

Electronic Properties of Unprecedented Bridging Organoimido-Substituted Hexamolybdate: New Insights from Density Functional Theory Study

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The organoimido functionalization of polyoxometalates (POMs) has drawn tremendous attention due to particular merits in fabricating POM-based hybrid materials with finely tunable properties. The electronic properties, orbital and bonding characters of unprecedented bridging organoimido-substituted hexamolybdate are investigated using density functional theory methods. Among the organoimido-bridged hexamolybdates, $[\text{Mo}_6\text{O}_{16}(\text{2,6-Me}_2\text{-NC}_6\text{H}_3)_2(\mu_2\text{-2,6-Me}_2\text{-NC}_6\text{H}_3)]^{2-}$ (3-Ar-1), which features two terminal and one bridging organoimido ligand, is more favorable. The calculations confirm that the three-center (3c) π bond originates from the coplanarity of bridging nitrogen atom with two Mo atoms and the hybridization of bridging nitrogen. The 3c bond stabilizes the organoimido-bridged anion 3-Ar-1. Compared with cis-bifunctionalized organoimido derivative $[\text{Mo}_6\text{O}_{17}(\text{2,6-Me}_2\text{-NC}_6\text{H}_3)_2]^{2-}$ (2-Ar), the bonding interaction between terminal organoimido ligand and hexamolybdate cluster in 3-Ar-1 is strengthened by the bridging organoimido. The results are in good agreement with the analysis of the Wiberg bond index of the Mo–N bond. The organoimido segment modifies the occupied molecular orbitals of organoimido hexamolybdates. The unoccupied molecular orbitals in 3-Ar-1 are largely nonbonding O_p and Mo_d orbitals in character, which resemble those of 2-Ar.

1. Introduction

Polyoxometalates (POMs) constitute a diverse class of inorganic oxometal clusters with defined structures based on octahedra of tungstic, molybdic, or vanadate oxides, which are characterized by an intriguing variety of architectures and topologies and applications in catalysis, biology, magnetism, nanoscience, optics, and medicine.¹ Over the past few years, there has been increasing interest in the chemistry of organically derivative POMs.^{1c,d} In organic–inorganic hybrid POMs, the delocalized electrons coexist in both the organic networks and the inorganic clusters. Such materials not only combine the advantages of organic materials but also contribute to explore the possible synergistic effects. Therefore, increasing attention is currently paid to make multifunctional hybrid materials by using covalently linked POMs and organic polymers. Among the organic derivatives of POMs, the organoimido derivatives of Lindqvist-type polyoxometalates (POMs), $[\text{M}_6\text{O}_{19}]^{n-}$, have attracted particular interest because the organic π electrons may extend their conjugation to cluster d electrons, thus resulting in strong d– π interactions.^{2,3} A number of organoimido derivatives of Lindqvist-type POMs have been synthesized.⁴ Essentially, one or even all six terminal oxo groups of a Lindqvist ion could be replaced with various organoimido ligands. The terminally substituted mono- and even multifunctionalized organoimido derivatives of POMs have been prepared with various imido-releasing reagents.⁵

Very recently, Wei and co-workers reported the first bridging organoimido-substituted POM, triply functionalized Lindqvist hexamolybdate $[\text{Mo}_6\text{O}_{16}(\text{2,6-Me}_2\text{-NC}_6\text{H}_3)_2(\mu_2\text{-2,6-Me}_2\text{-NC}_6\text{H}_3)]^{2-}$ (3-Ar-1), in which the bridging oxo group between two terminal organoimido ligands is replaced by a third

organoimido ligand.⁶ The most distinctive feature of the bridging organoimido ligand in 3-Ar-1 is that the bridging nitrogen atom shows typical sp^2 hybridization on account of its three-coordinate linking mode. The lowest energy electronic absorption bands for 3-Ar-1 show that the bridging arylimido ligand is not conjugated with the delocalized $\{\text{Mo}_4\text{O}_3\text{N}\}$ ring.

