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Some Aspects of the Electronic Structures of a Series of Trimeric Transition-Metal Cluster Complexes

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We report the results of approximate molecular orbital calculations on a series of trimeric transition-metal cluster complexes: $Fe_3(CO)_9(\mu_3\text{-}S)_2$, $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}CO)$, $Co_3Cp_3(\mu_3\text{-}S)_2{}^n$ (n = 0, 1+), $Co_3Cp_3(\mu_3\text{-}S)(\mu_3\text{-}CO)$, $Ni_3Cp_3(\mu_3\text{-}S)_2$, and $Ni_3Cp_3(\mu_3\text{-}CO)_2{}^n$ (n = 1−, 0). The various differences among the magnetic and structural characteristics are explained in terms of the different bonding capabilities of bridging carbonyls and sulfides. A novel analysis of the metal–metal bonding shows that despite no net occupation of predominantly metal–metal bonding orbitals there are attractive metal–metal interactions. These interactions are shown to be dominated by occupation of orbitals on the metal triangles which are predominantly valence s and p in character, not unlike the situation that would presumably be found on the corresponding metal surfaces.

Introduction

In the study of the electronic structures of transition-metal cluster complexes (TMCC's), one of the goals is to further understand the similarity and differences beteween conventional organometallic complexes and the chemisorption systems of surface chemistry.[1] We have been particularly interested in the relationship between the metal–metal (M–M) bonding in TMCC's[2-11] and that in bulk metals or on metal surfaces.

Theoretical results on naked clusters of transition-metal atoms indicate that the M–M interactions are dominated by the occupation of orbitals which are predominantly metal s and p in character.[12-20] The role played by the d orbitals is a matter of some controversy,[5] though it does appear to be a function of the metal,[19,20] being more important for the group 3B–7B elements than for the group 8 and 1B elements. However, the fact that they are much more contracted than are the s and p orbitals, especially for the group 8 and 1B metals, leads one to conclude that whatever their effect, the d orbitals are less important in the M–M bonding in these naked clusters, and presumably on clean surfaces, than are the s and p orbitals.

In the saturated cluster complexes common to organometallic chemistry, on the other hand, the metal s and p orbitals are commonly considered to be tied up in bonding to the ligands, and it is often presumed that the d orbitals are responsible for any M–M bonding. From this it follows that in a molecular orbital (MO) calculation one should expect to find the occupation of more predominantly metal d, bonding orbitals than corresponding antibonding orbitals by a number equal to the number of M–M bonds. However, no theoretical results with which we are familiar support this assignment when the M–M bond is bridged by a π acid[4,6] or at least when one acidic π orbital runs parallel to the M–M axis.[6] This is basically a reflection of the magnitude of the metal–ligand vs. the M–M interactions. The ligand orbitals that give rise to the primary interactions with the metals are typically much more diffuse than the metal d orbitals, thereby rendering the metal–ligand interactions stronger than the M–M d–d interactions. The implication of this fact is that the ordering and consequently the occupation of the MO's which are predominantly metal d in character will be more a function of the symmetry and character of the ligand orbitals rather than their M–M bonding or antibonding character. A π-acid-bridged

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(1) See, for example: Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem Rev.* **1979**, *79*, 91–137 and references cited therein.

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system, for example, can have a M–M antibonding MO stabilized relative to a direct bonding MO by virtue of the interaction between the M–M antibonding orbital and the π-accepting orbital of the ligand.[21]

The above discussion not only has pedagogical implications in understanding the M–M interactions in TMCC's, but also has direct structural implications in evaluating molecular symmetries and M–M internuclear distances in these complexes. The research group of Professor L. F. Dahl has performed numerous experimental studies aimed at elucidating the electronic contributions to the structural features of TMCC's.[9,10] They have done this primarily by deducing the M–M bonding or antibonding nature of the high-lying orbitals from the structures of various oxidized and/or reduced complexes. A series of trimeric TMCC's with triply bridging S's and/or CO's, many of which were originally prepared and characterized in the Dahl research group, provided us with an interesting set of systems with which to explore both the electronic effects on the observed structures, thereby checking Dahl's predictions, as well as to examine the nature of the bridged M–M interactions. This series consists of $Fe_3(CO)_9(\mu_3\text{-}S)_2$,[22] $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}CO)$,[23] $Co_3Cp_3(\mu_3\text{-}S)_2{}^n$ (n = 0, 1+),[9f,24] $Co_3Cp_3(\mu_3\text{-}S)(\mu_3\text{-}CO)$,[24] $Ni_3Cp_3(\mu_3\text{-}S)_2$,[25] and $Ni_3Cp_3(\mu_3\text{-}CO)_2{}^n$ (n = 1−, 0)[9g,26] (where Cp = cyclopentadienyl).

This study involves approximate MO calculations on the aforementioned systems as well as a novel analysis of the MO results designed to elucidate the origins of the M–M interactions.

Calculational Details

The molecular orbital (MO) method used throughout this study is that developed by Fenske and Hall.[27] The Fenske–Hall procedure is an approximate, nonempirical, MO scheme with the only adjustable parameters being the basis sets and the molecular geometries. In the past this scheme has provided good correlation with experimental data on mono- and binuclear organometallic complexes.[10,28] The present study is its first application to trinuclear systems.

The specifications of the basis sets are as follows: All core functions are taken to be the appropriate Clementi and Raimondi single-ζ functions.[29] For C, O, and S the valence functions are contractions of Roetti and Clementi's double-ζ functions,[30] and in the case of S a set of 3d functions is included with Slater exponent of 1.0. The metal valence functions are taken from the results of Richardson et al.[31] For a given metal atom these include single-ζ 4s and 4p functions with the same exponents and a set of contracted, double-ζ 3d functions.

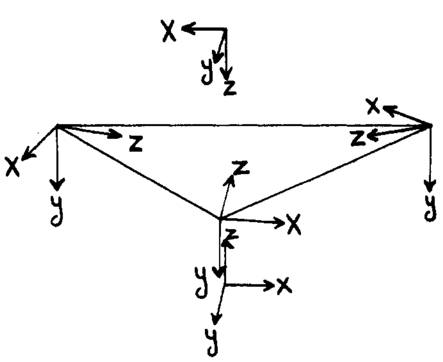

Figure 1. Coordinate system.

The molecular geometries were taken from the appropriate experimental results.[9f,22b,23,24b,25,26b] For the cases of $Fe_3(CO)_9(\mu_3\text{-}S)_2$, $Co_3Cp_3(\mu_3\text{-}S)_2{}^+$, and $Ni_3Cp_3(\mu_3\text{-}CO)_2{}^-$, which have C_{2v} symmetry in the solid state, we have also performed calculations imposing idealized D_{3h} symmetry on them. This was done by assigning to the odd M–M distance the value of the other two M–M distances as opposed to averaging the distances.

In analyzing our MO results we have employed a technique known as the natural hybrid orbital (NHO) analysis.[32] This is basically an MO localization technique, but unlike conventional localization procedures which first localize the orbitals and then decide whether or not they correspond to bonds or lone pairs, the NHO procedure tries to localize the orbitals specifically as bonds or as lone pairs. Details concerning the procedure can be found elsewhere.[32] We will present here only the necessary nomenclature used in discussing our results.

