally drive molecules away from symmetric side-on bonding.

The second type of perturbation is a modification of the ML_4 fragment geometry. This has a serious effect. Pyramidalization while maintaining a fourfold axis increases the energy of xz and yz and lowers the energy of z^2 in the ML_4 fragment illustrated in Figure 2.^{5a,b,8} Group overlaps with xz , yz , and z^2 orbitals increase as these orbitals become more directional by hybridizing with metal x , y , and z , respectively. The stabilization of the z^2 orbital affects the $\eta^1 - \eta^2$ Walsh diagram at both ends. In C_{4v} , η^1 structures, stabilizing the z^2 orbital by pyramidalizing the ML_4 fragment removes some of the driving force for bending the diatomic molecule in $\{MXY\}^8$ or $\{MXY\}^{10}$ systems. (This presupposes that z^2 is below $xz - \pi^*$; see ref 5a.) At the other extreme, in C_{2v} , η^2 structures, pyramidalization strongly stabilizes the z^2 orbital, as some X_2-L repulsion is relieved and the basal ligands move toward the node in the z^2 orbital. In between, in bent η^1 , this distortion is less favorable to the z^2 orbital, since there is a sizable admixture of diatomic π^* and metal xz , which opposes pyramidalization (see below). The net result is that the dip in energy of the $z^2 - n$ orbital in Figure 7 is lowered as the ML_4 fragment is made more pyramidal. $\{MXY\}^8$ molecules, in which this orbital is occupied, would be driven toward either the η^1 or η^2 extremes by increased pyramidalization. But on the η^2 side

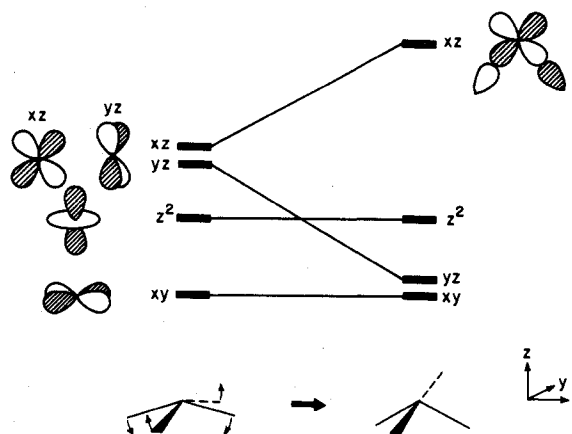


Figure 8. Change in energy of the four lower d-block orbitals of ML_4 as the fragment is deformed from C_{4v} to C_{2v} . In the square pyramid xz and yz are degenerate, each somewhat antibonding with two ligands in the base of the square pyramid. As one distorts to the trigonal-bipyramidal fragment, C_{2v} , one of these orbitals, the xz , is destabilized further by the same interaction, as shown. The other orbital, yz , is stabilized since the same motion removes the σ antibonding.

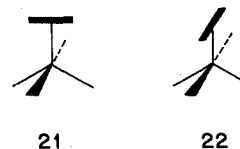
there is another possibility which must be discussed, namely, the loss of fourfold symmetry in the ML_4 fragment.

The distortion from a square-pyramidal C_{4v} geometry to a fragment of a trigonal bipyramid, C_{2v} , is shown by **19** \rightarrow **20**.



The effect of the distortion is illustrated in Figure 8. A distinction between the xz and yz planes is introduced by a destabilization of the ML_4 orbital in one plane, here xz , and a stabilization of the orbital in the other plane, yz . The simple rationale for this has been detailed elsewhere.^{5a,b,8} The incoming diatomic ligand will find its interactions in the xz plane enhanced and those in the yz plane diminished. The effect is dramatic on the η^2 side. The lowest orbital in Figure 7 is $xz + \pi^*$. It will be stabilized still further by the motion. A high-lying orbital is $yz - \pi$. It will be less destabilized by the same distortion. Thus both $\{MXY\}^4$ and $\{MXY\}^{10}$ complexes will deform the underlying ML_4 fragment toward a trigonal bipyramid if the steric constraints of the ligands allow it. The force driving this distortion will be greater in $\{MXY\}^{10}$ complexes, for there both orbitals are involved. Indeed, all known η^2 oxygen complexes of the $\{MXY\}^{10}$ type and some of the $\{MXY\}^4$ class conform to this notion.

