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## DFT Analysis of Electronic and Bonding Properties in Face-Bridged inorganic Octahedral Clusters $M_6L_{14}$ .

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### ABSTRACT

Several theoretical studies shown that in face-bridged octahedral transition metal clusters  $M_6L_{14}$  (M = transition metal; L =  $\pi$ -Donor Ligand) the optimal metallic electron (ME) count is of 24 but for many clusters experimentally synthesized, the ME count can vary from 20 to 24 for early transition metals such as molybdenum, tungsten and rhenium, and from 24 to 48 for late transition metals such as cobalt and palladium without altering the architecture of the octahedral cluster core. Density Functional Theory (DFT) calculations were carried out on the species with 20 to 24 metallic electron count in order to rationalize their electronic structure and to explain the conservation of octahedral metallic core for all electron counts.

**Keywords:** Transition metal, Cluster Compounds, Density Functional Theory (DFT), Electronic Structure, Frontier orbitals.

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## INTRODUCTION

A wide variety of compounds based on octahedral transition metal clusters have been obtained by solid-state synthesis and extensively investigated because of their remarkable and various physico-chemical properties [1-3]. Systematic efforts aimed at understanding the electronic structure and bonding of these compounds have been performed by developing topological electron counting theories [2, 4]. The Metallic octahedral compounds dominate the solid-state cluster chemistry of early transition metals with general formula  $M_6L_8^iL_6^a$ , where octahedral  $M_6$  cluster core is face-capped by eight inner ligands ( $L^i$ ) and additionally bonded to six apical ones ( $L^a$ ) (a = apical, i = inner according to the Schäfer and Schnering notation [5]) (see Figure1).

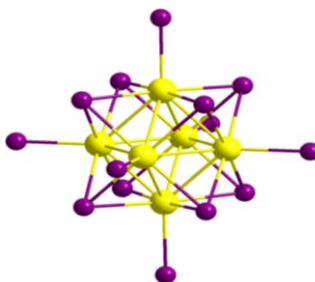


Figure1. Structural arrangement of  $[M_6L_8L_6^a]$  clusters.

Several theoretical studies of chemical bonding in these clusters indicates that metallic electrons occupy a set of 12 frontier orbitals, spanning  $a_{1g}$ ,  $t_{1u}$ ,  $t_{2g}$ ,  $t_{2u}$  and  $e_g$  in the ideal  $O_h$  symmetry. For clusters with halide ligands, the full occupation of these orbitals satisfy the closed shell requirement and leads to an optimal electron count equal to 24; whereas the ME count can vary from 20 to 24 for early transition metals such as molybdenum, tungsten and rhenium, owing to the topological properties of the frontier orbitals and to the metal and ligands nature (see Table 1 for a partial list) [6-16].

In this contribution, our aim is to analyse, using DFT calculations, the electronic structure of molybdenum and tungsten face-bridged octahedral clusters with  $\pi$ -donor ligands with 20 to 24 ME count, in order to explain the relationships that exist between the number of electrons available for metal-metal bonding and the structural arrangement of these cluster compounds.

## COMPUTATIONAL DETAILS

Density Functional Calculations were carried out on  $M_6L_{14}$  clusters, using the Amsterdam Density Functional (ADF) [17] program package developed by Baerends and Co-workers [18]. Becke exchange [19] and Perdew Correlation [20] non local gradient corrections were included in the local density approximation (LDA) [21]. Relativistic corrections in scalar zero order regular approximation (ZORA) [22] were incorporated. The numerical integration procedure applied for the calculations was developed by te Velde et al. [23]. The geometry optimisation procedure was based on the method developed by Versluis and Ziegler [24] and was followed by analytical vibrational frequencies calculations [25, 26]. The valence atomic

orbitals of transition metal and halide ligands were described by triple- $\xi$  Slater type orbitals (STO) [27] basis set augmented with a set of single- $\xi$  polarisation. A frozen core approximation was used to treat the core electrons [28].