For the purposes of this work there are two basic pieces of information which one obtains from an NHO analysis. These are (1) the polarization coefficients of the bonding orbitals and (2) the orbital character of the constituent hybrids. These terms will be defined presently. A bonding orbital between A and B, ϕ_{AB}, can be broken down into contributions from A, h_A, and contributions from B, h_B, as is described in eq 1.

$$\phi_{AB} = \lambda_A h_A + \lambda_B h_B \qquad (1)$$

Here the λ's are scalar and are referred to as the *polarization coefficients*. The h's, on the other hand, are normalized functions referred to as *hybrids*. Ordinarily the A and B will refer to particular atoms in a molecule in which case the term *hybrid* will have its conventional meaning. However, we are not restricted to assigning A and B identities as individual atoms. It is often convenient or even necessary to have A and B refer to groups of atoms. In this work, for example, we have always grouped the ten atoms of a Cp ligand or the two atoms of a carbonyl ligand together as one unit, and we have often grouped the three metal atoms together similarly. Hybrid orbitals arising from these groups of atoms are certainly not like the conventional hybrids. Therefore, we will refer to them as *delocalized hybrids*.

Unlike our MO procedure an NHO analysis does involve an empirical parameter. That parameter is a threshold value which is used to determine whether or not to designate a potential bonding orbital or lone pair orbital as being doubly occupied. For all of the NHO analyses in this work a value of 1.7 electrons was used. This value was found to yield the most information. Higher values, though more aesthetically pleasing, are unreasonable for use in the large systems studied here due to delocalization. Lower values, on the other hand,

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(21) In the context of antiferromagnetic coupling of weakly interacting metal dimers, Hoffmann and co-workers discuss the role of bridging ligand orbitals in the splitting patterns of the metal orbitals. These effects, which they designate as due to "through bond coupling", are analogous to the more substantial interactions presented here. Cf.: Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884–4899.

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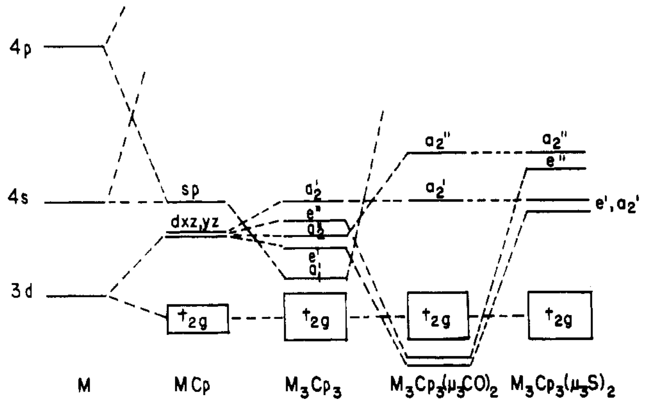

Figure 2. Summary of dominant features in electronic structures.

produce less physically meaningful results.

Molecular Orbital Results

Before considering any of the MO calculations in detail we will first present a framework from which we can effectively explain our results. Since we are primarily concerned with the effects that the bridging ligands have on the metal levels, we will develop separate pictures of the metal triangles with their terminal ligands and the bridging ligands before discussing the interactions between the two. Figure 1 shows the coordinate system used in all of these calculations and discussions. Figure 2 summarizes the features of the framework we are about to present.

The terminal ligands will have a large role in determining how the metal atoms may interact. The terminal group of concern here are the Cp^- or three terminally bound CO groups. Each has three low-lying donor orbitals: the e_1'' and a_2'' orbitals of the free Cp^- ligand, and the three 5σ orbitals of the free CO's. When these low-lying, ligand, donor orbitals interact with a metal atom, they will greatly destabilize three of the nine metal, valence orbitals. These destabilized orbitals will be predominantly valence s and p in character. The valence d orbitals will not be as greatly destabilized since they are not as diffuse as the s and p orbitals, though they will be split by the interaction with the ligand donor orbitals. The d orbitals will basically be split into two groups; those that can interact directly with the donor orbitals of the terminal ligands and those that cannot. Due to the similarity between the disposition of the terminally bound ligands and an octahedron cut in half by a plane perpendicular to one of its threefold rotation axis, Hoffmann often refers to the set of d orbitals which do not interact with the donor orbitals of the ligands as the "t_{2g}" set,[4] after their counterparts in O_h symmetry. With the coordinate systems for the metal atoms lined up along the threefold rotation axes of these "half-octahedra", the orbitals in the t_{2g} sets are primarily the d_{xy}, $d_{x^2-y^2}$, and d_{z^2} orbitals. The remaining d orbitals which do interact directly with the donor orbitals of the terminally bound ligands will be destabilized relative to the t_{2g} set. These are basically the d_{xz} and d_{yz} orbitals. The last of the nine metal, valence orbitals is in an orbital which is not strongly destabilized via interactions with the terminal ligands, is primarily s and p in character, and is directed away from the terminal ligands.

When three of these M–Cp or $M(CO)_3$ units are brought together to form a triangle, the metal levels will interact to form M–M bonding and antibonding orbitals.

The orbitals which are predominantly s and p in character and are not greatly affected by the terminal ligands will interact strongly with one another since they are so diffuse. This interaction gives rise to a low-lying M–M bonding orbital and a doubly degenerate pair of high-lying antibonding orbitals.

Since the M–M interactions for the d orbitals are smaller than the corresponding s and p metal–metal interactions, the separation of the metal d orbitals into a lower lying t_{2g} set and a higher lying set will be preserved through formation of the triangles. Jumping ahead slightly, the orbitals of primary importance in understanding the final MO results will be only those arising from the interactions of the higher lying set of d orbitals. Hence, they will be the only ones treated here. In D_{3h} symmetry the d_{xz} orbitals will give rise to a_2' and e' orbitals, and the d_{yz} orbitals will give rise to a_2'' and e'' orbitals. The e' and a_2'' orbitals are M–M bonding whereas the a_2' and e'' orbitals are M–M antibonding. These orbitals are depicted pictorially in Figure 3.

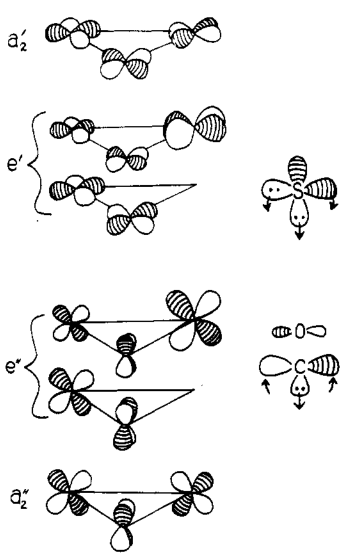

Figure 3. Pictorial representations of important metal and bridging ligand orbitals.

Both the CO and S bridging ligands possess three orbitals of interest to the bonding picture; one orbital of σ symmetry with respect to the threefold rotation axis of the metal triangle and two of π symmetry. These are, respectively, the 5σ and 2π orbitals for the CO and the $3p_z$ and $3p_x$ and $3p_y$ orbitals for the S. In D_{3h} symmetry, i.e., when the two triply bridging ligands are identical, the σ orbitals will transform as a_1' and a_2'' whereas the π orbitals will transform as e' and e''.