In the above discussion the location of the η^2 diatomic in the xz plane, as in **21**, was assumed. In the alternative ori-



entation, **22**, all of the interactions are mismatched. This conformation will be at high energy. The consequences could be stated in two ways. η^2 diatomic complexes will have high rotational barriers around the $M-X_2$ axis, especially so in $\{MXY\}^{10}$ case. Alternatively we can say that, if a diatomic were coordinated as in **22**, that it would be likely to undergo a Berry pseudorotation to **21**.

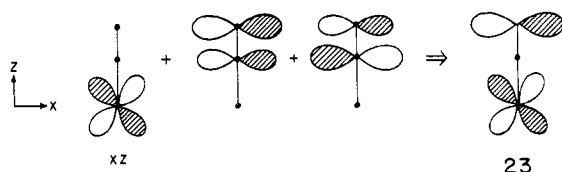
Still another perturbation one could imagine is the addition of a sixth ligand to give $ML_5(XY)$. The primary effect is a raising in energy of the z^2 orbital. This in turn manifests itself

most clearly in the $\{MX\}^8$ case where the enhanced resonance between $z^2 - n$ and $xz - \pi^*$ leads to a greater force driving the molecule to bend. This effect has been previously analyzed by Enemark and Feltham,² who termed it "stereochemical control of valence".^{2a}

$\{MX\}^6$ and Polarization

$\{MX\}^6$ is perhaps the most frequently encountered bonding situation, with $XY = CN^-, N_2, CO$ linearly coordinated in octahedral complexes. Coordinatively unsaturated ML_4XY complexes are rare.²⁵ Another ligand can be added trans to the diatomic without occupying any antibonding orbitals and in fact adds to the stability of the complex.

The ligands in question are such that for most metal atoms the d levels will lie between the π and π^* orbitals of the diatomic. We may now drop one of our simplifying assumptions, which artificially limited our view to π^* and d. The π orbitals are important as well, in that they shape the metal xz, yz pair in a characteristic "allylic" way shown in **23**.^{26,27}

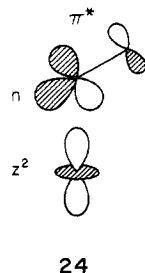


The orbital is polarized so that it accumulates electron density on the Y atom. The polarization effect is important, especially in reactivity of N_2 complexes.²⁸ Nevertheless, it is the π^* orbital of the diatomic which is important in accounting for the charge transfer and in contributing to metal-ligand bonding.²⁹

$\{MX\}^8$, Bending MCO, and Linearizing MOO

One or two electrons added to the $\{MX\}^6$ systems bring us to the class of $\{MX\}^7$ and $\{MX\}^8$ complexes. The odd-electron examples are limited in number,³⁰ a most interesting recent example being the quartet $\{MnOO\}^7$ example of $Mn(TPP)O_2$.^{30d} Five-coordinate $\{MX\}^8$ complexes with $CN, N_2,$ and NO as ligands are quite common, but only NO appears with any frequency in six-coordinate complexes.

The orbital that is occupied in $\{MX\}^7$ and $\{MX\}^8$ is $z^2 - n$ in Figure 7. Actually it could just as well be $xz - \pi^*$, for the ordering of these two η^1 levels is sensitive to all factors. If indeed the order is reversed, little will happen to change the predictions. $xz - \pi^*$ will take over the role played by $z^2 - n$, or alternatively one could think of an avoided crossing between these orbitals. Indeed, the downward slope of $z^2 - n$, which induces these compounds to bend, is due to its interaction with $xz - \pi^*$. In the linear form these σ - and π -type orbitals do not interact. As the molecule bends, the two orbitals mix with each other, as shown in **24**. One goes down and the other



goes up in energy. Which one goes down is determined by the level ordering for $M-X-Y = 180^\circ$ but in a sense is immaterial at significant bending angles, where the σ - π mixing is strong. The energy of this singly or doubly occupied MO drops with increasing slope as XY bends; it opposes the

linear-restoring tendencies of the lower occupied orbitals. When it is sufficiently steep, orientation **1** will no longer be a minimum and the stable geometry will be **2**.

