

in Table III. The modified Wolfsberg-Helmholz formula was employed.³⁷ The following bond lengths were used: C-C (olefin), 1.38 Å (for the comparison of free carbonyl and free ethylene, the C-O bond length was 1.22 Å and the C-C bond length was 1.34 Å); C-H, 1.08 Å; N-H, 1.01 Å; P-H, 1.42 Å; FeC(CO) = 1.78 Å (Fe(CO)₅, Fe(CO)₄); FeC(CO), 1.75 Å (CpFe(CO)₂); FeH, 1.7 Å; CO, 1.14 Å; PtCl, 2.2 Å; PtN, 2.14 Å; Fe to center of C₂H₄,

(37) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* 1978, 100, 3686.

1.88 Å (Fe(CO)₅(C₂H₄), Fe(CO)₄(C₂H₄), Fe to center of C₂H₄, 2 Å; Ni to center of C₂H₄, 1.88 Å; Pd to center of C₂H₄, 2 Å; Fe to center of Cp, 2.09 Å; Ni to center of Cp, 2.09 Å; C-C (Cp), 1.43 Å; FeP, 2.36 Å; NiP, 2.15 Å; NiC(CO), 1.82 Å. The angles in ML₅ and ML₃ were set to 90°. C(O)FeCO (equatorial) is 115° (Fe(CO)₄), PNiP is 110.5°, and HPH is 109.47°. The geometry of Cp₂WH(C₂H₄)⁺ was adapted from Cp₂NbC₂H₅(C₂H₄),²⁷ CpML = 125° (CpML₂, CpML). A pseudooctahedral geometry was assumed for CpML₂(C₂H₄). In Cp₂WH(C₂H₄)⁺ the angle CpWCp is 136°.

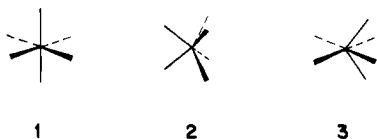
Deformations from Octahedral Geometry in d⁴ Transition-Metal Complexes

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Abstract: There are observed substantial deformations from octahedral symmetry in several diamagnetic d⁴ complexes of Mo(II) and W(II). Two of the compounds are of the stoichiometric type Mo(CO)₂L₂L'₂, and while both deform roughly along a C_{2v} mode, in one the carbonyls move together, while in the other they move apart. A detailed theoretical analysis of molecular distortions in ML₂L'₂L'' and ML₆ complexes is presented. It utilizes the additivity of effects of each ML₂, ML₂', ML₂' subunit and, within each unit, the angularly dependent σ- and π-donating or -accepting capability of the ligands. An M(CO)₂ subunit generates a double minimum in the total energy. In one of the minima the carbonyls move together and in the other they move apart. One of these minima is then deepened by the composite effect of the other ligands in the molecule.

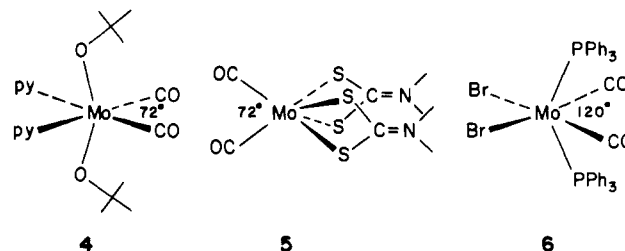
The preeminence of the octahedral geometry (1) in transition-metal six-coordination is assured by both steric and electronic factors.¹⁻³ Nevertheless, substantial departures from this poly-



hedral paradigm are well established. There is a reasonably well-populated class of trigonal prismatic complexes (2) as well as molecules intermediate in local symmetry between the octahedron and the trigonal prism.⁴ Still smaller is the group of complexes distorted toward a bicapped tetrahedron (3).⁵

Within the past year we noticed three crystal structures in which d⁴ six-coordinate complexes departed substantially from octahedral symmetry—Mo(O-*t*-Bu₂(CO)₂(py)₂ (4),⁶ Mo(CO)₂[S₂CN(*i*-Pr)]₂ (5),⁷ and an older MoBr₂(CO)₂(PPh₃)₂ structure (6),⁸ the last

brought to our attention by J. L. Templeton.^{9,10} The schematic structures 4-6 do not do justice to, but only indicate approximately, the deformations of these molecules. Compounds 4 and 6 are



distorted toward a bicapped tetrahedron,¹¹ and 5 is a trigonal prism.

In fact most d⁴ complexes are octahedral or close to octahedral in the solid state.^{12,13} A Jahn-Teller deformation, albeit weak,

(1) Kepert, D. L. *Prog. Inorg. Chem.* 1977, 23, 1-65 and references therein.

(2) Pearson, R. G. "Symmetry Rules for Chemical Reactions"; Wiley: New York, 1976.

(3) Hoffman, R.; Howell, J. M.; Rossi, A. R. *J. Am. Chem. Soc.* 1976, 98, 2484-2492 and references therein.

(4) For a leading review, see: Wentworth, R. A. D. *Coord. Chem. Rev.* 1972, 9, 171-187.

(5) (a) Guggenberger, L. J.; Titus, D. D.; Flood, M. T.; Marsh, R. E.; Orio, A. A.; Gray, H. B. *J. Am. Chem. Soc.* 1972, 94, 1135-1143. (b) E. A. McNeill, Ph.D. Dissertation, Cornell University, 1975. (c) McNeill, E. A.; Scholer, F. R. *J. Am. Chem. Soc.* 1977, 99, 6243-6249. (d) Vancea, L.; Bennett, M. J.; Jones, C. E.; Smith, R. A.; Graham, W. A. G. *Inorg. Chem.* 1977, 16, 897-902.

(6) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *J. Am. Chem. Soc.* 1979, 101, 7615-7617.

(7) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* 1980, 6568-6569.

(8) Drew, M. G. B.; Tomkins, I. B.; Colton, R. *Aust. J. Chem.* 1970, 23, 2517-2570.

(9) We are grateful to J. L. Templeton, University of North Carolina, for informing us of his work in this area.

(10) Another distorted d⁴ structure of W(CH₃)₂(PMe₃)₄ (Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* 1979, 926-927) is in fact a carbyne. (CH₃)W(CH₃)(PMe₃)₄: M. B. Hursthouse, private communication.

(11) The crystal structure of 6 is of limited accuracy. There appears to be an additional distortion from the idealized C_{2v} symmetry, a slight twist of the P-Mo-P unit around the axis which bisects C-Mo-C.

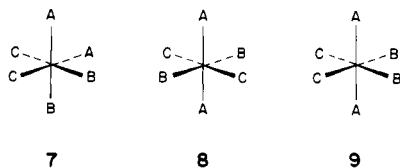
(12) (a) Ti(CO)₆ and Ti(N₂)₆, matrix-isolated species, are distorted to an unknown degree from O_h symmetry: Busby, R.; Klotzbücher, W.; Ozin, G. A. *Inorg. Chem.* 1977, 16, 822-828. (b) For references to the structures and chemistry of some d⁴ hexacyanides, see: Sharpe, A. G. "The Chemistry of Cyano Complexes of the Transition Metals"; Academic Press: New York, 1976; pp 44, 84-85. (c) For references to the structures and chemistry of some d⁴ hexahalides, see: Colton, R.; Canterford, J. H. "Halides of the First Row Transition Metals"; Wiley-Interscience: New York, 1969; pp 237, 238. Cotton, S. A.; Hart, F. A. "The Heavier Transition Elements"; Wiley-Halstead: New York, 1975; pp 60, 110. Griffith, W. P. "The Chemistry of the Rarer Platinum Metals: Os, Ru, Ir, and Rh"; Wiley-Interscience: New York, 1967; pp 53-57, 132-133, 231, 316.

might have been expected for some of the low-spin states arising from a t_{2g}^4 configuration of an O_hML_6 complex.¹⁴ The substituent pattern in 4–6 of course forces a lower symmetry. The Jahn–Teller theorem, strictly speaking, is not relevant to the problem. Nevertheless one might have thought that an electronic memory of the octahedral parentage would have led to an excursion along a t_{2g} or e_g vibration.¹⁴ What we found impressive about compounds 4–6 was that their deformation from octahedral symmetry was (a) substantial, (b) varied—here toward a bicapped tetrahedron, there toward a trigonal prism with carbonyls moving toward each other (4, 5), away from each other (6), and (c) not predictable from simple Jahn–Teller arguments.

Extended Hückel calculations, described in the Appendix, were carried out on models for 4 and 6, $Mo(CO)_2(OCH_3)_2(py)_2$ and $Mo(CO)_2(PH_3)_2Cl_2$, respectively. They reproduced qualitatively the experimentally observed trends. Wishing to understand why these molecules assume the deformed structures that they do, we began a general theoretical analysis of bonding in d^4 six-coordinate complexes. That is the subject of this paper. While the d^4 configuration was the impetus to this study, and will figure prominently in the discussion, the arguments are quite general and should form a basis for an analysis of octahedral deformation for any d-electron configuration.

Geometrical and Bonding Prelude

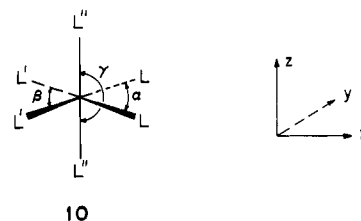
Ideally we should like to be able to predict the geometry of an arbitrary six-coordinate complex, even with six different ligands, if we are given the central metal and the six ligands. That is unlikely to happen. Suppose we set the more modest goal of encompassing the general stoichiometric type of 4–6, i.e., $MA_2B_2C_2(ML_2L_2'L_2'')$. The configurational possibilities are 7 (all ligands cis), 8 (all ligands trans), and 9 (two pairs cis, one trans). This assumes an octahedral starting point. If $A \neq B$



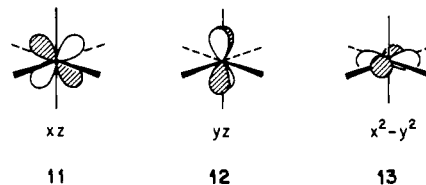
$\neq C$, then 7 has no symmetry, 8 has D_{2h} , and 9 C_{2v} symmetry. We will concentrate on structural type 9. It allows large changes in angular coordinates while retaining its basic symmetry. The general problem of isomer stability, while occasionally susceptible to a simple analysis,¹⁵ is a most difficult one, especially so if departures from the relatively transparent octahedral geometry are allowed. It is just those geometrical excursions which interest us.

The idealized octahedral geometry is a convenient reference point for our study. We show the coordinate system that we will use throughout this paper in 10; the structure also carries the notation of the angles: α and β in the xy plane and γ in the xz plane, bisecting the LML and $L'ML'$ angles.

The orbitals which we must consider are, of course, the octahedral t_{2g} set, shown in 11–13, capable of π bonding or anti-



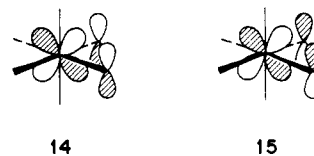
bonding. In a low-spin d^4 complex, two of these orbitals will be



occupied and one empty. Which orbitals are filled and which one is empty—that will control the geometry adopted by a given complex. Our aim is twofold—to establish the ordering in energy of the three orbitals and determine the slope of each orbital as a function of geometrical deformation, of each of the three angles. The energy ordering and the slopes will in turn depend on the electronic properties of the ligands, on their σ -donor and π -donor (D) or π -acceptor (A) capability.

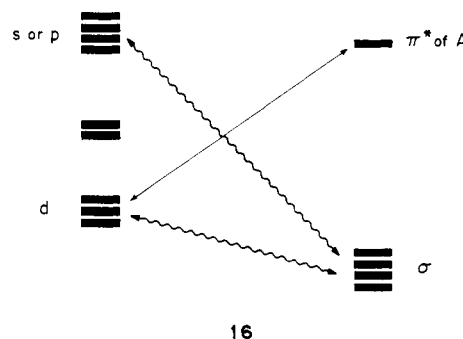
Hybridization, Nodal Surfaces, and Perturbation Theory

Most of the time we can describe the movement of the frontier orbitals by means of first-order perturbation arguments.¹⁶ Here the simplest protocol is to think about a decrease or increase in overlap. For instance, if the orbital in question were xz and L were a π acceptor, then simple inspection of 14 would tell that xz is stabilized by decreasing α and destabilized on increasing α . Note the importance of the basic phase relationship between



the d orbital and the ligand—if L were a π donor, then (15) the slope of xz with α would be precisely reversed.

