J. Am. Chem. Soc. **2001,** *123,* 2825−2829

Electron Delocalization and Magnetic State of Doubly-Reduced Polyoxometalates

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Received July 31, 2000. Revised Manuscript Received January 12, 2001

Abstract: Different mechanisms of spin pairing in doubly reduced polyoxometalates are studied on the basis of quantum-chemical DFT calculations. Using the nitrosyl derivative of decamolybdate $[Mo_{10}O_{25}(OMe)_6(NO)]^-$ (**I**) as an example, we elucidate an important role of the delocalization of "blue electrons". The charge distributions and spin states are studied for the series of isomers of **I** differing by positions of methyl groups (modeled by hydrogens). Three different states are calculated for each isomer: spin triplet, spin-restricted singlet, and a broken symmetry state. If the quasihomogeneous distribution of the "blue electrons" density is weakly perturbed by protonation, the delocalization mechanism is responsible for the spin pairing. It is evidenced by the singlet ground state given by a spin-restricted solution. If the perturbation of charge distribution is strong enough and the "blue electrons" density is localized at several metal centers, the exchange mechanism becomes active. A lowest energy broken symmetry state indicates the antiferromagnetic nature of the singlet ground state. The modulation of magnetic interactions in reduced polyoxoanions by external perturbations provides new possibilities for design of molecular magnetic materials.

Introduction

Polyoxometalates constitute a large group of polynuclear metal−oxygen anionic clusters. Their interesting and potentially valuable physical and chemical properties found impact in several disciplines such as catalysis, materials science, and medicine.[1−4] An important characteristic of polyoxometalates with only one nonshared oxo ligand per metal atom (type I in the Pope classification[5]) is their ability to accommodate one or several excess electrons.[6] This reduction is reversible and occurs with minimal structural modifications. The reduced systems frequently possess a deep blue color, which justifies their name "poly blues" or "heteropoly blues", if the polyoxoanion (POA) includes a heteroatom. The excess electrons in blue species are delocalized over numerous centers of the POA framework.

The electronic configuration of metal ions (more often these are Mo^{6+}, W^{6+}, and V^{5+}) in oxidized POA is d^0. If more than one excess electron is added to such a closed electronic shell system, in principle several spin states could arise. So for POA reduced by two electrons one can expect states with $S = 0$ or 1. The magnetic properties of different doubly reduced POA were studied by Baker with co-workers[7] using NMR. In all cases, a strong tendency to electron spin pairing was found. Even at room temperature no signs of the population of the spin triplet state have been observed. Similar behavior was found for other POA reduced by an even number of electrons. To explain the strong stabilization of the nonmagnetic ground state, Baker et al. proposed the existence of a multiroute antiferromagnetic exchange. However, this mechanism can be questioned. In fact, the same NMR data show that the blue electrons usually do not reside on adjacent metal atoms. It is difficult in this case of well separated spins to expect a very large antiferromagnetic exchange. Another explanation was proposed by one of us[8] and by Tsukerblat et al.[9] It was found that a strong stabilization of the spin singlet state can appear as a result of electron-transfer processes between metal centers. This effect was demonstrated by model Hamiltonian methods for POA with Keggin[8a,9a] and Dawson-type[9b] structures and for the decatungstate anion.[8b] However, oversimplified model Hamiltonian methods using some phenomenological electron-transfer parameters cannot elucidate the active mechanism in a particular compound. A quantum-chemical molecular orbital calculation should be a useful tool in such context. Numerous calculations of the electronic structure of polyoxoanions are known in the literature. If the earliest theoretical works on polyoxoanions were

