Theor Chem Acc (2006) 116: 509–513
DOI 10.1007/s00214-006-0088-2

REGULAR ISSUE

Serguei A. Borshch · Ekaterina M. Zueva

Electron localization versus delocalization and ferromagnetic coupling in mixed valence polyoxometalates

Received: 24 November 2004 / Accepted: 15 January 2005 / Published online: 14 February 2006

Abstract We show that the ferromagnetism, recently found in the doubly-reduced hexanuclear polyoxometalate $[V_6O_{12}(\mu_2\text{–}OCH_3)_4(L)_4]$ does not contradict to the proposed earlier delocalization mechanism of the stabilization of a spin-singlet state. The ground state triplet state yields from the internal and/or external complex asymmetry leading to the spin density localization.

Keywords Polyoxometalates · Ferromagnetism · Electron delocalization.

1 Introduction

Polyoxometalates (POM) constitute an important class of metal-oxygen anionic clusters, formed mainly by Mo, W, V in their highest oxidation states, with interesting and potentially valuable physical and chemical properties [1–3]. The remarkable possibilities of tuning their molecular and electronic structure have impact in such different disciplines as catalysis, medicine, and materials sciences. A special place in the POM chemistry is occupied by reduced species called, due to their intense blue color, “polyoxo blues” or “heteropoly blues”, if polyoxoanions contain a heteroatom. Addition of one or several electrons usually preserves the POM structure, and its high symmetry provides excellent possibilities for excess electron delocalization between metal centers. As in their oxidized state POM metal centers possess the d^0 electronic configurations, the reduction leads to appearance in the POM energetic spectrum of states characterized by a non-zero total spin. However, it has been found experimentally for clusters reduced by an even number of electrons, that only spin singlet ground state is populated even at room temperature. The strong stabilization of spin singlet ground state was initially explained by the presence of multiple channels of antiferromagnetic exchange between centers accepting magnetic electrons [4–8]. The further theoretical analysis based on model Hamiltonians of the Hubbard type suggested that the delocalization of excess electrons in reduced POM can result in singlet ground states [9–14]. The most common POM structures, such as Keggin, decatungstate, and Wells–Dawson, have been studied. The energy gap between ground singlet and first non-zero spin state is of the order of intramolecular transfer parameter. The high-level ab initio calculations [13] of local effective transfer integrals resulted in values in the range 0.5–1 eV, thus explaining the diamagnetic properties of doubly reduced polyoxoanions.

It seems natural that if the electron delocalization enhances the stabilization of a spin singlet state, the delocalization hindering must weaken this stabilization. This idea was illustrated in the study of model isomers of the experimentally observed system $[Mo_{10}O_{25}(OMe)_6(NO)]^-$, in which two excess electrons are delocalized over decanuclear cluster [15]. Changing the positions of methyl groups attached to different bridging oxygen atoms, we observed the strong decrease of the singlet-triplet gap in the cases, when methylation concerns oxygen bridges most efficient in the electron delocalization. The gap value changes from several thousands cm^{-1} to a few wave numbers. The transition from diamagnetism to an antiferromagnetically coupled state is also reflected in the nature of the ground state. If for the strong delocalization even spin-unrestricted DFT calculations converge to a spin-restricted solution, in the opposite case a broken symmetry type state has lowest energy. For some model isomers, with a particular choice of exchange-correlation functionals, we even obtained a spin-triplet ground state.

Recently synthesized hexanuclear oxo-alkoxo vanadium cluster gives the first experimental example of ferromagnetically coupled POM, reduced by even number of electrons [16]. We will show in this paper that this example does

S.A. Borshch (✉)
Laboratoire de Chimie, UMR 5182
CNRS – Ecole Normale Supèrieure de Lyon,
46 allée d’Italie, 69364 Lyon Cedex 07, France
E-mail: borchtch@ens-lyon.fr

E.M. Zueva
Department of Inorganic Chemistry,
Kazan State Technological University,
68 K. Marx street, 420015 Kazan, Russia
E-mail: zueva_e@kstu.ru

