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Bonding in Transition-Metal Cluster Compounds. 1. The $\mathrm{M_6(\mu_3\text{-}X)_8}$ Cluster

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The electronic structure of the transition-metal cluster moiety $\mathrm{M_6(\mu_3\text{-}X)_8}$, with idealized O_h symmetry, is examined for X = chalcogen, halogen, and carbonyl ligands. The role of the metal d electrons in metal–metal bonding is emphasized, and the structure of the metal cluster "d-band" is described in detail.

1. Introduction

In recent years numerous metal cluster compounds in which transition-metal atoms are part of a chemically bonded metal–metal network have been prepared and their chemical and physical properties characterized; two recent books survey much of the field.[1,2] I have emphasized elsewhere that (a) the *principal bonding interaction* between transition-metal atoms in cluster compounds is due to the *metal d electrons as in the bulk metals* and that (b) this conclusion is consistent with the electron-counting aspects of Wade's rules.[3,4] The first of these general points will be illustrated here by examining directly the electronic structure of cluster species in which eight chalcogen, halogen, or carbonyl ligands sit over the faces of an idealized metal atom octahedron, i.e. the $\mathrm{M_6(\mu_3\text{-}X)_8}$ moiety, examples of which can be found throughout the transition-metal block.[5-8] While there is a difference in the formal number of metal d electrons between say $\mathrm{Mo_6(\mu_3\text{-}Cl)_8Cl_6^{2-}}$ and $\mathrm{Co_6(\mu_3\text{-}CO)_8(CO)_6^{4-}}$, there are important similarities in both the metal cluster bonding and the cluster–ligand bonding to which I wish to draw attention.

A variety of molecular orbital calculations of the electronic structure of species containing the idealized octahedral $\mathrm{M_6(\mu_3\text{-}X)_8}$ cluster can be found in the literature.[9-19] These include the following: detailed studies of the archetype of the Chevrel phase materials $\mathrm{Mo_6X_8}$ (X = S, Se, Te) using both the LMTO[10] and extended Hückel[11] methods; studies of the halide cluster anion $\mathrm{Mo_6(\mu_3\text{-}X)_8X_6^{2-}}$ (X = Cl, Br, I) by extended Hückel, d-orbital overlap, and Xα methods;[14-17] extended Hückel studies of $\mathrm{Co_6}$ and $\mathrm{Co_6H_6}$ which were related to the electronic structure of $\mathrm{Co_6(\mu_3\text{-}CO)_8(CO)_6^{4-}}$.[18] All these clusters are based on an idealized structure in which the locations of the μ_3-ligand donor atoms define the corners of a cube circumscribing the octahedron. Since both the cube and the octahedron share the same point group symmetry, O_h, we can use the symmetry species of this group to classify the orbitals of both the metal cluster (section 3(a)) and the ligands (section 3(b)), and this simplifies an account of the bonding interactions in these clusters. It is worth emphasizing however that this particular point group symmetry does not greatly influence the final distribution of the bonding and antibonding molecular orbitals for the cluster compound, which is largely determined by the nearly spherical shape of the whole cluster.[3,20,21] Accordingly the discussion has a much wider range of application than just the clusters referred to here.

Most theoretical studies of the electronic structure of bare transition-metal clusters have used molelcular orbital models of the kind routinely used in solid-state physics such as the chemical pseudopotential method,[3,12] and a family of techniques that can be lumped together as "Xα methods". (Technically the Xα methods are all descendants of the KKR-band structure method for periodic solids;[44] they are based on the local density (LD) approximation to density functional theory.) Users of these methods *are* aware of the chemically more familiar techniques such as CNDO and extended Hückel (EH) and have tended to be skeptical as far as transition-metal systems are concerned.[16,17,22-24] While there may be general agreement over those features that are largely determined by symmetry, for example the distribution of bonding and antibonding molecular orbitals, there appears to be sharp disagreement as to the factors responsible for cluster bonding and the theoretical basis for Wade's rules. It is important therefore to assess critically these different approaches to the electronic structure of transition-metal systems, and this is the concern of section 2.

The plan of the paper is as follows: Section 2 is devoted to a critical assessment of various electronic structure methods that have been used for studying transition-metal clusters, and ends with a statement of the overall goal of these two papers, which is to establish the *general* importance of d-electron bonding in transition-metal cluster compounds. Section 3 is concerned with a particular class of clusters, the $\mathrm{M_6(\mu_3\text{-}X)_8}$ species, which are convenient exemplary cases; some extensions to other cluster types are given in the following paper. It is important to recognize at the outset that the paper is concerned with *general principles* illustrated by reference to selected examples, *not* induction on the basis of reviewing numerous cluster species. I analyze these octahedral cluster species by first studying the orbitals of two fragments, the octahedral $\mathrm{M_6}$ unit (section 3(a)) and the ligand polyhedron in the absence of the metal cluster core (section 3(b)), before allowing the orbitals of the two parts to hybridize (section 3(c)). Finally the main themes of the paper are drawn together in section 4. In the following paper I shall discuss the relationship between the qualitative arguments that enjoy much popularity in inorganic chemistry, for example Wade's rules and the isolobal principle and the view of transition-metal cluster bonding developed

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here—a view that has emerged from recent studies in theoretical physics.[3,4]

2. Electronic Structure Methods for Transition-Metal Systems

Xα methods have been used to look at M_8 and M_{13} clusters with O_h point group symmetry formed from Ni, Pd, and Cu,[23] and Xα calculations on octahedral M_6 clusters of Nb, Ta, Mo, and W are also available.[24] The results of these calculations can be reproduced quantitatively, and with much less computational effort, by the closely related LMTO method,[4,25,26] which was used by Nohl et al. in their Chevrel phase studies.[10] All these calculations show small metal clusters to be recognizable as fragments of the bulk metals as far as their *electronic structure* is concerned. In the simplest form of the LMTO method, namely the atomic sphere approximation (ASA),[4,10] one achieves a Hückel-like MO model that has the simplicity of the d-orbital overlap model of Cotton and Haas[15] combined with a more or less *quantitative* treatment of the d-orbital interactions in transition-metal clusters. Furthermore, in contrast to the quantum chemistry techniques referred to in section 1, these "Xα methods" have provided the basis for a deep analysis of the d-orbital interactions, which shows that *bonding between transition-metal atoms involves novel factors not found with the s- and p-bonded main-group elements.*[27-29] Specifically, there is no straightforward interpretation of transition-metal bonding in terms of the overlapping of the valence atomic orbitals.