Occasionally first-order perturbation theoretic arguments will not suffice. As the ligands move, the shape of the d orbitals changes. What happens is schematically shown in 16. Say that



we are interested in the interaction of some acceptor π orbitals with metal d functions, as indeed we are for our problem. A geometrical distortion takes place. As a result, the metal d functions begin to overlap with ligand σ functions, an overlap which vanished in the idealized octahedral starting point. The ligand

(13) Here is a sample of d^4 structures that are close to octahedral. (a) Glavan, K. A.; Whittle, R.; Johnson, J. F.; Elder, R. C.; Deutsch, E. *J. Am. Chem. Soc.* **1980**, *102*, 2103–2104. (b) Bandoli, G.; Clemente, D. A.; Mazzi, U. *J. Chem. Soc., Dalton Trans.* **1976**, 125–130; **1977**, 1837–1844. (c) Trop, H. S.; Davison, A.; Jones, A. G.; Davis, M. A.; Szalda, D. J.; Lippard, J. J. *Inorg. Chem.* **1980**, *19*, 1105–1117. (d) Swanson, B. I.; Ryan, R. R. *Ibid.* **1973**, *12*, 283–286. (e) Armstrong, J. R.; Chadwick, B. M.; Jones, D. W.; Sarneski, J. E.; Wilde, H. J.; Yerkess, J. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 1025–1029; (f) Gupta, M. P.; Milledge, H. J.; McCarthy, A. E. *Acta Crystallogr., Sect. B* **1974**, *30*, 656–661. (g) Muetterties, E. L.; Kirner, J. F.; Evans, W. J.; Watson, P. L.; Abdel-Meguid, S.; Tavanaiepour, I.; Day, V. W. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1056–1059. (h) Aslanov, L.; Mason, R.; Wheeler, A. G.; Whimp, P. O. *Chem. Commun.* **1970**, 30–31.

(14) (a) Jahn, H. A.; Teller, E. *Phys. Rev.* **1936**, *49*, 874. *Proc. R. Soc. London, Ser. A* **1937**, *161*, 220–235. (b) Herzberg, G. "Molecular Structure and Molecular Spectra. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules"; D. Van Nostrand: Princeton, 1966, pp 37–65. (c) Jotham, R. R.; Kettle, S. F. A. *Inorg. Chim. Acta* **1971**, *5*, 183–187.

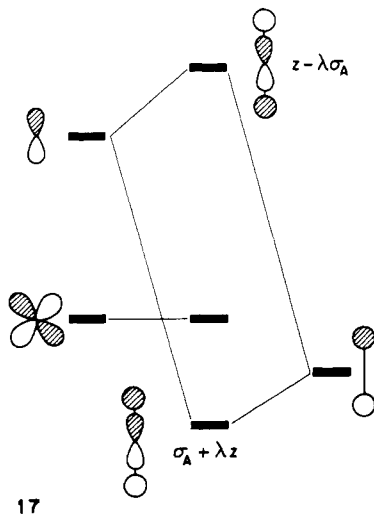
(15) Mingos, D. M. P. *J. Organomet. Chem.* **1979**, *179*, C29–C33. Burdett, J. K. *Inorg. Chem.* **1976**, *15*, 212–219. Reference 13b.

(16) For an introduction to perturbation theory, see: Heilbronner, E.; Bock, H. "The HMO Model and its Application"; Wiley: New York, 1976. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1–9. (c) Libit, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1974**, *96*, 1370–1383. (d) Imamura, A. *Mol. Phys.* **1968**, *15*, 225–238.

σ orbitals in turn overlap substantially with metal s and p functions. It follows that in second-order perturbation theory, metal s and p functions will mix into the d functions. Polarization or hybridization will result.

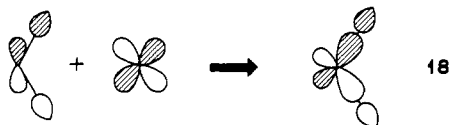
The formalism of second-order perturbation theory is not difficult,^{16c,d} but it is complex. Our experience in constructing explanations has taught us that if there is a way of circumventing second-order arguments it should be taken. Is there a simple way to estimate the shape of a hybridized d function after deformation? If so, one can use these hybridized or deformed orbitals in subsequent first-order bonding analysis.

There is a way of guessing the shape of a perturbed d orbital. Let us examine a model case and then move to the general conclusion. Consider the metal xz orbital and the deformation of lowering γ from 180° . In the idealized octahedral geometry, $\gamma = 180^\circ$, the antisymmetric ligand combination, σ_A in **17**, mixes strongly with the z orbital on the metal, not at all with xz . One

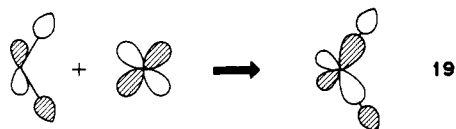


obtains bonding and antibonding combinations $\sigma_A + \lambda z$ and $z - \lambda \sigma_A$ where λ is a mixing coefficient.¹⁶ Now imagine γ decreased from 180° . Some $xz - \sigma_A$ overlap takes place. What happens to the three orbitals?

In first order $\sigma_A + \lambda z$ mixes into itself xz , in a bonding, stabilizing way, as sketched in **18**.¹⁶ The new metal orbital com-



ponent is hybridized toward the ligands. The highest orbital, $z - \lambda \sigma_A$, mixes into itself xz in an antibonding way, because it is above xz .¹⁶ The new highest orbital (**19**) has a metal component that is also hybridized toward the ligands.



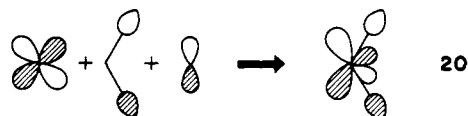
Now we come to the difficult part, which is xz . This d orbital mixes into itself σ_A in the first order and z in the second order. The mixing can be analyzed formally¹⁶ as follows:

$$xz' = xz^0 + \left(\frac{H'_{xz,\sigma_A}}{E^0_{xz} - E^0_{\sigma_A}} \right) \sigma_A + \left[\frac{H'_{xz,\sigma_A} H'_{\sigma_A,z}}{(E^0_{xz} - E^0_z)(E^0_{xz} - E^0_{\sigma_A})} \right] z$$

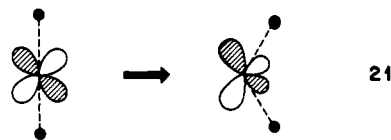
Or one can do two sequential first-order interactions—mix σ_A with z (done in **16**) to form $\sigma_A + \lambda z$ and $z - \lambda \sigma_A$ and then mix the last two orbitals in first order into xz . Either way, the mixing one obtains is as follows:

$$xz' = xz^0 - |\lambda'| \sigma_A - |\lambda''| z$$

or pictorially



The new xz is hybridized away from the ligands. Alternatively the nodal surfaces of the new xz have shifted toward the ligands (**21**); i.e., they have followed the ligands.



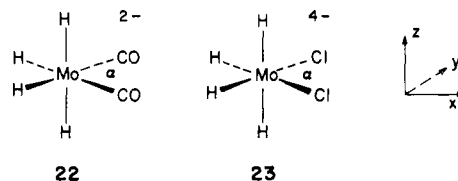
That was a specific case, but it can be generalized. In bonding orbitals, where most of the total energy of a molecule resides, orbitals will mix, hybridize, so as to produce maximum overlap. Nodal planes will arise, but they will be placed in between ligands. The σ^* antibonding counterparts of the σ orbitals will be hybridized in a similar manner—their high energy is derived from further nodes perpendicular to bond directions. In the whole set of MO's, we do have other orbitals which have smaller bonding/antibonding interactions than the σ -type MO's do. These are usually the frontier orbitals or are close in energy to them. The best examples here are nonbonding orbitals. But we can rank among them even other orbitals which have smaller interactions than σ and σ^* MO's do, for example, MO's based on π - (or δ -) type overlap. Is there any simple way to conjecture the shape of those orbitals? Yes, since the σ -type orbitals in the process of achieving greatest stabilization have already tailored the one-electron functions, pushed them into the bond regions. Orthogonality conditions must be obeyed by the entire set of wave functions, and so the nonbonding or nearly nonbonding orbitals must contain electron density where the ligands are not, i.e., in the region between the ligands. It follows that the nodal surfaces of such nonbonding orbitals will be directed toward the ligands. When we modify the shape of a molecule, the nonbonding orbitals will attempt to shift their nodes to follow the ligands. This fundamental idea is in agreement with basic notions of crystal field theory and also connects with Goddard's orbital phase continuity principle.¹⁷

The discussion of hybridization and second-order perturbation theory may have appeared as a digression. But it is not—these ideas are essential to a general analysis of the problem.

Influence of Ligand Pairs on Level Ordering

In analyzing the influence of ligand electronic properties on deformation modes of $ML_2L_2'L_2''$, we have found useful a pairwise decomposition. That is, we think about ML_2 , ML_2' , or ML_2'' separately first and trace the way they change the orbital level pattern as the respective angle, α , β , or γ varies. Then we reassemble the whole molecule, superimposing the individual trends.

Let us begin with the *cis* pairs ML_2 or ML_2' and allow them to vary from being a π acceptor, denoted as A, to a π donor, D. The actual calculations were carried out with carbonyls as acceptor models, a hypothetical *cis*- $Mo(CO)_2H_4^{2-}$ (**21**), and chlorides as donor models, *cis*- $MoCl_2H_4^{4-}$ (**22**). The parameters of the ex-



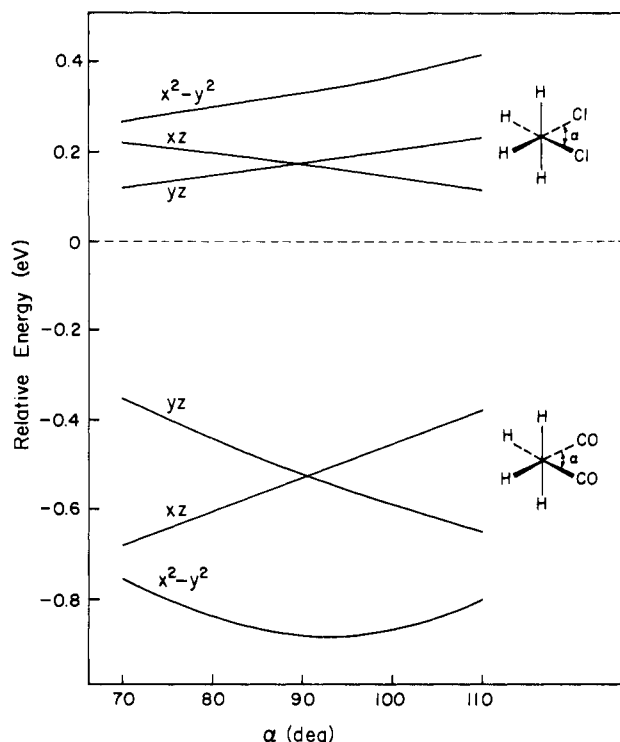
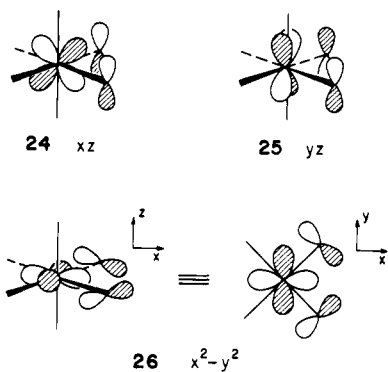


Figure 1. The d_{π} energy levels as a function of α for *cis*- $\text{Mo}(\text{CO})_2\text{H}_4^{2-}$ (bottom) and *cis*- $\text{MoCl}_2\text{H}_4^{4-}$ (top). Both molecules are on the same energy scale, whose zero corresponds to the energy of a noninteracting d orbital of Mo.

tended Hückel computations are specified in the Appendix. The hydrides completing the ligand set in these model compounds serve as π -innocent σ -bonding ligands.

