Electronic structure and magnetic anisotropy of the [Co$_4$(hmp)$_4$(CH$_3$OH)$_4$Cl$_4$] molecule

Tunna Baruah $^a$ and Mark R. Pederson $^a$, $^b$

$^a$Department of Physics, Georgetown University, Washington, DC 20057, USA

$^b$Center for Computational Materials Science, Code 6392, Naval Research Laboratory Washington, DC 20375-5000, USA

Accurate density-functional based calculations have been performed on the Co$_4$(hmp)$_4$(CH$_3$OH)$_4$Cl$_4$ molecular magnet where hmp is deprotonated hydroxymethyl pyridine. In addition to the experimentally observed staggered geometry, we identify two isomers, referred to as eclipsed and half-staggered/half-eclipsed, that are reasonably low in energy. Our calculations show that the magnetic anisotropy is strongly dependent on the pyridine-pyridine separation and that the three structures exhibit easy axis, easy plane and triaxial behavior. Other effects such as partial reprotonation of the hmp is considered.

The magnetic molecules containing transition metal atoms are being widely studied due to potential technological applications for information storage and quantum computing [1]. The magnetic molecules show magnetic hysteresis behavior reminiscent of single domain magnets and exhibit the phenomenon of quantum tunneling of magnetization. Observation of such behavior in a molecular magnet is greatly facilitated by a reasonably high net spin and a large magnetic anisotropy energy (MAE). A very recent experimental report of a single molecule magnet consisting of Co$_4$(hmp)$_4$(CH$_3$OH)$_4$Cl$_4$ [2] where hmp- is the deprotonated hydroxymethylpyridine, suggests that this molecule is quite promising since the magnetic anisotropy energy per transition metal atom is high (25-50K) compared to other magnetic molecules Fe$_8$-tacn [3], Mn$_{12}$-acetate [4-5,6,7] where it is (3-6K). The reported ferromagnetic ordering of the Co$_4$ molecule also differs qualitatively from the ferrimagnetic spin ordering observed in the Mn$_{12}$ and Fe$_8$. The negative anisotropy energy for a transition metal with more than 5 d electrons is also considered to be unusual.

In order to gain more insight into the properties of this molecule, we have carried out a detailed ab initio study of the electronic structure and magnetic anisotropy energy of [Co$_4$(hmp)$_4$(CH$_3$OH)$_4$Cl$_4$] for different conformers. Density functional theory [8,9] based all-electron, spin-polarized calculations were carried out with the NRLMOL code [10,11] within the generalized gradient approximation to the exchange-correlation functional [12].

In the experimentally obtained Co$_4$ cluster [2], the four cobalt atoms in the molecule are bonded to organic hydroxy-methyl-pyridine(hmp) ligands (Fig. 1(a)). The four Co(II) atoms and the four oxygens from the CH$_2$O$^-$ radicals of the hmp ligand form an inner cubane structure. The experimentally observed molecule exhibits S$_4$ point group symmetry and is made up of four units where each 22-atom unit (Fig. 1(b)) consists of Co$^{+2}$, Cl$^-$, CH$_3$OH and the hmp ligand. An eclipsed geometrical isomer (Fig. 2(a)) can be generated by continuously distorting the lower half of the staggered experimental geometry or from the inequivalent 22-atom complex from the group of order 4 generated from (xyz) → (-x,-y,z) and (xyz) → (y,x,-z). Another energetically competitive structure (Fig. 2(b)), which we refer to as half staggered and half eclipsed (HSHE), can be generated by rotating and appropriately reorienting only the Cl and ligands on the lower
half of the experimental structure. This structure has one symmetry operation [(xyz) → (x,-y,-z)]. Complete geometry optimizations were carried out for each conformer.

