Bonding Considerations in the Apex Bridged Complexes

Introduction

The M = M bonded complexes M₄(OR)₄ (M = Mo, W; R = Pr, Ne, Bu) show many striking features. The first thing is that the M₄(OR)₄ complexes provide a good source of electrons to ligands that are capable of being reduced upon coordination. As an example, carbon monoxide reacts with M₂(OR)₄ to give the adduct M₄(OR)₄ (μ-CO)₄, in which the C-O bond order may be reduced. The second thing is that the M₂(OR)₄ complexes are coordinatively unsaturated. Therefore, donor ligands rapidly react with the alkoxy M₂(OR)₄ (M = Mo, W; R = Pr, Ne, Bu) to give adduct M₄(OR)₄ L₄, in which one or two alkoxy groups are bridged. For example, acetylene and phosphorus react with the M₄(OR)₄ complexes to give the complexes of the type M₄(OR)₄ L₄ (RCCR)₄ and M(OR)₄ L₄ (PP)₄ (R = Pr, CH₃-Cu, Bu; L = py; R = H and Me), respectively. The geometry of the M₄(OR)₄ (μ-X) complexes is an open-based pyramidal for molybdenum atom through the agency of alkoxyl bridges, in which an incoming ligand may be sited at an apical position. The metal-metal complexes with alkoxyl bridges, in which access to two metals is controlled by the alkoxyl ligands, offer the possibility of activation of substrates.

Recently, Chishohm and coworkers 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-

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Appendix

The M-C and C-O distances for chromium and nickel complexes are based on the H(HO) CO(CO)₄ and Ni(CO)₄, 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.

References

Bonding and Electronic Considerations in the Apex Bridged M₄(OR)₄, L₄(μ-X) Complexes (M = Mo; R = t-Bu, l-Pr; L = Py; x = 0 or 2; X = CO, SO₂, HCCCH, H, and Cl)

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The molecular interaction of M₄(OR)₄ (μ-X)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 M₄(OR)₄ (μ-X) complexes (X = SO₂, H, and Cl) in order to compare the stability of the complexes. In the C₆H₆ 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 M₄(OR)₄(CO) complex. The comparisons and predictions in the stability of known and unknown complexes are the subject of this study.
Single-atom bridges such as Cl and H to small molecules such as CO, C2H2, and SO2, we decided to investigate the bonding in the complexes of the general type M2(OH)4(μ-X). Our procedure will be to construct the molecular orbitals of the M2(OH)4(μ-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 M4(OR)4(μ-X) complexes for which crystal structures are available. The first reported was the carboxyl-bridged M2(OR)4(μ-CO)(1). Recently, the crystal structure of M2(OR)4L4(RCCR)(2) has been reported. In this section, we discuss the bonding and electronic structure of the μ-CO and μ-HCCH apex bridged complexes. Furthermore, we would like to extend the general bonding features studied in both complexes to the μ-SO2 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 M4(OR)4(μ-X) with small molecules as bridges such as the CNR, and PR3 ligands. For the first step for a convenient 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 NH2 group. Now, we start from the orbitals of M2(OH)4(μ-OH)2. They are derived from those of an square based pyramidal geometry for each molybdenum atom. The fragment M2(OH)4(μ-OH)2 has a C2v symmetry. The important metal-based molecular orbitals are shown on the left side in the Figure 1. The geometry centered on molybdenum of M2(OH)4(μ-OH)2 can be thought as a combination of two square planar metal fragments. In the valence orbitals of the M2(OH)4(μ-OH)2 fragment, at high energy is a primarily metal xz orbital of 2b1 symmetry followed by an e set of x^2-y^2 and z^2 character. Some of metal σ character also mixes into it. The combination of xy and yz atomic orbitals would give rise to the 1a2 fragment MO's. The 3a1 orbital consists of the combination of x^2-y^2, z^2 and xz atomic orbitals. At lower energy are two a1 and b1, set of predominantly metal s, x^2-y^2, z^2 and xy character. At this point, we are in a position to explain the reason why the 3a1 metal-metal orbital in a bonding fashion is higher in energy than the 1b1 metal-metal orbital in a antibonding fashion. The reason may be derived from the interaction between the metal d orbitals and σ and π hybrids from the alkoxides. The 1b1, 3a1 and 1a2 orbitals including the interaction between the metal d orbitals and σ and π hybrids from the alkoxide are shown schematically in 1.

