periments with Fe(III) point to the importance (although not the essentiality[5b,c]) of ligand bridging. At the same time, our results underscore the extent to which Mo(IV) is stabilized in solution by trimerization. Each oxidation yields three Mo(VI)'s a net change of six units, yet in all cases, rates are governed by the initial 1e$^-$ and 2e$^-$ transaction. Ensuing redox acts and steps involving the breakup of partially oxidized Mo clusters proceed much more rapidly.

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Electronic Structure and Bonding in Trinuclear Molybdenum and Tungsten Cluster Compounds of M_3X_{13} Type

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This paper is concerned with some newly observed electronic properties of trinuclear cluster compounds belonging to the M_3X_{13} structural type and particularly with the way in which the preferred number of electrons in the compounds of this type is influenced by the identity of the ligand intimately associated with the metal cluster. The ground-state electronic structures of a number of trinuclear molybdenum and tungsten cluster compounds have been studied by employing SCF-Xα-SW molecular orbital calculations. The calculations have been performed for the molybdenum and tungsten systems with six, eight, and nine metal d electrons. The results have been shown to give consistent and satisfactory explanations for the electron populations and related properties of these compounds. The M-M bonding in these cluster compounds has been examined in detail by employing the results of the present calculations and compared with a long-established bonding scheme of less rigorous origin. Comparative studies have also been carried out on the followed trimolybdenum systems: $Mo_3(\mu_3\text{-}X)(\mu\text{-}Y)_3$ (X = O, Y = O, X = O, Y = Cl, X = S, Y = S). It has been found that the preferred oxidation levels in these systems are directly related to the significant differences in their electronic structures caused by different interactions between the metal atoms and the intimate ligand atoms.

Introduction

Discrete triangular M-M bonded cluster compounds of molybdenum and tungsten have received much attention in recent years in the study of bonds betwen transition-metal atoms.[1] Among several structurally distinct types of the compounds,[2-5] a particularly common and important structural type, often designated as M_3X_{13}, has been of continuing interest to us.[6-11] This structural type is characterized by a central M_3X_4 core about which there may be a considerable variety and arrangement of peripheral ligands. Within the M_3X_4 core, one of the four intimate ligands, X, is a triply bridging, or capping, atom above the plane of the equilateral triangle of the metal atoms and the three others are edge-bridging atoms below it. The capping and edge-bridging intimate ligands need not be the same, but in all cases the M_3X_4 unit retains C_{3v} symmetry. For the compound as a whole this symmetry may be lowered by the outer nine ligands. Electronically, the compounds within this type are usually further classified according to the number of electrons in the metal cluster that are primarily involved in metal-metal bonding.

There has been a continuing effort to formulate electronic descriptions of bonding in equilateral-triangular metal systems of various structural types.[12-14] The electronic structure of the molybdenum and tungsten compounds of the M_3X_{13} type has, thus far, been investigated only by use of the empirical Cotton-Haas MO method[12] and the Fenske-Hall method.[14] A simple but widely accepted formulation of the M-M bonding in the Mo and W systems is the one based on treatment of the Mo_3O_{13} unit by the Cotton-Haas method.[12] According to this scheme, the M_3X_{13} compounds should be stable when there are six metal d electrons available to enter the low-energy $1a_1$ and 1e metal cluster obitals, which correspond to three M-M σ-bonding orbitals. The compounds with seven or eight metal electrons might also be stable, since the additional electrons would occupy the next higher ($2a_1$) orbital, which is approximately M-M nonbonding. All higher MOs that are mainly localized in the M_3 cluster, namely, the 2e, 3e, and $1a_2$ orbitals, are M-M antibonding. Thus, the bonding scheme has given a satisfactory explanation for the existence of both six-electron systems, such as $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$,[6] and eight-electron systems, such as $[Mo_3OCl_3(O_2CCH_3)_3(H_2O)_3]^{2+}$.[7]

Recent work in our laboratory has revealed several important but previously unrecognized characteristics of this type of cluster compound. It has been found that while the systems with three μ-O or μ-S atoms appear to favor a six-electron population, the compounds with three μ-Cl atoms in place of the oxygen or sulfur atoms usually have eight metal d electrons[10] and, remarkably, they can even have nine electrons.[11] It has also been found that in spite of a close structural similarity between homologous molybdenum and tungsten species, their redox behavior can be very different.[10] These new discoveries apparently cannot be interpreted through the existing electronic descriptions of the structural type. Therefore, more detailed and more rigorous theoretical exploration of the electronic structures of this structural type was considered necessary. We have carried out molecular orbital calculations on a number of molybdenum and tungsten compounds of the M_3X_{13} type, employing the density functional SCF-Xα-SW method. We report here the results of calculations on some newly