## RESULTS AND DISCUSSION

### Qualitative approach

The structure of an octahedral cluster  $[M_6L_8L_6^a]$  can be described as consisting of six  $ML_5$  fragments because the local coordination around each metal atom in this cluster is square pyramidal. A qualitative study of a complex  $ML_5$  pseudo-octahedral enables us therefore to easily analyze the electronic structure of this type of octahedral clusters.

A fragment  $ML_5$  of symmetry  $C_{4v}$  can be obtained directly by metal-ligand interactions or simply by removing a ligand from a complex type  $ML_6$ . Converting a complex  $ML_6$  with  $O_h$  symmetry into a complex  $ML_5$  with  $C_{4v}$  symmetry causes lifting of degeneracy of the two levels  $e_g$  and  $t_{2g}$ . The  $t_{2g}$  level gives rise to two levels: level  $b_2$  ( $\delta$ ) which remains stable with pure metal character  $d_{xy}$  and a level  $e$  ( $\pi$ ) consisting of two hybrid molecular orbitals (MO) with predominant metal character  $d_{xz}$  and  $d_{yz}$ , this level is a bit destabilized because the reduction of metal-ligand binding character. The  $e_g$  level generates an undisturbed level  $b_1$  ( $\delta'$ ) predominantly formed with the  $d_{x^2-y^2}$  atomic orbital and of which lobes point toward the four ligands thus exhibiting a very antibonding metal-ligand character and a level  $a_1$  ( $\sigma$ ) consisting essentially by the  $d_{z^2}$  atomic orbital which is stabilized by the decrease of the metal-ligand antibonding character decreases [29]. This conversion is illustrated by the simple correlation diagram shown in Figure 2.

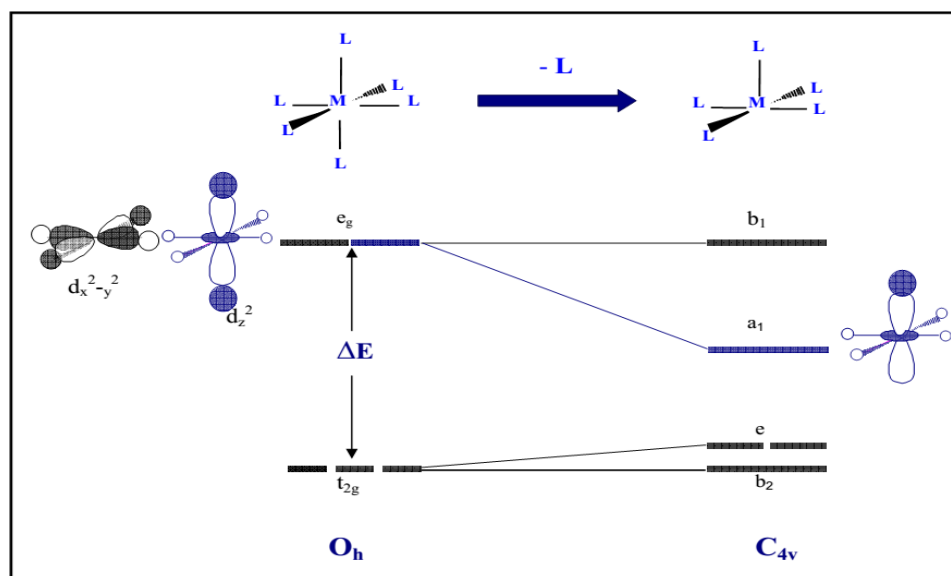


Figure 2: Correlation diagram of  $ML_6$  complex in  $O_h$  symmetry and  $ML_5$  in  $C_{4v}$  symmetry.

The frontier orbitals (FO) interaction of the six  $ML_5$  fragments, and after second order mixing among FO orbitals, two widely separated sets are obtained: 12 bonding and 12 antibonding MO's. Therefore, for a closed shell configuration, the complete occupation of all bonding MO's leads to the optimal count of 24 ME in these species (see figure 3).