The behavior of the t_{2g} set of Mo in **22** and **23** as a function of α in the region of small variations from the octahedral value of $\alpha = 90^\circ$ is shown in Figure 1. The interaction of $x^2 - y^2$ with a π donor or acceptor is inherently greater than that in xz and yz . That is obvious from angular overlap model considerations¹⁸ or the shape of the orbitals shown for the D case in **24–26**. The



A case orbitals are, of course, the same in shape, except that the CO π^* acceptor orbital now mixes in phase into the d function.

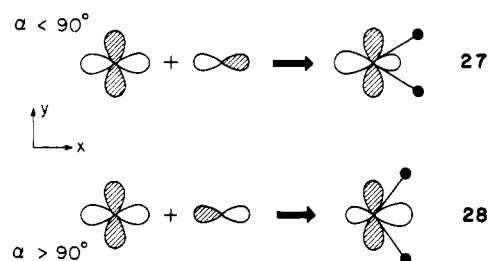
π -Acceptor functions on the ligand stabilize the t_{2g} set and π -donor functions destabilize it. The overlap active in this stabilization or destabilization is greater for $x^2 - y^2$, which is behind the level ordering in the central region of Figure 1.

Now we allow α to vary. At 90° the overlap of xz and yz with z on the ligands is precisely equal. As α increases, the overlap with xz diminishes and that with yz increases. As α decreases, precisely the reverse happens. Recalling once again that in the

acceptor case an increase in overlap is stabilizing, while for a donor the same increase is destabilizing, we easily understand the trends of Figure 1 for xz and yz .

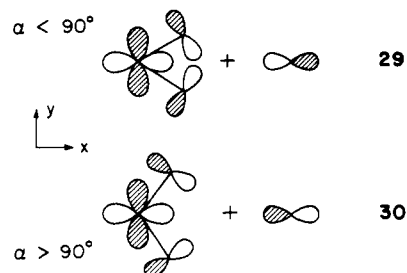
For $x^2 - y^2$ the dependence of energy on α is more complicated. As the angle α changes, $x^2 - y^2$ should lose π overlap with appropriate orbitals of ligands, and do so to the same extent in both directions of change of α . This effect should destabilize $x^2 - y^2$ for the case of acceptors and stabilize it for the case of donors. Examination of Figure 1 shows that our expectations are followed for the A case but not quite for D. It is here that we must turn to a consideration of hybridization—the $x^2 - y^2$ orbital changes shape as α changes.

In C_{2v} symmetry $x^2 - y^2$ can mix with s , x , and z^2 AO's of the metal. Since the interactions of both s and $x^2 - y^2$ AO's with ligand orbitals do not depend on α (s and z^2 do not distinguish directions in the xy plane), we may consider only hybridization of $x^2 - y^2$ with x . As discussed above, the prescription is that the model planes of a hybridized orbital are to follow the connecting lines between M and L's. A decrease of α will cause squeezing and an increase of α dilation of the lobe along the $+x$ direction. This is accomplished by x mixing as shown in **27** and **28**. Not that



the sign of mixing in of the x orbital changes at $\alpha = 90^\circ$. Indeed, this is what is observed in our calculations.

The x orbital which is thus mixed in has an overlap with the same ligand π orbital which interacts with $x^2 - y^2$ —the interaction may be augmented or diminished by this metal p -ligand p π bonding. The working out of the mixing is shown for the acceptor case in **29** and **30**. The extra interaction increases overlap



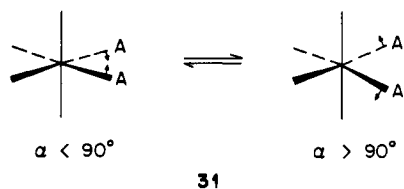
(therefore stabilization) for $\alpha > 90^\circ$ and decreases it for $\alpha < 90^\circ$. The opposite situation takes place for a donor.

To this analysis we must add another effect. As the angle α departs from 90° , $x^2 - y^2$ gains σ interaction with the ligands L. That interaction must destabilize this d orbital. As a consequence of the hybridization of $x^2 - y^2$ with x , the destabilization will be somewhat bigger for $\alpha < 90^\circ$.

Putting these three effects (the change of π overlap, the hybridization, and turning on of σ interaction) together, just counting their directions, we get the dependence of the energy of the $x^2 - y^2$ level on α in accordance with Figure 1. The data in Figure 1 are again based on extended Hückel calculations.

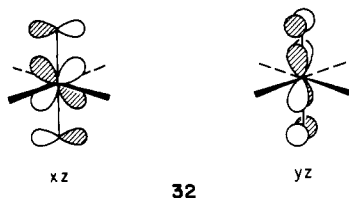
Though our analysis is not yet complete, for we have not considered the trans ligands, it is worthwhile to indicate what we have accomplished. If we understand the individual level slopes, we can predict the state energies which arise from any electron configuration. For instance suppose we have a d^4 complex with two cis acceptors and four ligands that are innocent in their π -bonding properties. Figure 1 shows that such a molecule should be stabilized by a departure of α up or down from 90° , with the $\alpha > 90^\circ$ minimum slightly more stable due to the behavior of $x^2 - y^2$. A double minimum, **31**, is the predicted result. The

(18) See: Burdett, J. K. *Chem. Soc. Rev.* **1978**, *7*, 507–526. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 113–146. Schäffer, C. E.; Jørgensen, C. K. *Mol. Phys.* **1964**, *9*, 401–412. Burdett, J. K. "Molecular Shapes"; Wiley-Interscience: New York, 1980.

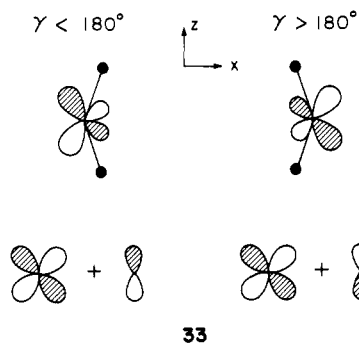


actual configuration energies are shown in Figure 2. The barrier due to the level crossing at $\alpha \sim 90^\circ$ is clearly visible. The interconversion of the two minima is strictly speaking a forbidden reaction. Of course the equilibrium geometry in each minimum is not set just by these frontier orbitals; there are other lower-lying orbitals in which steric repulsion in these one-electron calculations manifests itself, and it is the combination of the frontier orbital trends and these lower orbitals that creates the real minima.

We turn to the trans ligands L'' . These can have π interactions with xz and yz , as shown for the acceptor case in 32. As the angle



γ departs from 180° , only π overlap will be lowered for yz . No σ interaction turns on here nor does any hybridization of yz occur. That is to say the motion runs in the nodal plane of yz , and no metal orbital of the same symmetry is available for hybridization. For two acceptors/donors this level is pushed up/down, no matter in which direction γ changes. xz is different. Just as we analyzed for $x^2 - y^2$, all three effects— π bonding, hybridization, and σ bonding—are at work here. These act in the same way for both $\gamma < 180^\circ$ and $\gamma > 180^\circ$. The π interaction is diminished, destabilizing/stabilizing the level for $L'' =$ acceptor/donor. The σ interaction that is turned on as γ moves from 180° obviously destabilizes this level. The hybridization is what we analyzed in detail in the previous section; it is shown in 33. The additional



metal p -ligand p π bonding may be shown to stabilize the xz level for $L =$ acceptor and destabilize it for $L =$ donor. The effect is a minor one, since the nonvanishing π component of that interaction is small. In summary the main direct effects of ligands L'' upon changing γ should be a loss of π overlap for yz and for xz the gained σ interaction and the loss of its π overlap. The latter should be faster for the same change in γ than for yz because of the different angular dependence of π overlap for xz and yz . Except for ligand-ligand interactions or asymmetry of L'' , it does not matter whether $\gamma > 180^\circ$ or $\gamma < 180^\circ$ for these effects.

In Figure 3 we can see the orbital pattern for $\text{Mo}(\text{OH})_2\text{H}_4^{4-}$ and $\text{Mo}(\text{CO})_2\text{H}_4^{2-}$, both trans. In the dihydroxy compound the $\text{Mo}-\text{O}-\text{H}$ angle is taken as linear. This is not a good model for the real Chisholm complexes, and as we will discuss soon, the nonlinear $\text{M}-\text{O}-\text{R}$ grouping is crucial. But for the moment we only seek a model donor or acceptor, and the linear $\text{M}-\text{O}-\text{H}$ serves fine as a model, cylindrically symmetric, donor. The orbital trends may be seen to be in agreement with our qualitative analysis.

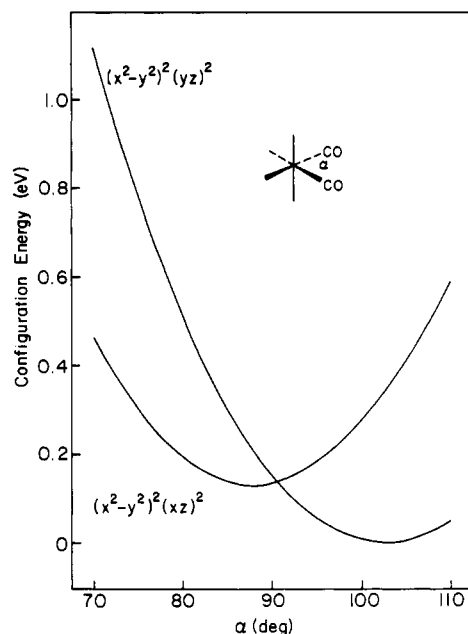


Figure 2. Configuration energies as a function of $\text{OC}-\text{M}-\text{CO}$ angle α for $\text{Mo}(\text{CO})_2\text{H}_4^{2-}$. The zero of the energy scale is arbitrary.

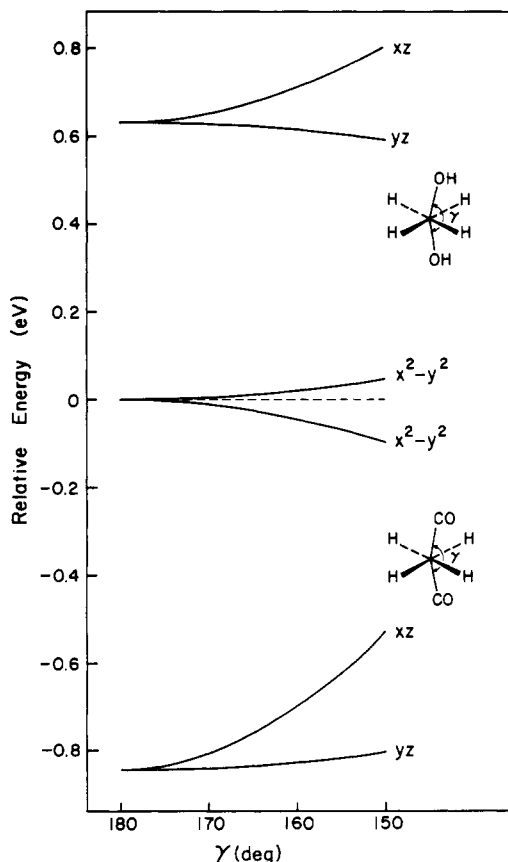


Figure 3. The d_x energy levels as a function of γ for $\text{trans-Mo}(\text{CO})_2\text{H}_4^{2-}$ (bottom) and $\text{trans-Mo}(\text{OH})_2\text{H}_4^{4-}$ (top). Both molecules are on the same energy scale, whose zero corresponds to the energy of a noninteracting d orbital of Mo. In the model hydroxide complex, the $\text{Mo}-\text{O}-\text{H}$ angle is kept at 180° .

