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Conformational Preferences in Mo_2L_6 Complexes

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Single-determinant STO-3G calculations on Mo_2H_6 and Mo_2F_6 show a favoring of staggered over eclipsed equilibrium geometries. The sizable rotation barrier calculated for the hydride (7.6 kcal mol^{-1}) reflects increased repulsion between the polar metal–hydrogen bonds in the eclipsed arrangement relative to the staggered. The smaller energy barrier found in Mo_2F_6 (1.0 kcal mol^{-1}) is a consequence of the fact that the MoF bonding orbitals are much lower in energy and more highly localized than their counterparts in Mo_2H_6. An eclipsed equilibrium conformation for $Mo_2(OH)_6$ is predicted with a barrier to rotation of 0.5 kcal mol^{-1}.

Introduction

The structure and reactivity of dinuclear complexes incorporating multiple metal–metal bonds have been subject to extensive scrutiny over the past two decades.[2] Among the most studied are triply bonded systems, M_2L_6, where M is Mo or W and L is alkyl, NR_2, or OR.[3] Thus far, all characterized complexes of this type exhibit staggered, "ethane-like" structures. Note, however, the theoretical arguments of Hoffmann and his co-workers,[4] which suggest considerable δ-antibonding character of the two π bonds in staggered M_2L_6 complexes and δ-bonding character of the corresponding linkages in eclipsed complexes. As a consequence, it is reasoned that the "natural" conformational preference in these systems is eclipsed; staggered M_2L_6 structures should be favored only where ligand–ligand repulsion is likely to be significant. Extended Hückel calculations have provided support; predicted preferences for eclipsed over staggered geometries are 11 kcal mol^{-1} in Mo_2H_6, 4 kcal mol^{-1} in Mo_2Cl_6, and 9 kcal mol^{-1} in $Mo_2(CO)_6$.

The underlying hypothesis in Hoffmann's analysis, that δ-symmetry functions will contribute significantly to the metal–metal π bonds, is, however, not supported by the results of Xα calculations on Mo_2L_6 complexes (L = OH, NH_2, NMe_2, CH_3) from the Cotton group.[5] Of the systems examined theoretically, only $Mo_2(CH_3)_6$ showed evidence supporting significant contribution of δ-symmetry functions to the π bonds. Conformational preferences were not examined. Generalized molecular orbital calculations by Hall[6] "suggest almost pure 4d π bonding" in Mo_2H_6 and yield an essentially zero barrier to rotation about the central metal–metal bond.

All barrier calculations performed to date have been based on assumed equilibrium structures; detailed parameters have been taken from crystal data on related compounds in *staggered* geometries. In particular, the generalized molecular orbital calculations of Hall on Mo_2H_6,[6a] in which only a very small rotation barrier was obtained, utilized the MoMo bond length and MoMoL bond angles in $Mo_2(NMe_2)_6$.[3] Only a single attempt has been made to account for equilibrium structure by theory,[6b] and no work has sought to assess possible changes in structure as a function of conformation. These subjects are discussed in this paper.

Table I. Calculated Equilibrium Geometries for Mo_2L_6 Complexes

structure (conformation)	geometrical parameter		
	r(MoMo), Å	r(MoL), Å	∠(MoMoL), deg
Mo_2H_6 (staggered)	2.134	1.673	96.0
(eclipsed)	2.160	1.672	98.7
Mo_2F_6 (staggered)	2.235	1.804	104.9
(eclipsed)	2.239	1.803	105.5
$Mo_2(OH)_6$ (staggered)[a]	2.258	1.854	109.4
(eclipsed)[b]	2.262	1.851	110.0

[a] r(OH) = 0.983 Å, ∠(MoOH) = 122.2°. [b] r(OH) = 0.982 Å, ∠(MoOH) = 123.0°.