### Density functional calculations

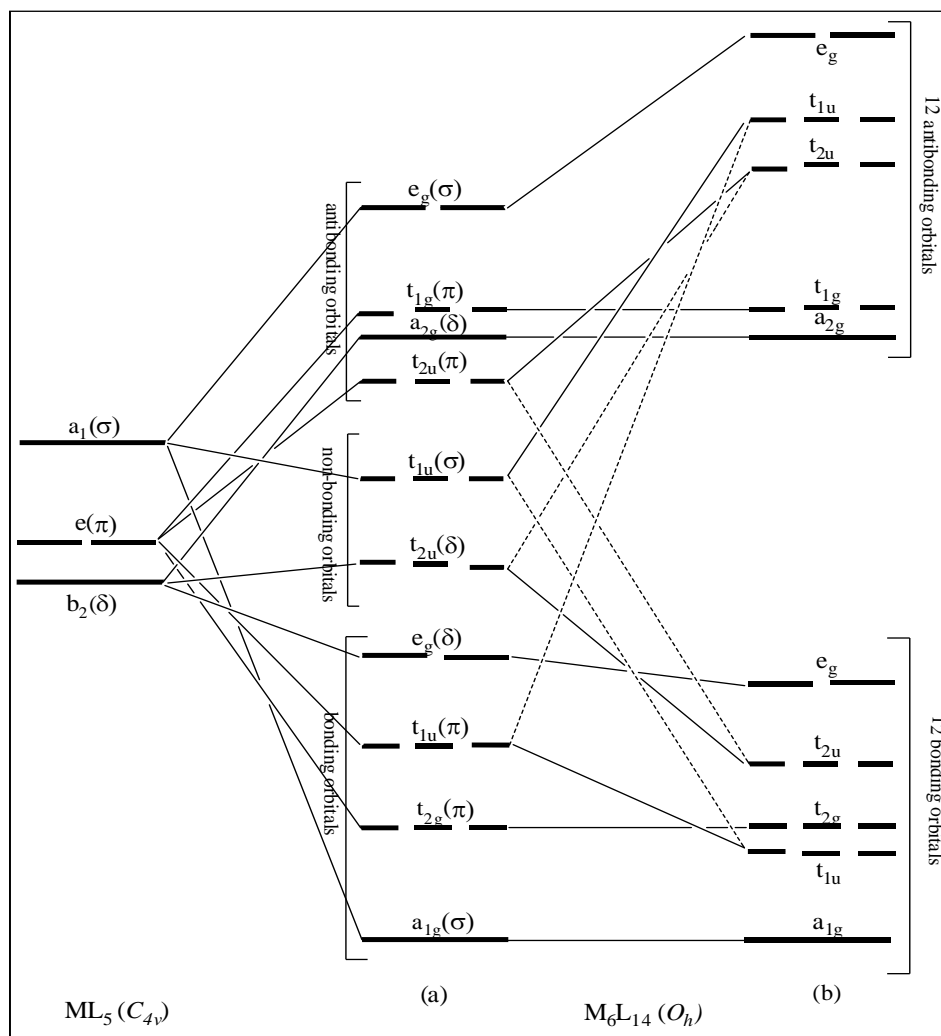


Figure 3: Qualitative molecular orbital diagram of  $M_6L_8L_6^i$  clusters before (a) and after (b) second order interaction of orbitals with the same symmetry.

Density Functional Theory calculations were first carried out on cluster models with optimal count of 24 ME then on electron deficient clusters respectively  $[(Mo_6Cl_8^i L_6^a)]^{2-}$  ( $L = Cl, Br, I$ ) and  $[Mo_6S_8^i (PH_3)_6^a]^n$  ( $n = 0, -1, -2$ ).

