Bonding Considerations in the Apex Bridged Complexes

Bull. Korean Chem. Soc., Vol. 9, No. 3, 1988 121

cal optimization. Since *ab initio* MO calculations give good information on the magnetic susceptibility, it can be said that the combination of EH and *ab initio* MO calculations would give more informations on the analysis of transition metal complexes.

Appendix

The M-C and C-O distances for chromium and nickel complexes are based on the H(HO) CCr(CO)₅ᵇ and Ni(CO)₄ᵇ, respectively. The P-H distance was assumed to be 1.42Å in both complexes. All calculations employed M-C-O angles of 180°. The extended Hückel calculations used a modified Wolfsberg-Helmholz formula with the parameters listed in Table 2. Orbital exponents and Hii's for Ni and Cr were obtained from previous work.

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Bonding and Electronic Considerations in the Apex Bridged M₂(OR)₆ Lₓ(μ-X) Complexes (M = Mo; R = -t-Bu, -i-Pr; L = Py; x = 0 or 2; X = CO, SO₂, HCCH, H, and Cl)

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The molecular interaction of $Mo_2(OR)_4(\mu-OR)_2$ unit has been studied for carbonyl and acetylene ligands by means of extended Hückel calculations. We have extended the extended Hückel calculations to unknown apex bridged $Mo_2(OR)_6(\mu-X)$ complexes (X = SO₂ H, and Cl) in order to compare the stability of the complexes. In the C₂H₂ and H apex bridged complexes, one finds a relatively small HOMO-LUMO gap. However, both complexes are stabilized due to Jahn-Teller distortion. The stability of both complexes is comparable to that of $Mo_2(OR)_6(CO)$ complex. The comparisons and predictions in the stability of known and unknown complexes are the subject of this study.

Introduction

The M=M bonded complexes $M_2(OR)_6^1$ (M = Mo, W; R = Pr, Ne, Bu) show many striking features.[2] The first thing is that the $M_2(OR)_6$ complexes provide a good source of electrons to ligands that are capable of being reduced upon coordination. As an example, carbon monoxide reacts with $M_2(OR)_6$ to give the adduct $M_2(OR)_6(\mu-CO)^3$, in which the C-O bond order may be reduced. The second thing is that the $M_2(OR)_6$ complexes are coordinatively unsaturated. Therefore, donor ligands rapidly react with the alkoxides $M_2(OR)_6$ (M≡M) to give adduct $M_2(OR)_6 L_x^4$, in which one or two alkoxy groups are bridged. For example, acetylene and phosphorus react with the $Mo_2(OR)_6$ complexes to give the complexes of the type $M_2(OR)_2L_x$ $(RCCR)^5$ and $M(OR)_6L_x(PP)^6$ (R = Pr, CH₂-t-Bu, Bu; L = py; R = H and Me), respectively. The geometry of the $M_2(OR)_6(\mu-X)$ complexes is an square based pyramidal for molybdenum atom through the agency of alkoxy bridges, in which an incoming ligand may be sitted at an apical position. The metal-metal complexes with alkoxy bridges, in which access to two metals is controlled by the alkoxy ligands, offer the possibility of activation of substrates.

Recently, Chishohm and coworks[7] reported the bonding in monocarbonyl adducts of dimolybdenum and ditungsten hexaalkoxides with the aid of nonparameterized Fenske-Hall calculations. Since we are interested in the electronic structure and stability of various apical ligands ranging from sin-
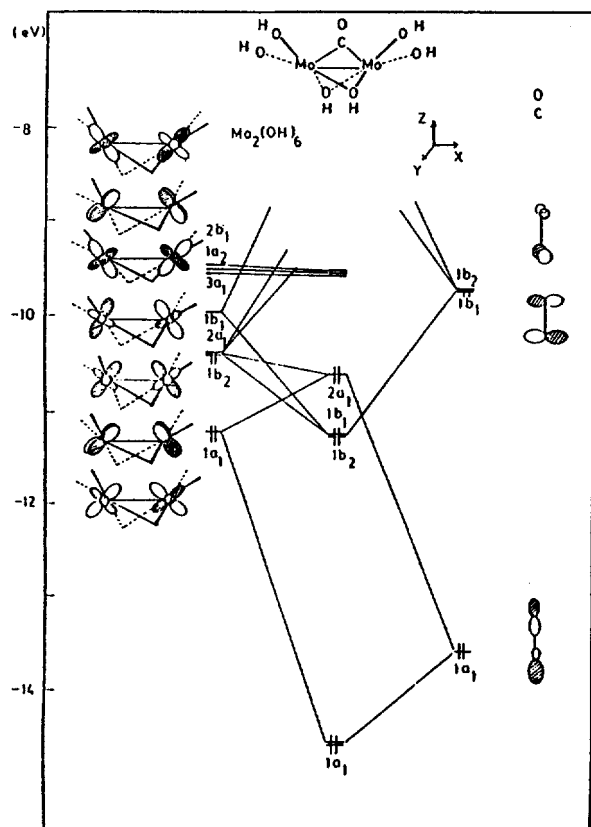
**Figure 1.** An orbital interaction diagram for $Mo(OH)_4(\mu\text{-}OH)_2$ ($\mu\text{-}CO$).