The greatest fundamental difference between these two ligands lies in the bonding role of the π orbitals. In S the π orbitals are low lying like the σ orbital and therefore make S a *π-donor* ligand. In CO, on the other hand, the π orbitals are high lying and consequently unoccupied, thereby making CO a *π-acceptor* ligand.

The most important interactions of the bridging ligands with the metal triangle involve the non-t_{2g} set of metal d orbitals, the bonding combination of the metal s and p orbitals not involved in bonding to the terminal ligands, and the σ and π orbitals of the bridging ligands mentioned above. The t_{2g} set of metal d orbitals is not appreciably involved in the bridge to triangle bonding since it is low in energy and its orbitals do not point toward the bridging ligands.

When the σ-donor orbitals of the bridging ligands interact with the metal triangle, they destabilize the metal valence orbitals of the same symmetries, the σ-acceptor orbitals. The bonding combination of the metal s and p orbitals which transforms as a_1' in D_{3h} will be strongly destabilized since it is so diffuse and consequently interacts strongly with the bridging ligands. The other metal orbital of appropriate symmetry and direction to function as a σ-acceptor orbital is the a_2'' combination of the d_{yz} orbitals. It will also be destabilized, though, since d orbitals are much more compact, not nearly as much as the a_1' orbital.

The π interactions accompanying the approach of the bridging ligands to the metal triangle are smaller than those

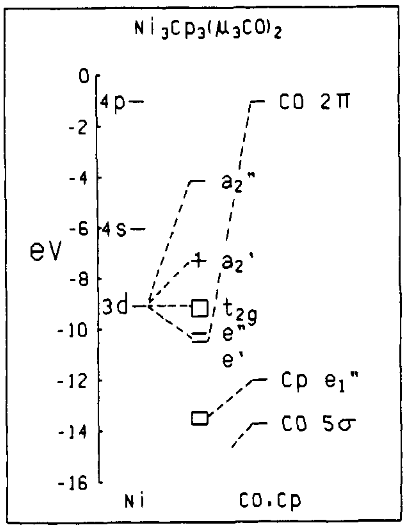

Figure 4. MO diagram for $Ni_3Cp_3(\mu_3\text{-}CO)_2$.

of the σ orbitals, though they determine many of the fine points of the electronic structure of these compounds. The difference between the S and CO π orbitals, i.e., their π-donor/acceptor character, is, of course, of paramount importance in determining the nature of the π interactions between the bridging ligands and the metal triangle: the π-donor S orbitals destabilizing the metal e′ and e″ orbitals and the π-acceptor CO orbitals stabilizing them.

Finally, there is one orbital of the metal triangle which, by symmetry, cannot interact directly with the bridging ligands. That orbital is the a_2' combination of the d_{xz} orbitals. Since it is purely M–M antibonding, it lies higher in energy than the other important metal d orbitals before allowing interactions with the bridging ligands. Whether or not the orbitals which get destabilized will end up at higher energies than the a_2' is, in part, a function of the metal and is one of the major concerns of the remainder of this section.

With this simple framework established we are prepared to discuss the details of the MO calculations.

Two Triply Bridging Carbonyls. The MO diagram from our calculation on $Ni_3Cp_3(\mu_3\text{-}CO)_2$ is presented in Figure 4. As expected, the e′ and e″ levels appear to be stabilized by their interaction with the CO 2π orbitals, and the a_2'' orbital is destabilized because of its interaction with the CO 5σ orbitals. A detailed study of the results suggests that the final e′ and e″ eigenvalues are a delicate balance between a variety of bonding and antibonding interactions among several orbitals on the metal and carbonyl centers. Our calculations show that the resultant stabilization of the e′ and e″ levels is sufficient to take them below the t_{2g} orbitals. This stabilization speaks to the very simple argument that π back-bonding increases as the energy of the donating orbitals prior to interaction approaches the energy of the CO 2π orbitals.[33] Such is the case here where the donating orbitals are energetically rather high before interacting with the CO 2π orbitals due to their interactions with the terminally bound Cp ligands.

The destabilization of the a_2'' orbital by the bridging CO 5σ orbitals is, as expected, considerably greater than the stabilization afforded by the M–M π bonding. As a result it is the highest lying of the levels which are predominantly metal d orbital in character.

Considering the Ni atom to be Ni(I) and consequently the Cp's to be Cp^-, one sees that there are 27 electrons to be placed in the predominantly metal orbitals. This allows for double occupation of all orbitals up through the t_{2g} set with the final electron being unpaired in the energetically isolated a_2' orbital.

This prediction of a $^2A_2'$ ground state supports the claims of Dahl et al.[10] They based their prediction on the increasing M–M distances as one goes from 26 to 27 to 28 electrons in the predominantly metal levels. This feature is compatible with the a_2' orbital being gradually filled since the a_2' orbital is M–M antibonding. It should be noted, however, that the increases in the M–M distances are small, only 0.02 or 0.03 Å/electron, thereby verifying the claim that the M–M interactions afforded by the d orbitals are very weak.

In 1962 Longuet-Higgins and Stone assessed that the unpaired electron resides in the a_2'' orbital and supported their assessment by showing that it leads to a qualitatively correct prediction of the perpendicular and parallel components of the electron **g** tensor.[34] However, using their same approximate evaluation of the **g** shifts, but placing the electron in the a_2' orbital, as we suggest, one also gets a similar qualitative match.[9b]

Schilling and Hoffman have carried out extended Hückel calculations on the heretofore unobserved $Co_3Cp_3(\mu_3\text{-}CO)_2$.[4e] By an extrapolation of their results to $Ni_3Cp_3(\mu_3\text{-}CO)_2$ one would also predict a $^2A_2'$ ground state, i.e., the unpaired electron in the a_2' orbital. Apart from this important similarity there is also an important difference between our results and those of Schilling and Hoffman. That is, in our calculations the e′ and e″ orbitals are stabilized below the t_{2g} set whereas Schilling and Hoffman leave them above the t_{2g} set. There are no definitive experimental results which suggest the correctness of either assignment. However, electronic spectra appear to indicate only one occupied orbital above the t_{2g} set.[35]

The energetic isolation of the a_2' orbital in $Ni_3Cp_3(\mu_3\text{-}CO)_2$ leads one to expect that in the anion the additional electron will also go into the a_2' orbital. This is, in fact, born out in the calculations and accounts for the observed diamagnetism in the complex.[36]

Two Triply Bridging Sulfides. The MO diagrams from our calculations on $Fe_3(CO)_9(\mu_3\text{-}S)_2$, (with D_{3h} symmetry), $Co_3Cp_3(\mu_3\text{-}S)_2$, and $Ni_3Cp_3(\mu_3\text{-}S)_2$ are present in Figure 5. Whereas the correct orbital ordering and occupations could basically have been reasoned out a priori in the case with the two triply bridging carbonyls, the cases with two triply bridging sulfides are not as intuitively obvious. The main difference between the disulfides and the dicarbonyl complex, as mentioned above, results from the S being a π donor and the CO being a π acceptor. Hence, in the disulfides the metal e′ and e″ levels are destabilized whereas they were stabilized in the dicarbonyl case. As one would expect from geometric arguments, the e″ orbitals are destablized more than the e′ orbitals since the e″ orbitals point toward the bridging atoms and the e′ orbitals are basically localized in the plane of the metal triangle. This fact coupled with the fact that the M–M bonding e′ levels are lower than the M–M antibonding a_2' level prior to interaction with the bridging ligands leads one to ask the question of what the final ordering will be of the a_2' orbital, which is not directly affected by the bridging ligands, and the e′ orbitals. Our computational results indicate that, in fact, the a_2' and e′ levels are typically very close in these complexes, with the e′ level about 0.4 eV below the a_2' level in the Fe complex, about 0.2 eV above the a_2' in the Co complex, and about 0.3 eV above the a_2' in the Ni complex. We would be hard pressed to demand a few tenths eV accuracy from our approximate method, hence we will resort to comparisons with experimental data to further elucidate the electronic structures of these compounds.

