ity of ultrasound-induced in situ radical formation in liquid CO_2, thereby substantially broadening the application potential for sonochemistry as it allows for the use of environmentally benign CO_2 to replace conventional organic solvents in many reaction systems.

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Closed-Shell Molecules That Ionize More Readily Than Cesium

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We report a class of molecules with extremely low ionization enthalpies, one member of which has been determined to have a gas-phase ionization energy (onset, 3.51 electron volts) lower than that of the cesium atom (which has the lowest gas-phase ionization energy of the elements) or of any other known closed-shell molecule or neutral transient species reported. The molecules are dimetal complexes with the general formula $M_2(hpp)_4$ (where M is Cr, Mo, or W, and hpp is the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine), structurally characterized in the solid state, spectroscopically characterized in the gas phase, and modeled with theoretical computations. The low-energy ionization of each molecule corresponds to the removal of an electron from the delta bonding orbital of the quadruple metal-metal bond, and a strong interaction of this orbital with a filled orbital on the hpp ligands largely accounts for the low ionization energies.

The phenomena of oxidation (electron loss) and reduction (electron gain) are fundamental to chemistry. Even when these processes do not occur as such, more complex chemical processes and properties, such as ionic and covalent bond formation and acid-base behavior, can be understood by analyzing them as a sum of oxidation and reduction steps. Tables of oxidation enthalpies, electron affinities, and electrode (redox) potentials are essential to understanding and teaching chemistry.

Molecules that are thermodynamically stable under normal conditions typically have closed shells of valence electrons and ionization enthalpies of at least 7 eV. The closed-shell molecule with the lowest ionization enthalpy (5.17 eV, vertical) is $[(\eta^5\text{-}C_5H_4{}^iPr)MoSe]_4$ (*1*). In general, values below 5 eV are observed only for molecules or atoms with at least one electron alone in an outer orbital, and even then additional conditions must apply. Typical examples are the alkali metal atoms, which are well known as powerful reducing agents (*2*). Lithium and sodium atoms have ionization enthalpies above 5 eV (5.39 and 5.14 eV, respectively), and only the heavier alkali metals have ionization enthalpies less than 5 eV, with the cesium atom having the lowest of all the elements at 3.89 eV (*3*). We report here measurements and modeling of a class of closed-shell molecules with extremely low ionization energies (IEs). One member of this class ionized at significantly lower energy than cesium atoms and far lower than any other molecules that have been chemically prepared up to this time (*4*–*6*).

We are currently studying the remarkable ability of the hpp ligand (the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine) to cause large negative shifts in the oxidation potentials of paddlewheel complexes of the $M_2(hpp)_4X_n$ ($n = 0, 1, 2$) type, as indicated in electrochemical studies. Recently we reported that the $Mo_2(hpp)_4$ molecule (*7*) (Fig. 1) is so easily oxidized that a chlorinated solvent such as CH_2Cl_2 oxidizes it essentially quantitatively to $Mo_2(hpp)_4Cl$ (*8*). In order to take the $Mo_2(hpp)_4Cl$ molecule to $Mo_2(hpp)_4Cl_2$ or others containing the $[Mo_2(hpp)_4]^{2+}$ unit, an additional (and stronger) oxidizing agent, such as O_2 or Ag^+, is required, but even this oxidation is facile and the product remarkably stable as compared with the reactivity of all other paddlewheel complexes of the $Mo_2{}^{4+}$ core (*9*).

There are a number of other cases in which $M_2(hpp)_4Cl_2$ molecules have been found to be much more accessible than analogous paddlewheel molecules in which

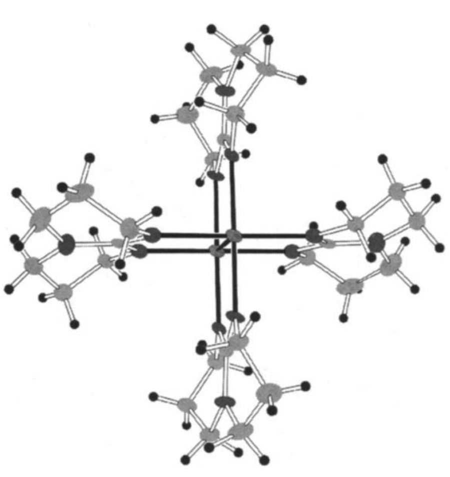

Fig. 1. A thermal ellipsoid drawing of the quadruply bonded $M_2(hpp)_4$ molecules (M = Mo and W) based on X-ray crystallography (*7, 8, 13*). The nonplanarity of the ligands is clearly shown. Distances: Mo–Mo = 2.067(1) Å; W–W = 2.162(1) Å; Mo–N(av) = 2.157[7] Å; W–N(av) = 2.128[5] Å.

