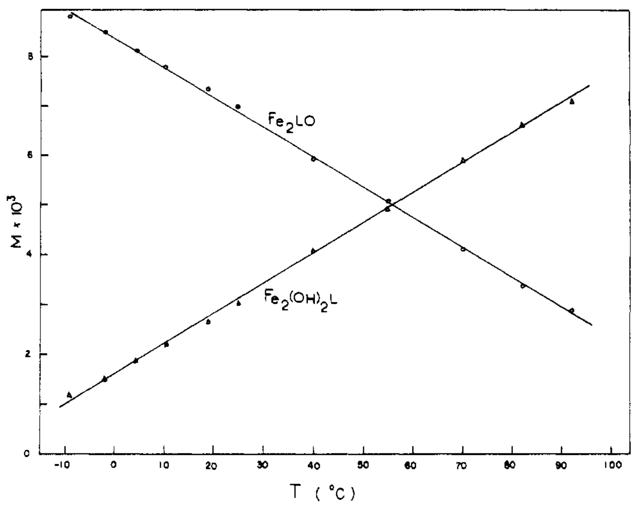
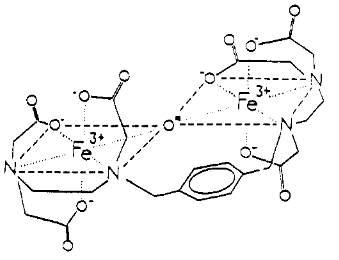


Figure 8. Concentrations of the intramolecular μ-oxo complex, Fe_2LO (L = PXED3A), and the dihydroxy chelate, $Fe_2(OH)_2L$, plotted as a function of temperature at $[Fe^{3+}]_T = 0.0200$ M, $[PXED3A]_T = 0.0100$ M, and pH 9.30.

probably deviates appreciably from the ideal 180° generally observed in other M–O–M systems.[26] Crystal structures of several μ-oxo Fe(III) complexes containing O and N donor groups[13,27,28] were also reported to have nonlinear Fe–O–Fe angles. The characteristic orange-red color, of the Fe(III)-PXED3A μ-oxo complex, has a molar extinction coefficient at 475 nm of 180, which is similar in magnitude to those reported for the analogous μ-oxo dimers of Fe(III)-HEDTA and Fe(III)-EDTA.[13,19] Although no evidence has been provided in this work on the structure of the Fe(III)-PXED3A μ-oxo chelate, the stoichiometry of complex formation, the equilibrium constants involved, and the electronic absorption spectrum indicate that the most reasonable structure of the μ-oxo dimer is that indicated schematically by formula **2**.



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Acknowledgment. This research was supported by Grant A-259 from the Robert A. Welch Foundation.

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Electronic Structure and Dissociation Energy of the Molybdenum-to-Molybdenum Triple Bond

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Generalized molecular orbital (GMO) and configuration interaction (CI) calculations are reported for the series N_2, P_2, As_2, Sb_2, and Mo_2H_6 in a large Gaussian basis set. Similar calculations are reported for Mo_2H_6 and $Mo_2(NH_2)_6$ in a smaller Gaussian basis set. The potential energy curve for Mo_2H_6 at the GMO–CI level has a minimum at 2.194 Å in excellent agreement with the Mo–Mo distance in a range of systems: $Mo_2(OCH_2CMe_3)_6$ at 2.222 Å, $Mo_2(NMe_2)_6$ at 2.214 Å, and $Mo(CH_2SiMe_2)_6$ at 2.167 Å. By comparing the calculated dissociation energies of the triply bonded diatomics and Mo_2H_6, we predict a dissociation energy for the molybdenum-to-molybdenum triple bond of 284 kJ mol^{-1}. The results indicate the importance of including the differential correlation energy, which in Mo_2H_6 contributes 70 kJ mol^{-1} to the dissociation energy. We find that the larger basis set increases the calculated dissociation energy by 40 kJ mol^{-1}. When we change the hydride ligand of Mo_2H_6 to an amino ligand in $Mo_2(NH_2)_6$, the dissociation energy increases 117 kJ mol^{-1}. A significant fraction of this increase is due to the π-donating ability of the NH_2 ligand, which results in an expansion of the Mo orbitals and a stronger bond. The relationship between the donor strength of the ligand and the expansion of the Mo orbitals may be responsible for much of the variation in the Mo–Mo triple-bond lengths.

Introduction

There has been considerable interest, recently, in determining the bond strengths of metal–metal bonds. Of particular interest are the bond strengths of multiply bonded metal–metal systems and their comparison to those of main-group multiple bonds. For experimental reasons a large fraction of this effort has been directed at determining the strength of the molybdenum-to-molybdenum and tungsten-to-tungsten double or triple bonds.[1-5]

The earliest experimental work was done on $Mo_2(N(CH_3)_2)_6$, for which the enthalpy of formation was accurately measured.[1] However, it was difficult to derive a value for the Mo–Mo triple-bond dissociation energy from this experiment because of the uncertainty in assigning a value for the Mo–$N(CH_3)_2$ bond energy and a formal oxidation state to the metal. The authors suggested a value of 592 ± 196 kJ mol^{-1} for the Mo–Mo triple-bond energy, but the error bars of the value are so large that a useful comparison to main-group bonds is prohibited.