gle-atom bridges such as Cl and H to small molecules such as CO, C_2H_2, and SO_2, we decided to investigate the bonding in the complexes of the general type $Mo_2(OH)_6(\mu\text{-}X)$. Our procedure will be to construct the molecular orbitals of the $Mo_2(OH)_4(\mu\text{-}OH)_2$ fragment and then interact these fragments with each different apex ligand. This study is based on extended Hückel calculations and symmetry arguments.

Small-Molecule Apex Bridges. There are two small-molecule apex bridged $M_2(OR)_6(\mu\text{-}X)$ complexes for which crystal structures are available. The first reported was the carbonyl-bridged $Mo_2(OR)_6(\mu\text{-}CO)(1)$. Recently, the crystal structure of $M_2(OR)_6L_2(RCCR)(2)$ has been reported. In this section, we discuss the bonding and electronic structure of the $\mu\text{-}CO$ and $\mu\text{-}HCCH$ apex bridged complexes. Furthermore, we would like to extend the general bonding features studied in both complexes to the $\mu\text{-}SO_2$ complex (3) as
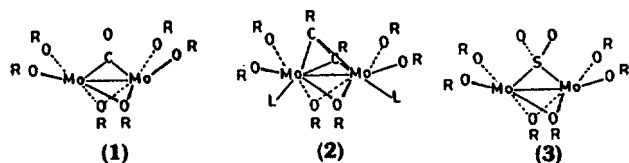
shown below. This approach, we hope, may be useful to the syntheses and to the prediction of stability of the general type $M_2(OR)_6$ ($\mu\text{-}X$) with small molecules as bridges such as the CNR, and PR_2 ligands. For the first step for a convinient computational method, we replaced the methyl groups on the acetylene and alkyl group on the alkoxides by hydrogens. We also replaced the pyridine group by NH_2 group. Now, we start from the orbitals of $Mo_2(OH)_4(\mu\text{-}OH)_2$. They are derived from those of an square based pyramidal geometry for

each molybdenum atom. The fragment $Mo_2(OH)_4(\mu\text{-}OH)_2$ has a C_{2v} symmetry. The important metal-based molecular orbitals are shown on the left side in the Figure 1. The geometry centered on molybdenum of $Mo_2(OH)_4(\mu\text{-}OH)_2$ can be thought as a combination of two square planar metal fragments. In the valence orbitals of the $Mo_2(OH)_4(\mu\text{-}OH)_2$ fragment, at high energy is a primarily metal xz orbital of $2b_1$ symmetry followed by an e set of $x^2\text{-}y^2$ and z^2 character. Some of metal s character also mixes into it. The combination of xy and yz atomic orbitals would give rise to the la_2 fragment MO's. The $3a_1$ orbital consists of the combination of $x^2\text{-}y^2$, z^2 and xz atomic orbitals. At lower energy are two a_i and b_i set of predominantly metal s, $x^2\text{-}y^2$, z^2 and xz character. At this point, we are in a position to explain the reason why the $3a_1$ metal-metal orbital in a bonding fashion is higher in energy than the $1b_1$ metal-metal orbital in a antibonding fashion. The reason may be derived from the interaction beween the metal d orbitals and σ and π hybrids from the alkoxides. The $1b_1$ $3a_1$ and $1a_2$ orbitals including the interaction between the metal d orbitals and σ and π hybrids from the alkoxide are shown schematically in 1.
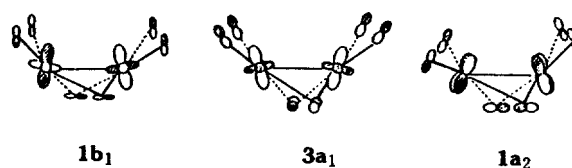