The crystal structures of isomorphous complexes  $Cs_2[(M_6Cl_8^i L_6^a)]$  ( $M = Mo$  or  $W$ ;  $L = Cl, Br, I$ ), have been determined from single-crystal X-ray diffraction [13]. The molybdenum atoms are at the corners of a nearly regular octahedron with mean distances of 2.615 Å for metal-

metal bonds and 2.540 Å for metal-ligands ones. Calculation were at first performed on  $[(M_6Cl^i_8)Cl^a_6]^{2-}$  using idealised geometry in  $O_h$  symmetry. After geometry optimisation, some variations affect bond distances, we have 2.661 for Mo-Mo, 2.531 for Mo-Cl<sup>i</sup> and 2.468 for Mo-Cl<sup>a</sup>. The DFT orbital diagram obtained schematically illustrated in Figure 4 complies with the qualitative one (Figure 3).

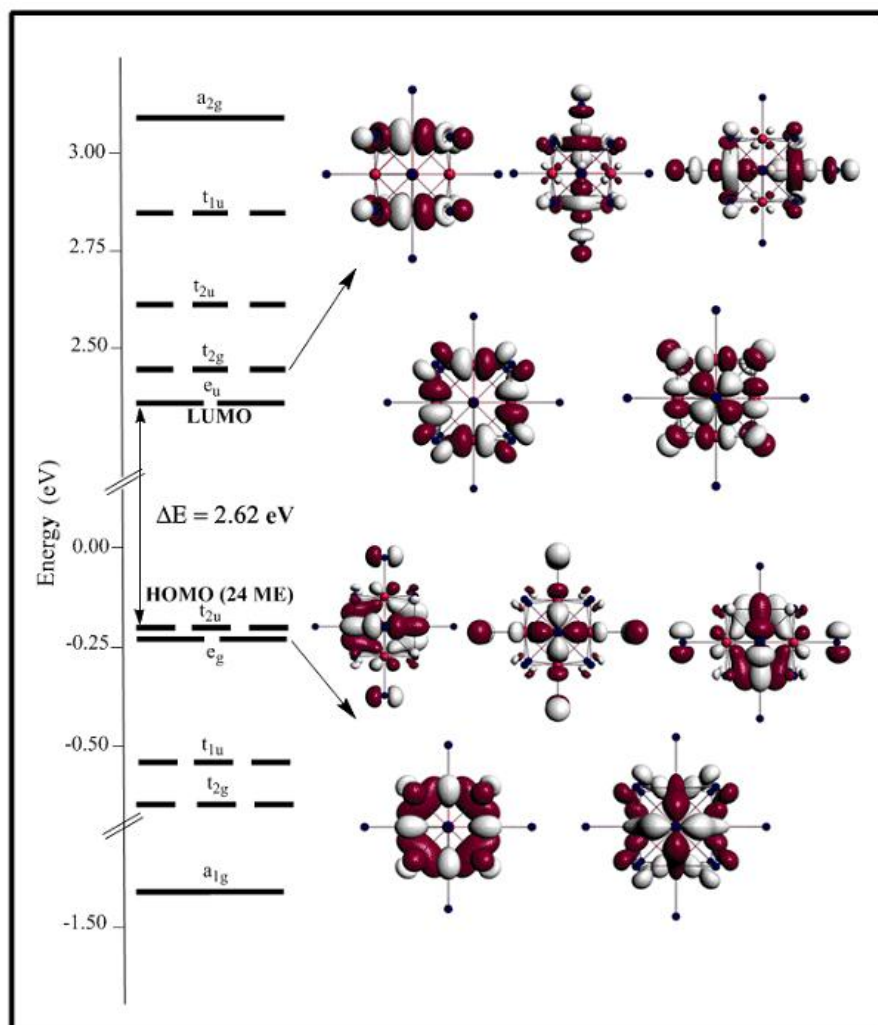


Figure 4: DFT molecular orbital diagram of  $[Mo_6Cl^i_8Cl^a_6]^{2-}$  in  $O_h$  symmetry.