How this crucial orbital can be useful in the understanding of the linear-bent nitrosyl dichotomy has been detailed in an earlier paper.^{5a} The better the σ - or π -donating capability of the basal ligands, the steeper the slope of this level and the more likely is the nitrosyl to bend. Fine details of the nitrosyl bending, for instance, why it bends in the sterically more hindered plane of $IrCl_2(NO)(PPh_3)_2$,³¹ also emerge from this analysis. Depending on the electronic characteristics of the other ligands, five-coordinate $\{MNO\}^8$ complexes can be linear or bent.¹⁶ All six-coordinate $\{MNO\}^8$ complexes are bent.

The five- or six-coordinate examples of geometry **2**, a bent $M-X-Y$, all contain the nitrosyl ligand. The ubiquitous nature of the linearly bonded cyanide, carbonyl, and dinitrogen ligands naturally prompted us to seek conditions that might harbor a bent exception. We are not interested in the minor distortions caused by unsymmetrical π bonding with the two acceptor orbitals of these ligands³² but are after a strong tendency to deform.

The strategy for maximizing the tendency to bend in $\{MX\}^8$ is clear from Figure 7 and structure **24**. An optimal match in energy and good overlap between π^* of XY and the z^2 orbital of the ML_n fragment are required.

Let us first try to decide which of the three ligands is the most likely candidate for bending—in other words, which is the strongest π^* acceptor.³³ One-electron orbital energies should be viewed with some caution, for, while they may correctly predict the relative ordering of π^*_{NO} vs. π^*_{CO} , they may give insufficient emphasis to the difference. It is instructive to remind ourselves of the distaste evoked by the electronic configuration of these ligands which we would have to write to make them isoelectronic with that commonly accepted for bent nitrosyls. They are $M^{2+}CO^{2-}$, M^+CN^{3-} , $M^{2+}N_2^{2-}$, and $M^{2+}NO^-$. The most unfavorable is CN^{3-} , and MO theory would concur that π^*_{CN} should be the highest in energy. The relative acceptor strength of N_2 vs. CO is difficult to decide and may in fact be a function of the total intramolecular environment.³³ In the free ligand the first electronic transition of CO is at slightly lower energy than that of N_2 .³⁴ The CO π^* coefficient at the bonding carbon is greater than that for N_2 . Our explorations of the bonding capabilities of N_2 and CO by interacting both with a test orbital favor CO . Stretching frequencies of N_2 and CO before and after coordination have been interpreted in terms of the nitrogen being a weaker σ donor and weaker π acceptor.³⁵ Therefore CO seems to be the best candidate.

In order to raise the energy of the z^2 we may use the strategy developed previously.^{5a} It is required that the other ligands should be good σ, π donors. Moreover, in the five-coordinate complexes the CO should be at the apex of a square pyramid.

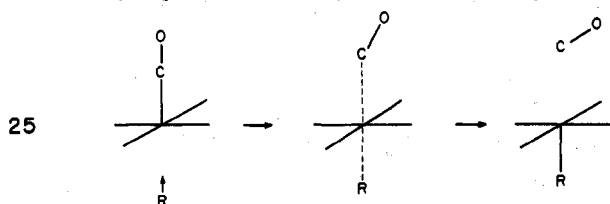
There appear to be no mononuclear complexes with a bona fide bent carbonyl, if we exclude the $<15^\circ$ deviations normally found in crystal structures and attributable to crystal-packing distortions. A structure reported to contain a strongly bent CO in $Ru(TPP)(CO)_2$ was later shown to be $Ru(TPP)(CO)(EtOH)$, with a normal carbonyl.³⁶ A square-pyramidal macrocyclic complex of $Co(I)$ contains an apical carbonyl group that is linear.³⁷ In carbonmonoxyhemoglobin,^{38a} carbonmonoxymyoglobin,^{38b} and carbonmonoxyerythrocytochrome^{38c} the oxygen atom of the carbonyl is definitely displaced off the axis of the heme group. A similar effect is found for the cyanide nitrogen in the structures of cyanometmyoglobin,^{39a} lamprey cyanomethemoglobin,^{39b} and cyanomethemoglobin.^{39c} It has been suggested, however, that the carbonyl or cyanide is not bent but that its carbon atom is also displaced from the heme axis in the same direction as the oxygen.^{38a,39c}

Although no bent carbonyl has been found, we remain hopeful that future structural studies or examinations of the M-C-O bending force constants may demonstrate a trend of increasing "softness" in the potential energy surface for bending as the criteria we enumerated above are satisfied.

