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A DFT Study on the Electronic and Redox Properties of $[PW_{11}O_{39}(ReN)]^{n-}$ (n = 3, 4, 5) and $[PW_{11}O_{39}(OsN)]^{2-}$

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DFT calculations were carried out to investigate the electronic and redox properties of nitrido-functionalized polyoxometalate species, $[PW_{11}O_{39}(ReN)]^{n-}$ (n = 3, 4, 5) and $[PW_{11}O_{39}(OsN)]^{2-}$. The rhenium- and osmium-nitrido effectively modify the electronic properties. The LUMOs in fully oxidized $[PW_{11}O_{39}(ReN)]^{3-}$ and $[PW_{11}O_{39}(OsN)]^{2-}$ are mainly concentrated on the Re and Os centers. The high-valent transition metals Re and Os modify the components and energies of the LUMO. The LUMO energies of $[PW_{11}O_{39}(ReN)]^{3-}$ and $[PW_{11}O_{39}(OsN)]^{2-}$ are lower than that of related Keggin $[PW_{12}O_{40}]^{3-}$. In addition, Re centers will prefer to accept the electrons in the first and second reduced process of fully oxidized $[PW_{11}O_{39}(ReN)]^{3-}$.

Introduction

Polyoxometalates (POMs) are anionic clusters of discrete structure commonly based on molybdenum or tungsten oxides.[1–3] Most POMs possess an extensive and reversible redox chemistry and some contain multiple unpaired d-electrons that make them useful in several fields including catalysis, material science, and magnetochemistry.

One of the important applications of POMs is based on their potential to act as an electron acceptor, which leads to the possibility of the formation of charge-transfer or electron donor-acceptor materials with interesting electronic and magnetic properties.[4,5] Over the past few years, research on POMs has greatly expanded to investigate functionalized POMs by the incorporation or coordination of organic or organometallic moieties to produce novel systems.[6–9] The modification and functionalization of POMs have provided the means to more fully exploit these desirable attributes. Rhenium is known to incorporate into Keggin structures by virtue of its appropriate radius and ability to form short terminal M=O bonds.[10] Three nitrido-functionalized polyoxometalate species, $(nBu_4N)_4[PW_{11}O_{39}(OsN)]$, $(nBu_4N)_4[PW_{11}O_{39}(ReN)]$, and $(nBu_4N)_3[PW_{11}O_{39}(ReN)]$, which feature the incorporation of $[Os^{VI}{\equiv}N]^{3+}$, $[Re^{VI}{\equiv}N]^{3+}$, and $[Re^{VII}{\equiv}N]^{4+}$ fragments into the framework of a Keggin-type heteropolyanion were reported by Maatta.[11] It is the first time that rhenium- and osmium-nitrido were inserted into the polyoxometalate. Several questions drew our attention. First, how does the rhenium- or osmium-nitrido modify the structural and electronic properties? Second, how are the redox properties of POMs modified by the rhenium-nitrido segment? Third, does the rhenium atom prefer to accept an electron when the $[PW_{11}O_{39}(ReN)]^{3-}$ is reduced? Following our investigations of the electronic properties, bonding nature, stabilities, and nonlinear optical properties of POMs,[12–16] density functional theory (DFT), which has been proven to be a significant tool for understanding and rationalizing the electronic and magnetic properties of polyanions,[17–26] was employed to pursue the questions mentioned above. Our main objective was to investigate the effect of high-valent metal nitrido on the electronic and redox properties of POMs.

Methodology

All calculations reported in this work were carried out with the ADF2005.01 program.[27] The local density approximation (LDA) characterized by the Vosko–Wilk–Nusair (VWN)[28] parameterization for correlation was used. Becke[29]and Perdew[30] gradient corrections were used for the exchange and correlation energy, respectively. Triple-ζ plus polarization Slater basis sets were used to describe the electrons of main group elements (O, C, H) and the valence electrons of all transitional-metal atoms (Re, Os, W). The internal or core electrons (1s–4d for Re, Os, W) were frozen and described by single Slater functions. The relativistic effects were taken into account by means of the zero-order regular approximation (ZORA).[31] The integration parameter in the molecular calculations, which determines the precision of the numerical integral, was set to 5.0. The default optimization convergence criteria in the ADF were used.

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For purposes of comparison, calculations were also carried out on $[PW_{12}O_{40}]^{3-}$. A short-hand notation is used for the polyanions, without oxygen atoms and anion charge, and it specifies the number of blue electrons as well as the substituted transition metal oxidation states (e.g. $[PW_{12}O_{40}]^{3-}$ = PW_{12}, $[PW_{11}O_{39}(ReN)]^{3-}$ = $PW_{11}ReN$, and $[PW_{11}O_{39}(ReN)]^{4-}$ = $PW_{11}ReN1e$, where e specifies the electrons which the polyanion accepted).

