Modelling electric field control of the spin state in the mixed-valence polyoxometalate [GeV$_{14}$O$_{40}$]$^{8-}$

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The two-electron reduced mixed-valence polyoxometalate [GeV$_{14}$O$_{40}$]$^{8-}$ presents an unusual paramagnetic behaviour as a consequence of the partial trapping of these electrons. The effect of applying an electric field is that of inducing antiferromagnetic coupling between the two delocalized electronic spins.

A recently emerging field namely Molecular Spintronics combines the ideas and concepts developed in spintronics with the unique possibilities offered by the molecular systems to perform electronic functions, to form self-organized nanostructures and to exhibit quantum effects at the nanoscale.[1] This new field offers the flexibility of molecular chemistry in the processing of materials, and uses the tools of molecular electronics with the goal of manipulating, measuring and addressing individual molecules. It also uses molecule-based materials for the fabrication of spintronic devices, in particular spin valves.[2]

One of the most challenging goals in this area is the use of individual magnetic molecules as active components of nano-spintronic devices. As the nano-fabrication of single-molecular devices becomes technically feasible, the manipulation of the spin state of a molecule through a physical stimulus may be achieved. An attractive strategy to reach this goal is that of using electric fields or currents instead of a magnetic field to achieve an all-electrical control of the nanodevice. This presents some advantages, namely: electric fields are easy to obtain (with gates or STM-tips), undergo fast switching ($\approx$ ps) and can be applied at the nanoscale. This enables adequate operating times and the spatial resolution needed to address a single molecular spin. Some interesting experiments on the electrical control of the spin state have recently been reported in spin-crossover nanoparticles.[3] Currently, most of the work in this area remains theoretical and deals with the following electrically switchable magnetic molecules: (1) spin-crossover metal complexes,[4] (2) valence-tautomeric metal complexes,[5] (3) dipolar metal complexes, such as asymmetric dimers[6] or molecular triangles formed by three antiferromagnetically coupled spins,[7] and (4) mixed-valence metal complexes.[8–10]

Relative to the last class of molecules, we showed that delocalized mixed-valence dimers with double-exchange interaction could be good candidates for the electric control of the spin state.[8] In these systems, under certain conditions (moderate vibronic coupling and a dominant double exchange over the antiferromagnetic superexchange), both the spin of the ground state and its dipole moment can be controlled by the application of an electric field. These magnetic MV dimers can be regarded as single-molecule analogues of multiferroic materials.

In this context, polyoxometalates (POMs) present some electronic and magnetic features that make them especially suitable in molecular spintronics.[1d] These molecular oxides present a well-defined, highly symmetric and robust cluster framework both in solution and in the solid state. Furthermore, they behave as "electron sponges" suffering only a minimal modification of their structures. Usually these "extra" electrons are delocalized over the whole cluster.[11] These reduced molecules are the so-called mixed-valence polyoxometalates (MV-POMs or hetero-polyblues). In recent years, MV-POMs have been rediscovered and suggested for a variety of applications.[10,12] In this regard, the [PMo$_{12}$O$_{40}$(VO)$_2$]$^{n-}$ di-capped Keggin anion has been proposed to fabricate a quantum logical gate.[9] In this MV-POM the exchange coupling between the two vanadium spins is different for even and odd numbers of electrons. Thus, an electrical control can be achieved by injecting an extra electron into the central MV molybdenum cluster *e.g.* using the tunneling current of a STM setup.

In this work we explore a different mechanism: the effect of an electric field on the magnetic properties of the MV poly-oxovanadate K$_2$Na$_6$[GeV$_{14}$O$_{40}$]·10H$_2$O (in short V14) (Fig. 1).[13] This system is formed by 12 diamagnetic V^V ions and 2 V^{IV} ions with spins $S = 1/2$. The unusual feature of this POM is that it is paramagnetic (two unpaired electrons) at least down to 1.7 K. This is in sharp contrast to the diamagnetic behavior observed in other 2e-reduced POMs with the Keggin structure.[14]

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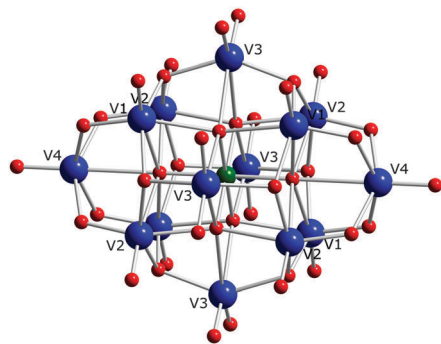
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Fig. 1 Schematic structure of the anion $[GeV_{14}O_{40}]^{8-}$, oxygen (red), vanadium (blue) and germanium (green).

