

He@Mo₆Cl₈F₆: A Stable Complex of Helium

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The electronic structure and chemical stability of the endo helium cluster, He@Mo₆Cl₈F₆, were investigated carefully by using density function theory. The results show that the cluster is significantly different from typical van der Waals systems: the bond distance between helium and molybdenum is only about 1.89 Å. Moreover, the bonding analysis clearly reveals considerable charge and bond order on the helium atom and bond order for He–Mo. The dissociation of He@Mo₆Cl₈F₆ to He + Mo₆Cl₈F₆ is prohibited by a barrier of 0.86 eV (19.8 kcal/mol), indicating that the cluster is chemically stable. However, no covalent He–Mo bonding was found so it is an analogue of He@adam. Comparison was also made with the isoelectronic system of [Mo₆Cl₈F₆]^{2−}.

Introduction

Since xenon hexafluoroplatinate was experimentally prepared in 1962,¹ many rare-gas compounds of Kr, Xe, and Rn have been found,² thereby leading to a new field of research. Especially in 2000, HArF was also prepared at low temperature,³ which is hitherto the only stable covalent compound of Ar. It is well-known that, due to larger polarizability, the heavier rare-gas elements are more readily bound than helium and neon. Up to now, several types of helium compounds have been reported experimentally, including cations (e.g., HeH⁺, which was found 70 years ago⁴), quasi-molecules in excited states (e.g., HeH⁵), and weakly bound van der Waals molecules (e.g., helium in carbon cages⁶ and the metal–helium system HgHe⁷). Yet, stable or metastable neutral covalent compounds of helium are still unknown experimentally. Nevertheless, some new kinds of neutral complexes of helium were theoretically predicted in the literature to be stable or metastable, including the following:

- Metastable complexes with uncommonly strong van der Waals interactions.^{8–16} For such molecules, the calculated binding energies of helium only amount to a few kcal/mol, and the topological analysis of the electron density distribution shows that there is no covalent bond formed on helium. For example, HeBeO.^{8–10}
- Pressure-induced complexes, which are a special kind of endohedrals (i.e., atom-in-cage systems). An example is the complex of He in adamantane (He@adam).¹⁷ It was found that the centered helium atom is protected by a barrier to dissociation of as large as 1.7 eV (39.2 kcal/mol). Different from most of the helium-in-cage systems (for instance, see ref 6), there are very strong repulsive interactions between helium and carbon atoms. The topological analysis of electron density by the atoms in molecules (AIM) method does not support any chemical bonds on helium,^{17a} although this argument has been disputed.^{17b}
- Quasi-covalent compounds. In 2005 Hu et al.¹⁸ predicted a helium-containing anion, FHeO[−]. Inspired from this

anion, Grochala recently calculated some derivatives by the density functional theory (DFT) and post Hartree–Fock methods and found that CsFHeO and N(CH₃)₄FHeO may exist at a very low temperature.¹⁹ For the latter, the dissociation energy in the He–O bond is computed as large as half an electronvolt, but a crossing of the singlet–triplet electronic states and the decomposition in the bending direction decrease the kinetic stability considerably.¹⁹ In our test calculations of FHeO[−] and CsFHeO, typical covalent molecular orbitals can be found between He and O as well as He and F. However, these compounds are not so simple from a topological analysis point of view. The positive Laplacians (∇²ρ) of the electron density suggest there are no covalent interactions between the atoms, meaning that they are not real covalent compounds. On the contrary, the negative values of the H(*r*) function suggested by Cremer and Kraka [ref 8c and references therein] indicate that the He–O bonds are covalent. The same should also be true for N(CH₃)₄FHeO.

- Covalent compounds. The only example is HHeF²⁰ presently. It was considered to be metastable with a strong covalent H–He bond,²⁰ but a high-level ab initio calculation by MRCI showed that the barrier between HHeF and H + He + F is only 0.5 kcal/mol.²¹ Subsequent quantum dynamics treatments indicated that its lifetime is extremely short, only 157 fs,²¹ though maybe somewhat longer in pressurized solid helium.²²

In addition, the HHeCCH molecule was also predicted to be stable by the B3LYP/6-31G** method with a barrier of 15 kcal/mol between HHeCCH and He + HCCH.²³ Our topological analysis, by using different functionals and basis sets, also reveals a covalent H–He bond in HHeCCH. Unfortunately, our high-level MRCI and CCSD(T) calculations could not confirm the existence of this configuration, so the artifactual stable HHeCCH molecule is completely a result of the defects of DFT.