Scheme 1

As seen in scheme 1, in $1a_2$, the set of four terminal hydroxide ligands are involved in strong π-bonding interaction with the dimetal fragments and the set of two bridged hydroxide ligands involved in weak π-bonding interaction with the eclipsed dimetal fragments. In the $3a_1$ orbital, the set of four terminal hydroxide ligands are involved in strong σ-bonding interaction with the dimetal fragment. On the other hand, the σ hybrids of the set of four terminal and two bridged hydroxides mix with the corresponding dimetal fragments in an antibonding fashion to produce Mo-O σ^* bonds. From these results, it may be said that the metal-metal bonding $3a_1$ orbital is destabilized compared to the metal-metal antibonding $1b_1$ due probably to the strong interaction between the metal d orbitals and the alkoxide σ and π hybrids rather than the metal-metal bond itself. The next topic we would like to discuss is the problem about specifying the electron count around the metal. If we count a bridging carbonyl as neutral, that would lead us to the oxidation state of Mo(III) with having $d^3\text{-}d^3$ dimetal fragments. In that case, the HOMO is the $1b_2$ metal-metal bonding orbital. The LUMO is the $1b_1$ metal-metal antibonding orbital. Another approach in electron account can be made by thinking of the bridging carbonyl as dinegative CO^{2-}.[15] In that case, the metal-metal fragments have a $d^2\text{-}d^2$ configuration. From now on, we will adapt a bridging carbonyl as dinegative by the reason of an appreciable interaction between the metal d orbital and ligand π orbital and for the sake of the consistency with other ligands followed.

The electronic structure of $Mo_2(OH)_4(\mu\text{-}OH)_2(\mu\text{-}CO)$ is most easily constructed by interacting a $Mo_2(OH)_4(\mu\text{-}OH)_2$ fragment with CO fragment. Figure 1 shows an orbital interaction diagram for $Mo_2(OH)_4(\mu\text{-}OH)_2(\mu\text{-}CO)$. On the left side of this figure are the important valence orbitals of the

$Mo_2(OH)_4(\mu\text{-}OH)_2$ fragment, having C_{2v} symmetry. Here we represent their interactions with carbon monoxide. Before combining a symmetry adapted linear combination, let us review the carbon monoxide frontier orbitals. Carbon monoxide has one low energy P_z orbital and two high energy P_x and P_y orbitals as shown in the Figure 1. In the low energy, the atomic P_z orbital on carbon interacts with the $1a_1$ metal-metal bonding fragment orbital in a bonding fashion to produce a M-C bonded molecular orbital, labelled the $1a_1$ on the center and an antibonding counterpart, $2a_1$, which is a predominantly metal $1a_1$ orbital. Carbon P_x and P_y orbitals mix into $1b_2$ and $1b_1$ on metal site to produce the $1b_2$ and $1b_1$ π bonding, respectively. The filled $1a_1$, $2a_1$ molecular orbitals and $1b_2$, $1b_1$ orbitals correspond to the σ and π bonds respectively. The four bonding combinations between carbon monoxide and metal fragment orbitals are represented in **4a-d**. At higher energy, the $3a_1$, $1a_2$ and $2b_1$ metal fragment orbitals does not overlap to an appreciable extent with the carbon monoxide atomic orbitals. The $3a_1$ and $1a_2$ orbitals are primarily metal-based orbitals, which mix into the σ and π hybrids of the alkoxide represented in scheme 1. The HO
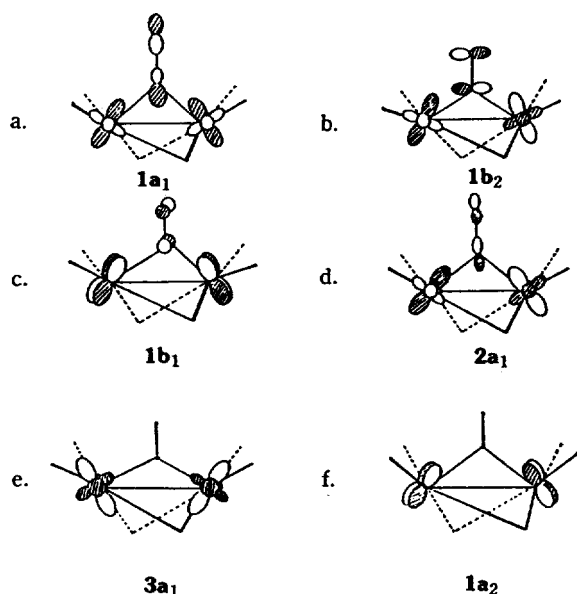
MO can be thought as representing a σ bond $2a_1$ orbital formed from the combination of carbonyl $1a_1$ orbital with metal-based $2a_1$ orbital. The $3a_1$ orbital is a mainly $3a_1$ metal-metal molecular orbital far above in energy as the LUMO. Since there is a relatively large gap(1.05eV) in energy between the HOMO and LUMO, a second-order Jahn-Teller distortion between $2a_1$ and $3a_1$ orbitals is not expected although the HOMO($2a_1$) and LUMO($3a_1$) have the same symmetry. In the consideration of the difference, it is also not surprising that related μ-CO apex bridged complexes such as $[W_2(OPr)_6 (\mu\text{-}CO)]_2$[8] and $Pt_2 (\mu\text{-}CO) Cl_2 (dam)_2$[9] (HOMO-LUMO gap; 3.23 eV) have been prepared.

