NOVEL LINEAR MANGANESE CLUSTERS OF A HEPTADENTATE BIS-β-DIKETONE LIGAND

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Introduction

One of us has recently synthesized a new potentially heptadentate ligand 1,3−bis−(3−oxo−3−(2−hydroxyphenyl)−propionyl)−2−methoxybenzene (H_5L).[1] The reaction in pyridine of this ligand with various $M(AcO)_2$ salts ($M=Ni^{II}$, Co^{II}, Mn^{II}) leads to very different products depending on the metal. A use of the Mn^{II} salt creates a linear zigzag tetranuclear cluster $[Mn_4(H_2L)_2(AcO)_2(py)_5]$ (**1**). Slow oxidation of **1** leads to formation of a novel mixed valence linear complex $[Mn_3(HL)_2(py)_6]$ (**2**), displaying an unprecedented asymmetric $Mn^{III}Mn^{III}Mn^{II}$ topology. The magnetic behavior of both complexes has been investigated by magnetometry and X-band EPR. In this report we employed High-Frequency and -Field EPR (HFEPR) to further probe the magnetic properties of the ground spin state of complex **2**.

Experimental

The HFEPR experiments at several frequencies were performed at the EMR Facility and 17-Tesla superconducting magnet.

Results and Discussion

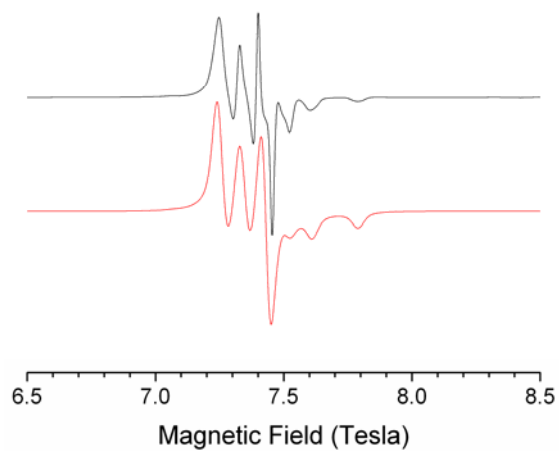

Figure 1. A 208 GHz HFEPR spectrum of complex **2** at 10 K (blue trace) and its simulation (red trace) using parameters as in text.

The g ~ 2 region of an exemplary HFEPR spectrum of **2** is shown in Fig. 1 together with its powder-pattern simulation using the following spin Hamiltonian parameters: $S = 5/2$, $D = +0.085$ cm^{-1}, $E = 0$, $g_{iso} = 2.00$. These parameters are characteristic for single-ion properties of Mn^{II} in reduced-symmetry environment. The well-resolved fine structure witnesses a lack of a significant magnetic inter-cluster exchange. Besides the strong g ~ 2 set of resonances shown in Fig. 1, which is typical for a Kramers (half-integer spin) system, there also appear at lower and higher fields multiple thermally-activated lines (not shown) characteristic for a non-Kramers (integer spin) system present in the cluster. The interpretation and analysis of those resonances is currently in progress.

Conclusions

The unusual mixed-valence linear trimeric Mn cluster **2** shows that the Mn^{II} ion is practically magnetically isolated from the rest of the molecule, as suggested by the Kramers-type ground spin state of the cluster. At the same time, the two Mn^{III} ions couple antiferromagnetically with each other, creating a diamagnetic ($S = 0$) dimeric state. The exchange constants between the Mn^{III} ions are very small, which results in a presence of low-lying thermally excited non-Kramers spin states.

Acknowledgements

This work was supported by the NHMFL.

References

[1] Aromì, G., *et al*., Eur. J. Inorg. Chem. 1940-1944 (2006).