Formally, each metal atom is in the +2 oxidation state to assign 2 electrons per bond in these species; however the analysis of results shows that the chemical bond is partially covalent with significant delocalization throughout the system. Table 2 report the Hirshfeld net charges where it appear clearly that our compounds possesse 24 metal electrons, without localized bonds (2 electrons / 2 centres). The inner ligands are slightly negative but apical ones are very largely negative which indicate that M-L<sup>i</sup> bonds are essentially covalent in nature, whereas M-L<sup>a</sup> bonds are rather ionic in character.

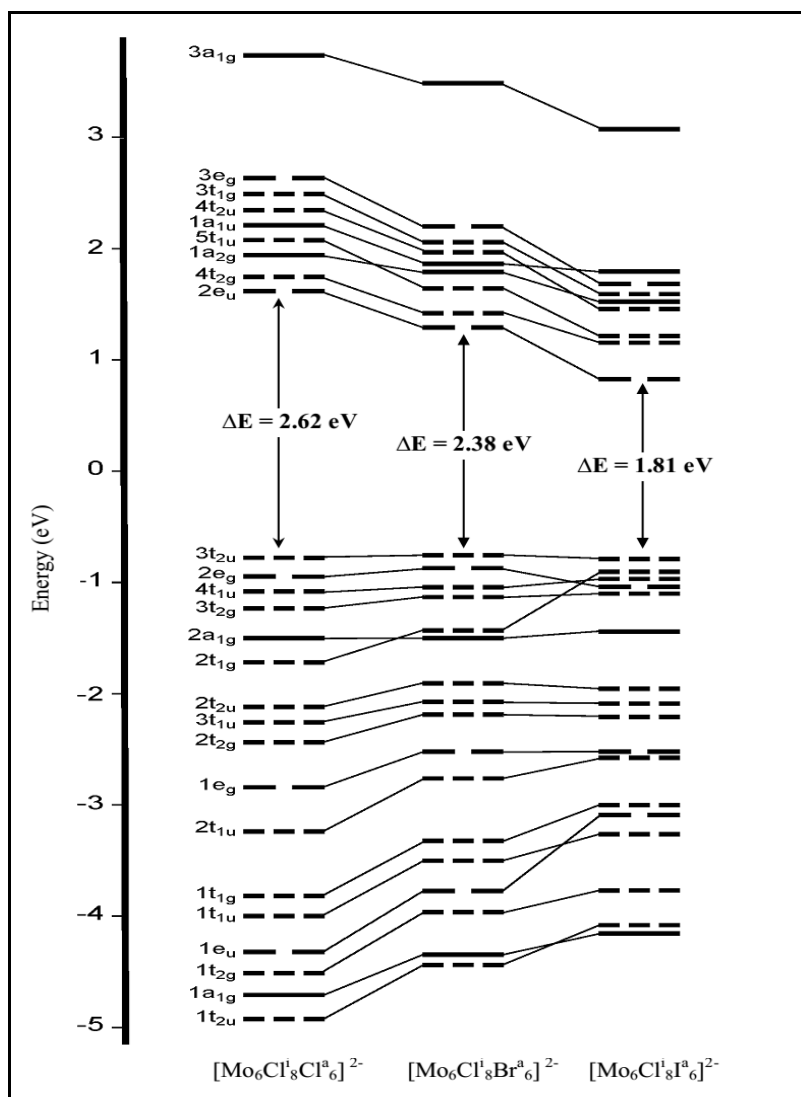


Figure 5: DFT correlation diagram of  $[\text{Mo}_6\text{Cl}_8\text{L}_6]^{2-}$  ( $\text{L} = \text{Cl}, \text{Br}, \text{I}$ ) in  $O_h$  symmetry