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Adedeji et al. later reported the thermochemical measurements for a series of metal–metal triple bonds including $Mo_2(N(CH_3)_2)_6$.[2] They calculated $\bar{D}$(Mo–$N(CH_3)_2$) from $Mo(N(CH_3)_2)_4$ and transferred this value unchanged to $Mo_2(N(CH_3)_2)_6$. They identified $\bar{D}$(Mo≡Mo) as 398 ± 18 kJ mol^{-1}, where these error bars represent only the experimental error in the enthalpy determinations. Again the uncertainty of transferring bond enthalpy contributions is well documented, an uncertainty compounded in this molecule because an error in $\bar{D}$(Mo–$N(CH_3)_2$) enters sixfold into the calculated value for $\bar{D}$(Mo≡Mo).

The large uncertainty in the first reported value suggested that this number could be calculated more precisely than it could be measured. Recently, we reported some preliminary theoretical results for the dissociation energy of a model compound, Mo_2H_6, in a small basis set.[3] By determining the difference between the calculated and experimental values for N_2 and P_2, we estimated the size of the basis set and correlation error and then extended this error to the dimolybdenum system. The dissociation energy was predicted to be 526 ± 63 kJ mol^{-1}.

Significant problems, however, existed in this calculation. First, the basis set was still too inaccurate to represent the system adequately. Second, the error estimate was computed by comparison to only two diatomics, N_2 and P_2. Third, although replacing the NMe_2^- ligands with H^- ligands was not expected to introduce large errors,[6] the differences in these two ligands did indicate that a better model compound might change the results. Fourth, because the Mo–Mo triple bond was more highly correlated than either the nitrogen or the phosphorus triple bond, the effects of different configuration interactions would influence the dissociation energy.

In this paper, we report calculations that attempt to minimize these sources of error. First, we have recalculated the dissociation energy of the model compound, Mo_2H_6, in a larger basis set so that we can more accurately describe the triple bond. Second, we have extended our calculations on triply bonded diatomics to include As_2 and Sb_2, also in large basis sets, in order to more accurately compare the diatomics and Mo_2H_6. Third, we have calculated the dissociation energy of $Mo_2(NH_2)_6$, a better model compound and one that allowed us to compare the effect of the two ligands, NH_2^- and H^-, in the same basis set. Fourth, we calculated the dissociation energy of Mo_2H_6 using several types of configuration interaction. Because the differential correlation energy was an important contribution in both the diatomics and Mo_2H_6, we were able to recover an equivalent fraction of the correlation energy.

Theory

Generalized Molecular Orbital Theory. The generalized molecular orbital (GMO) approach[7] is a limited type multiconfiguration self-consistent field (MCSCF) calculation. It provides an optimized set of primary orbitals for configuration interaction (CI) calculations and needs only modest additional effort beyond that needed for the Hartree–Fock–Roothaan (HF) or standard molecular orbital (MO) approach. In the standard MO approach for a 2*n*-electron closed-shell molecule, the MO's, which have been expanded in a basis set, are divided into doubly occupied and unoccupied sets as

$$(\phi_1 \text{---} \phi_n)^2 (\phi_{n+1} \text{---} \phi_m)^0 \tag{1}$$

In the GMO approach the previously doubly occupied orbitals are divided into a doubly occupied set (r set) and a strongly occupied set (t set), while the previously unoccupied orbitals are divided into a weakly occupied set (u set) and an unoccupied set (v set). These four sets of orbitals may be thought of as molecular core, valence, valence correlating, and virtual orbitals, respectively. The electronic configuration in the GMO framework may be written as

$$(\phi_1 \text{---})^2 (\text{---} \phi_n)^x (\phi_{n+1} \text{---})^y (\text{---} \phi_m)^0 \tag{2}$$

It is this shell structure, in which the orbitals are treated in sets with all orbitals in a set having equal occupation numbers, that led to the use of the name generalized molecular orbital theory.

The GMO wave function, which is consistent with the above orbital partitioning, is

$$\Psi = (1 - n_t n_u \lambda^2)^{1/2} \Psi_{oo} + \lambda \sum_t \sum_u \Psi_{tu} \tag{3}$$

where

$$\Psi_{oo} = |\phi_1 \bar{\phi}_1 \text{---} \phi_t \bar{\phi}_t \text{---} \phi_n \bar{\phi}_n| \tag{4}$$

$$\Psi_{tu} = |\phi_1 \bar{\phi}_1 \text{---} \phi_u \bar{\phi}_u \text{---} \phi_n \bar{\phi}_n| \tag{5}$$

and n_t and n_u are the number of orbitals in the t and u sets, respectively. Thus, the GMO wave function consists of a dominant single determinant Ψ_{oo}, plus a correlation function. This correlation function contains determinants constructed from all paired excitations from the strongly occupied (t) set to the weakly occupied (u) set. The total energy can be written as in eq 6, where h_i, J_{ij}, and K_{ij} are the one-electron, Coulomb,

$$E = \sum_i f_i h + \sum_i \sum_j (a_{ij} J_{ij} + b_{ij} K_{ij}) \tag{6}$$

and exchange integrals, respectively. In standard MO theory $f_i = 2.0$, $a_{ij} = 2.0$, and $b_{ij} = -1.0$. Because these coefficients do not depend on the orbital involved, one can solve the MO problem by the Roothaan procedure.[8] In a general MCSCF problem, these coefficients will depend on the individual orbitals involved. The real advantage of the GMO approach is that these coefficients depend on the set to which the orbitals belong but not on the individual orbitals. Thus, when the variation principle is applied to minimize the energy, the orbitals may be treated in groups as they are in the HF approach. Using a generalized coupling operator[9] to solve this problem, we only need to build two additional HF-like matrices beyond those needed in the ordinary MO approach. Thus, the efforts in obtaining optimized orbitals with the GMO procedure is only a small fraction of that needed by a general MCSCF calculation.