Methods, Results, and Discussion

Theoretical equilibrium structures for staggered and eclipsed forms of Mo_2H_6, Mo_2F_6, and $Mo_2(OH)_6$ (OH bonds assumed gauche to the metal–metal linkage) are presented to Table I. The theoretical structures have been obtained from single-determinant wave functions using the STO-3G minimal basis set.[7,8] Even though the theoretical model employed is among the simplest possible ab initio techniques, previous work has shown that it is capable of reproducing the experimental geometries of a variety of transition-metal organometallics as well as structures obtained from higher level calculations.[7b,10]

The following points are worthy of mention:

Calculated metal–metal bond lengths in Mo_2F_6 and $Mo_2(OH)_6$ are significantly longer than that in Mo_2H_6, for both staggered and eclipsed geometries. This is consistent with the available experimental X-ray data:[3] The calculated MoMo distance in staggered Mo_2H_6 (2.134 Å) is close to the experimental value in $Mo_2(CH_2SiMe_3)_6$ (2.167 Å),[3] while those in staggered Mo_2F_6 (2.235 Å) and $Mo_2(OH)_6$ (2.258 Å) are close to the range of values found in the remaining known complexes (2.20–2.24 Å).[3] MoMoL bond angles are also sensitive to the nature of the ligands. Those calculated for staggered Mo_2H_6 (96.0°) are close to the corresponding MoMoC angles in $Mo_2(CH_2SiMe_3)_6$ (100.6°).[3] Bond angles in staggered forms of Mo_2F_6 and $Mo_2(OH)_6$ are larger (104.9 and 109.5°, respectively), consistent with the range of values

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(1) Chevron Fellow.

(2) For a recent and extensive reivew see F. A. Cotton and R. A. Walton, "Multiple Bonds Between Metal Atoms", Wiley-Interscience, New York, 1982.

(3) For reviews see: (a) ref 2, p 199; (b) M. H. Chisholm and F. A. Cotton, *Acc. Chem. Res.*, **11**, 356 (1978).

(4) T. A. Albright and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 7736 (1978); (b) A. Dedieu, T. A. Albright, and R. Hoffmann, *ibid.*, **101**, 3141 (1979).

(5) B. E. Bursten, F. A. Cotton, J. C. Green, E. A. Seddon, and G. G. Stanley, *J. Am. Chem. Soc.*, **102**, 4579 (1980).

(6) (a) M. B. Hall, *J. Am. Chem. Soc.*, **102**, 2104 (1980); (b) R. A. Kok and M. B. Hall, *Inorg. Chem.*, **22**, 728 (1983). In this work the MoMo bond length in Mo_2H_6 was optimized by assuming values for the remaining geometrical parameters. No rotational barrier was reported.

(7) (a) First-row main group: W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969). (b) First- and second-row transition metals: W. J. Pietro and W. J. Hehre, *J. Comput. Chem.*, **4**, 241 (1983).

(8) All calculations have been performed with use of the GAUSSIAN 83[9] program on Harris Corp. Slash 6, H100, and H800 digital computers. Standard gradient procedures have been followed.

(9) R. F. Hout, Jr., M. M. Francl, E. S. Blurock, W. J. Pietro, D. J. DeFrees, S. K, Pollack, B. S. Levi, R. Steckler, and W. J. Hehre, to be submitted for publication in *QCPE*.

(10) M. M. Francl, W. J. Pietro, R. F. Hout, Jr., and W. J. Hehre, *Organometallics*, **2**, 281 (1983).

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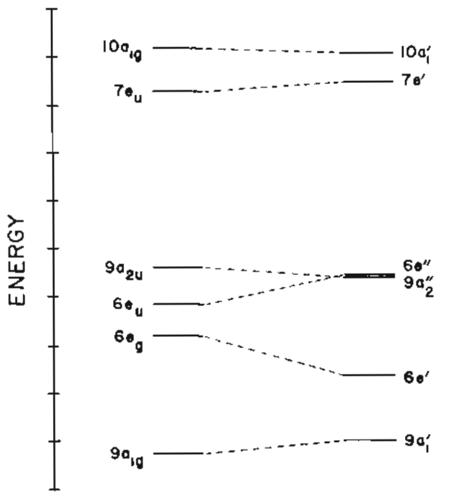

Figure 1. Energy correlation diagram connecting occupied valence molecular orbitals of staggered (left-hand side) and eclipsed (right-hand side) conformers of Mo_2H_6.