This difference derives from the structure of V14. It favors the localization of the two extra electrons at the two extremes of the molecule to minimize the Coulomb repulsion, and prevents the electrons from hopping from one side of the molecule to the other. It was found that the central square $[GeV_4O_{12}]$ acts as a barrier owing to its high orbital energy.[15] With this electronic distribution one can expect that an electric field will help the electrons overcome the Coulomb repulsion and the central barrier and will promote an antiferromagnetic coupling between the spins when they are in adjacent vanadium sites. This will make the system switch its ground spin state from a paramagnetic situation (2 independent spins $S = 1/2$) to an antiferromagnetic situation ($S = 0$).[15]

To model the spin coupling in this molecule we have assumed an effective Hamiltonian that takes into account the electron transfer t of a single electron between two vanadium sites, the exchange coupling J and the Coulomb repulsion V.

$$\hat{H} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \left(t_{ik} \sum_\sigma c_{k\sigma}^+ c_{i\sigma} - J_{ij} S_i S_j + V_{ij} n_i n_j \right) + \sum_{i=1}^{N} n_i \left(\varepsilon_i + \vec{r}_i \vec{E} \right)$$

Into this Hamiltonian a new term ε was added to account for the influence of an electric field $\vec{E}$ on an electron in coordinates $\vec{r}_i$. This term assumes a linear interaction of the electric dipole created by the asymmetric distribution of the two electrons with the external electric field, which has been applied along the molecular axis (V4–V4).

The results showed that in the absence of an electric field, the singlet–triplet energy gap obtained from the diagonalization of the t–J model Hamiltonian using the local parameters optimized by using *ab initio* methods is close to zero (0.16 cm^{-1} ≈ 0.2 K), in agreement with the paramagnetic behavior experimentally observed. When the electric field is applied, a step-like feature appears at *ca.* 6.5 V nm^{-1} (Fig. 2). Such behaviour is attributed to the stabilization of the singlet spin state and the consequent opening in the singlet-to-triplet energy gap that is due to the very strong antiferromagnetic coupling between the two $S = 1/2$ spins induced by the electric field when the energy barrier has been overcome and the two electrons are located on adjacent V sites. In addition, this switching of the magnetic properties is
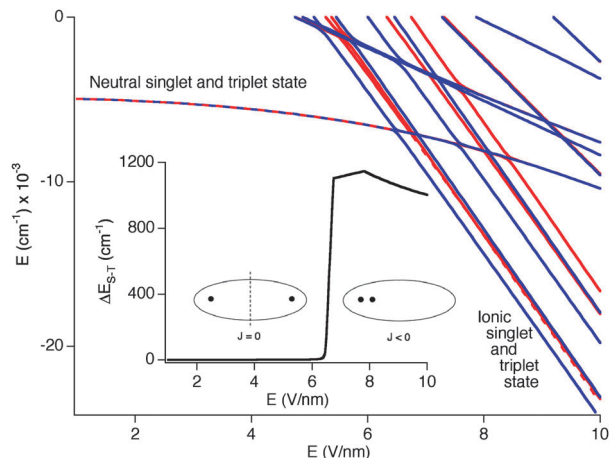

Fig. 2 Energy level scheme as a function of the external electric field (red: singlet states, blue: triplet states). Inset: energy gap between the ground singlet and the lowest triplet state, with a schematic representation of the electron distribution.

very abrupt (with only a change of 0.2 V nm^{-1} the energy gap is increased by about four orders of magnitude).

The above qualitative description can be refined by calculating the electron occupation on each vanadium site in the presence of **E**. The analysis of the composition of the wave functions showed that, at zero field, both triplet and singlet spin states have very similar distributions, with the electrons mostly located at the apical vanadium sites (87% at the two V4 sites) and 13% at the base of the square pyramids (V1 and V2).

The population of initially equivalent atoms at both sides of the molecule begins to imbalance when an electric field is applied. As can be seen in Fig. 3, equivalent sites are differentiated when a minimum field is applied (solid lines *versus* dashed lines). One of them is strongly stabilized, and therefore its population increases, while the other is destabilized in the same proportion. As the electric field is increased, an abrupt jump occurs in the population of the different sites (at 6.5 V nm^{-1} for the
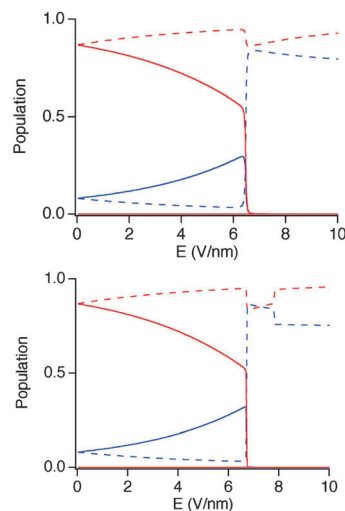

Fig. 3 Single site electronic population as a function of the external electric field for singlet (left) and triplet (right). Red lines: V4, blue lines: bases of the pyramids. Solid lines *vs.* dashed lines: the two sides of the molecule.

singlet states and 6.8 V nm^{-1} for triplet states). The population of one of the apical vanadium ions goes straight to zero as its electron density is transferred to the V1 and V2 centres on the other side. In this region where the two electrons are in the same half of the molecule, the energy levels are slightly different for the singlet and triplet due to the exchange interaction (Fig. 3).