Details of the computational procedure have been given previously.[7] The choice of orbitals for each of the GMO sets is usually straightforward. Often the strongly occupied set (t) and the weakly occupied set (u) are respectively the filled valence orbitals and the virtual orbitals expected in a minimal basis calculation. Although the filled orbitals from a HF calculation resemble the natural orbitals of extensive CI calculations, the virtual orbitals usually do not bear a similar resemblance. Our previous results for H_2O and N_2[7] in large Gaussian basis sets showed that the GMO orbitals, both strongly occupied and weakly occupied, resembled the natural orbitals of an all single- and double-excitation CI calculation. The similarity of the orbitals was reflected both in the overlap between the GMO's and the MO's and in the correlation energies obtained with either set of orbitals.

Configuration Interaction. In the CI calculation it was important that we allow only excitations in the molecule that

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would vanish in the fragment. This insured that the molecule would dissociate into the proper HF fragments. After determining a set of GMO's with the strongly occupied set being the σ and two π orbitals of the triple bond and the weakly occupied set their antibonding counterparts, we did several types of configuration interaction calculations that met these conditions. First we did a full CI calculation within the triple bond, allowing excitations from the bonding orbitals of the triple bond into their antibonding counterparts. This scheme results in spin- and symmetry-adapted configurations for the diatomics and Mo_2H_6, respectively. Then, to improve this value for the correlation energy, we included other important correlations in the molecule by allowing excitations out of the *ns* orbital for the diatomics and the Mo–H bond for Mo_2H_6 but without enlarging the weakly occupied space. We then examined the effect of allowing excitations out of the semivalence 4s and 4p orbitals of Mo_2H_6.

In an effort to recover an equivalent fraction of the correlation energy from both the diatomics and Mo_2H_6, we next calculated the differential correlation energy. In this GMO calculation the orbitals involved in the triple bond, σ, π_x, π_y, π_y^*, π_x^*, and σ^*, were kept fixed and the GMO procedure was used to determine correlating orbitals for the remaining valence electrons, the *ns* orbitals of the diatomics, and the Mo–H bonds of Mo_2H_6. The differential correlation energy, which vanishes for the fragments, resulted from simultaneous excitation of a single electron in the triple bond to its antibonding orbital and of an electron in a different region of the molecule to its antibonding orbital. For diatomics this meant a single excitation from the *ns* orbital to the *ns** orbital and a single excitation in the triple bond. For Mo_2H_6 this involved a single excitation from the Mo–H bonding orbital to the Mo–H antibonding orbital and a single excitation in the triple bond. This was found to have a large effect on the dissociation energy both for the diatomics and for Mo_2H_6.

Theoretical Details

Geometry. The bond distances for N_2 and P_2 were taken from Huheey,[10] and the bond distances for diarsenic and diantimony were estimated with use of Badger's rule.[11] The values used for these four diatomics were 1.098, 1.893, 2.13, and 2.53 Å, respectively.[12]

The geometry of Mo_2H_6 was based on the crystal structure of $Mo_2(N(CH_3)_2)_6$.[13] The Mo–Mo bond length and the Mo–Mo–H bond angle were the same as the average values in $Mo_2(N(CH_3)_2)_6$, 2.214 Å and 103.7°, respectively. The Mo–H bond length was taken to be 1.60 Å, a typical bond length for transition-metal hydrides, and the geometry was assumed to be staggered and to have D_{3d} symmetry.

The geometry of $Mo_2(NH_2)_6$ was also based on the crystal structure of $Mo_2(N(CH_3)_2)_6$ with the same Mo–Mo bond length and Mo–Mo–N bond angle and the same Mo–N bond length (1.98 Å) and Mo–N–H bond angle (133.4°). Like Mo_2H_6, the geometry of $Mo_2(NH_2)_6$ was assumed to be staggered and to be D_{3d}.

In all of the calculations reported the Mo–L geometry remained fixed. Therefore the potential energy curve and dissociation energy refer to changing and breaking only the Mo–Mo bond.

Basis. The basis functions employed in this study were obtained from a least-squares fit of a linear combination of Gaussians to near-Hartree–Fock-quality Slater-type functions.[14] The program, GEXP, processes the functions from the 1s orbital outward, keeping each orbital of higher *n* quantum number orthogonal to the previous ones. This procedure results in an efficiently nested representation of the function.[15] In this study, the number of Gaussians used for each function was increased until the integral error of the fit was less than 2×10^{-4} for valence functions and 5×10^{-4} for core functions. It was found that three Gaussians per atomic orbital were sufficient, except for N 2p, As 3d, Mo 3d, and Mo 4d, where four Gaussians were used.

Table I. Dissociation Energies for Group 5A Diatomics and Mo_2H_6 Based on CI Involving the Triple Bond[a]

	exptl[b]	calcd	error
N_2	944	806	138
P_2	487	301	186
As_2	381	242	139
Sb_2	301	172	129
Mo_2H_6	266[d]	118	148[c]

[a] All values in kJ mol^{-1}. [b] Reference 17. [c] Average of above values. [d] Our prediction.

Table II. Dissociation Energies for Group 5A Diatomics and Mo_2H_6 Based on CI Including Differential Correlation from Other Valence and Semivalence Electron Pairs[a]

	exptl[b]	calcd	error
N_2	944	876	68
P_2	487	355	132
As_2	381	288	93
Sb_2	301	212	89
Mo_2H_6	284[d]	188	96[c]

[a] All values in kJ mol^{-1}. [b] Reference 17. [c] Average of above values. [d] Our prediction.