The $Fe_3(CO)_9(\mu_3\text{-}S)_2$ and $Co_3Cp_3(\mu_3\text{-}S)_2$ complexes are electronically equivalent as far as the number of predominantly

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[33] Caulton, K. G.; Fenske, R. F. *Inorg. Chem.* **1968**, *7*, 1273–1284.

[34] Longuet-Higgins, H. C.; Stone, A. J. *Mol. Phys.* **1962**, *5*, 417–424.

[35] Maj, J.; Rives, A. B., unpublished research results.

[36] Maj, J.; Dahl, L. F., to be submitted for publication.

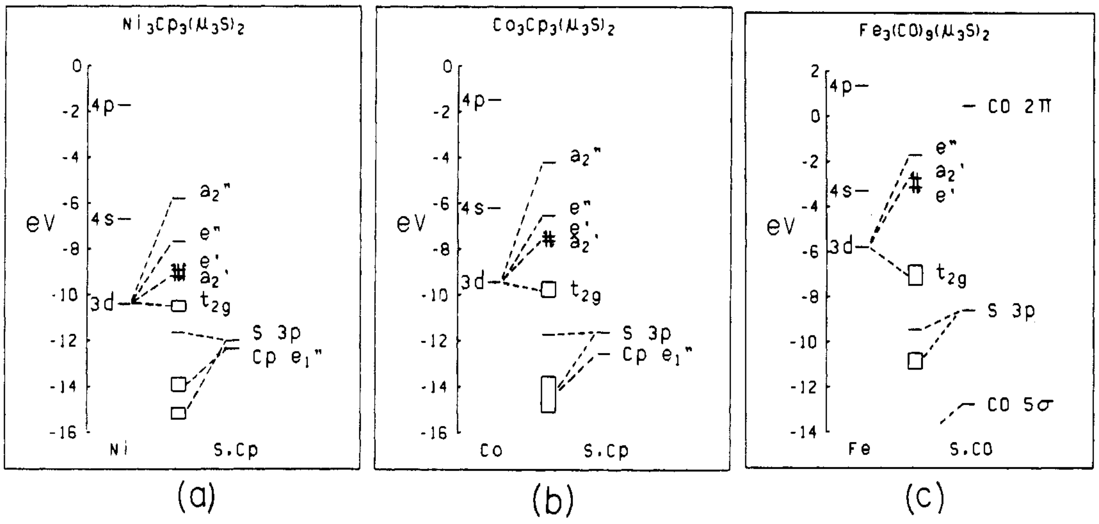

Figure 5. MO diagrams for (a) $Ni_3Cp_3(\mu_3\text{-}S)_2$, (b) $Co_3Cp_3(\mu_3\text{-}S)_2$, and (c) $Fe_3(CO)_9(\mu_3\text{-}S)_2$.

metal electrons is concerned, each having 20 electrons in the metal levels. This amounts to doubly occupying all of the orbitals up through the t_{2g} sets and having two electrons left over to place in the a_2' and/or e' orbitals. The resulting possible configurations would give rise to $^3A_2'$ (e'^2), $^1E'$ (e'^2), $^1A_1'$ (e'^2), $^3E'$ $(a_2'e')$, $^1E'$ $(a_2'e')$, and $^1A_1'$ $(a_2'^2)$ states. Traditional MO arguments would claim that in $Fe_3(CO)_9(\mu_3\text{-}S)_2$, for instance, the two electrons beyond the t_{2g} set would go into the e' orbitals and triplet couple to give a $^3A_2'$ ground state. However, when the highest occupied MO (HOMO) and lowest unoccupied MO (LUMO) are close together, and when the atomic orbitals which go into making them up do not overlap one another substantially, as is the case here with the $3d_{xz}$ atomic orbitals, regular MO arguments may break down as in the popular case of the dissociating H_2 molecule.[37] Here certain experimental observations can be used to help develop a clearer picture of the electronic structure of this compound.

The metal atoms in the diamagnetic $Fe_3(CO)_9(\mu_3\text{-}S)_2$ molecule form a very distorted triangle with two short sides (2.6 Å) and one long side (3.4 Å).[22b] This suggests that in idealized D_{3h} symmetry the ground state would have been $^1E'$, the singlet spin state accounting for the diamagnetism and the E' state giving rise to the distortion via the Jahn–Teller theorem. Upon distortion, the a_2' and one of the e' orbitals in D_{3h} both transform as the b_1 representation in the C_{2v} symmetry of the molecule and mixing of the two orbitals can occur. Our MO results on the distorted complex confirm this. The HOMO is a mixture of 40% a_2' orbital and 60% e' orbital. Furthermore the HOMO, which is energetically isolated from the LUMO, is antibonding on the long side of the triangle in accord with the structural data. Thus, the makeup of the HOMO in the distorted complex indicates that the most appropriate description in D_{3h} afforded by a single configuration would be $^1E'$ $(a_2'e')$.

The electronically equivalent $Co_3Cp_3(\mu_3\text{-}S)_2$ complex is somewhat more complicated. It has crystallographically imposed threefold rotational symmetry (space group $P6_3/m$)[24b] and hence appears to have idealized D_{3h} point group symmetry. Its magnetism is temperature dependent.[24b] At high temperatures it has a temperature-independent magnetic moment indicative of a triplet state and obeys the Curie–Weiss Law. However, below 190 K its susceptibility drops and becomes zero by about 130 K indicating, of course, a singlet state. The investigators who carried out the magnetic work suggested that they were seeing a crossover of the a_2' $(3d_{xz})$ and e' $(3d_{z^2}$, not $3d_{xz})$ orbital energies, at low temperatures the a_2' orbital being lowest and doubly occupied, giving rise to the singlet state, and at high temperatures the e' levels being lowest and doubly occupied, giving rise to the triplet state. We suggest an alternative explanation. Presumably at low temperatures $Co_3Cp_3(\mu_3\text{-}S)_2$ will be like $Fe_3(CO)_9(\mu_3\text{-}S)_2$ and will have a $^1E'$ $(a_2'e')$ ground state. At higher temperature the stabilization afforded by the singlet spin coupling will be overcome and the $^3E'$ state will become populated.