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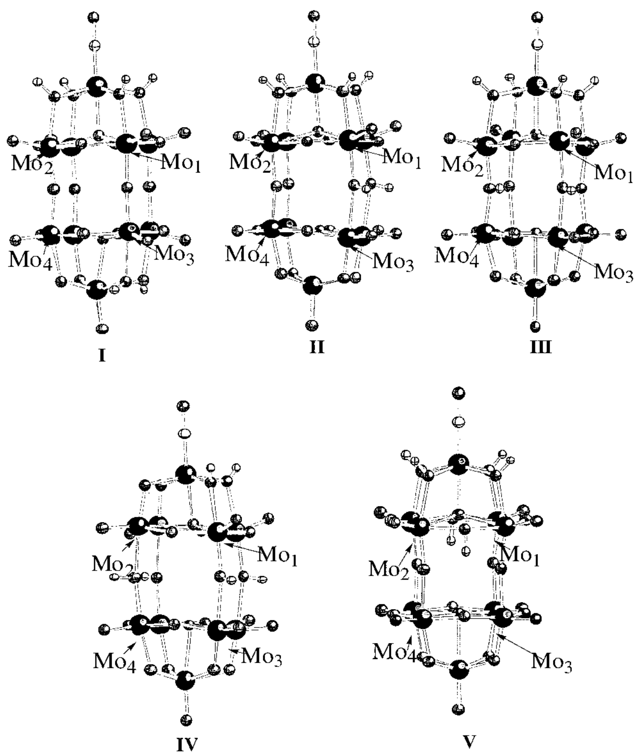

Figure 1. Ball-and-stick representation of structure of **I** and its isomers. Only nonequivalent equatorial molybdenum atoms are numbered; equivalent symmetry metal centers are primed, Mo′, in the text.

performed with the simplest semiempirical Hückel method,[10] the more rigorous ab initio or DFT calculations of rather large polyoxoanions began to appear.[11] To our knowledge, only one study[11g] deals with quantum-chemical calculations of spin states in polyoxometalates.

The electron delocalization in POA takes place due to the strong interaction between localized metal orbitals, which in similar octahedral oxygen environments have close energies. A high symmetry of the metal−oxygen framework is also favorable for the intramolecular electron transfer. The electron delocalization can, however, be modified by some chemical and structural perturbations. For example, the introduction of substitutes into the metal−oxygen framework breaks the equivalence of adjacent metal centers and/or modulates the orbital interactions through bridging atoms. Reducing in this way the electron transfer in doubly reduced polyoxometalates one can hope to pass from the spin pairing controlled by the delocalization to the more common antiferromagnetic (or ferromagnetic) exchange. This transition can be analyzed by quantum chemical calculations.

The recently reported by Proust et al. nitrosyl derivative of decamolybdate $[Mo_{10}O_{25}(OMe)_6(NO)]^-$ (**I**, Figure 1)[12] presents an excellent possibility for verifying this hypothesis. The molecular structure of this system is closely similar to the structure of the well-studied decatungstate anion,[13,14] $[W_{10}O_{32}]^{4-}$, which consists of two halves of five edge-sharing octahedra connected through four quasilinear W−O−W bridges. In comparison with the hypothetical molybdenum counterpart, $[Mo_{10}O_{32}]^{4-}$, in **I** one terminal oxygen ligand is formally replaced by nitrosyl, and six bridging oxygens are replaced by methoxo ligands. In fact, the two methoxo ligands in **I** are disordered over three positions but we will consider the two positions with preferential population. The electronic configuration of **I** merits special consideration. If we assume that the Mo(NO) fragment has the charge +3, as in all known oxonitrosyl molybdates,[12] the rest of the molecule can be formally considered as a mixed-valence cluster containing seven Mo^{6+} and two Mo^{5+}. Thus this part of **I** is doubly reduced in comparison with $[Mo_{10}O_{32}]^{4-}$. The oxidized parent for **I** must be written as $[Mo_{10}O_{25}(OMe)_6(NO)]^+$. It was proposed that two "excess" electrons in the reduced compound have been delocalized over eight equatorial molybdenum sites.[12] Unfortunately, **I** was obtained in insufficient amount to be studied by electronic spectroscopy and magnetochemical methods. The conclusion about electron delocalization was done on the basis of Extended Hückel study and the structural data. The latter do not allow Mo^{6+} and Mo^{5+} sites to be distinguished. The doubly populated HOMO obtained in the calculations, which is well separated in energy, is homogeneously distributed over eight equatorial molybdenum sites. The nondegeneracy of the HOMO suggests a nonmagnetic state for **I**. However, the idealized high symmetry, constraining eight equatorial molybdenum atoms to be equivalent, was imposed in the calculations. The electron delocalization found in the calculations may result from this assumption. In fact, the methylation of some bridging oxygen atoms, as well as the nitrosyl ligand in the upper half of the cluster, introduces a nonequivalence of the metal centers. Full geometry optimizations should give credible information about the electronic distribution and magnetic state of **I**. Furthermore, we can construct model isomers of **I** differing by positions of the methyl groups. Although these isomers are hypothetical, we must note that for the four-electron reduced cluster $[Mo_{10}O_{24}(OMe)_7(NO)]^{2-}$ two isomers were synthesized.[12] In one isomer only bridging oxygens between axial and equatorial molybdenum atoms are methylated (as in **I**), whereas in the second one a methoxo ligand separates two molybdenum atoms belonging to the same equatorial plane. It is quite natural to suppose that methoxo ligands in different positions will result in variation of the electron delocalization pattern and thus modulate the singlet−triplet gap. The analysis of this phenomenon in terms of the transition from delocalization to antiferromagnetic pairing of electronic spins will be presented in this paper.

