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Electronic and Molecular Structures of the Octahedral $Cp_6M_6A_8$, Trigonal-Bipyramidal $Cp_5M_5A_6$, and Tetrahedral $Cp_4M_4A_4$ Clusters

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So that the structures and magnetic properties of $Cp_6Ti_6(\mu_3\text{-}O)_8$, $Cp_5V_5(\mu_3\text{-}O)_6$, and $Cp_4Cr_4(\mu_3\text{-}O)_4$ ($Cp = \eta^5\text{-}C_5H_5$) could be explained, molecular orbital calculations (extended Hückel approximation) have been performed on clusters of general formula $Cp_6M_6(\mu_3\text{-}A)_8$, $Cp_5M_5(\mu_3\text{-}A)_6$, and $Cp_4M_4(\mu_3\text{-}A)_4$. For each of the clusters there are orbitals representing C–H, C–C, M–C, and M–A bonds, as well as nonbonding orbitals localized on A at low energies. There is then a group of 12 orbitals at higher energy which are essentially completely metal d in character when M lies to the right of Mn in the periodic table but contain increasing contributions from Cp as one moves to the left. These 12 orbitals contain the "excess" metal electrons, over and above those required for M–Cp and M–A bonding (two "excess" electrons in the case of $Cp_6Ti_6A_8$, eight for $Cp_5V_5O_6$, and twelve for $Cp_4Cr_4O_4$). Their energy level ordering is determined by a combination of three interactions: M–M bonding, M–Cp back-donation, and donation of the nonbonding pair of electrons on A to M. For $Cp_6M_6A_8$ the ordering of these 12 orbitals in O_h symmetry is $a_{1g} < 1e_g < t_{2u} << a_{2g} <<< t_{1u} < 2e_g$; in $Cp_6Ti_6O_8$ the metal contribution to a_{1g}, which contains the two excess electrons, is exclusively d_{z^2} and $d_{x^2-y^2}$. The two electrons may be considered as being at the center of the octahedron. For $Cp_5V_5O_6$ the order in D_{3h} symmetry is $1a_1' \approx 1e' <<< e'' \approx 2a_1' < 2e' << a_2'' < 3a_1' < 3e'$. Since $1a_1'$ and $1e'$ are localized almost completely on the equatorial V atoms and e'' almost completely on the axial V atoms, the electronic structure may be described as a pair of electrons on each of the equatorial V atoms and a single electron on each axial V. This is in accord with the V–O and V–Cp distances. For $Cp_4Cr_4O_4$ the ordering of the 12 orbitals in T_d symmetry is $e << 1t_2 << t_1 \lesssim< 2t_2 < a_1$, which differs from that previously suggested for $Cp_4M_4A_4$ clusters. Calculations on distorted $Cp_4M_4A_4$ clusters of D_{2d} symmetry with either four long and two short or two long and four short M–M distances, or of D_2 symmetry with two short, two intermediate, and two long distances, are used to predict the structures of $Cp_4M_4A_4$ clusters according to the number of "excess" electrons in the 12 orbitals. The predictions are compared to observations.

Introduction

In earlier papers we described the preparation, structures, and physical and chemical properties of $(\eta^5\text{-}C_5H_5)_5V_5(\mu_3\text{-}O)_6$ and $(\eta^5\text{-}C_5H_5)_4Cr_4(\mu_3\text{-}O)_4$ (hereafter referred to as $Cp_5V_5O_6$ and $Cp_4Cr_4O_4$, respectively).[1,2] Previously Caulton and co-workers had structurally characterized $Cp_6Ti_6O_8$.[3] Each of these clusters consists of an approximately regular polyhedron (octahedron, trigonal bipyramid, or tetrahedron for $Cp_6Ti_6O_8$, $Cp_5V_5O_6$, or $Cp_4Cr_4O_4$, respectively) with oxygen atoms placed above the triangular faces. The metal–oxygen distances are those of M–O single bonds. A Cp ring caps each metal atom, the M–Cp distances being normal. The geometries of the clusters are illustrated in Figures 1–3.

In the present paper we address ourselves to certain problems of this cluster series. The first problem is as follows: does the series $Cp_6Ti_6O_8$, $Cp_5V_5O_6$, $Cp_4Cr_4O_4$ represent something more than an aesthetically pleasing sequence of clusters? For instance, is $Cp_5Cr_5O_6$ capable of existence? This question brings us to the placing of these clusters in a general context. Whereas $Cp_6Ti_6O_8$ appears to have only one close relative, the recently prepared $[((C_2H_5)_3P)_6Fe_6S_8]^{2+}$,[4] and $Cp_5V_5O_6$ has none, $Cp_4Cr_4O_4$ is a member of the series of $[Cp_4M_4A_4]^{n+}$ cubane-like clusters elegantly studied by Dahl and co-workers.[5-14] These clusters are listed in Table I. However, the model proposed by Dahl to explain these clusters[8,15] predicts that $Cp_4Cr_4O_4$ would be of T_d symmetry and diamagnetic, in contrast to the D_2 symmetry, and antiferromagnetism actually observed for this cluster.[1] This discrepancy is the second problem that we address. The third problem is the details of the structures and magnetic properties of $Cp_6Ti_6O_8$, $Cp_5V_5O_6$, and $Cp_4Cr_4O_4$. Diamagnetic $Cp_6Ti_6O_8$ is a regular octahedron with relatively short Ti-Ti distances (2.891 Å) (which nevertheless do not represent an exceptionally strong interaction of the Ti atoms) and equivalent Ti–O distances. In $Cp_5V_5O_6$, which is paramagnetic ($\mu_{eff} = 0.93\ \mu_B$ at 293 K), the V–V distances are essentially all equal, averaging 2.748 Å (again representing a definite but not exceptionally strong interaction), but the V(ax)–O distances (averaging 1.861 Å) are very much shorter than the V(eq)–O average of 1.992 Å. The V(ax)–Cp perpendicular distances average 1.997 Å, significantly longer than the V(eq)–Cp average of 1.973 Å.[2,11] The antiferromagnetic $Cp_4Cr_4O_4$ has three pairs of Cr–Cr distances averaging 2.898, 2.826, and 2.707 Å; the Cr–O distances are all equal (1.937 Å). The Cr–Cr distance represents approximately a single bond.[11]

In order to attack these problems, we have performed molecular orbital calculations on the three clusters in question, as well as on a variety of other $Cp_mM_m(\mu_3\text{-}A)_n$ and some $L_mM_m(\mu_3\text{-}A)_n$ clusters (L = terminal ligand other than Cp) related to $Cp_mM_mO_n$. The results presented here produce a general model for clusters of this type.

Results and Discussion

General Valence Bond Approach. Before discussing the molecular orbital model for these complexes, it is useful to

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Table I. Geometry and Magnetism of $Cp_4M_4A_4$ Clusters

cluster	no. of "excess" electrons	symmetry	M-M dist, Å	symmetry type	magnetic moment, μ_B	ref
$Cp_4Co_4S_4$	24	C_2	3.236, 3.299, 3.315, 3.343 (each × 2)	T_d with slight distortion	diamag	5
$[Cp_4Co_4S_4]^+$	23	D_{2d}	3.172 × 4, 3.330 × 2	distorted T_d	1.73	5
$Cp_4Co_4P_4$	20	D_{2d}	2.504 × 2, 3.630 × 4	${D_{2d}}^{B\,a}$	diamag	6
$Cp_4Fe_4S_4$	20	D_{2d}	2.65 × 2, 3.365 × 4	${D_{2d}}^{B\,a}$	diamag	7-9
$[Cp_4Fe_4S_4]^+$	19	D_2	2.652, 3.188, 3.319 (each × 2)	${D_{2d}}^{B\,a}$	paramag	8, 10
$[Cp_4Fe_4S_4]^{2+}$	18	D_{2d}	2.834 × 4, 3.254 × 2	${D_{2d}}^{A\,a}$	diamag	8
$Cp_4Cr_4O_4$	12	D_2	2.702, 2.826, 2.898 × 2	distorted ${D_{2d}}^{A\,a}$	antiferromag	1, 11
$Cp_4Fe_4(CO)_4$	12	T_d	2.506-2.530	T_d	diamag	12
$[Cp_4Fe_4(CO)_4]^+$	11	D_{2d}	2.506, 2.478 2.467, 2.484 (each × 2)	distorted T_d	2.07	13
$Cp_4V_4(CO)_4$	0			T_d	paramag	14

[a] ${D_{2d}}^A$ and ${D_{2d}}^B$ refer to two long and four short M-M distances or four long and two short M-M distances, respectively.