Now we turn to the SO_2 bridged $Mo_2(OR)_6$ complex. Thus far, any crystal structures for $Mo_2(OR)_6(\mu\text{-}SO_2)$ complexes have not been reported in spite that the related $Pd_2(\mu\text{-}SO_2) Cl_2(dpm)_2$[10] and $Rh_2(\mu\text{-}SO_4) Cl_2(dpm)_2$[11] have been well documented. However, we would like to extend the bonding in monocarbonyl adduct of dimolybdenum to a SO_2 bridged $Mo_2(OR)_6$ complex in order to predict the stability of $Mo_2 (OR)_6(\mu\text{-}SO_2)$ complex energetically. In the treatment of Mo_2
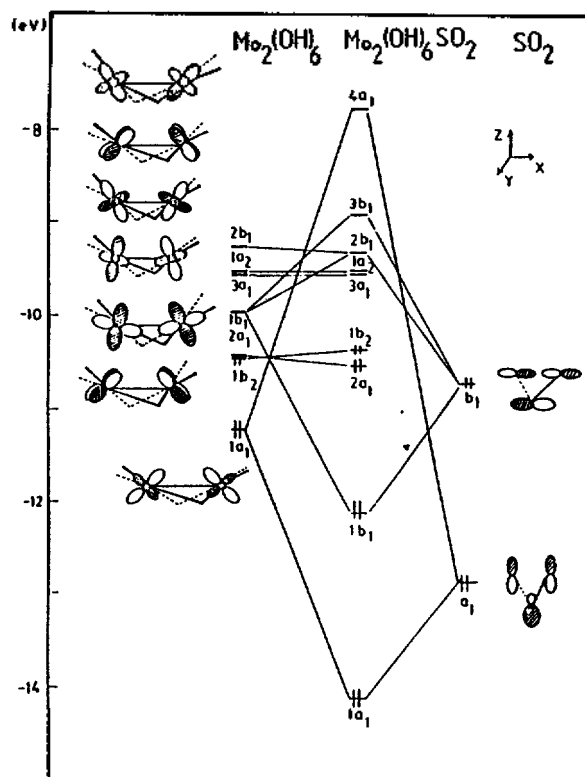

Figure 2. An orbital interaction diagram for $Mo(OH)_4(\mu\text{-}OH)_2$ $(\mu\text{-}SO_2)$.

$(OR)_6(\mu\text{-}SO_2)$ complex, we assumed that the bridged carbonyl group in $Mo_2(OR)_6(\mu\text{-}CO)$ was replaced with SO_2 group, with the distance and angle in $Mo_2(OR)_6$ exactly same. Figure 2 is the interaction diagram for $Mo_2(OH)_6$ $(\mu\text{-}SO_2)$. As before, we continue with $d^2\text{-}d^2$ formalism and so we have SO_2^{2-}. On the left side of this figure are the important valence orbitals of the $Mo_2(OH)_4(\mu\text{-}OH)_2$ fragment in an exactly same manner to the $Mo_2(OH)_6(\mu\text{-}CO)$ complex. On the right side of this figure are the valence orbitals of SO_2^{2-} fragment. The filled a_1 orbital of SO_2^{2-} interact very strongly with the $1a_1$ orbital of $Mo_2(OH)_6$ to produce σ and σ^*bonds. The filled b_1 orbital of SO_2^{2-}, mainly sulfur P_y mixes strongly with both $1b_1$ and $2b_1$. The result is a three-orbital pattern of the b_1 Mo's in the composite. This pattern is very similar to that of $Rh_2(\mu\text{-}SO_2) Cl_2(dpm)_2^{2-}$ (dpm $= Ph_2PCH_2PPh_2$)[12]. The HOMO is the $1b_2$ orbital, which is a predominantly metal xz and yz character. Our calculations reveal the HOMO to be actually nonbonding. This is in contrast with that of $Rh_2 (\mu\text{-}SO_2) Cl_2(dpm)_2^{2-}$. The $3a_1$ orbital in the $Mo_2 (OH)_6(\mu\text{-}SO_2)$ complex is a primarily $3a_1$ metal metal molecular orbital as the LUMO. Since there is a reasonably large gap (0.81 eV) in energy between the HOMO and LUMO, it may be reasonable to predict that unknown SO_2 bridged $Mo_2 (OH)_6$ complex could be prepared.