What theoretical tools should allow us to conclude about the mechanism of spin pairing? The broken symmetry (BS) approach in Density Functional Theory (DFT) introduced by Noodleman[15] is a powerfull tool in the study of exchange interactions for rather large molecular systems. It was shown that with a suitable choice of the exchange-correlation potential the BS method provides antiferro- or ferromagnetic exchange parameters for bi- and polynuclear complexes of transition

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metals with sufficiently high accuracy.[16] The BS method supposes a relatively weak interaction between metal centers and is reminiscent of the valence bond formalism. In the BS state, which is a fictive state, the spin density asymmetry in different parts of molecule is introduced. It allows one to calculate under some assumptions the singlet−triplet energy gap taking into account the multiconfigurational character of the singlet wave function within the DFT. However, if the spin singlet arises through strong bonding, a most stable singlet state is given by a spin restricted solution. The densities of α and β spins are equal over the whole molecule. The transition from the BS to the spin restricted solution will be considered in our study as a manifestation of the regime change in spin pairing.

Computational Details

Calculations were carried out with the ADF2.3 program.[17] Triple-ζ basis sets were taken to describe the valence electrons of all atoms with added polarization functions for oxygen and nitrogen atoms. An approximation of frozen core was used up to the 4p state for molybdenum (with scalar relativistic corrections explicitly introduced in the potential) and up to the 1s states for oxygen and nitrogen atoms. The LDA approximation was employed, with the exchange-correlation potential of Vosko, Wilk, and Nusair.[18] Gradient corrections to exchange (Becke[19]) and correlation (Perdew[20]) were also incorporated in a pertubative way based on the local SCF density.

Restricted calculations of singlet states were done with geometry optimization under constraints of the symmetry groups C_s or C_{2v}, according to the case. Structures of triplet states were also optimized. The broken-symmetry states were calculated in geometry optimized for the corresponding triplet states. To generate a broken-symmetry state, an asymmetry of spin polarization was introduced for molybdenum atoms bearing principal contributions of spin density in the triplet state.

Calculations with the B3LYP functional,[19] implemented in the GAUSSIAN-94 package,[21] were also done. The basis we used was the LANL2DZ,[22] which includes the Huzinaga−Dunning double-ζ basis set for oxygen, nitrogen, and hydrogen atoms, the Hay and Wadt effective core potentials[23] with relativistic effects, and double-ζ valence basis set for molybdenum. Only single-point calculations were done for the geometries optimized with the LDA functional. For the broken symmetry, we used the geometry of the most stable state between the singlet state obtained by a restricted calculation and the triplet state.

Results and Discussion

The structures of **I** and its isomers, numerated from **II** to **V**, studied in this work are presented in Figure 1. For the sake of simplicity, we substitute methyl groups for hydrogen atoms. The notation **I** will be used afterward for the hydrogen-substituted model $[Mo_{10}O_{25}(OH)_6(NO)]^-$ of the experimentally studied complex. The symmetry group is C_s or C_{2v} for isomers with hydrogen atoms in cis or trans positions, respectively.