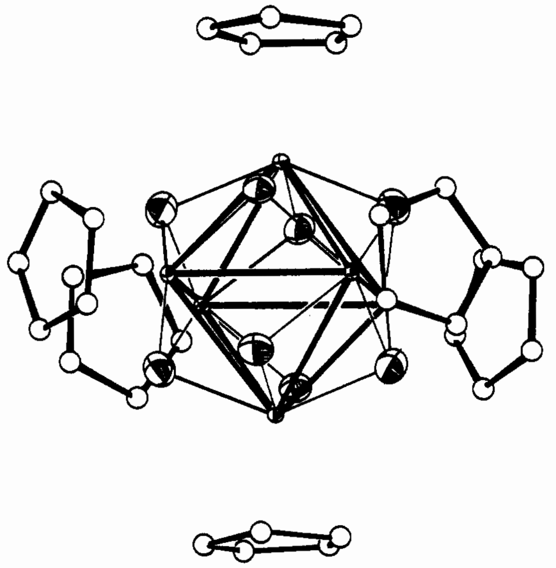

Figure 1. Geometry of $Cp_6Ti_6O_8$. The diagram is redrawn from that given in ref 3.

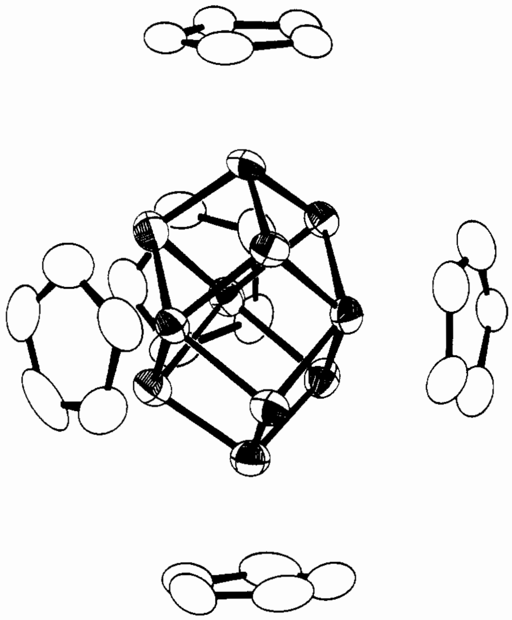

Figure 2. Geometry of $Cp_5V_5O_6$.

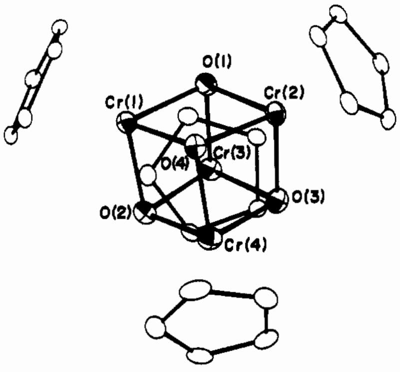

Figure 3. Geometry of $Cp_4Cr_4O_4$. All $Cp_4M_4A_4$ clusters have a cubane-like basic structure.

Table II. Number of Electrons and Orbitals Available in $Cp_mM_mA_n$ Clusters

	$Cp_6M_6A_8$	$Cp_5M_5A_6$	$Cp_4M_4A_4$
no. of electrons available[a]	$62 + 6n$	$49 + 5n$	$36 + 4n$
no. of electrons required	84	66	48
excess electrons	$6n - 22$	$5n - 17$	$4n - 12$
no. of metal orbitals available	54	45	36
no. of metal orbitals required	42	33	24
excess orbitals	12	12	12

[a] In arriving at the number of available electrons, each μ_3-A atom is considered to provide four electrons if it is a group 6 element (O or S) and three if it is in group 5. The metal provides n electrons, where n is the group number of M in the periodic table.

present a simple valence bond picture. If we assume that each η^5-C_5H_5 ring brings five electrons from its π orbitals to the cluster, each metal its 3d and 4s electrons, and each oxygen four electrons (leaving a lone pair on each oxygen atom), the total available electrons per cluster is as listed in Table II. Since the structures of $Cp_6Ti_6O_8$, $Cp_5V_5O_6$, and $Cp_4Cr_4O_4$ show that the M-Cp distances are normal and that the M-(μ_3-O) distances are those appropriate to an M-O single bond, it can be assumed that six electrons are required for the metal-Cp bonding, and six electrons also are required for the three M-O bonds formed by each μ_3-oxygen. The total number of electrons required for M-Cp and M-(μ_3-A) bonding in each cluster is given in Table II on this basis. The difference between the "available" electrons and the "required" electrons is the "excess" electrons belonging to the cluster. For $Cp_6Ti_6O_8$ there are two "excess" electrons, for $Cp_5V_5O_6$, eight, and for $Cp_4Cr_4O_4$, twelve. Many of the problems given in the Introduction in fact reduce to the problem of assigning these "excess" electrons and assessing their effect on the cluster. The valence bond approach is limited in its capacity to deal with these electrons. Gillespie, using valence-bond arguments, has

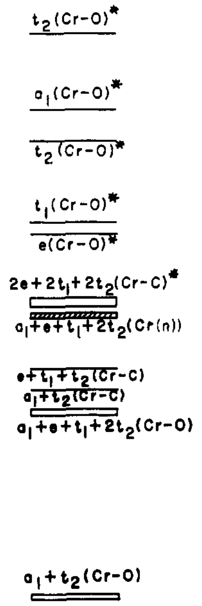

Figure 4. Energy level ordering in $Cp_4Cr_4O_4$. The C–H and C–C bonding and antibonding orbitals have been omitted. The shaded Cr(*n*) orbitals are the 12 "excess" orbitals referred to in the text.

suggested that the two excess electrons in 86-electron octahedral clusters such as $Cp_6Ti_6O_8$ are located in the center of the octahedron.[16] This would explain the diamagnetism of $Cp_6Ti_6O_8$. For $Cp_5V_5O_6$ the D_{3h} symmetry of the molecule (η^5-C_5H_5 being treated as a disk) requires a similar symmetry in the electronic arrangement, and this can only be achieved by placing a pair of electrons on each of the equatorial V atoms and a single electron on each axial V. This arrangement explains the paramagnetism of $Cp_5V_5O_6$. Also, because the axial V atoms are now formally V(IV) and the equatorial V(III), the shorter V(ax)–O and longer V(ax)–Cp distances, when compared to the distances involving the equatorial V atoms, are also explained. The effect on the V–V distances is not predictable. The valence bond approach cannot cope with the distortion or antiferromagnetism of $Cp_4Cr_4O_4$.