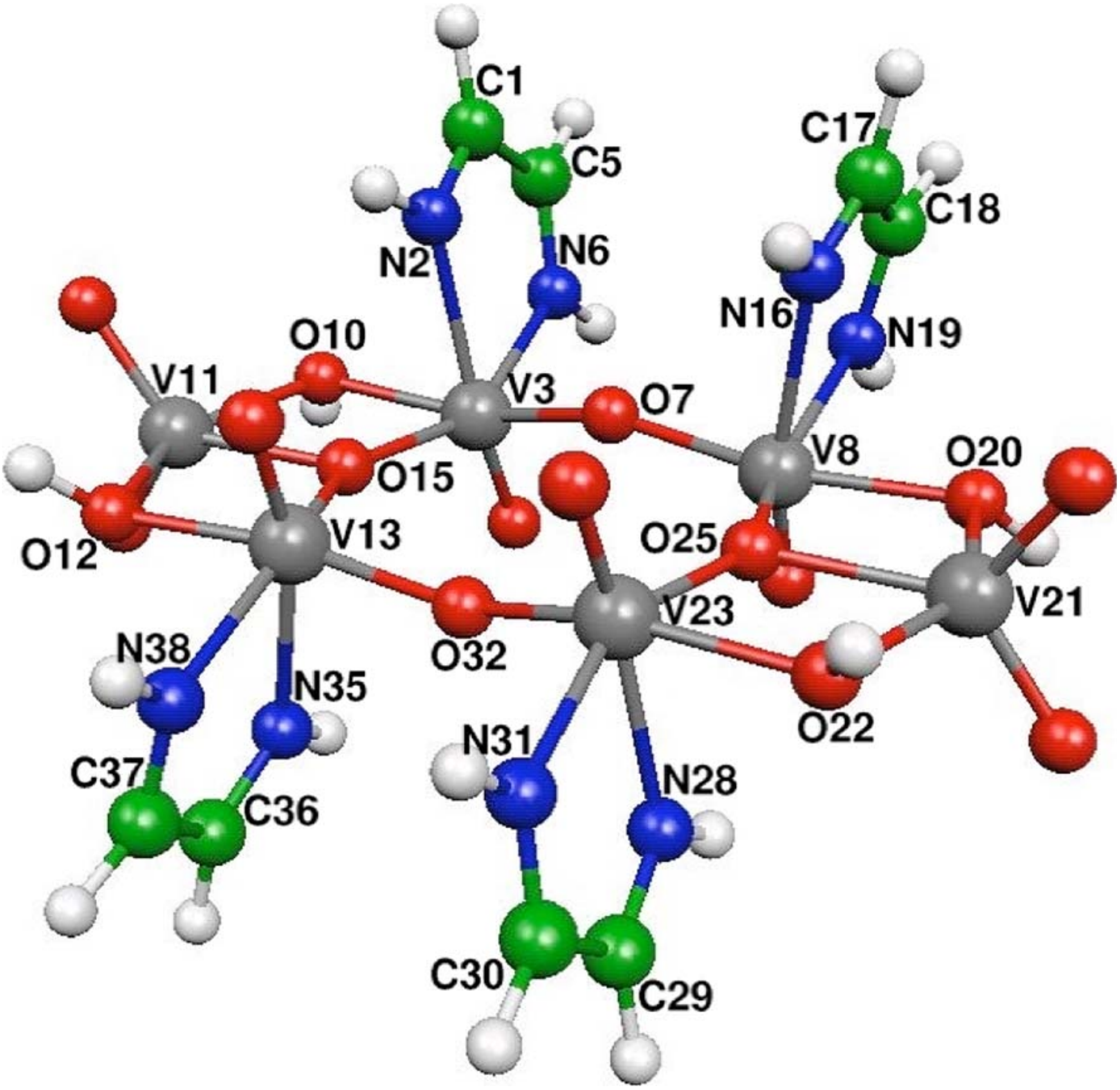

Fig. 1 Ball-and-stick representation of the hexanuclear vanadium complex $[V_6O_{12}(\mu_2 - OCH_3)_4(L)_4]$. Ligands L are replaced by the model ligand [HN = CH–CH = NH].

not contradict our previous conclusion about the delocalization stabilization of the spin singlet state. The ferromagnetic ground state results from the cluster disymmetry (intrinsic and induced by external perturbations), which breaks the electron delocalization.