For deficient species, calculations have been performed on idealised model in  $O_h$  symmetry of experimental structure of  $[\text{Mo}_6\text{S}_8^i(\text{PH}_3)^a_6]^n$  ( $n = 0, -1$ ) [6-7]. For 22 EM clusters, calculations are carried out on reduced  $[\text{Mo}_6\text{S}_8^i(\text{PH}_3)^a_6]^{2-}$  directly by adding 1 electron to idealized 20 EM cluster model in  $O_h$  symmetry. The exploration of the DFT molecular orbital diagram indicate that among bonding levels, the HOMO  $e_g$  is partially occupied with only 2 electrons. We expect a distortion of the metal octahedron core such as a pseudo-tetragonal elongation along the metal-metal bonds found in reduced compounds with 21 EM count. The distortion may be driven by the Jahn-Teller effect [30] resulting from  $3E_g$  ground state in  $O_h$  symmetry. The HOMO-LUMO energy gap calculated is equal to 0.795 eV. The Mulliken and Hirshfeld computed net charges for 20, 21 and 22 EM are reported in table 3. The values are clearly different with those of 24 EM, this is due to the nature of ligands and their electronic properties. Based on these results, clusters with intermediate electron counts from 20 to 24 electrons should be favoured with distorted octahedral core [6-16]. Compared to 24 ME species,

the same relatively octahedral unit is observed with some significant lengthening of Mo-Mo distances and some shortening of the M-L<sup>i</sup> separations (see Table1).

**Table 1:** Examples of early transition metal octahedral clusters with  $\pi$ -Donor Ligands.

Cluster	ME <sup>a</sup>	d <sub>M-M</sub> (Å) <sup>b</sup>	Reference
[Mo <sub>6</sub> S <sub>8</sub> <sup>i</sup> (PEt <sub>3</sub> ) <sub>6</sub> <sup>a</sup> ]	20	2.66	6
[Mo <sub>6</sub> Se <sub>8</sub> <sup>i</sup> (PEt <sub>3</sub> ) <sub>6</sub> <sup>a</sup> ]	20	2.70	6
[W <sub>6</sub> S <sub>8</sub> <sup>i</sup> (PEt <sub>3</sub> ) <sub>6</sub> <sup>a</sup> ]	20	2.68	7
[Mo <sub>6</sub> S <sub>8</sub> <sup>i</sup> (PEt <sub>3</sub> ) <sub>6</sub> <sup>a</sup> ] <sup>-</sup>	21	2.67	6
[Mo <sub>6</sub> Se <sub>8</sub> <sup>i</sup> (PEt <sub>3</sub> ) <sub>6</sub> <sup>a</sup> ] <sup>-</sup>	21	2.71	6
[Nb <sub>6</sub> I <sub>8</sub> <sup>i</sup> (NH <sub>2</sub> CH <sub>3</sub> ) <sub>6</sub> <sup>a</sup> ]	22	2.75	8
[W <sub>6</sub> Cl <sub>8</sub> <sup>i</sup> Cl <sub>6</sub> <sup>a</sup> ] <sup>-</sup>	23	2.63	9
[W <sub>6</sub> Cl <sub>8</sub> <sup>i</sup> Cl <sub>6</sub> <sup>a</sup> ] <sup>2-</sup>	24	2.61	10
[Mo <sub>6</sub> Cl <sub>8</sub> <sup>i</sup> Cl <sub>6</sub> <sup>a</sup> ] <sup>2-</sup>	24	2.62	11
[Mo <sub>6</sub> Br <sub>8</sub> <sup>i</sup> Br <sub>6</sub> <sup>a</sup> ] <sup>2-</sup>	24	2.63	12
[Mo <sub>6</sub> Cl <sub>8</sub> <sup>i</sup> Br <sub>6</sub> <sup>a</sup> ] <sup>2-</sup>	24	2.62	13
[Mo <sub>6</sub> Cl <sub>7</sub> <sup>i</sup> S <sup>i</sup> Cl <sub>6</sub> <sup>a</sup> ] <sup>3-</sup>	24	2.62	14
[Re <sub>6</sub> Se <sub>6</sub> <sup>i</sup> Cl <sub>2</sub> <sup>i</sup> Cl <sub>6</sub> <sup>a</sup> ] <sup>2-</sup>	24	2.61	15
[Re <sub>6</sub> Se <sub>5</sub> <sup>i</sup> Cl <sub>3</sub> <sup>i</sup> Cl <sub>6</sub> <sup>a</sup> ] <sup>-</sup>	24	2.61	15
[Re <sub>6</sub> Se <sub>4</sub> <sup>i</sup> Cl <sub>4</sub> <sup>i</sup> Cl <sub>6</sub> <sup>a</sup> ]	24	2.61	16

