High-Frequency and -Field EPR of a Dinuclear Y^{III}-Co^{II} Coordination Complex Exhibiting Slow Relaxation of the Magnetization

E. Colacio, J. Ruiz (U. of Granada, Spain, Chemistry); E K. Brechin (U. of Edinburgh, United Kingdom, Chemistry), J. Krzystek (NHMFL)

Introduction

A dinuclear coordination complex, [Co(μ-L)(μ-OAc)Y(NO_3)$_2$] (**1**) (H_2L is the compartmental ligand *N*,*N*',*N*"-trimethyl-N,N"-bis(2-hydroxy-3-methoxy-5-methylbenzyl)diethylenetriamine), comprising one diamagnetic Y^{III} and one high-spin Co^{II} metal center was magnetically investigated by *dc* and *ac* susceptibility techniques. The magnetic results show that **1** exhibits slow relaxation of the magnetization in the presence of a small applied magnetic field of 1000 Oe, with an effective thermal energy barrier of 20 K, and, therefore, from the magnetic point of view, it can be considered as a single-ion magnet (SIM). In order to disclose the relaxation mechanism for this compound, it would be very helpful if the sign of the single-ion anisotropy parameter *D* were known. Magnetization *vs* H/T results seems to indicate that D = +32 cm^{-1} (a negative value of ~ –9 cm^{-1} is also possible). We thus undertook an HFEPR study to differentiate between these two possible situations.

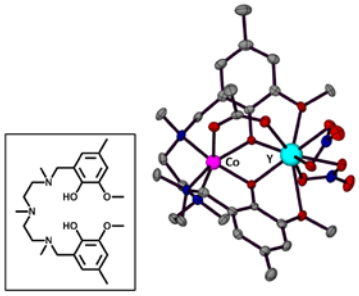

Figure 1. Molecular structure of complex **1**.

Experimental

HFEPR experiments were conducted at the NHMFL EMR Facility, using its 15/17 T superconducting magnet.

Results and Discussion

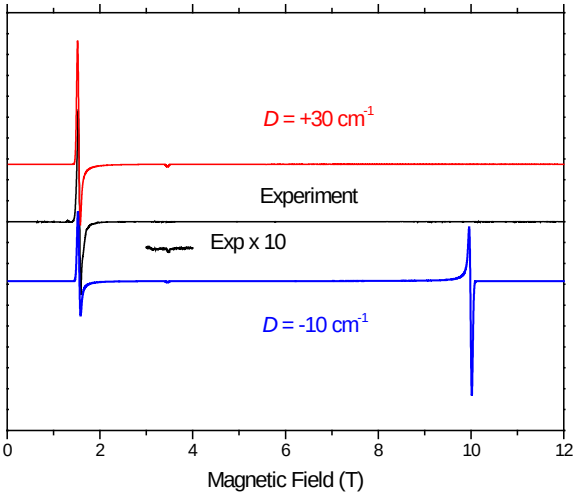

Figure 2. A 101.2 GHz EPR spectrum of 1 at 10 K (black trace) accompanied by powder-pattern simulations using two different *D* values as indicated. The g-matrix was [2.37, 2.4, 2.1].

Figure 2 shows a 101 GHz spectrum of **1** at 10 K. Two simulations are also provided, using spin Hamiltonian parameters delivered by magnetometry, in particular with a negative, and positive *D* value. It is clearly established that *D* is positive, thus the ground spin state is the M_S = ±1/2 Kramers doublet.

Conclusions

Only two examples of Co^{II} mononuclear complexes with D > 0 exhibiting SIM behavior have been reported (with either pseudotetrahedral[1] or octahedral[2] rhombic geometries). In the pseudotetrahedral case the relaxation process can be reasonably explained by a spin-phonon bottleneck mechanism, but not so in the rhombic octahedral complex, which exhibits a thermal energy barrier similar to that observed in complex **1**. From susceptibility and magnetization vs H/T data, the rotation of the magnetization for **1** would require an energy barrier of $E_a = 2|D| = 64$ cm^{-1}, a value which is four times greater than that experimentally observed ($E_a \approx 17.0$ cm^{-1}). Consequently, new physics involving a smaller energy barrier must be involved.

Acknowledgements

This work was supported by the MEC (Spain) (Project CTQ2011-24478), the Junta de Andalucía (FQM-195 and Project of Excellence P08-FQM-03705), the University of Granada, and the NHMFL.

References

[1] Zadrozny, J.M., *et al.*, Chem. Commun., **48**, 3897-3929 (2012).
[2] Vallejo, J., *et al.*, J. Am. Chem. Soc., **134**, 15704-15707(2012).