Along with the experimental achievements on the organoimido-substituted Lindqvist hexamolybdates, we investigated the stability and electronic properties of organoimido-substituted hexamolybdates⁷ using the density functional theory (DFT) method, which appears to be a powerful and effective computational tool to study POMs.^{8–11} The bonding character between organoimido and $[\text{Mo}_6\text{O}_{19}]^{2-}$ in terminal organoimido-substituted hexamolybdate has been studied in previous work.^{7a} The results show that the strong $\text{Mo}\equiv\text{N}$ triple bond can be formed through the $\text{N} \rightarrow \text{Mo}$ σ donation, $\text{N} \rightarrow \text{Mo}$ π donation, and $\text{N} \leftarrow \text{Mo}$ π back-donation in the formation of the arylimido-substituted hexamolybdates. This strong interaction generates a strong electronic communication between organoimido and $[\text{Mo}_6\text{O}_{19}]^{2-}$. Therefore, the nonlinear optical (NLO) properties of organoimido-substituted hexamolybdates have been predicted by using DFT methods.^{7b–d}

From computational results using DFT methods, we demonstrate the stability, bonding character, and electronic properties of the first bridging organoimido-substituted hexamolybdate. The current work can provide new insights into understanding the stability, bonding, and orbital character of organoimido-substituted hexamolybdate derivatives.

2. Computational Details

The DFT calculations in this work were carried out using the ADF2006.01 program.¹² The local density approximation (LDA) characterized by the Vosko–Willk–Nusair (VWN)¹³ parametrization for correlation was used. The generalized-

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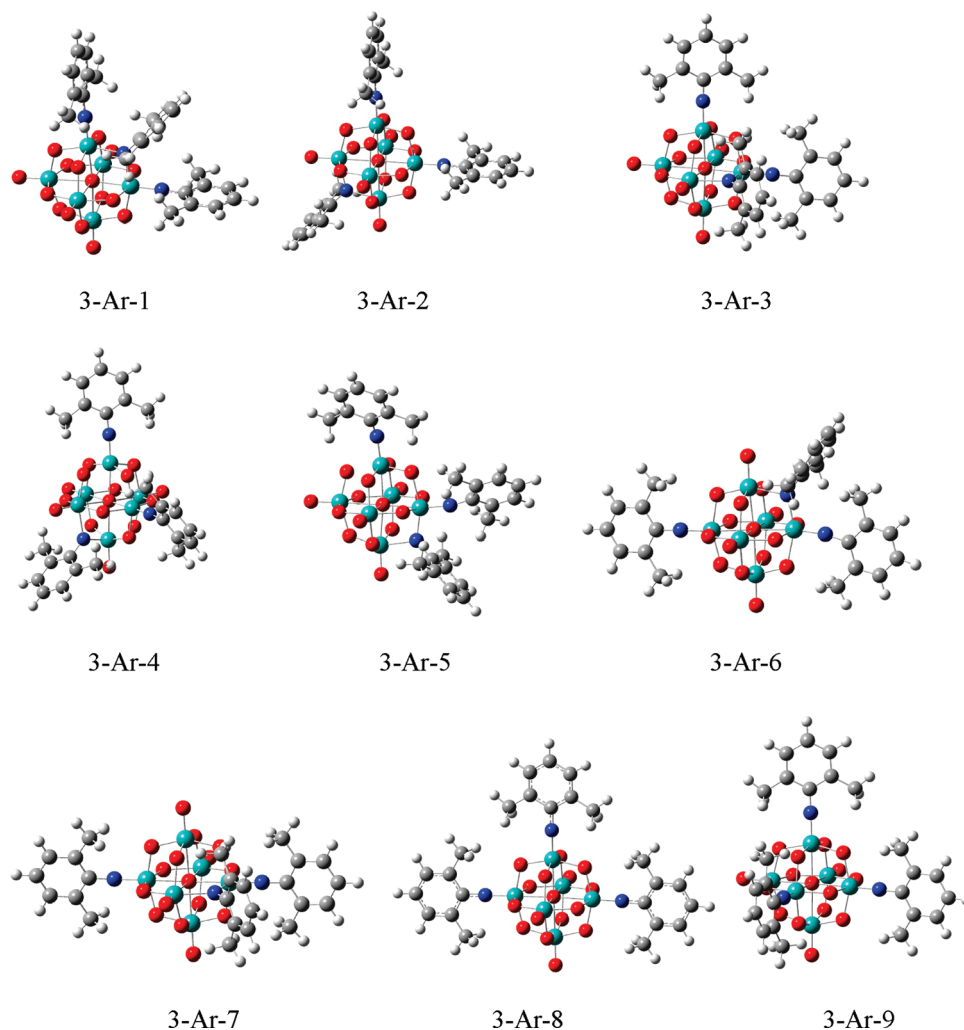