The overlaps of the valence s and p orbitals are large, but as far as bonding is concerned the resulting one-electron stabilization energy is outweighed by electron correlation and core-valence orthogonality effects, which ensure that when the nearest-neighbor separation is close to that of the equilibrium crystal structure the *net effect* of the s and p electrons is to act *against bonding.* This is because the valence s and p electrons are repelled by the *cores* of adjacent transition-metal atoms, and this effectively raises their energy. This repulsive force is counterbalanced by an *attractive force between metal atoms due to the d electrons,* even though the d orbitals on neighboring atoms have small overlap integrals ($\lesssim 0.1$). Moreover, the d electrons account quantitatively for the bonding as judged by calculation of the cohesive energy per atom, U, (or equivalently, the metal–metal bond energy $b = 2U/z$, where z is the coordination number). In Hückel theory language, *the resonance integrals involving d orbitals on adjacent atoms are large even though these orbitals give small overlap integrals.*[4,27,30,31]

This picture of bonding in transition metals remains valid provided that the effective number of d electrons per atom, N_d, is less than 10, a circumstance that is guaranteed by electronic configuration and/or hybridization throughout the transition-metal block until the group 11[52] metals are reached. Since the demonstration in the late 1970's that these ideas are in accord with a quantitative theory of transition-metal properties such as atomic radius and crystal structure, bond energy, and compressibility,[28,29] they have become the orthodoxy of metal physics; in the absence of any serious rival theory these ideas about bonding in metals are no longer controversial. Despite their obvious significance for the putative relationship between transition-metal clusters and metal surfaces, they have yet to be widely taken up in transition-metal chemistry.

Now, in the light of the above discussion it is clear that the application of the extended Hückel (EH) method to transition-metal systems (clusters, surfaces, bulk solid) is problematic. In this approach the Hückel theory resonance integrals, H_{ij}, connecting orbitals i and j are taken to be simply proportional to the corresponding orbital overlap integrals, S_{ij}

$$H_{ij} = k\left(\frac{H_{ii} + H_{jj}}{2}\right)S_{ij} \qquad i \neq j$$

where the constant k is usually assigned a value ≈ 1.7 irrespective of the type (s, p, d) of orbital involved, and H_{ii} and H_{jj} are interpreted as the energies (VSIP's etc) for orbitals i and j, respectively.[32,33] As far as I am aware there is no quantitative EH calculation in the literature of the electronic structure of a transition-metal cluster, surface, or bulk crystal. The reason for this is not hard to find; the only variables in the EH method are the orbital energies $\{H_{ii}\}$ and the overlap integrals $\{S_{ij}\}$, and these do not give enough freedom to account quantitatively for transition-metal band structures that arise from a subtle interplay of electron repulsion energies (correlation) and the valence orbital resonance integrals.[28] Quantitative accuracy is not claimed for the EH method of course, but even so, care is needed in assessing the qualitative picture that results from such calculations. The skepticism of physicists concerned with transition metals arises because of the *variability* of the EH parameterizations that have been used; some are much more "right" than others! Because semiempirical MO models cannot guarantee internally their own consistency in different applications, it is absolutely vital that the results of such calculations be checked against available experimental results and other theoretical methods. Photoelectron spectroscopy and visible/UV absorption spectroscopy are generally the most useful experimental technique for assessing molecular orbital energy level schemes.

The limitations as far as transition-metal systems are concerned are seen in some EH parameterizations addressed specifically to metal clusters.[18,34,35] These calculations used atomic d orbitals that generate small overlap integrals ($S \lesssim 0.1$) when the nearest-neighbor bond length is close to that found in the equilibrium bulk metal; the EH ansatz for the resonance integrals H_{ij} inevitably produced a *narrow* band of states centered about the atomic d-orbital energy. For this reason, attention was focused on the (large) overlaps of the metal valence s and p orbitals, which were reported as generating MO's bonding between the metal atoms, as well as a set of highly antibonding MO's characteristic of the structure of the cluster. These EH calculations suggest a correspondence between the electronic structure of the transition-metal cluster and that of a main-group-element cluster, and from this result it is only a small step to the much used analogy between transition-metal cluster compounds and isostructural boranes. Thus, for example, Lauher reported that transition-metal cluster chemistry could be rationalized by examining the position of cluster MO's relative to the energy of the metal's atomic p orbital,[34,35] and Mingos and Forsyth suggested that the analogy between boranes and transition-metal cluster compounds has its basis in the similar s- and p-orbitals overlap integrals in isostructural clusters, which lead to similar MO splitting patterns.[18] One can hardly fail to notice that this EH picture of a transition-metal cluster, if taken at face value, would preclude any plausible analogy between the bonding and electronic structure in transition-metal clusters and their compounds and transition-metal surfaces and their chemistry (e.g. chemisorption, catalysis) because of the discrepancy in the weight attached to the bonding effects of the d-electrons—all important in transition-metal surfaces and the bulk[27-29] and negligible in these EH descriptions of a metal cluster. The information available from photoelectron spectroscopy and other physical properties is quite definitely in favor of the d-electron bonding model for transition-metal cluster compounds[10,16] and cannot be reconciled with narrow cluster d bands. The metal surface–metal cluster analogy[36] has of course been much exploited

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and finds support from experimental techniques such as photoelectron spectroscopy and visible/UV absorption spectroscopy that are used to probe electronic structure[3,4,37-45]

More recent parameterizations of the extended Hückel model[11,38] have used expanded valence d orbitals that give rise to much more substantial d-orbital overlap integrals and hence much larger d-orbital resonance integrals for equilibrium geometries. Theoreticians may object to the use of expanded d orbitals as a "patch up" of the method that does not capture the correct nature of transition-metal bonding,[27] and this defect more or less rules out a quantitative treatment; nevertheless, the essential point here is that, at the qualitative level, the electronic structure calculated with the *new* parameterization for transition-metal clusters and surfaces[11,38] certainly comes much more into agreement with well-established metal physics results and, for example, correctly identifies the prime role of the metal d electrons in chemisorption of CO.[4,38] This recent development in EH methodology requires that reconsideration be given to the conclusions about metal cluster compounds drawn from earlier EH calculations.[18,34,35] Exactly what might be made of the borane analogy will be discussed in the following paper;[42] however, it is appropriate to note at this stage that extended Hückel calculations have provided a valuable insight into the *cluster–ligand* bonding modes.