Our discussion has been limited to cylindrically symmetrical π donors and acceptors, i.e., substituents such as CO and Cl, which bear two orthogonal π systems. The extension of the analysis to single-faced π donors or acceptors, those which distinguish one π orbital from another, e.g., CR_2 , NR_2^- , RCO , etc., follows an obvious course. The molecules 4-6 which stimulated our interest contain two such ligands, the dithiocarbamate group and the bent

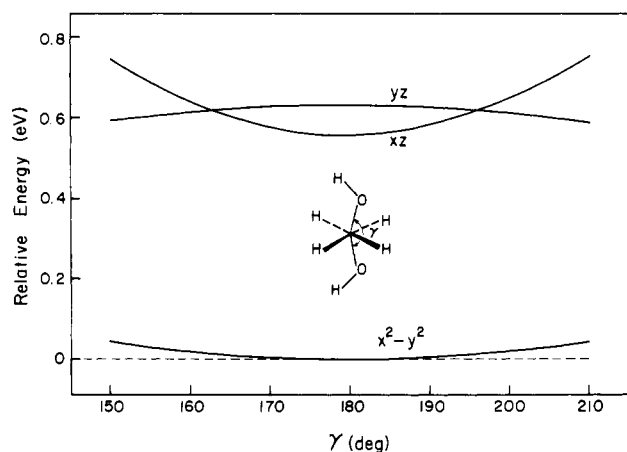
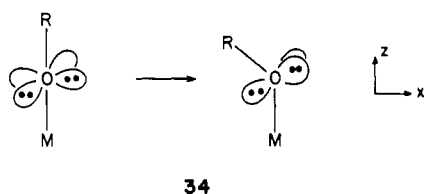


Figure 4. The d_{π} energy levels of $trans\text{-Mo}(\text{OH})_2\text{H}_4^{4+}$ as a function of γ . The difference between this figure and Figure 3 is that here the Mo-O-H unit is nonlinear, Mo-O-H angle 141° .

tert-butoxy ligand. Let us take a brief look at the latter, because the compound in which it occurs (4) is one we wish to study in detail. The two oxygen lone pairs of an OR group become non-equivalent as the group bends (34). The lone pair orthogonal



34

to the bending plane, the xz plane in 34, is obviously the better π donor, since it lies at higher energy and is approximately pure $2p$ on O. If we take an M-O-H angle of 141° , as in 4, and study the effect of bending (change in γ) in $trans\text{-Mo}(\text{OH})_2\text{H}_4^{4+}$ with two such bent MoOH groups, we get the d level changes plotted in Figure 4. Now the yz level, the one which interacts better with the oxygen lone pairs, is at higher energy at $\gamma = 180^\circ$. Otherwise the levels move in a similar way to Figure 3.

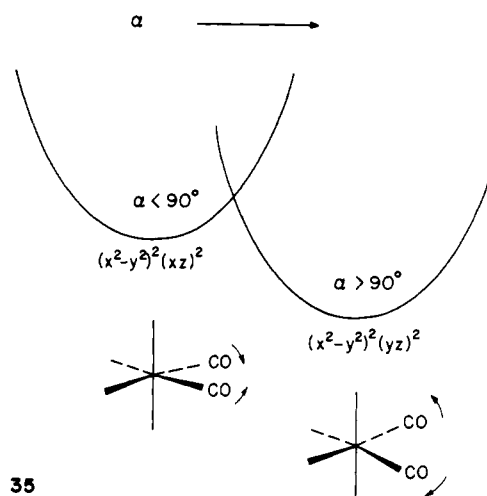
In concluding our analysis of the trans ligand pair, an important point to note is that the hybridization creates a coupling between the motion of trans ligands L'' and π interactions of ligands in the xy plane. The phase relation of mixing of z into xz depends on the direction in which the ligands L'' move in the xz plane. Then the z orbital mixed into xz is able to improve or worsen the π -type interaction with ligands in the xy plane. For example, if $\gamma > 180^\circ$, the π interaction with ligands L will be stronger than for $\gamma = 180^\circ$ and still stronger than for $\gamma < 180^\circ$ (see 32). That will, of course, stabilize/destabilize the level if $L = \text{acceptor/donor}$. As the z AO of the metal is already most favorably oriented for π interaction with ligands in the xy plane, that effect is going to be an important one.

Assembling $\text{Mo}(\text{CO})_2(\text{PR}_3)_2\text{Br}_2$ and $\text{Mo}(\text{CO})_2(\text{OR})_2(\text{py})_2$

Now that we have analyzed in detail the level ordering and orbital slopes for $cis\text{-ML}_2$ and $trans\text{-ML}''_2$, $L = \text{D, A}$, we can put the individual effects of ligands together and think of the deformations of actual d^4 six-coordinate complexes. The situation becomes more intelligible if we find and start with the major interactions. Then the orbital pattern can be tuned by less important effects. The major interactions, of course, will decide the occupation of d_{π} levels.

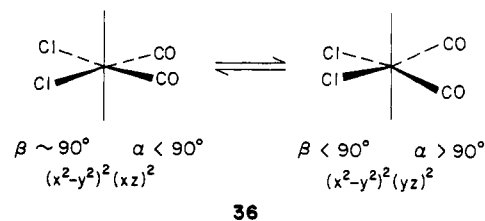
The outstanding π -accepting ability of carbonyls is well-known. Figures 1 and 3 just confirm this—note how the d orbitals are much more stabilized by interactions with CO's than they are destabilized by the donors Cl and OH. Since the phosphines or the pyridines are neither good donors nor acceptors, we are led to expect that for both $\text{Mo}(\text{CO})_2(\text{PR}_3)_2\text{Br}_2$ and $\text{Mo}(\text{CO})_2(\text{OR})_2(\text{py})_2$ the carbonyls dominate the electronic picture. This implies a level ordering $x^2 - y^2$ below xz and yz . It follows from

our previous discussion that we will have *in principle* a double minimum, as illustrated in 35.



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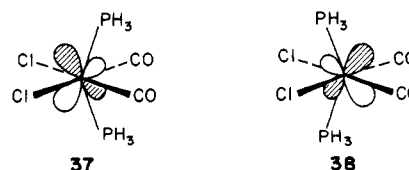
Consider first $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2\text{Br}_2$, which we model in detailed calculations by $\text{Mo}(\text{CO})_2(\text{PH}_3)_2\text{Cl}_2$. The Cl ligands will not switch the basic level pattern but will add their own influence on the angle β , Cl-Mo-Cl. Referring back to Figure 1, we see that in the configuration $(x^2 - y^2)^2(yz)^2$ β should be $< 90^\circ$, since $x^2 - y^2$ and yz both favor $\beta < 90^\circ$. For the configuration $(x^2 - y^2)^2(xz)^2$, the influences of $x^2 - y^2$ and yz are opposite and β should remain near 90° . We are now at the stage of 36, with the angular preferences



36

of $L = \text{CO}$ and $L' = \text{Cl}$ satisfied. Before we start considering the angle P-Mo-P(γ), we should remind ourselves that from the point of view of the total energy, the more the LUMO is destabilized by either σ or π bonding, the lower the total energy of the molecule. This is the Angular Overlap Model viewpoint;¹⁸ qualitative destabilization of the LUMO implies a corresponding stabilization of some occupied molecular orbital(s). The advantage of focusing on the LUMO is that occasionally it concentrates in one orbital the antibonding interactions whose bonding counterparts may be diffused over several orbitals.

Now we consider the axial phosphines. In our calculations these have essentially no π -donating nor -accepting capability. For instance in octahedral $trans\text{-Mo}(\text{PH}_3)_2\text{H}_4^{2-}$ xz and yz are pushed up only 0.057 eV above $x^2 - y^2$. As γ changes from 180° (bending in the xz plane), the xz orbital will be destabilized. This is a σ effect. Destabilization produces hybridization, a mixing of z into xz , as illustrated in 33. If $\gamma < 180^\circ$, the hybridization is toward the halogens, 37. This will increase the interaction of xz with

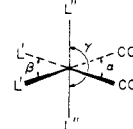


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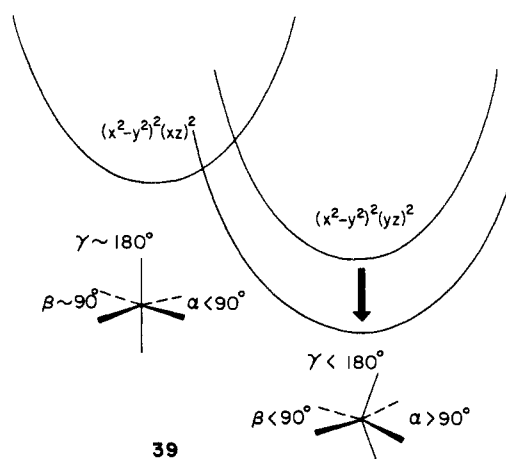
the halogens. If $\gamma > 180^\circ$, the hybridization is toward the carbonyls, 38. This will increase the interaction with the carbonyls.

Bending the phosphines toward the halogens, $\gamma > 180^\circ$, turning on a greater interaction with the carbonyls, might seem to stabilize the configuration $(x^2 - y^2)(xz)^2$. So it does, from the π -bonding viewpoint. But remember that changing γ from 180° is σ destabilizing—it turns on some σ antibonding that z admixture

Table I. Observed Structural Parameters of $\text{Mo}(\text{CO})_2(\text{PPh}_3)_2\text{Br}_2$ and $\text{Mo}(\text{CO})_2(\text{O}-t\text{-Bu})_2(\text{py})_2$ and the Optimized Computed Structures of Models for These


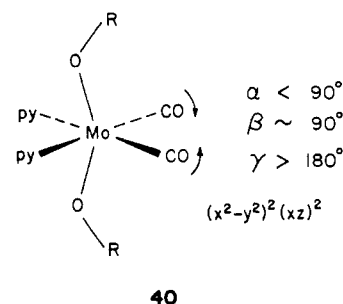
	obsd, deg ($L' = \text{Br}$, $L'' = \text{PPh}_3$)	calcd, deg ($L' = \text{Cl}$, $L'' = \text{PH}_3$)	obsd, deg ($L' = \text{py}$, $L'' = \text{O}-t\text{-Bu}$)	calcd, deg ($L' = \text{py}$, $L'' = \text{OCH}_3$)
α	110	98	72	86
β	83	82	85	83
γ	128	170	204	192

tries to counteract but does not do entirely. In the net balance σ antibonding clearly wins out over π bonding—the $(x^2 - y^2)(xz)^2$ configuration is destabilized by a change of γ from 180° . The other configuration, $(x^2 - y^2)(yz)^2$, has xz empty. The higher xz is the greater the gap between the filled orbitals and it and the more stable the configuration. A change in γ , only in the direction of $\gamma < 180^\circ$, will produce that effect. Schematically, we have the situation of **39**.



To put it another way the assumption that xz is the LUMO allows all of the stabilizing effects to develop themselves in mutual accord and to their full extent. The same cannot be said about the second possibility, a yz LUMO. There, both the parameters β and γ would be set by two contradicting effects. Hence it seems a reasonable conjecture that the stable configuration is $(x^2 - y^2)(yz)^2$, with its associated geometrical pattern of $\alpha > 90^\circ$, $\beta < 90^\circ$, and $\gamma < 180^\circ$. This agrees with the experimental structure and our extended Hückel calculations, both listed in Table I. In Chisholm's $\text{Mo}(\text{O}-t\text{-Bu})(\text{CO})_2(\text{py})_2$ there are again two carbonyls with excellent π -accepting ability. For clarity in the following discussion we choose $L = \text{CO}$, $L' = \text{py}$, and $L'' = \text{OR}$. The OR groups can be considered as reasonably good π donors. In the actual structure the O-R bonds lie in the xz plane. A consequence of this fact is that the π -donating ability is better toward the yz orbital than the xz orbital. In the experimental structure the pyridine rings take up a position perpendicular to the xy plane. Their π interactions are thus directed toward the $x^2 - y^2$ orbital, but in any case they are not great—the ligand is not an especially good π donor or acceptor. No matter what the deformation is, the two *cis*-carbonyls will keep the $x^2 - y^2$ orbital at the lowest energy position amid the three d levels. The question is again which of the xz and yz orbitals is going to be the HOMO and which the LUMO for the d^4 configuration. Let us start with the assumption that the yz is the LUMO. Such an ordering is favored by the better π -donating ability of the OR group toward yz . As we concluded earlier, the configuration $(x^2 - y^2)(xz)^2$ favors $\alpha < 90^\circ$, i.e., a closing of the OC-Mo-CO angle. If the pyridine does not have much π -bonding ability, there is no reason for β

to depart from 90° . Changing γ in either direction from 90° destabilizes the xz HOMO, by a σ effect. Least destabilization will occur if maximum π bonding is preserved, and this is achieved by bending the OR's toward the pyridines, away from the carbonyls, **40**.