For all the diatomics, the most diffuse component of the valence s orbital was split off to form a double-ζ representation while the two most diffuse components of the valence p orbital were split off to form a triple-ζ representation. In addition, each diatomic had a single s and p GTO at the midpoint of the bond (bond-centered functions). The exponents for the bond-centered s and p functions on N_2, P_2, As_2 and Sb_2 were 1.4 and 0.6, 0.4 and 0.4, 0.4 and 0.2, and 0.4 and 0.2, respectively. These exponents were obtained by optimizing the HF energy while varying the bond-centered s function followed by the bond-centered p function.

Two basis sets were employed for the molybdenum in this study. The smaller basis set was used for the Mo in $Mo_2(NH_2)_6$ and was the same as the one used in the previous calculation on Mo_2H_6,[3] that is, (13s10p8d)/[5s4p3d]. The most diffuse component of the 4d orbital was split off to form a double-ζ representation. The Mo basis was also augmented by an s function, exponent 0.10, and a p function, exponent 0.10. The basis set for the N and H consisted of fully contracted orbitals made up of three Gaussians each.

The molybdenum in Mo_2H_6 was represented by a larger basis set in order to obtain a more accurate picture of the bonding region between molybdenums. The basis set was also improved to approximate the same quality basis set as the diatomics so that the comparison between the two systems would be valid. The H atom was not improved because of the hypothetical nature of the hydride ligand and because the Mo–Mo bond was the region of greater interest. The Mo basis set consisted of (14s10p8d)/[7s5p4d], in which the 4s and 4p orbitals were split to form double-ζ representations and the 4d orbital was split to form a triple-ζ representation. The molybdenum was also augmented by two extra s functions, exponents 0.13 and 0.043, and an extra p function, exponent 0.124. Finally the basis set included single bond-centered s and p GTO's, both with exponents of 0.5 (also obtained by energy optimization).

Calculations. All calculations were carried out on an Amdahl 470 V/6 in double precision at Texas A&M University's Data Processing Center. The integrals and the Hartree–Fock–Roothaan (HF)[8] calculations were done with the ATMOL 3 system of programs.[16] The

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GMO calculations were done with a program written by M.B.H. The CI calculations were done with a package written by Dr. C. T. Corcoron, Dr. J. M. Norbeck, and Professor P. R. Certain. This package, which was written for a Harris computer, was modified by T. E. Taylor and M. B. Hall for the Amdahl 470 V/6.

Results and Discussion

Diatomics and Mo_2H_6. Since the accurate calculation (±10 kJ mol^{-1}) of the dissociation energy of even the hypothetical compound Mo_2H_6 would be difficult, its dissociation energy was predicted through comparison with those of a series of triply bonded diatomics. Tables I and II give the dissociation energies for N_2, P_2, As_2, and Sb_2 as compared to that for Mo_2H_6 at various levels of CI. Table I shows the results of calculations involving all excitations of the six electrons of the triple bond into the corresponding antibonding orbitals. This resulted in a calculated dissociation energy shown in the middle column. The difference between this value and the experimental dissociation energy is listed as the error, resulting largely from inadequate basis sets and insufficient CI calculations that did not recover enough correlation energy. By using very similar basis sets for all the diatomics, we expected this calculational error to remain fairly constant. We found this to be true. We then averaged this difference and used the average to approximate the calculational error in our Mo_2H_6 dissociation energy. The calculational error, added to the calculated dissociation energy for Mo_2H_6, produced a value of 266 kJ mol^{-1} as an approximate experimental dissociation energy.

Table II shows similar results, but these are CI calculations that include the differential correlation energy. The large increase in the dissociation energy for Mo_2H_6 demonstrates how important the differential correlation energy is to this molecule.

Two things about Table II are important to note. First, this calculation supports the idea that the calculational error is fairly constant. Including the differential correlation energy for the diatomics brought the error down by about 50 kJ mol^{-1} for every system. Second, the final value of the dissociation energy for Mo_2H_6 in the improved calculation was not significantly different. Although the calculated value improved by 67% (the error went down), the predicted dissociation energy changed only 18 kJ mol^{-1} from 266 to 284 kJ mol^{-1} in the second calculation. This implies that employing better CI calculations would not appreciably affect our final dissociation energy. We would expect this trend of balance between smaller errors and larger calculated values to continue.

Potential Energy Curve. Figure 1 shows a potential energy curve for Mo_2H_6. As expected, the CI calculation affects the curve by lowering total energies. It also increases the curvature of the potential energy plot, thus lowering the force constant for the system. This occurs because the CI calculation includes, in contrast to single-determinant calculations, which emphasize only the configurations at the equilibrium distance, configurations that are important at long internuclear distances as well. The CI calculation further affects the curve by increasing the equilibrium bond length. The minimum for the single-determinant curve occurs at 2.092 Å while the minimum for the CI curve occurs at 2.193 Å, very close to our assumed bond length of 2.214 Å.