In an analogous fashion to the carbonyl bridged $Mo_2(OR)_6$ $(\mu\text{-}CO)$ complex, the acetylene in $Mo_2(OR)_6Py_2(RCCR)$ complex was sitted to the apex bridged position where the geometry of acetylene is perpendicular to the metal-metal fragment. The central M_2C_2 unit is typical of those commonly found in dinuclear organometallic complexes, e.g. $Co_2 (CO)_6(RCCR)$[13], $Cp_2M_2(CO)_4(HCCH)$[14] where $M = Mo$ and W and $(COD)_2Ni_2(RCCR)$[15]. In preparation for the construction of an interaction diagram for the $Mo_2(OR)_6Py_2(RCCR)$, it is
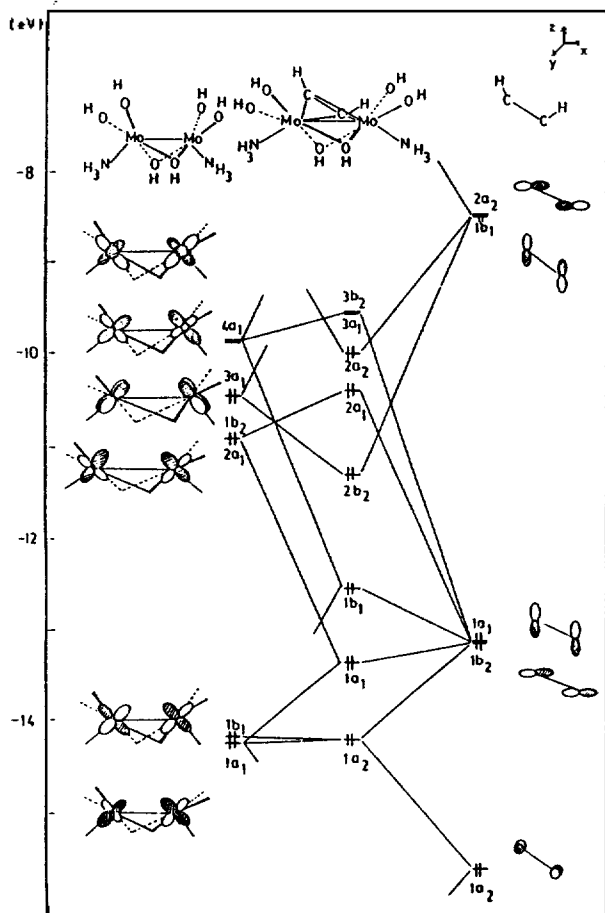
Figure 3. An orbital interaction diagram for $Mo(OH)_4(NH_2)_2$ (μ-OH)$_2$(HCCH).

Figure 4. An orbital interaction diagram for $Mo(OH)_4(\mu$-OH)$_2$ (μ-H).

