

Electronic structures of $[M_3(\mu_3-X)(\mu_2-S_2)_3]^{4+}$ ($M=Mo, Ti$) cluster compounds and the effects of the μ_3-X cap to the self-assembly in cluster synthesis

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Abstract

The electronic structures and bonding in one class of trinuclear transition-metal cluster compounds having the cores $[Ti_3(\mu_3-O)(\mu_2-S_2)_3]^{4+}$ (**1**), $[Mo_3(\mu_3-S_2)_3]^{4+}$ (**2**) and $[Mo_3S_4]^{4+}$ (**3**) are discussed in terms of the results of molecular orbital (MO) calculations using the CNDO/2-LMO method. There are certain strong bonding interactions between the metal atoms in clusters **2** and **3**, but no significant metal-metal bonding is found in cluster **1**. The existence of one four-centred bond consisting of three skeletal Mo atoms and the μ_3 cap in cluster **2** is of particular importance for shedding light on the nature of the self-assembly syntheses. From the analysis of the localized MO (LMO) we conclude that the μ_3-O cap and the μ_3-S cap have an important effect on the self-assembly of the trinuclear clusters.

INTRODUCTION

The members of one class of trinuclear molybdenum cluster compounds possessing the $[Mo_3S_4]^{4+}$ (**3**) core have been synthesized and structurally characterized by X-ray crystallography. It is indicated that this kind of cluster has the characteristic of forming a so-called "loose" coordination structure [1]. In the light of the structure, reactivity and the molecular orbital (MO) theory calculation [2], it is believed that the $[Mo_3S_3]$ cluster ring in the $[Mo_3S_4]^{4+}$ cluster fragment has quasi-aromatic stability. Recently, members of another class of trinuclear titanium and molybdenum cluster compounds containing μ_3-O and μ_3-S , i.e. $[Ti_3(\mu_3-O)(\mu_2-S_2)_3]^{4+}$ (**1**) and $[Mo_3(\mu_3-S)(\mu_2-S_2)_3]^{4+}$ (**2**), have been synthesized. However, the geometrical structures and the reactivity of these cluster molecules show that they have no quasi-aromatic stability and that there is no direct Ti-Ti bonding in cluster fragment **1**. The geometrical structures of **1** and **2** are akin to each other owing to the

similar cluster skeleton $[M_3(\mu_3-X)(\mu_2-X_2)_3]$. It is of importance to inspect the role played by μ_3-X ($X=O$ or S) on the stability of these clusters and on the bonding pattern of such cluster fragments.

In a comprehensive review of the chemical bonding in several structural types of trinuclear molybdenum cluster, Bursten et al. [3] calculated the electronic structure of the $[Mo_3(\mu_3-O)(\mu_2-O)_3]^{4+}$ fragment and compared the different contributions of the capping oxygen and the bridging oxygen to the structural stability of the cluster skeleton. The conjugation effect between the three bridging sulphur atoms and the three molybdenum atoms in $[Mo_3(\mu-S)(\mu_2-S)_3]^{4+}$ clusters has been discussed previously [2]. In order to elucidate the electronic structures of clusters 1 and 2 and in order to find the differences and connections between the electronic factors of clusters 1-3 we studied the electronic structures of the corresponding cluster fragments using a semiempirical approach of MO theory, paying particular attention to the effects of μ_3-X on the stability of the cluster skeleton. The calculated results show that the μ_3-O and μ_3-S atoms play the main role in the self-assembly of cluster synthesis, which is essential to the formation of these kinds of cluster.

CALCULATION

The geometrical models of the clusters 1-3 and one $TiSCl_4$ complex (4) are shown in Fig. 1.

The model molecules were assumed to possess ideal D_{3h} symmetry (1), C_{3v} symmetry (2 and 3) and C_{4v} symmetry (4). The geometrical parameters of

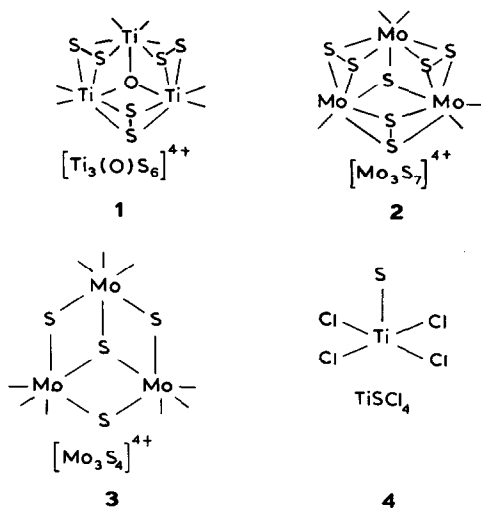


Fig. 1. Structures of model molecules 1-4.