As seen in scheme 1, in 1a2, 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 σ-bonding interaction with the eclipsed dimetal fragments. In the 3a1 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 3a1 orbital is destabilized compared to the metal-metal antibonding 1b1 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-d^3 dimetal fragments. In that case, the HOMO is the 1b1 metal-metal bonding orbital. The LUMO is the 1b1 metal-metal antibonding orbital. Another approach in electron account can be made by thinking of the bridging carbonyl as dinegative CO^2-. In that case, the metal-metal fragments have a d^2-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 M2(OH)4(μ-OH)2(μ-CO) is most easily constructed by interacting a M2(OH)4(μ-OH)2 fragment with CO fragment. Figure 1 shows an orbital interaction diagram for M2(OH)4(μ-OH)2(μ-CO). On the left side of this figure are the important valence orbitals of the

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Figure 1. An orbital interaction diagram for Mo(OH)4(μ-OH)2 (μ-CO).
Mo₆(OH)₆(μ-OH)₂ fragment, having C₆₅ 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 Pₓ orbital and two high energy Pᵧ and Pz orbitals as shown in the Figure 1. In the low energy, the atomic Pₓ orbital on carbon interacts with the 1a₁ metal-metal bonding fragment orbital in a bonding fashion to produce a M-C bonded molecular orbital, labelled the 1a₁ on the center and an antibonding counterpart, 2a₁, which is a predominantly metal 1a₁ orbital. Carbon Pᵧ and Pz orbitals mix into 1b₂ and 1b₁ on metal site to produce the 1b₂ and 1b₁ π bonding, respectively. The filled 1a₁, 2a₁, molecular orbitals and 1b₂, 1b₁ 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 3a₁, 1a₂ and 2b₁ metal fragment orbitals do not overlap to an appreciable extent with the carbon monoxide atomic orbitals. The 3a₁ and 1a₂ 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 2a₁ orbital formed from the combination of carbonyl 1a₁ orbital with metal-based 2a₁ orbital. The 3a₁ orbital is a mainly 3a₁ metal-metal molecular orbital far above in energy as the LUMO. Since there is a relatively large gap (1.05 eV) in energy between the HOMO and LUMO, a second-order Jahn-Teller distortion between 2a₁ and 3a₁ orbitals is not expected although the HOMO(2a₁) and LUMO(3a₁) have the same symmetry. In the consideration of the difference, it is also not surprising that related μ-CO apex bridged complexes such as [W₆(OR)₆(μ-CO)]²⁺ and Pt₂(μ-CO)Cl₂(dam)₂ (HOMO-LUMO gap; 3.23 eV) have been prepared.

Now we turn to the SO₂ bridged Mo₆(OR)₆ complex. Thus far, any crystal structures for Mo₆(OR)₆(μ-SO₂) complexes have not been reported in spite that the related Pd₂(μ-SO₂) Cl₂(dpm) and Rh₂(μ-SO₂) Cl₂(dpm) have been well documented. However, we would like to extend the bonding in monocarbonyl adduct of dimolybdenum to a SO₂ bridged Mo₆(OR)₆ complex in order to predict the stability of Mo₆(OR)₆(μ-SO₂) complex energetically. In the treatment of Mo₆ (OR)₆(μ-SO₂) complex, we assumed that the bridged carbonyl group in Mo₆(OR)₆(μ-CO) was replaced with SO₂ group, with the distance and angle in Mo₆(OR)₆ exactly same. Figure 2 is the interaction diagram for Mo₆(OH)₆ (μ-SO₂). As before, we continue with p²d¹ formalism and so we have SO₂ 2p. On the left side of this figure are the important valence orbitals of the Mo₆(OH)₆(μ-OH)₂ fragment in an exactly same manner to the Mo₆(OH)₆(μ-CO) complex. On the right side of this figure are the valence orbitals of SO₂ 2p fragment. The filled a₃ orbital of SO₂ 2p interacts very strongly with the 1a₁ orbital of Mo₆(OH)₆ to produce σ and π bonds. The filled b₁ orbital of SO₂ 2p, mainly sulfur Pₓ mixes strongly with both 1b₁ and 2b₁. The result is a three-orbital pattern of the b₁ Mo₆'s in the composite. This pattern is very similar to that of Rh₂(μ-SO₂) Cl₂(dpm) (dpm = Ph₂PCH₂PPh₂)⁶. The HOMO is the 1b₂ orbital, which is a predominantly metal px and py character. Our calculations reveal the HOMO to be actually nonbonding. This is in contrast with that of Rh₂(μ-SO₂) Cl₂(dpm).⁶ The 3a₁ orbital in the Mo₆ (OH)₆(μ-SO₂) complex is a primarily 3a₁ 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 SO₂ bridged Mo₆ (OH)₆ complex could be prepared.