A further point becomes clear on consideration of the valence bond model. With the assumption of localized orbitals, each μ_3-oxygen atom requires three orbitals for bonding to the metal. Similarly, each η^5-C_5H_5 ring requires three metal orbitals. Each metal atom provides nine orbitals, and we see that, for all clusters listed in Table II, there are 12 metal orbitals in excess of those required for M–(μ_3-A) and M–Cp bonding. These orbitals can accommodate up to 24 "excess" electrons. In the molecular orbital model electrons in excess of 24 can be accommodated in antibonding orbitals, but this will be at the expense of M–A or M–Cp bonding, and we therefore predict that neutral $Cp_6M_6A_8$ clusters will only be obtainable for M from Ti through Mn (and the second- and third-row congeners), $Cp_5M_5A_6$ for M from Ti through Fe, and $Cp_4M_4A_4$ for M from Sc through Co. With an appropriate charge, clusters of other metals become possible, as do mixed-metal clusters.

The molecular orbital model, to which we now turn, therefore attacks the essential problem of these clusters, the arrangement of the "excess" electrons in the 12 "excess" orbitals.

Molecular Orbital Model. General Considerations. In general, the molecular orbital calculations confirm the idea that the essential problem is the assignment of "excess" electrons in 12 "excess" orbitals. At the very lowest energies are occupied C–H and C–C bonding orbitals. For all $Cp_mM_mA_n$ clusters there are then sets of occupied orbitals at low energy that are mainly localized on A (the "lone pairs"). There is then a closely grouped set of occupied orbitals corresponding to M–C and M–A bonds. After a large energy gap appear 12 orbitals mainly localized on M. After a further small energy gap there come the M–C antibonding orbitals and after these the M–A antibonding orbitals, which are spread over a wide range of energies. The energy levels are illustrated for $Cp_4Cr_4O_4$ in Figure 4. Since no clusters with more than 24 "excess" electrons are known, further discussion will be restricted to the 12 "excess" orbitals. That part of the 12 "excess" orbitals which is metal in character is overwhelmingly d orbital in nature. The metal s and p orbitals lie at higher energy and participate mainly in the antibonding M–A orbitals.

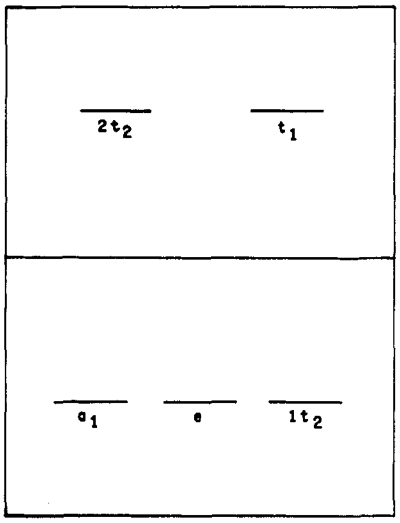

Figure 5. Energy level diagram for the 12 "excess" orbitals of $Cp_4M_4A_4$ clusters as proposed by Dahl and co-workers.[15]

Because there are far more of them than of the other clusters, it is convenient to begin the detailed discussion of the molecular orbital model with $Cp_4M_4A_4$ clusters. Many of the principles governing these clusters are applicable to the larger ones.

$Cp_4M_4A_4$ Clusters. In a series of papers Dahl and coworkers have analyzed the molecular and electronic structures of many of the cubane-like $Cp_4M_4A_4$ clusters listed in Table I.[5-8,10,12,13,15] In essence the Dahl model is similar to that shown in Figure 4 for $Cp_4Cr_4O_4$ in that it focuses on the 12 metal orbitals remaining after the M–A and M–Cp bonds have been accounted for. These orbitals are of $a_1 + e + t_1 + 2\ t_2$ symmetry. Dahl suggests these orbitals are used to form M–M bonds lying along the edges of the idealized tetrahedron of metal atoms. These edge bonds transform as $a_1 + e + 1t_2$, leaving a strongly antibonding $t_1 + 2t_2$ set (see Figure 5). As an example, in $Cp_4Fe_4S_4$ there are 12 electrons in $a_1 + e + 1t_2$ and 8 in $t_1 + 2t_2$. This necessitates a Jahn–Teller distortion and predicts six occupied bonding and four occupied antibonding orbitals and a net bond order of 2. This nicely explains the Fe–Fe distances in $Cp_4Fe_4S_4$ (Table I). Other $Cp_4M_4A_4$ clusters are explained similarly. However, this model predicts $Cp_4Cr_4O_4$, with 12 "excess" electrons filling $a_1 + e + 1t_2$, to be of exact T_d symmetry and diamagnetic, in contradiction to the observed D_2 symmetry and antiferromagnetism of this cluster.

The calculations reported here do not support the energy level order given by Dahl but give the order $e < 1t_2 < t_1 < 2t_2 < a_1$ (Figure 6). The reasons for this change in order are twofold. In addition to the metal–metal interaction assumed by Dahl, interaction of the "lone pair" of electrons on the bridging A ligand, of $a_1 + t_2$ symmetry, with the metal is

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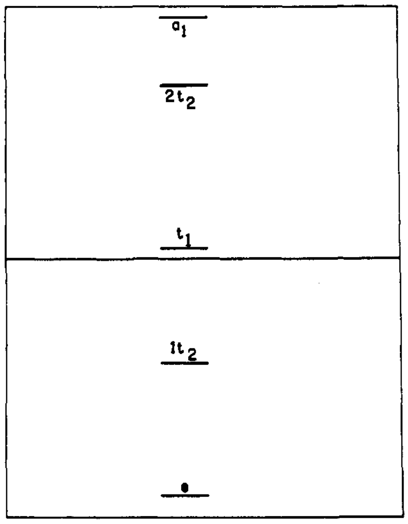

Figure 6. Energy level diagram for the 12 "excess" orbitals of $Cp_4M_4A_4$ clusters.

possible. Also, back-bonding of metal electrons to Cp via the empty $e + t_1 + t_2$ orbitals on the rings is possible. The three interactions are illustrated in Figure 7. The interaction of the filled A-ligand orbitals pushes the previously nonbonding $a_1 + t_2$ metal orbitals to higher energy, leaving $e + t_1 + t_2$ nonbonding. Back-bonding to the Cp ring makes $e + t_1 + t_2$ bonding, leaving $a_1 + t_2$ nonbonding. Back-bonding is particularly important toward the left of the transition metals; our calculations indicate 60% contribution of the Cp ring to $e + t_1 + 1t_2$ for $Cp_4Ti_4N_4$ vs. 2% for $Cp_4Co_4S_4$. Contribution of the A ligand to a_1 and $2t_2$ is more restricted (from 1% in $Cp_4Co_4O_4$ to 17% in $Cp_4Fe_4P_4$) but more drastic in its effect because of the energy gap between the participating orbitals. As expected the contribution increases as the electronegativity of A decreases.

A simple combination of the three interactions is not possible. However, inspection of Figure 7 suggests the ordering $e = 1t_2 < t_1 < a_1 < 2t_2$, which is remarkably close to the calculated $e < 1t_2 < t_1 < 2t_2 < a_1$ of Figure 6. The calculations also provide further evidence for the three interactions. The energy and composition of the e orbital, which is invariably the orbital of least energy, are independent of A in a series of $Cp_4M_4A_4$ clusters of the same M. This e orbital varies from a high of 96% metal d-orbital character in $Cp_4Co_4A_4$ to a low of 47% in $Cp_4Ti_4A_4$. The nonmetal part is from the C of the Cp ring, showing the importance of M–Cp back-bonding in clusters of the early transition metals. The a_1 orbital has significant contributions from the metal and A but not from the rings. On the other hand $2t_2$ has a ring contribution of 17% in $Cp_4Ti_4N_4$, decreasing to 1% for the Fe and Co clusters. The behavior of $1t_2$ and t_1 is less regular. While A makes no contribution to t_1, the partitioning of this orbital between the ring and the metal is influenced by A, and the relative energies of t_1 and $1t_2$ vary widely. In $Cp_4Co_4P_4$ t_1 is actually below $1t_2$ in energy. This does not significantly affect the general conclusions because both orbitals are triply degenerate. The positions of a_1 as the highest and e as the lowest of the 12 "excess" orbitals never vary.