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other bridging ligands form the blades of the paddlewheel. We have recently isolated (*10*) $[Os_2(hpp)_4Cl_2]PF_6$, the first structurally characterized compound among several thousand M_2^{n+} compounds (*11*) to contain an M_2^{7+} core.

The W_2^{n+} compounds are always considerably easier to oxidize than their Mo_2^{n+} analogs (*11*), and so we have already investigated the series of compounds $W_2(hpp)_4$, $W_2(hpp)_4Cl$, and $W_2(hpp)_4Cl_2$ (*12*). In this work, $W_2(hpp)_4$ was obtained only in the form of $W_2(hpp)_4 \cdot 2NaHBEt_3$, $NaHBEt_3$ having been used as a reducing agent. In order to obtain the simple crystalline compound $W_2(hpp)_4$, we have used potassium metal in tetrahydrofuran and obtained the crystalline substance by benzene extraction (*13*). $W_2(hpp)_4$ is so easy to oxidize that it can be taken directly by chloroalkanes to $W_2(hpp)_4Cl_2$.

The Mo and W compounds are crystallographically isomorphous, and their molecular structures are similar (Fig. 1) except for the M–M distances, which are 2.067(1) Å for the Mo compound and 2.162(1) Å for the W compound. The difference, 0.095 Å, is typical for such Mo/W homologous pairs, and both are within experimental error of being the shortest known (*14*) for compounds containing Mo_2^{4+} or W_2^{4+} quadruple bonds, respectively.

The photoelectron spectra of three homologous $M_2(hpp)_4$ molecules, with M = Cr (*7*), Mo (*7*), and W (*12*, *13*), have been measured and are shown in Fig. 2. The He I gas-phase photoelectron spectra of the three $M_2(hpp)_4$ molecules were recorded by means of an instrument and experimental methods that have been described previously (*15*–*18*). The first ionization peak of each molecule was modeled analytically with an asymmetric Gaussian peak as described elsewhere (*19*). The results of the photoelectron spectroscopy measurements are presented numerically in Table 1. The ionizations do not show any particularly unusual features except for their extremely low IEs. The He self-ionization, which appears as the sharp band at 4.99 eV on the He I IE scale, as shown in the spectrum of the $Mo_2(hpp)_4$ molecule, is a convenient reference point for the low IEs (*20*). The trend in the IEs from the dichromium to the dimolybdenum to the ditungsten molecule is exactly as expected based on previous studies of quadruple-bonded dimetal molecules with strong donor ligands (*21*). For example, Table 2 shows a comparison of the first IEs of these molecules with the first IEs of the related $M_2(DPhF)_4$ molecules (DPhF is *N*,*N*′ diphenylformamidinate). The IE shift from $M_2(DPhF)_4$ to $M_2(hpp)_4$ is the same 1.46 eV (with an experimental certainty of ±0.03 eV) in each case of Cr, Mo, and W. The shift does not diminish as the ionizations move from the IE of the Cr_2 complex to the very low IE of the W_2 complex, a range of 1.24 eV. This result indicates that saturation has not occurred and an asymptotic limit has not been approached, which suggests that appropriate chemical modifications of the ligand could produce even lower IEs for the molecules.

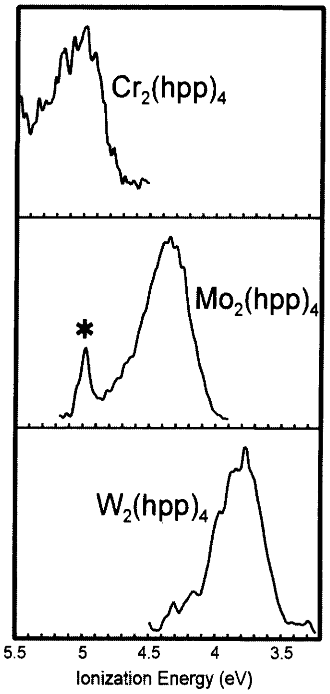

Fig. 2. He I photoelectron spectra of the first ionization bands of $M_2(hpp)_4$ molecules. The peak marked with an asterisk is the He self-ionization.