Results and Discussion

The Effect of the Rhenium- or Osmium-Nitrido Segment on Geometrical Structure

The Keggin anion is made of an assembly of 12 MO_6 octahedrons sharing their corners or edges with a central XO_4 tetrahedron. The metal–oxygen bonds in the Keggin framework can be divided into three sets according to whether their oxygen atoms are tetrahedral (O_a), bridging (O_b), or terminal (O_t). From the point-of-view of structure, the transition metals Re and Os are inserted into a lacunary position of PW_{12}. At the same time, Re and Os link to the nitrogen atom instead of the terminal oxygen atom (O_t). Figure 1 shows the optimized structure of $PW_{11}ReN$, and other structures in this article are all similar to it.

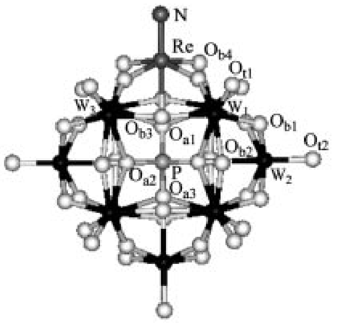

Figure 1. The calculation model $PW_{11}ReN$.

Some selected bond lengths are listed in Table 1. Compared with PW_{12}, the bonds in $PW_{11}ReN$ are lengthened, while the bonds in $PW_{11}OsN$ are shortened. The calculated atomic radii[32] of tungsten, rhenium, and osmium are 1.93, 1.88, and 1.85 Å, respectively. The $PW_{11}OsN$ is contracted when the osmium-nitrido segment substitutes the W=O unit because the radius of Os^{VIII} is smaller than that of W^{VI}. Although the radius of Re^{VII} is slightly smaller than that of W^{VI}, the cluster size of $PW_{11}ReN$ is enlarged. This may be due to the slightly weak interaction between Re and its adjacent atoms compared with related bonds in PW_{12}. As Poblet demonstrated that the reduction of a fully oxidized anion is accompanied by an expansion of the geometry,[33] the bonds in single- and double-electron reduced polyanions of $PW_{11}ReN$ are elongated. So, the reduced polyanions are loosened by adding reduced electrons. The lengthening of the bond would lead to a weakening of the bond strength, and then the electronic properties would be changed.

Table 1. Selected bond lengths [Å] of systems.

	PW_{12}	$PW_{11}ReN$	$PW_{11}ReN1e$	$PW_{11}ReN2e$	$PW_{11}OsN$
W_1–O_{b1}	1.938	1.941	1.958	1.969	1.922
W_1–O_{b2}	1.938	1.943	1.979	1.975	1.909
W_3–O_{b3}	1.932	1.932	1.936	1.936	1.936
W_1–O_{t1}	1.725	1.726	1.735	1.746	1.720
W_2–O_{t2}	1.725	1.726	1.734	1.744	1.719
P–O_{a1}	1.555	1.554	1.553	1.553	1.562
P–O_{a2}	1.555	1.556	1.558	1.560	1.555
P–O_{a3}	1.555	1.558	1.561	1.563	1.555
W(Re, Os)–P	3.608	3.619	3.654	3.655	3.573
Re(Os)–N		1.678	1.680	1.686	1.676
Re(Os)–O_{b4}		1.930	1.982	1.985	1.900

Electronic Properties of Fully Oxidized $PW_{11}ReN$ and $PW_{11}OsN$

For fully oxidized polyanions, one of the remarkable properties concerns redox behavior. The molecular orbital distribution will give reasonable information about the redox properties of $PW_{11}Re$ and $PW_{11}Os$. In order to investigate the effect of the rhenium- or osmium-nitrido segment on the electronic properties of polyanions, the frontier molecular orbitals (FMO) of PW_{12}, $PW_{11}ReN$, and $PW_{11}OsN$ are compared. For Keggin anion PW_{12}, the ground-state configuration is typical of a fully oxidized polyanion for which the highest molecular orbital (HOMO) delocalizes over oxo-ligands, and the lowest molecular orbital (LUMO) delocalizes over the d-shells of tungsten atoms with some antibonding participation of oxygen orbitals (Figure 2).[24] The LUMO is a doubly degenerate orbital of symmetry e, and the LUMO+1 is a triply degenerate orbital of symmetry t_1.