The other possible configuration is $(x^2 - y^2)^2(yz)^2$. The HOMO is stabilized by a departure of γ from 180° , thus lessening the π antibonding with yz . The direction of change of γ might be such as to destabilize the xz LUMO. This is accomplished by hybridizing xz away from the carbonyls, $\gamma < 180^\circ$.

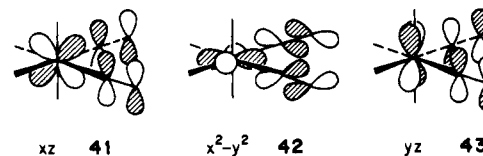
We think that the $(x^2 - y^2)(xz)^2$ configuration is much to be preferred, because it utilizes the π -bonding capability of the OR group. Indeed this is likely to be the electronic configuration of the observed structure, for its geometry (Table I) agrees with our qualitative reasoning and optimized calculated structure. A theoretical analysis very similar to ours has been independently derived by Templeton and Ward.⁷ Note also the resemblance of our computed energy minima to one of the symmetrical waypoints on a potential energy surface of a t_{1u} bending manifold, as beautifully illustrated by Lohr, Bartell, and co-workers¹⁹ in their discussion of the XeF_6 structure. An ideal complete discussion of the geometries of $d^4 \text{ML}_6$ complexes should include such a vibrational analysis.

Ligand-Ligand Interactions

There are two kinds of interactions among the ligands that one might have to worry about, loosely to be called steric and electronic. Concerns about ligand bulk might be raised by the PPh_3 or $\text{O}-t\text{-Bu}$ groups. In the experimental structures no significant short interatomic contacts were observed (except for the OC...CO distance in **4**). The ligands are big, no doubt about it, but we think their bulk so to speak "follows" the electronic structure-determining factors, rather than setting the structure.

Electronic interactions between ligands might be the donor-acceptor type (e.g., halogen lone pair-carbonyl π^*) or direct bonding or antibonding interactions caused by occupation of specific orbitals. In either case they are detectable from the population analysis. We find none that would change the qualitative analysis of the deformation trends given above. But in $\text{Mo}(\text{CO})_2(\text{OR})_2(\text{py})_2$, where α is expected to be $< 90^\circ$, and in fact is 72° , there is an intriguing bonding interaction between the carbonyls. The C-C overlap population is 0.1273 at $\alpha = 72^\circ$. This is a substantial number, from our experience, definitely indicative of incipient bonding. Its significance is enhanced by the fact that it rises steadily to that value as α is decreased from 90° , as shown in Figure 5.

The bonding OC...CO interaction comes from the level pattern. Filled are xz and $x^2 - y^2$ orbitals, **41** and **42**, both C-C bonding.



Empty is yz orbital, **43**, C-C antibonding. This is obviously a

(19) (a) Bartell, L. S.; Gavin, R. M., Jr. *J. Chem. Phys.* **1968**, *48*, 2466-2483. (b) Wang, S. Y.; Lohr, L. L., Jr., *Ibid.* **1974**, *60*, 3901-3915.

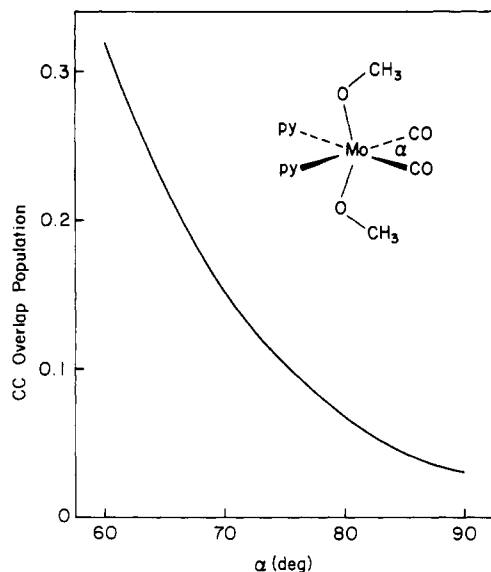


Figure 5. Computed CC overlap population between the carbonyls as a function of α in $\text{Mo}(\text{CO})_2(\text{OCH}_3)_2(\text{py})_2$.

good situation for C-C bonding.

Could the carbonyl-carbonyl interaction be improved further? Perhaps, it can be done by (a) increasing γ , to improve the mixing in **41**, and (b) improving the ability of $x^2 - y^2$ to interact with carbonyls. A detailed orbital analysis shows that good donor substituents in the other equatorial sites (L') would help. It would be nice to achieve the coupling of two carbonyl ligands into the C_2O_2 unit. The latter molecule, the formal dimer of carbon monoxide, has been discussed several times in the literature²⁰ but never synthesized. Coordinated to the metal, it is formally a $\text{C}_2\text{O}_2^{2-}$ ligand. The coupling would thus constitute an oxidation at the metal, at least formally. One would not think that is a likely process for what is already an electron-deficient 16 electron center, but a simple symmetry analysis shows that it is a symmetry-allowed process if one uses the two electrons in $x^2 - y^2$. We will explore the conditions for carbonyl coupling elsewhere—it should be mentioned here that coupling of coordinated nitrosyls^{21a} and isocyanides^{21b} is an experimental reality.

The reader's attention is also directed to a remarkable recent structure, that of $\text{MoO}_2[\text{CH}_3\text{NHCH}_2\text{C}(\text{CH}_3)_2\text{S}]_2$.^{22a} This is formally a $\text{Mo}(\text{VI})$, d^0 compound; so it does not fall into the general category of d^4 complexes studied in this paper. Yet it exhibits a related strong deformation from octahedral symmetry and a near approach of the two sulfur atoms in the inner coordination sphere. Partial S-S bonding is taking place.^{22a} We also mention briefly here a recently synthesized low-spin d^4 complex of $\text{Mo}(\text{II})$, $\text{Mo}(t\text{-BuS})_2(t\text{-BuNC})_4$.^{22b} In this molecule the *cis*-thiolate ligands move apart, angle S-Mo-S 115° . A theoretical analysis, to be reported elsewhere,^{22b} makes use of the arguments

(20) Hirst, D. M.; Hopton, J. D.; Linnett, J. W. *Tetrahedron Suppl.* **1963**, 2, 15. Gimarc, B. M. *J. Am. Chem. Soc.* **1970**, 92, 266-275. Bodov, N.; Dewar, M. J. S.; Harget, A.; Haselbach, E. *Ibid.* **1970**, 3854-3859. Fleischer, J.; Beckers, M.; Scharf, H.-D. *Tetrahedron Lett.* **1973**, 4275-4276. Haddon, R. C. *Ibid.* **1972**, 3897-3900. Beebe, N. H. F.; Sabin, J. R. *Chem. Phys. Lett.* **1974**, 24, 389-394. Haddon, R. C.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1975**, 97, 1645-1649.

(21) (a) Bhaduri, S.; Johnson, B. F. G. *Trans. Met. Chem.* **1978**, 3, 156-163. Bhaduri, S.; Johnson, B. F. G.; Pickard, A.; Raithby, P. R.; Sheldrick, G. M.; Zuccaro, C. I. *J. Chem. Soc., Chem. Commun.* **1977**, 354-355. See also: Meyer, C. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1976**, 98, 1364-1371. Hendriksen, D. E.; Meyer, C. D.; Eisenberg, R. *Inorg. Chem.* **1977**, 16, 970-972. Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, 96, 3325-3326. Gwost, D.; Caulton, K. G. *Inorg. Chem.* **1974**, 13, 414-417. (b) Lam, C. T.; Corfield, P. W. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, 99, 617-618.

(22) (a) Stiefel, E. I.; Miller, K. F.; Bruce, A. E.; Corbin, J. L.; Berg, J. M.; Hodgson, K. O. *J. Am. Chem. Soc.* **1980**, 102, 3624-3626. (b) Kamata, M.; Yoshida, T.; Otsuka, S., to be published. Kamata, M.; Hirotsu, K.; Higuchi, T.; Tatsumi, K.; Hoffmann, R.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, 103.

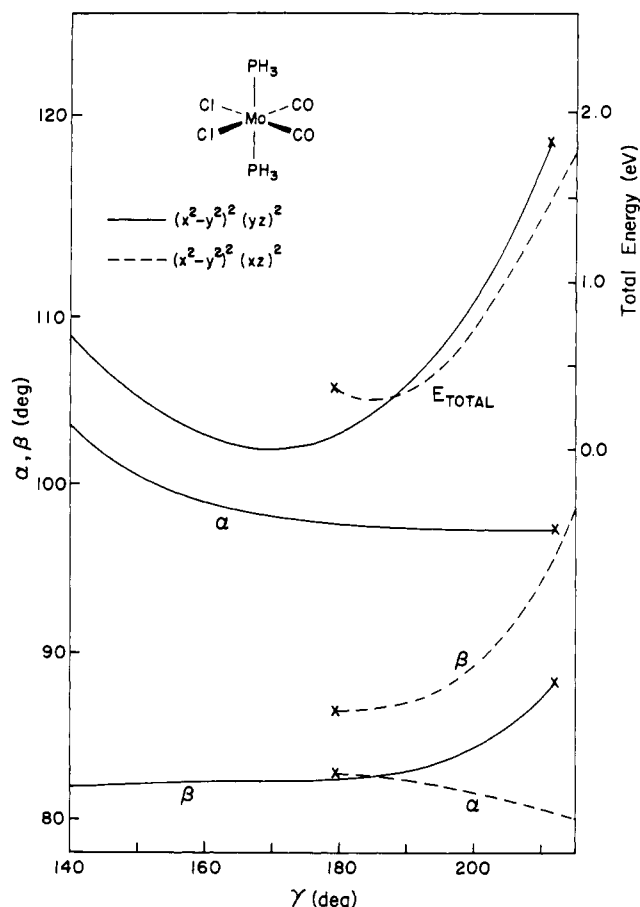
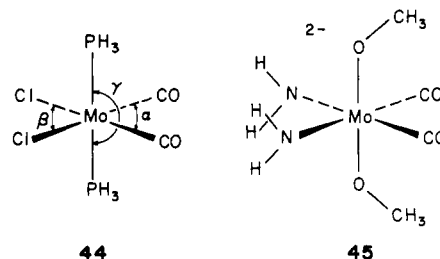


Figure 6. $\text{Mo}(\text{CO})_2(\text{PH}_3)_2\text{Cl}_2$ within C_{2v} symmetry. The plotted values of α and β are those optimized for a fixed value of δ . Crosses at ends of curve show where the xz and yz levels intersect and the valleys end. The α and β curves refer to the scale at left. The total energies of the two configurations are also plotted, marked E_{TOTAL} , and refer to the scale at right. The zero of this energy scale is at the minimum energy of the more stable configuration. Two configurations are plotted. The solid lines are for $(x^2 - y^2)^2(xz)^2$ and the dashed lines for $(x^2 - y^2)^2(yz)^2$.

tested in this paper to analyze the single minimum characterizing this particular ligand set.

Further Details of the Computed Energy Surfaces

We have previously presented in tabular form the angular parameters of the computed optimum geometries of $\text{Mo}(\text{CO})_2(\text{PH}_3)_2\text{Cl}_2$ (**44**) and $\text{Mo}(\text{CO})_2(\text{OCH}_3)_2(\text{py})_2$. Another model that



was studied for the Chisholm complexes was $\text{Mo}(\text{CO})_2(\text{OCH}_3)_2(\text{NH}_2)_2^{2-}$ (**45**). Here the pyridines were replaced by amides, for reasons of computational economy. At this point we should like to present a more detailed description of the outcome of these calculations.