Figure 1. Structures of trifunctionalized organoimido hexamolybdates. Color code: Mo, blue; O, red; N, dark blue; C, gray; H, white.

gradient approximation (GGA) was employed in the geometry optimizations by using the Beck¹⁴ and Perdew¹⁵ exchange-correlation (XC) functional. The zero-order regular approximation (ZORA) was adopted in all the calculations to account for the scalar relativistic effects.¹⁶ The basis functions were Slater-type sets. Triple- ζ plus polarization basis sets were used to describe the valence electrons of all the atoms, whereas for transition metal molybdenum atom, a frozen core composed of 1s to 3spd shells was described by means of single Slater functions. Moreover, the value of the numerical integration parameter used to determine the precision of numerical integrals was 6.0. All of the structures herein discussed were optimized in the presence of a model solvent, accounted for with the conductor-like screening model (COSMO)¹⁷ implemented as part of the ADF code. To define the cavity surrounding the molecules, we used the solvent-excluding-surface method and a fine tesserae. The ionic radii for the polyanion atoms, which actually define the size of the solvent cavity where the target molecule remains, were chosen to be 1.26 Å for Mo atom. The radii for O, C, N, and H are 1.52, 1.70, 1.55, and 1.20 Å, respectively. The dielectric constant (ϵ) utilized in the computations was set equal to 37.5 for modeling of the effects of acetonitrile. The Wiberg bond indices were calculated by NBO at the BP86 level involving the effective core potential (ECP) on the metal atoms, using the Gaussian 03 program.¹⁸ In Gaussian 03 calculations, the LANL2DZ basis set associated with the pseudopotential was used to describe the metal atoms,

and the 6-31G(d) basis set was used to describe the C, N, O, and H atoms. The optimized structures are sketched in Figure 1.

3. Results and Discussion

3.1. Stability. There are seven geometric isomers for trifunctionalized organoimido derivatives of hexamolybdates bearing two terminal ligands and one bridging ligand: if the two terminal ligands are mutually cis, there are five geometric isomers (3-Ar-1 to 3-Ar-5); if the two terminal ligands are mutually trans, there are two possible geometric isomers (3-Ar-6 and 3-Ar-7). For a tris-imido complex with three terminal ligands, there are two geometric isomers, mer- and fac-isomer (3-Ar-8 and 3-Ar-9). The organoimido-bridged anion 3-Ar-1 was obtained by Wei and his co-workers, and it was confirmed that the bridging oxo group between two terminal organoimido ligands could be replaced by a third organoimido ligand.⁶ Table 1 shows the relative energies of nine trifunctionalized organoimido hexamolybdates. For the organoimido-bridged anions 3-Ar-1 to 3-Ar-7, anion 3-Ar-1 is more stable in energy (only the energy for 3-Ar-3 is slightly lower than that of 3-Ar-1), while compared with the organoimido-terminal anions 3-Ar-8 and 3-Ar-9, anion 3-Ar-1 is high in energy. It is clear that the organoimido-bridged anion 3-Ar-1 is not thermodynamically favorable compared with organoimido-terminal anions.