The importance of the M–Cp and M–A interactions is beautifully illustrated by the calculations on $Cp_4Fe_4(CO)_4$. Here the M–A interaction is not possible, and also metal electrons will be back-donated to CO in preference to Cp because of the lower energy of the π^* orbitals on CO compared to that on Cp.[17] Hence of the three interactions shown in Figure 7 only the M–M is possible. In agreement with this, the calculation of the levels for $Cp_4Fe_4(CO)_4$ gives $e < a_1 < 1t_2 < t_1 \approx 2t_2$ for the 12 "excess" orbitals. This result is similar to the Dahl model. Since $Cp_4Fe_4(CO)_4$ has 12 excess electrons, it is therefore expected to be diamagnetic and of T_d symmetry, as is observed. Very surprising is the observation that $Cp_4V_4(CO)_4$ is paramagnetic,[14] since it has zero "excess" electrons. Its structure has not been determined; we are tempted to suggest that, if it really is paramagnetic, then it is not a cubane-like molecule.

In Table I are listed the known $[Cp_4M_4A_4]^{n+}$ clusters, the number of "excess" electrons, the symmetry, and the important magnetic and structural details. It is seen that several of the clusters are highly distorted from T_d symmetry. Three types of distortion may be distinguished: a D_{2d} structure with four long and two short M–M distances, a D_{2d} structure with two long and four short M–M distances, and a D_2 structure with two long, two intermediate, and two short M–M distances. Smaller further distortions of these severe ones are also observed; in column 5 of Table I are given the effective symmetries with only the severe distortion considered. In order to understand these distortions, we have calculated the energy level diagrams for the three severely distorted structures. The results for the 12 "excess" orbitals of interest are presented in diagrammatic form in Figure 8. This diagram shows the stabilization energy for each orbital calculated for each geometry according to the formula $(E_1 - E_A)/\Delta E$, where E_1 is the energy of the appropriate orbital of the 12 "excess" orbitals, E_A is the average energy of the 12 "excess" orbitals, and ΔE is the difference in energy between the orbital of lowest and the orbital of highest energy within the 12-"excess"-orbital set. For each geometry the stabilization energies so calculated were averaged over all $Cp_4M_4A_4$ clusters for which calculations were performed. The diagram is normalized to take account of the approximately 17% higher center of gravity for the T_d structure relative to that of the distorted structures. The structure that will be observed can be predicted from this diagram, initially in terms of a severe distortion and then in detail. This is accomplished by a combination of Jahn–Teller and Walsh arguments. In Table III are listed the predicted structures of $Cp_4M_4A_4$ clusters with from 1 to 24 "excess" electrons. With the exception of $[Cp_4Fe_4S_4]^{2+}$ the predicted and observed structures agree well.

A number of interesting points of detail arise from Figure 8 and Table III. The higher average energy for a T_d cluster suggests that with 24 "excess" electrons and no M–M bonds a $Cp_4M_4A_4$ cluster will distort. The direction of distortion cannot be predicted. The Co–Co distances in $Cp_4Co_4S_4$ average 3.298 Å, which is nonbonding, but the cluster has C_2 rather than T_d symmetry.[5] For $Cp_4Fe_4S_4$[7-9] and $Cp_4Co_4P_4$[6] with 20 "excess" electrons we predict the $D_{2d}{}^B$ structure (four long and two short M–M distances), as observed. Figure 8 suggests that these clusters will have two unpaired electrons, whereas they are observed to be diamagnetic. Diamagnetism can be achieved either by having $2a_1$ below $3e$ in energy in the $D_{2d}{}^B$ structure (these orbitals have very similar energies) or by making a slight distortion toward D_2 symmetry. Whereas $Cp_4Fe_4S_4$ must adopt the former solution, since the structure is essentially of D_{2d} symmetry,[7-9] $Cp_4Co_4P_4$ adopts the latter, since the four long Co–Co distances come in two sets of 2.624 and 2.637 Å.[6] In the case of 12-electron clusters such as $Cp_4Cr_4O_4$, the predicted distortion is initially to $D_{2d}{}^A$, with 4 electrons in 2e. However, 2e and $1b_2$ are extremely close in energy, and hence a further dynamic Jahn–Teller distortion to D_2 will occur. Even in D_2 the very similar energies of $2b_2$, $1b_1$, and $2b_3$ will lead to temperature-dependent occupation of these levels. We therefore expect anomalous magnetic behavior and D_2 symmetry for 9–12 electrons.

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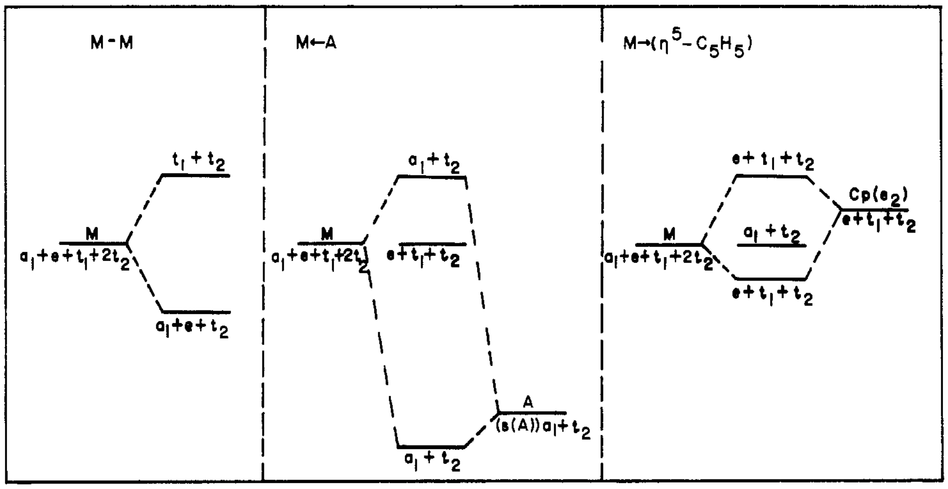

Figure 7. Effect of M–M, A–M, and M–Cp interactions on the 12 "excess" orbitals of $Cp_4M_4A_4$ clusters, determined by symmetry alone.