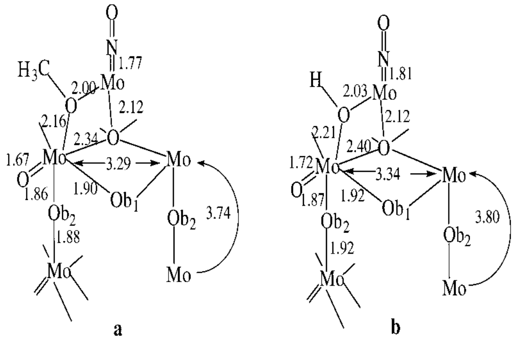

Figure 2. Comparison between crystallographic data of $[Mo_{10}O_{24}(OMe)_6(NO)]^-$ (a) and optimized selected bond distances of the model cluster $[Mo_{10}O_{24}(OH)_6(NO)]^-$ (b). The different types of bridging oxygens are indicated (O_{b1} belongs to the equatorial plane and O_{b2} lies between the two planes).

Table 1. Mulliken Charges on Molybdenum Atoms, LUMO-HOMO Gap for Spin Restricted Solution ($\Delta\epsilon$), and Spin-Restricted Singlet−Triplet (isomers **I**−**III**) or Broken-Symmetry State−Triplet (isomers **IV**−**V**) Gap (ΔE)

	Q_{Mo1}	Q_{Mo2}	Q_{Mo3}	Q_{Mo4}	$\Delta\epsilon$ (eV)	ΔE (eV)
$[Mo_{10}O_{25}(OH)_6(NO)]^+$	2.29	2.28	2.32	2.33		
I	2.20	2.20	2.19	2.23	1.09	0.85
II	2.15	2.15	2.18	2.23	0.90	0.55
III	2.13	2.18	2.17	2.25	0.66	0.39
IV	2.12	2.17	2.14	2.18	0.55	0.083
V	2.09	2.09	2.21	2.22	0.21	0.031

The Electronic Structure of I. Calculations show that for this anion the most stable state is a singlet obtained within the spin-restricted method. All tentative attempts to obtain a broken symmetry state also converge to the same solution without spin polarization.

The optimized structural features of the POA framework are found in good agreement with the crystallographic data as shown for selected bond distances on Figure 2. The mean Mo−Mo separations are equal to 3.34 and 3.80 Å within the equatorial planes and between two planes, respectively. The corresponding experimental values are 3.29 and 3.74 Å. A crude measure of excess electron distribution can be given by Mulliken charges. The comparison of charges in **I** and its nonreduced parent $[Mo_{10}O_{25}(OH)_6(NO)]^+$ (Table 1) shows that the extra charge is almost homogeneously distributed between the eight equatorial molybdenum sites. The composition and energies of several highest occupied orbitals and the LUMO are presented in Figure 3. The orbitals 130 and 131 are localized on the Mo(NO) fragment and are well separated from the HOMO 132. It explains a relatively small Mulliken charge value of 1.77 for the nitrosyl-linked molybdenum atom. The high π acceptor power of the nitrosyl ligand guarantees a noninterference of the Mo(NO) group into the blue electron delocalization. The HOMO is formed essentially as a nonbonding orbital in the interaction of the eight equatorial molybdenum atoms in twelve Mo−O−Mo fragments. The weights of eight Mo atoms in HOMO are very close. It proves, as well as Mulliken charges, the delocalization of two excess electrons over equatorial Mo sites. Two Mo−O−Mo interactions are responsible for the electron delocalization, namely within the same equatorial plane and between two planes. The antibonding contribution in the