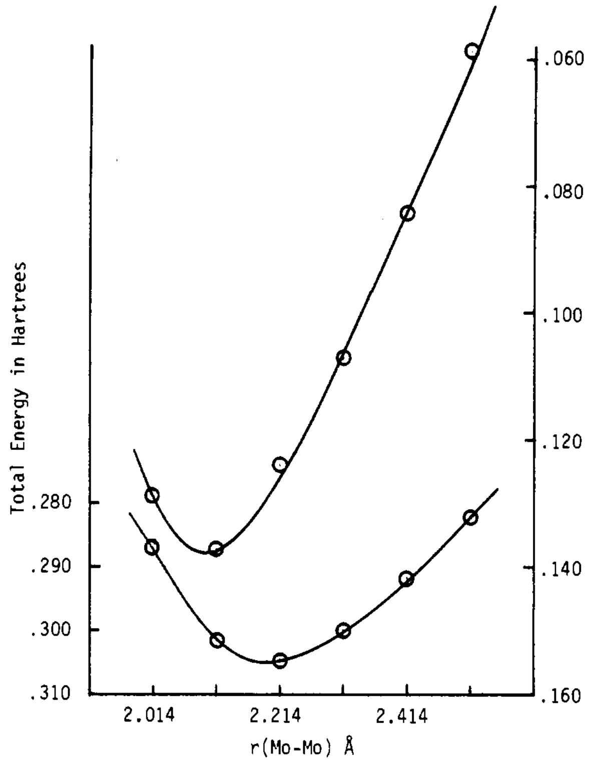

Figure 1. Potential energy curve for Mo_2H_6. The top curve represents the single-determinant energy and has its minimum at 2.092 Å. The scale on the right side of the graph represents the absolute value of the single-determinant energy plus 7897 hartrees. The bottom curve represents the CI energy and has its minimum at 2.193 Å. The scale on the left side of the graph represents the absolute value of the CI energy plus 7897 hartrees. The bond distance used in calculating the dissociation energies was 2.214 Å.

Electron Density. We have analyzed the effect of electron correlation by comparing the electron density maps for Mo_2H_6. Figure 2 shows the result at the CI level. At the top of the figure we have plotted the total electron density in a plane including the two molybdenum atoms and two opposite hydrogen atoms. We generated the middle plot by subtracting spherical ground-state atomic densities in the same basis set, resulting in the static deformation density. This middle plot shows the changes in the electron density that occur when forming the molecule from its constituent atoms. The bottom map, formed by subtracting the HF electron density from the GMO–CI electron density, shows the effect of electron correlation on the density. The following discussion will concentrate on the Mo–Mo region because of the hypothetical nature of the H$^-$ ligand and because of the minimal H basis set.

The deformation density map clearly shows a buildup of density between the Mo atoms. As would be expected for multiple bonds, this buildup is elongated perpendicular to the bond direction because of strong π bonding. When we add CI as shown in the correlation density map, the electron density is diminished in the bond region and increased close to the atoms. Although the changes in electron density when electron correlation is introduced are only a small fraction of the deformation density, they are still responsible for large changes in the bond energy.

The strongly and weakly occupied natural orbitals of our best CI with differential correlation are shown in Figure 3. Only one of the two perpendicular π and π^* orbitals are shown. As expected, the antibonding orbitals have a node between the metal centers, while the bonding orbitals do not. These orbital maps provide a graphic illustration of what electron correlation does to the total energy and electron density. In HF all the

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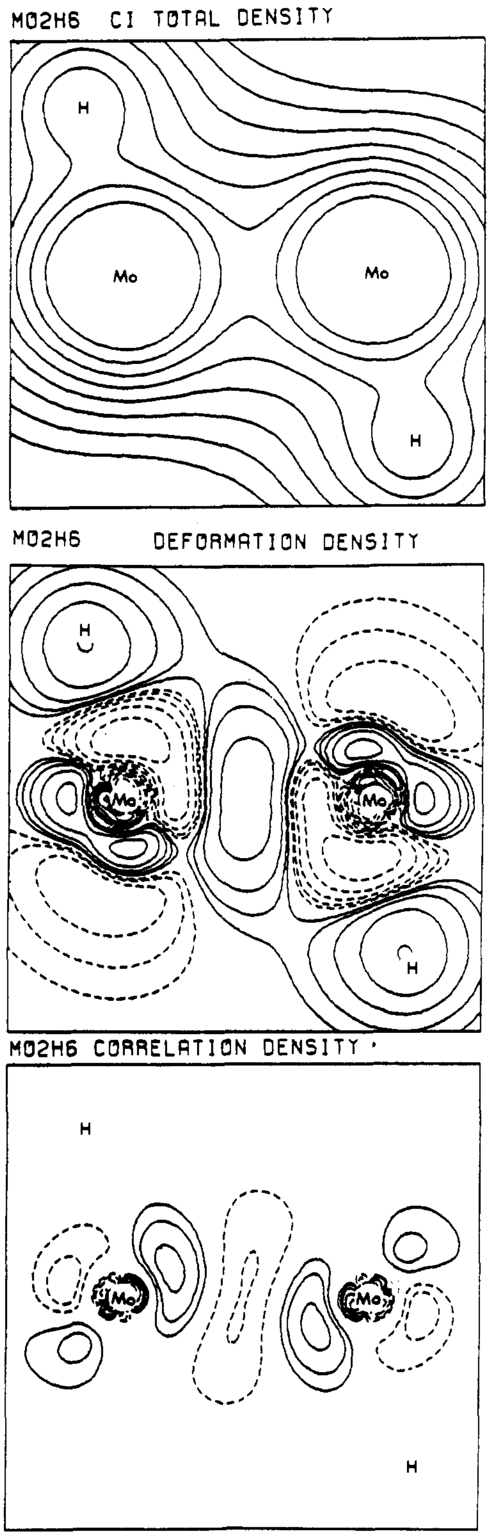

Figure 2. Electron density maps for Mo_2H_6. These plots are 8 by 8 au. The largest contour marked is 3.91×10^{-3} e/(au)^3. This is $^1/_{256}$ e/au^3 or 0.026 e/Å^3. Adjacent contours differ by a factor of 2 in all maps. The top map is the GMO–CI total electron density map of Mo_2H_6. The middle map represents the difference between the total electron density distribution and ground-state atomic densities. The bottom map represents the difference between the GMO–CI and HF total electron density maps.