On the other hand, during the past three decades, there have been a large number of reports of inorganic metallic cage clusters made up of main group elements²⁴ or transition-metal elements.²⁵ Among these cage-like compounds, the endohedrals have been attracting great attention because of their unique

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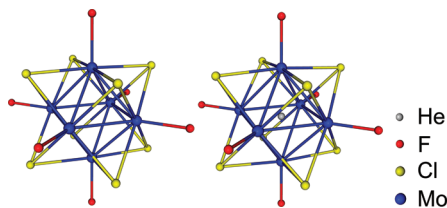


Figure 1. Optimized structures of $[\text{Mo}_6\text{Cl}_8\text{F}_6]^{2-}$ (left) and $\text{He@Mo}_6\text{Cl}_8\text{F}_6$ (right) by O3LYP-c/VTZ. There are six molybdenum atoms lying at the vertices of a regular octahedron, each connected with a fluorine atom, and eight chlorine atoms at the vertices of a regular cube. For $\text{He@Mo}_6\text{Cl}_8\text{F}_6$, the helium atom occupies the center.

structures and novel properties. Up to now, the endo atoms reported experimentally range from light atoms to 5d transition-metals (ref 26 and references therein). This raises an interesting question: is there a stable and non van der Waals helium-in-metallic-cage compound? It is clear that, to capture the helium atom and form a decent helium-metal chemical bond, the empty metallic cage should be very compact with a relatively small inner diameter. The hexanuclear M_6 cluster, well-known in solid state chemistry, is a potential candidate. For $[\text{Mo}_6\text{Cl}_8\text{F}_6]^{2-}$, both experimental²⁷ and theoretical²⁸ researches show that the center-Mo distance is only about 1.8 Å. There are six molybdenum atoms lying at the vertices of a regular octahedron, each connected with a fluorine atom, and eight chlorine atoms at the vertices of a regular cube (O_h symmetry, see Figure 1). Since the center-Mo distance is much smaller than the van der Waals lower limit between He and Mo (see below), we envisage that the $\text{He@Mo}_6\text{Cl}_8\text{F}_6$ cluster, obtained by replacing the two extra electrons of $[\text{Mo}_6\text{Cl}_8\text{F}_6]^{2-}$ by an endo helium atom, may also have a short He-Mo chemical bond.

Here we investigate both $[\text{Mo}_6\text{Cl}_8\text{F}_6]^{2-}$ and $\text{He@Mo}_6\text{Cl}_8\text{F}_6$ by using DFT to find whether or not there is a covalent He-in-cage structure.

Computational Details

For the sake of computational efficiency, relativistic effective core potentials (RECP) for F, Cl, and Mo were used in the present calculations. The effects of spin-orbit coupling (SOC) were not considered as they vanish to first order for closed-shell systems. The valence basis sets of triplet- ζ quality (denoted as VTZ) were used in most of the calculations (for details and references, see the Supporting Information), whereas the ANO-VQZ basis sets (quadruple- ζ contracted in the manner of atomic natural orbitals, see the Supporting Information) were used in some single point calculations.

To select a suitable exchange-correlation functional, the geometry of $[\text{Mo}_6\text{Cl}_8\text{F}_6]^{2-}$ was first fully optimized with various functionals under the O_h symmetry. The details and results are documented in the Supporting Information. It turns out that the O3LYP-c^{29,30} functional performs best and was therefore used to study $\text{He@Mo}_6\text{Cl}_8\text{F}_6$. It should be noted that there are two formulas for O3LYP²⁹ differing in the weight of the nonlocal exchange.³⁰ The commonly used parameter in most program packages is 0.8133 (denoted as O3LYP-c), whereas in Gaussian 03³¹ it is 0.8133×1.43169 .³⁰ In addition, there may be two other variants of O3LYP according to the published total energy benchmarks and the quantum chemistry programs used.³² To the best of our knowledge, tests of the reliability of O3LYP-c have never been published, so the conclusions about other variants of O3LYP^{32,33} may not be suitable for O3LYP-c. For our studied systems, we found that the distance changes from $[\text{Mo}_6\text{Cl}_8\text{F}_6]^{2-}$ to $\text{He@Mo}_6\text{Cl}_8\text{F}_6$ can be looked on approximately