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Table I. Upper Valence Molecular Orbitals for $[M_3OCl_6(O_2CH)_3]^-$ with M = Mo and W[a]

$[Mo_3OCl_6(O_2CH)_3]^-$												$[W_3OCl_6(O_2CH)_3]^-$											
		% charge							Mo angular contribn, %					% charge							W angular contribn, %		
level	*E*, eV	Mo	Cl_b	Cl_t	O_c	O	C	H	s	p	d	level	*E*, eV	W	Cl_b	Cl_t	O_c	O	C	H	s	p	d
21e	−6.845	78	6	5	10	0	0	1			100	21e	−5.915	78	6	4	10	1	1	0		1	99
$7a_2$	−7.064	87	7	4	0	2	0	0			100	$7a_2$	−5.979	87	8	3	0	2	0	0		1	99
20e	−8.337	85	4	3	0	7	1	0			100	20e	−7.549	88	3	2	0	6	1	0			100
$15a_1$	−9.088	78	12	3	0	5	2	0		1	99	$15a_1$	−8.647	79	12	1	1	5	2	0		1	99
19e	−9.360	29	2	66	0	2	0	0		1	99	19e	−9.158	35	2	60	0	3	0	0		2	98
$14a_1$	−9.383	26	2	71	0	1	0	0		4	95	$14a_1$	−9.272	24	2	73	0	0	0	0	1	7	92
18e	−9.735	3	7	86	1	2	0	0				18e	−9.648	2	6	89	1	1	0	0			
$6a_2$	−9.747	3	7	88	0	2	0	0				$6a_2$	−9.655	2	7	89	0	2	0	0			
$13a_1$	−10.277	17	1	78	4	0	0	0	3	24	74	$13a_1$	−10.329	22	1	74	3	0	0	0	1	24	75
17e	−10.566	39	7	43	0	10	0	0	1	3	96	17e	−10.457	45	4	37	1	13	0	0		1	99
16e	−10.612	23	1	47	3	25	0	1	7	6	87	16e	−10.752	15	3	62	3	16	0	0	16	20	64
$12a_1$	−10.980	10	24	5	0	48	4	8	9	22	69	$12a_1$	−11.226	13	28	8	1	40	3	6	11	18	71
15e	−11.328	8	57	8	0	20	2	4				$5a_2$	−11.441	0	14	0	0	86	0	0			
$5a_2$	−11.383	0	16	0	0	84	0	0				15e	−11.451	6	68	6	0	16	2	2			
$11a_1$	−11.387	55	8	23	6	5	2	1	1	1	97	$11a_1$	−11.520	45	10	22	9	10	2	2	2	3	95
14e	−11.565	5	26	2	0	65	1	1				14e	−11.728	6	20	1	0	71	1	1			
$4a_2$	−11.687	6	22	3	0	68	1	0				$4a_2$	−11.821	6	25	2	0	66	1	0			
13e	−12.038	13	46	6	0	27	3	5	1	17	83	13e	−12.200	12	41	6	0	32	3	6	1	25	74
12e	−12.226	25	6	5	0	64	0	0	1	3	97	12e	−12.334	23	6	5	0	65	1	0	1	5	95
$10a_1$	−12.819	19	65	0	1	10	3	2	1	5	94	$10a_1$	−12.911	18	65	0	1	10	3	2	1	9	90
11e	−12.831	17	64	2	1	13	1	2	13	4	83	11e	−13.045	16	60	2	3	14	2	3	18	7	75
$3a_2$	−13.040	24	42	2	0	31	1	0		1	99	$3a_2$	−13.089	21	44	2	0	32	1	0		1	99
$9a_1$	−13.224	16	68	0	3	8	2	3	54	13	33	10e	−13.571	15	32	1	2	41	8	1	4	6	90
10e	−13.450	21	42	1	0	30	5	1	3	5	93	$9a_1$	−13.991	22	59	0	0	10	3	5	56	9	35
9e	−13.941	11	12	1	8	55	13	0	4	5	91	9e	−14.016	15	25	1	5	44	9	0	10	7	93
$8a_1$	−14.243	7	4	0	3	69	16	0				$8a_1$	−14.311	7	5	0	3	69	15	0			

[a] The HOMO is the $15a_1$ orbital in both cases; % charge indicates relative amount of charges in the atomic spheres, and metal angular contribution is given only when >10%; Cl_b and Cl_t = bridging and terminal chlorine atoms; O_c = capping oxygen atom.

characterized Mo and W species with eight and nine electrons, as well as calculations on three six-electron Mo cluster compounds that differ from each other in the μ-X atoms, in order to see how changes in the intimate ligand in the central M_3X_4 core affect the relative stabilities of different oxidation levels of the metal atoms.