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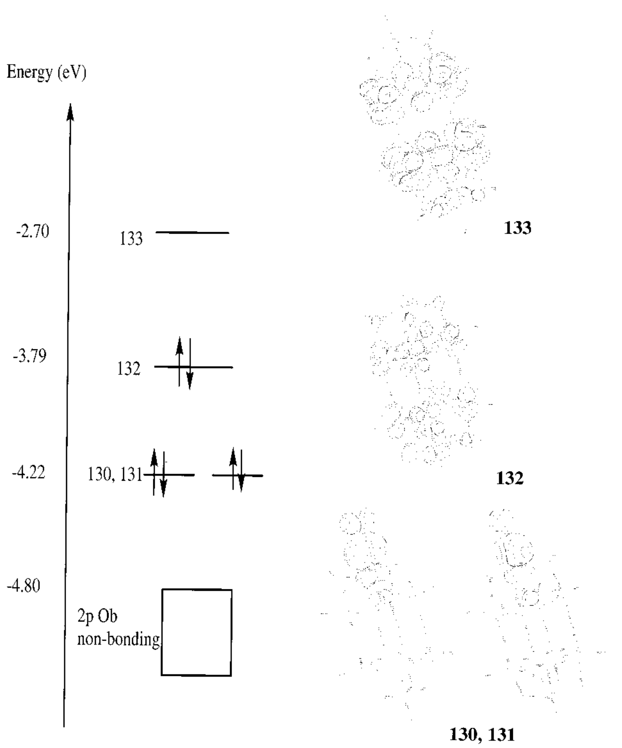

Figure 3. Composition and energies of several highest occupied orbitals and LUMO in isomer **I**.

LUMO between molybdenum atoms and bridge oxygens in the plane suggests that the equatorial interaction is weaker. The protonation of bridging oxygens between equatorial and axial metal centers does not interfere in this interaction and does not break the electronic delocalization keeping the eight equatorial molybdenum atoms quasiequivalent. We also performed calculations of the experimental system with methoxo bridges and found the same results as with the protonated bridges. The singlet−triplet gap is reduced, but still remains very large (0.76 eV). The Mulliken charges for the equatorial molybdenum atoms varying from 2.18 to 2.22 again reflect the quasihomogeneous delocalization of electrons.

Magnetic State of I and Its Isomers. The failure to obtain a broken-symmetry solution for **I** reveals the delocalization mechanism of the spin singlet stabilization. A diamagnetic ground state appears due to the nondegenerate well-separated HOMO (Table 1). This separation is explained by the strictly nonbonding character of the HOMO imposed by the quasi-D_{4h} symmetry of the central part of the cluster, as opposed to the antibonding character of the LUMO. The corresponding value of the singlet−triplet gap is much higher than could be expected for antiferromagnetic exchange interactions.

Our goal is to modulate the electron delocalization to change the relative stabilization of singlet state and, if possible, the mechanism of this stabilization. To be efficient, a perturbation must be located on the electron delocalization pathway. So, in our model isomers we protonated different bridging oxygens between equatorial molybdenum atoms. The expected effect of the protonation is to reduce the HOMO-LUMO gap by mixing HOMO with some of its antibonding counterparts.

For the first two isomers **II** and **III** (Figure 1) two bridging oxygens between equatorial planes are protonated. They are placed in the cis or trans position, leading to the symmetry C_s or C_{2v}, respectively. The ground state in both cases is found to be a singlet spin-restricted solution. The two optimized structures demonstrate a breaking of electronic communication between equatorial planes through protonated oxygen atoms. This is evidenced by the elongation and dissymmetrization in the Mo−O(H)−Mo unit. The corresponding Mo−O distances become equal to 1.99 and 2.35 Å for isomer **II** and 2.03 and 2.28 Å for isomer **III**. The bonds are shorter for molybdenum atoms belonging to the upper half of the cluster, which contains nitrosyl. Composition of the HOMO (Figure 4) and the Mulliken charges in **II** and **III** (Table 1) reflect the concentration of an excess of electronic density in the upper equatorial plane, accompanied by the reduction of the HOMO-LUMO gap. Due to different symmetry, the atoms with maximal electronic density are more separated in isomer **III**. Although the degree of the electron charge localization in **II** and **III** is higher than that in **I**, the ground state formed by the spin restricted solution indicates that the delocalization mechanism is still operative. However, the singlet−triplet gap is reduced (Table 1) and a smaller value is found for the more localized isomer **III**.