TABLE 1: Optimized Geometries (in Å), HOMO (T_{2u} or E_g), LUMO (E_u or E_g), and HOMO-LUMO Gap (ϵ , in eV) of $[\text{Mo}_6\text{Cl}_8\text{F}_6]^{2-}$ and $\text{He@Mo}_6\text{Cl}_8\text{F}_6$ (X = He or the Cage Center)

cluster	$R_{\text{X-Mo}}$	$R_{\text{Mo-F}}$	$R_{\text{X-Cl}}$	E_{HOMO}	E_{LUMO}	ϵ
$[\text{Mo}_6\text{Cl}_8\text{F}_6]^{2-}$						
O3LYP-c/VTZ	1.821	1.978	3.044	0.01	3.90	3.89
O3LYP-c/ANO-VQZ ^a				0.17	4.04	3.87
2c-SVWN5 ^b	1.82	1.98	3.11			3.4 ^c
expt ^d	1.834	1.994	3.046			~3.7
$\text{He@Mo}_6\text{Cl}_8\text{F}_6$						
O3LYP-c/VTZ	1.888	1.879	3.035	-7.36	-3.68	3.68
O3LYP-c/ANO-VQZ ^a				-7.29	-3.63	3.66

^a Computed at the O3LYP-c/VTZ structure. ^b Reference 28.

^c Computed by the two-component relativistic SAOP potential at the optimized structure of 2c-SVWN5. The HOMO is E_g .²⁸ ^d Reference 27. See Supporting Information for the HOMO-LUMO gap.

as constants and are nearly independent of the functionals.³⁴ Since O3LYP-c obtains the best structure for $[\text{Mo}_6\text{Cl}_8\text{F}_6]^{2-}$, the results should also be reliable for $\text{He@Mo}_6\text{Cl}_8\text{F}_6$.

The calculations with O3LYP-c were performed by using PC-GAMESS³⁵ and Gaussian 03³¹ (for analytical frequencies only³⁶), whereas GAMESS,³⁷ modified versions of NWChem,³⁸ and PC-GAMESS³⁵ were used for the other functionals. At the optimized structures, the harmonic vibrational frequencies were obtained analytically³⁶ and the vertical excitation energies were calculated with time-dependent DFT (TD-DFT). The natural bond orbital (NBO) analysis was carried out by the NBO program³⁹ via the PC-GAMESS interface, and the molecular orbitals were plotted by using the MacMolPlt program.⁴⁰

Results and Discussion

The structures of $[\text{Mo}_6\text{Cl}_8\text{F}_6]^{2-}$ and $\text{He@Mo}_6\text{Cl}_8\text{F}_6$ optimized by using the hybrid O3LYP-c functional are plotted in Figure 1, where the helium atom occupies the center denoted as X. The results are further summarized in Table 1. To have a first glance at the chemical stability, the energy gap between the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals is also given therein.

It is seen from Table 1 that the results for $[\text{Mo}_6\text{Cl}_8\text{F}_6]^{2-}$ by the O3LYP-c functional are in good agreement with the available experimental values.²⁷ The same is expected also for $\text{He@Mo}_6\text{Cl}_8\text{F}_6$.³⁴ For comparison, we may estimate the van der Waals lower limit and the standard covalent distance for the He-Mo bond ($R_{\text{He-Mo}}$) by using the atomic van der Waals radius (R_{vdW}),⁴¹ ionic radius (R_{ion}),⁴² and covalent radius (R_{cov})⁴³ with the following formulas:⁴⁴

$$R_{\text{vdW}}(\text{He-Mo}) = R_{\text{vdW}}(\text{He}) + R_{\text{ion}}(\text{Mo}^{2+}) = 1.40 + 0.83 = 2.23 \text{ Å} \quad (1)$$

and

$$R_{\text{cov}}(\text{He-Mo}) = R_{\text{cov}}(\text{He}) + R_{\text{cov}}(\text{Mo}) = 0.46 + 1.38 = 1.84 \text{ Å} \quad (2)$$

The optimized $R_{\text{He-Mo}}$ for $\text{He@Mo}_6\text{Cl}_8\text{F}_6$ is only 1.89 Å, being much shorter than the above estimated distances of $R_{\text{vdW}}(\text{He-Mo})$ and closer to $R_{\text{cov}}(\text{He-Mo})$. Compared with $[\text{Mo}_6\text{Cl}_8\text{F}_6]^{2-}$, the X/He-Mo distance is elongated by about 0.07 Å whereas the Mo-F bond length is shortened by about 0.1 Å.