In the ADF program, the bonding energy (E_B) analysis can effectively described as the fragment relative effect on bonding

TABLE 1: Relative Energies for Nine Trifunctionalized Organoimido Hexamolybdates (kcal/mol)

	3-Ar-1	3-Ar-2	3-Ar-3	3-Ar-4	3-Ar-5	3-Ar-6	3-Ar-7	3-Ar-8	3-Ar-9
E	0.0	2.35	−0.77	0.58	3.78	3.18	0.84	−9.22	−8.68

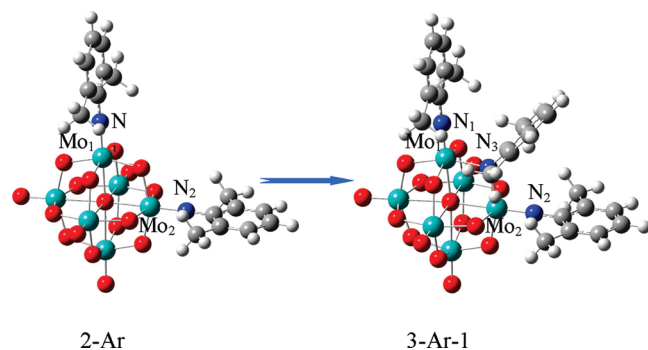
TABLE 2: Bonding Energies (in eV) for Seven Trifunctionalized Organoimido Hexamolybdates

	3-Ar-1	3-Ar-2	3-Ar-3	3-Ar-4	3-Ar-6	3-Ar-8	3-Ar-9
E_P	1749.3199	1743.7742	1744.2602	1743.5515	1743.8227	1746.2262	1745.2907
E_E	−413.2502	−412.8480	−412.5368	−412.5383	−412.7676	−412.7784	−412.6052
E_O	−1857.4461	−1852.5381	−1853.2906	−1852.5828	−1852.5886	−1855.1730	−1854.4492
E_B	−529.1073	−529.0052	−529.1617	−528.9940	−528.8472	−529.5070	−529.4260

TABLE 3: Optimized Bond Length (Å) of 2-Ar and 3-Ar-1^a

	2-Ar	3-Ar-1
Mo ₁ –O _c	2.2545	2.2305
Mo ₁ –N ₁	1.7782(1.6624) ^b	1.7777(1.7345) ^b
N ₁ –C ₁	1.3704	1.3719
Mo ₁ –N ₃		2.0377

^a The Wiberg bond indices of Mo₁–N₁ are also listed in parentheses. ^b The Wiberg bond index of Mo₁–N₁.

**Figure 2.** Structures of difunctionalized and trifunctionalized organoimido hexamolybdates.

stability. According to the transition state method of Ziegler and Rauk,¹⁹ the molecular bonding energy (E_B) can be decomposed as

$$E_B = E_E + E_P + E_O \quad (1)$$

where E_E , E_P , and E_O are the electrostatic interaction, Pauli repulsion, and orbital mixing term, respectively. Descriptions of the physical meaning of these properties have been given by Landrum, Goldberg, and Hoffmann,²⁰ and by Bickelhaupt and Baerends.²¹ E_E is an electrostatic term whose contribution is primarily dominated by the nucleus–electron attractions. The Pauli repulsion acts as the destabilizing effect, which is caused by the larger energy shift of antibonding orbitals to bonding orbitals. E_O results from the mixing of occupied and unoccupied orbitals. Therefore, E_E and E_O show stabilizing effects. E_B is a total molecular bonding energy relative to the sum of the single atoms.

Further insight can be obtained if the molecular bonding energy (E_B) is decomposed as E_O , E_P , and E_E . The results obtained by applying eq 1 to the trifunctionalized organoimido hexamolybdates are given in Table 2. For five organoimido-bridged anions (3-Ar-1 to 3-Ar-4, and 3-Ar-6), the Pauli repulsion is of larger magnitude in 3-Ar-1, while the orbital mixing and electrostatic effects are more favorable in 3-Ar-1.

