Using partial orbital momentum quenching in a Co(II) complex to control magnetic properties: a computational study

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Transition metal compounds exhibiting sharp transition in magnetic properties upon temperature change or external perturbation attract intense attention for their potential industrial applications. There are several strategies to prepare such compounds, however in all the reported cases a change in spin- or oxidation-state of the transition metal ion is responsible for the control of magnetic properties. We would like to introduce a new approach using paramagnetic compounds with large angular momentum contribution, and controlling this contribution by distorting the crystal field and orbital quenching.

Fig. 1. The structure of **1**.

To explore such an approach, we performed DFT calculations on Co(II) complex, [Co(L)(NO3)2], (**1**) (where L: 2,6-di(pyrazol-1-il)pyrazine) (see Figure 1). High-spin cobalt(II) complexes generally show magnetic properties deviating significantly from Curie-law due to large angular momentum contribution characteri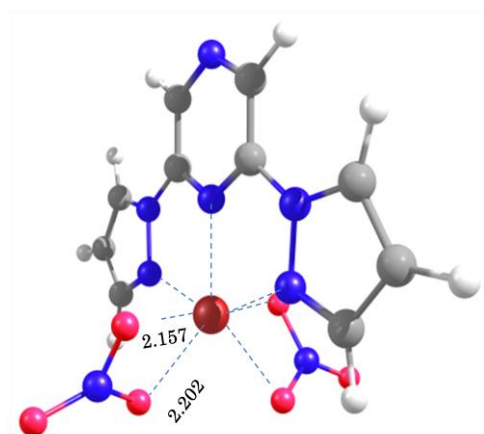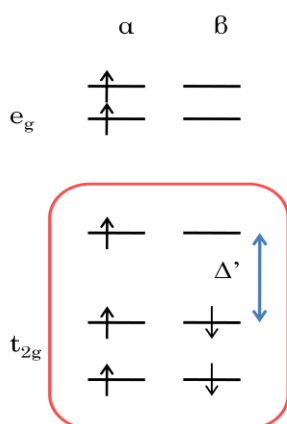stic to the $^4T_1$ state [1]. With two beta electrons on the three t_{2g} orbitals the orbital quenching is very sensitive to the distortions of the ligand field and the degeneracy of these orbitals (see Figure 2). It has been reported that **1** has a phase transition around 235 K with a hysteresis of 10 K, which transition is followed by a magnetic susceptibility change from $\chi_m T$ = 2.80 (at 225K) to 2.92 cm^{3}K/mol (at 245 K) [2]. Detailed powder-X ray investigations on **1** and the value of magnetic susceptibility excludes the possibility that spin-crossover would be responsible for the abrupt change in the magnetic data. Therefore, in both phases the cobalt ions are in high-spin state with different orbital quenching.

Fig. 2. Co^{2+} high-spin ion in distorted octahedral ligand-field.

We explored two scenarios. One is an isomerisation between two states with two distinct potential minima at single molecular level. The other possibility is that the phase transition is essentially lattice based, and the intermolecular forces distort the molecule that way that the orbital quenching is smaller in the high-temperature phase. For the calculations the Gaussian'03 software package have been used. The geometry optimizations and relaxed scans were performed at B3LYP/6-31+G* level. For the fragment molecular orbital (FMO) analysis, the diffuse functions were left out to avoid unphysical results.

The relaxed scans showed that the nitrate ions can coordinate the cobalt ion in **1** two different ways: acting as bidentate or monodenate ligand. The complex with bidentate nitrates is only slightly more stable than the complex with mixed bidentate-unidentate with an energy difference of 1.9 kcal / mol, and the potential energy barrier between the two isomers is 2.5 kcal / mol at single molecule level. However, crystallographic studies showed that there is no such drastic structural change in solid phase around the transition temperature, and the nitrate ions of the coordination sphere remains bidentate. Therefore we considered the transition as it is essentially lattice based, and investigated a model where external forces distort the molecule along the normal modes, shifting the energy of the orbitals relevant for the angular momentum contribution to magnetic susceptibility. We performed a fragment molecular orbital (FMO) analysis of **1** using $[Co(L)]^{2+}$ and the nitrate ions as fragment, and scanned the orbital overlaps along the normal modes of the $\{CoN_3O_4\}$ chromophore. The analysis showed that the energies of the empty |xz> and the filled |xy> and |yz> β orbitals are sensitive to the position of nitrate ligands, due to the significant overlap with those. Our analysis also showed that displacing the nitrate oxygens from their equilibrium position results in a reduced interaction between the cobalt(II) ion and the orbitals of the nitrate ion, which leads to smaller splitting of the orbitals relevant to the quenching of the angular momentum. Such a reduction is qualitatively consistent with the observed magnetic susceptibility values for the two high-spin phase.

Reference:
[1] O. Kahn: Molecular Magnetism, 1993, VCH Publisher; F. E. Mabbs, D. J. Machin: Magnetism and Transition Metal Complexes, 1972, Chapman & Hall.
[2] O. Sato et al. (manuscript in preparation).