found in amino-, alkoxy-, and siloxy-substituted complexes.[3]

Hall's calculations[6b] suggest a significant *increase* in the bond strength of the metal–metal linkage in $Mo_2(NH_2)_6$ relative to Mo_2H_6. Note, however, that experimental structures for dimethylamino and related complexes as well as those presented here for Mo_2F_6 and $Mo_2(OH)_6$ exhibit metal–metal bond lengths that are significantly longer than those found in the corresponding alkyl and hydride systems. Hall suggests that π donation from the NH_2 groups in $Mo_2(NH_2)_6$ leads to a sizable increase in the population of the molybdenum 5p orbitals, which are more diffuse than the underlying 4d functions; therefore, the metal valence shell expands and the metal–metal bond strengthens. The present calculations do not support such an assertion. The lone pairs on the ligands in Mo_2F_6 and in $Mo_2(OH)_6$ (as well as those in the variety of known alkoxy, amino, and siloxy compounds) interact with the π-symmetry metal–metal bonding molecular orbitals. This interaction yields lower energy combinations that are primarily metal–ligand bonding and higher energy combinations that are primarily metal–metal π bonding. Since such an interaction is not possible in Mo_2H_6, the metal–metal π orbitals in Mo_2F_6 and in $Mo_2(OH)_6$ are destabilized, relative to the corresponding π orbitals in Mo_2H_6, and bond lengthening (weakening) follows. Our assertion is further supported by atomic size measurements;[11] F and OH substituents (and presumably NH_2 as well) are far more effective than hydrogen in *removing* electron density from the molybdenum centers. It is also in accord with atomic charges based on $X\alpha$ calculations,[5] which show that the molybdenums in $Mo_2(OH)_6$ are more positively charged than those in $Mo_2(NH_2)_6$, which in turn are more positive than the metals in $Mo_2(CH_3)_6$. One would think that a reduction in electron density around the metal centers would lead to decreased bonding between the two molybdenums and to an increase in the metal–metal bond length.

The metal–metal bond length in staggered Mo_2H_6 is predicted to be significantly (0.026 Å) shorter than that in the corresponding eclipsed complex; the MoMoH bond angle is found to be 2.8° smaller. For comparison, the corresponding differences between the staggered and eclipsed conformers of Mo_2F_6 and $Mo_2(OH)_6$ are minuscule. Eclipsed Mo_2H_6 is 7.6 kcal mol^{-1} higher in energy than the staggered form. The staggered form of Mo_2F_6 is also predicted to be the stable

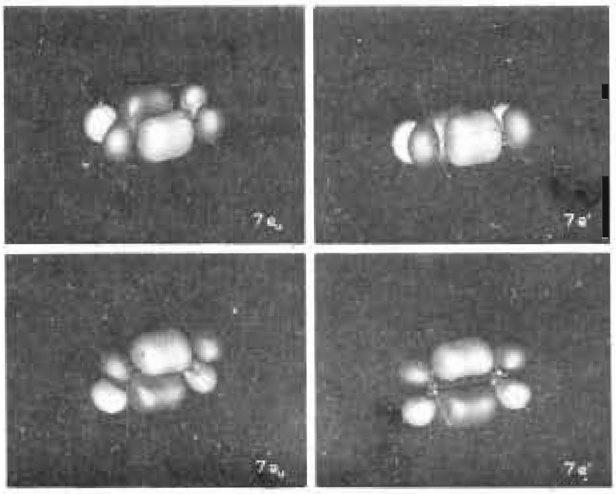

Figure 2. π-Bonding molecular orbitals in staggered (left) and eclipsed (right) conformers of Mo_2H_6.