To simplify the problem and reduce the dimensionality of the energy hypersurface, we have kept constant all the bond lengths and the local geometry of ligands. The geometries are specified in the Appendix. We have also kept the geometry of the basic framework under a constraint of C_{2v} symmetry. The total energy of the compounds is then a function of the angles α , β , and γ defined in **10** or **44** and **45**. A common feature for both surfaces

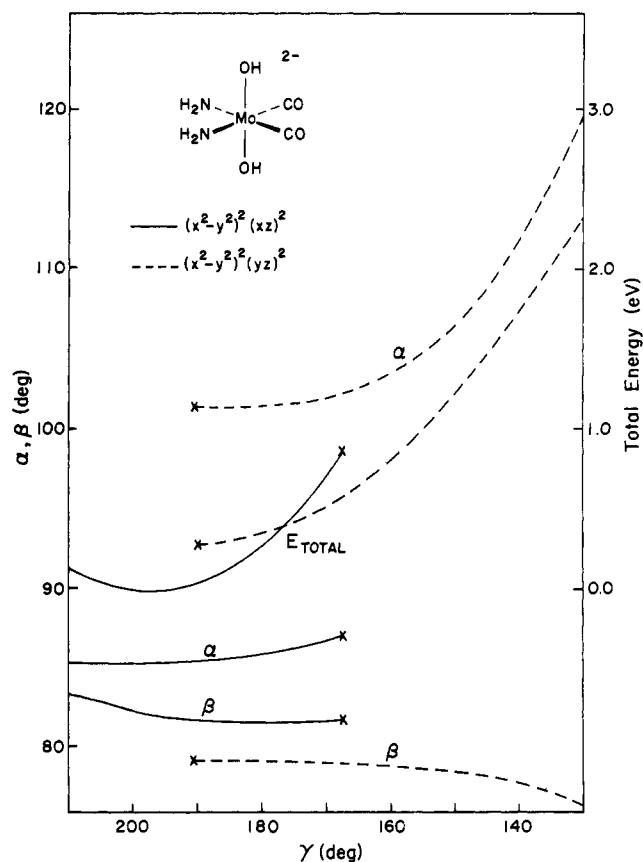


Figure 7. $\text{Mo}(\text{CO})_2(\text{OCH}_3)_2(\text{NH}_2)_2^{2-}$ within C_{2v} symmetry. The plotted values of α and β are those optimized for a fixed value of γ . Crosses at ends of curves show where the xz and yz levels intersect and the valleys end. The α and β curves refer to the scale at left. The total energies of the two configurations are also plotted, marked E_{TOTAL} , and refer to the scale at right. The zero of this energy scale is at the minimum energy of the more stable configuration. Two configurations are plotted. The solid lines are for $(x^2 - y^2)^2(yz)^2$ and the dashed lines for $(x^2 - y^2)^2(xz)^2$.

is that there are only two valleys on them. These valleys correspond to the configurations $(x^2 - y^2)^2(xz)^2(yz)^0$ and $(x^2 - y^2)^2(yz)^2(xz)^0$. We have chosen one of the angles, γ , as an independent variable and explored in more detail only the bottoms of these valleys. The results are shown in Figure 6 for $\text{Mo}(\text{CO})_2(\text{PH}_3)_2\text{Cl}_2$ and in Figure 7 for $\text{Mo}(\text{CO})_2(\text{OCH}_3)_2(\text{NH}_2)_2^{2-}$. The given values of the angles α and β are optimized for fixed values of γ , and these optimized α and β are plotted in the figures, along with the total energy.

The energy scales on which the total energy is plotted are very different for the two molecules. Note that the valleys "go past each other", finishing at a point where the xz and yz levels finally cross each other. This is marked on both figures by a cross. Such a continuatoin of the two valleys is a typical feature of constrained surfaces for forbidden reactions.²³ The quantitative results of EH calculations presented here are in agreement with the previous qualitative analysis.

For the former complex [$\text{Mo}(\text{CO})_2(\text{PH}_3)_2\text{Cl}_2$, Figure 6] there exists a distinct minimum of the total energy for either electronic configuration. The lower energy minimum agrees in its trends of distortion with the actual complex.⁸ The EH total electronic

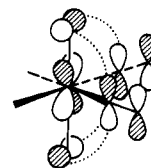
energy is 0.24 eV below that of the same complex with an octahedral geometry and 0.32 eV below the higher energy minimum. The separation between HOMO (yz) and LUMO (xz) is calculated here as 0.43 eV.

In the case of the optimized geometry with a higher energy, the deformation is again in accord with the qualitative arguments presented earlier. Now the separation between HOMO (xz) and LUMO (yz) is only 0.08 eV.

Could the existence of two minima with significantly different geometry be a reason for the low quality of the X-ray data of **6**? Certainly it would be interesting to have more crystallographic studies of molecules in this family, to see whether in some case both minima could be realized.

In the case of the $\text{Mo}(\text{CO})_2(\text{OR})_2(\text{NH}_2)_2^{2-}$ molecule, only one of the two valleys on the energy surface reaches its minimum. This minimum lies 0.36 eV below the energy for the octahedral geometry. The energy difference between HOMO (xz) and LUMO (yz) is 0.27 eV for the optimized geometry. Again, the trend of distortion for the optimized geometry agrees with qualitative arguments.

The cause for the failure of the second valley to reach a minimum, and for the unanticipated variation with γ , can be traced to another ligand-ligand interaction that we did not discuss in the previous section. This is a weak antibonding interaction between y AO's of the oxygen atoms of the OR groups and z AO's of the carbonyls within the yz HOMO (**46**). Because $\alpha > 90^\circ$,



46

this effect can outweigh the destabilization of the LUMO, xz , through hybridization.

The reader will note that we compute but small gaps between filled and unfilled levels for both the models for **4** (0.25 eV) and **6** (0.43 eV). **4** is definitely diamagnetic, low spin, at room temperature, and **6** probably so. Now the extended Hückel procedure of course does not compute directly the difference in energy between low-spin and high-spin configurations. It has been our experience that a gap of at least 0.5–1.0 eV between HOMO and LUMO is typically calculated for molecules which are known to be low spin. So these small gaps are surprising. Perhaps spin-orbit coupling should be taken into account—one wishes that we understood better the magnetic properties of second and third row transition metals.

Some General Observations on $\text{ML}_2\text{L}'_2\text{L}''$ Complexes

With the assistance of the qualitative arguments presented above, it is possible to conjecture about distortion trends in a general $d^4\text{-ML}_2\text{L}'_2\text{L}''$ transition-metal complex. The basic feature required for a large departure from a pseudo octahedral geometry, within C_{2v} symmetry, is a splitting of the d_x levels in the pattern one below two. In the molecules discussed above this is accomplished by two *cis*-carbonyls, i.e., by two outstanding *cis* π acceptors. In some sense the condition for distortion here is equivalent to a condition for maximum realization of a second-order Jahn-Teller distortion.²

Two strong trans acceptors would cause a splitting of d_x levels in the reverse sense, two below one. Such a splitting would provide the possibility of deformation and/or low stability for d^2 transition-metal complexes. But quite aside from the greater kinetic instability likely from the electronic deficiency, the diversity of properties probably would be smaller than for d^4 complexes, because only one geometry controlling level would be occupied.

For low-spin d^4 complexes in general, two electronic configurations, each with distinct geometrical consequences, must be explored. For each electronic configuration the existence of two well-defined minima is not a priori excluded. Furthermore, even

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(24) Bellard, S.; Rubinson, K. A.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1979**, *35*, 271–274. See also: Rubinson, K. A. *J. Am. Chem. Soc.* **1976**, *98*, 5188–5190. Barton, T. J.; Grinter, R.; Thomson, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 608–611. Schmidling, D. J. *J. Mol. Struct.* **1975**, *24*, 1–8. Formally isoelectronic $\text{CpM}(\text{CO})_3$ units, $M = \text{Cr}, \text{Mo}, \text{W}$, do dimerize: Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086–1090. *J. Am. Chem. Soc.* **1974**, *96*, 749–754. Goh, L.-Y.; D'Aniello, M. J., Jr.; Slater, S.; Muetterties, E. L.; Tavaniapour, I.; Chang, M. I.; Fredrich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192–197.

if a deformation should occur to increase the energy gap between HOMO and LUMO, the separation of the two configurations or minima may not be big enough to preclude the possibility of temperature-dependent phenomena (e.g., magnetic properties and stereochemical nonrigidity). This is because the gap depends on nuclear motion and the switching of occupation of molecular orbitals can be achieved by nuclear motion.

d^4 ML_6 Complexes

To give symmetry arguments their full play, we turn our attention from $ML_2L_2'L_2''$ to the general problem of deformation in d^4 ML_6 transition-metal complexes. These are relatively rare compounds— $Ti(CO)_6$ and $Ti(N_2)_6$ have been claimed in a matrix,^{12a} there are some hexacyanides, e.g., of Cr(II) and Mn(III),^{12b} and hexachlorides and fluorides of the $MnCl_6^{3-}$, $RuCl_6^{2-}$, IrF_6^- , and PtF_6^- type.^{12c} Accurate structural information is rare. There is also the long standing structural problem of the related d^5 $V(CO)_6$ for which a crystal structure recently has become available.²⁴ This molecule is very close to octahedral and shows no evidence for association in the solid. While $V(CO)_6$ does not have a d^4 configuration, it shares with the d^4 complexes the problem of a hole in the t_{2g} set.

To examine the basic σ electronic structure of such complexes, we have studied a hypothetical MoH_6^{4+} . π -donating and -accepting effects were then introduced in $MoCl_6^{4+}$ and $V(CO)_6^{+}$. Some calculations were also done on $V(CO)_6$ itself.

In general, octahedral d^4 - ML_6 complexes should be a subject to first order Jahn-Teller (FOJT) distortion.¹⁴ This classical analysis tells us that there are two (and only two) symmetry lowering motions available for lowering the total electronic energy and removing orbital state degeneracy. Those are a motion of t_{2g} symmetry, leading to a descent in symmetry from O_h to D_{3d} symmetry, and a deformation coordinate of e_g symmetry, lowering the symmetry of the molecule from O_h to D_{4h} . It should be recalled that the FOJT prescribes only which distortion must *start* for a symmetric system possession electronic degeneracy. It does not tell us anything about where a distortion ends. Nor can it exclude other deformations, whose cause is not bound to first-order correction terms in the energy.¹⁴

MoH_6^{4+}

MoH_6^{4+} is the simplest possible model for octahedral d^4 transition-metal complexes with σ -type interactions only. A reasonable value for a Mo-H distance might be 1.7 Å; for instance a neutron diffraction study of Cp_2MoH_2 gives Mo-H = 1.685 Å.²⁵ Extended Hückel calculations would not be expected to give a good Mo-H distance and they do not, Mo-H optimizing at a much too short 1.257 Å. We would not normally seek that minimum, but we did so in this case, for we wished to examine the tetragonal distortion, in which bond length vary.

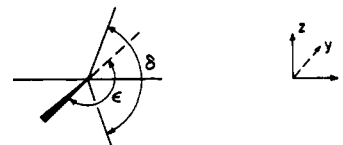
The perfectly octahedral hexahydride of course has a pure metal d t_{2g} set. The trigonal deformation, $O_h \rightarrow D_{3d}$, splits t_{2g} into $a_{1g} + e_g$. Only the e_g orbital is affected, destabilized by the deformation. The total energy (calculated for the lowest one-electron energy configuration) favors the ideal octahedron at both Mo-H distances (1.7 and 1.257 Å). The tetragonal deformation, $O_h \rightarrow D_{4h}$, does not affect the t_{2g} block at all. If carried out at the EH optimum geometry, it also is destabilizing.