Table 1. First ionization bands of $M_2(hpp)_4$ molecules, where M = Cr, Mo, and W. All IEs are reported in eV.

Molecule	Vertical IE*	Width to high IE†	Width to low IE‡	Onset IE§
$Cr_2(hpp)_4$	5.00	0.46	0.27	4.76
$Mo_2(hpp)_4$	4.33	0.48	0.36	4.01
$W_2(hpp)_4$	3.76	0.47	0.28	3.51

*The intensity of the ionization band at energy *E* is given by the skewed Gaussian form $C(E) = A \times \exp[-(4\ln 2) \times (\{E - P\}/W)^2]$, where *P* is defined as the vertical IE and *W* is the half-width of the band on the high IE side if $E > P$, or *W* is the halfwidth of the band on the low IE side if $E < P$. †The ionization peak positions are reproducible to ±0.02 eV (≈3σ level). ‡The widths are reproducible to ±0.04 eV (≈3σ level). §The low-energy onset of the band is defined as the vertical (peak) IE minus 0.9 times the width to low IE. The accuracy of the ionization onset energy is estimated to be ±0.05 eV.

The first IEs of these molecules are compared with the first ionizations of atoms and other known and characterized molecules with ionizations below 5 eV in Table 3 (*22*–*26*). The onset of the ionization of $W_2(hpp)_4$ is nearly 0.4 eV lower in energy than for Cs. The low IEs listed in Table 3 are, in every other case, associated with electron configurations that have unpaired spins. Most often, the atoms and molecules with lowest IEs have just one electron beyond filled shells. The $(\eta^6\text{-}C_6Et_6)(\eta^5\text{-}C_5Me_5)Fe$ and $(\eta^5\text{-}C_5Me_5)_2Co$ molecules each have a single electron beyond the favored 18-electron valence configurations, and the electron is in an orbital that is net antibonding between the metal

Table 2. Comparison of first vertical IEs of $M_2(DPhF)_4$ and $M_2(hpp)_4$ molecules where M = Cr, Mo, and W. The vertical IEs are in eV ±0.02 eV; shifts are ±0.03 eV.

	$M_2(DPhF)_4$	$M_2(hpp)_4$	Shift
M = Cr	6.44	5.00	1.44
M = Mo	5.80	4.33	1.47
M = W	5.23	3.76	1.47

Table 3. First ionizations of atoms and chemically prepared and isolated molecules below 5 eV. Transient and low-temperature species detected in molecular beam techniques are discussed in the text. All of the dinuclear molecules have closed-shell singlet $\sigma^2\pi^4\delta^2$ configurations.

Molecule or atom	Spin state	IE (eV)	Type	Ref.
$W_2(hpp)_4$		3.514	Onset	This work
$W_2(hpp)_4$		3.76	Vertical	This work
Cs	Doublet	3.89	Atomic	(*3*, *22*, *23*)
$(\eta^6\text{-}C_6Et_6)\ (\eta^5\text{-}C_5Me_5)Fe$	Doublet	3.95	Onset	(*23*)
$Mo_2(hpp)_4$		4.01	Onset	This work
Fr	Doublet	4.07	Atomic	(*22*, *23*)
Rb	Doublet	4.18	Atomic	(*3*, *22*, *23*)
$(\eta^6\text{-}C_6Et_6)(\ \eta^5\text{-}C_5Me_5)Fe$	Doublet	4.21	Vertical	(*23*)
$Mo_2(hpp)_4$		4.33	Vertical	This work
K	Doublet	4.34	Atomic	(*3*, *22*, *23*)
$Cp(\eta^6\text{-}C_6Et_6)Fe$	Doublet	4.54	Vertical	(*24*)
$Cp(\eta^6\text{-}C_6Me_6)Fe$	Doublet	4.68	Vertical	(*24*)
$(\eta^5\text{-}C_5Me_5)_2Co$	Doublet	4.71	Vertical	(*25*)
$Cp(\eta^6\text{-}C_6H_3(CMe_3)_3)Fe$	Doublet	4.74	Vertical	(*24*)
$Cr_2(hpp)_4$		4.76	Onset	This work
$(\eta^5\text{-}C_9Me_7)_2Co$	Doublet	4.89	Vertical	(*26*)
$(\eta^5\text{-}C_5Me_5)_2Cr$	Triplet	4.93	Vertical	(*25*)
$Cr_2(hpp)_4$		5.00	Vertical	This work

