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Bistability of Magnetization without Spin-Transition in a High-Spin Cobalt(II) Complex due to Angular Momentum Quenching

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In this communication we describe a new mechanism that causes an abrupt change in the magnetic susceptibility of transition metal complexes through orbital quenching of the angular momentum, instead of controlling their spin state. Functional materials showing a sudden change in magnetic susceptibility, even hysteresis, associated to temperature change or other external perturbation[1−3] have attracted great attention. Such materials, e.g., spin-crossover complexes[4] and valence tautomeric complexes,[5] are potentially useful as molecular memories, switches, or spintronics.[6] The magnetization change is generally obtained by triggering a transition between different spin states, so the change of spin contribution to magnetic susceptibility is responsible for the control of magnetic properties. However, the magnetic susceptibility of transition metal compounds can also contain a nonvanishing contribution of orbital multiplicity. This contribution can be quenched by distorting the ligand field, which offers an alternative opportunity to alter magnetic properties. To demonstrate this approach, we studied various Co(II) complexes with nitrate ligands. High-spin cobalt(II) compounds often show a large orbital momentum partially quenched by spin−orbit coupling and the distortion of the ligand field.[7] Nitrate ions can adopt different coordination modes:[8] symmetric bidentate, asymmetric bidentate with a difference between the M−O(N) bond distances of 0.4−0.7 Å, and monodentate coordination. Isomerization between these modes induced by external perturbation has also been reported;[9] therefore nitrates can form a very flexible ligand environment. We found that [Co(NO_3)$_2$(L)] (L: 2,6-di(pyrazol-1-yl)pyrazine), **1**, exhibits bistability connected to a phase transition that distorts the environment of the cobalt and alters the angular contribution to magnetic susceptibility.

The mononuclear complex, **1**, has been synthesized from solutions of Co(NO_3)$_2$·6H_2O and 2,6-di(pyrazol-1-yl)pyrazine.[10,11] The magnetic susceptibility of **1** was measured between 5 and 270 K (see Figure 1) and shows a hysteresis between 228 and 240 K.

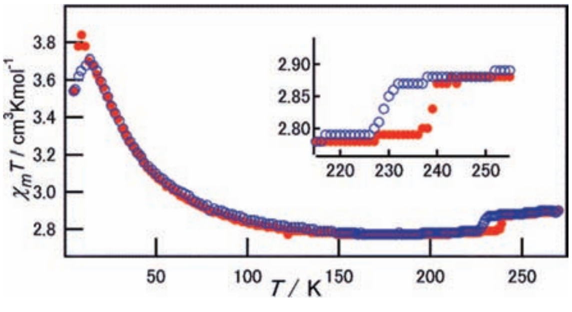

Figure 1. Temperature dependence of $\chi_m T$ for **1** in cooling (blue ○) and heating mode (red ●).

The $\chi_m T$ values below and above the transition (2.8 and 2.9 cm^3 K mol^{-1}, respectively) are significantly higher than the value for low-spin cobalt(II) (0.37 cm^3 K mol^{-1}), and they are between the values of high-spin cobalt(II) complexes with a fully quenched (1.88 cm^3 K mol^{-1}) and unquenched (5.49 cm^3 K mol^{-1}) angular momentum. Powder XRD measurements were performed between 210 and 260 K, and two distinct, pure phases were observed below and above the transition temperature. This excludes the possibility that the hysteresis is due to a spin transition of a smaller part of the sample (impurity or inhomogenity), and conventional spin-crossover cannot explain the hysteresis. At low temperature, **1** also shows an irregular magnetic behavior, which is under further investigation in our laboratory.

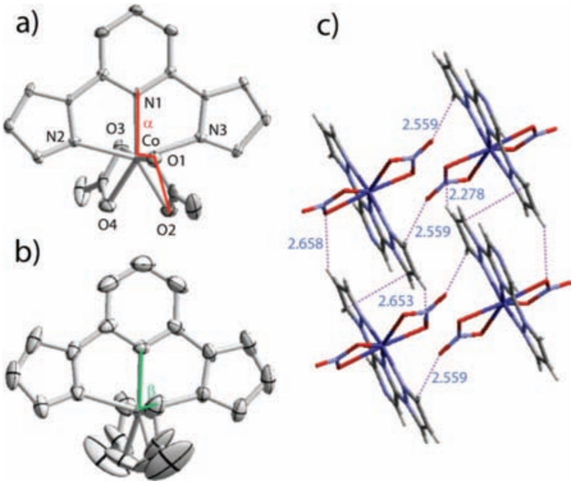

Figure 2. ORTEP view of **1** at 123 (a) and 296 K (b). H atoms of the ligand are omitted for clarity; (c) packing of **1** at 296 K (projected along [0 1 0]) (Co, navy; O, red; N, light blue; C, gray; H, white).

Crystal analysis of **1** was successfully performed at both 123 (Figure 2a) and 296 K (Figure 2b). At 123 K, **1** has a monoclinic space group $C2/c$; the asymmetric unit cell consists of two complex molecules. At 296 K, **1** has a triclinic space group $P\bar{1}$, and there is one molecule in the asymmetric unit cell. The unit cell packing shows strong intermolecular interactions at both temperatures between the nitrate ions and the pyrazol of ligand L. Strong intermolecular interactions generally play an important role in abrupt phase transitions and transitions with hysteresis. The cobalt(II) remains seven-coordinated at both temperatures, and the two nitrate ions coordinate in a symmetric bidentate fashion in an approximate C_2 symmetry. Two significant changes occur in the structure of **1** at 296 K compared to the low temperature structure: (1) the nitrate ions are twisted along the dihedral angles N1−Co−O1−O2 and N1−Co−O3−O4 (α) from an average of 157.9° to 173.0°; (2) the nitrate ions show large displacements, most probably due to structural disorder. The dihedral angle α is monitoring the angle

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between the pseudo C_2 axis going through the Co−N1 bond and the plane of the nitrate ions. The disorder of nitrate is realized in this plane, and the dihedral angle α remains in a narrow range. Comparing the IR spectra of **1** recorded between 160 and 300 K (see Figure S1 in Supporting Information) with characteristic bands previously reported[9,12] also supports the conclusion that both nitrates remain symmetric bidentate in the whole temperature range.

