Molecular and Electronic Structures of Clusters of the General Formulas $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_6$ and $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ (M = d-Block Element, A = Group 16 Element)

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The molecular and electronic structures of $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_6$ and $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ (M = Ti, V, Mo; A = O, Se) are compared. Extended Hückel molecular orbital calculations show that the $M_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ structure cannot exist unless the M_4 tetrahedron is severely distorted by lengthening of the $M^{apical}\text{–}M^{basal}$ distance, because the μ_2-A–μ_3-A nonbonded interaction is repulsive. The $M_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ structure can exist with a small distortion. The $M_4(\mu_2\text{-}A)_6$ structure is preferred over $M_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ when M–A multiple bonding is important, that is when A = O. There are 12 cluster orbitals for $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_6$ and 9 for $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$. The ordering of the energy levels is dependent on A, because the cluster orbitals are the antibonding counterparts of the M–A bonding interaction. Apart from the lowest energy orbital, $1a_1$, there is little M–M interaction in any of the cluster orbitals.

Introduction

Clusters of general formula $[L_nM]_4(\mu_2\text{-}A)_6$ (L = ligand, M = metal, A = main group atom) with an adamantane-like $M_4(\mu_2\text{-}A)_6$ core (Figure 1) are relatively common for d^{10} and main group metals M. Examples are $\{[XZn]_4(\mu_2\text{-}X)_6\}^{2-}$ (X = Cl, Br, I),[1,2] $[MeSn]_4(\mu_2\text{-}S)_6$, and $[SP]_4(\mu_2\text{-}S)_6$.[3,4] Clusters of this type were not known until recently for non-d^{10} transition elements when A is an atom, although examples exist when A is a group, e.g. in $\{[(PhS)M]_4(\mu_2\text{-}SPh)_6\}^{2-}$ (M = Mn, Fe, Co).[5-8] Two examples containing non-d^{10} transition metals M, combined with oxygen as element A have now been prepared: $[(\eta\text{-}C_5Me_5)M]_4(\mu_2\text{-}O)_6$ (M = Ti,[9] V;[10] Figure 2). These contain formally d^0 and d^1 metal ions.

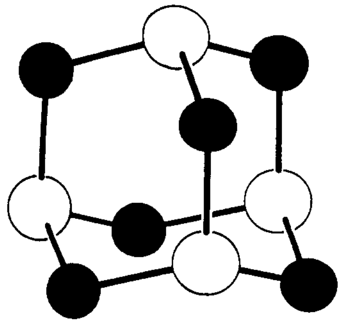

Figure 1. $M_4(\mu_2\text{-}A)_6$ adamantane-like core of $[L_nM]_4(\mu_2\text{-}A)_6$.

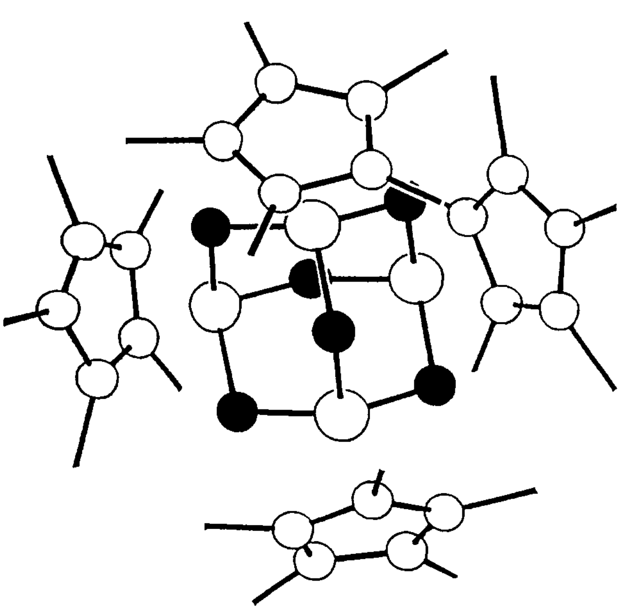

Figure 2. Molecular structure of $[(\eta\text{-}C_5Me_5)M]_4(\mu_2\text{-}O)_6$ (M = Ti, V).[9,10]

Recently, three clusters having an alternative to the $[L_nM]_4(\mu_2\text{-}A)_6$ structure have been prepared. These are $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ (Figure 3),[11] $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$ (Figure 4),[12] and $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ (Figure 5),[13] with the $M_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ core shown in Figure 6. In the latter two clusters, one η-C_5R_5 ligand is replaced by terminal or bridging oxo ligands to give the $[(\eta\text{-}C_5Me_5)Mo(\mu_2\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_2(R)$ unit (Figure 7). The clusters $[(\eta\text{-}C_5Me_5)Ti]_4(\mu_2\text{-}O)_6$ and $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ are particularly interesting since they have a common formula, $[(\eta\text{-}C_5R_5)Ti]_4A_6$, with A = group 16

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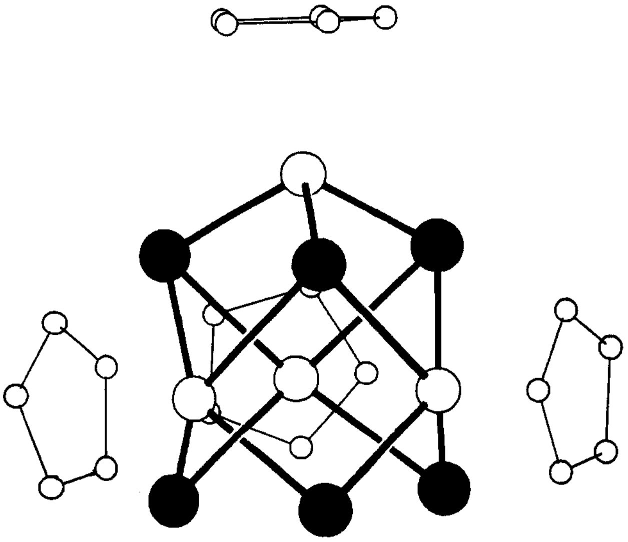

Figure 3. Molecular structure of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$.[11]