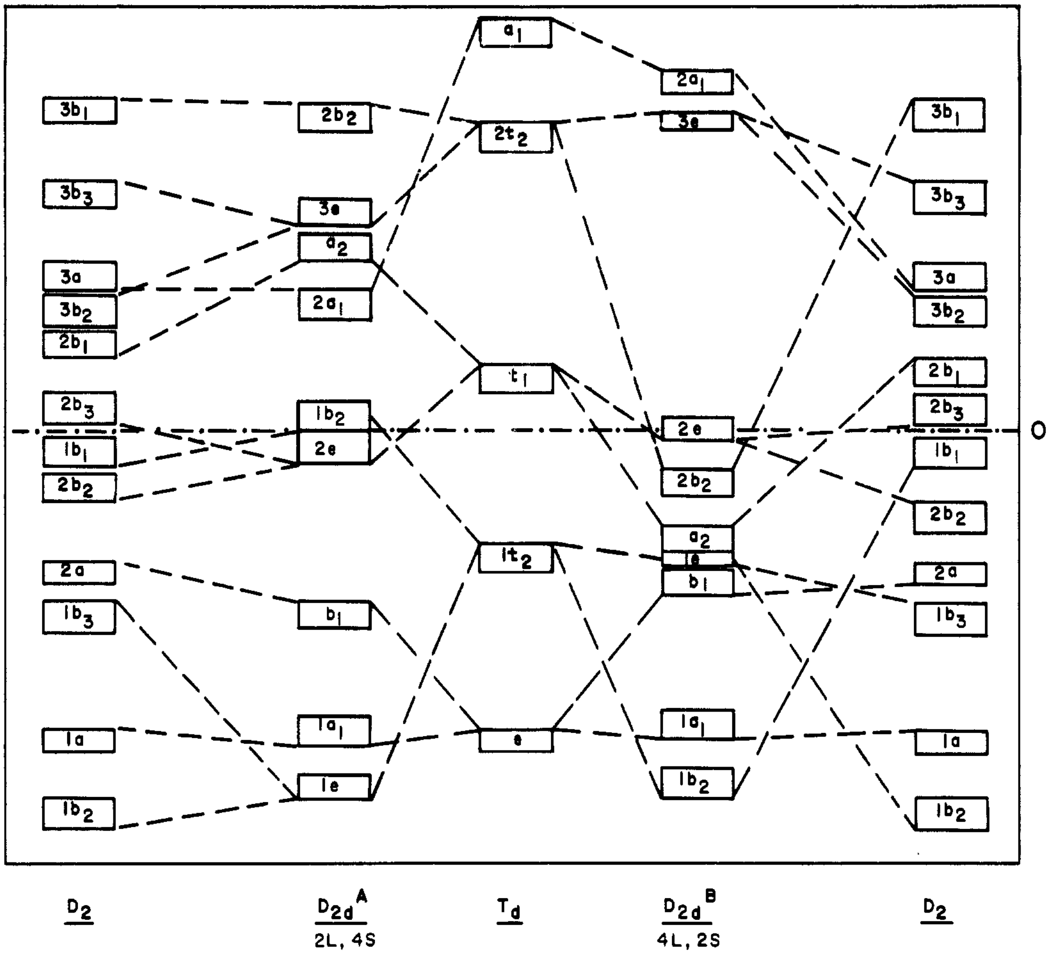

Figure 8. Distortions of the cubane-like structure of $Cp_4M_4A_4$ clusters. The M–M distances (Å) are as follows: T_d, 2.81; $D_{2d}{}^A$, two of 3.365 and four of 2.65; $D_{2d}{}^B$, four of 3.365 and two of 2.65; D_2, two of 3.365, two of 3.022, and two of 2.632. All M–C are 2.258 Å and all M–A 1.933 Å.

$Cp_4Cr_4O_4$ is of D_2 symmetry and antiferromagnetic.[1] Note that Figure 8 predicts that at low temperature a 12-electron cluster will be diamagnetic and of $D_{2d}{}^A$ symmetry. We are presently investigating $Cp_4Cr_4O_4$ at low temperature. One caveat to the situation with 9–12 electrons and the $D_{2d}{}^A$ or D_2 symmetry is in order. The $D_{2d}{}^A$ ground state involves the e and b_2 orbitals, the product of which contains neither b_1 nor b_2, which are the Jahn–Teller-active vibrations.[18] Exact $D_{2d}{}^A$ symmetry cannot be present in these clusters; however, we have only performed calculations for idealized symmetry.

The symmetry of $[Cp_4Fe_4S_4]^+$, with 19 "excess" electrons, is predicted to be D_2 with one unpaired electron, as is observed.[8,10] For $[Cp_4Co_4S_4]^+$ with 23 "excess" electrons the present model marginally predicts D_2 instead of the observed $D_{2b}{}^B$ structure. However, the energy differences are small, as are the differences in Co–Co bond distances in this cluster. The major failure of the present model is $[Cp_4Fe_4S_4]^{2+}$ with 18 "excess" electrons. This is predicted to be diamagnetic and

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Table III. Predicted Structures of $Cp_4M_4A_4$ Clusters for Various Numbers of "Excess" Electrons

	stabilization energy, arbitrary units									
	T_d		$D_{2d}{}^{A\,a}$		$D_{2d}{}^{B\,a}$		D_2			
no. of electrons	energy	symmetry[a]	energy	symmetry[b]	energy	symmetry[a]	energy	symmetry[b]	predicted structure	no. of unpaired electrons
1	49	e*	66	e*	65	b_2	70	b_2	D_2	1
2	98	e	114	e	114	b_2	123	b_2	D_2	0
3	147	e*	161	e*	136	a_1	162	a	D_2	1
4	196	e	211	e	194	a_1	200	a	$D_{2d}{}^A$	0
5	218	t_2*	253	a_1	210	e*	221	b_3	$D_{2d}{}^A$	1
6	239	t_2*	294	a_1	226	e	243	b_3	$D_{2d}{}^A$	0
7	261	t_2	316	b_1	243	e*	259	a	$D_{2d}{}^A$	1
8	283	t_2*	337	b_1	259	e	275	a	$D_{2d}{}^A$	0
9	304	t_2*	339	e*	277	b_1	284	b_2	$D_{2d}{}^{A\,c}$	*c*
10	326	t_2	342	e	293	b_1	291	b_2		
11	324	t_1*	344	e*	308	a_2	295	b_1		
12	322	t_1*	347	e	323	a_2	297	b_1		
13	320	t_1	346	b_2	322	e*	294	b_3		
14	318	t_1*	344	b_2	321	e	291	b_3	$D_{2d}{}^A$	0
15	316	t_1*	321	a_1	318	e*	279	b_1	$D_{2d}{}^A$	1
16	314	t_1	293	a_1	316	e	267	b_1	$T_d/D_{2d}{}^{B\,d}$	0/2[d]
17	278	t_2*	246	b_2	314	b_2	246	b_2	$D_{2d}{}^B$	1
18	242	t_2*	200	b_2	307	b_2	226	b_2	$D_{2d}{}^B$	0
19	204	t_2	165	e*	261	e*	205	a	$D_{2d}{}^{B\,e}$	1
20	171	t_2*	130	e	214	e	184	a	$D_{2d}{}^B$	2[f]
21	135	t_2*	95	e*	148	e*	167	b_3	D_2	1
22	99	t_2	60	e	120	e	116	b_3	$D_{2d}{}^B/D_2{}^d$	0
23	49	a_1	38	a_2	69	a_1	66	b_1	$D_{2d}{}^B/D_2{}^d$	1
24	0	a_1	17^7	a_2	17^7	a_1	17[g]	b_1	not $T_d{}^g$	0

[a] $D_{2d}{}^A$ and $D_{2d}{}^B$ refer to two long and four short and two short and four long M–M distances, respectively; the M–M distances are given in the caption to Figure 8. [b] Starred symmetries are required to be Jahn–Teller distorted. [c] Because of the closeness in energy of b_2 and 2e in $D_{2d}{}^A$, it is expected that 9–13 electrons will give rise to dynamic Jahn–Teller distortions and anomalous magnetic properties. [d] The energy differences are insufficient to decide between the given alternatives in these cases. [e] The predicted $D_{2d}{}^B$ structure must be Jahn–Teller distorted. A small distortion of the basically $D_{2d}{}^B$ structure is actually observed in $[Cp_4Fe_4S_4]^+$. [f] A small distortion of the $D_{2d}{}^B$ structure will produce diamagnetism; see text. [g] The overall energy is higher for the T_d structure than for any of the others, which are themselves equal within 1%; the diagram has been normalized to the T_d structure.

of $D_{2d}{}^B$ symmetry (two short and four long Fe–Fe distances); it is actually diamagnetic but of $D_{2d}{}^A$ symmetry (two Fe–Fe distances of 3.254 Å, four of 2.834 Å).[8] A possible reason for this failure is that the increase in effective nuclear charge in the dication alters the energy levels of the 12 "excess" orbitals. The extended Hückel method cannot accommodate this change. The calculated stabilization energies for $Cp_4Fe_4S_4{}^{2+}$ are not significantly different from the average values used in Table III, and a different prediction is therefore not obtained by using individual stabilization energies.

It is in theory possible to relate the total energy of electrons in the 12 "excess" orbitals to bond orders and M–M distances in the $Cp_4M_4A_4$ clusters. Such a relation would allow predictions of the magnitude of the distortions expected for various configurations. We have been deterred from this investigation by the large number of calculations for various combinations of distances required to produce a complete picture.