If overlaps between ligand orbitals and relatively low-lying cluster MO's derived from the s and p atomic orbitals of the metal atoms are considered, the overall division between bonding/nonbonding/weakly antibonding and strongly antibonding MO's of clusters can be established.[18,20,21,34,35] This gives a rationalization of the valence electron count in metal cluster carbonyl compounds if it is assumed that only the strongly antibonding cluster MO's cannot be used in ligand bonding. These arguments have also been used to rationalize some of the chemistry of cluster carbonyl compounds; they are qualified however by their failure to deal adequately with the metal d electrons.

There is probably now very little disagreement among rival methods of calculation (chemical pseudopotential,[12] extended Hückel,[11] LMTO,[10] Xα[16]) for transitional-metal cluster compounds as far as the overall *qualitative* picture is concerned. There is however a need to integrate the d-electron bonding model for transition-metal systems with other areas of cluster chemistry. It is the purpose of these two papers to show that (a) the metal cluster–metal surface analogy finds its rationale in the d-electron bonding model for metal–metal bonds and that (b) this model *can be integrated* with the ideas formalized in Wade's rules and the isolobal principle,[39,40,41] which, however, must be interpreted in terms *consistent* with what we now know about the d-electron energy levels in cluster compounds.[42]

3. The Electronic Structure of $M_6(\mu_3\text{-}X)_8$ Clusters

(a) The Metal Cluster. Figure 1 shows a schematic energy level diagram for an octahedral transition-metal cluster, M_6, based on literature calculations;[10-18,24,34] the molecular orbitals are labeled by their symmetry species in the point group O_h, and I have assumed that the nine valence s, p, and d orbitals of each metal atom contribute to the valence electronic structure of the cluster. The precise ordering of the symmetry labels varies from one calculation to another because of the different amounts of hybridization they invoke, but all calculations agree on the gross features of the diagram, for example the separation of the levels into what can be loosely called "the d band", "the s band", "the p band", the presence of the energy gaps between the d-like levels and the s-like levels, and the unsymmetrical division of the 30 d-like levels into 13 "bonding" and 17 "antibonding" levels. It also seems to be agreed that the "p band" has a considerable gap dividing 11 very high levels from the other MO's of s- and p-orbital character. These features do not seem to be sensitive to the particular metal chosen for the calculation: this is just as expected from metal physics, of course.[26-29]

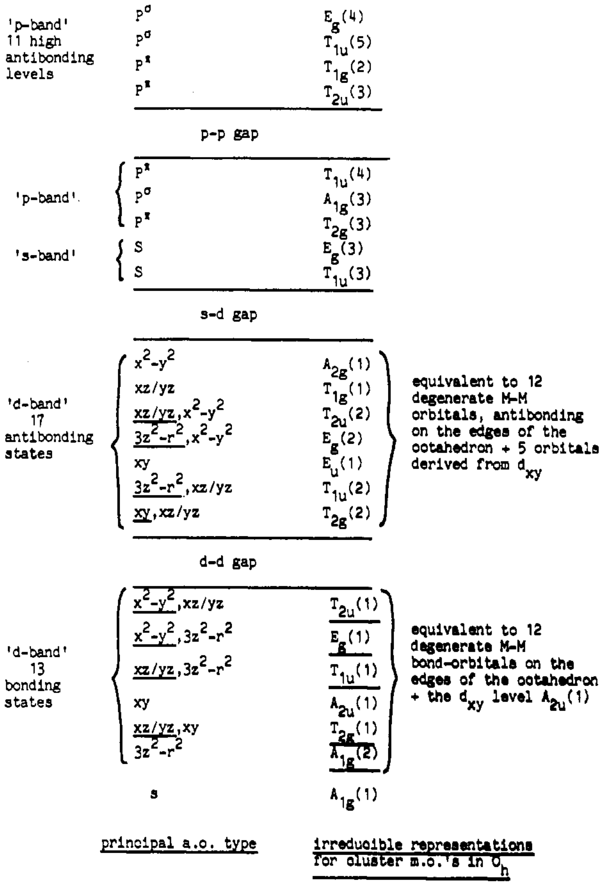

Figure 1. Orbitals for the octahedral transition metal cluster, M_6. An underlined d orbital is the major component in the corresponding MO; the underlined MO's are the M–M bonding orbitals.

On the other hand the *quantitative* aspects of the diagram, the energetics, do vary from metal to metal and also discriminate between different calculational schemes. For example, an early EH calculation on a Co_6 cluster with the metal–metal bond length set at 0.25 nm suggests that the d band covers an energy range of about 1.1 eV, i.e. $E[A_{1g}(2)] - E[A_{2g}(1)] \approx 1.1$ eV; this was characterized as a "narrow band of states", and was therefore largely ignored in the subsequent discussion of cluster bonding, in which attention was focused on the overlaps of the metal s and p orbitals[18]—subsequent EH calculations on metal clusters omitted numerical information on the energy levels but invoked the same qualitative picture.[18,34,35]

In contrast, the metal physics literature[4,19,26,28,29] suggests that this EH d-band width for Co_6 is *too small* by a factor of at least 2,[53] and recognition of this discrepancy goes some way towards explaining how bonding between transition-metal atoms can be attributed primarily to the d-electron levels. Furthermore since overlap integrals involving d orbitals are a less reliable guide to estimating interactions (e.g. Hückel resonance integrals) than we have become accustomed to in the case of s- and p-orbital overlaps, we should not be surprised to discover that the d band of the bare cluster has some significant interaction with the ligands. This will be described below and in the following paper[42] and is crucially important for the electronic structure of the metal cluster com-

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(a)

	Localized orbital description	symmetry species of m.o.'s for a cube (O_h)	No. of levels
24 p-orbitals from the 8μ_3-ligands (chalcogens, halogens)	high-energy: can be associated with σ^*-antibonds on cube-edges.	$t_{1u}(2), \underline{t_{2g}(2)}, \underline{a_{2u}(1)}, t_{1g}(1), \underline{e_u(1)}$	12
	low-energy: can be associated with σ-bonds on cube edges	$\underline{a_{1g}(1)}, \underline{e_g(1)}, \underline{t_{1u}(1)}, t_{2u}(1), t_{2g}(1)$	12