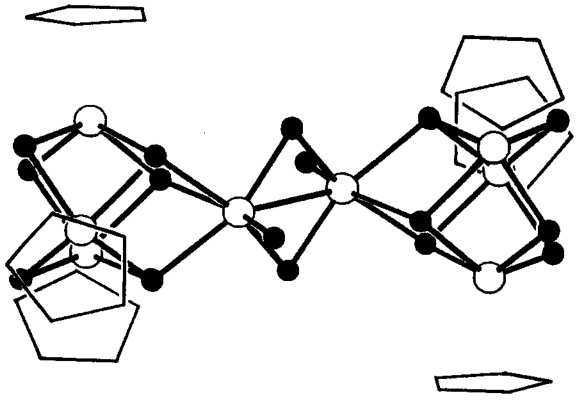

Figure 4. Molecular structure of $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$.[12]

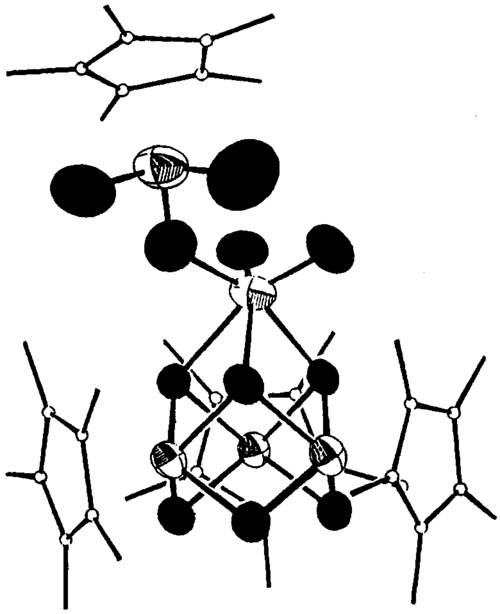

Figure 5. Molecular structure of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$.

element. There is more steric repulsion in $M_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ than in $M_4(\mu_2\text{-}A)_6$ because of the eclipsed arrangement of the A atoms in the former. Therefore it is not clear why $[(\eta\text{-}C_5Me_5)Ti]_4(\mu_2\text{-}O)_6$ and $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ adopt the observed structures.

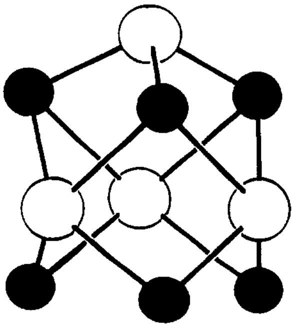

Figure 6. $M_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ core of $[L_nM]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$.

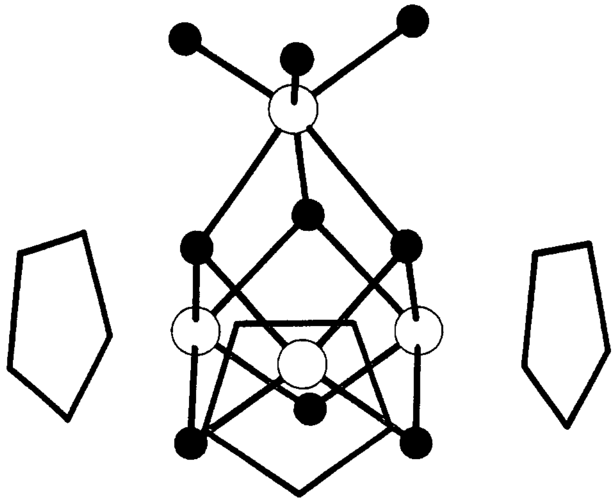

Figure 7. $\{[(\eta\text{-}C_5R_5)Mo(\mu_2\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_3\}^-$ core of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$.

The present work explores the relationship between the $M_4(\mu_2\text{-}A)_6$ and $M_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ structures and discusses the reasons for the occurrence of one or the other.

Results and Discussion

Comparison of the $M_4(\mu_2\text{-}A)_6$ and $M_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ Structures. Extended Hückel calculations on $M_4(\mu_2\text{-}O)_6$ and $M_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ cores (M = Ti, V, Mo, without $\eta\text{-}C_5H_5$ ligands), using a regular tetrahedron for the metal atoms, proved that the $M_4(\mu_2\text{-}O)_6$ structure was always of lower total energy for any reasonable M–O distances. For $M_4(\mu_2\text{-}Se)_6$ and $M_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ there were no significant differences in the total energies. Therefore we first discuss the reason for the difference between the oxide and selenide cases.

The $M_4(\mu_2\text{-}A)_6$ and $M_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ structures are related by the motions shown in Figure 8. In essence, three A atoms rotate by 60°, changing from two- to three-coordinate, converting the staggered (octahedral) arrangement of A atoms into the eclipsed (trigonal pyramidal) arrangement. As the three A atoms rotate, the repulsion between the three- and the two-coordinate A atoms increases markedly. The repulsion is reduced by a down- and inward movement of the two-coordinate A atoms, but this movement increases the repulsion between the two-coordinate A atoms themselves. The effect of the two types of repulsion on the total energy is shown in Figure 9 for $Mo_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ with Mo–Mo = 3.00 Å and Mo–O = 1.93 Å. The minimum energy occurs at an O^2–O^3 distance of 2.15 Å and an O^2–O^2 distance of 2.55 Å (A^3 = three-coordinate A atom, A^2 = two-coordinate A atom). In $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$ the observed

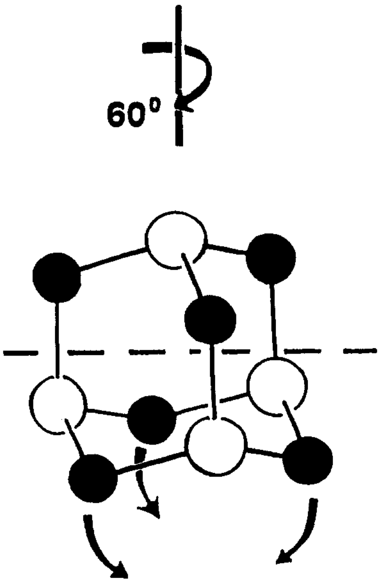

Figure 8. Movements required to convert $M_4(\mu_2\text{-}A)_6$ into $M_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$.