Table III. Dissociation Energy for the Mo-Mo Triple Bond[a]

Comparison of Basis Sets for Mo_2H_6

Mo (13s10p8d)/ [5s4p3d]	Mo (14s10p8d)/ [7s5p4d] with interbond s + p
76	118

Comparison of Ligand System

Mo_2H_6	$Mo_2(NH_2)_6$
76	193

[a] All values are in kJ mol^{-1} and are without the differential correlation energy and without the estimated error.

strongly occupied orbitals have two electrons in them and the weakly occupied have none. The HF calculation does not take into account the dynamic electron–electron repulsion that results from the proximity of the two electrons in the same orbital. When excitations are allowed to antibonding orbitals, orbitals that contain nodes between the metal centers mix into the ground state. This allows the electrons to spend more time on opposite centers, thereby reducing the electron–electron repulsion and lowering the total energy. In other words, CI allows the electrons to separate spatially and it increases the probability that if one electron is on one Mo atom, the other electron of the pair is on the other Mo atom.

Bond Enthalpy Plots. Recently Cavell et al.[5] have published tentative bond enthalpy vs. bond length plots for Mo–Mo linkages. Figure 4 is a similar plot that includes our new calculated value for the Mo–Mo bond energy. The points in the graph correspond to dissociation energies based on nearest-neighbor and next-nearest-neighbor distances in the metal A.2. crystal, $r = 2.725$ Å and $r = 3.14$ Å, and on experimental and spectroscopic studies of the dissociation energy of gaseous Mo_2, $r = 1.929$ Å.[18,19] A value of 143 kJ mol^{-1} was calculated for Mo metal at 2.725 Å, 29 kJ mol^{-1} for Mo metal at 3.14 Å, and 406 kJ mol^{-1} for gaseous Mo_2. Our result of 284 kJ mol^{-1} for the Mo–Mo triple bond at 2.214 Å lies very close to the smooth curve drawn through the other three points.

Comparison of Basis Set and Ligand System. Table III shows the bond energy of the Mo–Mo triple bond as calculated from various basis sets and model compounds. The values are for the simplest CI and have not been corrected for the estimated error. The top part of the table gives the results for calculations on Mo_2H_6 involving only excitations of electrons in the triple bond to their corresponding antibonding orbitals. By improving the basis set in the Mo–Mo bonding region, we were able to increase the calculated dissociation energy by 40 kJ mol^{-1}. This demonstrates the importance of choosing an adequate basis set for describing metal–metal bonding. However, we do not expect to see a similar improvement by enlarging the basis set still further. Calculations comparing basis sets to dissociation energies for N_2 confirmed that the basis set chosen was very near the HF limit for the diatomics. The Mo_2H_6 large basis set was chosen in order to be comparable in accuracy to that for the diatomics. Thus, although there is usually more room for improving transition-metal basis sets as compared to those for main-group compounds, we do not expect the basis set error to be a significant factor in our final value.

The bottom part of Table III shows the results for calculations on two model compounds where both Mo atoms have the same basis set. Again, these dissociation energies represent calculations done with CI on the triple bond only. In this case there is a large difference in the dissociation energy when the H^- ligand is replaced by NH_2^-. Although we originally felt that the bond strength would be relatively insensitive to the ligands,[6] it appears that the difference between typical ligands and H^- is significant. However, this difference may be artificially large, because of the small Mo basis set. In this sit-

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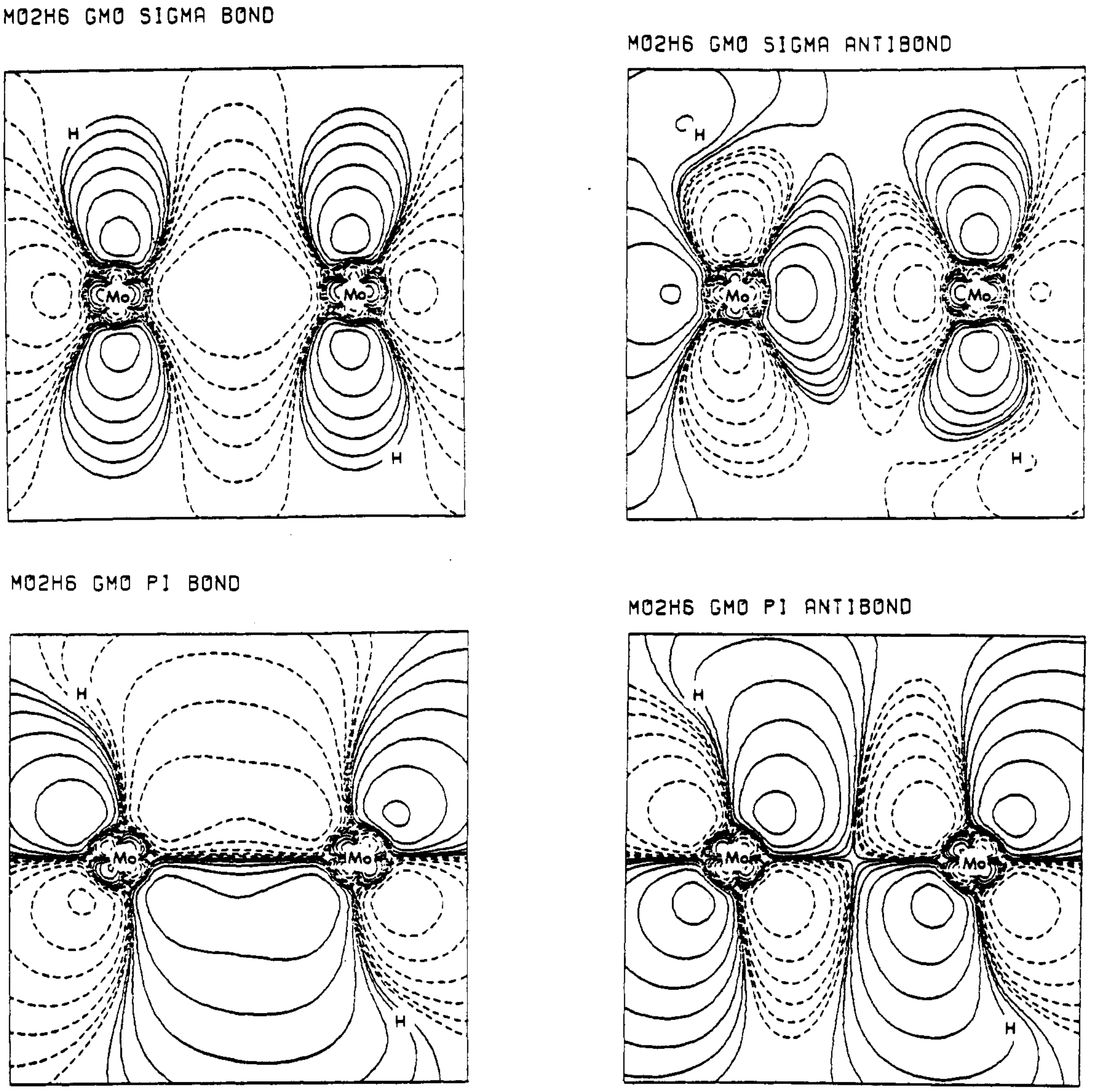