convenient to visualize the bonding interaction between the acetylene and $Mo_2(OR)_6Py_2$ unit with use of the simple model of $Mo_2(OH)_6(NH_2)_2^{2+}$. The dimeric $Mo_2(OH)_6(NH_2)_2^{2+}$ unit completes a confacial bioctahedral geometry by interacting with acetylene. Figure 3 shows an orbital interaction diagram for $Mo_2(OH)_6(NH_2)_2$(HCCH). The frontier orbitals of $Mo_2(OH)_6(NH_2)_2^{2+}$ fragment, having C_{2v} symmetry are shown on the left side in Figure 3. There are four filled orbitals. At high energy is a primarily metal d orbital of $4a_1$ and $5a_1$ symmetry. The frontier orbitals of acetylene fragment in perpendicular geometry with respect to the dimetal unit are shown on the right side in Figure 3. Here we take acetylene as a dianionic ligand $C_2H_2^{2-}$ as reported elsewhere[16]. Linear acetylene has doubly degenerate π and doubly degenerate π* orbitals. The π orbital in the plane of the molecule mixes with the $1a_1$ and $2a_1$ orbital of $Mo_2(OH)_6(NH_2)_2^{2+}$ fragment to produce M-C σ and σ* bonds. The π orbital of acetylene levelled in $2a_2$ interacts with the corresponding orbital of $Mo_2(OH)_6(NH_2)_2^{2+}$ to produce a π-bond. The five bonding combination between acetylene and metal fragment orbitals are represented in **5a-e**.

The HOMO, $2a_2$, of the complex is the antibonding combination of acetylene $2a_2$ (0.3 p_x) and metal fragment $1a_2$ (0.48xy + 0.40yz). The $2a_2$ orbital has 25% acetylene character. The resultant large contribution of acetylene character in the complex may give rise to the attack of another acetylene toward the bonding consisted of the acetylene p_x and metal d orbitals. In fact, the neopentoxy
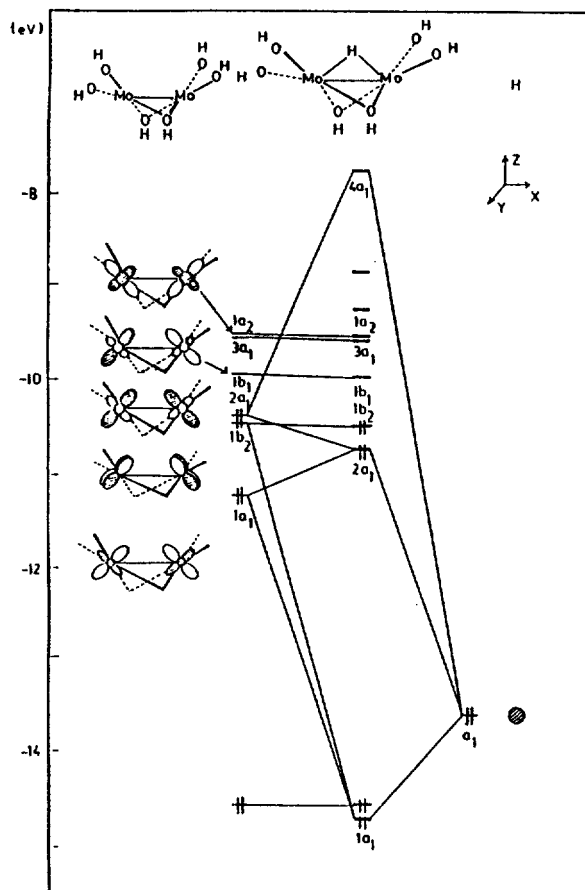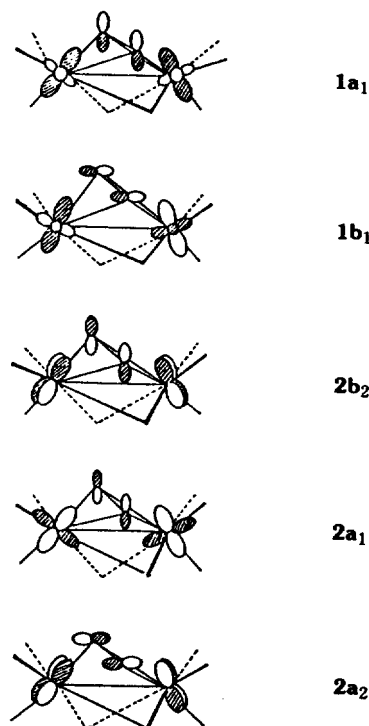

1a$_1$

1b$_1$

2b$_2$

2a$_1$

2a$_2$

compound $Mo_2(ONe)_6(\mu$-$C_4H_4)$[16] was synthesized through the reaction between $Mo_2(ONe)_6$ Py_2(ac) and one equivalent of acetylene. The $3a_1$ orbital is a predominantly $4a_1$ metal-