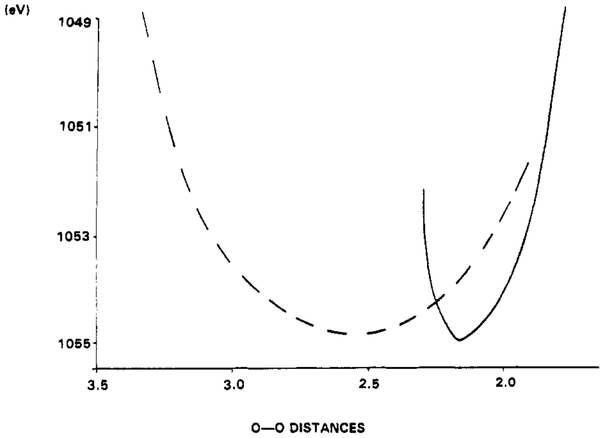

Figure 9. Total energy of $Mo_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ as a function of O^2–O^3 (—) and O^2–O^2 (- - -) distances.

O^2–O^3 distances are not significantly different from one another and average 2.44 Å; the O^2–O^2 distances average 2.78 Å. Thus, the O^2–O^3 distance calculated for an idealized $Mo_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ structure is shorter by 13.4% than the observed nonbonding contact, whereas the calculated O^2–O^2 distance is 9.0% shorter. The O^2–O^3 interaction is calculated to be repulsive (antibonding, see below), and it is this interaction which is responsible for the higher energy of the $M_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ structure compared to $M_4(\mu_2\text{-}O)_6$. Dramatic proof of this was obtained when $V_4(\mu_2\text{-}O)_6$, with V–V = 3.00 Å and V–O = 1.81 Å, was compared to $V_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$, with V–V = 3.00 Å, V^b–O^2 = 1.81 Å, V^b–O^3 = 1.90 Å, and V^a–O^3 = 1.90 Å (M^a = apical M atom, M^b = basal M atom). The calculated O^2–O^3 distance was reduced to 1.70 Å, and the total energy increased by 12 eV. Thus it is concluded that the $M_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ structure will not be stable with respect to $M_4(\mu_2\text{-}O)_6$ without significant distortion of the M_4 tetrahedron, as occurs in $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$.

The effect of Se^2–Se^3 and Se^2–Se^2 repulsions on the total energy of $Ti_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ with Ti–Ti = 3.375 Å and Ti–Se = 2.56 Å is shown in Figure 10. Both curves are flatter than the corresponding ones for $Mo_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$. The minimum energy occurs for Se^2–Se^3 = 3.15 Å and Se^2–Se^2 = 3.35 Å. The Se^2–Se^3 distances in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ average 3.28 Å, and the Se^2–Se^2 distances, 3.67 Å. The calculated Se^2–Se^3 contacts are only 4% smaller than the observed values, and therefore an undistorted $M_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ structure may be stable.

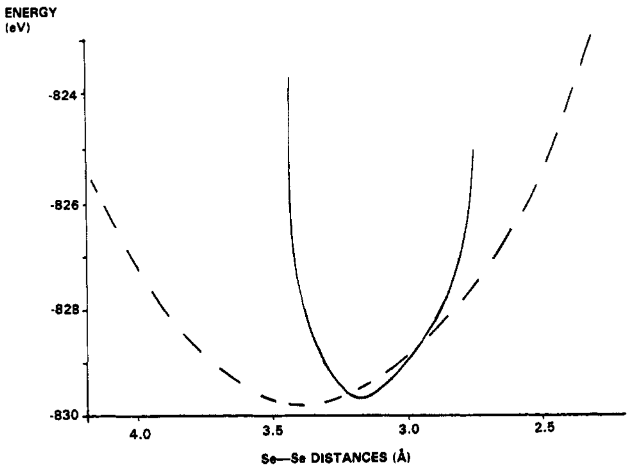

Figure 10. Total energy of $Ti_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ as a function of Se^2–Se^3 (—) and Se^2–Se^2 (- - -) distances.

Comparison of the $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_6$ and $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ Structures. The calculations established that the $M_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ core was markedly unstable with respect to $M_4(\mu_2\text{-}O)_6$ when the M_4 unit was an undistorted tetrahedron. In fact the clusters $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$ are distorted, having Mo^a–Mo^b distances of 3.31 Å and Mo^b–Mo^b distances of 2.73 and 2.74 Å, respectively.[12,13] The distortion in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ is much less severe, the Ti^1–Ti^b distances averaging 3.46 Å and Ti^b–Ti^b averaging 3.29 Å.[11] The questions are as follows. Why does $[(\eta\text{-}C_5H_5)Ti]_4Se_6$ have the $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ structure, whereas $[(\eta\text{-}C_5Me_5)Ti]_4O_6$ is $[(\eta\text{-}C_5Me_5)Ti]_4(\mu_2\text{-}O)_6$, and why is the highly distorted $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_2R$ unit preferred to $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)]_3(\mu_2\text{-}O)_3Mo(O)_2R$? Note that there was no interconversion between $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ and $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_6$, as judged by NMR methods.

The first possible reason for the observed structures is the different steric repulsions of the $\eta\text{-}C_5R_5$ ligands (R = H, Me). The average Ti–Ti distance in $[(\eta\text{-}C_5Me_5)Ti]_4(\mu_2\text{-}O)_6$ is 3.25(3) Å.[9] In $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ the Ti^a–Ti^b distances average 3.462(4) Å and the Ti^b–Ti^b distances, 3.288(4) Å.[11] Obviously, there would be no steric problem in interchanging the $\eta\text{-}C_5Me_5$ and $\eta\text{-}C_5H_5$ ligands in these compounds. The average Mo^b–Mo^b distance in $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$ is 2.737(1) Å,[12,13] and the Cr–Cr distances in the undistorted cubane $[(\eta\text{-}C_5Me_5)Cr(\mu_3\text{-}O)]_4$ average 2.834(2) Å.[14] It is concluded that steric differences between $\eta\text{-}C_5H_5$ and $\eta\text{-}C_5Me_5$ do not determine the structure adopted by $[(\eta\text{-}C_5R_5)M]_4A_6$.