Computational Procedures

The SCF–Xα–SW method[15] was employed in the calculations of the ground-state electronic structures of representative M_3X_{13} type trinuclear cluster compounds of molybdenum with six, eight, and nine metal d electrons and of tungsten with eight electrons. The geometry of all compounds calculated was idealized to C_{3v} symmetry. Schwartz's α atomic exchange parameters[16] were used in all calculations. A valence electron weighted average of the atomic α values was used in each case for the intersphere and outer-sphere regions. Overlapping atomic sphere radii were taken as 89% of the atomic number radii calculated by the molecular superposition program.[17] The outer-sphere radius in each case was made tangential to the outermost atomic spheres. For compounds with negative charges a Watson sphere with the same positive charges and with the same radius as the outer sphere was used. Relativistic corrections[18] were included in the calculations for the tungsten compound.

The coordinates for the eight-electron systems, $[M_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(O_2CH)_3Cl_3]^-$ (M = Mo, W), were determined from the crystal structures of the newly characterized Mo and W species,[10] namely, $[M_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(O_2CCH_3)_3Cl_3]^-$. The bond lengths and angles of the actual compounds were averaged and used for the model ones. As for the nine-electron system, two Mo compounds, $[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(O_2CH)_3Cl_3]^{2-}$ and $[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(O_2CH)_3(PH_3)_3]^+$, were calculated. While the first one is directly related to the actual compound $[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(O_2CCH_3)_3Cl_3]^{2-}$,[11] the second compound was a model for two actually characterized species,[11] $Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(O_2CCH_3)_3Cl(PMe_3)_2$ and $[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(O_2CCH_3)_3Cl_2PMe_3]^-$.

The calculations on six-electron systems were carried out for three molybdenum compounds differing from each other by their edge-bridging atoms, namely $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(OH)_6(H_2O)_3]^{2-}$, $[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(OH)_6(H_2O)_3]^+$, and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PH_3)_3]^{2-}$. The compound edge-bridged by oxygen atoms was taken as a model for $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(C_2O_4)_3(H_2O)_3]^{2-}$,[6] and the atomic coordinates used in its calculations were obtained by using the averaged bond lengths and angles of the real compound. Since no actual example of a six-electron compound with μ-Cl atoms has been reported, the bond lengths and angles in it were assumed to be Mo–Mo = 2.65 Å, Mo–O(capping) = 2.00 Å, Mo–Cl = 2.42 Å, Mo–O = 2.09 Å, Mo–O_w(water) = 2.15 Å, Cl–Mo–Cl = 88°, O–Mo–O = 80°, O–Mo–O_w = 85°, and O_c–Mo–O_w = 168°. Finally, the bond distances and angles in the compound with μ-S were taken from the structural data of an actural six-electron system, $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dmpe)_3]^+$.[9]

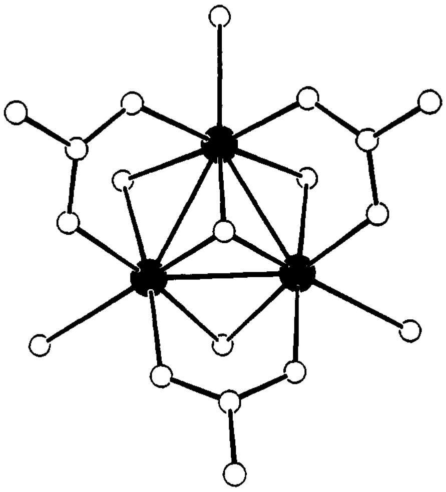

Figure 1. Molecular structure of the formular $Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(O_2CH)_3X_3$. Metal positions are indicated by filled circles.

Results and Discussion

Eight- and Nine-Electron Systems. The Mo and W cluster compounds with eight and nine metal d electrons that we will consider first all belong to a specific structural type, $M_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(O_2CH)_3X_3$ (X = Cl, PH_3), which is shown schematically in Figure 1. We shall first, and mainly, focus on the results for the calculations on the eight-electron systems, and a relatively brief presentation for the nine-electron systems will then follow. The results of the Xα-SW calculations on $[Mo_3OCl_6(O_2CH)_3]^-$ and $[W_3OCl_6(O_2CH)_3]^-$, both with eight metal d electrons, are