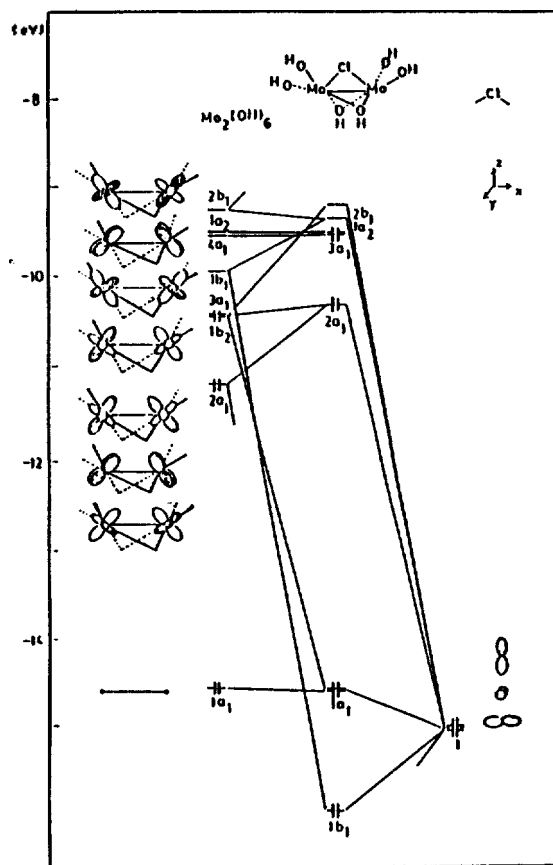**Figure 5.** An orbital interaction diagram for $Mo(OH)_4(\mu\text{-}OH)_2$ (μ-Cl).

Table 1. Extended Hückel Calculation Parameters

atom	orbital	Hii(eV)	i1	$(C_1)^a$	i2	$(C_2)^a$	ref
M_o	5s	−8.34	1.96				b
	5p	−5.24	1.90				
	4d	−10.50	4.54	(0.6097)	1.90	(0.6097)	
C	2s	−21.4	1.625				b
	sp	−11.4	1.625				
O	2s	−32.3	2.275				b
	2p	−14.8	2.275				
H	1s	−13.6	1.30				c
S	3s	−20.0	2.122				d
	3p	−11.0	1.827				
	3d	−8.0	1.500				
Cl	3s	−26.3	2.183				b
	3p	−14.2	1.733				
N	2s	−26.00	1.95				b
	2p	−18.60	1.95				

$^a C_1$ and C_2 are coefficients in a double- ζ expansion. ^{b}R. H. Summerville, R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 7240 (1976). ^{c}R. Rein, N. Fukuka, H. Win, G. A. Clarke and F. E. Harris, *J. Chem. Phys.*, **45**, 4773 (1966). ^{d}M. M. L. Chen, R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 1647 (1976).

metal bonded orbital slightly above in energy as the LUMO. The HOMO-LUMO energy gap(0.47 eV) is relatively small. One might inquire as to why the complex $Mo_2(OR)_6$ Py_2 (HCCH) can be isolated in spite of small energy difference between the HOMO-LUMO. The answer lies in the second-order Jahn-Tellar distortion. Since the HOMO(a_2) and LUMO(a_1) become of the same symmetry(a in C_2), they mix together. Therefore, the energy level of HOMO gets down, resulting in the stabilization of the molecule. Our calculation on the HOMO-LUMO is similar to that of $W_2(\mu\text{-NMe})_2$ (μ-C_2Me_2) Cl_4Py_2 reported by Hoffmann and coworker.[17]

Single-Atom Apex Bridges. In this section we would like to extend the bonding of small-molecule apex bridged complexes to that of single atom apex bridged complexes such as H^- and Cl^-. Although the complexes of the type $Mo_2(OR)_6$ (μ-X)(X = H, Cl) have not been isolated, recently Chisholm and coworkers reported the synthesis of $W_4(\mu\text{-H})_2(OPr)_{14}$[18], which is one of the few transition metal hydrido alkoxides. Our interest is to investigate the bonding of a hydride-bridged dinuclear complex in order to predict the stability of the complex. Our theoretical analysis begins with $Mo_2(OH)_4$ (μ-$OH)_2$(μ-H). In Figure 4 is shown the interaction diagram for H^- with the $Mo_2(OH)_4(\mu\text{-}OH)_2$ fragment. The filled s orbital of the H^- fragment interacts strongly with the orbitals of the dimetal fragment $1a_1$ and $2a_1$ in a bonding and antibonding fashion to produce $1a_1$ bonding and $2a_1$ bonding, respectively. The $2a_1$ orbital of a composite is formed by a three orbital pattern through the interaction of the $1a_1$ and $2a_1$ from $Mo_2(OH)_6^{+1}$ and $1a_1$ from H^- fragment. The $1b_2$ is essentially nonbonding as the HOMO. The HOMO-LUMO

energy gap (0.38 eV) is small. In an identical manner with that disscussed in $Mo_2(OR)_6$ Py_2(HCCH), the HOMO $1b_2$ gets down more than a calculated value, resulting in the stabilization of the complex. Thus, it is not surprising that the complex $W_4(\mu\text{-H})_2(OPr)_{14}$ can be isolated.