DFT calculations were carried out on at the B3LYP/6−31+G* level of theory with Gaussian 03.[13] Optimizations started from different geometries, including the experimental structures at high and low temperatures and converged to a single potential minimum, which is close to the low-temperature structure. The geometry changes associated with the transition of **1** are most probably induced by the strong intermolecular interactions in the lattice. To investigate the effect of these geometrical changes on the electronic state of **1**, relaxed scans were performed symmetrically rotating in-phase the dihedral angles N1−Co−O1−O2 and N1−Co−O3−O4 (α) and rotating the N1−Co−O1/N1−Co−O3 angle (β) keeping α constant. Angle β simulated the disorder of the nitrates at high temperature. The electronic ground state of **1** is $(d_{(xz)+(yz)})^2(d_{xy})^2(d_{(xz)-(yz)})^1(d_{z^2-y^2})^1(d_{x^2})^1$ in all geometries. The orbital contribution to the susceptibility is a result of the admixture of the excited states to the ground state due to spin−orbit coupling, and this contribution is inversely proportional with the energy gap between the excited states and ground state. TDDFT calculations showed that the two lowest excited states are with one β electron excited from d_{xy} to $d_{(xz)-(yz)}$ ($\Delta E1$) and from $d_{(xz)+(yz)}$ to $d_{(xz)-(yz)}$ ($\Delta E2$). In Figure 3, the calculated $\Delta E1$ and $\Delta E2$ are shown together with estimated g values along α and β. The excited-state energies show a significant drop as the dihedral angle of the nitrates, α, approaches 180°, which also results in an increase of g. However, these energies and g are less sensitive to the changes of β; therefore the disorder of nitrates does not significantly influence the magnetic properties of **1**. Though the calculations significantly underestimate the orbital contribution to the magnetization,[15] our findings are in good qualitative agreement with the observed increase of susceptibility at high temperature.

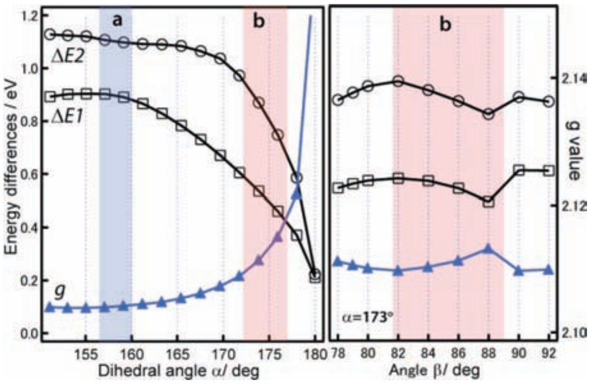

Figure 3. Excitation energies $\Delta E1$ (□), $\Delta E2$ (○) and g value (blue ▲) monitored along the α and β angles. Colored areas correspond to experimental geometries at 123 K (blue, **a**) and 296 K (red, **b**).

In summary, we observed bistability in the magnetic susceptibility of **1**, where the change of magnetization can only be explained as a result of the quenching of the orbital angular momentum. Our investigation showed that the symmetric twisting of the nitrate ligands is the most important structural change responsible for the change in magnetic properties. Utilizing orbital quenching can be a new strategy to construct molecular switches and spintronics,[6] and similar quenching may also play an important role in cobalt spin-crossover materials where complex lattice dynamics can control the electronic state of cobalt through distorting the coordination environment.[16]

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Supporting Information Available: Temperature dependent IR and XRD data, crystallographic structures, detailed discussion of DFT calculations, and complete ref 13. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Synthesis of ligand L was carried out analogous to ref 11. ^{1}H NMR (270 MHz, 25°C, $CDCl_3$): $\delta = 6.56$ (dd, $J = 1.6$, 2.6 Hz, 2 H, pyrazole), 7.83 (d, $J = 1.6$ Hz, 2 H, pyrazole), 8.52 (dd, $J = 0.7$, 2.6 Hz, 2 H, pyrazole), 9.21 (s, 2 H, pyrazine). In a test tube a solution of ligand L in acetone (0.02 mol/L) was slowly layered on a solution of $Co(NO_3)_2 \cdot 6H_2O$ in acetone (0.02 mol/L). Violet/purple prismatic crystals of **1** appeared after 1 or 2 days. Elemental analysis: observed value (element, theoretical value) = 30.22% (C, 30.40%), 2.11% (H, 2.04%), 28.11% (N, 28.36%).
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(14) At the single molecule level, the geometry with dihedral angles N1−Co−O1−O2/N−Co−O3−O4 symmetrically approaching 180° as observed at high temperature is in fact a transition state with an ∼4 kcal/mol barrier between two equivalent potential wells.
(15) DFT is a single-reference method and, therefore, less accurate when applied in systems with orbitally near-degenerate ground states such as **1**. TDDFT most probably significantly overestimates such small excitation energies.
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