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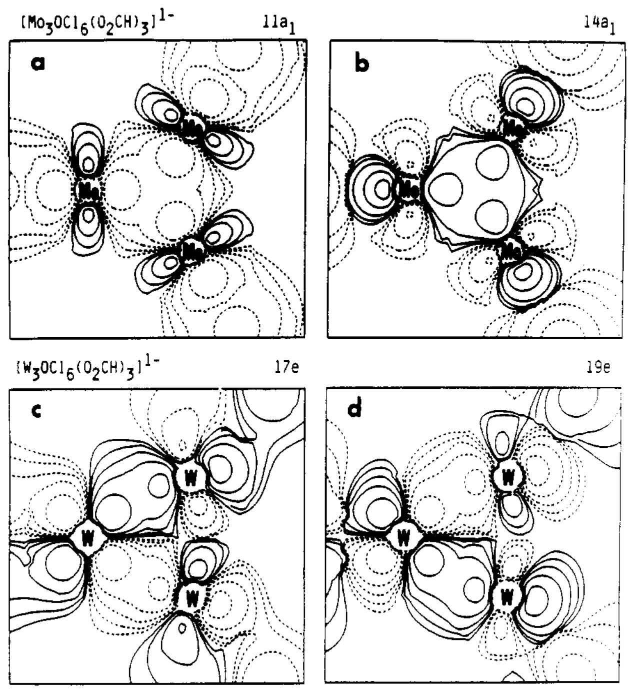

Figure 2. Contour plots of (a) the $11a_1$ orbital and (b) the $14a_1$ orbital in $[Mo_3OCl_3(O_2CH)_3]^-$ and (c) the 17e orbital and (d) the 19e orbital in $[W_3OCl_3(O_2CH)_3]^-$. Dashed lines indicate negative contour values. Contour values used in all plots are as follows: 0.005, 0.01, 0.02, 0.04, 0.08, and 0.16. All contours are plotted on the M_3 plane.

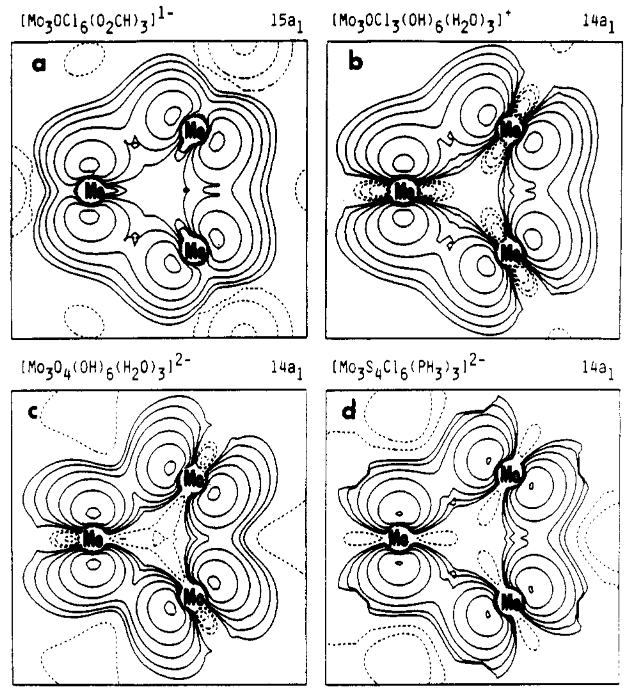

Figure 3. Contour plots of (a) the $15a_1$ orbital in $[Mo_3OCl_3(O_2CH)_3]^-$, (b) the $14a_1$ orbital in $[Mo_3OCl_3(OH)_6(H_2O)_3]^+$, (c) the $14a_1$ orbital in $[Mo_3O_4(OH)_6(H_2O)_3]^{2-}$, and (d) the $14a_1$ orbital in $[Mo_3S_4Cl_6(PH_3)_3]^{2-}$.

presented in Table I. Listed in the tables are the MO energies, the relative charge contributions of the atomic spheres, and the metal atom angular contributions for the upper valence molecular orbitals. The lower valence MOs that are not listed represent the 3s lone pairs on the chlorine atoms, the bonding between the metal atoms and the capping oxygen atom, and the bonding within the acetate ligands. For both compounds, the HOMO and LUMO are the $15a_1$ and 20e orbitals, respectively. As can be seen clearly, the ordering of the molecular orbitals on the left part of Table I for the Mo compound is very similar to that on the right for the W compound.

Let us start by considering the metal-metal bonding in the compounds. When we are looking at the molecular orbitals in Table I that are concerned with M-M interation, we may naturally compare them with the metal cluster orbitals given by the Cotton-Haas method.[12] For both the Mo and the W compounds the three virtual orbitals shown in Table I, namely, 20e, $7a_2$, and 21e, are all mainly derived from metal atomic orbitals and are all M-M antibonding in character. These orbitals correspond directly to the Cotton-Haas orbitals that are also M-M antibonding. According to the Cotton-Haas bonding scheme, there should be two MOs of a_1 and e symmetry, respectively, that are strongly M-M bonding and accommodate six metal electrons. This is in essence also the case in our present results, but the situation appears more complicated due to interactions of the metal orbitals with the lone pairs on the terminal chlorine atoms. Thus, for the a_1-type M-M bonding, both $11a_1$ and $14a_1$ orbitals (see Table I) in the two cluster compounds have the same M-M bonding character, but the former is also M-Cl(terminal) bonding and the latter M-Cl(terminal) antibonding. This is illustrated clearly by the contour plots of the two orbitals in the Mo cluster compound in parts a and b of Figure 2, respectively. The same situation applies to the M-M bonding orbitals of e symmetry, namely, the 17e and 19e orbitals in Table I, as shown by the contour plots of the orbitals in parts c and d of Figure 2 for the W cluster compound.