In an analogous fashion to the carbonyl bridged Mo₆(OR)₆ (μ-CO) complex, the acetylene in Mo₆(OR)₆Py₂(RCCR) complex was sited to the apex bridged position where the geometry of acetylene is perpendicular to the metal-metal fragment. The central Mo₆C₆ unit is typical of those commonly found in dinuclear organometallic complexes, e.g. CO₂ (CO)₆(CP₂)₆, CO₂(CO)₂(CO)₂(COCH₃)₄ where M = Mo and W and (COD)₆(Ni₂(RCCR))²⁺. In preparation for the construction of an interaction diagram for the Mo₆(OR)₆Py₂(RCCR), it is
convenient to visualize the bonding interaction between the acetylene and Mo$_2$(OH)$_6$Py$_2$ 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 cofacial biotahedral 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$$^{2+}$ fragment, having C$_2v$ symmetry, are shown on the left side in Figure 3. There are four filled orbitals. At high energy is a primarily metal d orbital of 4a$_1$ and 5a$_1$ symmetry. The frontier orbitals of acetylene fragment in perpendicular geometry with respect to the dimetal unit are shown on the right side in Figure 3. Here we take acetylene as a diatomic ligand C$_2$H$_2$$^-$ as reported elsewhere. Linear acetylene has doubly degenerate $\pi$ and doubly degenerate $\pi^*$ orbitals. The $\pi$ orbital in the plane of the molecule mixes with the 1a$_1$ and 2a$_1$ orbital of Mo$_2$(OH)$_6$(NH$_2$)$_2$$^{2+}$ fragment to produce M-C $\sigma$ and $\sigma^*$ bonds. The $\pi$ orbital of acetylene levelled in 2a$_2$ interacts with the corresponding orbital of Mo$_2$(OH)$_6$(NH$_2$)$_2$$^{2+}$ to produce a $\pi$-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 compound Mo$_2$(ONe)$_6$(\mu-C$_5$H$_2$)$_6$ 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-
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 MoO(OH)₂ Py₂ (HCCH) can be isolated in spite of small energy difference between the HOMO-LUMO. The answer lies in the second-order Jahn-Teller distortion. Since the HOMO(a₁) and LUMO(a₄) become of the same symmetry in C₂, 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 W₆(μ-NMe₃) (μ-C₂Me₂) Cl₂Py₂ reported by Hoffmann and coworkers.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 Mo₂(OH)₆ (μ-X(OH) = H, Cl) have not been isolated, recently Chisholm and coworkers reported the synthesis of W₆(μ-H)₂(OPr)₁₄, which is one of the few transition metal hydroxido 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 Mo₂(OH)₄ (μ-OH)(μ-H). In Figure 4 is shown the interaction diagram for H⁺ with the Mo₂(OH)₄ (μ-OH)₂ fragment. The filled orbital of the H⁺ fragment interacts strongly with the orbitals of the dimetal fragment 1a₁ and 2a₁ in a bonding and antibonding fashion to produce 1a₁ bonding and 2a₁ bonding, respectively. The 2a₁ orbital of a composite is formed by a three orbital pattern through the interaction of the 1a₁ and 2a₁ from Mo₂(OH)₄ and 1a₁ from H⁺ fragment. The 1b₂ is essentially nonbonding as the HOMO. The HOMO-LUMO energy gap (0.38 eV) is small. In an identical manner with that discussed in Mo₂(OH)₄ Py₂(HCCH), the HOMO 1b₂ gets down more than a calculated value, resulting in the stabilization of the complex. Thus, it is not surprising that the complex W₆(μ-H)₂(OPr)₁₄ can be isolated.

In Figure 5 is shown the interaction diagram for the Cl⁻ and Mo₂(OH)₄ (μ-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 SO₂ 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 Mo₂(OH)₄ fragment compared with the analogous one in the SO₂ case. For example, the 1a₁ orbital in Mo₂(OH)₄ (μ-SO₂) formed by the interaction of a σ character form 5² with 1a₁ orbital from Mo₂(OH)₄ fragment is stronger than the corresponding orbital 1b₁ of a p character from Cl⁻ and 1b₁ orbital from Mo₂(OH)₄ fragment due to the difference in energy of two orbitals and the effective overlap. The LUMO is mainly the antibonding combination of 1b₁ orbital from Mo₂(OH)₄ fragment and chlorine p₃, and lies 0.18 eV above the HOMO. As noted before, the SO₂-bridged Mo₂(OH)₄ (μ-SO₂) complex has its LUMO -0.81 eV 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(1a₁) and LUMO(2a₁) 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 Mo₂(OH)₄ (μ-Cl) complex can not be isolated.

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

Table 1. Extended Hückel Calculation Parameters

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

Appendix

Extended Hückel calculations were performed with the parameters listed in Table 1. The geometry for \( \text{Mo}_2\text{O}_4\text{H}_4 \) (\( \mu\text{-OH})_2(\mu\text{-X}) \) was taken from the experimental structure of the tert-butyl derivative, except Mo-O-H angles of 104.5 were used. Bond lengths for calculations involving \( \text{Mo}_2\text{O}_6 \) \( \text{Py}_2(\text{HCCH}) \) were taken from the experimental structure for \( \text{Mo}_2\text{O}_4\text{-Pr}_3(\text{Py})_2(\text{HCCH}) \).

References


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 choice 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 alkyl lithium clusters are now believed to be formed by multi-