(b)

	Localized orbital description	symmetry species of m.o.'s for a cube (O_h)	No. of levels
24 orbitals from the $1\pi x$, $1\pi y$ and 5σ-levels of the $8\mu_3$-CO ligands	high-energy: can be associated with individual carbonyl 5σ-levels	$\underline{a_{1g}(1)}, \underline{t_{1u}(2)}, \underline{t_{2g}(2)}, \underline{a_{2u}(1)}$	8
	low-energy: can be associated with individual carbonyl 1π-levels	$\underline{e_g(1)}, t_{2u}(1), t_{1u}(1), t_{2g}(1), \underline{e_u(1)}$	16

Figure 2. Molelcular orbitals, listed in order of increasing energy, for the ligand polyhedron in $M_6(\mu_3\text{-}X)_8$ clusters in the absence of the metal core: (a) chalcogens and halogens; (b) carbonyls. Underlined orbitals are responsible for the principal cluster–ligand bonding overlaps.

pound because for metals to the left of the Ni triad the HOMO–LUMO gap is *in* the d band of the cluster compound. We shall also be led to the important conclusion that the d-band levels are involved significantly in cluster chemistry simply because the *number of occupied levels in the d band changes as ligands are added or removed.*[42] This is actually in agreement with earlier discussions,[18,34] except that here attention is focused on the crucial contribution made by the d electrons.

(b) The μ_3-Ligand Orbitals. The eight ligands in the ideal $M_6(\mu_3\text{-}X)_8$ cluster lie at the corners of a cube circumscribing the octahedron, and accordingly the molecular orbitals of the ligand polyhedron can be classified by using irreducible representations of the point group O_h. With chalcogen and halogen ligands, the orbitals relevant to metal–ligand bonding are the ligand valence p orbitals. For the cube of ligands they form two groups of 12 MO's, which we may call "bonding" and "antibonding" (see Figure 2a) since each set can be shown to have that character with respect to the edges of the cube.[10] All of these ligand polyhedron MO's for chalcogenide clusters lie below the bottom of the metal cluster d band (see Figure 1) with the possible exception of the $a_{2u}(1)$, $t_{1g}(1)$, and $e_u(1)$ levels, which are above the metal $A_{1g}(2)$ level for the 4d and 5d elements in the middle of the transition-metal series. The position is similar for the halide clusters of the same elements.[10,16]

A similar discussion can be given for the ligand orbitals of the group 8–10[52] metal cluster carbonyls. Molecular orbital calculations indicate that the carbonyl 3σ and 4σ orbitals have a negligible interaction with a metal atom or cluster and that the principal cluster–ligand interaction is mediated through the occupied 5σ orbital, which is the HOMO in the free CO molecule, and corresponds to the classical lone pair on the carbon atom.[3,4,43] Both the occupied and the unoccupied carbonyl π levels also interact with the cluster and must be taken account of. Calculations on carbonyl polyhedra, e.g. $(CO)_6$ and $(CO)_{12}$ in the structures appropriate to the Ni and Pt carbonyl clusters, indicate that the 5σ and the π levels interact and broaden out into "bands". Those derived from the 5σ and 1π levels nearly overlap ($E(5\sigma)-E(1\pi) \approx 2$ eV for free CO), with the "1π band" remaining below the "5σ band"; in the calculations reported in ref 3 the "2π band" turned out to cover about three-fifths of the energy range of the "1π band". With this information about carbonyl interactions we can list in order of increasing energy the symmetry-adapted combinations for the carbonyl cube that can be derived from the $1\pi_x$, $1\pi_y$, and 5σ levels of the CO molecule (see Figure 2b).

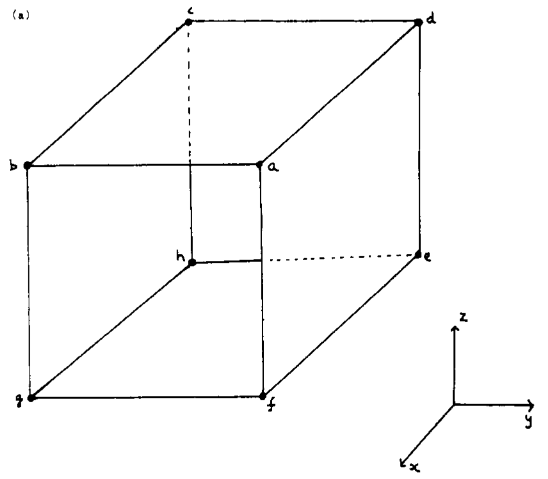
An extremely important difference between the neutral chalcogen and halogen ligands and CO is that the orbitals classified in Figure 2b for the latter are all fully occupied, whereas the neutral atomic ligands have incomplete atomic p subshells and can accept electrons from the metal cluster. The LUMO's in the free CO molecule are the degenerate antibonding levels $2\pi_x$ and $2\pi_y$, which lie about 5–6 eV above the HOMO, 5σ; the 2π levels are therefore of similar energy to the cluster s band for group 8–10 metals[54] and lie above the HOMO of the bare metal cluster.

It is helpful to choose the ligand orbitals in a way that facilitates the comparison among the chalcogenides, halides, and carbonyls. In the idealized $M_6(\mu_3\text{-}X)_8$ cluster structure, the bond axis of a carbonyl ligand lies on a bond diagonal of the cube formed by the ligands, and the σ-, π-symmetry classification of the CO orbitals is with respect to this direction. Rather than thinking in terms of bonding/antibonding combinations over the edges of the cube, it is much more convenient here to choose the cube body diagonals as quantization axes for the atomic orbitals of chalcogen and halogen ligands; at each atomic ligand one p orbital is then radially directed along a body diagonal like the carbonyl 5σ orbital, while the two orthogonal p orbitals are *tangential* to the shpere circumscribing the cube, just like the carbonyl π orbitals. A more detailed description of the polyhedron MO's generated by the *radially directed* ligand orbitals is given in Figure 3. Figure 3 also summarizes the classification of these MO's in Stone's angular-momentum-based description of cluster bonding, which exploits the fact that the ligands sit on the surface of a sphere.[20,21]