The HOMO or the $15a_1$ orbital in both compounds has a dominant contribution from the metal atoms, and the pair of electrons that occupy it can be correctly described as metal cluster electrons. This orbital should correspond to the $2a_1$ orbital in the Cotton-Haas scheme. However, in contrast to the nonbonding nature of the $2a_1$ orbital that was inferred from the simple empirical calculation on Mo_3O_{13}, the present calculations show that the $15a_1$ orbital contributes significantly to the M-M bonding in the $[M_3OCl_6(O_2CCH_3)_3]^-$ compounds. This is indicated clearly by the contour plot of the orbital in Figure 3a. It may be mentioned that the same situation has also been found in our previous study for trinuclear cluster compounds of niobium of the M_3X_{13} type.[13d] The strong M-M bonding character of the orbitals of this type in the Nb compounds gave a consistent and satisfactory explanation for the considerably shorter Nb-Nb bond distance in the eight-electron system than that in the six-electron system, both have a central Nb_3Cl_4 core.

The three occupied and M-M bonding a_1 orbitals show an interesting contrast in the types of electron density distribution they describe. The two ($11a_1$ and $14a_1$) that correspond to the Cotton-Haas $1a_1$ orbital both concentrate the bonding electron density within the M_3 triangle. In contrast the $15a_1$ orbital places the bonding electron density immediately outside of the edges of the triangle. We may choose a local coordinate system on each metal atom in such a way that the z axis points toward the center of the M_3 plane with the x axis in the plane and the y axis perpendicular to the plane. Thus, the M-M bonding in the $11a_1$ and $14a_1$ orbitals may be described as due to overlap of the d_{z^2} orbitals of the metal atoms. The M-M bonding type represented by the $15a_1$ orbital, on the other hand, may be shown mainly due to overlap of the $d_{x^2-y^2}$ orbitals.

The remaining molecular orbitals in Table I represent essentially the lone pairs of the ligands of various types and the bonding between the metal atoms and the ligands. It may be noted again that each of these MOs in the Mo cluster compound correlates very well in its character with the MO of the same label in the W cluster compound. The resemblance of the overall molecular bonding features in $[Mo_3OCl_6(O_2CH)_3]^-$ with those in $[W_3OCl_6(O_2CH)_3]^-$ is consistent with the great similarity in the structural features of the Mo and W compounds.[10]

Detailed analysis of the results also reveals certain differences between the electronic structures of the Mo and W compounds, and these differences account well for the fact that some observed characteristics of the compounds are not identical for both $[Mo_3OCl_6(O_2CCH_3)_3]^-$ and $[W_3OCl_6(O_2CCH_3)_3]^-$. It may be seen from Table I that, although the HOMOs and LUMOs in both compounds have almost identical bonding character, the HOMO-LUMO energy gap in the Mo compound is 0.35 eV smaller than the gap in the W compound, indicating that addition of an electron to the LUMO would be energetically easier for the Mo compound. This is consistent with the observations on their electrochemistry,[10] where it was found that, while both compounds could be reduced, the reduction of the W compound is more difficult. The most significant different between the two compounds, however, is their oxidation behavior. As shown by their cyclic voltammetry,[10] while both reversible reduction and oxidation were observed in the W case, only reversible reduction was found in the case of Mo compound. In order to have a explanation for this behavior from an electronic structure point of view, we have calculated ionization potentials of the $15a_1$ orbitals (the HOMOs) in both compounds by using the spin-restricted Slater transition-state method.[15] The results of the calculations predict that the first ionization of the Mo compound would occur at 0.4 eV higher energy than the first ionization of the W compound. Evidently this leads to a greater disruption of the structure and hence to irreversibility.