Figure 3. Strongly and weakly occupied natural orbitals of Mo_2H_6. The left side represents the σ- and π-bonding orbitals while the right side represents their antibonding counterparts.

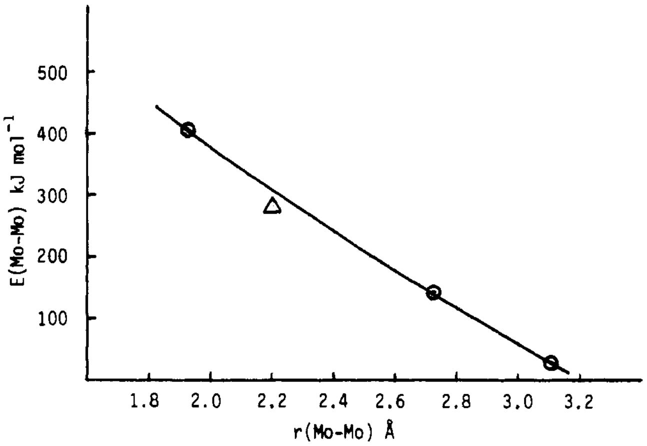

Figure 4. Bond enthalpy against bond length plot for Mo–Mo bonds. See the section Bond Enthalpy Plots in the text for a complete explanation of the points. The open triangle is the calculated value reported in this paper.

uation the larger number of functions on the NH_2^- ligand serve to make up the deficit on the Mo atom and allow the Mo atom to make better use of its functions in forming the metal–metal bond. Calculations accurate enough to determine if this actually occurs here are not presently possible.

The NH_2^- ligand increases the dissociation energy by so much because N is a much better π donor than H^-. This can be seen in the total atomic orbital populations as well as in the fragment orbital plots. The orbital populations indicate that the valence p_x and p_y orbitals in $Mo_2(NH_2)_6$ have about 2 times more electron density than those in Mo_2H_6. The shift in electron density and corresponding expansion of the orbitals can also be clearly seen in the orbital plots of the fragments MoH_3 and $Mo(NH_2)_3$ (Figure 5). The σ orbitals of the two compounds shown at the top of Figure 5 have about the same spatial extent. If we look at the π orbitals at the bottom of Figure 5, however, we see that the contours on $Mo(NH_2)_3$ have expanded considerably as compared to those on MoH_3. This expansion in the fragment orbitals leads to greater overlap in the dimer and thus to a larger dissociation energy. The effect of this expansion is also seen in the occupation numbers of the natural orbitals, which are $\sigma^{1.88}\pi^{3.73}\pi^{*0.27}\sigma^{*0.12}$ for Mo_2H_6 and $\sigma^{1.89}\pi^{3.74}\pi^{*0.26}\sigma^{*0.11}$ for $Mo_2(NH_2)_6$. The larger occupation of the σ and π orbitals and smaller occupation of the π^* and σ^* orbitals lead to a large actual (as opposed to formal) bond order for $Mo_2(NH_2)_6$. In other words, the simple HF description $\sigma^2\pi^4$ is more accurate for $Mo_2(NH_2)_6$ than for Mo_2H_6. Again, we must be cautious not to take the quantitative difference too seriously, since it may be smaller in