TABLE 1

CNDO/2 parameters for titanium and molybdenum

Atom	Orbital	Orbital exponent	$(I_f + A_f)/2^a$ (eV)	$\beta_f^0 X^b$ (eV)
Ti	4s	1.075	3.77	-7.0
	4p	0.675	0.690	-7.0
	3d	2.283	4.140	-18.0
Mo	5s	1.71	3.250	-6.0
	5p	0.41	0.830	-4.0
	4d	2.05	2.580	-6.5

^a I_f , ionization energy; A_f , electron affinity for f atomic orbitals.^b $\beta_f^0 X$, bonding parameters of the f atomic orbitals of the metal atoms.

the four structural models were taken from refs. 3-5 and 7. The electronic structures of all the model molecules were calculated using the semiempirical MO method. The canonical MOs were obtained from a CNDO/2 method of unrestricted spin and were subsequently transformed to localized MOs by means of a unitary transformation defined by the energy-localization scheme of Edmiston and Ruedenberg. The basis functions of the ns , np , $(n-1)d$ and the ns , np valence orbitals were adopted for metal and non-metal atoms, respectively. The exponents, the electronegativities and the bonding parameters of the atomic orbitals (AOs) for the metal atoms are listed in Table 1, and the CNDO/2 parameters for the other non-metal atoms were taken from ref. 8.

RESULTS AND DISCUSSION

Localized molecular orbitals (LMOs) for 1-4

Based on the CNDO/2-LMO calculations for the four model molecules under consideration, the orbital energies, atomic orbital contributions and bonding character of the α -spin occupied LMOs for the model molecules 1, 2 and 4 are listed in Table 2. The results for model molecule 3 have been reported in ref. 2.

It can be seen from Table 2 that only one $\sigma(\text{Ti-S})$ single bond instead of a double Ti-S bond was found for TiSCl_4 and that the Ti-S bonding is stronger than the Ti-Cl bonding, causing the facile reaction of TiSCl_4 to $[\text{Ti}_3\text{O}(\text{S}_2)_3\text{Cl}_6]^{2-}$ by a self-assembly procedure in the presence of air.

Owing to the fundamental similarity of the geometrical structures of clusters 1 and 2, the energy level sequence for the two clusters (as listed in Table 2) is essentially the same, i.e. there are very comparable bonding types in both clusters. Especially noteworthy is the distinction between the π -bonding patterns