It is less easy to assess the different electronic influences of $\eta\text{-}C_5H_5$ and $\eta\text{-}C_5Me_5$, because the $M_4(\mu_2\text{-}A)_6$ structure is only known with $\eta\text{-}C_5Me_5$ whereas $M_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ occurs with both $\eta\text{-}C_5H_5$ and $\eta\text{-}C_5Me_5$. However, the $\eta\text{-}C_5R_5$ ligand will have an electronic influence on the metal, not on the coordination number of A, and as discussed below, the electronic structure of the metal is not a factor

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[14] Bottomley, F.; Chen, J.; MacIntosh, S. M.; Thompson, R. C. *Organometallics* **1991**, *10*, 906.

in determining which of the two molecular structures will be adopted.

Another possible reason is the number of cluster electrons and their configuration. These are determined by the identity of the metal M, the formal oxidation state of which is +4 (regarding $\eta\text{-}C_5R_5$ as having a −1 charge and the group 16 element as −2). A detailed analysis (see below) showed that the cluster orbitals are essentially pure metal d and, with one exception, nonbonding in character, as in other clusters of this type such as $[(\eta\text{-}C_5R_5)Cr(\mu_3\text{-}O)]_4$.[15,16] Since $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_6$ have 12 cluster orbitals but $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ only 9, clusters with more than 18 cluster electrons (which have not yet been prepared) will strongly favor $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_6$. There is one orbital in $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_6$ which is strongly bonding with respect to the M–M interaction within the M_4 tetrahedron and one orbital in $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ which is strongly bonding with respect to the M^b–M^b interaction within the M_3 basal plane, but occupation of this orbital (e.g. when M = V or Mo) does not determine which of the two structures is adopted.

A further possibility is that A^2–A^3 bonding along the axis of the trigonal pyramid of A atoms stabilizes $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$, as has been suggested previously for other $[(\eta\text{-}C_5R_5)M]_mA_n$ clusters.[17] Such A^2–A^3 bonding implies that the resonance form $[(\eta\text{-}C_5H_5)M]_4(\mu_3\text{-}\eta^2\text{-}A_2)_3$ makes a significant contribution to the structure of $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$. This argument was most easily tested by calculations on $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$. The diselenide structure $[(\eta\text{-}C_5H_5)Ti]_4(\mu_3\text{-}\eta^2\text{-}Se_2)_3$ contains formally Ti_4^{10+} and six cluster electrons, whereas the selenide $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ contains Ti_4^{16+} and no cluster electrons. Thus the extended Hückel calculations should show significant Se–Se overlap integrals and also a significant contribution of Ti orbitals to the highest occupied molecular orbitals of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$. Neither of these predictions was borne out by calculations on the $Ti_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ core, nor on $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ itself. The Se^2–Se^3, Se^2–Se^2, and Se^3–Se^3 overlap populations were all small and negative (−0.019, −0.001, and −0.007 respectively). These may be compared to the Ti–Se overlap populations which were in the range +0.261 to +0.543. Thus all of the Se–Se interactions are antibonding. The highest occupied molecular orbitals of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ form a set of eight, spanning a range in energy of 0.067 eV. There was a contribution of Ti d orbitals to this set, but it was small (maximum of 5% to any one orbital) and somewhat less than the contribution to these orbitals in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_6$. Thus neither the Se–Se overlap populations nor the contribution of Ti orbitals to the highest occupied molecular orbitals supports the concept of Se^2–Se^3 bonding in these clusters. Calculations on an idealized $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ cluster gave a similar result.

The final possibility is that M–A multiple bonding is important in determining which of the structures is adopted. Multiple bonding between a three-coordinate oxygen atom and a metal will be minimal, but that involving a two-coordinate oxygen atom may be extensive. Multiple bonding between O and M has been identified as a major contributor to the stability of the $M(\mu_2\text{-}O)M$ unit.[18,19] The average Ti–O distance of 1.837(3) Å in $[(\eta\text{-}C_5Me_5)Ti]_4(\mu_2\text{-}O)_6$ is in the range 1.75–1.85 Å[20,21] usually observed in complexes containing the six-coordinate $(\eta\text{-}C_5R_5)TiL_2(\mu\text{-}O^-)$ unit. These distances are shorter than those for Ti–O where multiple bonding is not possible because of a higher coordination number of Ti or O, where the range is 1.95–2.15 Å.[20,22] The average Mo^b–O^2 distances in $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$ are 1.930(8) and 1.954(2) Å, respectively. Where multiple bonding is present, Mo–O^2 distances are in the range 1.85–1.90 Å;[20,23,24] otherwise the range is 1.95–2.05 Å.[20,23,25] Thus the Mo–O^2 distances in $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$ suggest that there is little Mo–O multiple bonding in these compounds. The average Ti^b–Se distance in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ (2.508(3) Å) is in the range normally observed for a Ti–Se single bond (2.37–2.64 Å[11,26–28]) and is in fact longer than the average Ti^a–Se^3 distance of 2.389(3) Å. This indicates that there is little Ti–Se^2 multiple bonding.

Multiple bonding in these compounds can be assessed by comparative extended Hückel calculations on $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}A)_6$ and $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ (A = O, Se). However, a problem arises in estimating the distances in the two unknown clusters $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ and $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_6$. As indicated above, if the Ti–Ti and Ti–O distances of $[(\eta\text{-}C_5Me_5)Ti]_4(\mu_2\text{-}O)_6$ are used to model $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$, the O^2–O^3 distance will be reduced to an impossible value. Increasing the Ti–Ti distance to obtain reasonable Ti–O and O^2–O^3 distances will automatically decrease the Ti–O overlap population and thus the estimate of Ti–O multiple bonding. Conversely, using the long Ti–Se^2 distance of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ to model $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_6$ will lead to an underestimate of the multiple bonding in the latter cluster. For $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ the Ti–Ti and Ti–O distances were fixed at the same values as for the average Mo–Mo and Mo–O distances in the $[(\eta\text{-}C_5Me_5)Mo(\mu_2\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_2R$ unit in $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$ (Mo^a–Mo^b = 3.31 Å, Mo^b–Mo^b = 2.735 Å, Mo^a–O^3 = 2.175 Å, Mo^b–O^3 = 2.03 Å, Mo^b–O^2 = 1.93 Å). Since Mo and Ti have similar radii (2.01 and 2.00 Å, respectively), this should result in a reasonable estimate of multiple bonding. For $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_6$ the Ti–Ti distance was taken as the average Ti–Ti distance in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$.