<sup>a</sup> Metallic electron count.

<sup>b</sup> Averaged metal-metal distance.

**Table 2:** Computed Hirshfeld and Mulliken Net Charges in selected [Mo<sub>6</sub>Cl<sub>8</sub><sup>i</sup>L<sub>6</sub><sup>a</sup>]<sup>2-</sup> models.

Cluster	Hirshfeld Net Charge			Mulliken Net Charge		
	Mo	Cl <sup>i</sup>	X <sup>a</sup>	Mo	Cl <sup>i</sup>	X <sup>a</sup>
[Mo <sub>6</sub> Cl <sub>8</sub> <sup>i</sup> Cl <sub>6</sub> <sup>a</sup> ] <sup>2-</sup>	0.145	-0.046	-0.418	0.444	-0.172	-0.548
[Mo <sub>6</sub> Cl <sub>8</sub> <sup>i</sup> Br <sub>6</sub> <sup>a</sup> ] <sup>2-</sup>	0.144	-0.049	-0.412	0.372	-0.116	-0.551
[Mo <sub>6</sub> Cl <sub>8</sub> <sup>i</sup> Cl <sub>6</sub> <sup>a</sup> ] <sup>-</sup>	0.138	-0.040	-0.418	0.268	-0.090	-0.467

**Table 3:** Computed Hirshfeld and Mulliken Net Charges in selected [Mo<sub>6</sub>S<sub>8</sub><sup>i</sup>(PH<sub>3</sub>)<sub>6</sub><sup>a</sup>]<sup>n</sup> models.

Cluster	Hirshfeld Net Charge			Mulliken Net Charge		
	Mo	S <sup>i</sup>	(PH <sub>3</sub> ) <sup>a</sup>	Mo	S <sup>i</sup>	(PH <sub>3</sub> ) <sup>a</sup>
[Mo <sub>6</sub> S <sub>8</sub> <sup>i</sup> (PH <sub>3</sub> ) <sub>6</sub> <sup>a</sup> ]	0.212	-0.199	-0.143	0.479	-0.227	-0.548
[Mo <sub>6</sub> S <sub>8</sub> <sup>i</sup> (PH <sub>3</sub> ) <sub>6</sub> <sup>a</sup> ] <sup>-</sup>	0.228	-0.173	-0.164	0.402	-0.173	-0.339
[Mo <sub>6</sub> S <sub>8</sub> <sup>i</sup> (PH <sub>3</sub> ) <sub>6</sub> <sup>a</sup> ] <sup>2-</sup>	0.212	-0.199	-0.279	0.479	-0.227	-0.509

## CONCLUSION

The density functional calculations performed on inorganic face-bridged octahedral clusters with  $\pi$ -Donor ligands have shown that, for the molybdenum and tungsten clusters, the complete occupation of the Metal-Metal bonding MOs fulfills the closed-shell requirement with 24 ME count. According to MO diagrams, the HOMO e<sub>g</sub> level is lying in the middle of large energy gap between the bonding t<sub>2u</sub> and antibonding a<sub>2g</sub> levels and the energy gap is controlled by the nature of apical ligands L<sup>a</sup> and their contribution in molecular orbitals which is in

agreement with the existence of two favoured closed-shell electron counts of 20 and 24, as well as with intermediate one of 21, 22 and 23.

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