TABLE 4: Fragment Analysis ΔE_O , ΔE_E , ΔE_P , and ΔE_B (eV) for 2-Ar and 3-Ar-1

	2-Ar	3-Ar-1
ΔE_O	−15.4570	−15.8519
ΔE_E	−13.2428	−13.9479
ΔE_P	14.6925	15.4278
ΔE_B	−14.0073	−14.3720

So the orbital mixing term appears as the dominant stability factor in five organoimido-bridged anions. Next, the energies of two organoimido-terminal anions (3-Ar-8 and 3-Ar-9) and organoimido-bridged anion 3-Ar-1 are compared. The orbital mixing and electrostatic effects of 3-Ar-1 are still more favorable than two organoimido-terminal anions. Nevertheless, the Pauli repulsions are of smaller magnitude in organoimido-terminal anions and determine the stability. The Pauli contribution provides a measure of steric interactions,²² and the “less crowded” structures of organoimido-terminal anions seem to be of major importance in this case.

From the structure, the anion 3-Ar-1 can be regarded such that the bridging oxo group between two terminal organoimido ligands is replaced by a third organoimido ligand (Figure 2). The optimized bond lengths for 2-Ar and 3-Ar-1 are listed in Table 3, and the Wiberg bond indices of Mo₁–N₁ are also included. In the Lindqvist-type anion, the oxygen atom that links with six metal atoms is named as the central oxygen atom (O_c). According to the C_{2v} symmetry, the Mo₁–N₁ bond is equivalent to the Mo₂–N₂ bond. From anion 2-Ar to 3-Ar-1, the bond Mo₁–O_c is shortened from 2.2545 Å in 2-Ar to 2.2305 Å in 3-Ar-1. It confirms that the central oxygen is closer to the organoimido-bearing Mo atoms. The Mo₁–N₁ bond is also shortened from 2-Ar to 3-Ar-1, and the Wiberg bond index of Mo₁–N₁ is increased from 1.6624 to 1.7345. That means the Mo₁–N₁ bond is strengthened by a third organoimido ligand. The strong bond is helpful to construct three-dimensional network structures.

In the following, the bond changes from 2-Ar to 3-Ar-1 are analyzed in detail. In previous work^{7a} the significant covalent character of the molybdenum–nitrogen interaction is confirmed, which is helpful to construct the three-dimensional structures. A fragment approach to the molecular structures of the poly-anions can provide further insight into the bonding stability.²³ Herein, the formulas of [Mo₆O₁₆(2,6-Me₂-NC₆H₃)₂(μ₂-2,6-Me₂-NC₆H₃)₂]^{2−} (3-Ar-1) and [Mo₆O₁₇(2,6-Me₂-NC₆H₃)₂]^{2−} (2-Ar) are abbreviated to [Mo₆O₁₆(NAr)₃]^{2−} and [Mo₆O₁₇(NAr)₂]^{2−}, respectively. For comparison with the bonding energy between terminal organoimido (NAr) segment and hexamolybdate in difunctionalized 2-Ar ([Mo₆O₁₇(NAr)₂]^{2−}) and trifunctionalized 3-Ar-1 ([Mo₆O₁₆(NAr)₃]^{2−}), the following decompositions are defined

TABLE 5: Occupancy, Orbital Hybridization (Orbital Coefficients), and Orbital Type of 3-Ar-1

bond	occupancy	bond orbital
Mo ₁ –N ₃ –Mo ₂	1.9322	0.4407(d ^{99.91%})Mo+0.7833(p ^{100%})N+0.4384(d ^{99.57%})Mo
Mo ₁ –N ₃	1.7369	0.3561(s ^{8.50%} p ^{4.69%} d ^{86.82%})Mo+0.9344(s ^{30.10%} p ^{69.89%})N
Mo ₂ –N ₃	1.7557	0.3736(s ^{12.27%} p ^{19.45%} d ^{68.27%})Mo+0.9276(s ^{30.10%} p ^{69.89%})N

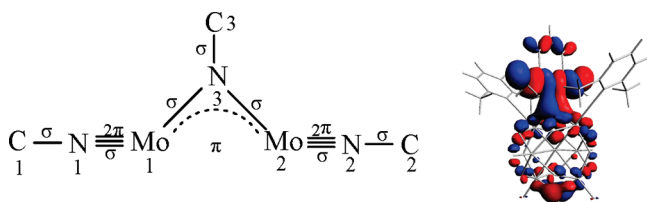
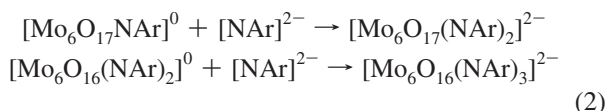


Figure 3. Bonding model for 3-Ar-1 and the corresponding molecular orbital.