The starting parameters for the experimentally reported staggered geometry were taken from the reported isostructure of the [Ni₄(hmp)₄(CH₃OH)₄Cl₄] molecular crystal. Upon relaxation, the volume of the molecule increases due to the repulsion of the hmp ligands in parallel positions. The eclipsed structure was found to be higher in energy than the staggered structure by 2.77 eV. Since this energy difference is probably due to intraplanar and interplanar steric repulsions, we have been motivated to look at the half-staggered and half-eclipsed geometry as well. We find that the relaxed HSHE geometry is only 0.79 eV above the experimental geometry. The cohesive energy was found to be approximately 4.7 eV/atom for all structures.

The spin-projected total density of states (DOS) as well as the Co d density of states of the staggered structure are shown in Fig. 3. The figure shows that the states near the Fermi level arises mainly from the Co atoms. These states also contain minor contributions from the oxygen and chlorine atoms. The Co d majority states are fully occupied. The figure shows that both the HOMO and the LUMO belongs to the minority spin Co d levels. The HOMO-LUMO gap in the staggered structure is 0.55 eV. The gap is found to be highly sensitive to the orientation of the ligands. In the eclipsed structure, the HOMO-LUMO gap is small (0.09 eV), while for the HSHE structure, it is 0.41 eV. This leads to interesting magnetic behavior in the three structures. The values of the gap and the MAE of the three conformers are summarized in Table 1.

Our calculations have shown that the states near the Fermi level are dominated by the cobalt d states with both the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) belonging to the minority spin Co d levels. The HOMO-LUMO gap in the staggered structure is 0.55 eV. The gap is found to be highly sensitive to the orientation of the ligands. The calculated magnetic anisotropy energy of the uniaxial, optimized staggered structure was found to be 23 K although the initial structure, based on experimental parameters, showed a high value of MAE of 57 K. The separation between pyridine rings was found to increase upon optimization which in turn increased the HOMO-LUMO gap. The HOMO-LUMO gap for the initial geometry of the experimental structure was found to be 0.09 eV. This observation opens up an
exciting possibility of altering the MAE by manipulating the pyridine-pyridine separations, in particular, by the application of pressure. It may be mentioned here that Yang et al. have established that the magnetization barrier is $\sim 100-200$ K. The large discrepancy between the theoretical and experimental values further supports the possibility that the MAE may exhibit significant pressure dependencies. So crystal packing effects may play an important role here.

The eclipsed structure, on the other hand, shows a more promising magnetic behavior (Table 1). In this case, the magnetization has easy, medium and hard axes. The easy axis lies along the axis of the molecule as in the experimental structure. The energy barrier between the easy and the medium axes is 95K while that between the medium and hard axes is 65K. This leads to a rather large D parameter of -3.55K and an E parameter of -0.91K. Interestingly, the MAE of the HSHE structure (50K) lies between the MAE of the staggered and the eclipsed structures. However, this geometry has an easy plane of magnetization. Thus, changing the orientation of the ligands significantly, albeit indirectly, influences the magnetic behavior of the Co$_4$ through band gap changes.

One possible way of achieving an overall easy axis is through the orthogonal hard axis alignment model in which each cobalt exhibits a local easy plane and the intersection of easy planes between the lower and upper Co atoms determines an easy axis. Another way is for each atom to exhibit a local easy axis along the global uniaxis. Within the second-order perturbation theory, and the LCAO method used here, it is possible to decompose the anisotropy hamiltonian into a sum of 4-center terms by expanding the relevant matrix elements into their atomic constituents. Because the Co d states are localized and dominate the behavior near the Fermi level, one expects that the single-center diagonal terms will be primarily responsible for the anisotropy energy. We have determined numerically that this is an excellent approximation and find that in all structures, the local alignments are identical with the local hard axis lying along the in-plane Co-O bond in the cubane (Co and O are attached to two parallel ligands) and the local medium axis lying along the Co-N bond (Fig. 4). This leads to the situation where the local hard and easy axes lie on a plane bisecting the molecule. For the case of the staggered structure, the local hard axes of the upper and lower Co atoms are orthogonal, which leads to the global easy axis lying along the axis of the molecule. In the other two structures, the local hard axes are aligned parallel and the competition between the medium and the local easy axes leads to a triaxial alignment in one and to an easy plane of alignment in the other. For the latter, the easy and the medium axes are nearly degenerate.