Let us now turn to the nine-electron systems. The calculated molecular orbitals for the nine-electron Mo compound, $[Mo_3OCl_6(O_2CH)_3]^{2-}$, have features very similar to those shown in Table I for the $[Mo_3OCl_6(O_2CH)_3]^-$ compound with eight electrons. The results for another nine-electron system, $[Mo_3OCl_3(O_2CH)_3(PH_3)_3]^+$, also show an overall similarity, except for some changes that are apparently due to replacement of Cl atoms in the terminal positions by PH_3 groups. Thus, the only characteristic difference in their electronic structures is that the LUMO (the 20e orbital) in the eight-electron system has been occupied by a single electron and become the HOMO in the nine-electron systems. Thus, the nine-electron system, $[Mo_3OCl_6(O_2CH)_3]^{2-}$, is obtained from the eight-electron system, $[Mo_3OCl_6(O_2CH)_3]^-$, by adding an electron to the M–M antibonding 20e orbital, without any other significant electronic change. The M–M bond order in the nine-electron systems is decreased, but by only $^1/_6$ as compared to the eight-electron system. At the same time, the reduction of the mean oxidation state of the Mo atoms from +3.33 to +3.0 should be accompanied by a decrease in the Coulombic repulsion between the metal atoms for the nine-electron system. As a result, one would not expect any significant lengthening of the M–M bonds in the nine-electron system. This is consistent with the very small increase observed in the average Mo–Mo distances, namely, from 2.580 Å in $[Mo_3OCl_6(O_2CCH_3)_3]^-$ [10] to 2.604 Å in $[Mo_3OCl_6(O_2CCH_3)_3]^{2-}$.[11] It may also be noted from Table I that, for the eight-electron Mo compound, the HOMO($15a_1$)–LUMO(20e) gap (0.75 eV) is considerably smaller than the energy gap between the LUMO and the next higher $7a_2$ orbital (1.27 eV). Correspondingly, in the nine-electron $[Mo_3OCl_6(O_2CH)_3]^{2-}$ compound, the calculated energy gap between the $15a_1$ and 20e orbitals is 0.82 eV, and the HOMO(20e)–LUMO($7a_2$) gap is 1.29 eV. Therefore, the stability of the nine-electron systems of the same structural type as the eight-electron systems is credible. Our results even suggest that the existence of stable ten-electron systems of this type might not be impossible.

It should be mentioned that in our calculations we have imposed C_{3v} symmetry on the nine-electron systems, which resulted in the electronically degenerate ground states of the systems due to the partial occupation of the 20e orbital. As a result of this, one would naturally expect Jahn–Teller distortion to be observed in the actual structures of the systems. However, as indicated by the crystal structure data for $[Mo_3OCl_6(O_2CCH_3)_3]^{2-}$,[11] the maximum difference in any given type of bond lengths is no more than 0.021 Å, and there is no correlation betwen the differences for different types of bonds. It is difficult to know whether to attribute such small differences to the Jahn–Teller effect or to the packing in the crystal. Therefore, the distortions, if any, are almost completely negligible, which is consistent with the electronic structure of the system in that there is only one electron delocalized over three M–M bonds and operating to induce the Jahn–Teller effect. The structural features of the compound also militate against a large distortion. In addition to the direct M–M bond between them, each pair of Mo atoms is also rigidly bridged by an acetate ligand and a chlorine atom. We might thus expect that the force constant could be very large for any nontotally symmetric vibration within the metal triangle, so that the net energy gained by the system from the Jahn–Teller distortion would be almost negligible in such a case.

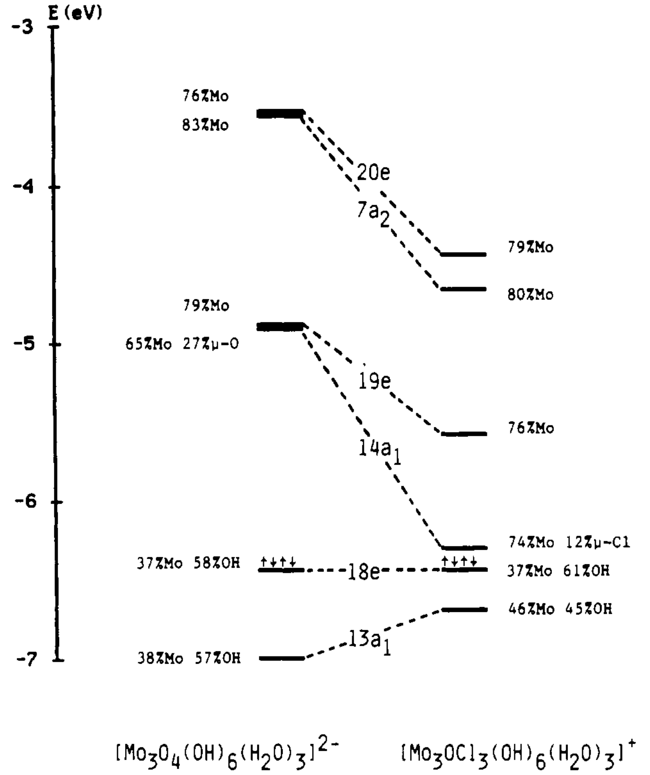

Figure 4. Molecular orbital diagrams for $[Mo_3O_4(OH)_6(H_2O)_3]^{2-}$ and $[Mo_3OCl_3(OH)_6(H_2O)_3]^+$.