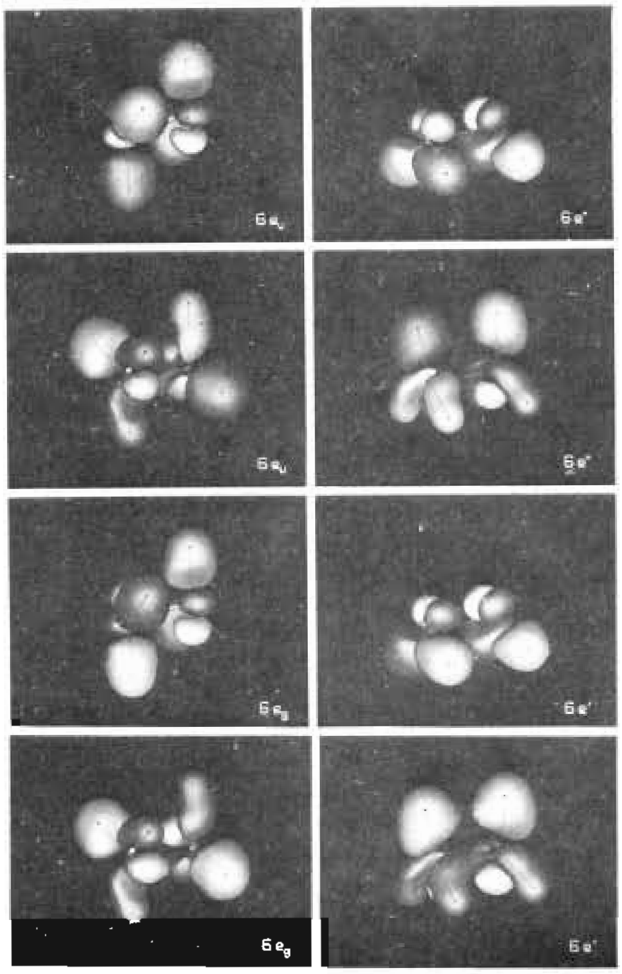

Figure 3. Degenerate MoH bonding molecular orbitals in staggered (left) and eclipsed (right) conformers of Mo_2H_6 $6e_u$ [$6e''$] (top) and $6e_g$ [$6e'$] (bottom).

conformer, although the eclipsed structure is only 1 kcal mol^{-1} higher in energy. On the other hand, $Mo_2(OH)_6$ is found to prefer an eclipsed equilibrium conformer with a barrier to rotation (through a staggered structure) of 0.5 kcal mol^{-1}. (Interestingly, there appears to be a good linear relationship between the STO-3G metal–metal bond length of the preferred conformer and the calculated energy of the eclipsed conformer relative to the staggered form. This perhaps points to a steric origin for the barrier.) As mentioned previously all structurally characterized Mo_2L_6 complexes exhibit staggered geometries,

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[11] Determined by best sphere fits to calculated total electron densities. See: (a) R. F. Hout, Jr. and W. J. Hehre, *J. Am. Chem. Soc.*, **105**, 3728 (1983); (b) M. M. Francl, R. F. Hout, Jr., and W. J. Hehre, *ibid.*, in press.

but experimental evidence does exist for facile rotation about the MoMo triple bond in some systems. Recent work from Chisholm's laboratory[12] suggests a wide range of values for metal-metal rotation barriers: <8 kcal mol^{-1} in 1,1-Mo_2(O-*t*-Bu)$_2R_4$, R = CH_2SiMe_3; 14.0 kcal mol^{-1} in 1,1-$Mo_2(NMe_2)_2R_4$; 15.6 kcal mol^{-1} in 1,2-$Mo_2(NMe_2)_2R_4$; >16 kcal mol^{-1} in *anti*-1,2-$Mo_2Cl_2(NMe_2)_4$.

The very low barriers reported by Hall for Mo_2H_6,[6a] obtained from Hartree-Fock as well as partially correlated molecular orbital models, may be due to the use of assumed equilibrium geometries. STO-3G calculations using these geometries (taken, as previously mentioned, from the crystal structure of $Mo_2(NMe_2)_6$)[3] reveal an energy difference of only 0.5 kcal mol^{-1} between the staggered and eclipsed forms of Mo_2H_6, the former being the preferred. For comparison, Hall's data place the energy of the staggered conformer 0.1 kcal mol^{-1} below that of the eclipsed form.