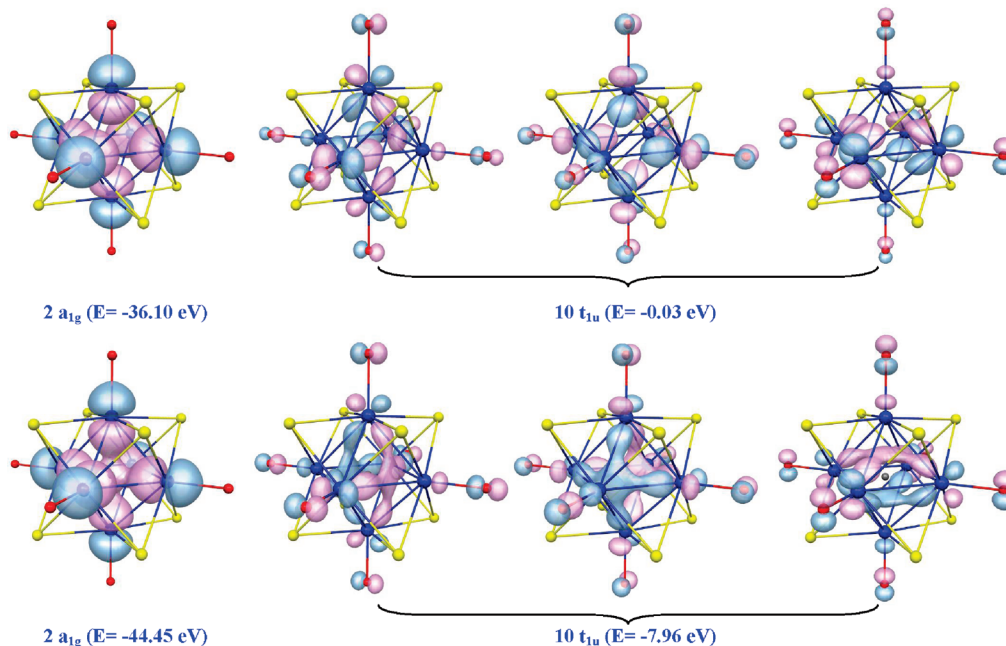


Figure 2. Typical molecular orbitals of [Mo₆Cl₈F₆]²⁻ (upper panel) and He@Mo₆Cl₈F₆ (lower panel) by O3LYP-c/ANO-VQZ. Contour value = 0.04 (2 a_{1g}) or 0.07 (10 t_{1u}).

On the other hand, the X/He—Cl distance is marginally changed. Overall, the internal volume of the Mo₆ cage is enlarged by 11% going from [Mo₆Cl₈F₆]²⁻ to He@Mo₆Cl₈F₆, indicating a larger pressure in the latter.

There are in total 92 occupied orbitals in both He@Mo₆Cl₈F₆ and [Mo₆Cl₈F₆]²⁻, excluding the core ones replaced by RECPs. Because of the pressure of the cage there is noticeable electronic rearrangement upon the formation of the He—Mo bonds. The second a_{1g} (2a_{1g}) and the tenth t_{1u} (10t_{1u}) become bonding orbitals between helium and molybdenum; see the lower panel in Figure 2. Compared with the corresponding orbitals of [Mo₆Cl₈F₆]²⁻ (upper panel), remarkable overlaps can be identified between the He atomic orbitals and the Mo₆ cage orbitals in 2a_{1g} and 10t_{1u}. The 2a_{1g} orbital of [Mo₆Cl₈F₆]²⁻ is composed mainly of the Mo 4p atomic orbitals, but further there is mixed in some He 1s character in the case of He@Mo₆Cl₈F₆. Similarly, the 10t_{1u} orbital of [Mo₆Cl₈F₆]²⁻ is essentially atomic Mo 4d and F 2p with some He 2p character in He@Mo₆Cl₈F₆. As a result, the HOMO—LUMO gap of He@Mo₆Cl₈F₆ is smaller by 0.2 eV than that of [Mo₆Cl₈F₆]²⁻.