TABLE 2

The α -spin occupied LMOs for molecules 1, 2 and 4^a

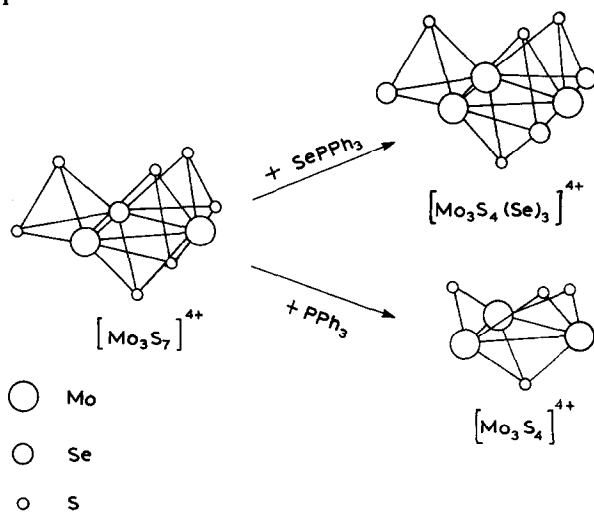
Model molecule	Orbital order	E_i (a.u.)	Composition of LMO (%)	Bonding character
TiSCl ₄	6	-0.766	Ti (14.3) + S (85.5)	$\sigma(\text{Ti-S})$ (X)
	7-10	-0.648	Ti (13.2) + Cl (86.3)	$\sigma(\text{Ti-Cl})$ (4X)
[Ti ₃ OS ₆ Cl ₆] ²⁻	1-3	-0.712	S _{b1} (46) + S _{b2} (49)	$\sigma(\text{S}_{b1}\text{-S}_{b2})$ (3X)
	13	-0.626	O (92)	1 (O) (X)
	17-19	-0.560	Ti (11.5) + O (83.6)	$\sigma(\text{Ti-O})$ (3X)
	20-22	-0.440	Ti (14) + Cl (83.6)	$\sigma(\text{Ti-Cl})$ (3X)
	23-25	-0.428	Ti (11.2) + Cl (87.9)	$\sigma(\text{Ti-Cl})$ (3X)
	29-34	-0.362	Ti (9) + S _b (87.9)	$\sigma(\text{Ti-S}_b)$ (6X)
	35-40	-0.350	Ti (8.7) + S _b (89)	$\sigma(\text{Ti-S}_b)$ (6X)
[Mo ₃ S ₇ Cl ₆] ²⁻	1-3	-0.854	S _{b1} (44.4) + S _{b2} (51.2)	$\sigma(\text{S}_{b1}\text{-S}_{b2})$ (3X)
	13	-0.810	S _c (95.4)	H (S _c) (X)
				Mo Mo
	17-19	-0.640	Mo ₁ (13.1) + Mo ₂ (13.1) + Mo ₃ (13.1) + S _c (61)	σ_m ($\begin{array}{c} \diagup \\ \text{S} \\ \diagdown \end{array}$) (3X)
				 Mo
	20-25	-0.573	Mo (24.8) + S _{b2} (72.4)	$\sigma(\text{Mo-S}_{b1})$ (6X)
	26-31	-0.525	Mo (18) - S _{b2} (78)	$\sigma(\text{Mo-S}_{b2})$ (6X)
	32-34	-0.520	Mo (30.7) + Cl (73.1)	$\sigma(\text{Mo-Cl})$ (3X)
	35-37	-0.516	Mo (24.1) + Cl (73.1)	$\sigma(\text{Mo-Cl})$ (3X)
	50-52	-0.210	Mo ₁ (33.7) + Mo ₂ (32.7) + Mo ₃ (32.5)	M(M-M) (3X)

^a σ , 1 and M denote the σ -bond, lone-pair electron and metal-metal bond respectively; σ_m indicates a multicentre bond. S_{b1} and S_{b2} denote the bridging S atoms which lie above and below the plane containing the three Mo atoms respectively; S_c denotes μ_3 -S; X denotes bonding character. The lone pair orbitals of the S_b bridging and Cl atoms are not included in this table.

of 1 and 2 and that of 3. The large conjugated π -bonding system, as characterized by the three-centred two-electron π -bond of three Mo-S_b-Mo in the ring of cluster 3, could not exist in 1 and 2; in 2 all nine d orbitals of one molybdenum atom are utilized to form σ -bonds with the ligands, and the bridging sulphur atoms adopt sp³ hybridization in both the clusters. We found that three of the four hybridization orbitals are used in constructing the M-S_b and S_b-S_b bonds, whereas the remaining one is occupied by the lone-pair electrons.

However, some remarkable differences can be seen from the data in Table 2. First, in cluster 2 there are three Mo-Mo bonds lying in the zone of the highest occupied orbitals, which is consistent with the typical analysis of the chemical bonding for transition-metal cluster compounds. Conversely, there are no Ti-Ti bonds in cluster 1 owing to the lack of a d electron for forming a

1



Scheme 1.