Thus neither of the two distortions predicted by the FOJT theorem provides a lower calculated total energy. In the tetragonal distortion the degeneracy of t_{2g} is not even removed. It appears that we have a failure of the FOJT theorem within the constraints of the extended Hückel model. But this is not quite right. The Jahn and Teller reasoning is based on the linear first-order perturbation theory term in energy and is, of course, valid without exception for a many electron system. But in the simplified one-electron picture of the EH method, the t_{2g} orbitals of MoH_6^{4+} are not only degenerate but also are *not involved* in any bonding. The first-order perturbation energy term has no handle with which

to offset these orbitals. It would if, for instance, we added $2p$ functions to the hydrogen basis sets, but even then the force of first-order term would be tiny.

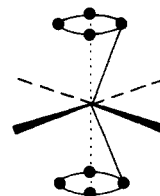
We have already mentioned that FOJT arguments cannot exclude other deformations, ones which are not based on the first-order perturbation energy term. In fact we have explored every mode of symmetry descent in which one changes solely the angles within MoH_6^{4+} . The only deformation which provides MoH_6^{4+} with a lower total energy is one to C_{2v} symmetry.

Two such C_{2v} geometries are possible. The first one is described by the same angles α , β , and γ as for $ML_2L_2'L_2''$ complexes (11). The second one bends two axial Mo-H bonds toward one of the equatorial hydrogens, as shown in 47. In 47 δ is the trans angle



47

in the xz plane and ϵ the trans angle in the xy plane. Both C_{2v} distortions are ever so slightly stabilizing. That in the C_{2v} geometry where axial bending is in between the equatorial ligand 11 optimizes at $\alpha = 91.3^\circ$, $\beta = 90.2^\circ$, and $\gamma = 156.2^\circ$ at 0.028 eV (0.64 kcal/mol⁻¹) below the octahedron. The other C_{2v} bending, in a plane containing equatorial ligands, optimizes at $\delta = 158.0^\circ$ and $\epsilon = 180.4^\circ$ at 0.024 eV (0.56 kcal/mol⁻¹) below the octahedron. This is at Mo-H = 1.7 Å. For a shorter Mo-H distance the minima deepen. For instance, for Mo-H = 1.257 Å the C_{2v} minimum is at $\alpha = 91.3^\circ$, $\beta = 90.2^\circ$, and $\gamma = 148.6^\circ$, 1.9 kcal/mol⁻¹ below the octahedron. Given the octahedral symmetry there are 12 minima of each type. An easy precession of axial hydrogens around the octahedral geometry follows from the small difference in energy between the C_{2v} minima and the lack of barriers between them (48).



48

Though the extent of deformation is small and the associated energy minimum is shallow, it is of interest to elucidate the origins of the distortion. The departure from O_h into either C_{2v} symmetry follows a coordinate which is totally symmetric in C_{2v} . It follows solely from symmetry considerations that along this coordinate the ideal octahedral geometry must be at either a minimum or a maximum of the total electronic energy and the first-order perturbation term in energy must be zero at this point. Furthermore, at least near this point, the change of E_T must be governed by second- (or higher) order terms. It can be shown by using the Imamura approach^{16d} that the driving force for $O_h \rightarrow C_{2v}$ deformation is the second-order energy term and the stabilizing effect comes from b_2 molecular orbitals. One of these is descended from the t_{2g} set in O_h .

An alternative interpretation of the deformation utilizes our previous notions concerning hybridization. Any C_{2v} departure of a hydrogen from ideal octahedral geometry turns on σ -type interaction with at least one of the d_x AOs of the metal. This always has destabilizing consequences for the d_x AO. As long as only one such d-block AO is destabilized, there is no harm, for one d_x AO must in fact be vacant for a d^4 complex. In fact the destabilization of the one AO has consequences in M-L bonding levels below the d block: the d orbital hybridizes a p function and thus improves a M-L bonding orbital. We have already used this type of reasoning for $ML_2L_2'L_2''$ complexes.

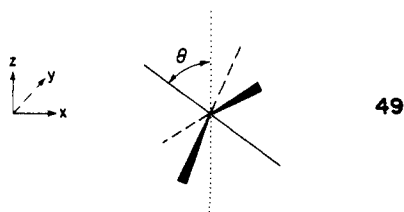
Note that the same argument would cause a d^6 complex to remain at an octahedral geometry—the formerly vacant d_x orbital

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is now occupied, and as usual destabilization in the higher MO of a pair of interacting ones overcomes stabilization in a lower one.

MoCl₆⁴⁻

Chloride ligands provide p orbitals to interact with the metal t_{2g} set. That means the FOJT effect must manifest itself even in EH calculations. As mentioned above, there are two vibrational coordinates which should decrease the total energy and remove orbital degeneracy: t_{2g}(O_h → D_{3d}) and e_g(O_h → D_{4h}). For the first of these it is convenient to choose a coordinate system with the z axis along a C₃ axis of the octahedron (49). Then one of

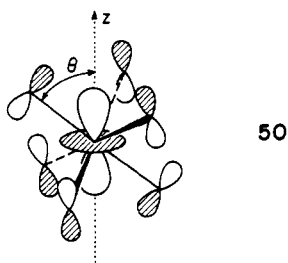


the t_{2g} AO's is pure z² and the other two are a linear combination of xz, yz with x² - y², and xy.²⁶ The deformation may be measured by the angle θ between the ligands and the z axis.

A small departure of the angles from the octahedral value ($\theta = \tau = 54.79^\circ$) in either direction lowers the total energy and removes the degeneracy of t_{2g} orbitals. The minima of E_T occur at $\theta = 53.98^\circ$, energy 0.0096 eV below the octahedron, and $\theta = 55.12^\circ$, with E_T decreased by 0.0024 eV. This is for a Mo-Cl bond length of 2.50 Å, maintained throughout the deformation.

The descent in symmetry from O_h to D_{3d} of course produces a splitting of t_{2g} into a_{1g} + e_g. The ordering of these levels is a_{1g} below e_g for $\theta > \tau$ and e_g below a_{1g} for $\theta < \tau$. Thus the deeper minimum is a true one, but the more shallow one, $\theta > \tau$, is a minimum only within the D_{3d} constraint and is subject to a further symmetry-lowering deformation. Throughout this section the total energy is the lowest extended Hückel configuration energy, i.e., it corresponds to the configuration (a_{1g})²(e_g)² for $\theta > \tau$ and (e_g)⁴ for $\theta < \tau$.

The rationale for the observed splitting (a_{1g} above or below e_g) is easiest made by focusing on the a_{1g} z² orbital (50). The overlap



between the z² and a ligand p orbital is not optimized at $\theta = \tau$ but in fact for $\tau = 45^\circ$.²⁷ Thus a moderate decrease in θ from the octahedral value will increase π overlap and an increase in θ will decrease it. Increasing overlap implies destabilization of the d orbital for a donor substituent. The e_g set behaves in a reverse way.

For MoCl₆⁴⁻ extended Hückel calculations provide, accidentally, a reasonable optimized MoCl distance of 2.42 Å. Figure 8 shows a surface for a tetragonal distortion (O_h → D_{4h}), starting from an octahedron with that distance. Again there occur two minima: a lower one with E_T = 0.210 eV below the saddle point of the octahedron, two axial bond lengths of 2.59 Å and four equatorial ones of 2.33 Å, and a higher one with a stabilization of 0.095 eV, axial bonds of 2.28 Å and equatorial ones of 2.50 Å. The known

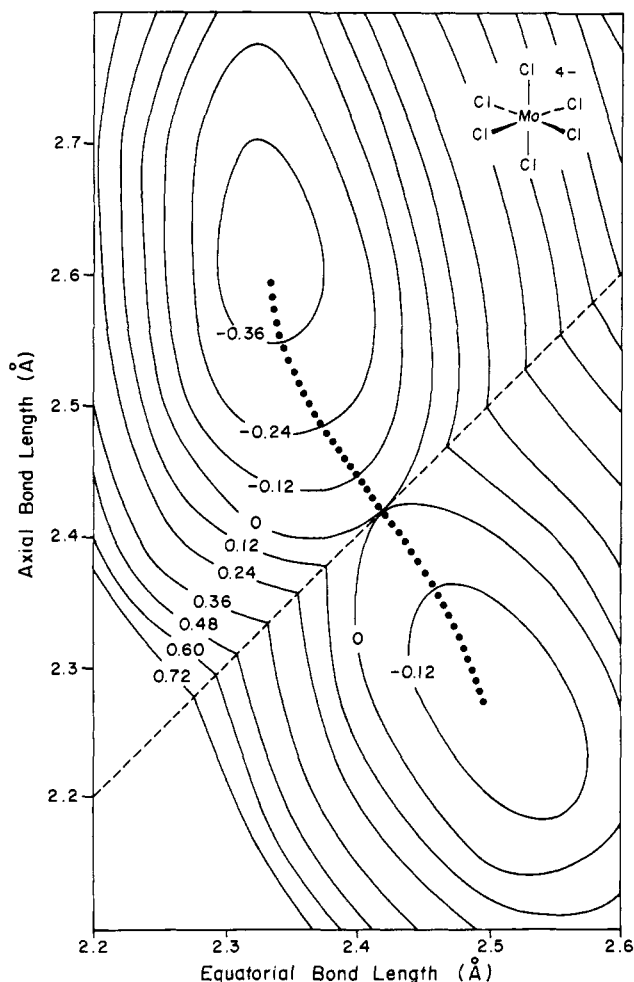


Figure 8. A potential energy surface for the O_h → D_{4h} distortion of MoCl₆⁴⁻. The contours are in eV relative to an energy zero at the most stable octahedron. The electronic configurations switch at the dashed line. The heavy dotted line connects the two minima within a D_{4h} constraint.

crystal structures of d⁴ halides show no departure from octahedral symmetry, within their limited accuracy.^{13c}

The symmetry analysis here is also familiar. In D_{4h} t_{2g} correlates with b_{2g}(xy) and e_g(xz and yz). Elongation along the z axis, contraction in the equatorial plane destabilizes b_{2g}, stabilizes e_g for the donor case. The reverse splitting obtains for contraction along z axis and elongation in the equatorial plane. The former splitting is the desired one, for it creates a closed shell configuration.

The O_h → C_{2v} deformation does not provide MoCl₆⁴⁻ with an energy minimum. It appears that the first-order Jahn-Teller effects operative in trigonal and tetragonal distortions are substantially stronger than the second-order effects that are required to produce the C_{2v} distortion. π bonding with halides is weaker than with carbonyls and the d orbitals are destabilized, less susceptible to hybridization through ligand σ functions. Finally this may be a case where ligand-ligand interactions, here between Cl lone pairs, are significant in setting steric constraints to departure from the octahedral polytope.

V(CO)₆⁺ and V(CO)₆

d⁴ V(CO)₆⁺ must also be subject to a FOJT effect. When we take into account that CO is a π acceptor, while Cl is a donor, the sense of the stabilizing O_h → D_{3d} and O_h → D_{4h} distortions is reversed for V(CO)₆⁺ as compared to MoCl₆⁴⁻. Furthermore we find that in distinction to MoCl₆⁴⁻, a strong O_h → C_{2v} distortion takes place in V(CO)₆⁺.