The procedure adopted for assessing the multiple bonding was to compare the Ti–A^2 overlap integral in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ with that of Ti–A in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}A)_6$ when the Ti–A distances were varied. It was found that the Ti–Se overlap integral in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_6$ was proportionally equal to the Ti–O overlap

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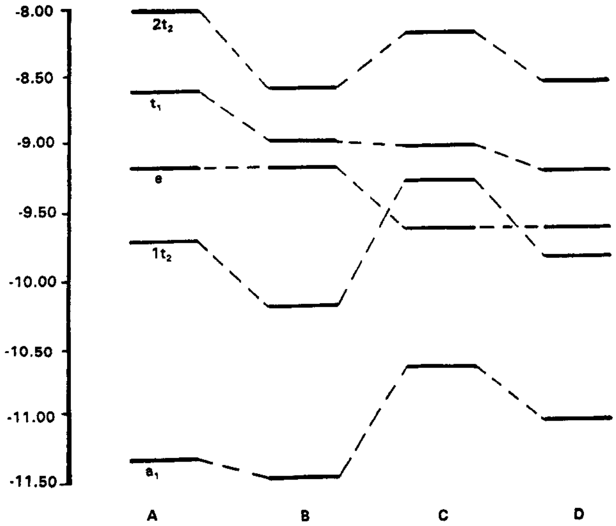

Figure 11. Energies of the cluster orbitals of $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_6$ as a function of the Mo–Mo and Mo–O distances. Key: (A) Mo–Mo = 2.73 Å, Mo–O = 1.81 Å; (B) Mo–Mo = 2.73 Å, Mo–O = 1.93 Å; (C) Mo–Mo = 3.00 Å, Mo–O = 1.81 Å; (D) Mo–Mo = 3.00 Å, Mo–O = 1.93 Å.

integral in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}O)_6$ with a Ti–O distance of 1.84 Å, when the Ti–Se distance was 2.10 Å. Thus multiple bonding in the hypothetical $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_6$ would only equal that achieved in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}O)_6$ if the Ti–Se distance was considerably shorter than ever observed. The shortest Ti–Se distance in a compound containing $\eta\text{-}C_5R_5$ appears to be 2.369(2) Å in $[(\eta\text{-}C_5H_5)_2Ti][(\eta\text{-}C_5H_5)ClTi](\mu_2\text{-}Se)_2)$.[28]

It is concluded that the $M_4(\mu_2\text{-}A)_6$ structure will be preferred when M–A multiple bonding is important. Thus, in general, for A = O the $M_4(\mu_2\text{-}O)_6$ structure will be the rule, for A = Se the $M_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ structure will be common. The $[(\eta\text{-}C_5Me_5)Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_2(R)$ unit of $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$ adopts the $M_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ structure and not the $M_4(\mu_2\text{-}A)_6$ structure because of extensive multiple bonding to the terminal oxygen atoms within the $Mo(O)_2(OR)$ group. The molybdenum orbitals which otherwise would be available for π-bonding within the $M_4(\mu_2\text{-}O)_6$ framework are used to form terminal Mo–O multiple bonds.

Relationship of the Cluster Orbitals of $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_6$ to Those of $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$. The energy levels of the 12 cluster orbitals of $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}O)_6$ (M = Ti, V) were described previously.[10] Figure 11 shows the levels for the model cluster $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_6$ and also shows the effect of changing the Mo–Mo and Mo–O distances on the energies of the cluster orbitals. The M–A σ-interactions of the $M_4(\mu_2\text{-}A)_6$ unit span the representations $a_1 + e + t_1 + 2t_2$. The M–M bonding interactions span the representations $a_1 + e + t_2$.[29] Within the $M_4(\mu_2\text{-}A)_6$ core, the p orbitals on A, whose principle axis is normal to the plane containing an $M(\mu\text{-}A)M$ unit, will carry the overwhelming portion of any M–A π-interaction. These orbitals span the symmetries $t_1 + t_2$. It is seen from Figure 11 that the $1t_2$, t_1, and $2t_2$ orbitals all decrease markedly in energy as the Mo–O distance increases. The a_1 orbital also decreases in energy, but far less markedly, and the e orbital does not change in energy. This shows that the cluster orbitals of t_1 and t_2 symmetries are the antibonding counterpart of the Mo–O σ- and π-interactions. The reduction in energy of the a_1 orbital as the Mo–O distance increases must be due to a contribution from the antibonding Mo–O σ-interaction. When the Mo–Mo distance is increased, the energies of the a_1 and $1t_2$ orbitals increase, showing that these orbitals are involved in Mo–Mo bonding. The e, t_1, and $2t_2$ orbitals decrease in energy as the Mo–Mo distance increases. These orbitals are antibonding with respect to the Mo–Mo interaction. Detailed analysis of the overlap populations supports these conclusions.

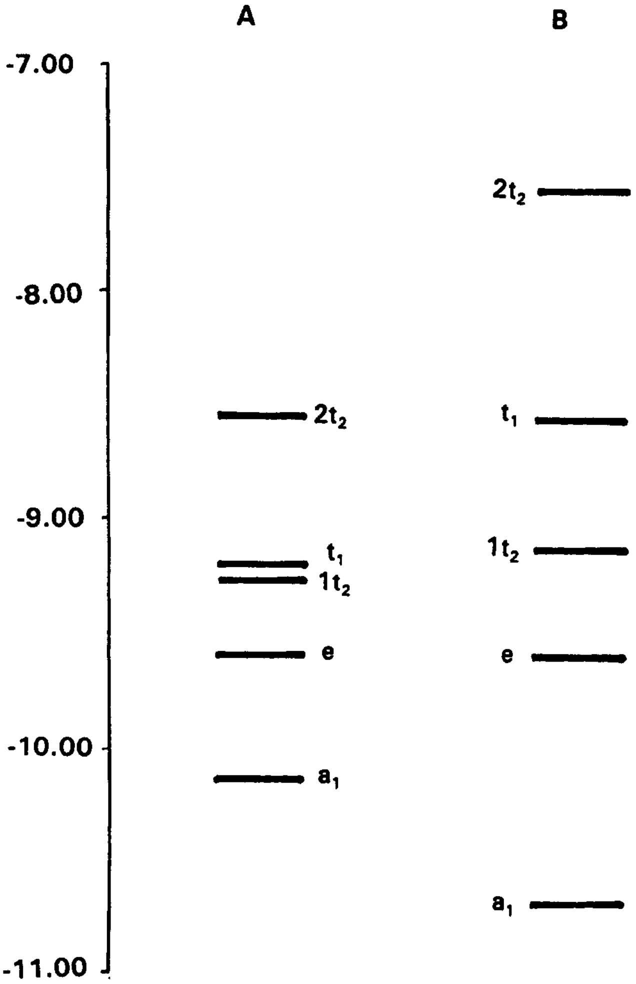

Figure 12. Energies of the 12 cluster orbitals of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}O)_6$ (A) and the model $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_6$ (B).

