The quantum chemical study of isotropic and anisotropic magnetic properties of molecular magnets

E.A. Suturina[1], N.P. Gritsan[1], L. Ungur[2], L.F. Chibotaru[2]

[1] Institute of Chemical Kinetics and Combustion, SB RAS, Novosibirsk, Russia

[2] Division of Quantum and Physical Chemistry, Katholieke Universiteit Leuven, Belgium

liza.suturina@gmail.com

The field of molecular magnetism grows essentially over the past two decades. Significant progress has been achieved in the synthesis and investigation of different types of molecular magnetic materials. Note, that nowadays quantum chemistry plays a crucial role in the understanding and analysis of the magnetic properties.

In most cases, the magnetic properties of three-dimensional bulk molecular magnets can be described using isotropic spin-Hamiltonian ($\hat{H} = -2\Sigma J_{ij}\hat{S}_i\hat{S}_j$), where only isotropic exchange spin coupling is taken into account. In contrast, in the case of anisotropic systems, such as single molecular magnets, the anisotropy caused by electron spin-orbit coupling in metal centers determines the magnetic properties [1].

Here we report results of our calculations for both the isotropic and anisotropic molecular magnets.

The first investigated system is the anion radical salt of [1,2,5] thiadiazolo [3,4-c] [1,2,5] thiadiazolidyl with bis(toluene)chromium. Parameters of the Heisenberg spin-Hamiltonian have been calculated at the CASSCF/NEVPT2 and broken-symmetry DFT levels, and the complex magnetic motifs featuring the dominance of the antiferromagnetic (AF) interactions have been revealed.

The second system of interest is the heterometallic cluster $[Co_2^{III}Mn_2^{II}(hmp)_6Br_2(CH_3CN)_2]$ $Mn^{II}Br_4$. The DFT calculations of the exchange interactions revealed that AF interactions between core Mn^{II} cations determine the magnetic properties.

The third system under study is a layered $[Co_3^{II}(2,2'-bpdo)_4(H_2O)_4[W^V(CN)_8]_2]\cdot 8H_2O$ network [2]. In this system, the bulk magnetic anisotropy is confronted with a local anisotropy of Co complexes. According to the CASSCF/RASSI/SINGLE_ANISO *ab initio* calculations this material is characterized by a strong axial anisotropy of the trans,cis,cis-$[Co^{II}(\mu-NC)_2(H_2O)_2(2,2'-bpdo)]$ moieties represented by g_x = 2.06, g_y = 2.95 and g_z = 7.30, and a planar anisotropy of the trans,cis,cis-$[Co^{II}(\mu-NC)_2(H_2O)_2(2,2'-bpdo)_2]$ moieties represented by g_x = 5.40, g_y = 4.82 and g_z = 2.28. These values well reproduce the anisotropy of magnetic properties observed in the experiment.

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[2] Chorazy, S., Podgajny, R., Majcher, A.M. et al. *Cryst. Eng. Comm.*, 15: 2378-2385, 2013.