2 Phenomenological treatment

The hexanuclear cluster $[V_6O_{12}(\mu_2{-}OCH_3)_4(L)_4]$ (Fig. 1), where L is a bidentate nitrogen-donor organic ligand, has a formal composition $[V_2^{IV}V_4^{V}]$.[9] Two symmetry-related vanadium ions form $[VO_5]$ coordination cores with distorted trigonal bipyramidal geometry and can be clearly identified as V^V centers. Four remaining vanadium atoms form a tetranuclear centrosymmetric unit with $[VN_2O_4]$ strongly distorted octahedral coordination sites. Should the tetranuclear unit have the maximal possible symmetry C_{2h}, it could produce ideal conditions for the delocalization of two excess electrons between four equivalent vanadium centers. Symmetry reduction to C_I, expressed by the displacement of bridging oxygen atoms from central positions, distinguishes between two pairs of equivalent vanadium atoms and results in a partial localization of the electronic density within one pair.

The interesting feature of the hexanuclear clusters is a weak ferromagnetic coupling between two “excess” electrons. It is a first example of the ferromagnetic exchange in doubly reduced polyoxometalates. The experimental observation agreed with the results of the UHF calculations of the exchange parameter for a simplified model system [16]. However, these calculations, neglecting the electronic correlation, do not provide insight into the mechanism of the ferromagnetic interaction. One can suppose that the localization of electronic density due to the symmetry lowering is non-innocent in the stabilization of a spin triplet ground state.

Since two electrons within a cyclic tetranuclear unit generate the magnetic state of the hexanuclear cluster, let us consider a simple model two-electron four-center system. Such a system was firstly studied in order to analyze the electronic properties of the tetranuclear mixed-valence POM $[W_4O_8Cl_8(H_20)_4]^{2-}$ [17]. Using as a basis two-electron radical and ionic singlet states,

$$\begin{aligned}\phi_{ij}^{S} &= \frac{1}{\sqrt{2}}\left(\phi_i(1)\phi_j(2)+\phi_i(2)\phi_j(1)\right),\\ \phi_{ii}^{S} &= \phi_i(1)\phi_i(2),\end{aligned} \tag{1}$$

and triplet states

$$\phi_{ij}^{T} = \frac{1}{\sqrt{2}}\left(\phi_i(1)\phi_j(2)-\phi_i(2)\phi_j(1)\right), \tag{2}$$

where ϕ_i is a one-electron function, localized at ith center of a square cluster, and diagonalizing in this basis the Hubbard hamiltonian

$$\mathbf{H}_\mathrm{el} = t\sum_{i,j,\sigma}\mathbf{a}_{i,\sigma}^{+}\mathbf{a}_{j,\sigma} + U\sum_{i,\sigma}\mathbf{n}_{i,\sigma}\mathbf{n}_{i,-\sigma} \tag{3}$$

one can obtain the energy spectrum presented on Fig. 2. It can be easily seen that for any value of the electron transfer parameter the ground state is a singlet. A ground triplet state can result from the stabilization of the first excited ^{3}E state. The energy of this orbitally degenerate electronic term can be affected by the Jahn-Teller effect through the interaction with the b_1 vibrations, active in $D_{4\mathrm{h}}$ symmetry. This vibronic interaction must reduce the symmetry of the cluster and lower the energy of one of the components of the ^{3}E state. The most straightforward way to introduce the vibronic interactions in our system is to account for the interaction with the local totally symmetric distortions (breathing vibrations) q_i, accompanying localization of excess electrons at metal centers. This interaction governs the transition between localized and delocalized regimes in mixed-valence polynuclear clusters [18]. The matrix elements of this interaction can be written in the two-electron basis as

$$\langle ii|\,\mathbf{H}_v\,|ii\rangle = 2\lambda q_i,\ \langle ij|\,\mathbf{H}_v\,|ij\rangle = \lambda(q_i+q_j), \tag{4}$$

where λ is the vibronic constant. The local coordinates can be grouped into symmetrical combinations:

$$\begin{aligned}Q_a &= \tfrac{1}{2}(q_1+q_2+q_3+q_4),\\ Q_b &= \tfrac{1}{2}(q_1-q_2+q_3-q_4),\\ Q_{e1} &= \tfrac{1}{\sqrt{2}}(q_1-q_3),\\ Q_{e2} &= \tfrac{1}{\sqrt{2}}(q_2-q_4),\end{aligned} \tag{5}$$

and the nuclear coordinates depending electronic energies can be obtained by the diagonalization of the full electronic Hamiltonian $\mathbf{H}_v + \mathbf{H}_\mathrm{el}$. In order to determine potential surfaces one must add the elastic energy

$$E_v = \frac{k}{2}\sum_i q_i^2, \tag{6}$$

and the energies of stable states will be given by the energies of the minima of corresponding sheets of adiabatic surfaces. If we perform these calculations for different choices of the parameters, we find that the behavior of the energy gap between the first excited triplet and the ground singlet state can be represented as in Fig. 3. It shows that the vibronic interaction strongly reduces the energy gap. However, the crossing of triplet and singlet states does not take place. For a rather strong vibronic coupling not only the triplet is stabilized due to the Jahn-Teller effect, but the energy of the ground singlet level is lowered due to vibronic mixing with higher lying levels (Fig. 2). The asymmetry induced by the chosen part of vibronic interaction is not sufficient to lead to a triplet ground state. However, the interaction with other molecular vibrations can provide an additional source of internal asymmetry as well as external factors such as the influence of counter-ions or solvent molecules in the vicinity

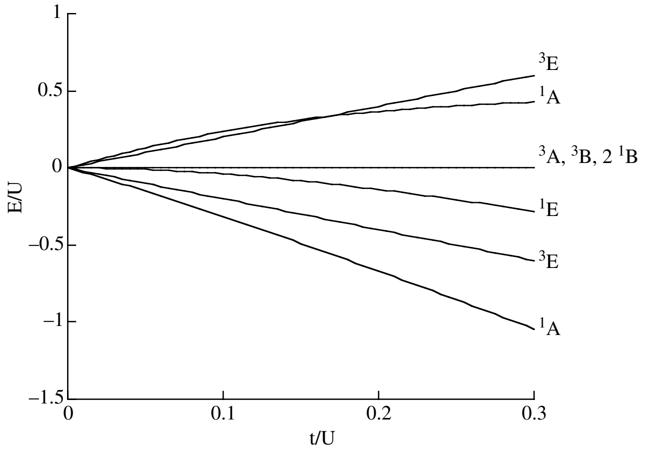

Fig. 2 The energy levels of a two electrons-four center model system

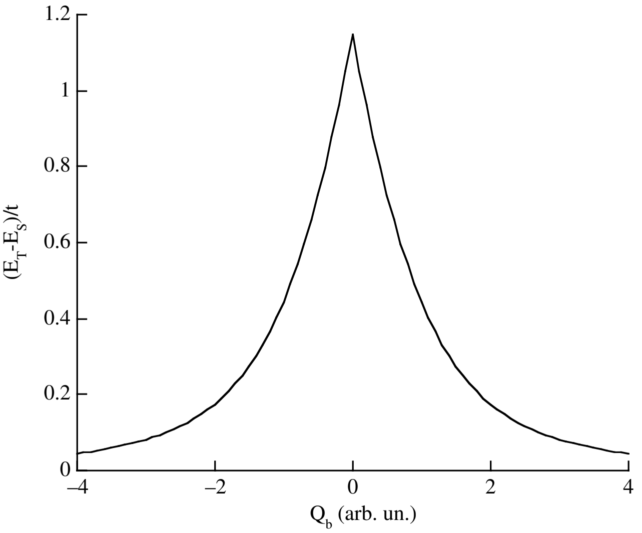

Fig. 3 The dependence of the triplet-singlet gap on vibronically active Q_b-coordinate

Table 1 Dependence of the gap between triplet and BS states on the position of the bridging oxygen atom in model complexes

V3–O7	1.813	1.837	1.861	1.885	1.909	1.933	1.958	1.982	2.006	2.030	2.054
V8-O7 (Å)	1.813	1.789	1.765	1.741	1.717	1.693	1.669	1.645	1.621	1.597	1.573
$E_T - E_{BS}(\mathrm{cm}^{-1})$	9.9	9.6	9.1	8.0	6.6	5.0	3.0	1.0	−2.5	−5.1	−7.7

of the complex. In the next section we will illustrate the role of the asymmetry in the stabilization of the ferromagnetic state using DFT calculations.