Such electronic redistributions may further be reflected in the excitation spectra. To check this, the vertical excitation energies for the low-lying symmetry-allowed ¹T_{1u} states were computed by using TD-DFT with the O3LYP-c functional. The simulated absorption spectra are plotted in Figure 3. The first ¹T_{1u} excited state of [Mo₆Cl₈F₆]²⁻ results from the transition of HOMO (T_{2u}) → LUMO+1 (T_{2g}). The calculated excitation energy is 3.51 eV, being close to the 2c-SAOP result of 3.39 eV.²⁸ The second ¹T_{1u} state stems from the HOMO—2 (T_{1u}) → LUMO+1 (T_{2g}) transition with the energy of 3.63 eV. For the He@Mo₆Cl₈F₆ cluster, the positions of these two absorption bands are nearly the same. Yet, a lower state appears at 3.29 eV, which results mainly from the HOMO—1 (T_{2u}) → LUMO+1 (A_{2g}) transition. For the higher states, no simple correspondence between these two systems can be established because the relative energies of the frontier orbitals are different.

To gain more insight into the nature of the He—Mo bond, the NBO analysis was extended. The NBO charge and bond order (Wiberg index) are documented in Tables 2 and 3,

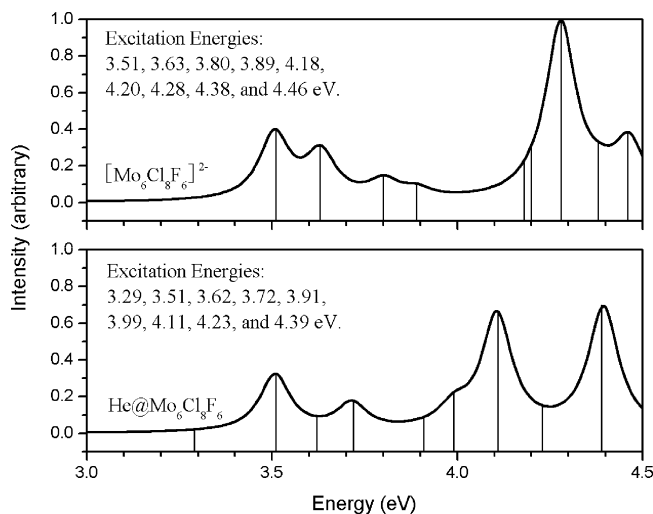


Figure 3. Simulated absorption spectra of [Mo₆Cl₈F₆]²⁻ and He@Mo₆Cl₈F₆ by TD-DFT/O3LYP-c/VTZ for the bright (¹T_{1u}) states.

TABLE 2: NBO Charge on Each Atom for the O3LYP-c Functional

cluster	basis set	Mo	Cl	F	He
[Mo ₆ Cl ₈ F ₆] ²⁻	VTZ	0.27	0.01	−0.61	
	ANO-VQZ	0.38	−0.06	−0.63	
He@Mo ₆ Cl ₈ F ₆	VTZ	0.32	0.09	−0.50	0.38
	ANO-VQZ	0.43	0.02	−0.52	0.34

respectively. There is an a_{1g}-donation of 0.06e from He to Mo on each He—Mo bond and the net charges on He are +0.34 (by ANO-VQZ), being consistent with the population of 1.61e on the He 1s orbital. Moreover, the population of 0.05e on the He 2p reveals some t_{1u}-type back-donation. Both the He—Mo bond order of 0.10 and the gross He bond order of 0.74 are much larger than typical van der Waals interactions, indicating strong interactions between He and Mo.

To confirm the stability of the optimized structures, the harmonic vibrational frequencies were computed by O3LYP-c.

TABLE 3: NBO Wiberg Bond Index for the O3LYP-c Functional

cluster	basis set	bond order				total bond order by atom			
		He–Mo	Mo–Mo	Mo–Cl	Mo–F	He	Mo	Cl	F
[Mo ₆ Cl ₈ F ₆] ^{2−}	VTZ		0.69	0.43	0.49		5.55	1.71	0.78
	ANO-VQZ		0.68	0.42	0.47		5.47	1.67	0.77
He@Mo ₆ Cl ₈ F ₆	VTZ	0.09	0.61	0.46	0.65	0.67	5.49	1.82	0.98
	ANO-VQZ	0.10	0.59	0.45	0.63	0.74	5.42	1.79	0.98