Whether the consequence of even the best electronic conditions will be the bent CO is a point worthy of further discussion. It is likely that one of our proposed complexes—a six-coordinate d^8 carbonyl complex—will decompose ejecting CO or its trans ligand. It is a 20-electron complex. Why this should happen to CO and not to NO must have to do again with the weaker π^*_{CO} acceptor orbital. It cannot interact sufficiently with the filled z^2 even though the antibonding $z^2 - n$ interaction has been partially alleviated by bending. This dims hope for a stable, bent CO structure. Just as the CO is about to bend, it also departs. It does suggest an interesting idea about the displacement reaction



The CO may depart in a non-least-motion reaction path, 25,



swinging sideways so as to retain a lingering $\pi^* - z^2$ bonding interaction. Conversely, an attacking carbonyl may prefer to approach in a nonlinear manner.⁴⁰

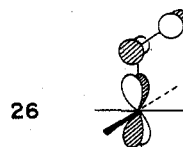
When we labeled the six-coordinate $\{MCO\}^8$ system as a 20-electron complex, we were assigning the eight electrons to the metal. In the corresponding nitrosyl complexes two more electrons are typically assigned to the nitrosyl. A similar charge distribution in carbonyl or dinitrogen complexes would make these $(CO)^{2-}$ or N_2^{2-} . While this is just a formalism, it would indicate that such a coordinated ligand would be extremely reactive with respect to attack by Lewis acids. This point has been made by Enemark and Feltham.^{2a,d}

The dioxygen ligand, discussion of which we have delayed to this point, also forms complexes of the $\{MXY\}^8$ class. There is no doubt that the π^* orbitals of O_2 are lowest in energy among the ligands covered so far. The downward trend in the $XY \pi^*$ energies as one proceeds from N_2 or CO to O_2 may be used to rationalize the observed experimental structures. The energetic remoteness of the π^* 's of CO, CN^- , and N_2 from metal z^2 precluded a strong $\sigma - \pi$ interaction. Hence the great difficulty in stabilizing a bent CO ligand. With NO the π^* levels have descended so as to be energetically closer to z^2 . Therefore on occasion, under auspicious circumstances, a bent NO ligand could be observed. With O_2 , where the π^* levels have descended still further, there is little question that the ligand will bend. Indeed, the difficulty will be in avoiding a strong $\sigma - \pi$ interaction. A linear O_2 ligand should be the oddity here. There are some 60 dioxygen complexes for which crystal structures are available.^{7,18} Approximately half of these contain only one O_2 unit per metal.⁴¹ None of these contains O_2 in configuration 1.⁴²

Let us speculate on how the M-O-O bond might be linearized. One orbital of the $xz, yz - \pi^*$ set is filled and favors bending. We wish to decrease the magnitude of its downward slope. Ironically the way to accomplish this is once again by raising the energy of z^2 , just as in our strategy for bending MCO. There is no contradiction here. Whereas the $ML_5 z^2$ orbital was most likely below π^* of CO and needed to be pushed up to maximize interaction, in the case of O_2 the $ML_5 z^2$ orbital is probably above π^* of O_2 and pushing it further up in energy will minimize the $\sigma - \pi$ interaction that causes

bending. Again the way to raise the $ML_5 z^2$ is to make the ligands good donors, especially the one trans to the O_2 binding site.