The bonding energy relative to the fragments described by eq 2 is given by

$$\Delta E_B = \Delta E_E + \Delta E_P + \Delta E_O \quad (3)$$

The results are shown in Table 4. As compared to 2-Ar, the Pauli repulsion of 3-Ar-1 is larger than that of 2-Ar due to the third organoimido, while the orbital mixing term and the electrostatic term in 3-Ar-1 are decreased. Finally, the bonding energy between NAr and [Mo₆O₁₆(NAr)₂] is lower than that in 2-Ar. It suggests that the bonding interaction between terminal NAr and cluster is strengthened by the third organoimido, which is in good agreement with the analysis of Wiberg bond index on Mo₁–N₁. It would be helpful for the stability of 3-Ar-1 as well as constructing three-dimensional structures.

3.2. Bonding Character. The question with which we are concerned is why the bridging oxo group between two terminal organoimido ligands could be replaced by a third organoimido ligand. In order to analyze the bonding character for organoimido-bridged anions, the bonding character between Mo and N centers was investigated using NBO theory, and the results are summarized in Table 5. The simple model was sketched from 3-Ar-1 and shown in Figure 3. The corresponding molecular orbital is also presented.

The Mo≡N triple bond in terminal-substituted organoimido hexamolybdate derivatives has been demonstrated in the experiment^{2c,d} and theoretical calculation.^{7a} In 3-Ar-1, Mo₁–N₁, and Mo₂–N₂ are still triple bonds. The nitrogen atoms of the terminal organoimido ligands show typical sp hybridization, while the nitrogen atom of bridging organoimido ligand has sp² hybridization due to its three-coordinate mode. From Table 5, it can be seen that there are a Mo₁–N₃ σ bond (comprised of s^{8.50%}p^{4.69%}d^{86.82%} Mo orbital and s^{30.10%}p^{69.89%} N orbital) and a Mo₂–N₃ σ bond (comprised of a s^{12.27%}p^{19.45%}d^{68.27%} Mo orbital and s^{30.10%}p^{69.89%} N orbital). At the same time, Mo₁–N₃–Mo₂ formed three-center (3c) π bond (Mo–N_{bri}–Mo), which is comprised of d^{99.91%} Mo₁ orbital, p^{100%} N orbital, and d^{99.57%} Mo₂ orbital. The analysis from the corresponding molecular orbital shows that the p orbital of bridging N and d orbitals of two molybdenum atoms give the main contributions. It supposes that the 3c π bond originates from the coplanarity of bridging nitrogen atom with two Mo atoms (Mo₁ and Mo₂) and the