TABLE 4: Harmonic Vibrational Frequencies (in cm^{−1}) Computed by O3LYP-c/VTZ (Absorption Intensities (in km/mol) in Parentheses)

cluster	mode	frequency					
		1	2	3	4	5	6
[Mo ₆ Cl ₈ F ₆] ^{2−}	A _{1g}	296	305	557			
	E _g	187	216	509			
	T _{1g}	154	244				
	T _{2g}	133	194	245	348		
	A _{2u}	279					
	E _u	184					
	T _{1u}	146 (12)	218 (0)	277 (4)	350 (233)	514 (1089)	
		149 ^a	224 ^a	278 ^a	372 ^a	437 ^a	
		151 ^b			343 ^b	516 ^b	
	T _{2u}	101	189	282			
He@Mo ₆ Cl ₈ F ₆	A _{1g}	290	324	665			
	E _g	206	241	630			
	T _{1g}	168	243				
	T _{2g}	134	201	255	347		
	A _{2u}	300					
	E _u	194					
	T _{1u}	131 (12)	226 (2)	277 (1)	340 (123)	621 (1078)	902 (0)
	T _{2u}	106	193	274			

^a Computed by 2c-SVWN5.²⁸ ^b Experimental T_{1u} frequencies.²⁷

The results are collected in Table 4, to be compared with the available experimental and theoretical values. The computed infrared frequencies of [Mo₆Cl₈F₆]^{2−} are in better agreement with the experimental values²⁷ than the ones by 2c-SVWN5.²⁸ Comparable frequencies were also found for He@Mo₆Cl₈F₆, except for an additional dark T_{1u} mode at 902 cm^{−1}, which is mainly due to the vibration of He. Moreover, the T_{1u} frequency at 621 cm^{−1} of He@Mo₆Cl₈F₆ is blue-shifted by about 100 cm^{−1} because the motions of fluorine and helium atoms are combined in this absorption. The remaining vibrational modes are due to internal motions of the cage. Noticeably, compared with [Mo₆Cl₈F₆]^{2−}, the third A_{1g} and E_g modes of He@Mo₆Cl₈F₆ are also blue-shifted by about 100 cm^{−1}. Both of the modes correspond to the Mo–F stretching, so the blue shifts should be ascribed to the shortened Mo–F bond length in He@Mo₆Cl₈F₆.

The dissociation energy was also computed to further confirm the stability of He@Mo₆Cl₈F₆. There are two sites for helium to escape from the Mo₆ cage. One is the midpoint of a Mo–Mo bond (X₁) where the symmetry decreases from O_h to C_{2v}, while the other is the center of a trimolybdenum plane (X₂) with C_{3v} symmetry. The equilibrium distances X–X₁ and X–X₂ are 1.206 and 1.090 Å, respectively. The potential energy curve (PEC) is constructed by moving the helium atom in the X–X₁ and X–X₂ directions. At each point the He–X₁ or He–X₂ distance is fixed whereas the other coordinates are fully optimized. The scanned PEC is shown in Figure 4. In the X–X₂ direction, the energy increases incrementally even when the helium atom moves out of the cage because of the repulsion between the He and Cl atoms. In the X–X₁ direction, however, the PEC has a maximum at about R_{X–He} = 1.206 Å where the helium atom is still inside the cage. After the helium atom moves out of the cage, the total energy decreases rapidly. So the

dissociation can only take place in the X–X₁ direction. The computed dissociation energy is 0.91 (21.0 kcal/mol) and 0.86 eV (19.8 kcal/mol) before and after the ZPE correction, indicating that this endohedral system is chemically stable. The total energy of He@Mo₆Cl₈F₆ is 3.48 eV (80.3 kcal/mol) higher than that of the He + Mo₆Cl₈F₆ system, being much smaller than that of He@adam (about 6.5 eV).^{17b} So the He@Mo₆Cl₈F₆