The only reported structure of a six-coordinate $\{MOO\}^8$ complex appears to be the "picket fence" iron-porphyrin-imidazole complex determined by Collman and co-workers.⁴³ It is bent, with an M-O-O angle of $\sim 136^\circ$. The general features of the level pattern of Figure 7 may also be probed by $\{MOO\}^9$ complexes. The odd electron should reside in the next orbital—the π^* (out of the plane of bending), 26. As



it is antisymmetric about the plane of bending, changes in the symmetric orbitals which lie in the plane are independent of its influence. Support for this assignment of electronic configuration also comes from ESR studies^{44,45} and ab initio calculations.^{6j}

Our calculations on model compounds confirmed that an increase in electropositivity of the trans σ -donor ligand lessened the energy gain from a linear to bent O_2 distortion. Rohmer, Dedieu, and Veillard carried out ab initio calculations on $Co(acacen)(O_2)L$ where $L = \text{none}, H_2O, CN^-$, and CO in the three different geometries.^{6j} They found the stabilization energy of the $(\pi_g^a)^2(\pi_g^b)^1$ configuration as the Co-O-O angle decreased from 180 to 120° to be 0.052 au for $L = \text{none}$. This stabilization decreases as the trans σ donation improves, to 0.046 au for $L = H_2O$ and to 0.032 au for $L = CN^-$. The large Co-O-O angle of 153° in $Co(CN)_5O_2^{3-}$ ⁴² in comparison with the values of 126° in $Co(bzacen)(py)(O_2)$,^{46a} 136° in $Co(salen-C_2H_4-py)(O_2)$,^{46b} and 119° in $Co(t-Bsalten)(bzImid)(O_2)$ ⁴⁷ can also be attributed to the trans influence. Brown and Raymond⁴² ascribed it to the weak Co-O-O angle bending force constant in these compounds and the electrostatic repulsion of dioxygen and the adjacent cyanide anions.⁴⁸

Our previous paper^{5a} discussed the tendency, barely perceptible in $\{MNO\}^8$ structures, for the bent nitrosyl to move its nitrogen off the coordination axis, the distortion shown in 3. The deformation follows from the important interaction illustrated in 24. Motion of the NO group as a whole to the left would lower the $n - z^2$ overlap and increase that of z^2 with π^* . There is some indication of this "kinking" distortion in $IrCl_2(NO)(PPh_3)_2$,³¹ $IrI(CH_3)(NO)(PPh_3)_2$,⁴⁹ and a nitrosylcobalt porphyrin derivative.⁵⁰ Obviously this geometry change is a way-point between 2 and 4.

In conclusion we might note the further specific directions in which our general work might be extended. One could inquire whether a ligand set or geometry exists which could convert the transition state for oxidative addition into an intermediate, i.e., whether a real $\{MXY\}^{12}$ complex could be designed. A second point for constructive speculation is the design of complexes of diatomics such as C_2 or A_2^+ , where A is a noble gas. A third departure would be to establish the link between oxidative addition or geometrical deformation in mononuclear complexes and the geometrics of adsorption on well-defined metal surfaces. A recent study by Rhodin and co-workers nicely systematizes the available information for molecular and dissociative adsorption of CO, N_2 , and NO on metals.⁵¹

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Appendix

The calculations which underlie the qualitative arguments used in this paper are of the extended Hückel type.⁵² The basis set included single Slater-type functions for all orbitals except metal 3d or 5d, which were approximated by double- ζ functions. The metal atoms studied were Ir, Ti, and Fe. For Ir^{5a} and Ti,⁵³ as well as C, N, O, and H,^{5a} the parameters were taken from earlier work. For Fe and a pseudoligand L bearing σ orbitals alone the following parameters were used: Fe 4s, $\zeta = 1.90$, $H_{ii} = -9.99$ eV; Fe 4p, $\zeta = 1.90$, $H_{ii} = -5.97$ eV; Fe 3d, one Slater exponent 5.35, coefficient 0.5505, other Slater exponent 2.0, coefficient 0.626, $H_{ii} = -12.63$ eV; pseudoligand L 2s, $\zeta = 1.95$, $H_{ii} = -13.4$ eV.

