Manganese(III) Complexes with Dcadpz Ligand: Precursors for Rational Synthesis of Homo-/Hetero-Metallic Trinuclear and Tetranuclear Clusters

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Introduction

In coordination chemistry, ligands can facilitate the formation of multi-metal structures and help controlling the magnetic interactions between metal centers. In our earlier work, we obtained a pentadentate ligand, di(pyrazolecarbimido)aminate ($dcadpz^-$) generated via an *in situ* addition of pyrazole to dicyanamide, and applied it to rationally assemble a family of trinuclear complexes of the type $[M\{M'(dcadpz)_2\}M]$ ($M = Co^{II}, Ni^{II}$, $M' = Cu^{II}, Ni^{II}$).[1] Here we report on magnetic properties of the two mononuclear manganese(III) precursors used in the clusters synthesis, $[Mn^{III}(dcadpz)_2(NO_3)]\cdot MeCN$ (**1**) and $[Mn^{III}(dcadpz)_3]\cdot H_2O$ (**2**) using magnetometric and resonance (HFEPR) techniques, with the purpose of better modeling properties of the clusters.

Experimental

The EMR Facility with its 17 T superconducting magnet was used in this experiment. Polycrystalline samples of **1** and **2** were used 'as is'.

Results and Discussion

The Mn(III) ions are coordinated in a square-pyramid environment by four nitrogen atoms from two $dcadpz^-$ ligands and one oxygen atom of NO_3^- in **1**, and in a slightly distorted octahedral geometry by six nitrogen atoms from three $dcadpz^-$ ligands in **2**. This difference in coordination has a dramatic effect on magnetic properties of the complex, since **1** shows properties typical for a high-spin ($S = 2$) Mn(III) complex while **2** is found to exist in low-spin state ($S = 1$) at low temperatures, with a possible crossover to a high-spin state at about 270 K. A representative EPR spectrum of **2** is shown in **Fig. 1**. It agrees well with that expected from an $S = 1$ spin state, with a large positive zero-field splitting term D in the spin Hamiltonian.

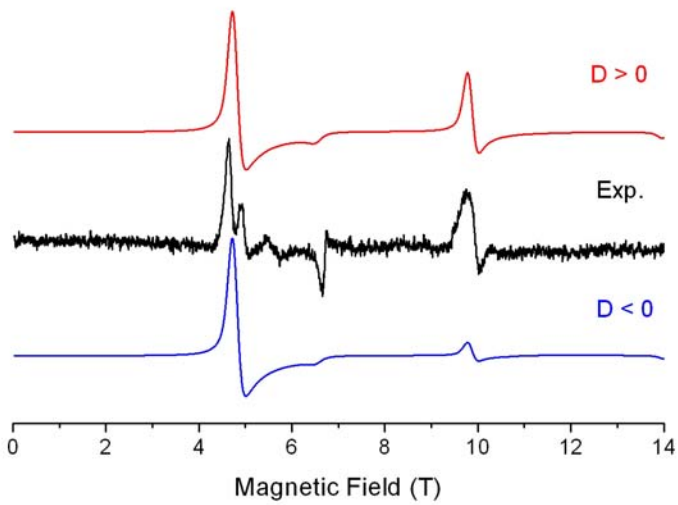

Figure 1. EPR spectrum of polycrystalline **2** at 610 GHz and 5 K (black trace) accompanied by powder-pattern simulations (colored traces) using spin Hamiltonian parameters: $S = 1$, $D = +15.9\ cm^{-1}$, $E = 0$, $g_x = g_y = 2.07$, $g_z = 2.00$ (red trace), and same parameters but negative sign of D (blue trace). The doubling of the parallel turning point at 5 T may result from a different solvent content in the crystal, and is not reproduced in the simulations.

Conclusions

Using the same ligand but different synthetic procedures one can achieve mononuclear Mn(III) complexes of very different magnetic properties. Spin Hamiltonian parameters obtained for the complexes involved in the current study will allow to better understand the magnetic properties of the clusters constructed from these complexes.

Acknowledgements

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References

[1] Zheng, L.-L., *et al*., Inorg. Chem., **46**, 9548-9557 (2007).