A comment is in order on the use of an energy level diagram averaged over a large number of $Cp_4M_4A_4$ clusters as against the energy level diagrams for individual clusters. It is felt that a general diagram that is on average correct but may be incorrect in detail is far more useful at this stage than particular diagrams. Many $Cp_4M_4A_4$ clusters await discovery. Also the individual diagrams are close to the average in the majority of cases (with 1–24 electrons and 16 $Cp_4M_4A_4$ clusters there are 384 individual cases). All of the known clusters have the same predicted structure with use of either the averaged or the individual diagram. In one case, $Cp_4Cr_4O_4$, the averaged diagram predicts $D_{2d}{}^A$ with a ground state in which the occupied 2e level is extremely close in energy to the unoccupied $1b_2$, leading to a further dynamic Jahn–Teller distortion. The individual diagram predicts $D_{2d}{}^B$ with the occupied a_2 level extremely close to the unoccupied e level, again leading to a dynamic Jahn–Teller distortion. In summary, the averaged diagram is at least as useful as the individual ones, gives the same result in all cases, and is of far more predictive value.

Cubane-like clusters without Cp ligands can be accommodated in the scheme presented here. Those known, $(NO)_4Co_4(\mu_3\text{-}NC(CH_3)_3)_4$,[19] $(CO)_{12}Co_4(\mu_3\text{-}Sb)_4$,[15] $(CO)_{12}Os_4(\mu_3\text{-}O)_4$,[20] and $(CO)_{12}Re(\mu_3\text{-}A)_4$ (A = OH,[21] OCH_3,[22] SCH_3[23]), all have terminal ligands which are extremely effective π acceptors (NO, CO). For $(NO)_4Co_4(NR)_4$ we assume that four electrons on each Co are strongly involved in π donation to NO. This leaves 16 "excess" electrons to be accommodated in the 12 "excess" orbitals. Since π donation to the terminal ligands has been accounted for, and there are no lone pairs on NR to interact with the metal, the only interaction splitting the 12 orbitals is Co–Co, and the Dahl model applies.[19] For $(CO)_{12}Co_4Sb_4$ and $(CO)_{12}Os_4O_4$ we expect π back-donation to CO to be even greater than to Cp; interaction of lone pairs on Sb or O with the metal is also possible. Hence the energy level order shown in Figure 6 will apply. Since both $(CO)_{12}Co_4Sb_4$ and $(CO)_{12}Os_4O_4$ have 24 "excess" electrons, a basically T_d structure with long M–M distances is expected, as is observed.[15,20] Both the present and the Dahl models predict this structure. For $(CO)_{12}Re_4A_4$ an intermediate situation occurs;[21–23] the A lone pairs are not available, but π donation to CO will be extensive. However, these clusters have 24 "excess" electrons, and long Re–Re distances and a T_d structure (as observed) are expected

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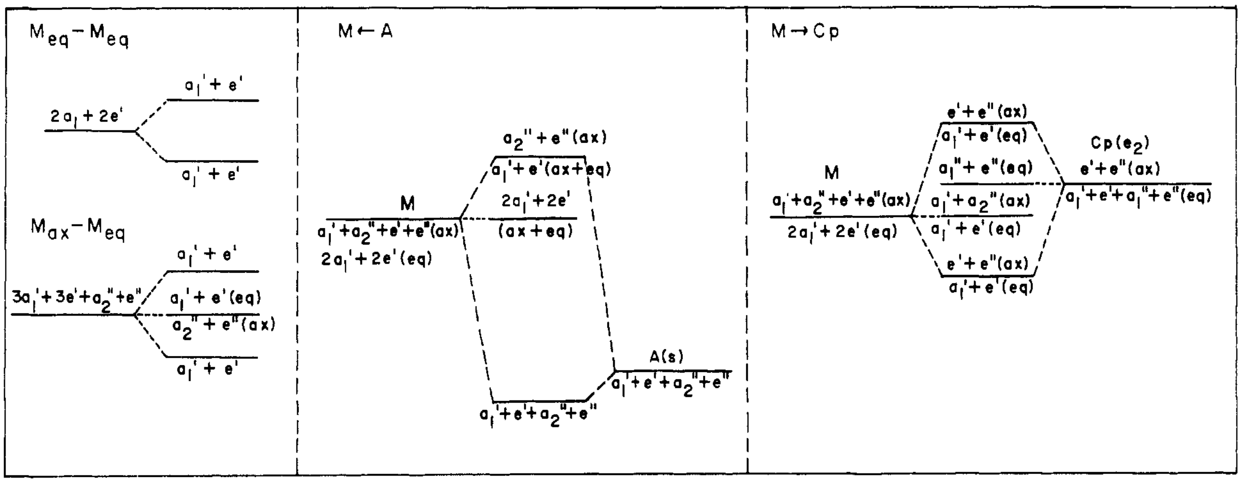

Figure 9. Effect of M–M, A–M, and M–Cp interactions on the 12 "excess" orbitals of $Cp_5M_5A_6$ clusters as determined by symmetry.

whatever the energy level order.

Two interesting clusters, $(NO)_4Fe_4(\mu_3\text{-}S)_4$ and $(NO)_4Fe_4(\mu_3\text{-}S_4)_2(\mu_3\text{-}NC(CH_3)_3)_2$,[21] fall in between the carbonyls and nitrosyls discussed above. The former has 16 "excess" electrons and the latter 14 (four electrons on each Fe having been used in Fe–NO π bonding). There remain the S–Fe and Fe–Fe interactions, and we expect the energy order $e \approx 1t_2 < t_1 < a_1 << 2t_2$ or $e \approx 1t_2 < a_1 < t_1 << 2t_2$. Our calculations support the former ordering and predict that $(NO)_4Fe_4S_4$ will be of T_d symmetry and diamagnetic, as observed.[20] For $(NO)_4Fe_4S_2(NR)_2$ we expected and calculate $e \approx 1t_2 < a_1 < t_1 << 2t_2$ and thus expect a distortion. We can predict neither direction nor magnitude; the cluster in fact has C_{2v} symmetry.[24]

$Cp_5M_5A_6$ Clusters. Again we have 12 "excess" metal orbitals remaining after formation of M–Cp and M–(μ_3-A) bonds. These can be divided into a set of $a_1' + a_2'' + e' + e''$ symmetries localized on the axial M atoms and a set of $2\ a_1' + 2\ e'$ symmetries localized on the equatorial M atoms. The three interactions that split the energies of these orbitals are the same as for $Cp_4M_4A_4$ clusters, namely, M to Cp back-donation, lone-pair interaction between A and M, and M–M interactions. These interactions are shown individually in Figure 9, and the calculated average energy levels for $Cp_5M_5A_6$ clusters are shown in Figure 10. Again the order of energy levels is remarkably close to that expected from a composite of the symmetry-determined interactions. Also, shown in Figure 10 are the percentages of the orbitals localized on the axial or equatorial metal atoms. It will be noted that the a_2'' and e'' orbitals, which should be localized solely on the axial metal atoms in D_{3h} symmetry, have an equatorial component. This arises because the actual static symmetry of the $(\eta^5\text{-}C_5H_5)_5M_5A_6$ clusters used in the calculations was C_s. However, the effective localization of the orbitals is clear.

So far the only known $Cp_5V_5A_6$ cluster is $Cp_5V_5O_6$ with eight "excess" electrons. These would fill the $1a_1'$ and $1e'$ orbitals and half-fill the e'' orbital. Thus $Cp_5V_5O_6$ is expected to have two unpaired electrons. The observed magnetic moment of 0.93 μ_B[11] is lower than expected for two unpaired electrons, possibly because of the close proximity of $2a_1$ to e''. In addition it is seen that the eight electrons are partitioned, the six occupying $1a_1'$ and $1e'$ being almost completely localized on the equatorial V atoms and the two occupying e'' being localized on the axial V atoms. Thus the molecular orbital approach gives the same result as the valence bond approach, with the same consequences for the V–O and V–Cp distances (see above).