metal-metal bond with the Ti atom and this is probably the reason why the Ti-Ti bond (3.140 Å) in **1** is longer than the Mo-Mo bond (2.755 Å) in **2**. Secondly, in cluster **1** the three sp^3 hybridized orbitals of the $\mu\text{-O}$ cap form three Ti-O bonds with the atomic orbitals of three Ti atoms, while in cluster **2** the $\mu_3\text{-S}$ cap atomic orbitals form three four-centred two-electron bonds of $\text{Mo}(1) + \text{Mo}(2) + \text{Mo}(3) + \text{S}_c(\mu_3)$ with the skeletal Mo atoms. Furthermore, the energy levels and the strength of the 12 Ti-S_b bonds are quite close to each other in **1** but those of the 12 Mo-S_b bonds in **2** are so different that they can be roughly divided into two groups, in line with the conclusion drawn in ref. 7 that in these kinds of the thiohalide molybdenum cluster compound the sulphur atoms of the μ_2 ligands are structurally non-equivalent. It is for this reason that the non-equivalent sulphur atoms belonging to two different groups possess distinct characteristics with respect to chemical reactions (see Scheme 1). This reaction shows that the cluster fragment $[\text{Mo}_3\text{S}_4]$, where the sulphur atom is situated in the upper position relative to the Mo_3 plane, is rather stable to many chemical reactions. This stability originates not only from the stabilization of electron delocalization due to the formation of a large conjugated π -bond [2], but also, in our point of view, from the role played by the $\mu_3\text{-S}$ cap.

The effect of the $\mu_3\text{-O}$ and $\mu_3\text{-S}$ atoms on the self-assembly in cluster synthesis of 1-3

The $\mu_3\text{-O}$ and $\mu_3\text{-S}$ atoms, denoted O_c and S_c for brevity, occupy a position above the centre of the triangular plane composed of the three metal atoms.

The atomic orbitals of S_c and O_c are all sp^3 hybridized. However, according to Cotton's bonding picture of atomic clusters, the metal atoms combine with the ligands in d^2sp^3 hybrids, and the three hybridized orbitals of O_c or S_c then bond to the d^2sp^3 hybrid orbitals provided by each of the three metal atoms. The bonding patterns are depicted as follows.

It can be seen from Table 3 that the Mulliken bond order of $Mo-S_b$ is greater than that of $Mo-S_c$ in $[Mo_3S_4]$, which is in agreement with the conclusion reached by investigating the $[Mo_3O_4]$ fragment [8]. However, in **2**, because of the four-centred bond of the three Mo atoms and the S_c atom, the Mulliken bond order of the $Mo-S_b$ bond is much smaller than that of the $Mo-S_c$ bond, thus giving rise to the two reactions shown in Scheme 1.

In summary, we conclude that there is a stable structural fragment $[Mo_3S_4]$ in **2**, which results from the cooperative effect of both the adjoining interaction of the σ bonding of the μ_3-S cap and the conjugation effect of the σ bonding S_b bridge and the skeletal Mo atoms. In addition, as pointed out in ref. 4, the $[Ti_3O(S_2)_3Cl_6]^{2-}$ cluster may be generated from the TiS_4 compound by a

TABLE 3

Mulliken bond order of the $M-X_c$ ($X=O$ or S) and $M-S_b$ in $[Ti_3O(S_2)_3]^{4+}$, $[Mo_3S(S_2)_3]^{4+}$ and $[Mo_3S_4]^{4+}$

Skeleton molecule	Metal (orbital)–ligand (orbital)	Mulliken bond order	
		X_c ($X=O$ or S)	$X=S_b$
$[Ti_3O(S_2)_3]^{4+}$	Ti(s)–X(s)	0.0419	
	Ti(p)–X(s)	0.0409	0.0614
	Ti(d)–X(s)	0.0283	0.1376
	Ti(s)–X(p)	0.0032	0.0082
	Ti(p)–X(p)	0.0146	0.0416
	Ti(d)–X(p)	0.1119	0.0539
$[Mo_3S(S_2)_3]^{4+}$	Mo(s)–X(s)	0.0560	0.0405
	Mo(p)–X(s)	0.0045	0.0014
	Mo(d)–X(s)	0.0346	0.0014
	Mo(s)–X(p)	0.0711	0.0259
	Mo(p)–X(p)	0.0183	0.0635
	Mo(d)–X(p)	0.1987	0.0002 0.1450
$[Mo_3S_4]^{4+}$	Mo(s)–X(s)	0.0672	0.0816
	Mo(p)–X(s)	0.0061	0.0062
	Mo(d)–X(s)	0.0391	0.0434
	Mo(s)–X(p)	0.0894	0.1046
	Mo(p)–X(p)	0.0038	0.0040
	Mo(d)–X(p)	0.2361	0.3295

procedure of self-assembly during the clusters synthesis. No metal-metal bond is formed in the titanium cluster as titanium has fewer valence electrons than does molybdenum.

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