Effects of Edge-Bridging Ligands. As a result of the observation that the oxidation levels of the metal atoms are strongly affected by the μ-X atoms in the Mo cluster compounds of the M_3X_{13} type,[10] we have investigated the electronic structures of three such compounds all having six metal electrons but differing in their central Mo_3X_4 cores by the μ-X atoms. Our Xα-SW calculations on $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(OH)_6(H_2O)_3]^{2-}$, $[Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3(OH)_6(H_2O)_3]^+$, and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PH_3)_3]^{2-}$ show that the overall bonding in these six-electron systems is similar to that in the eight- and nine-electron systems discussed above. Therefore, we present the results briefly in Figure 4, where we show the two highest occupied MO levels and the four lowest unoccupied levels but only for the two compounds with μ-O and μ-Cl atoms, respectively, for simplicity and clarity. In Figure 4, the MO levels of the compound with the Mo_3OCl_3 core have been moved upward so that its 18e level matches the same level of the compound with the Mo_3O_4 core. For the cases of Mo_3O_4 and Mo_3OCl_3, the Mo–Mo bonding represented by the lower energy Cotton–Haas a_1 orbital is distributed again over two MOs, the $13a_1$ orbital in Figure 4 and another a_1 orbital not shown, due to the interaction of the metal orbital with the terminal oxygen lone pairs. The e-type Mo–Mo bonding in these two compounds is also distributed over two orbitals. As a matter of fact, the $13a_1$ and 18e orbitals in Figure 4 correlate directly with the $14a_1$ and 19e orbitals, respectively, in Table I for the eight-electron compounds and have bonding features very similar to those shown in Figure 2b,d. Except for the $14a_1$ orbitals, which are the LUMOs for the six-electron systems, the remaining unoccupied MOs in Figure 4 correspond directly with the virtual MOs in Table I. We particularly note that the listed MOs in Figure 4 for $[Mo_3OCl_3(OH)_6(H_2O)_3]^+$ have a close resemblance to the six highest MOs in Table I for $[Mo_3OCl_6(O_2CH)_3]^-$ both in their relative energy spacing and their characteristics. As for $[Mo_3S_4Cl_6(PH_3)_3]^{2-}$, the overall M–M bonding is similar to that in the other six-electron systems, although some occupied MOs have different characters due to changes of the ligands surrounding the M_3X_4 core. For example, the LUMO (also $14a_1$) and the MOs higher in the Mo_3S_4 case correlate well with the virtual MOs in Figure 4, but the HOMO now is the $13a_1$ orbital, which is mainly Mo–P bonding.

A significant difference in the electronic structures of the six-electron compounds with different μ-X atoms can be seen immediately from Figure 4. Compared to case in the compound with the μ-Cl atoms, very large HOMO–LUMO energy gaps, 1.53 and 1.22 eV, have been predicted for the two six-electron compounds with μ-O and μ-S atoms, respectively. The large HOMO–LUMO gap is apparently caused by the very strong interaction between the metal atoms and the μ-O or μ-S atoms, which raises the energy of the LUMOs in the compounds due to their Mo–(μ-X) antibonding character. As shown by our calculations, the $14a_1$ orbitals (the LUMOs) in $[Mo_3O_4(OH)_6(H_2O)_3]^{2-}$ and $[Mo_3S_4Cl_6(PH_3)_3]^{2-}$ have considerably larger contributions from the μ-O atms (27%) and the μ-S atoms (34%), respectively, than those provided by the μ-Cl atoms (12%) to the corresponding orbital in $[Mo_3OCl_3(OH)_6(H_2O)_3]^+$. The contour plots of the orbitals (Figure 3c,d) further indicate that the character of the $14a_1$ orbitals is dominated by the Mo–(μ-X) (X = O, S) antibonding rather than the M–M bonding role. On the contrary, the same type of antibonding effect between the Mo and μ-Cl atoms is obviously much less prominent in the $14a_1$ orbital of the compound that has a Mo_3OCl_3 core. Here the orbital is still predominantly M–M bonding. This is made very clear by comparing the contour plot of the orbital in Figure 3b for $[Mo_3OCl_3(OH)_6(H_2O)_3]^+$ with those in parts c and d of Figure 3 for $[Mo_3O_4(OH)_6(H_2O)_3]^{2-}$ and $[Mo_3S_4Cl_6(PH_3)_3]^{2-}$, respectively. These figures may also be compared with the contour plot of the $15a_1$ orbital in Figure 3a for the eight-electron system. It is clear then that the large HOMO–LUMO energy gap and the weakened M–M bonding character in the LUMO are factors that strongly disfavor an eight-electron population for the M_3O_4 or M_4S_4 core. Conversely, the observed eight- or nine-electron populations in the systems with the M_3OCl_3 core is favored by their electronic structures, which are characteristically different from those of the systems with the M_3O_4 or M_3S_4 core.