(c) The Metal Cluster–Ligand Polyhedron Interactions. In the previous section, 3b, the ligand orbitals were classified as either "radial" or "tangential", and it is convenient to take separately the two groups of ligand polyhedron MO's that they generate; these may also be referred to as "radial" and "tangential". Since the interactions between the metal cluster and ligand polyhedron orbitals have been analyzed in detail for the Chevrel phase cluster Mo_6S_8,[10,11] I shall start with this species. The chalcogen polyhedron has eight MO's of radial type; these are the levels $a_{1g}(1)$, $t_{1u}(1)$, $t_{2g}(2)$, and $a_{2u}(1)$ in Figure 2a. These orbitals hybridize strongly with metal cluster orbitals of the same symmetry; $a_{1g}(1)$ and $t_{1u}(1)$ interact with cluster orbitals that are mainly metal s orbital in character, $A_{1g}(1)$ and $T_{1u}(3)$, respectively, and $t_{1u}(1)$ also hybridizes weakly with $T_{1u}(2)$ in the metal cluster d band (see Figure 1). On the other hand the higher energy radial orbitals $t_{2g}(2)$ and $a_{2u}(1)$ have a strong bonding interaction with the cluster orbitals of the same symmetry derived from the metal d_{xy} orbitals, and in the case of $t_{2g}(2)$ there is also hybridization with the cluster orbital $T_{2g}(3)$ derived from the metal p orbitals.

The bonding is markedly heteropolar in character, and the net result of these strong interactions is that the occupied cluster–ligand bonding orbitals are mainly radial ligand orbital in character, while their antibonding orbital partners are mainly metal orbital in character: in effect, the metal orbitals are swept up in energy (strongly destabilized) by their interactions with the ligands. In particular it should be noted that the metal cluster orbital $A_{2u}(1)$ interacts so strongly with the μ_3-ligands that it is pushed up in energy well above *the top of the d band*; thus after hybridization with the radial ligand orbitals, there remain only 12 orbitals below the d–d gap. The modified d band of the cluster compound lies in a gap caused by the strong hybridization between the ligand polyhedron radial orbitals and metal cluster orbitals of matching symmetry and good overlap; as might be expected on overlap grounds, this picture is not altered by the interaction between the cluster and the ligand polyhedron tangential orbitals, which we now discuss.

Of the ligand polyhedron tangential MO's, only $e_g(1)$ and $e_u(1)$ have a strong interaction with the metal cluster: $e_g(1)$ hybridizes strongly with the metal s-orbital level $E_g(3)$, and also mixes weakly with $E_g(1)$ in the cluster d-band such that $E_g(1)$ is destabilized to become the highest energy level below the d–d gap. $e_u(2)$ has a strong bonding interaction with the cluster level $E_u(1)$ derived from the metal d_{xy} orbitals such that $E_u(1)$ moves toward the top of the antibonding part of the d band in the cluster compound. The remaining group of tangential ligand levels, $t_{2u}(1)$, $t_{2g}(1)$, $t_{1u}(2)$, and $t_{1g}(1)$, have either only a weak or a negligible interaction with the metal cluster; $t_{2u}(1)$ interacts weakly with both $T_{2u}(1)$ and $T_{2u}(2)$ from the cluster d-band and with the much higher $T_{2u}(3)$. $t_{2g}(1)$ and $t_{1u}(2)$ have negligible hybridization with the



(b)

O_h symmetry species of m.o.	Cube Vertices							
	a	b	c	d	e	f	g	h
a_{1g}	+	+	+	+	+	+	+	+
t_{1u}	+	+	+	+	−	−	−	−
	+	+	−	−	−	+	+	−
	+	−	−	+	+	+	−	−
t_{2g}	−	+	−	+	+	−	+	−
	−	+	+	−	+	+	−	−
	−	−	+	+	−	+	+	−
a_{2u}	−	+	−	+	−	+	−	+

(c)

irreducible representations in rotation group O(3)		irreducible representations in cubic group O_h
S	→	a_{1g}
P	→	t_{1u}
D	→	$t_{2g} + e_g$
F	→	$a_{2u} + t_{1u} + t_{2u}$

Figure 3. (a) Donor atoms of the eight μ_3-ligands defining the vertices of a cube circumscribing the M_6 unit. They also lie on the surface of a sphere with origin at the intersection of the cube bond diagonals (not shown). (b) "Radial" ligand orbitals with lobes directed at the center of the cube combining with phase relationships. a_{1g} is bonding over the whole cube, the t_{1u} set is bonding over cube faces, and the t_{2g} set is bonding over diagonally opposite pairs of edges; at any vertex (e.g. *c*), a_{2u} is antibonding with respect to the nearest neighbors (b, d, h) and the second nearest neighbor (f) and is bonding with respect to the next nearest neighbors (a, e, g). For a carbonyl ligand the radial orbital is the 5σ orbital; for a chalcogen or halogen atomic ligand we can choose this radial direction (the body diagonal) as the quantization axis for the p orbitals. Then the two orthogonal atomic p orbitals play a role analogous to that of the π orbitals in CO (the "tangential" orbitals). (c) MO's formed from ligand orbitals on a sphere circumscribing the cube related to the point group O_h by descent of symmetry, O(3) → O_h. The MO's in Figure 3b are described in Stone's scheme[20,21] as follows: $a_{1g} \leftrightarrow S^\sigma$; $t_{1u} \leftrightarrow P^\sigma(P_z{}^\sigma,P_x{}^\sigma,P_y{}^\sigma)$; $t_{2g} \leftrightarrow D^\sigma(D_{xy}{}^\sigma,D_{yz}{}^\sigma,D_{xz}{}^\sigma)$; $a_{1u} \leftrightarrow F^\sigma(F_{xyz}{}^\sigma)$. The e_g pair ($D_{z^2}{}^\sigma$ and $D_{x^2-y^2}{}^\sigma$) do not occur here because the corresponding spherical harmonics $Y_{2,0}$ and $(Y_{2,2} + Y_{2,-2})$ are zero at the cube vertices. The a_{2u} orbital is $F_{xyz}{}^\sigma$; other F^σ functions either vanish (t_{2u}) or are combinations of ones already found ($t_{1u} \leftrightarrow P^\sigma$).

cluster, while $t_{1g}(1)$ interacts weakly with the $T_{1g}(1)$ level from the antibonding part of the d band.