The spin transition from a paramagnetic to a strongly anti-ferromagnetic $S = 0$ ground state has also been confirmed using broken-symmetry DFT calculations performed on the whole molecule. In these calculations, a similar change in the spin state was found above a critical value of the electric field of 11.5 V nm^{-1}. Moreover, this approach qualitatively confirmed the electron distribution in the polyoxometalate framework, both before and after the transition. The predicted singlet-to-triplet gap is also very large (it sharply increases to 800 cm^{-1} at 12.5 V nm^{-1} reaching a value of 1400 cm^{-1} at 15 V nm^{-1}). The difference in the critical field between both approaches can be explained considering the electric polarization and the electronic shielding effect on the molecule. As the effective Hamiltonian calculations do not take them into account, the critical field predicted by this method can be significantly underestimated.

In conclusion our calculations have shown that the V14 molecule works as a switch, undergoing a sudden and reversible transition from a paramagnetic to an antiferromagnetic ground spin state when an electric field along the molecular axis is applied. Notice that to obtain experimental evidence for this switching behaviour, we face two limitations that are intrinsic to this molecule. The first one concerns the high electric field needed to reach the switching of the spin state (of the order of 10 V nm^{-1}). The second one concerns the high negative charge of this type of mixed-valence molecules. This last feature presents formidable experimental difficulties in order to maintain the number of electrons in the cluster when it is contacted with metallic electrodes.

Notes and references

1 (*a*) L. Bogani and W. Wernsdorfer, *Nat. Mater.*, 2008, **7**, 179–186; (*b*) J. Camarero and E. Coronado, *J. Mater. Chem.*, 2009, **19**, 1678–1684; (*c*) S. Sanvito, *Chem. Soc. Rev.*, 2011, **40**, 3336–3355; (*d*) J. M. Clemente-Juan, E. Coronado and A. Gaita-Ariño, *Chem. Soc. Rev.*, 2012, **41**, 7464.
2 V. A. Dediu, *Nat. Phys.*, 2013, **9**, 210–211.
3 F. Prins, M. Monrabal-Capilla, E. A. Osorio, E. Coronado and H. S. J. van der Zant, *Adv. Mater*, 2011, **23**, 1545–1549.
4 A. R. Rocha, V. M. Garcia-Suarez, S. W. Bailey, C. J. Lambert, J. Ferrer and S. Sanvito, *Nat. Mater.*, 2005, **4**, 335–339.
5 A. Droghetti and S. Sanvito, *Phys. Rev. Lett.*, 2011, **107**, 047201.
6 N. Baadji, M. Piacenza, T. Tugsuz, F. Della Sala, G. Maruccio and S. Sanvito, *Nat. Mater.*, 2009, **8**, 813–817.
7 A. Palii, B. Tsukerblat, J. M. Clemente-Juan and E. Coronado, *J. Phys. Chem. C*, 2012, **116**, 4999–5008.
8 (*a*) C. Bosch-Serrano, J. M. Clemente-Juan, E. Coronado, A. Gaita-Ariño, A. Palii and B. Tsukerblat, *ChemPhysChem*, 2012, **13**, 2662–2665; (*b*) C. Bosch-Serrano, J. M. Clemente-Juan, E. Coronado, A. Gaita-Ariño, A. Palii and B. Tsukerblat, *Phys. Rev. B*, 2012, **86**, 024432.
9 J. Lehmann, A. Gaita-Ariño, E. Coronado and D. Loss, *Nat. Nanotechnol.*, 2007, **2**, 312–317.
10 J. Lehmann, A. Gaita-Ariño, E. Coronado and D. Loss, *J. Mater. Chem.*, 2009, **19**, 1672–1677.
11 (*a*) J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. Tsukerblat, *Chem. Phys.*, 1995, **195**, 1–15; (*b*) J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. Tsukerblat, *Chem. Phys.*, 1995, **195**, 17–28.
12 S. Bertaina, S. Gambarelli, T. Mitra, B. Tsukerblat, A. Müller and B. Barbara, *Nature*, 2008, **453**, 203–206.
13 L. H. Bi, U. Kortz, M. H. Dickman, S. Nellutla, N. S. Dalal, B. Keita, L. Nadjo, M. Prinz and M. Neumann, *J. Cluster Sci.*, 2006, **17**, 143–165.
14 (*a*) M. Kozik, C. F. Hammer and L. C. W. Baker, *J. Am. Chem. Soc.*, 1986, **108**, 2748–2749; (*b*) M. Kozik and L. C. W. Baker, *J. Am. Chem. Soc.*, 1987, **109**, 3159–3160; (*c*) M. Kozik, N. Casañ-Pastor, C. F. Hammer and L. C. W. Baker, *J. Am. Chem. Soc.*, 1988, **110**, 7697–7701; (*d*) M. Kozik and L. C. W. Baker, *J. Am. Chem. Soc.*, 1990, **112**, 7604–7611; (*e*) N. Casañ-Pastor and L. C. W. Baker, *J. Am. Chem. Soc.*, 1992, **114**, 10384–10394.
15 N. Suaud, Y. Masaro, E. Coronado, J. M. Clemente-Juan and N. Guihéry, *Eur. J. Inorg. Chem.*, 2009, 5109–5114.