and the ligands. In the $M_2(hpp)_4$ molecules, the first ionizations correspond to electrons in orbitals that are bonding between the metals.

A few transient neutral molecules with IEs comparable to those reported here have been produced in molecular beams and detected by mass spectrometry. Of these, the lowest reported IE for a closed-shell neutral species is 3.7 ± 0.1 eV for Cs_2 (*27*), which is still higher than we observed for $W_2(hpp)_4$. The lowest IE we have found reported for any neutral species is for Cs_2Cl, again produced only as a transient in molecular beams, with a measured IE onset of 3.4 ± 0.2 (*28*). This energy is the same, within experimental uncertainty, to the ionization onset of $W_2(hpp)_4$ at 3.51 ± 0.05 eV. Cs_2Cl again has one electron beyond the filled shell.

To obtain insight into why this class of molecules has unprecedentedly low IEs, while at the same time they have exceptionally short (and thus, presumably, strong) M–M bonds, electronic structure calculations were carried out. The geometry of the $M_2(hpp)_4$ molecules for M = Mo and W was fully optimized (*29–31*) both at the Hartree-Fock (HF) and the density functional theory (DFT) (B3LYP) (*32–36*) levels of theory. The resulting geometric parameters were in excellent agreement with the experimental measurements (*37*).

The calculated vertical IEs of 3.50 eV for $W_2(hpp)_4$ and 3.85 eV for $Mo_2(hpp)_4$ are about 10% smaller than the corresponding experimental values. The difference of the vertical IEs of the $M_2(hpp)_4$ molecules, (Mo versus W), is 0.35 eV, only 60% of the experimental result (0.57 eV).

Orbital analysis shows that both $Mo_2(hpp)_4$ and $W_2(hpp)_4$ molecules have the electronic configuration of $\sigma^2\pi^4\delta^2$. The highest occupied molecular orbital (HOMO) of these two molecules displays δ-bond character. A detailed analysis of the molecular orbitals reveals that the δ orbitals of the metal cores strongly interact with the b_2 orbitals of the $(hpp)_4{}^{4-}$ ligand groups, and the δ* orbitals of the metal cores strongly interact with the b_1 orbitals of the ligand groups. Four resulting δ-type orbitals are shown in Fig. 3, denoted as $\delta + L_{b2}$, $\delta - L_{b2}$, $\delta^* + L_{b1}$, and $\delta^* - L_{b1}$, respectively. In contrast to the $M_2(DPhF)_4$ molecules, where the linear combination of the δ orbital from the metal core with both the occupied b_{2g} orbital and the unoccupied b^*_{2g} orbital from the formamidinate ligands