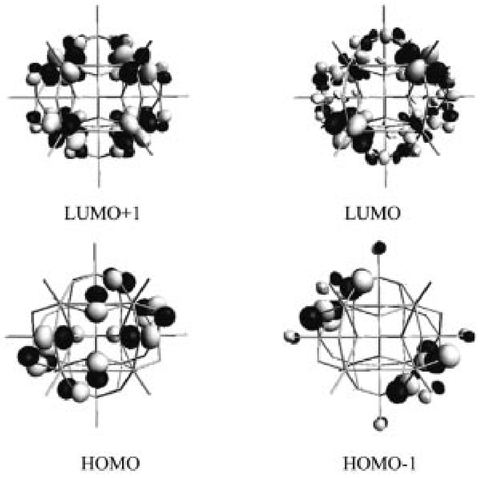

Figure 2. The molecular orbitals of PW_{12}.

The doubly degenerate HOMO and LUMO in PW_{12} split into two orbitals of symmetry a' and a'' in $PW_{11}ReN$ and $PW_{11}OsN$. The HOMO in $PW_{11}ReN$ is mainly delocalized over the bridge oxygen atoms, but the nitrogen atom has a contribution (6.58%; Figure 3). The LUMO is quite different from that of PW_{12} and is mainly localized on the Re atom (39.76%), although there is some contribution from the tungsten atoms (16.46%). The LUMO+1 in $PW_{11}ReN$ concentrates on the tungsten and bridge oxygen atoms, which is similar to the LUMO in PW_{12}. It can be proposed that the rhenium-nitrido segment mainly modifies the unoccupied orbitals and the redox properties would be modified as the redox property of a polyanion depends on the energy and compositions of the LUMO. The LUMO energy and the HOMO–LUMO energy gap are lower than that of PW_{12} (Figure 4), so the electron transition between HOMO and LUMO is much easier.

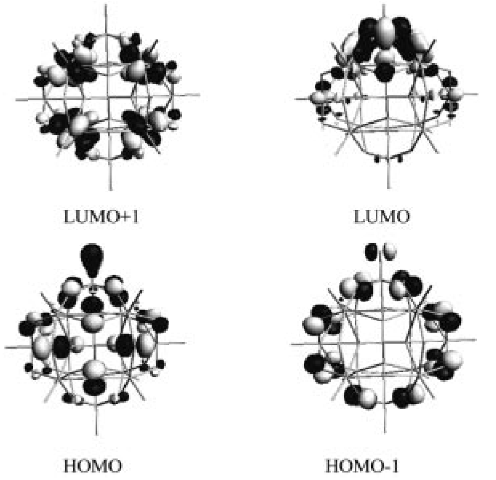

Figure 3. The molecular orbitals of $PW_{11}ReN$.

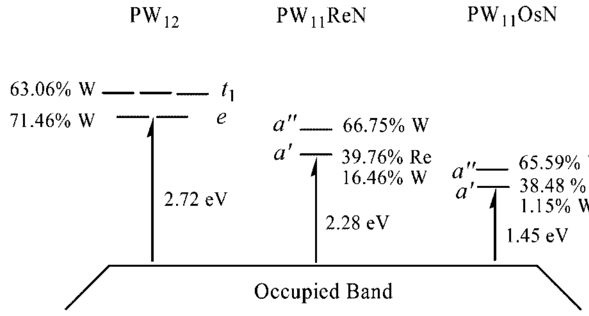

Figure 4. The energy level of PW_{12}, $PW_{11}Re$, and $PW_{11}Os$.

Let us now consider the osmium–nitrido substituted derivative $PW_{11}OsN$. The FMOs are presented in Figure 5. Here, the situation is somewhat different. The HOMO and HOMO-1 for $PW_{11}OsN$ are similar to PW_{12}, whereas the lowest metal orbitals are mainly localized on osmium (38.48%), and the contribution of tungsten atoms is only 1.15%. The d-osmium orbitals are lower in energy than the tungsten orbitals and strong competition between the osmium and tungsten orbitals would occur; $PW_{11}OsN$ tends to have a lower HOMO–LUMO energy gap and LUMO energy as presented in Figure 4.

The question we are now concerned with is whether tungsten or high-valent transition-metal Re or Os accept the extra electrons when the cluster is reduced. Taking $PW_{11}Re$ as an example, we investigated the reduction process in detail. It is known that the redox properties depend on the energy and composition of the LUMO, as the LUMO formally delocalizes over the metal atoms, which determine the redox properties of POMs.[21]

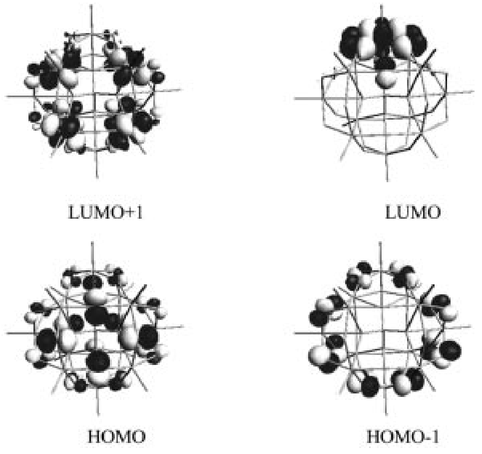

Figure 5. The molecular orbitals of $PW_{11}OsN$.