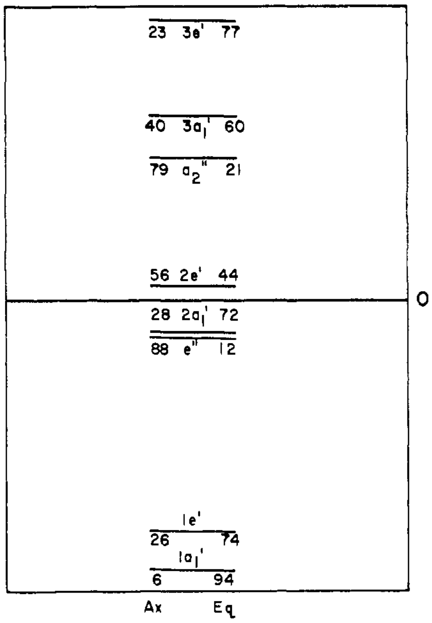

Figure 10. Energy level diagram for the 12 "excess" orbitals of $Cp_5M_5A_6$ clusters. Numbers are percentages of the orbital localized on the axial or equatorial metal atoms.

The six electrons occupying the $1a_1'$ and $1e'$ orbitals are bonding with respect to both the V(eq)–V(eq) and the V(ax)–V(eq) interactions, whereas the two occupying e'' are nonbonding with respect to both interactions. Analysis of the V–V interactions reveals no significant difference between V(eq)–V(eq) and V(ax)–V(eq) overlap. Hence equal V–V distances throughout the cluster would be expected. This is observed. Nevertheless, the average V–V distance, 2.748 Å, is shorter than would be expected for a cluster in which formally only six electrons are available for nine V–V bonds. An authentic V–V single bond appears to exist in $Cp_2V_2(CO)_5$ and has a V–V distance of 2.46 Å.[25]

We finally note the closeness in energy of the e'' HOMO and $2a_1'$ LUMO of $Cp_5V_5O_6$ (see Figure 10). This raises the possibility of abnormal magnetic behavior and a second-order Jahn–Teller distortion on heating $Cp_5V_5O_6$ above room temperature. We have not been able to investigate this for technical reasons.

$Cp_6M_6A_8$ Clusters. Once again we have 12 "excess" metal orbitals of $a_{1g} + a_{2g} + 2\ e_g + t_{1u} + t_{2u}$ symmetries split by the

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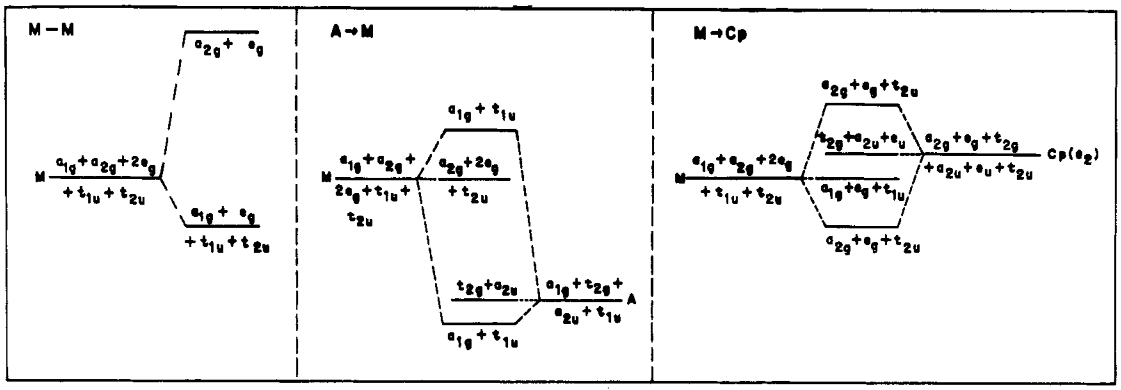

Figure 11. Effect of M–M, A–M, and M–Cp interactions on the 12 "excess" orbitals of $Cp_6M_6A_8$ clusters as determined by symmetry.

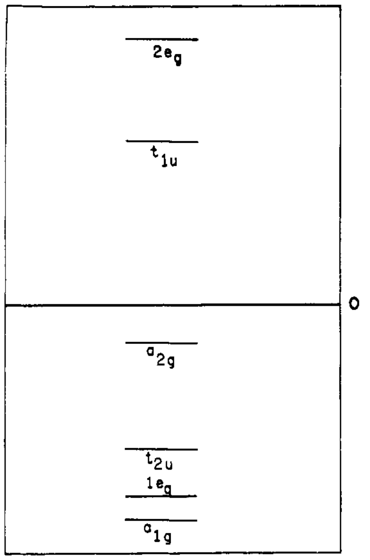

Figure 12. Energy level diagram for the 12 "excess" orbitals of $Cp_6M_6A_8$ clusters.

same three interactions (M–M, A–M, M–Cp). The effect of the three interactions determined by symmetry alone is shown in Figure 11 and the calculated energy level order in Figure 12. It is noteworthy that the M–Cp interaction becomes more important in the $Cp_6M_6A_8$ clusters, because we are dealing with metals to the left of Mn of necessity. The closeness of a_{1g}, $1e_g$, and t_{2u} in energy is also noteworthy.

In $Cp_6Ti_6O_8$, which is the only known example of this type of complex, there are two "excess" electrons, which would occupy a_{1g} in agreement with the diamagnetism of this complex.[3] This orbital is almost 100% metal d in character, specifically d_{z^2} from the two Ti atoms lying along the z coordinate and $d_{x^2-y^2}$ from the four Ti atoms lying along x and y. The coefficients are such that the lobes pointing into the octahedron are positive. Hence the simple idea that the two electrons are located in the center of the octahedron is confirmed. Although the electrons are bonding with respect to the Ti–Ti interaction, the average Ti–Ti distance of 2.891 Å[3] does seem short for a cluster with only two electrons for 12 Ti–Ti edge bonds.

Recently $[((C_2H_5)_3P)_6Fe_6S_8]^{2+}$, with μ_3-S atoms over triangular faces of an octahedron of Fe atoms having terminal R_3P ligands, has been prepared.[4] This can be accommodated in the present scheme if four electrons on each Fe are regarded as nonbonding (they will in fact be involved in π bonding to the R_3P ligand). There are then six "excess" electrons to be filled into the 12 orbitals depicted in Figure 12. The cluster has a magnetic moment of 6.04 μ_B at 291 K and of 5.66 μ_B at 91 K. We propose that at 291 K the six "excess" electrons half-occupy each of the a_{1g}^1, $1e_g^2$, and t_{2u}^3 orbitals, so that the cluster has six unpaired electrons. At low temperature the configuration is $a_{1g}^2 1e_g^2 t_{2u}^2$ with four unpaired electrons. Because $1e_g$ and t_{2u} are close in energy, the alternative arrangements of a_{1g}^1, t_{2u}^3, $1e_g^2$ and a_{1g}^2, t_{2u}^3, $1e_g^1$ are also possible. The magnetism will be unchanged. The Fe–Fe distances of 2.605–2.655 Å[4] indicate considerable Fe–Fe interaction, as is to be expected if six electrons occupy six strongly bonding orbitals. Note also that the low-temperature form of $[((C_2H_5)_3P)_6Fe_6S_8]^{2+}$ must be distorted because the ground state is t_{2u}^2 or e_g^1.

