High-Frequency and -Field EPR Experiments on a Mononuclear Single-Molecule Magnet Based on a Manganese(III) Complex

J. Vallejo, A. Pascual-Álvarez, J. Cano, I. Castro, R. Ruiz-García, M. Julve, F. Lloret, E. Pardo (U. of Valencia, Spain, Inorganic Chemistry and Inst. for Molecular Science); J. Krzystek (NHMFL); G. De Munno, D. Armentano (U. of Calabria, Italy, Chemistry and Chemical Technology); W. Wernsdorfer (Institut Néel, Grenoble, France)

Introduction

The past few years have seen a trend within the area of single-molecule magnetism to shift from large polynuclear complexes of metal ions with high *S* numbers to much simpler mononuclear species. The first known examples of single-molecule magnet were complexes of lantanides and actinides, and within the transition metals, cobalt and iron [1]. In this report we present HFEPR results on what is the first known mononuclear Mn(III) complex that displays the properties of a single-molecule magnet: $Ph_4P[Mn(opbaCl_2)(py)_2]$ (**1**) [$H_4opbaCl_2$ = *N,N'*-3,4-dichloro-*o*-phenylenebis(oxamic acid), py = pyridine, and Ph_4P^+ = tetraphenylphosphonium cation] (Fig. 1) [2].

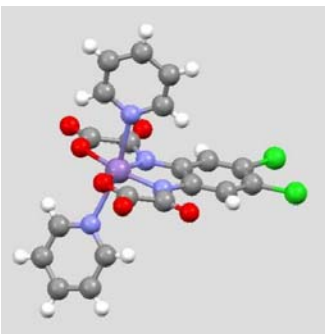

Figure 1. Perspective view of **1**.

Experimental

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

Results and Discussion

The magnetic properties of **1** were investigated in Valencia and Grenoble, and the complex showed slow relaxation as detected via frequency-dependent ac susceptibility in magnetic field, and a magnetic field hysteresis at low temperatures (not shown). The crystal structure was solved in Calabria. The coordination sphere is represented by a distorted octahedron, with a Jahn-Teller elongation. This geometry predisposes the complex to have negative zero-field splitting (zfs), which in turns correlates with its magnetic properties. The zfs parameters were very accurately determined from HFEPR spectra (Fig. 2) at both low (10 K) and high (280 K) temperatures, and were found to be at 10 K: $D = -3.421(2)$ cm^{-1}, $E = -0.152(2)$ cm^{-1} ($|E/D| = 0.044$), $B^4_0 = B^4_2 = 0$, $B^4_4 = 32(5) \times 10^{-4}$ cm^{-1}, with very slightly anisotropic *g*-tensor [1.994(2), 1.997(2), 1.978(7)]. At 280 K the relevant parameters are: $D = -3.246(2)$ cm^{-1}, $E = -0.115(1)$ cm^{-1}; ($|E/D| = 0.035$), $B^4_0 = B^4_2 = 0$; $B^4_4 = 23(3) \times 10^{-4}$ cm^{-1}; g = [2.001(1), 2.000(1), 1.990(3)].

Conclusions

The magnetic properties of **1** as obtained via HFEPR correlate very well with those delivered by magnetometry, and also with the results of quantum-chemical calculations. In particular, the relaxation activation energy (12.7 cm^{-1}) agrees with the value of $4|D| = 13.7$ cm^{-1}.

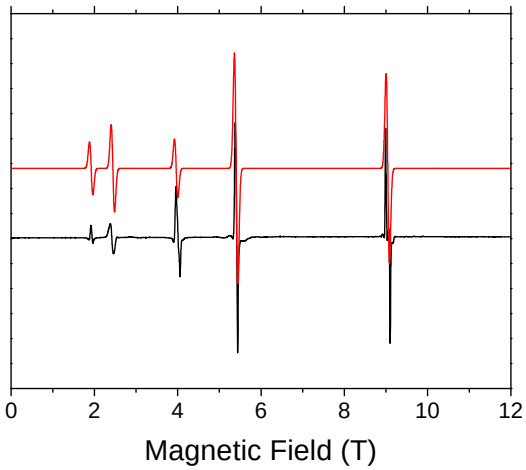

Figure 2. HFEPR spectrum of a single crystal of **1** at 10 K and 203 GHz (black trace) and its simulation using spin Hamiltonian parameters as text (red trace).

Acknowledgements

This work was supported by the MICINN (Spain) (Project CTQ2010-15364), the Generalitat Valenciana (Spain) (Projects PROMETEO/20. 09/108, GV/2012/051 and ISIC/2012/002), the MiUR (Italy) through the Centro di Eccellenza CEMIF.CAL (Grant CLAB01TYEF), and the NHMFL.

References

[1] (a) Ishikawa, N., *et al*., J. Am. Chem. Soc., **125**, 8694-8696 (2003); (b) Meihaus, K.R., *et al*., Inorg. Chem., **50**, 8484-8489 (2011); (c) Zadrozny, J.M., *et al*., J. Am. Chem. Soc., **133**, 20732-20734 (2011); (d) Harman, W.H., *et al*., J. Am. Chem. Soc., **132**, 18115-18126 (2010).
[2] Vallejo, J., *et al*., Angew. Chem. Int. Ed., in print, DOI: 10.1002/anie.201308047 (2013).