3 DFT calculations of the hexanuclear polyoxometalate

The DFT calculations of the experimentally studied complex with $L = 5, 5' - \mathrm{me_2bipy}$, for which the X-ray structure is available [16], and of model systems have been performed with the ADF package [19,20]. The experimental system was calculated at experimental centro-symmetrical geometry with V3–O7 and V8–O7 distances equal respectively to 1.917 and 1.707 Å. A double-ζ Slater type orbital basis set was employed to describe valence electrons. The Vosko, Wilk, and Nusair exchange-correlation potential [21] was used to construct the local part of the energy functional, and the Becke [22] and Perdew [23] gradient corrections were added to the exchange and correlation energy functionals, respectively. We used the broken-symmetry (BS) technique developed by Noodleman et al. [24] to calculate the singlet–triplet gap. The monodeterminantal BS state is a mixed spin state with $M_S = 0$, and the calculated value of the singlet–triplet gap depends on the assumption about the overlap between magnetic orbitals. As in our analysis we are mainly interested in a qualitative behavior of the gap, we considered the monodeterminantal BS solution as an approximation to the singlet state of antiferromagnetically coupled systems.

The DFT calculations resulted in the energy gap between the triplet and BS states equal to $-40.1\ \mathrm{cm}^{-1}$. The experimental measurements for clusters with L = phen and bipy also gave the ferromagnetic exchange parameter, but a little bit weaker, $-6\ \mathrm{cm}^{-1}$ and $-8.5\ \mathrm{cm}^{-1}$. One can conclude that the results of DFT calculations correctly predict the sign and are in a good agreement in magnitude of the exchange parameter. It is interesting to note that in both high-spin and BS states the spin density is predominantly localized on V3 and V23 atoms (≈ 0.8), but a non-negligible part is also on V8 and V13 atoms (≈ 0.2). This result shows that the system is much less localized than presented by the UHF calculations [16].

In order to simplify the calculations necessary to analyze the role of electron localization, we replaced ligand L by the model ligand [HN = CH–CH = NH], as it has been done also in the UHF calculations [9]. If we maintain in the calculations of the model complex the experimental geometry of the $\mathrm{V_6O_{12}(\mu_2 - OCH_3)_4}$ core, we again obtain a ferromagnetic ground state with a slightly diminished energy gap of $-22.5\,\mathrm{cm}^{-1}$. A part of spin density in the model system is transferred to the rings due to conjugation effects.

The highest possible symmetry of our molecular system is C_{2h}. If we impose this symmetry and perform calculations with the geometry optimization, we obtain four vanadium atoms V3, V8, V13, and V23 that are structurally equivalent. The bridging oxygen atoms are found in middle positions with the V3–O7 and V8–O7 distances equal to 1.813 Å. The symmetrization of the geometry leads to the change in the energy gap sign. The antiferromagnetic singlet becomes a ground state and the exchange parameter is now equal to $9.9\ \mathrm{cm}^{-1}$. Due to the high symmetry the spin density value is the same for all four vanadium atoms forming the ring: 0.309 in the triplet state, and 0.297 (positive for V3, V8 and negative for V13 and V23) in the BS state.

In order to confirm that the asymmetry and resulting electron localization are at the origin of a ferromagnetic state, we performed a series of calculations for model C_i structures obtained from the optimized C_{2h} geometry. The C_i structures were generated by small displacements of O7 and O32 atoms parallel to the axis connecting V11 and V21 atoms. Single point calculations have been performed with a triple-ζ plus polarization STO basis set. The results of the calculations are presented in Table 1.