It is seen from Figure 12 that the cluster orbitals of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}O)_6$ span a much smaller range of energy than those of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_6$. This is a consequence of the greater spatial extent of the Se orbitals compared to O, resulting in greater Ti–Se overlap.[16] The relative ordering of the cluster orbitals was the same in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}O)_6$ and $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_6$. However, the e, $1t_2$, and t_1 orbitals were very close in energy for all $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}O)_6$ (M = Ti, V, Mo) and the energies were very dependent on the M–O and M–M distances. Thus variations in the distances and/or the metal involved may affect the ordering of these three energy levels. This makes the prediction of the ground state electron configuration and magnetic behavior of $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}O)_6$, where M = metal from groups 5–8, for which e, t_1, and $1t_2$ will be populated, very difficult. In $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_6$, the e and $1t_2$ orbitals are of very similar energy and therefore this diagram must also be used with caution when

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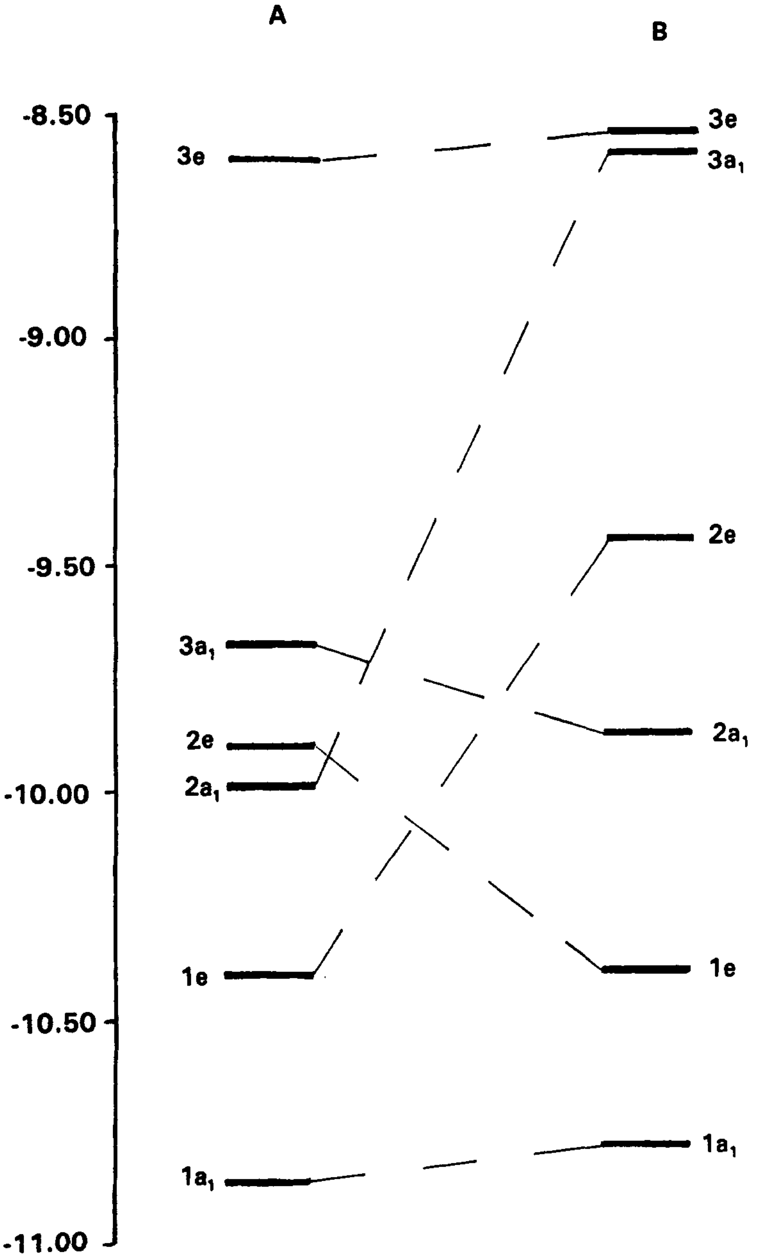

Figure 13. Energies of the nine cluster orbitals of $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ (A) and $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ (B).

predicting electronic configurations. The e orbital remains at the same energy in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}O)_6$ and $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_6$. This is expected, since this orbital contains no contribution from the ligands.

For $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ there are only 9 cluster orbitals compared to the 12 in $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_6$, as a consequence of the formation of three M^a–A^3 bonds. The energy level ordering in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ is shown in Figure 13, which also shows the diagram for the model cluster $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$. An analysis of the contributions of atomic orbitals to the molecular orbitals shows that the relationship between the energy level orderings in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ and $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ is quite complicated, as indicated by the connections shown in Figure 13. The reason for the large changes in energy on going from one cluster to the other is again due to the greater spatial extent of the Se orbitals compared to O. The 1e and $2a_1$ orbitals are essentially pure d orbitals localized on M^a, 1e being $d_{x^2-y^2}$ and d_{xy}, $2a_1$ being d_{z^2}. These orbitals are nonbonding with respect to the M^a–M^b interaction and are completely independent of any M^b–M^b interaction. The other orbitals shown in Figure 13 are mainly localized in the M^b_3 plane. The 2e orbital of $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ is antibonding by symmetry with respect to the M^b–M^b interaction. *It therefore decreases in energy as the* Mo^b–Mo^b distance increases on going from $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ to $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$. The $3a_1$ orbital of $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ ($2a_1$ of $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$, Figure 13) is bonding by symmetry with respect to the M^b–M^b interaction and would therefore be expected to rise in energy as the M^b–M^b distances increase on going from Mo/O to Ti/Se. However this orbital contains an antibonding contribution from the M^b–A^2 interaction.