Extension to Other Clusters. The most obvious extension of the present work would be to other clusters obeying Euler's theorem. These are pentagonal-bipyramidal $Cp_7M_7A_{10}$ and triangular $Cp_3M_3A_2$. Both of these have the 12 "excess" orbitals we have seen above. $Cp_3M_3A_2$ clusters have been discussed already by Hoffmann[26] and Dahl[27] and their coworkers. Some preliminary calculations on $Cp_7M_7A_{10}$ clusters have shown that the A–A intramolecular distance is crucial to the energy level order. We are presently attempting to synthesize such clusters.

Finally we note that our analysis suggests that any $Cp_mM_mA_n$ cluster having more than zero but less than 24 "excess" electrons should be capable of existence. Therefore the sequence $Cp_6Ti_6O_8$, $Cp_5V_5O_6$, $Cp_4Cr_4O_4$ is nothing more than an aesthetically satisfying series, and we are actively pursuing the search for other clusters, particularly $Cp_5Cr_5O_6$ and $Cp_4V_4O_4$.

Caveat. We have not explored $Cp_mM_mA_n$ clusters for second- or third-row metals. The larger size and higher energies of the d orbitals of the metals would be expected to increase the M–M and M→Cp interaction at the expense of A→M. This would result in a change in the energy level order, and particularly for $Cp_4M_4A_4$ drastic changes from first-row clusters might occur (an energy level order of $e \approx t_2 < a_1 \approx t_1 < t_2$ could be predicted).

Methods

Initial calculations were of the INDO/2 variety, as used in the programs developed by Zerner and co-workers.[28,29] However, the INDO/2 approximation proved unsatisfactory for the problem in hand for several reasons. First, in order to obtain acceptable computational core sizes and times, it was necessary to introduce fictitious $(H)_5$ in place of the C_5H_5 rings. Although this approximation appears to have been successfully used elsewhere,[30] it did not work in the present case because the total number of electrons in the cluster is crucial and

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Table IV. Extended Hückel Parameters (eV)[a]

	H	C	N	O	P	S	Ti	V	Cr	Mn	Fe	Co	Ni
$-H_s$	13.6	19.84	25.69	32.89	18.66	21.11	7.15	6.55	6.90	7.18	7.08	7.31	7.54
$-H_p$		10.93	13.20	15.80	10.78	12.39	4.47	3.99	4.20	3.61	3.86	3.78	3.92
$-H_d$							6.19	6.08	6.59	10.36	8.13	8.88	9.89

[a] ζ values were obtained from Slater's rules.

because π back-bonding to the Cp rings is important. Second, the results obtained from the INDO/2 method depend on the total number and multiplicity of the electrons specified. Since one major goal of this work was to obtain a general model suitable for a large number of electronically different clusters, the dependence of the results on the electronic input was not acceptable. We therefore turned to the extended Hückel approximation, again using programs written by Zerner.[31,32] For the transition metals, 3d, 4s, and 4p orbitals were used, for C, N, and O, 2s and 2p were used, for S and P, 3s and 3p were used, and, for H, the 1s was used. The distances were taken from the published structures of the clusters.[1-13] However, the ring distances were kept constant regardless of which cluster was being analyzed: C–C, 1.4 Å; C–H, 0.91 Å; C–C–C angle, 108°; C–C–H angle, 120°. Similarly the M–C distances were held constant at 2.26 Å for all clusters. Minor deviations in M–A and M–M distances or angles were averaged to obtain a structure with the highest symmetry possible.

An annoying problem with symmetry was encountered. With the assumption that the energy barrier to free rotation of an η^5-C_5H_5 ring is very small, the effective symmetries of $Cp_6M_6A_8$ are O_h, of $Cp_5M_5O_6$, D_{3h}, and of $Cp_4M_4A_4$, T_d. However, a necessarily static η^5-C_5H_5 ring reduces the symmetries to at best D_3 for $Cp_6M_6A_8$, C_s for $Cp_5M_5A_6$, and D_{2d} for $Cp_4M_4A_4$. This symmetry reduction was a further reason for abandoning the INDO/2 calculations since the unrestricted Hartree–Fock method does not retain the symmetry restriction of the molecular orbitals. Convergence problems and wide deviations from the expected degeneracies of orbitals were found. In reporting the extended Hückel results, we have used the symmetry labels of the idealized symmetry. In general we are confident that the grouping of orbitals according to the higher symmetry has been accurately followed for $Cp_4M_4A_4$ ($T_d \rightarrow D_{2d}$ or D_2), moderately confident for $Cp_6M_6A_8$ ($O_h \rightarrow D_3$), but less confident for $Cp_5M_5A_6$ ($D_{3h} \rightarrow C_s$).

Calculations of energy levels and orbital contributions for $Cp_6M_6A_8$ were performed on $Cp_6M_6O_8$ where M = Ti, Cr, or Mn, for $Cp_5M_5A_6$ on $Cp_5V_5O_6$, $Cp_5V_5S_6$, $Cp_5Mn_5O_6$, $Cp_5Fe_5S_6$, $Cp_5Ni_5O_6$, and $Cp_5Ni_5S_6$, for $Cp_4M_4A_4$ in T_d symmetry on $Cp_4Ti_4A_4$ (A = N, O) and $Cp_4M_4A_4$ (M = Cr, Fe, or Co, A = N, O, P, or S), for $Cp_4M_4A_4$ in $D_{2d}{}^A$ symmetry (two long/four short) on $Cp_4Ti_4O_4$, $Cp_4Cr_4O_4$, $Cp_4Fe_4S_4$, and $Cp_4Co_4S_4$, for $Cp_4M_4A_4$ in $D_{2d}{}^B$ symmetry (four long/two short) also on $Cp_4Ti_4O_4$, $Cp_4Cr_4O_4$, $Cp_4Fe_4S_4$, and $Cp_4Co_4S_4$, and for $Cp_4M_4A_4$ in D_2 symmetry on $Cp_4M_4A_4$ (M = Ti, Cr, Fe, or Co and A = O or S). As discussed in the Results and Discussion above, the important orbitals were found to be the 12 "excess" orbitals in each case. It was found that the ordering of the energy levels of these 12 orbitals was dependent on the type of cluster ($Cp_6M_6A_8$, $Cp_5M_5A_6$, or $Cp_4M_4A_4$). Within a given type the *relative* ordering of the energy levels was not significantly dependent on M and essentially totally independent of A. The absolute energies varied markedly with M and slightly with A, as expected, but the relative energies of the 12-orbital set did not. Since we were interested in devising as general a model as possible and since orbital energies calculated by the extended Hückel method are not accurate enough for any conclusions about the absolute energies to be drawn, the energies of each orbital of a given symmetry within the 12-orbital set were scaled and averaged over all M and A for a given $Cp_mM_mA_n$ cluster. The scaled energy, E_s, is defined as

$$E_s = ((E_1 - E_A)/\Delta E) \times 100$$

where E_1 = energy of the particular orbital, E_A = mean energy of 12 "excess" orbitals, and ΔE = difference in energy between the orbital of highest and the orbital of lowest energy in the set. All energies were taken in atomic units, so that E_s is dimensionless. The E_s values were then averaged. As an example the scaled energy of the e″ orbital of $Cp_5V_5O_6$ is

$$E_s = ((-0.235784) - (-0.232640))/((-0.217787) - (-0.243787)) \times 100 = -12.1$$

For $Cp_5V_5S_6$ the scaled energy of the e″ orbital is −17.4, for $Cp_5Mn_5O_6$, +4.5, for $Cp_5Fe_5S_6$, −6.3, for $Cp_5Ni_5O_6$, +8.3, and for $Cp_5Ni_5S_6$, −8.3; the average scaled energy for $Cp_5M_5A_6$ is therefore −5.2. The calculated energies for all clusters have been deposited as supplementary material.

The parameters for the orbitals are given in Table IV.

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Supplementary Material Available: Listings of orbital energies (Tables 1–6) (6 pages). Ordering information is given on any current masthead page.

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