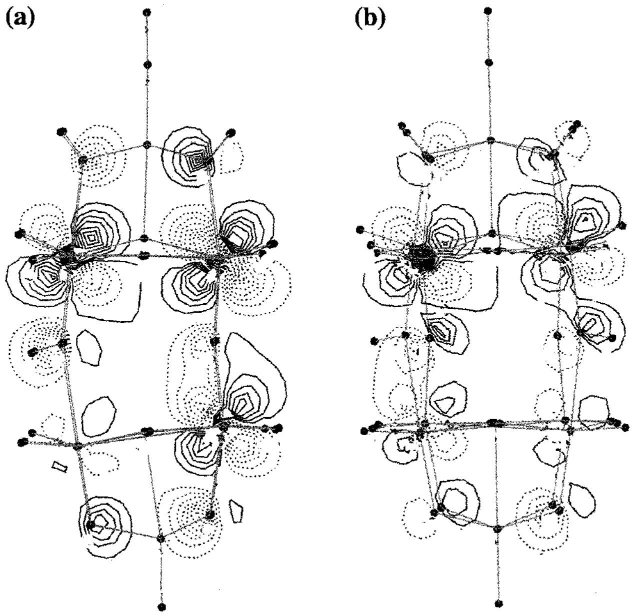

Figure 4. HOMO projection on the plane of the four molybdenum atoms Mo$_{1-4}$ for isomer **II** (a) and isomer **III** (b).

If we protonate all four oxygen atoms forming bridges between two halves, we obtain isomer **IV**. The frontier orbitals become closer in energy (Table 1). In this case, a more stabilized state is given by the broken-symmetry solution. This solution describes preferential localization of α density on atoms Mo$_1$−Mo$_1'$ and β density on atoms Mo$_4$−Mo$_4'$. This polarization is rather weak, $\rho_\alpha - \rho_\beta = \pm 0.012$. Nevertheless, the lowest energy broken symmetry state unambiguously shows that the antiferromagnetic exchange participates now in the spin pairing in the ground singlet state. The relationship between the broken-symmetry state−triplet energy gap and the singlet−triplet energy gap varies from $\Delta E_{ST} = E_{BS} - E_T$ to $\Delta E_{ST} = 2(E_{BS} - E_T)$ depending on the overlap of magnetic orbitals.[15a] The broken-symmetry state−triplet energy gap found equal to 0.083 eV shows that in any case the singlet−triplet gap is also strongly reduced. It falls now in the range more characteristic for the Heisenberg exchange in polynuclear complexes. The Mulliken charges indicate that electron localization on several molybdenum atoms continues to increase.

As was mentioned below, the electron delocalization takes place within equatorial planes and between them. Interactions through the first pathway are more weak and can be more easily perturbed by the protonation. It is confirmed by the calculations

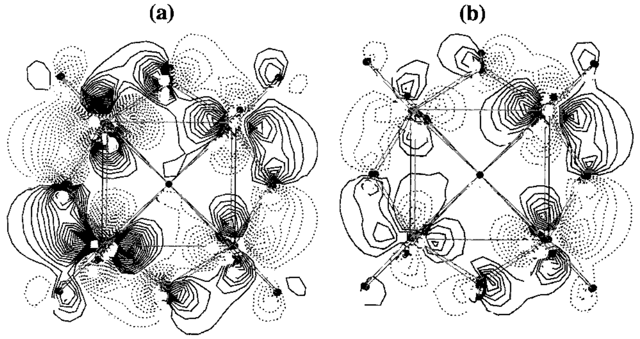

Figure 5. The isomer **V** SHOMO projection on the upper equatorial plane for α (a) and β (b) spin.

of isomer **V**, in which two equatorial bridging oxygens are protonated (Figure 1). The bonds Mo−O(H) become weaker with distances going from 1.92 to 2.11 Å. We obtain a broken symmetry state with much more pronounced spin polarization at molybdenum centers than in **IV**, equal to ±0.16. This effect can be easily seen from SHOMO's plot (Figure 5), which clearly shows space separation of α and β densities. We find for the isomer **V** a highest degree of electron charge localization on the upper half leading to the Mulliken charges 2.09. Correspondingly, the broken-symmetry state−triplet separation becomes as small as 0.03 eV.