We attribute the differences between the Co and Fe complexes to differences in the character of the atomic contributions to the e' and a_2' MO's. These atomic contributions will be difficult not only because the metals are different but also because the terminal ligands are different. The effect of changing from Fe to Co(I) is to contract the orbitals slightly thereby allowing them to interact with neighboring centers less strongly. The different effects of Cp^- and $(CO)_3$ ligands has been treated before by Pinhas and Hoffmann.[4g] They basically showed that the three carbonyls cause more polarization of the frontier d orbitals with s and p orbitals than do Cp rings. In the cases here the Fe orbitals would allow more Fe–Fe interaction due to their increased 4s and 4p character. Hence, both the changes in metal and changes in the terminal ligands would cause stronger M–M interactions in the Fe complex as compared to the Co complex, thereby making the singlet/triplet separation smaller in the Co complex; apparently small enough to be thermally surmountable.

We suggest that the apparent D_{3h} point symmetry of the Co complex is an artifact of the symmetry imposed by the space group ($P6_3/m$) and is not the true point symmetry. By this, we mean that the molecule is likely distorted; however, disorder in packing makes the molecule appear to possess threefold rotation symmetry. It should be noted that from the small interaction among the 3d orbitals we would not expect a large distortion from the threefold rotation symmetry.

When one oxidizes the $Co_3Cp_3(\mu_3\text{-}S)_2$ molecules to the monocation, the molecule becomes distorted with one short side (2.45 Å) and two long sides (2.65 Å). The average Co–Co distances in the cation are smaller than in the neutral, thereby indicating the antibonding nature of the electron that was removed. Since the e' orbital is bonding, it must have been the antibonding a_2' electron that was removed. Hence the ground state of the cation in idealized D_{3h} symmetry must be $^2E'$. The spacial degeneracy of the ground state accounts for the observed distortion. This time, however, the electron resides in an orbital which is bonding between the two Co atoms or the short side of the triangle.

Schilling and Hoffmann[4c] in their treatment of Co_3Cp_3-

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[37] Goddard, W. A.; Dunning, T. H.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368–376.

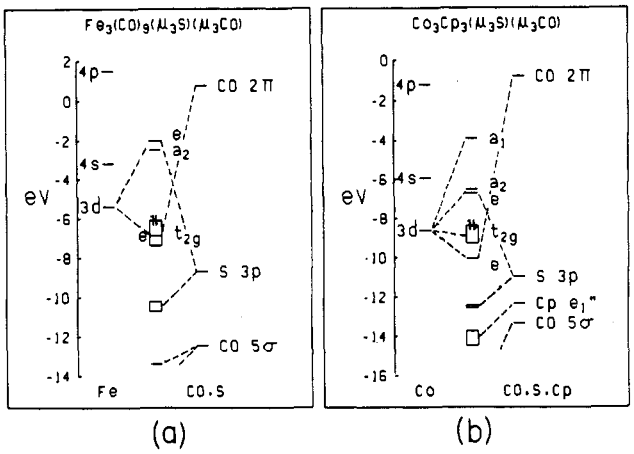

Figure 6. MO diagrams for (a) $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}CO)$ and (b) $Co_3Cp_3(\mu_3\text{-}S)(\mu_3\text{-}CO)$.

$(\mu_3\text{-}S)_2{}^n$ (n = 0, 1+) have the e′ ($3d_{xz}$) orbital greatly destabilized thereby leaving the a_2' orbital energetically isolated and necessarily the recipient of the electrons remaining after the filling of the t_{2g} set. This accounts for the experimentally observed shortening of the average Co–Co distance on oxidation. However, it cannot explain the consequent distortion to C_{2v} symmetry nor the magnetic behavior of the neutral species. The high-spin character of the neutral species is given recognition in a later article.[4m]

The $Ni_3Cp_3(\mu_3\text{-}S)_2$ system differs from the Fe and Co disulfides in that it contain three more electrons in the metal levels. These three electrons fill all but one hole in the a_2' and e′ orbitals thereby causing the molecule to have either a $^2A_2'$ or $^2E'$ ground state. Our results suggest that the a_2' level is lowest thereby suggesting that the ground state may be $^2E'$. The experimental structural data indicate that $Ni_3Cp_3(\mu_3\text{-}S)_2$ has D_{3h} point symmetry, and hence one would not expect a spacially degenerate ground state since it would cause a Jahn–Teller distortion which is not observed. Once again, though, the observed space group, $P6_3/m$,[25] imposes the threefold rotational symmetry on the molecules. Hence, we cannot say unambiguously that the individual molecules will have threefold rotational symmetry. The Ni 3d orbitals are not only the most contracted but they are also separated by the largest distances on the three metals studied here. These facts again lead one to expect that any Jahn–Teller distortion of the $^2E'$ state of the triangle would be small.

There are some other interesting systems with two triply bridging S's which are not unlike $Ni_3Cp_3(\mu_3\text{-}S)_2$. These are the $M_3L_6(\mu_3\text{-}S)_2{}^{2+}$ complexes with M = Ni and Pt and L = phosphine.[38] These diamagnetic systems involve three d^8 square-planar complexes which all share two ligands, the bridging sulfides. The $Ni_3Cp(\mu_3\text{-}S)_2$ cluster that we have been concerned with is just one electron short of having three diamagnetic d^8 Ni atoms, and each Ni center in the cluster has one unoccupied 3d orbital, the $3d_{yz}$ orbital, which resembles the high-lying b_{1g} orbital of a conventional square-planar complex. This straightforward connection between our $Ni_3Cp_3(\mu_3\text{-}S)_2$ results and these other complexes gives credence to our orbital ordering scheme.

Apparent from our results on the disulfides is the need for a strong link between theory and experiment when examining systems of this size. At this point in time the theory is necessarily too approximate and many of the experimental results too complicated to allow for unambiguous explanations of many phenomena. Advances in the near future will likely depend on input from both theory and experiment.

Table I. M–X–M Bond Angles (Deg)

	X = S	X = CO		X = S
$Ni_3Cp_3(\mu_3\text{-}CO)_2$		76.5	$Ni_3Cp_3(\mu_3\text{-}S)_2$	80.3
$Co_3Cp_3(\mu_3\text{-}S)(\mu_3\text{-}CO)$	65.4	78.7	$Co_3Cp_3(\mu_3\text{-}S)_2$	76.9
$Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}CO)$	72.4	78.6	$Fe_3(CO)_9(\mu_3\text{-}S)_2$ (C_{2v})	71.0, 98.2

Mixed Triply Bridged Systems. The MO diagrams showing the results of our calculations on $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}CO)$ and $Co_3Cp_3(\mu_3\text{-}S)(\mu_3\text{-}CO)$ are present in Figure 6. As may have been expected the electronic structures of these systems represent a cross between their dicarbonyl and disulfide counterparts.

Both of these systems have idealized C_{3v} point symmetry. The absence of a horizontal mirror plane allows the mixing of orbitals which were necessarily separate in D_{3h} symmetry: e′ with e″, a_1' with a_2'', and a_2' with a_1''. The mixing of the e′ and e″ orbitals produces two e sets, one which points toward the triply bridging CO and another which points toward the triply bridging S. The e set which points toward the triply bridging CO is stabilized by virtue of the interaction with the CO 2π orbitals. The other e set is destabilized by virtue of the interaction with the S p_π orbitals. As is the case with the dicarbonyl and disulfides, the a_2 orbital is unable by symmetry to directly interact with the bridging ligands, and the a_1 (formerly the a_2'' orbital) is destablized by interaction with the σ orbitals of the bridging ligands.