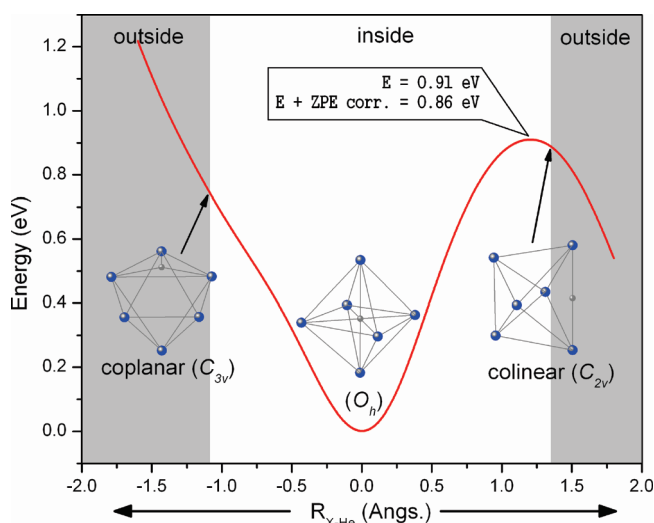


Figure 4. Dissociation of He@Mo₆Cl₈F₆ for the helium atom trapped inside and outside the cage as a function of the direction between the cage center and He. In the positive direction, He moves toward the midpoint of a Mo–Mo bond and dissociates to the energy asymptote of −3.48 eV (−80.3 kcal/mol). In the negative direction, He moves toward the center of a trimolybdenum plane. The helium atom is marked in gray and the molybdenum atoms in blue, whereas the fluorine and chlorine atoms are not shown for simplification.

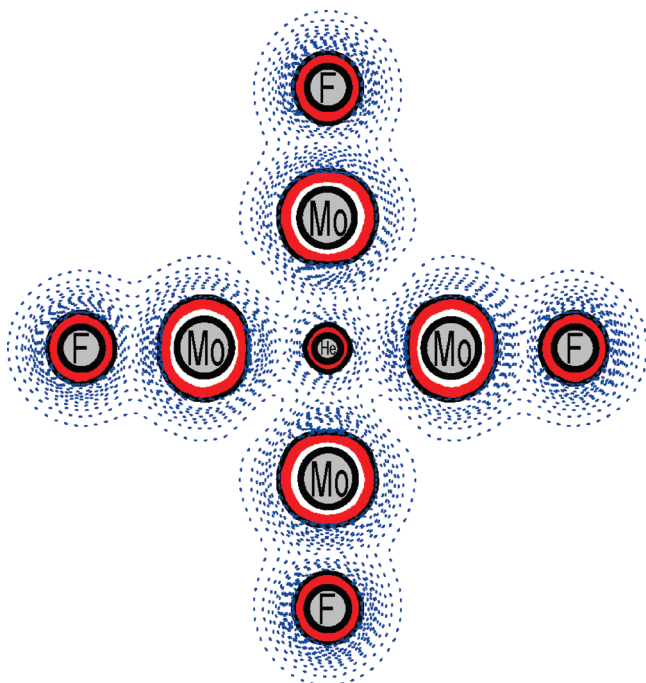


Figure 5. Contour diagram of the Laplacian ($\nabla^2\rho$) of He@Mo₆Cl₈F₆ in the x - y plane. The red, black, and blue lines, respectively, indicate negative, zero, and positive Laplacian of the electron density.

cluster has a greater possibility to be stable experimentally, if it could be formed. The large barrier to dissociation would be difficult to overcome.

There are other molybdenum cages²⁸ with inner diameters larger than that of [Mo₆Cl₈F₆]²⁻. The corresponding helium-doped clusters should be less stable than the one investigated here. Furthermore, He@Mo₆F₈F₆ is expected to be more stable than He@Mo₆Cl₈F₆ studied here, although the [Mo₆F₈F₆]²⁻ cage has not been discovered experimentally.

From the calculated He–Mo bond distance and bond orders only, it is difficult to say whether there are covalent interactions between He and Mo atoms or not. Therefore a topological analysis of the electron density distribution was performed. Figure 5 shows the contour map of the Laplacian in the x - y plane. It is seen that the Laplacian is positive (blue) between He and Mo atoms. This reveals that there are no covalent contributions, and the endo helium atom is constrained only by the Mo–Mo bond instead of the covalent He–Mo bond, being similar to the case of He@adam.¹⁷

Conclusions

We have investigated an endohedral compound, He@Mo₆Cl₈F₆, that encapsulates a central helium atom inside a Mo₆Cl₈F₆ cage. The optimized structure shows that the He–Mo bond is much stronger than typical van der Waals interactions. Its chemical stability is confirmed by all the criteria: HOMO–LUMO gap, NBO bonding analysis, blue shifts in vibrational frequencies, and a significant barrier along the dissociation channel. Although the molybdenum cage is very compact and the optimized He–Mo distance is very short, no He–metal covalent bonding was found. Nevertheless, He@Mo₆Cl₈F₆ is a good candidate for a stable helium-containing complex.

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were performed on the Lonestar Linux Cluster of Texas Advanced Computing Center (TACC).

Supporting Information Available: Full descriptions of the basis sets and the results of [Mo₆Cl₈F₆]²⁻ by different density functionals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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