The LUMO of $PW_{11}Re$ is composed of 39.76% Re and 16.46%W contributions. It is more likely that Re will prefer to accept extra electrons when the cluster is reduced. In order to investigate the reduced center, the reduced species $PW_{11}Re1e$ and $PW_{11}Re2e$ were calculated. Table 2 shows the spin density for two reduced species of $PW_{11}Re$, which indicates that the extra electron in the monoreduced $PW_{11}Re1e$ localizes on the Re center with a 0.67 spin alpha electron. This suggests that $PW_{11}Re^{VII}$ is reduced to $PW_{11}Re^{VI}$ when the cluster accepts one electron.

Table 2. Spin density (α-β) for $PW_{11}Re1e$ and $PW_{11}Re2e$.

	$PW_{11}ReN1e$	$PW_{11}ReN2e$
Re	0.6700	0.6533
W	0.0008~0.0456	0.0081~0.1618

The LUMO in monoreduced $PW_{11}Re1e$ has a participation of Re orbitals (35.23%), and the contribution of tungsten increases to 27.36% (Figure 6). The spin density analysis indicates that 65% of the spin density is localized over the Re center and the rest of the spin density is delocalized over the polar tungsten atoms. The HOMO is entirely localized over the oxygen atoms. The additional electron mainly goes to the sphere of Re and $PW_{11}Re^{VI}N$ would be reduced to $PW_{11}Re^{V}N$. In addition, the LUMO in $PW_{11}Re2e$ has a little participation of the Re orbitals (1.91%). So, this suggests that the first and second reduced process of $PW_{11}ReN$ is $Re^{VII} \rightarrow Re^{VI} \rightarrow Re^{V}$, which is in agreement with the experimental investigation.[11]

Conclusions

The effect of rhenium or osmium-nitrido on the electronic and redox properties of POMs was investigated by means of density functional calculations. The above results can be summarized in three principal conclusions: (1) Re and Os mainly modified the unoccupied orbitals of $[PW_{11}O_{39}(ReN)]^{3-}$ and $[PW_{11}O_{39}(OsN)]^{2-}$, especially the

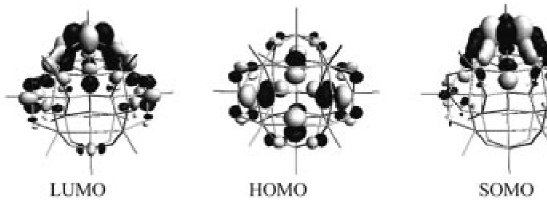

Figure 6. The molecular orbitals of $PW_{11}ReN1e$.

LUMO. The LUMO of fully oxidized $[PW_{11}O_{39}(ReN)]^{3-}$ is quite different from that of $[PW_{12}O_{40}]^{3-}$ and is localized on the Re atom, and the tungsten atoms also contribute to some extent. The LUMO of $[PW_{11}O_{39}(OsN)]^{2-}$ is mainly localized on osmium, and the contribution from the tungsten atoms is quite small. (2) Compared to Keggin $[PW_{12}O_{40}]^{3-}$, the LUMO energy in $[PW_{11}O_{39}(ReN)]^{3-}$ and $[PW_{11}O_{39}(OsN)]^{2-}$ is lower than that of $[PW_{12}O_{40}]^{3-}$, and the electron transition between HOMO and LUMO of nitrido-functionalized polyoxometalate species $[PW_{11}O_{39}(OsN)]^{2-}$ and $[PW_{11}O_{39}(ReN)]^{3-}$ is much easier compared with that of Keggin $[PW_{12}O_{40}]^{3-}$. (3) The Re center prefers to accept the extra electrons in the first and second reduced process of $PW_{11}ReN$, so the reduced process is $[PW_{11}O_{39}(Re^{VII}N)]^{3-} \rightarrow [PW_{11}O_{39}(Re^{VI}N)]^{4-} \rightarrow [PW_{11}O_{39}(Re^{V}N)]^{5-}$.

Supporting Information (see footnote on the first page of this article): Cartesian coordinates for the BP/TZP optimized $[PW_{11}O_{39}(ReN)]^{3-}$, $[PW_{11}O_{39}(ReN)]^{4-}$, $[PW_{11}O_{39}(ReN)]^{5-}$, $[PW_{11}O_{39}(OsN)]^{2-}$, and $[PW_{12}O_{40}]^{3-}$ structures.

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