Apart from the location of the stabilized e orbitals, our results are in basic accord with those of Schilling and Hoffmann[4c] on $Co_3Cp_3(\mu_3\text{-}S)(\mu_3\text{-}CO)$. In the Co case as in the case of $Ni_3Cp_3(\mu_3\text{-}CO)_2$ the e levels are stabilized below the t_{2g} set. However, in the Fe case the e levels are stabilized into the midst of the t_{2g} set. This is not unexpected since the t_{2g} set in $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}CO)$ is stabilized by π back-bonding with the terminal CO 2π orbitals, whereas in $Co_3Cp_3(\mu_3\text{-}S)(\mu_3\text{-}CO)$ the t_{2g} set is not stabilized since the Cp's do not function as π-accepting ligands.

The two systems we are treating here are electronically equivalent as far as the metal orbitals are concerned, each having 22 electrons to place in these levels. As usual, 18 electrons go into filling the t_{2g} set, thereby leaving 4 electrons to place in the stabilized e set. The HOMO is energetically isolated from the LUMO in this description. Hence, our results are in accord with the experimentally observed diamagnetism and symmetric triangles.

Nature of the M–M Interactions

In none of the MO results does one find among the predominantly metal levels three more occupied M–M bonding MO's than occupied M–M antibonding MO's. In fact, it could be argued that only in the $Ni_3Cp_3(\mu_3\text{-}S)_2$ complex are there more M–M bonding electrons than antibonding electrons, and in that case there is only one more M–M bonding electron.

From this one should not be led to the conclusion that the attractive M–M interactions are nonexistent. If there were no attractive M–M interactions, the M–X–M bond angles (see Table I) would necessarily be greater than or equal to 90° since it would be the bonding of the metal atoms to the sp^n ($0 < n < \infty$) orbitals of the bridging ligands that would hold the clusters together. However, since the M–X–M bond angles are less than 90°, we conclude that the M–M interactions are indeed attractive.

An NHO[32] analysis of the MO result, as discussed in the section on calculational details, provides a technique for more clearly describing in a conventional framework the bonds that exist in a complex. Hence, in order to elucidate the nature of the M–M interactions in the complexes being considered

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[38] (a) Ghilardi, C. A.; Midollini, S.; Sacconi, L. *Inorg. Chim. Acta* **1978**, *31*, L431–L432. (b) Chatt, J.; Mingos, D. M. P. *J. Chem. Soc. A* **1970**, 1243–1245.

here, we have carried out NHO analyses of our MO results.

We began by looking for direct M–M bonds and were somewhat surprised to find that the results of these NHO calculations basically reflected the conclusions obtained from a cursory view of our MO results. That is, no conventional M–M bonds were found to exist. It was impossible to carry out the necessary orthogonalization of the various hybrid orbitals on each center since any bonding orbital found involving two metal atoms was strongly involved with other M–M and metal–ligand bonds. This supports the contention that any M–M bonding is not localized and is strongly affected by the bonding to the ligands.[7,15,39] This problem prevented these NHO calculations from yielding meaningful information. Hence, we have not reported our results for these calculations.

The NHO calculations in which the metal atoms are treated individually fails not only in describing the M–M bonding but also in describing the direct metal atom to bridging ligand bonding. Typically when one thinks of bridging ligands he thinks of forming bonds from the ligand to each of the atoms to be bridged. In terms of symmetry orbitals this involves performing a unitary transformation of the ligand to metal substrate, bonding, symmetry orbitals to give appropriate localized, bridge-bonding orbitals. This transformation to localized orbitals is possible if and only if the proportion of bridge character to substrate character is the same in all of the bonding, symmetry orbitals.[38] For instance, so that the three bonding symmetry orbitals of a triply bridged system, ψ_σ and two ψ_π's, could be mixed together to form localized bonding orbitals, ψ_σ and the ψ_π's must have the same amount of contribution from the metal substrate atomic orbitals and the same amount of contribution from the bridging ligand orbitals. This was not the case in our original NHO calculations; hence, we were unable to discuss the bonding in these systems in terms of individual metal atoms bonding to bridging ligands.

These problems associated with our original NHO calculations, in particular these considerations of describing bridge bonding, led us to carry out another set of NHO analyses, this time grouping all three metal atoms together as one substrate unit rather than treating them individually. This would certainly produce a better picture of the bridge bonding and perhaps give some insight into the M–M bonding as well.

In all cases the NHO analyses show nine delocalized hybrids on each metal triangle. These delocalization lone pairs represent the t_{2g} set of orbitals, and as such, their occupation results in no net M–M bonding interactions.

In examining the M–M interactions we will be concerned here with three sorts of delocalized hybrid orbitals in these calculations, the π-donor and π- and σ-acceptor delocalized hybrids on the metal triangle. These orbitals will be labeled as chemical intuition would indicate. That is, the M_3–μ_3-CO σ bond is described as a metal delocalized σ-acceptor hybrid accepting electron density from a delocalized donor hybrid on the carbonyl, while the M_3–μ_3-CO π bond is described as a carbonyl delocalized acceptor hybrid accepting electron density from a delocalized π-donor hybrid on the metal triangle. Both the M_3–μ_3-S σ and π bonds involve delocalized acceptor hybrids on the metal accepting electron density from donor hybrids on the sulfur. Our results concerning the makeup of the delocalized hybrids and the polarization of the resultant bonds are given in Tables II and III. It is imperative for what is to follow, as well as for relating the NHO perspective to what has been said previously, that the reader realize that NHO's incorporate into the delocalized hybrid orbitals contributions from both the uppermost orbitals, which are mainly 3d metal, and the very low-lying canonical orbitals that are principally ligand in character. The metal contributions in these low-lying orbitals are composed primarily of 4s and 4p orbitals. Hence the NHO delocalized orbitals can have orbitals character which is quite different from the highest occupied canonical orbitals.

In the cases of the delocalized acceptor hybrids, the metal 4s and 4p atomic orbitals make up the major components in these delocalized hybrids. At the M–M distances which we are using here (i.e., "single bond" distances and longer), the only metal atomic orbitals that overlap orbitals on neighboring metal centers to any appreciable degree are just these 4s and 4p atomic orbitals. Hence, any appreciable occupation of these delocalized acceptor hybrids would therefore give rise to a substantial M–M interaction.

The polarization coefficients indicate the degree of occupation of the delocalization hybrids. In Table II one notices that the polarization coefficients of the metal triangle delocalized acceptor hybrids are much larger than one would have expected from looking at the MO's which most closely resemble these donor/acceptor bonds. The large polarization coefficients indicate substantial occupations of these delocalized acceptor hybrids: between $^2/_3$ and 1 full electron. Hence we conclude that the occupation of these orbitals accounts for the dominant M–M interactions in the clustes studied here and presumably in all bridged TMCC's. One should note, however, that we have not yet discussed the M–M bonding or antibonding character of these interactions.