The discussion by Cotton and co-workers of the analogous face-bridged halide clusters[16] shows them to be similar to the Chevrel phase clusters. Although they make no explicit comment about the role of the metal s orbitals, one can hardly doubt that the above discussion is applicable. They identify the hybridization of the radial ligand orbitals $t_{2g}(2)$ and $a_{2u}(1)$ and the tangential orbital $e_u(1)$ with the metal d_{xy} orbitals as the principle ligand–cluster bonding interaction, and this justifies the exclusion of the metal d_{xy} orbital from the earlier discussion by Cotton and Haas[15] of d-orbital overlaps in metal clusters of this structure. As in the Chevrel phase case the metal–metal bonding $E_g(1)$ and $T_{2u}(1)$ levels are weakly destabilized by metal–ligand interactions such that $E_g(1)$ once again becomes the highest energy of the 12 metal–metal bonding levels below the d–d gap. In the discrete halide anions these 12 levels are fully occupied, but there is some uncertainty as to whether $E_g(1)$ or a mainly ligand level is the HOMO.

Just as the 4 valence MO's for methane can be transformed into 4 degenerate tetrahedral bond orbitals,[48] so also a similar transformation can be applied to the 12 low-energy d-orbital states $A_{1g}(2)$, $T_{1u}(1)$, $T_{2g}(1)$, $T_{2u}(1)$, and $E_g(1)$ (Figure 1) to give 12 degenerate bond orbitals, each one being directed (essentially) along an edge of the octahedron. Note that a set of edge bond orbitals for an octahedron cannot be based on atomic s and p orbitals because they do not span appropriate irreducible representations of the symmetry group for the octahedron. The construction of bond orbitals for an octahedron of transition-metal atoms is discussed by Nohl et al.;[10] at its simplest, it involves forming orthonormal d^4 hybrids at each metal atom, with d_{xy} excluded for the reasons given above. A two-center bond orbital can then be formed by taking the in-phase overlaps of two d^4 hybrids that point at each other. Atomic d orbitals are *even* under inversion in the origin (nucleus) and so, in contrast to sp^n hybrids, the "back lobes" of a d^4 hybrid are identical with the "front lobes" involved in this bonding combination; this fact is important in the metal–metal bonding in *metal cluster condensation* where the metal octahedra may share vertices, edges, or faces.[10,49]

If we now turn to the group 8–10 metal cluster carbonyls based on the $M_6(\mu_3\text{-}CO)_8$ unit, an analogous discussion can be given, although here the antibonding orbitals in the cluster d band play a role because the metals have more d electrons (atomic configurations $d^7s^1 \rightarrow d^9s^1$). This discussion is less quantitative than for the chalcogen and halogen clusters because there do not seem to be accurate MO calculations for a carbonyl based on the $M_6(\mu_3\text{-}CO)_8$ core; however, some years ago we made a study of the Ni and Pt clusters $[M_3(CO)_6]_n{}^{2-}$ ($n = 1, 2$),[3] and taking those results together with what has been learned about metal–metal and metal–ligand interactions from the detailed studies of molybdenum cluster species,[3-16] some definite conclusions as to what may be expected can be put forward.

A guiding principle in my argument is that the 12 bonding orbitals in the lower part of the metal cluster d band will preserve enough of their integrity when bonding to the μ_3-ligands occurs for it to be possible to keep them together as the group of *occupied orbitals primarily responsible for metal–metal bonding in the cluster carbonyl.* In effect we are declaring that the existence of a set of d-orbital M–M bonding levels is a feature common to all transition-metal cluster compounds *irrespective* of the nature of the ligands; of course the *number* of M–M bonding levels depends on the structure of the ligand polyhedron and need not be 12 as in the face-bridged species discussed here, and obviously a localized bond model for M–M bonding will only be appropriate in special cases. We shall also have to pay attention to the antibonding orbitals of d-orbital parentage if the valence electron count requires their occupation, but the cluster MO's derived from the 12 M–M edge-bonding orbitals identified for the face-bridged octahedral M_6 unit should be seen as having the primary role in metal–metal bonding for this structure. Metal physics suggests that analogous statements hold for transition-metal cluster compounds with other structures/nuclearity whenever the nearest-neighbor metal contacts are similar to those found in the bulk metals and the number of d electrons per atom calculated after allowance for hybridization is less than 10.[3,4]

As for the metal cluster carbonyl interactions, we should expect to find a similar pattern to that described above for the chalcogenides and halides, for the overlaps of orbitals of radial and tangential type should be similar in all three cases. Unlike the chalcogen and halogen clusters however, we also have to consider

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the empty 2π orbitals that lie above the cluster d band. According to the synergic bonding mechanism, their main function is to facilitate "back-bonding" from the metal cluster through hybridization with the metal d orbitals. Their role is important, but it must not be overemphasized. We know from studies of chemisorption of CO on transition-metal surfaces that *dissociative adsorption* of CO occurs through transfer of electron density into the 2π orbitals and that this is a favorable process for the metals to the left of groups 8–10 because their d bands are reasonably close in energy to the empty 2π levels of the CO molecule. These metals do not form polynuclear cluster carbonyls. In the group 8–10 metals the d-band energy moves down sharply thereby greatly reducing the interaction with the carbonyl 2π orbitals, and *associative adsorption* ensues.[4] It is reasonable to suppose that similar factors are important for transition-metal clusters; there is an excellent correlation between the formation (or otherwise) of transition-metal cluster carbonyls and associative (dissociative) chemisorption of CO on metal surfaces, and this is part of the chemical evidence for the metal surface–metal cluster analogy.[4,36,37,38] On the basis of these general arguments, we are led to the following scheme for the $M_6(\mu_3\text{-CO})_8$ moiety.

The eight radial orbitals derived from the lone pairs of the face-bridging carbonyls (see Figures 2b and 3) can be expected to interact strongly with the cluster orbitals ($A_{1g}(2)$, $T_{1u}(3)$) and ($A_{2u}(1)$, $T_{2g}(2)$) derived from the metal s and d_{xy} orbitals, respectively, as well as the unoccupied metal orbital $t_{2g}(3)$ which is of p-orbital character (Figure 1), to form eight strong bonds, which are mainly ligand orbital in character. As before, the main contribution of these metal orbitals is to the antibonding combination, which for symmetries A_{1g}, A_{2u}, and T_{1u} may reasonably be assumed to lie above the top of the d band, as in the chalcogen and halogen clusters. By this scheme (see Figure 4) $T_{2g}(1)$ remains a metal–metal cluster bonding orbital (as discussed earlier), while the antibonding $T_{2g}(2)$ is regarded as being better suited for μ_3-ligand bonding because of its predominantly d_{xy} character.