In Figure 5 is shown the interaction diagram for the Cl^- and $Mo_2(OH)_4(\mu\text{-}OH)_2$ fragment. On the right side of Figure 5 is one σ and two π-type extra low-lying orbitals of the Cl fragment. They are topologically analogous to the σ and π levels of SO_2 except that the coefficients on the atoms are weighted with respect to the electronegativity of sulfur and chlorine. Three extra low-lying orbitals present for the Cl^- fragment result in a poorer bonding with the corresponding orbitals from $Mo_2(OH)_6$ fragment compared with the analogous one in the SO_2 case. For example, the $1a_1$ orbital in $Mo_2(OH)_6(\mu\text{-}SO_2)$ formed by the interaction of a sp character form S^{2-} with $1a_1$ orbital from $Mo_2(OH)_2$ fragment is stronger than the corresponding orbital $1b_1$ of a p character from Cl^- and $1b_1$ orbital from $Mo_2(OH)_6$ fragment due to the difference in energy of two orbitals and the effective overlap. The LUMO is mainly the antibonding combination of $1b_1$ orbital from $Mo_2(OH)_6$ fragment and chlorine p_x and lies 0.16eV above the HOMO. As noted before, the SO_2 bridged Mo_2 $(OH)_6(\mu\text{-}SO_2)$ complex has its LUMO −0.81eV above the HOMO. The reason for this difference between the two similar complexes lies in those three extra low-lying orbitals present for the Cl^- fragment. Since there is a small HOMO-LUMO energy gap, the HOMO($1a_2$) and LUMO($2b_1$) become of the different symmetry, which does not give rise to the second-order Jahn-Teller distortion, and the compound is electronically paramagnetic, it may be said that the chlorine bridged $Mo_2(OH)_4(\mu$-Cl) complex can not be isolated.

From our calculations, some important results are summarized as in Table 2.

Table 2. Some Important Results for Apex Bridged Complexes

Complex	μ-CO	μ-SO₂	μ-H	μ-Cl	μ-C₂H₂
HOMO orbital	2a₁	1b₂	1b₂	3a₁(1a₂)	2a₂
LUMO orbital	3a₁	3a₁	1b₁	2b₁(4a₁)	3a₁
HOMO-LUMO gap(eV)	1.05	0.81	0.38	0.16	0.47
Electron Counting	d²-d²	d²-d²	d³-d³	d³-d³	d²-d²
Prediction to Stability	stable	stable	stable	unstable	stable

University for his discussion and encouragement and assistance in most of the calculations.

Appendix

Extended Hückel calculations[19] were performed with the parameters listed in Table 1. The geometry for Mo₂(OH)₄ (μ-OH)₂(μ-X) was taken from the experimental structure of the tert-butyl derivative[20] except Mo-O-H angles of 104.5 were used. Bond lengths for calculations involving Mo₂(OH)₆ Py₂(HCCH) were taken from the experimental structure for Mo₂(O-i-Pr)₆(Py)₂(HCCH).

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Ab Initio Studies of Lithium Bonded Complexes with H₂O Molecule

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Lithium bonded complexes with H₂O molecule were investigated theoretically by varying the substituent of lithium compound as follows; LiH, LiLi, LiCH₃, LiNH₂, LiOH, LiF, and LiCl. Some hydrogen bonded complexes with H₂O molecule were also investigated to be compared with lithium bonded analogues. Electron correlation effect on the structures and energies of lithium bond was also investigated through MP2 and MP4 corrections. Unlike hydrogen bond with H₂O molecule, lithium bonded complexes with H₂O molecule were found to be interacting linearly with H₂O molecule. Electron correlation effect was very small for lithium bonded complexes. The lithium bond energies were found to be less affected by the choise of substituent of lithium compound.

Introduction

Hydrogen bonds have long been studied in a great detail

by theoreticians and spectroscopists; however, lithium bonds have not been studied so much. Although oligomeric alkyllithium clusters are now believed to be formed by multi-