Occupation of the $1a_1$ orbital of $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}O)_6$ (M = Ti, V), which is strongly M–M bonding, stabilizes $[(\eta\text{-}C_5R_5)V]_4(\mu_2\text{-}O)_6$ compared to $[(\eta\text{-}C_5R_5)Ti]_4(\mu_2\text{-}O)_6$.[10] In $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$, the $1a_1$ orbital is localized exclusively on the basal M atoms and is bonding with respect to these atoms (see Figure 14). In $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ this orbital is not occupied. The Ti^b–Ti^b

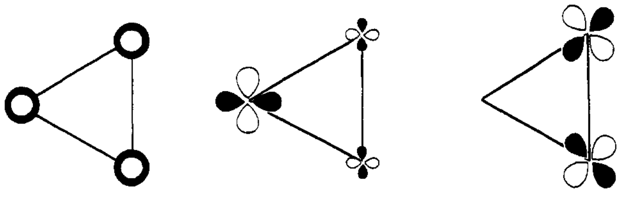

Figure 14. Contributions of the metal d orbitals to the $1a_1$ orbital of $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$.

distances average 3.29 Å, and the Ti^a–Ti^b, 3.46 Å. The longer Ti^a–Ti^b distance is due to the Se^2–Se^3 nonbonding repulsion discussed above. The difference in the distances is not large (0.17 Å), and the Ti–Ti distances in $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$ are comparable to those in related clusters. Examples are $[(\eta\text{-}C_5H_4Me)Ti]_5(\mu_3\text{-}Se)_6$, where Ti–Ti = 3.299–3.379(3) Å,[30] $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se_2)_2(\mu_2\text{-}Se)(\mu_3\text{-}Se)_2(\mu_4\text{-}O)$ (Ti–Ti = 3.114–3.464(4) Å[28]), $(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)_2TiCl(\eta\text{-}C_5H_5)$ (Ti–Ti = 3.399(2) Å[28]), and $[(\eta\text{-}C_5H_5)_2Ti(\mu\text{-}Se)_2Ti(\eta\text{-}C_5H_5)]_2(\mu\text{-}Se)$ (Ti–Ti 3.421(4) Å[27]). On the other hand, in $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$ the average Mo^b–Mo^b distance of 2.735 Å is not only much shorter (0.58 Å) than the Mo^a–Mo^b distance (3.31 Å) but also considerably shorter than that observed in polyoxomolybdates such as $[(\eta\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$ (Mo–Mo = 3.288(4), 3.297(4) Å[31]) and $[(\eta\text{-}C_5Me_5)Mo_6O_{18}]^-$ (Mo–Mo = 3.263(2), 3.314(2) Å[23]). The Mo^b–Mo^b distances approach those of 2.575(1) Å in $[(\eta\text{-}C_5H_5)Mo]_3(\mu\text{-}Cl)(\mu_3\text{-}\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-}C_4(CF_3)_4)(\mu_3\text{-}O)$, for which Mo–Mo multiple bonding was proposed.[32] The very short Mo^b–Mo^b distance is ascribed to the occupation of the a_1 orbital, which is bonding over the three Mo^b atoms (see Figure 14). In the model cluster $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$, the orbitals next in energy are 1e and $2a_1$, which are almost completely localized on the apical Mo atom and, although occupied, contribute nothing to the Mo^b–Mo^b interaction. The Mo^b–Mo^b overlap integrals are 0.066, which may be compared to the overlap integrals of Mo^b–O^2 (0.212), Mo^b–O^3 (0.257), and Mo^a–O^3 (0.121). Calculations on the $\{[(\eta\text{-}C_5H_5)Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_3\}^-$ unit present in $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $(\eta\text{-}C_5Me_5)Mo_8O_{16}$ show that the orbitals 1e and $2a_1$ of $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ are pushed to a higher energy because they contain a contribution from d orbitals of Mo^a which are involved in multiple bonding to the terminal oxygen atoms. In $\{[(\eta\text{-}C_5H_5)Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_3\}^-$ the energy level ordering is $1a_1 < 1e < 2a_1$, and 1e is occupied by two electrons. This orbital is almost completely localized on the Mo^b atoms of $\{[(\eta\text{-}C_5H_5)Mo(\mu\text{-}O)]_3(\mu_3\text{-}O)_3Mo(O)_3\}^-$ but is antibonding by symmetry with respect to the Mo^b–Mo^b interaction. Thus the Mo^b–Mo^b overlap integral of 0.051 is due to the $1a_1$ orbital, which carries all of the Mo^b–Mo^b bonding interaction.

In $[(\eta\text{-}C_5H_5)Ti]_4(\mu_2\text{-}Se)_3(\mu_3\text{-}Se)_3$, the Ti^a—Se^3 distances average 2.389(3) Å, which is shorter than the average Ti^b—Se^3 distance of 2.700(4) Å. This difference is expected since the Ti^a atom is six-coordinate but Ti^b is seven-coordinate. On the other hand, in $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ and $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$ the Mo^a—O^3 distances average 2.168(7) and 2.182(3) Å, respectively, which are longer than the Mo^b—O^3 averages of 2.030(7) and 2.031(2) Å. The lengthening of the Mo^a—O^3 distances is due to the strong *trans* influence of the M—O unit. In $(\eta\text{-}C_5Me_5)_4Mo_5O_{11}$ there are two Mo^a=O and one Mo^a—O—Mo units. The Mo^a—O^3 distances *trans* to Mo^a=O are 2.194(7) and 2.251(8) Å. *Trans* to Mo^a—O—Mo the Mo^a—O^3 distance is 2.060(7) Å. In $(\eta\text{-}C_5Me_5)_6Mo_8O_{16}$ there is one Mo^a=O and two Mo^a—O—Mo units. The Mo^a—O distances are 2.260(2), 2.137(2), and 2.150(2) Å, respectively.