Next we must consider the interactions of the cluster with the carbonyl orbitals of π symmetry (Figure 2b). If we assume that the 12 M–M bond orbitals are little affected by these π interactions, the following cluster orbitals in the d band can be expected to hybridize with the tangential orbitals of the carbonyl polyhedron: $T_{1u}(2)$, $E_u(1)$, $E_g(2)$, $T_{2u}(2)$, $T_{1g}(1)$, $T_{2g}(2)$. With the possible exception of the orbitals of E symmetry, the interactions should be less strong than for the carbonyl radial orbitals because, as in the chalcogenides and halides, the overlaps are poorer and the energy separation between cluster and ligand polyhedron levels is greater. These orbitals have been selected because they are the lowest energy orbitals of the metal cluster available for hybridization after the strong metal–metal and metal–ligand bonding interactions have been dealt with. $E_g(2)$ is preferred to $E_g(3)$, because the latter is expected to be important for bonding with additional terminally bonded ligands in the exo positions; this will be discussed in the following paper.[42] The interactions between the 1π levels and the cluster orbitals are expected to stabilize the 1π levels since they are lower in energy, so that the metal cluster orbitals, which contribute mainly to the cluster–ligand antibonding combinations, will be *destabilized.* However these roles are reversed when we consider hybridization between the cluster orbitals and the empty 2π levels on the ligands; although these on average are further away in energy, they may be expected to overlap with the cluster orbitals better than their 1π partners, and it is reasonable to expect that the *net* effect is that the 1π and 2π levels are pushed apart while the cluster d-band orbitals are relatively unaffected *in energy*, being "squeezed" from above and below. This is certainly what was found in the calculations on the Ni and Pt cluster carbonyls;[3] while there was little change in the energies of the cluster "d-band" levels, these were found to have hybridized with both sets of carbonyl π levels, indicating that the 2π levels have a role as acceptor orbitals as envisaged in the classical synergic bonding mechanism.[3]

In conclusion it therefore seems reasonable to suggest that the main effect of the π interactions is to shift upward the energies of the orbitals in the d-band with some rearrangement of these levels; $E_u(1)$ and $T_{2g}(2)$ would be expected to be destabilized most by the virtue of their d_{xy} character. However, the π interactions are not expected to alter the position of the HOMO, which is determined by the strong hybridization of the metal cluster with the ligand polyhedron radial orbitals, and is located at the resulting "s–d" gap of the cluster compound. Accordingly we would expect to find the $M_6(\mu_3\text{-CO})_8$ moiety with a valence electron count of 74, corresponding to occupancy of the 8 M–CO bonding orbitals and the 29 orbitals remaining in the cluster "d band". Since we do not expect highly charged species, this effectively limits the possibilities to the Co and Ni triads; the $M_6(\mu_3\text{-CO})_8$ moiety is found in the clusters $Co_6(CO)_{14}{}^{4-}$, $Rh_6(CO)_{14}{}^{4-}$, and $Co_4Ni_2(CO)_{14}{}^{2-}$. This valence electron count and the hybridization of the d band with the ligand orbitals ensures that the effective number of d electrons per atom remains close to the value found in the corresponding bulk metals. Even though most of the "antibonding" d-orbital levels are occupied, the d electrons are still responsible for the metal–metal bonding. Although a detailed analysis has not yet been made, the above discussion appears to be consistent with some recent chemical pseudopotential calculations on $Co_6(CO)_{14}{}^{4-}$,[19] which are not yet finished or published.

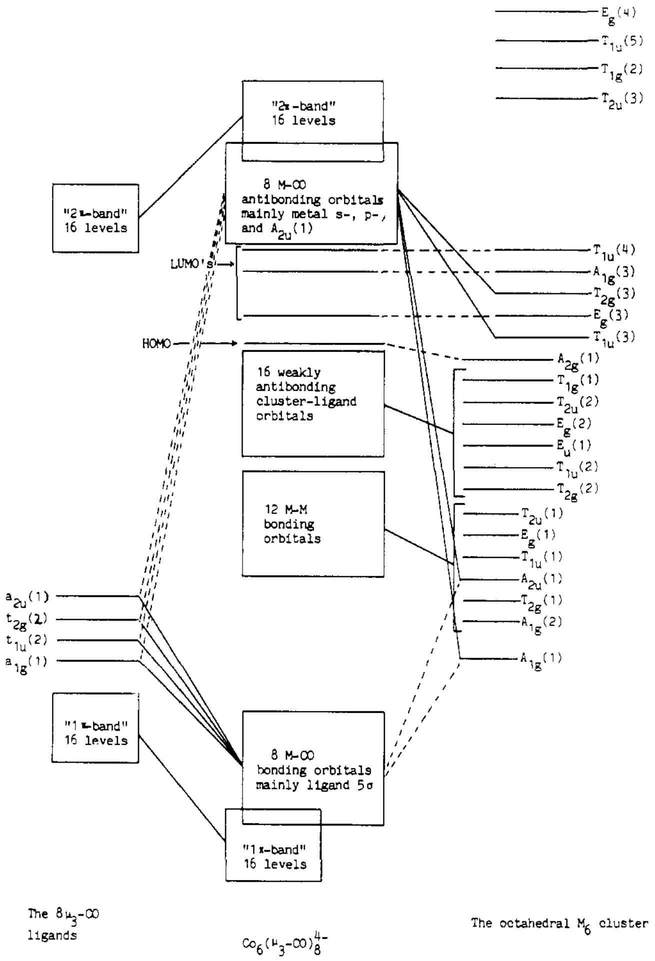

Figure 4. Schematic energy level scheme for the $Co_6(\mu_3\text{-CO})_8{}^{4-}$ cluster fragment formed from $(CO)_8$ and the octahedral Co_6 unit. The cluster has 74 valence electrons occupying 8 strongly bonding cluster–ligand orbitals, 16 weakly antibonding cluster–ligand orbitals, and 13 orbitals associated with the metal cluster. The 6 cluster LUMO's are responsible for bonding to 6 further terminal ligands, but the HOMO shown in the figure is not altered.