The M–M interactions we are developing here are not necessarily bonding interactions. The nature of the interactions depends on the symmetry and makeup of the localized acceptor hybrids. Delocalized hybrids which function as σ-acceptor orbitals will necessarily be M–M bonding, whereas delocalized hybrids which function as π-acceptor or π-donor orbitals will be part M–M antibonding as a result of contributions from the 4s, $4p_y$, and $4p_z$ atomic orbitals and part M–M bonding as a result of contributions from the $4p_x$ atomic orbitals. These arguments indicate that occupation of both σ- and π-delocalized hybrids will tend to oppose one another as far as their effects on the M–M interactions are concerned. Considerations must be made for the makeup of these orbitals in order to determine the net M–M antibonding character of the substrate to bridging ligand bond.

The σ bonds from the metal substrates to the bridging ligands are not strongly dependent on the identity of the bridging ligand. All of the metal triangle delocalized σ-acceptor hybrids have roughly the same makeup, about 75% 4s and 4p and 25% 3d, whether they are involved in a bond to a bridging carbonyl or a bridging sulfide. Their polarization coefficients are also nearly the same for the two types of bonds, both bonds being approximately 50% metal substrate and 50% bridging ligand in character.

The π bonds connecting the metal substrates with the bridging ligands will not be nearly so similar as the σ bonds since the bridging carbonyl is a π-acceptor ligand and the bridging sulfide is a π-donor ligand. These properties are reflected in the polarization coefficients, the bonds to the bridging carbonyls being strongly polarized toward the neutral triangles and the bonds to the bridging sulfides polarized towards the sulfides.

Despite the dissimilarity in the π bonding as manifested by the polarization coefficients, there is an important similarity in the orbital character of the π-delocalized hybrids on the metal triangle. That similarity is that both the acceptor and donor π-delocalized hybrids, except in $Ni_3Cp_3(\mu_3\text{-}S)_2$, have a much greater contribution from the 3d orbitals than do the σ-delocalized hybrids. The ramification of this fact is that the antibonding M–M interactions resulting from the occupation of the π-delocalized hybrids are diminished as compared to

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(39) Braterman, P. S. *Struct. Bonding Berlin* **1971**, *10*, 57–86.

Table II. Polarization Coefficients for the M_3–X Bond Orbitals

	$^{\sigma}M_3$–CO		$^{\pi}M_3$–CO		$^{\sigma}M_3$–S		$^{\pi}M_3$–S	
	M_3	CO	M_3	CO	M_3	S	M_3	S
$Ni_3Cp_3(\mu_3\text{-}CO)_2$	0.73	0.68	0.88	0.48				
$Co_3Cp_3(\mu_3\text{-}S)(\mu_3\text{-}CO)$	0.73	0.69	0.87	0.50	0.67	0.74	0.58	0.81
$Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}CO)$	0.71	0.70	0.81	0.58	0.68	0.73	0.62	0.78
$Ni_3Cp_3(\mu_3\text{-}S)_2$					0.68	0.73	0.59	0.80
$Co_3Cp_3(\mu_3\text{-}S)_2$					0.69	0.72	0.61	0.79
$Fe_3(CO)_9(\mu_3\text{-}S)_2$					0.68	0.73	0.67	0.74

Table III. Percent Characters of Metal Delocalized Hybrids in the M_3–X Bonds

	$^{\sigma}M_3$–CO			$^{\pi}M_3$–CO			$^{\sigma}M_3$–S			$^{\pi}M_3$–S		
	% 3d	% 4s	% 4p	% 3d	% 4s	% 4p	% 3d	% 4s	% 4p	% 3d	% 4s	% 4p
$Ni_3Cp_3(\mu_3\text{-}CO)_2$	25	20	55	70	3	27						
$Co_3Cp_3(\mu_3\text{-}S)(\mu_3\text{-}CO)$	26	19	54	72	4	24	21	23	56	42	12	46
$Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}CO)$	31	14	55	*a*	*a*	*a*	26	18	56	49	12	39
$Ni_3Cp_3(\mu_3\text{-}S)_2$							27	23	50	27	28	45
$Co_3Cp_3(\mu_3\text{-}S)_2$							24	22	54	43	12	45
$Fe_3(CO)_9(\mu_3\text{-}S)_2$							27	17	56	52	8	40

[a] Due to a strong delocalization with the π-back-bonding levels of the terminal CO's, the M_3–CO π bond is unable to be defined unambiguously.

those of the σ-delocalized hybrids because of the small interactions among the 3d orbitals or neighboring metal centers. (The $Ni_3Cp_3(\mu_3\text{-}S)_2$ system will be treated separately at the end of this section.)

With all of this information in hand, we conclude that the M–M interactions are dominated by the occupation of delocalized hybrids which are used in bonding a metal triangle to a triply bridging ligand and are constructed largely of metal 4s and 4p atomic orbitals. There is an attractive M–M interaction resulting from occupation of the delocalized σ-acceptor hybrid. This attractive M–M interaction dominates the M–M interactions since occupation of the M–M antibonding π-delocalized hybrids has a decidedly smaller effect due to the larger participation of metal 3d orbitals in these delocalized hybrids. Also, the antibonding character of the π-delocalized hybrids is not as strong as the bonding character of their counterpart σ-delocalized hybrids since the π-delocalized hybrids have some M–M bonding contribution arising from the $4p_x$ character. We assign the role played by the 3d atomic orbitals in M–M bonding to be secondary to that of the 4s and 4p atomic orbitals.

This description of the M–M bonding is not unrelated to the theoretical framework Lauher[2a] has established for explaining the structure and stoichiometries of TMCC's. That is, our delocalized hybrids which function as acceptor orbitals on the metal triangles are similar to Lauher's cluster valence MO's (CVMO's) of predominantly s and p character. Since the CVMO's are basically M–M bonding, the large occupation we have shown them to have gives rise to the attractive M–M interactions.

The analogy between this work and Lauher's, however, is not all together precise. The fact that all of the clusters studied here, except for the mixed-bridge systems, have more than the magic number of 48 cluster valence electrons necessitates mixing some of Lauher's high-lying antibonding orbitals into the delocalized acceptor hybrids. This helps account for the longer M–M distance in these clusters as compared with the electron-precise, mixed-bridged systems. Recently Anderson et al. have utilized arguments quite in line with those presented here in describing the bonding in $Fe_2(CO)_6S_2$.[7]

$Ni_3Cp_3(\mu_3\text{-}S)_2$ is the single exception to our conclusion concerning the decreased M–M antibonding character of the π-delocalized hybrids on the metal triangle resulting from an increased 3d atomic orbital participation. This is also the system with the largest M–M distances even though there are more M–M bonding MO's occupied than in any of the other disulfides. We attribute the attractive M–M interactions in the system again to the dominance of the M–M bonding character of the π-delocalized hybrid. However, its dominance is not so clear-cut in this case since the π-delocalized hybrid is rather strongly M–M antibonding due to its small 3d atomic orbital contribution. We attribute the large M–M distance in this cluster to this high M–M antibonding character of the π-delocalized hybrid.