The results in Figure 4 also show that for $[Mo_3O_4(OH)_6(H_2O)_3]^{2-}$ the LUMO is not only Mo–(μ-O) antibonding and weakly Mo–Mo bonding in character but also almost degenerate with the Mo–Mo antibonding 19e orbital in energy. This may imply that if a compound of similar type but containing seven or eight metal d electrons were to be obtained, the Mo–Mo bond distance would be essentially unchanged or could be even longer than in the case of the six-electron system. This has been found to be true in Mo_3O_{13} in solid state.[19] It may be noted that the Mo–Mo bond distance is shorter in the six-electron system with the Mo_3O_4 core (2.49 Å) than in the eight-electron system with the Mo_3OCl_3 core (2.58 Å). As we have seen, the M–M bonding effects should be obviously stronger in the eight-electron system, since the two more electrons both go to the MO that is M–M bonding. In addition, the less positive charges on the metal in the eight-electron system should also favor a shorter M–M distance. Therefore, the observed longer Mo–Mo distance in $[Mo_3OCl_6(O_2CCH_3)_3]^-$ must be mainly attributed to the larger size of the μ-Cl atom in the Mo_3OCl_3 core. The acetate ligand that bridges a pair of Mo atoms in the eight-electron system could be another steric factor favoring the longer Mo–Mo distance. The structural data for a newly characterized trinuclear cluster compound of tungsten[20] show that the distance between the pair of W atoms bridged by two acetate ligands is 0.15 Å longer than that between a pair of W atoms bridged by one acetate ligand and one chlorine atom.

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Synthesis and Characterization of Edge-Sharing Bioctahedral Complexes of Zirconium(III) and Hafnium(III) That Contain Long Metal–Metal Single Bonds: $Zr_2I_6(PMe_3)_4$, $Hf_2I_6(PMe_2Ph)_4$, and $Zr_2I_6(PMe_2Ph)_4$

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The reduction of MI_4 (M = Zr, Hf) with 1 equiv of Na/Hg amalgam, followed by addition of 2 equiv of phosphine, produces in moderate yields the edge-sharing bioctahedral complexes $Zr_2I_6(PMe_3)_4$ (**1**), $Hf_2I_6(PMe_2Ph)_4$ (**2**), and $Zr_2I_6(PMe_2Ph)_4$ (**3**). Each compound was characterized by single-crystal X-ray diffraction studies. $Zr_2I_6(PMe_3)_4$ (**1**) crystallizes from *p*-xylene in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 9.752$ (2) Å, $b = 14.909$ (2) Å, $c = 11.420$ (2) Å, $\beta = 96.32$ (2)°, $V = 1650.3$ (6) Å^3, and $d_{calc} = 2.501$ g/cm^3 for $Z = 2$. The structure was refined to $R = 0.040$ and $R_w = 0.050$ for 1512 reflections having $I > 3\sigma(I)$. $Hf_2I_6(PMe_2Ph)_4$ (**2**) crystallizes from toluene in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 11.083$ (2) Å, $b = 11.455$ (2) Å, $c = 10.081$ (2) Å, $\alpha = 106.12$ (1)°, $\beta = 112.17$ (1)°, $\gamma = 84.70$ (1)°, $V = 1138.4$ (3) Å^3, and $d_{calc} = 2.438$ g/cm^3 for $Z = 1$. The structure was refined to $R = 0.037$ and $R_w = 0.051$ for 2855 reflections having $I > 3\sigma(I)$. $Zr_2I_6(PMe_2Ph)_4$ (**3**) is isomorphous to **2** with unit cell dimensions $a = 11.132$ (2) Å, $b = 11.503$ (2) Å, $c = 10.118$ (2) Å, $\alpha = 106.17$ (1)°, $\beta = 112.21$ (1)°, $\gamma = 84.86$ (1)°, $V = 1151.9$ (3) Å^3, and $d_{calc} = 2.157$ g/cm^3 for $Z = 1$. The structure was refined to $R = 0.024$ and $R_w = 0.039$ for 2794 reflections having $I > 3\sigma(I)$. Each of the three complexes has a metal–metal distance of ~3.4 Å. Molecular orbital calculations on the model complex $Zr_2I_6(PH_3)_4$, at the Fenske–Hall level, were conducted to evaluate the bonding between the metal centers. The calculations indicate that the HOMO is metal–metal bonding and mainly composed of metal d_{z^2} and $d_{x^2-y^2}$ σ-type orbitals.

Introduction

Although the first examples of edge-sharing bioctahedral complexes of zirconium(III) were reported as early as 1981,[1] it is only within the past few years that further examples of these species,[2] as well as hafnium(III) analogues,[3,4] have been described. These new compounds constitute a significant addition to the

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