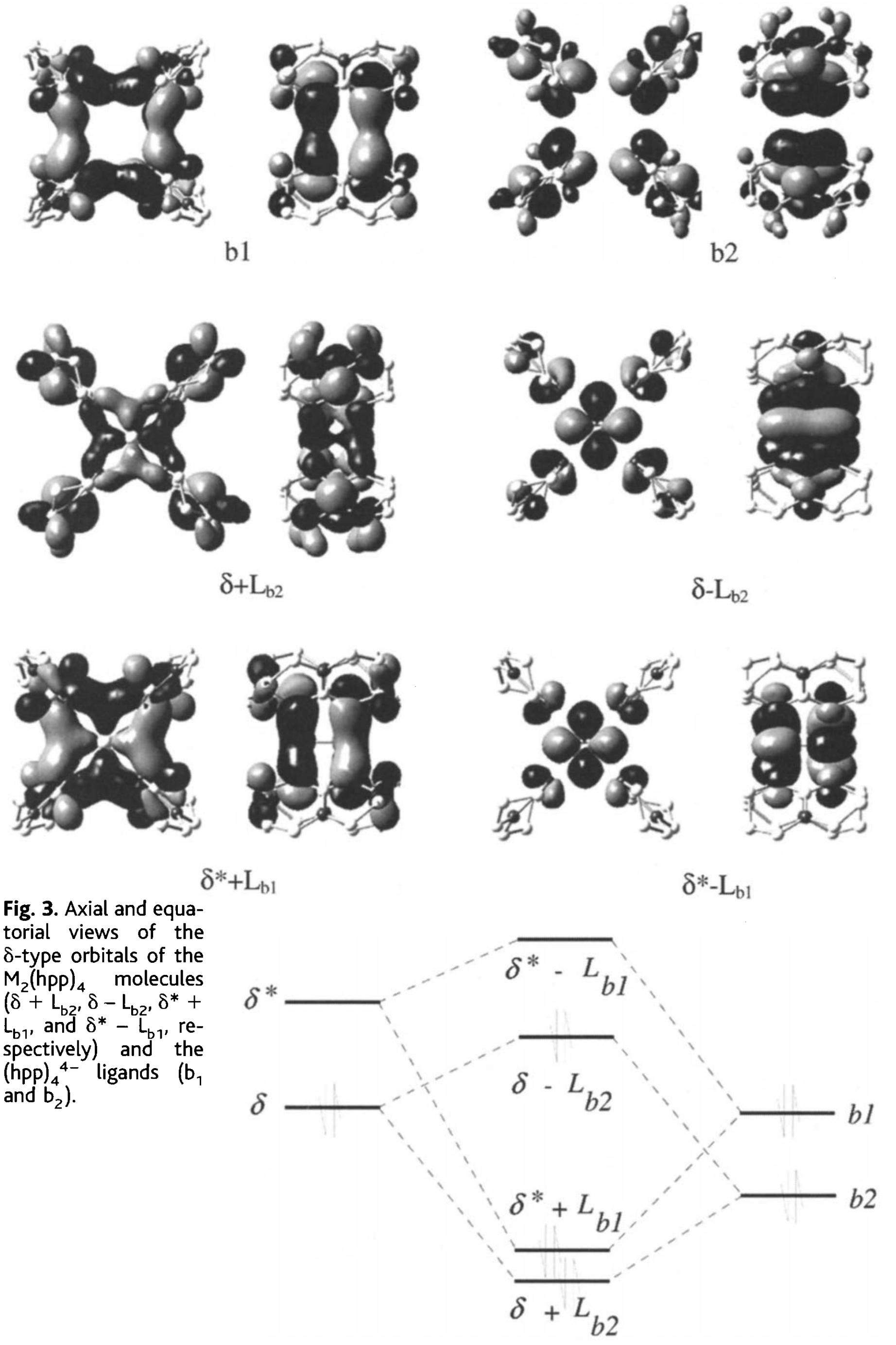

Fig. 3. Axial and equatorial views of the δ-type orbitals of the $M_2(hpp)_4$ molecules ($\delta + L_{b2}$, $\delta - L_{b2}$, $\delta^* + L_{b1}$, and $\delta^* - L_{b1}$, respectively) and the $(hpp)_4{}^{4-}$ ligands (b_1 and b_2).

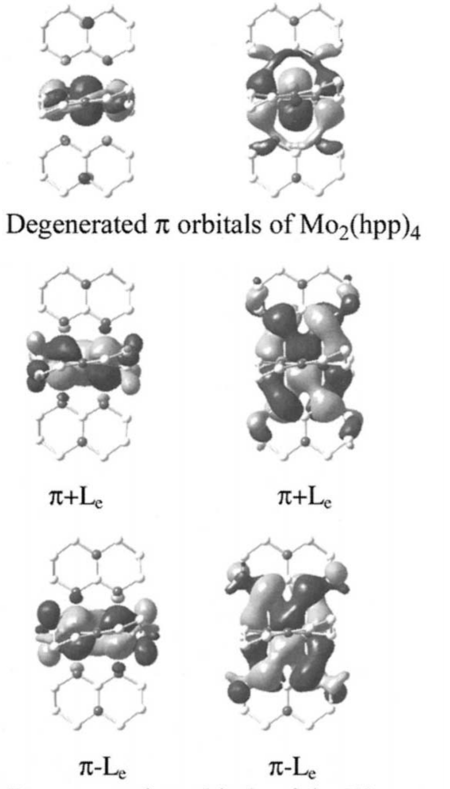

Fig. 4. The Mo-dominated π bonding orbitals of $Mo_2(hpp)_4$ **(top)** and the two sets of the π bonding orbitals of $W_2(hpp)_4$ **(bottom)**.