The results clearly demonstrate that by increasing the degree of spin density localization we reduce the gap between triplet and singlet state and finally invert it. The transition to the triplet ground state appears for more pronounced displacements of O7 and O32 atoms than those found in the experimental geometry. However, symmetry in the real system is also reduced by the displacements from the central positions of O15 and O25 atoms, which are ignored in our model. The ferromagnetism observed for a family of reduced polyoxometalates does not contradict the delocalization mechanism of the spin-singlet stabilization. The asymmetry of the system is sufficiently high to hinder the delocalization and to stabilize the spin-triplet state.

4 Conclusions

The fine-tuning of magnetic interactions in reduced POM creates new possibilities for the design of molecular magnetic materials. Our theoretical work shows that structural perturbations can modulate the character of electronic pairing in reduced POM. In some cases the sign of effective exchange parameter can be inverted leading to a ferromagnetic ground state. However, the ferromagnetism cannot be excluded in POM with delocalized electronic distributions. The high symmetry of POM results in sets of degenerate vacant orbitals, which can be filled by reducing electrons. Non-complete filling of degenerate orbital must, according to the Hund rules, produce a high-spin ground state. The elucidation of this mechanism is under way now.

Acknowledgements Among other achievements, Jean-Paul Malrieu contributed a lot in our knowledge of magnetism of delocalized electrons. It is a great pleasure for us to dedicate this paper to him. EMZ thanks the CRDF(REC-007) and Russian Ministry of Education for the financial support.

References

1. Pope MT, Müller A (eds) (1994) Polyoxometalates: from platonic solids to anti-retroviral activity. Kluwer, Dordrecht
2. Pope MT, Müller A (eds) (2001) Polyoxometalate chemistry: from topology via self-assembly to applications. Kluwer, Dordrecht
3. Borras-Almenar JJ, Coronado E, Müller A, Pope MT (eds) (2003) Polyoxometalate molecular science. Kluwer, Dordrecht
4. Kozik M, Casañ-Pastor N, Hammer CF, Baker LCW (1988) J Am Chem Soc 110:7697
5. Acerete R, Casañ-Pastor N, Bas-Serra J, Baker LCW (1989) J Amer Chem Soc 111:6049
6. Casañ-Pastor N, Bas-Serra J, Coronado E, Pourroy G, Baker LCW (1991) J Am Chem Soc 113:5658
7. Casañ-Pastor N, Baker LCW (1992) J Am Chem Soc 114:10384
8. Kirby JF, Baker, LCW (1995) J Amer Chem Soc 117:10010
9. Borshch SA, Bigot B (1993) Chem Phys Lett 212:398
10. Borshch SA (1998) Inorg Chem 37:3116
11. Borras-Almenar JJ, Clemente JM, Coronado E, Tsukerblat BS (1995) Chem Phys 195:1
12. Borras-Almenar JJ, Clemente JM, Coronado E, Tsukerblat BS (1995) Chem Phys 195:17
13. Suaud N, Gaita-Ariño A, Clemente-Juan JM, Sanchez-Marin J, Coronado E (2002) J Amer Chem Soc 124:15134
14. Suaud N, Gaita-Ariño A, Clemente-Juan JM, Coronado E (2004) Chem Eur J 10:4041
15. Duclusaud H, Borshch SA (2001) J Amer Chem Soc 123:2825
16. Manos MJ, Tasiopoulos AJ, Tolis EJ, Lalioti N, Woolins JD, Slawin AMZ, Sigalas MP, Kabanos TA (2003) Chem Eur J 9:695
17. Girerd JJ, Launay JP (1983) Chem Phys 74:217
18. Bersuker IB, Borshch SA (1992) In: Prigogine I, Rice SA (eds) Advances in Chemical Physics, vol. 81. Wiley, Chichester, p 703
19. Fonseca Guerra C, Snijders JG, te Velde G, Baerends EJ (1998) Theor Chem Acc 99:391
20. ADF2000.02, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com
21. Vosko SH, Wilk L, Nusair M (1980) Can J Phys 58:1200
22. Becke AD (1986) J Chem Phys 84:4524
23. Perdew JP (1986) Phys Rev B 33:8822
24. Noodleman L, Norman JG Jr (1979) J Chem Phys 70:4903
25. Noodleman L (1981) J Chem Phys 74:5737