The present theoretical results for Mo_2H_6 may be rationalized with the aid of an orbital-energy correlation diagram connecting staggered and eclipsed forms (Figure 1). (Here, in order to separate energy differences due to conformation from those associated with other geometry changes, bond lengths and angles for the eclipsed conformer have been constrained to those of the staggered form. This results in a modest increase in barrier to 9.4 kcal mol^{-1}.) Note that the energy of the $7e_u$ molecular orbitals ($7e'$ in the eclipsed structure) that constitute the two π bonds is essentially unaffected. Furthermore, orbital photographs[13] of these orbitals in staggered and eclipsed complexes (Figure 2) are visually nearly identical. Thus, the calculations at this level do not support significant participation of δ-symmetry functions in the π bonds. The only significant change in energy levels noted between the staggered and eclipsed conformers is an increased splitting of the $6e_g$ and $6e_u$ levels ($6e'$ and $6e''$ in the eclipsed form). The molecular orbitals to which these correspond are essentially the bonding ($6e_g$) and antibonding ($6e_u$) combinations of the metal-hydrogen linkages on the two MoH_3 fragments. It is clear from the orbital photographs in Figure 3 that the two fragments interact more strongly in an eclipsed geometry than in a staggered arrangement.

Rotation barriers in Mo_2F_6 and $Mo_2(OH)_6$ would be expected to be smaller, as here the metal-ligand bonding molecular orbitals are much lower in energy (compared to the hydride) and more tightly localized. Their energies are not significantly affected upon twisting.

Even though the present quantum-chemical calculations are relatively simple, they present a picture of the bonding in Mo_2L_6 complexes that is consistent both with the known experimental structures and with the apparent absence of stable eclipsed forms. They suggest that conformation is dictated in large part by vicinal interactions between metal-ligand bonding orbitals.

Registry No. Mo_2H_6, 83636-49-1; Mo_2F_6, 67480-54-0; $Mo_2(OH)_6$, 64438-94-4.

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Structure and Bonding in Thiazyl Fluorides

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Electronic structure calculations at the SCF and, in part, at the CEPA level are reported for SN^+, NSF, NSF_3, $[HNSF]^+$, $[HNSF_3]^+$, and $[CH_3NSF]^+$. The equilibrium distance obtained for SN^+, r_e = 1.44 ± 0.01 Å, is expected to be definitive. Computed equilibrium distances and the results of a population analysis show a marked stabilization of SN and SF bonds if electrons are removed from the thiazyl group, e.g. in going from NSF to NSF_3 or by complexing NSF or NSF_3 with electron acceptors. This effect appears to be correlated with the increasing positive net charge on sulfur. The population analysis indicates that bonding to acceptors is most likely at the nitrogen end, with NSF_3 being a better donor than NSF.

Introduction

The chemistry of thiazyl fluoride (NSF) and thiazyl trifluoride (NSF_3)—which has recently been reviewed in detail by Glemser and Mews[2]—shows some interesting and fascinating features. In adducts with electrophilic compounds, e.g. $A(NSF_{(3)})_n$, A = Ni^{2+}, Co^{2+}, etc., one finds always a strengthening of SN and SF bonds (as measured by bond distances and the corresponding infrared frequencies). This is in marked contrast with the corresponding behavior of ligands such as CO, SN^+, and OPF_3.[3,4]

In this article we report and discuss results of electronic structure calculations for the systems SN^+, NSF, NSF_3, $[HNSF]^+$, $[HNSF_3]^+$, and $[CH_3NSF]^+$, where H^+ and CH_3^+ serve as simple (and strong) electron acceptors. These investigations mainly deal with the properties of the SN bond and its changes—due to different chemical environments—in order to get a better understanding of the chemistry of thiazyl fluorides. The present results are certainly more accurate for the smaller systems (SN^+ and NSF), which also serve as test cases for approximations—use of pseudopotentials, neglect of electron correlation—made in the treatment of the "larger" molecules.

The results of the present computations together with an analysis of bonding and electron distributions yield a consistent model that allows for a rationalization of experimental facts. A crucial role for an understanding of the chemistry of NSF

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