In conclusion, we show that the magnetization of the Co$_4$ molecule varies strongly with the orientation of the various ligands. While the staggered and eclipsed structures have a preferred axis of magnetization, the intermediate structure has a preferred plane of magnetization. For the higher energy isomer, the energy barrier between the hard and the medium axis is quite high ($\sim 95$K). This is especially interesting in view of the small number of transition metal atoms in the molecule. Our results suggest that the anisotropy energy may be strongly varied by manipulating the pyridine-pyridine spacing and ligand orientation. Determining a means for constraining the ligands by either chemical, physical or electrostatic means would be a worthwhile investigation.

1. Acknowledgment

The authors gratefully acknowledge the financial support by ONR grant N0001400WX2011.

REFERENCES

1. M. N. Leuenberger and D. Loss, Nature 410 (2001) 789 (2001).
2. E.-C. Yang, D. N. Hendrickson, W. Wernsdorfer, M. Nakano, R. Sommer, A. L. Rheingold, M. Ledezma-Gairaud, and G. Christou, cond-mat/0109219.
3. A.-L. Barra, P. Brunner, D. Gatteschi, Ch. E. Schulz, and R. Sessoli, Europhys. Lett. 35 (1996) 133.
Table 1
The magnetic moment(\(\mu\)), HOMO-LUMO gap (\(\Delta\)), magnetic alignment energies, with respect to the easy axis, and type of magnetic alignment of the three different structures of the Co\(_4\) molecule. H and M correspond to hard and medium axes respectively. S, E and HSHE pertain to staggered, eclipsed and half-staggered/half-eclipsed structures respectively.

| Struc. | \(\mu\) | \(\Delta\) (eV) | Energy (K) | H | M | Type               |
|--------|--------|----------------|------------|---|---|--------------------|
| S      | 12     | 0.55           | 23         | 23 |   | Easy axis          |
| E      | 12     | 0.09           | 160        | 95 |   | Triaxial           |
| HSHE   | 12     | 0.41           | 50         | 10 |   | \(\sim\) Easy plane |

4. R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, Nature 365(1993) 141.
5. S. M. J. Aubin, M. W. Wemple, D. M. Adams, H.-L. Tsai, G. Christou, and D. N. Hendrickson, J. Am. Chem. Soc. 118 (1996) 7746.
6. M. R. Pederson and S. N. Khanna, Chem. Phys. Lett. 307 (1999) 253.
7. M. R. Pederson and S. N. Khanna, Phys. Rev. B 59 (1999) R693.
8. P. Hohenberg and W. Kohn, Phys. Rev. 136 (1964) B864.
9. W. Kohn and L.J. Sham, Phys. Rev. 140 (1965) A1133.
10. M. R. Pederson and K. A. Jackson, Phys. Rev. B, 41 (1990) 7453.
11. K. A. Jackson and M. R. Pederson, Phys. Rev. B 42 (1990) 3276.
12. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
13. A. Escuer, M. Font-Bardía, S. B. Kumar, X. Solan, and R. Vicente, Polyhedron 18 (1999) 909.
14. M.R. Pederson and S.N. Khanna, Phys. Rev. B 60 (1999) 9566.
15. J. Kortus, S. N. Khanna and M. R. Pederson, to be published.

Figure 1. (a) The geometry of the lowest-energy staggered structure in which the hydrogen atoms are not shown. (b) The inequivalent building block of each molecule which consists of the Co\(^{2+}\), Cl\(^-\), CH\(_3\)OH and the hmp\(^-\) ligands.

Figure 2. The optimized (a) eclipsed and (b) half-staggered half-eclipsed geometries in which the hydrogen atoms are not shown.
Figure 3. The total and Co-d majority and minority spin density of states of the staggered Co₄ molecule.

Figure 4. The local easy, medium and hard axes on a representative Co atom. Only the cobalt-oxygen cube part of the whole molecule is shown.