All previous results were obtained in the LDA approximation with the nonlocal BP corrections to the exchange-correlation energy. This method has been used in many calculations of magnetic interactions. However, it is known that the LDA overestimates electron delocalization[24] and the best DFT results for exchange parameters are obtained with the mixed B3LYP functional.[25] We performed calculations with this method using the geometry optimized within the LDA. For the isomers **I**−**III** the ground states are again given by the delocalized spin-restricted solution. The singlet−triplet gap is, however, reduced and in the three isomers it has values of 0.6, 0.46, and 0.18 eV, respectively. We succeeded also in finding in all these cases broken-symmetry solutions, but they always lie higher in energy. For isomer **IV** it is a triplet state that has the lowest energy, but with a small stabilization (0.0027 eV) relative to the broken symmetry state. A lowest energy broken symmetry state was found for isomer **V**, with an important polarization of spin, $\rho_\alpha - \rho_\beta = \pm 0.40$, and stabilization relative to the triplet state was very weak (0.001 eV). Thus, the overall results found with the B3LYP functional are similar to those presented above. The main difference concerns values of the singlet−triplet gap overestimated for the LDA functional. However, the tendency is respected and the mechanism of spin pairing remains the same for all isomers.

The comparative study of the five isomers demonstrated the transition from the delocalization to the magnetic exchange mechanism of spin pairing in reduced polyoxometalates. This transition appears as a result of the chemical bonding perturbation by the protonation of bridging oxygen atoms in Mo−O−Mo fragments. In other words, it can be considered as a change from strong to weak intercenter interaction. It is accompanied by stronger localization of the excess electron density on several metal centers. The change of regime is displayed in the value of singlet−triplet gap, which is essentially lower for systems with spatially separated α and β spin densities. Although the ΔE_{ST} approaches the values one can expect for exchange-coupled systems, the physical picture cannot be adequately described by the Heisenberg exchange Hamiltonian. The degree of electron delocalization still remains rather high and the unpaired electron density is concentrated not at one but at several metal centers.

Concluding Remarks

The competition of localization and delocalization is well-known in chemistry. At the fundamental level it is manifested, for example, in such effects as the appearance of symmetry-broken Hartree−Fock solutions in molecular systems.[26] Similar phenomena can be found in polynuclear transition metal clusters. Balance of localization and delocalization factors were also studied by DFT methods in a series of papers by Stranger and co-workers.[27] They considered the bonding in face-shared metal−halogen octahedra M_2X_9 with the electronic configuration d^3−d^3. The strongly interacting σ electrons are predisposed to form delocalized metal−metal bonds, whereas the δ electrons resist better the delocalization and for some metals give antiferromagnetically coupled pairs. The former situation corresponds to a spin-restricted solution and the latter one is better described by a broken-symmetry state. The transition between different regimes is achieved by a change of the nature of metal and/or bridging ligands. In our case the position of the protonation sites is decisive. As there are only two excess electrons in our systems, the separation into strongly and weakly interacting electrons cannot be done. If for M_2X_9 complexes one can obtain intermediate ground state spin values between $S = 3$ and 0, for doubly reduced POA we only have a choice between $S = 0$ and 1. A case of very strong intercenter interaction, when a broken symmetry calculation converges to the restricted solution, recently has been found for model μ-oxo copper dimers.[28]

Polyoxometalates have been found to be a versatile building block for the construction of molecular magnetic materials. The important feature of many magnetic systems based on POM is the coexistence of localized and delocalized magnetic electrons. In particular, delocalized blue electrons of reduced polyoxometalates can also be involved in magnetic interactions. As can be seen from our theoretical study, the introduction of substitutions into the POA framework can modulate the character of electronic pairing and the stabilization energy of different spin states. In principle, in some cases the sign of effective exchange coupling can be inverted leading to a ferromagnetic ground state of reduced POA. The fine-tuning of magnetic interactions in reduced polyoxometalates creates new possibilities for the design of molecular magnetic materials.

Acknowledgment. The authors are greatly indebted to A. Proust and P. Gouzerh for their encouragement and insights. We also would like to thank J. M. Mouesca and J. P. Malrieu for very useful discussions on the Broken Symmetry method and V. Robert for the critical reading of the manuscript.

JA002815D

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