

Redox Control of the SIM Behavior in Cobalt(II) Compounds

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Introduction

Single-ion magnets (SIMs) have attracted much attention in the last decades because of their relevance to molecular electronics as qubits, the smallest unit of information [1]. The particular behavior of a single-molecule magnet arises as a sum of the control of the ground state or the magnetic couplings and the local zfs tensors and their relative orientations. The unique requisite in SIMs of a local zfs that guarantee a ground Kramers doublet makes them much more electable materials. The design of switchable SIMs in which a controlled external stimulus can set off/defuse the magnetization blocking should be the subsequent step to adapt them to technological applications. One strategy for that purpose consists of the coordination of redox-active ligands to the $[\text{Co}(\text{Mephen})_2]^{2+}$ building block, which is a known precursor of octahedral SIMs [2]. The use of ferrocene mono- and di-carboxylic acids as redox-active groups to obtain discrete magnetic switchable cobalt(II) SIMs is the base of this project, namely $\text{Fc-CO}_2\text{H}$ and $\text{Fc}-(\text{CO}_2\text{H})_2$, to form more sophisticated structures.

Experimental

The EMR Facility of the NHMFL Tallahassee was used including its 15/17 T superconducting magnet.

Results and Discussion

The reactions of an acetonitrile solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and dmphen with $\text{Fc-CO}_2\text{H}$ and $\text{Fc}-(\text{CO}_2\text{H})_2$ in acetonitrile and methanol afford $[\text{Co}(\text{dmphen})_2\text{Fc-CO}_2](\text{ClO}_4) \cdot \text{Et}_2\text{O}$ (**1**) and $\{[\text{Co}(\text{dmphen})(\text{H}_2\text{O})_2]_2\text{Fc}-(\text{CO}_2)_2\}(\text{ClO}_4)_2 \cdot \text{MeCN}$ (**2**). Dc-magnetic studies suggest a large axial zero-field splitting. The HFEPFR studies confirm the large and positive D value for both compounds [$g_{\perp} = 2.63$, $g_{\parallel} = 2.27$, $E/D = 0.15$ (**1**) and $g_{\perp} = 2.53$, $g_{\parallel} = 2.26$, $E/D = 0.16$ (**2**)]. Whereas ac-magnetic measurements under a dc-magnetic field reveal frequency-dependence of χ_M'' below 8 (**1**) and 6 K (**2**), a fast relaxation of the magnetization occurs for their oxidized forms, which support the switchable nature of these systems.

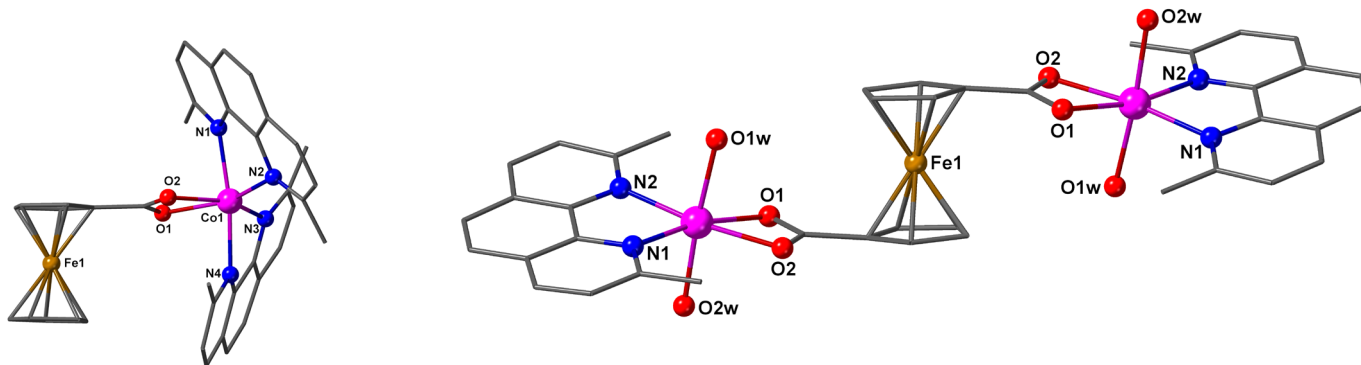


Fig.1 Views of the molecular geometries of the two cobalt/iron complexes under study.

Conclusions

Octahedral cobalt(II) complexes **1** and **2** display large and positive zfs and, as expected, behave as SIMs. The oxidation of the ferrocene redox-active group quenches this peculiar magnetic behavior probably as a result of a magnetic coupling between the cobalt(II) ions and the paramagnetic ferricinium species.

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References

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