leads to only a slight energy destabilization for the δ-like HOMO (*21*), the strong antibonding interaction between the δ orbital of the metal core and the b_2 orbital of the hpp ligands causes a marked energy destabilization for the δ-type HOMO ($\delta\text{-}L_{b2}$) in the $M_2(hpp)_4$ compounds.

To understand the extent to which the slightly lower IE of $W_2(hpp)_4$ as compared to $Mo_2(hpp)_4$ is intrinsic to the M_2 cores or caused by the coordinating effects of the ligands, the IEs of the M_2^{4+} cores also have been calculated at the DFT level of theory. The IE difference between W and Mo for the M_2^{4+} core is evaluated to be 0.29 eV, implying that the lower IE of the W compound is intrinsic. However, because the IE difference for $M_2(hpp)_4$ is calculated to be 0.06 eV larger, the interactions between the ligands and the metals may be slightly stronger for W.

These interactions can be further understood by an analysis of the orbital energies for the $\delta + L_{b2}$ and $\delta - L_{b2}$ orbitals. The energy splitting for $\delta + L_{b2}$ and $\delta - L_{b2}$ is 3.46 eV for the W complex, 0.18 eV larger than that of 3.28 eV for Mo. Also the splitting for the $\delta^* + L_{b1}$, and $\delta^* - L_{b1}$ amounts to 6.12 eV and 5.98 eV for W and Mo, respectively. A relatively stronger mixing between the ligands and the W core compared to the Mo core can be seen in the π type orbitals (Fig. 4). Because of their interaction with the *e* orbitals of the ligands $(hpp)_4^{4-}$, the degenerate π bonding orbitals of the W core split into two sets that are close in energy. However, the π bonding orbitals of the $Mo_2(hpp)_4$ are clearly Mo-dominated and are less influenced by the ligands in these calculations.

Because of the ease with which the $M_2(hpp)_4$ molecules can lose an electron (much more easily than the sodium atom, for example) the question could be asked: Will these substances dissolve in liquid ammonia to give blue solutions containing solvated electrons? They do not. The reason sodium dissolves is that a major contribution to its behavior with liquid ammonia is the solvation energy of the Na^+ ion, presumably by six NH_3 molecules in the primary coordination sphere of a small ion with a high charge-to-radius ratio. This energy more than compensates for the heat of atomization of Na metal. The $M_2(hpp)_4$ molecules, although they surrender the electron more easily than the Na atom and have much lower heats of vaporization, have much smaller solvation energies. The positive charge is spread over two larger metal atoms, each of which could bind only one NH_3 molecule. In solvents with little or no polarity, however, where the neutral molecules themselves are already soluble and in the presence of an electron acceptor (such as an electrode), the $M_2(hpp)_4$ molecules are better reductants than alkali metal atoms.

The special properties of these molecules offer a new class of reductants and electron reservoirs for known chemical and materials processes and offer possibilities for novel chemical transformations and behavior. The chemical behavior of molecules that lose an electron as easily as found for these $M_2(hpp)_4$ molecules is expected to be unprecedented in certain respects. As already reported (*8*, *13*), they react immediately with chlorocarbons. They also react with electron acceptors such as 7,7′,8,8′-tetracyanoquinodimethide (TCNQ) and buckminsterfullerene.

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37. Specifically, the Mo–Mo bond length of 2.090 Å at the DFT level is only 0.023 Å longer than that from the crystal data. The Mo–N distance of 2.187 Å agrees well with the experimental value of 2.157 Å. Theoretical predictions of 2.180 Å and 2.200 Å for the W–W and W–N atomic distances are close to the crystal values of 2.162 Å and 2.128 Å, respectively. Moreover, the bond length difference of 0.090 Å for W_2 and Mo_2 compounds is in excellent accord with the experimental observation of 0.095 Å.
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