Perhaps an equally important feature of the bonding in the $Ni_3Cp_3(\mu_3\text{-}S)_2$ complex is the exact makeup of the delocalized hybrids and how this relates to the description of the molecule given in the section on the MO results. One sees in Table III that the ratio of 3d/4s/4p is about 1/1/2 for both delocalized hybrids. In other words, what we have here are basically dsp^2 hybrid orbitals. (Here the term, hybrid, is used with its conventional meaning.) The dsp^2 hybrids give rise to a square-planar complex which is, in fact, just what we claimed after examining our MO results: three square-planar complexes all sharing two triply bridging ligands. Our ability to talk about this system in terms of three separate Ni atoms with dsp^2 hybridization is a reflection of the very weak M–M interactions in this complex as compared to the others studied here.

Summary and Conclusions

The results of our calculations have basically served two purposes. (1) They have supported the idea that bridging systems do not have the number or type of direct M–M bonds as would be predicted from conventional electron-counting schemes. We have lent credence to our results by explaining certain structural and magnetic data. (2) Our NHO results have led us to suggest that it is the metal valence s and p atomic orbitals which dominate the M–M interactions in these bridged systems. Also the bonding of the bridging ligands is best described in terms of bonding to a metal substrate rather than to individual metal atoms.

From these features one sees that the M–M bonding in systems such as the ones studied here is not unlike what it would presumably be on a transition-metal surface. As mentioned in the Introduction, the M–M bonding on surfaces is dominated by occupation of orbitals made largely from valence s an p orbitals, just as we have suggested here for these systems. Apparently the bonding in TMCC's is not as different from the bonding of chemisorbed species on transition-metal surfaces as one would have been led to believe from discussions like that given in the Introduction.

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Registry No. $Fe_3(CO)_9(\mu_3\text{-}S)_2$, 22309-04-2; $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}CO)$, 74520-99-3; $Co_3Cp_3(\mu_3\text{-}S)_2$, 11105-79-6; $[Co_3Cp_3(\mu_3\text{-}S)_2]^+$, 81316-25-8; $Co_3Cp_3(\mu\text{-}S)(\mu_3\text{-}CO)$, 37328-31-7; $Ni_3Cp_3(\mu_3\text{-}S)_2$, 58396-47-7; $[Ni_3Cp_3(\mu_3\text{-}CO)_2]^-$, 81205-88-1; $Ni_3Cp_3(\mu_3\text{-}CO)_2$, 12194-69-3.

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Reevaluation of the Crystal Structure Data on the Expanded-Metal Compounds $Li(NH_3)_4$ and $Li(ND_3)_4$

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Existing X-ray diffraction data (Mammano and Sienko, 1968) and neutron diffraction data (Chieux, Sienko, and DeBaecker, 1975) on the solid lithium–ammonia compounds have had to be reevaluated in the light of recent magnetic studies which indicate absence of the 82 K solid–solid transition in the deuterated compound. X-ray reflections observed at 77 K, which were previously interpreted as a mixture of hexagonal and body-centered-cubic phases, are better indexed as a single body-centered-cubic phase. Solid-phase II of $Li(NH_3)_4$, stable below 82 K, appears to belong to space group $I\bar{4}3d$, a = 14.93 Å, with 16 lithium atoms and 16 nitrogen atoms on Wyckoff position c and 48 nitrogens on Wyckoff position e. The same structure holds for $Li(ND_3)_4$. Below 25 K, extra reflections appear, corresponding to formation of a superstructure with period $2a$. This coincides with onset of what appears to be antiferromagnetic ordering below this temperature.

Introduction

A most remarkable feature of the lithium–ammonia phase diagram (Figure 1) is an extraordinarily deep eutectic at 20 MPM (mole percent metal) and 89 K.[1] A great deal of indirect evidence has accumulated which suggests that a compound, $Li(NH_3)_4$, is formed at or near this composition. Such evidence includes the following: the enthalpy of solution of Li in NH_3 is relatively large and negative (−38 kJ/mol), like that of Ca in NH_3 (−80 kJ/mol) and unlike that of Na in NH_3 (~0 kJ/mol);[2] the vapor pressure of the saturated $Li-NH_3$ solution is very small (32 torr at 0 °C) compared to that of $Na-NH_3$ (1700 torr at 0 °C);[3] the conductivity of solid lithium–ammonia is considerably greater than that of liquid $Li-NH_3$, whereas the reverse is true for $Na-NH_3$;[4] the heat capacity of the $Li-NH_3$ mixture is in excess of that computed from the sum of the components, an excess which peaks at 20 mole % Li;[5] solid $Li-NH_3$ shows a thermal transition at 82 K, corresponding to a break in the conductivity–temperature curve.[4] More direct evidence comes from X-ray diffraction patterns on solid $Li-NH_3$ that are neither those of Li nor NH_3.[6] Mammano and Sienko examined powder samples of 20 mol % lithium-in-ammonia solutions at 77 K and concluded that $Li(NH_3)_4(s)$ exists in two phases: a cubic form with a_0 = 9.55 Å stable between 82 and 89 K, and a hexagonal form having a = 7.0 Å and c = 11.1 Å, stable below 82 K.[6] Kleinman et al. found similar results but disagreed on the possible choice of space group for the hexagonal phase, claiming $P6_3$ rather than $P6_3mc$.[7]

Recently, in a magnetic investigation of lithium–methylamine solutions,[8] we remeasured the low-temperature magnetic susceptibility of $Li(NH_3)_4$ in order to verify certain unusual features of the temperature dependence as reported by Glaunsinger, Zolotov, and Sienko.[9] Not only were the gross features of temperature dependence, discontinuities at 89 and 82 K, and tendency to antiferromagnetism at very low temperatures reproduced, but the quantitative values themselves were duplicated. This last was no small feat since the forces involved were tiny and large corrections for core diamagnetism and sample container had to be applied. Fortunately, in collaboration with Landers and Dye,[10] we had worked out in the meantime a method of decomposing lithium–cryptate electride in situ in the magnetic apparatus so corrections for bucket and core diamagnetism could be made by direct measurement. Applying this technique to $Li-NH_3$, we were able to measure the *net electronic susceptibility* of $Li(NH_3)_4$ and also that of $Li(ND_3)_4$ with great accuracy. A most surprising result was that, although the susceptibilities of $Li(NH_3)_4$ and $Li(ND_3)_4$ were identical within experimental error (e.g., $(60 \pm 3) \times 10^{-6}$/mol of Li at 89 K) in the liquids above 89 K and in the solids below 82 K, there was no trace of solid phase I in the magnetic behavior of $Li(ND_3)_4$. In other words, deuteration apparently suppresses the solid–solid transition at 82 K of $Li(NH_3)_4$. Confirmation of this fact is given by the DTA studies of DeBaecker,[11] who found with $Li(ND_3)_4$ no heat effect at 82 K.

Chieux, Sienko, and DeBaecker[12] have done low-temperature neutron diffraction studies on powder samples of $Li(ND_3)_4$ and $Li(NH_3)_4$. They found that the pattern of the deuterated compound could be indexed uniquely as a body-centered-cubic phase (a = 14.83 Å at 30 K; a = 14.93 Å at 60 K). Because the electronic magnetic susceptibility of $Li(NH_3)_4$ is identical in magnitude and temperature dependence with that of Li-

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