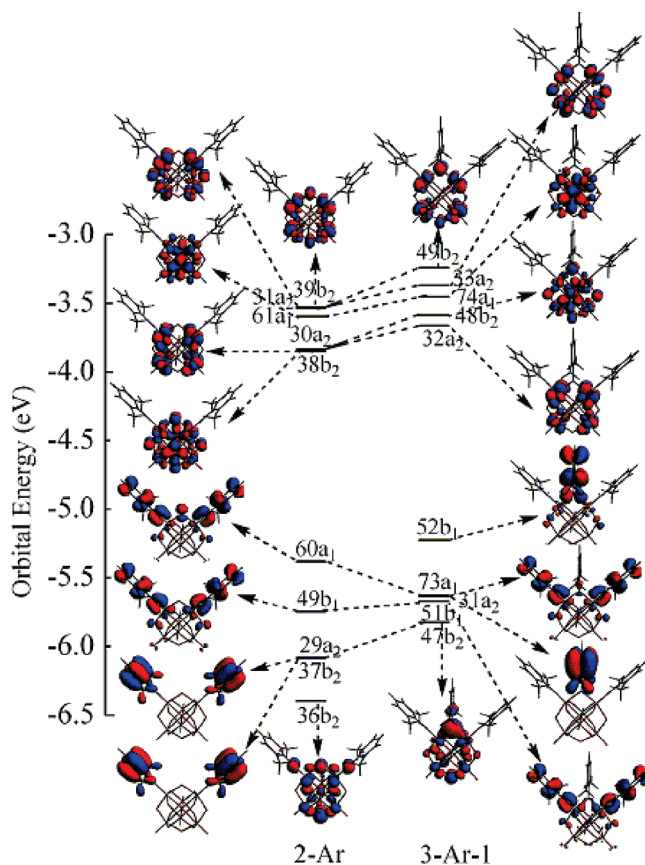


Figure 4. Frontier molecular orbital energy level diagram for 2-Ar and 3-Ar-1.

hybridization of bridging nitrogen. The result implies that the anion 3-Ar-1 is stabilized by 3c bond.

3.3. Orbital Character. The organoimido segment modifies the occupied molecular orbitals of organoimido hexamolybdates in previous work.^{7a} The orbital energy diagrams of 2-Ar and 3-Ar-1 are illustrated in Figure 4. The orbital energy levels are shifted up from 2-Ar to 3-Ar-1. The 60a₁ and 38b₂ orbitals are the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 2-Ar. In anion 2-Ar, the HOMO (60a₁) and HOMO–1 (49b₁) mainly concentrate on the organoimido segments, and N atom from organoimido and Mo atom which bonds with N atom form dπ bonding orbitals. The 29a₂ and 37b₂ are near degenerate orbitals, which have the contributions from p orbitals of carbon atoms and s orbitals of hydrogen atoms. The 36b₂ orbital mainly locates on the p orbitals of oxygen atoms from hexamolybdate and p orbitals of nitrogen atoms. The HOMO (52b₁) of 3-Ar-1 mainly concentrates on the bridging organoimido. The 73a₁ and 31a₂ are near degenerate orbitals, and the 73a₁ orbital corresponds to the HOMO (60a₁) of 2-Ar. The 31a₂ orbital is from the bridged organoimido. So the bridged organoimido ligand modifies the occupied molecular orbitals. The 38b₂ (LUMO) and 30a₂ of 2-Ar are near degenerate orbitals, which concentrate on the d orbitals (Mo) and p orbitals (O), while by introducing the bridging organoimido, the 32a₂ (LUMO) and 48b₂ of 3-Ar-1

are separated by 0.0748 eV. The orbital distributions of unoccupied molecular orbitals in 3-Ar-1 are similar to those of 2-Ar. From the frontier molecular orbitals (MOs), it can be seen that the organoimido ligands modify the occupied molecular orbitals. It suggests that the charge transfer under external electric field is originated from the organoimido segments to hexamolybdate.

4. Conclusions

The stability, bonding, and orbital character of unprecedented bridging organoimido-substituted hexamolybdate are investigated using the density functional theory method. Compared with trifunctionalized organoimido-terminal hexamolybdate anions, 3-Ar-1 is high in energy. So the organoimido-bridged anion 3-Ar-1 is not thermodynamically favorable. The bonding analysis was carried on the organoimido-bridged anions and shows that the orbital mixing and electrostatic effects are more favorable in 3-Ar-1. The bonding stabilities in 2-Ar and 3-Ar-1 are further studied by a fragment approach. From 2-Ar to 3-Ar-1, the bonding interaction between terminal organoimido ligand and hexamolybdate cluster is strengthened by the third bridging organoimido. The results are in good agreement with the analysis of the Wiberg bond index of Mo–N bond (N atom is from the terminal organoimido ligand). In 3-Ar-1, Mo–N_{br}–Mo formed a three-center (3c) π bond that originates from the coplanarity of bridging nitrogen atom with two Mo atoms (Mo₁ and Mo₂) and the hybridization of bridging nitrogen. The organoimido segment modifies the occupied molecular orbitals of organoimido hexamolybdates.

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Supporting Information Available: Cartesian coordinates of 3-Ar-1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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