From the point of view of symmetry the problem of the O_h → D_{3d} deformation is the same one as for MoCl₆⁴⁻. The shape of the a_{1g} orbital for D_{3d} V(CO)₆⁺ is the same as for MoCl₆⁴⁻ (see

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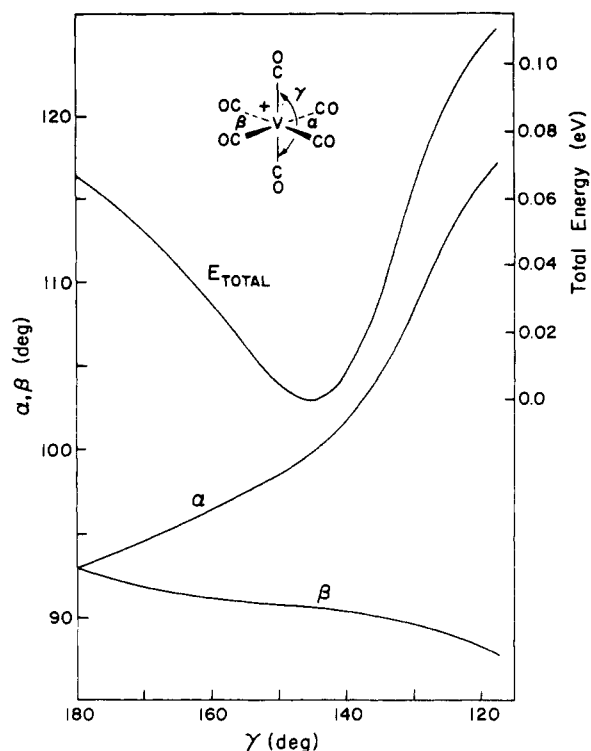


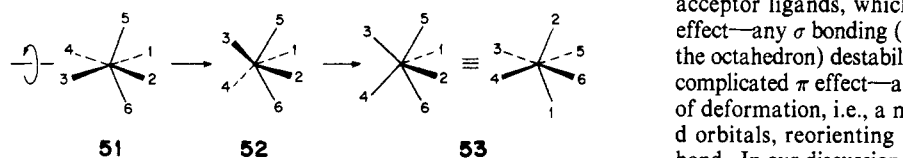
Figure 9. The $O_h \rightarrow C_{2v}$ distortion of $V(CO)_6^+$. The plotted values of α and β are those optimized for a fixed value of γ . They refer to the scale at left. The total energy is also plotted, referring to the scale at right, with an arbitrary energy zero.

47), except for the phase relation between z^2 and π orbitals of ligands. One can easily see that the direction of the $O_h \rightarrow D_{3d}$ distortion which destabilizes the a_{1g} orbital (and stabilizes the e_g orbitals) is to increase the angle θ from the octahedral value τ . This is in accord with EH calculations. These afford an energy minimum for $\theta = 56.4^\circ$, a total energy of 0.0376 eV below the octahedral one, and a nondegenerate electronic configuration. The greater $\Delta\theta = 1.69^\circ$ as compared with $\Delta\theta = 0.76^\circ$ for $MoCl_6^{4-}$ agrees with the greater capacity for π interaction of the carbonyls. The opposite change of θ gives a higher energy minimum but only under the D_{3d} constraint, since the splitting of the d_{π} levels here is one below two.

An EH calculation yields for the octahedral $V(CO)_6^+$ an optimum V-C bond length of 1.52 Å, which is too short. The $O_h \rightarrow D_{4h}$ distortion obeys the FOJT effect but was not examined in greater detail.

Unlike $MoCl_6^{4-}$ the $V(CO)_6^+$ is stabilized by an extensive $O_h \rightarrow C_{2v}$ distortion. Referring to the above defined angles the energy minimum of the C_{2v} $V(CO)_6^+$ molecule lies at $\alpha = 99.6^\circ$, $\beta = 90.6^\circ$, and $\gamma = 145.1^\circ$ and is 0.09 eV below the octahedral geometry. A cut along the bottom of a valley on the energy surface is shown in Figure 9, as a function of the angle γ .

The C_{2v} distortion in this molecule is so severe that it does not take much energy to approach the geometry of a bicapped tetrahedron. For instance it takes only 0.11 eV in our calculations to come to $\alpha = \gamma = 117^\circ$ and $\beta = 86^\circ$. This is geometry 51. To



rotate the plane of C_3-M-C_4 around the twofold axis takes little energy, 0.02 eV to reach 52. Regenerating 53 completes a rearrangement. $V(CO)_6^+$ should be a highly fluxional molecule.

The carbonyls bend easily along a C_{2v} coordinate, because they are outstanding π acceptors. They stabilize the metal d_{π} levels, enhancing their ability to hybridize the σ -bonding orbitals. Finally,

in agreement with the conclusion of Figures 1 and 2, two *trans*-carbonyls should bend toward an angle opened up between two *cis*-carbonyls.

While information on $V(CO)_6^+$ is not available, to our knowledge, we do have crystal structures of two d^4 ML_6 systems. One is $Tc(NCS)_6^{3-}$.^{13c} The coordination geometry is approximately octahedral. The complex is not diamagnetic but has a magnetic moment characteristic of two unpaired electrons. A structure is also available for $Mn(CN)_6^{3-}$.^{13e}

Even if one had a spin-paired configuration for these molecules, there is no guarantee that any deformation of the complex would have been observed. Crystal packing forces can easily override the minute energies for deformation from an octahedron that we calculate. Nevertheless it is interesting to examine such structures and seek out structures with variable counterions. If there is a soft surface, once in a while crystal packing forces will conspire to give a molecule that is strongly deformed.

$V(CO)_6$ has five electrons in the t_{2g} set. The level that is destabilized in any deformation that was advantageous for $V(CO)_6^+$ is now single filled. This should attenuate any deformation tendencies. For example, the angular excursion along the D_{3d} coordinate is to $\theta = 55.5^\circ$ and is worth only 0.0084 eV (for V-C 1.90 Å). No deformation toward C_{2v} is computed—the destabilization of the singly occupied MO simply overrides the tendencies of the lower levels. The molecule should remain very close to octahedral and apparently does so in the solid state.²⁴

In concluding our discussion of ML_6 complexes, we note once again, with disappointment, the relative *inutility* of elegant Jahn-Teller arguments, first order or second order, in guiding us to geometrical predictions in these molecules, not to speak of the less symmetrical $ML_2L_2'L_2''$. Burdett²⁸ has made this point, too.

Conclusions

The starting point for this research effort was an observation of substantial geometrical deformations from the perfect octahedron in three low-spin d^4 Mo(II) and one W(II) complexes. In a general way, one might have expected a first-order or second-order Jahn-Teller deformation in a molecule that must have only two of three relatively low-lying levels (the t_{2g} set) occupied. But what type of deformation? The curious feature was that in two of the compounds, both of the type $Mo(CO)_2L_2L_2''$, the *cis*-carbonyls departed substantially from their ideal octahedral angle. In 4 they came together and in 7 they moved apart.

The problem that presented itself so obviously here is the basic query of structural chemistry: Why do molecules have the structures that they do? Ideally we would have liked to predict the geometry of any d^4 complex. Realistically we settled on C_{2v} deformations in $ML_2L_2'L_2''$ complexes, with a subsequent brief return to more symmetrical ML_6 structures. Jahn-Teller arguments did not provide much guidance. We were able to implement a protocol for predicting the preferred geometry of any $ML_2L_2'L_2''$ by (a) partitioning the problem into pairwise additive effects of ML_2 , ML_2' , and ML_2'' subunits and (b) within each ML_2 set using the σ and π -donating or -accepting capability of L as the main control of the ordering in energy, and change in energy with angular deformation, of the three crucial d block levels.

In the analysis of each ML_2 subunit three factors were essential: (1) a first-order π effect—how overlap of ligand π orbitals varied with angle—here it was important to distinguish between donor and acceptor ligands, which naturally had opposite effects; (2) a σ effect—any σ bonding (and such was turned on by departure from the octahedron) destabilized some subset of the d levels; (3) a more complicated π effect—a hybridization of the d functions as a result of deformation, i.e., a mixing of metal s and p character into the d orbitals, reorienting them, and so changing their ability to π bond. In our discussion of hybridization we found useful a general principle that nonbonding orbitals will change, as ligands move, in such a way as to keep the ligands as much as possible in the nodal planes of such orbitals.

Table II. Parameters Used in Extended Hückel Calculations

orbital	H_{ii} , eV	ξ_1	ξ_2	C_1^a	C_2^a	
V	3d	-11.00	4.70	1.70	0.4755	0.7052
	4s	-8.81	1.30			
	4p	-5.52	0.875			
Mo	4d	-11.06	4.54	1.90	0.5899	0.5899
	5s	-8.77	1.96			
	5p	-5.60	1.90			
W	5d	-10.37	4.982	2.068	0.6685	0.5424
	6s	-8.26	2.341			
	6p	-5.17	2.309			
P	3d	-7.00	1.40			
	3s	-18.60	1.60			
	3p	-14.00	1.60			
S	3s	-20.00	1.817			
	3p	-13.30	1.817			
Cl	3s	-30.00	2.033			
	3p	-15.00	2.033			

^a Coefficients in a double- ξ expansion.

In general, a given ML_2 subunit, e.g., $M(CO)_2$, generates a double minimum in the total energy. In one configuration the ligands move together and in the other they move apart. The singling out of one of these two minima as the deeper one for a specific molecule is a consequence of the composite effect of the ML_2 , ML_2' , and ML_2'' subunits.

We found we could rationalize the observed C_{2v} deformations. The understanding that we achieved and the procedure evolved

in this analysis is, however, more important than the specific molecules which led us to the problem. The way is clear to an analysis of deformations in any coordination geometry, for any d-electron configuration.

Acknowledgment. We are grateful to J. L. Templeton for bringing several structures to our attention and to him and M. H. Chisholm for informing us of their work prior to publication. Helpful comments were made by the referees. Thanks are due to IREX for making possible the stay of Pavel Kubáček at Cornell, the National Science Foundation for its generous support of our work through research Grant CHE 7828048, and the Materials Science Center at Cornell University, (MSC Grant DMR-7681083). Pavell Kubáček would like to express his appreciation for the hospitality of our research group at Cornell. We are grateful to J. Jorgenson for the drawings and O. Eisenstein and D. Hoffman for their help in the processing of this paper.

Appendix

All calculations were performed by using the extended Hückel method,²⁹ with weighted H_{ij} 's.³⁰ Unless mentioned the experimental bond lengths were used.

The values for the H_{ij} 's and orbital exponents are listed in Table II. The parameters for C, N, O, and H are the standard ones.²⁹

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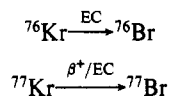
Reactions of Recoil Bromine Formed by the $^{76,77}\text{Kr} \rightarrow ^{76,77}\text{Br}$ Systems with Simple Hydrocarbons. Solid-Phase Reactions¹

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Abstract: Bromine atoms formed by the systems $^{76}\text{Kr} \rightarrow ^{76}\text{Br}$ and $^{77}\text{Kr} \rightarrow ^{77}\text{Br}$ were allowed to react with simple hydrocarbons in the solid phase at 77 K and the products of the reactions studied. The product distributions for the two systems varied greatly, and these variations are discussed in terms of the charge and kinetic energy of the two recoiling bromine species. It is concluded that the product differences are due to altered radical environments arising from charge neutralization for ^{76}Br and recoil energy dissipation for ^{77}Br .

In this study activation of bromine atoms from krypton decay will be considered. The parent-daughter systems used to generate such bromine atoms are



Relevant physical data for these processes are shown in Table I.

These two systems are interesting to compare because the decay mode and energy released in each process is different, leading to contrasts in the initial charge states and recoil energies of the two

bromine atoms. As shown in Table I, the recoil energies are 7.5 eV for ^{76}Br , 67.5 eV for electron-capture decay formation of ^{77}Br , and 7.2 eV (average; 37.8-eV maximum) for positron decay formation of ^{77}Br .

Determination of the initial charge states is somewhat more complicated. For the electron-capture case, the atom is formed with a high positive charge (average $\sim 5+$) due to inner-shell electron-capture process and the subsequent electron cascade which results in the emission of Auger electrons and x radiation.⁸ For the case of positron decay the atom would simply be left with a net 1- charge due to the loss of the 1+ charged positron. Therefore all of the ^{76}Br atoms would be formed with at least a 1+ charge since ^{76}Kr decays nearly 100% via electron capture. For the ^{77}Br case, 16% would be formed as in the ^{76}Br case and 84% would initially be formed as $^{77}\text{Br}^-$. There are two factors which modify these considerations to give the net charge spectra shown in Figure 1 for ^{77}Br and Figure 2 for ^{76}Br . These are the processes of electron shake-off and internal conversion of the γ -rays from the excited bromine nuclei.

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