4. Conclusions

In this paper I have examined in detail the electronic structure of the transition-metal cluster moiety $M_6(\mu_3\text{-X})_8$ with idealized point-group symmetry O_h. This cluster is commonly found as the building-block in the halides and chalcogenides (Chevrel phases) of transition metals in groups 5 and 6 (with limited possibilities for substitution from groups 7–10)[5-8] and is also found in some carbonyls of transition metals from groups 8–10, which may be taken as exemplary cases from the family of carbonyl clusters. The approach adopted here is to consider separately the electronic structure of the metal cluster and the polyhedral shell of ligands, before allowing the valence orbitals of these two fragments to hybridize. This is very convenient for exhibiting the similarities between these cluster species.

The discussion in section 3 can be summarized briefly by saying that the frontier MO's of the bare metal cluster of atomic s- and p-orbital parentage *plus a limited number of d-orbital parentage* contribute to the *cluster–ligand bonding*;[34] this theme will be explored in more detail in the following paper.[42] On the other hand the *electrons occupying the low-energy orbitals below the d–d* gap in the d band of the cluster compound are responsible for the *metal–metal bonding* in the metal cluster core. The principal difference between halides and chalcogenides on the one hand and carbonyls on the other is that, for the former, this d–d gap becomes the HOMO–LUMO gap of the cluster compound, whereas in the carbonyls the antibonding d orbitals weakly hybridized with tangential orbitals of the ligand polyhedron are also occupied, so their HOMO–LUMO gap is related to the s–d gap of the metal cluster (see Figures 1 and 4).

This description is consistent with the general principles[4,27–29,50] that govern bonding between transition-metal atoms with M–M bond lengths close to that found in the equilibrium structure of the bulk metals when the number of d electrons per atom is less than 10:

(i) Electrons occupying MO's of atomic d-orbital parentage produce a net attractive force between neighbouring metal atoms that accounts for the M–M bond energy.

(ii) Electrons occupying MO's of atomic s- and p-orbital parentage produce a net repulsive force between neighbouring metal atoms because those electrons are repelled by the cores of adjacent transition-metal atoms. In cluster compounds the main contribution of the metal atomic s and p orbitals is to the *unoccupied* antibonding cluster–ligand MO's; thereby the number of s and p electrons is kept low, being determined essentially by the d/s,p hybridization of levels below E_{HOMO} (cf. the bulk metals[28,29]). These principles do *not* apply in clusters of main-group elements ($N_d = 0$), or metals from group 11 (for which $N_d = 10$). Palladium is a borderline case because of the narrowness of its d band.[4,50]

The electronic structure of metal cluster compounds can be calculated by typical metal physics methods such as Xα or the chemical pseudopotential method; such calculations lead to energy level schemes that seem broadly consistent with spectroscopic and other physical measurements.[2–4,9,10,12,13,16,17,37,43,45,49–51] Some recent extended Hückel parameterizations[11,38] are also consistent with this picture; however, earlier EH calculations that lead to "narrow" cluster d bands cannot be regarded as trustworthy as far as metal–metal bonding is concerned in metal cluster compounds at or near their equilibrium geometries.

The general bonding ideas presented in this paper should be applicable to transition-metal cluster compounds as a whole; in the following paper[42] I shall widen the discussion by examining the relationship of d-electron bonding in metal cluster compounds to the isolobal principle and the analogy with borane clusters.[41] The importance of the d-band levels for the electronic structure of metal cluster compounds has obvious implications for theories of cluster chemistry.

Acknowledgment. It is a pleasure to acknowledge helpful discussions with Prof. O. K. Andersen, Dr. A. J. Stone, Prof. K. Wade, and Dr. A. M. Woolley.

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(52) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confustion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(53) This is a big effect; the bond energy between transition-metal atoms is directly proportional to the d-band width (the energy separation of the lowest bonding MO and the highest antibonding MO originating from atomic d orbitals) and so a factor of 2 means that the bond energy is only half of what it ought to be. Obviously such a result cannot be taken seriously.

(54) For example, the calculations reported in ref 3 gave $E_{2\pi} \approx -8.2$ eV in the free CO molecule. This compares with the following metal s-orbital energies for the $d^{n-1}s^1$ configuration: Fe, −7.10 eV; Co, −7.33 eV; Ni, −7.54 eV; Ir, −11.36 eV; Pt, −11.50 eV.[3,46,47]

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Bonding in Transition-Metal Cluster Compounds. 2. The Metal Cluster–Borane Analogy

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Following the detailed discussion of the transition-metal cluster moiety $M_6(\mu_3\text{-}X)_8$ in the preceding paper, a more general account of the importance of the d electrons in transition-metal cluster chemistry is presented. The putative analogy with borane clusters (and their derivatives) is examined critically. Although an *isolobal* relationship exists between, e.g., BH and appropriate ML_n fragments (e.g. conical $Fe(CO)_3$), *this does not imply* that the BH and ML_n fragments behave in electronically similar ways when cluster formation occurs, even when structurally related clusters are formed. Nonidentical isolobal fragments have orbital differences that manifest themselves in interfragment resonance integrals and require a qualitative distinction to be drawn between the bonding modes and detailed electronic structures of (i) transition-metal cluster compounds and (ii) boranes, carboranes, and their metalla derivatives; an analysis developed in the electronic structure theory of transition-metal systems shows why this is the case. The isolobal principle and Wade's rules owe their generality and utility to being *symmetry-based* statements; the *energetics and details* of the electronic structure of cluster compounds however are a separate matter requiring appropriate methods of theoretical chemistry.

1. Introduction

In the preceding paper, a detailed account of the electronic structure of the transition-metal cluster moiety $M_6(\mu_3\text{-}X)_8$ was presented for X = chalcogen, halogen, and carbonyl ligands.[1] The approach used there was to analyze the orbitals for two fragments, the octahedral M_6 unit and the ligand polyhedron in the absence of the metal cluster core, before allowing the orbitals of the two parts to hybridize. Such an approach builds on recent studies of the electronic structure of transition metals[2–6] and exploits the

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(1) Part 1: Woolley, R. G. *Inorg. Chem.*, preceding paper in this issue.

(2) Andersen, O. K. *Phys. Rev. B*: *Solid State* **1975**, *12*, 3060.

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