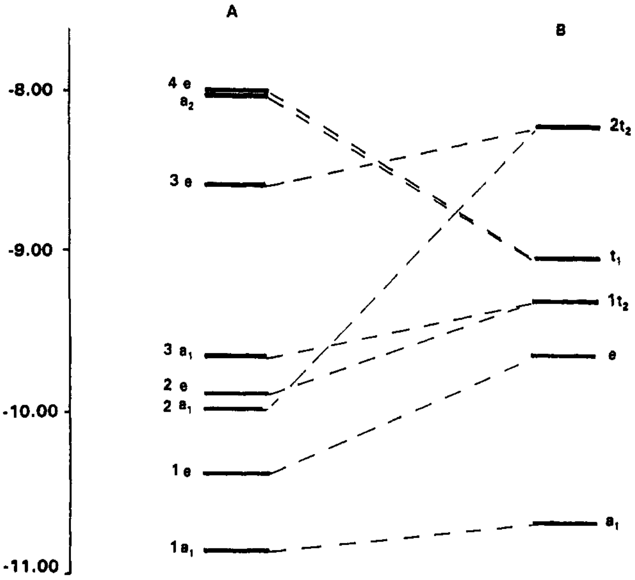

Figure 15. Relationship between the cluster orbitals of $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ (A) and those of $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_6$ (B).

In the calculations on $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ and $\{[(\eta\text{-}C_5H_5)Mo]_3(\mu_3\text{-}O)_3Mo(O)_3\}^-$ it was found that, as with $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}O)_6$, some of the cluster orbitals were very close in energy (for example $2a_1$ and 2e, Figure 13). The energies of these orbitals (particularly $2a_1$) were dependent on the Mo–O and Mo–Mo distances. Therefore prediction of ground state electronic configurations and magnetic properties of clusters with electrons in these orbitals will be uncertain.

The relationship between the cluster orbitals of $[(\eta\text{-}C_5H_5)Mo]_4(\mu\text{-}O)_6$ and those of $[(\eta\text{-}C_5H_5)Mo]_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ is shown in Figure 15. Two features of the correlation diagram are obvious. The first is that the cluster orbitals increase in energy on going from the $Mo_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ structure to $Mo_4(\mu\text{-}O)_6$. This is a consequence of the Mo–O antibonding contribution of oxygen to the cluster orbitals, as discussed above. The second is that the three orbitals which are pushed to high energy as a result of the formation of three σ-bonds on going from $Mo_4(\mu\text{-}O)_6$ to $Mo_4(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3$ come solely from the t_1 set. This is due to symmetry. The three new bonds formed on going from $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_6$ to $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ involve only the three basal M atoms. The six M^b–A^3 σ-bonds span the representations $a_1 + a_2 + 2e$, whereas the three M^a–A^3 σ-bonds span $a_1 + e$. Since t_1 and t_2 of $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_6$ (T_d) correlate with $a_2 + e$ and $a_1 + e$ of $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ (C_{3v}) respectively, formation of the three new M^b–A^3 σ-bonds requires that t_1 be used.

As discussed above, the primary force which decides whether the $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_6$ or the $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ structure is adopted is M–A multiple bonding. The occupancy of the cluster orbitals by any number of electrons will play only a very minor role, as is clear from Figure 15. Electron counts from 1 to 14 favor the $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ structure. Since the a_2 and 4e

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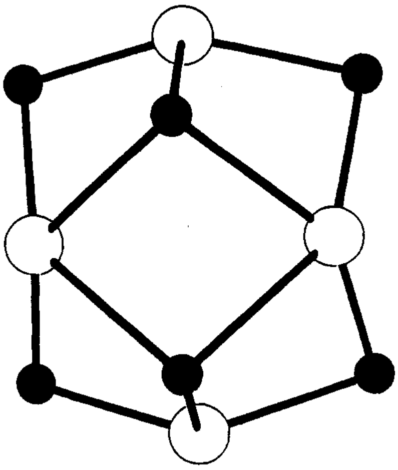

Figure 16. $M_4(\mu_2\text{-}A)_4(\mu_3\text{-}A)_2$ core of $[L_nM]_4(\mu_2\text{-}A)_4(\mu_3\text{-}A)_2$.

orbitals of the $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_3(\mu_3\text{-}A)_3$ structure are antibonding with respect to the M^a–A^3 interaction, 18–24 cluster electrons can only be accommodated by the $[(\eta\text{-}C_5H_5)M]_4(\mu_2\text{-}A)_6$ structure.

Other $[(\eta\text{-}C_5R_5)M]_4A_6$ Structures. Two other structures for $[L_nM]_4A_6$ are possible. The first has the $M_4(\mu_2\text{-}A)_4(\mu_3\text{-}A)_2$ core shown in Figure 16. However, in the compounds of this type which are known, for example $[M_2Cl_2((S(CH_2)_2NMeCH_2)_2)]_2$ (M = Zn,[33] Cd[34]), the metal atoms lie in an approximate plane.[33,34] The butterfly of metal atoms is opened so wide that a rectangle is formed. There are no $[(\eta\text{-}C_5R_5)M]_4(\mu_2\text{-}A)_4(\mu_3\text{-}A)_2$ examples of this type. The second structure has the $\{[M(\mu_2\text{-}A)_2M](\mu_2\text{-}A)\}_2$ core shown in Figure 17. The metal atoms again form a rectangle. We have not found any examples of this type.

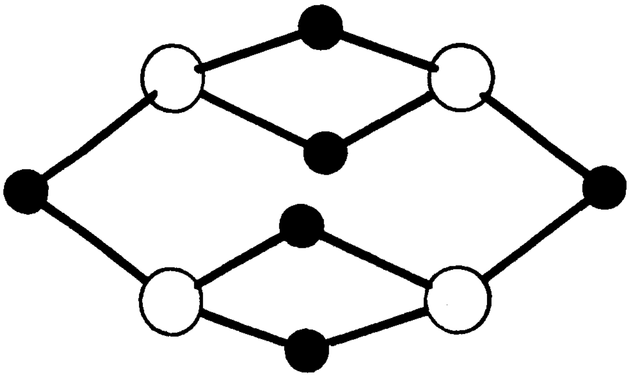

Figure 17. $\{[M(\mu_2\text{-}A)_2M](\mu_2\text{-}A)\}_2$ core of $[L_nM]_4(\mu_2\text{-}A)_6$.

Experimental Section

All calculations were of the extended Hückel type, using the programs of Hoffmann and co-workers.[35] The parameters for Ti,[36] Mo,[38] and Se[39] were taken from the literature. The M–C_5H_5(centroid) distance was taken as 2.034 Å, the C–C distances were 1.40 Å, and the C–H distances were 0.96 Å. The M–O and M–Se distances are given in the text.

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