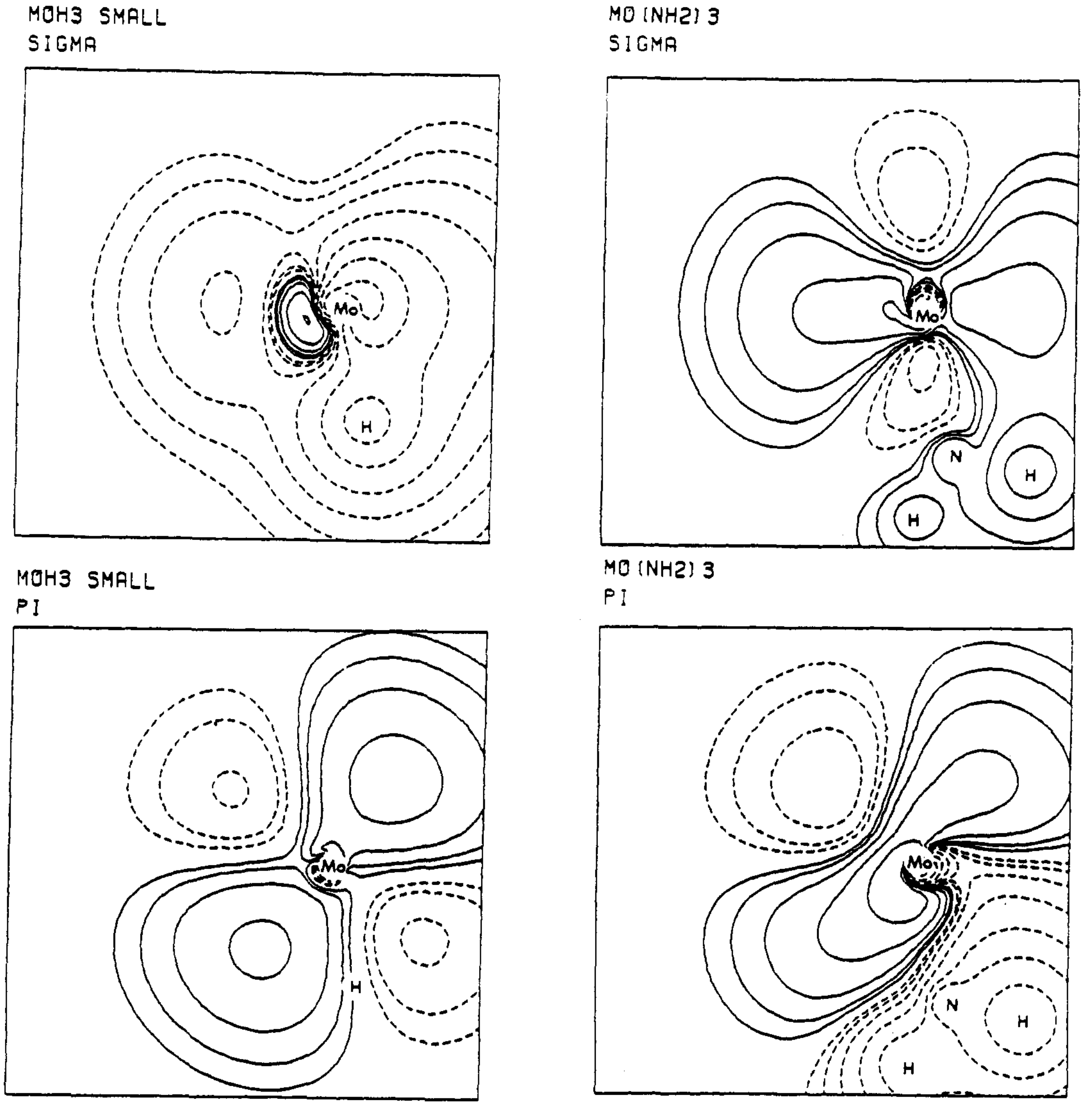

Figure 5. Singly occupied fragment orbitals of MoH_3 and $Mo(NH_2)_3$. The left side represents the σ– and π–fragment bonding orbitals of MoH_3 while the right side represents the same orbitals of $Mo(NH_2)_3$.

calculations with large Mo basis sets.

The change in size of the Mo orbitals as a function of ligand may be a key factor in the variation of the Mo–Mo triple-bond distances. In the series $Mo_2(OCH_2CMe_3)_6$,[20] $Mo_2(NMe_2)_6$,[21] and $Mo_2(CH_2SiMe_3)_6$[22] the bond distances are 2.222, 2.214, and 2.167 Å. The Xα calculations suggest that the molybdenum charges are 1.43+, 1.16+, and 0.61+, respectively.[4] Our calculations would suggest that as the charge on the Mo decreases the Mo orbitals expand, the Mo–Mo overlap increases, and the Mo–Mo bond becomes stronger and shorter.

Our results yield a bond energy of 284 kJ mol^{-1} for the molybdenum–molybdenum triple bond in Mo_2H_6, placing it below the bond energy of a carbon–carbon single bond and almost equal with the boron–boron single-bond energy. Results with more realistic ligands suggest a somewhat stronger bond in the actual compounds. Calculations comparing group 5A diatomics with Mo_2H_6 show that the calculational error associated with a series of compounds with the use of similar basis sets appears to be independent of the magnitude of the dissociation energy and can thus be extended to new compounds. CI calculations show the importance of CI in general and especially of the inclusion of differential correlation energy when attempting to calculate dissociation energies in transition-metal systems. The calculations comparing basis sets and ligand systems indicate the importance of adequate basis sets to describe metal–metal bonding and good model compounds to take into account factors like π-electron donation. Finally, our dissociation energy for the Mo–Mo triple bond fits in well with expected values as derived from bond enthalpy vs. bond length plots. Our previous preliminary estimate[3] now appears to have been too large.

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Registry No. Mo, 7439-98-7; N_2, 7727-37-9; P_2, 12185-09-0; As_2, 23878-46-8; Mo_2H_6, 83636-49-1; $Mo_2(NH_2)_6$, 64448-85-7.

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