The L_4MXX calculations were done for the following geometries: ML_4 fragment square planar, pyramidal (trans L-M-L angles 150°), and C_{2v} (trans L-M-L angles 120 and 180°); M-L distance 2.11 Å. The diatomic C_2 , N_2 , or O_2 was assigned a uniform X-X distance of 1.46 Å and placed at a 1.75-Å M-X distance in η^1 and a 1.75-Å M to center of X_2 separation in η^2 . CO, NO, and CN^- ligands were also studied, with geometrical parameters given in earlier work.^{5a} In the construction of Figure 1 the diatomics were calculated at their equilibrium distances. In addition to the pseudoligand L other ligands on the metal were examined, including CO, Cl, and NH_3 .

The general Walsh diagram of Figure 7 was checked with the following primitive model for the reaction coordinate, which did not do justice to the kinking region: The M-X-Y angle was first changed gradually from 180 to 90°. Then the XY diatomic was moved sideways until its midpoint came to the ML_4 axis.

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Seven-Coordination. A Molecular Orbital Exploration of Structure, Stereochemistry, and Reaction Dynamics

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A systematic molecular orbital analysis of seven-coordinate molecules is presented, with an emphasis on the basic electronic structure, substituent site preferences, and pathways for interconversion of various geometries. Conformations studied in detail include the pentagonal bipyramid (PB), capped octahedron (CO), and capped trigonal prism (CTP). With respect to σ or electronegativity effects the following conclusions are reached for the optimum site of substitution in a d⁴ complex by a better σ donor: PB equatorial (eq), CO capping site (c), CTP edge (e). For π effects the following preferences are deduced for d⁴ systems substituted by an acceptor and d⁰ by a donor (> means preferred): PB ax > eq, eq_{||} > eq_⊥; CO (cf = capped face, uf = uncapped face, c = capping site) cf > c > uf, cf_⊥ > cf_{||}, uf_⊥ > uf_{||}; CTP (qf = quadrilateral face, e = edge, c = capping site) qf ~ e > c, qf_⊥ > qf_{||}, e_⊥ > e_{||}, c_⊥ > c_{||}. These preferences are reversed for the d⁴ donor substituent case. The agreement with information available from structural studies is good, though often the same conclusions would be reached from steric arguments. All pathways of polytopal rearrangement in seven-coordination are of low energy.

In the seemingly complex yet quite simply ordered¹ structural scheme for inorganic chemistry, seven-coordination occupies a niche that is formally analogous to five-coordination. Neither five- nor seven-coordinate complexes can achieve as meritorious a structural form as their nearest coordination neighbors, four, six, and eight; and consistently, each is a less common coordination form than their nearest neighbors. A partial explanation for the "discontinuities" at five- and seven-coordination may be derived from the graph shown in Figure 1. There is a much less effective packing arrangement in progressing from four- to five- or from six- to seven-coordination and a quite modest penalty in ligand repulsion effects for a return to a more uniform spatial array of ligands in a further progression from five- to six- (essentially no penalty) or seven- to eight-coordination.² Nevertheless, five^{3,4} and seven-coordinate^{5,6} complexes are isolable and well-defined molecular entities, although seven-coordination forms are by far the less common of the two presumably because of steric as well as electronic penalties incurred in the construction of

complexes of high coordination number. The role of seven-coordination is significant when viewed in the light of reaction intermediates or transition states in associative reactions of six-coordinate complexes, oxidative addition reactions of five-coordinate complexes, and, most importantly, dissociative reactions of eight-coordinate complexes. An understanding of mechanism in these reaction regimes requires delineation of the electronic and steric factors that direct structural and stereochemical trends in seven-coordination. This paper is addressed to the issue of electronic controls.

Structural studies^{5,6} and calculations⁷⁻¹⁰ suggest that seven-coordination has in the general¹¹ case a potential surface that is not distinguished by a deep minimum corresponding to one polytopal¹² form. This situation, analogous to that established for the five-coordination family, in part reflects the simple geometric fact that seven points cannot be arranged so as to describe a regular polyhedron. The number of nonisomorphic polyhedra with seven vertices is large, 34. Each of these polyhedra has been illustrated by Britton and Dunitz.¹³ Within this complete set, just three high-symmetry polyhedra^{5,6,14} suffice to describe the established elements of

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