High-Field EPR Studies of Single-Ion Magnets with Giant Axial Magnetic Anisotropy

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Introduction

The motivation behind this project involves designing new single-ion single-molecule magnets (SI-SMMs) with giant magnetic anisotropies, particularly trigonal bipyramidal (TBP) Ni^{II} complexes with orbitally degenerate ground states.[1] However, such species are highly susceptible to Jahn-Teller-type distortions that lift the orbital degeneracy, thereby ultimately limiting the anisotropy. To this end, [Ni(Hdabco)(dabco)Cl_3] and [Ni(Me-dabco)$_2$$Cl_3$] were synthesized using the rigid dabco (= 1,4-diazabicyclo[2.2.2]octane) ligand in the hope of suppressing these Jahn-Teller effects.[2] High-field EPR studies then play a crucial role for precise elucidation of the spin Hamiltonian parameters which describe the magnetic anisotropy.

Experimental

Multi-frequency, low temperature EPR measurements based on a cavity perturbation technique were performed in the DC facility in magnetic fields to 35 T. The sample was placed in a rotating cavity to obtain the required orientation of the single-crystal with respect to the applied field.

Results and Discussion

Oriented single-crystal high-field EPR measurements were successfully performed at 4.2 K on the spin S = 1 trigonal bipyramidal (TBP) [$Ni^{II}Cl_3$(Me-dabco)$_2$] complex. Multiple resonances were observed at a frequency of 81 GHz, of which a single peak shifts rapidly to magnetic fields of 35 T and beyond over a very narrow angle range, as seen in Fig. 1(a). An analysis of this angle dependence suggests a huge easy-axis anisotropy with a zero-field-splitting (zfs) parameter, $|D| > 300$ cm^{-1}, associated with first order spin-orbit coupling. This value is considerably larger than previously reported for a Ni^{II} TBP complex,[1] and is thought to be due to the rigidity of the ligand that prevents Jahn-Teller type effects that can reduce D. This is confirmed by the small value of the rhombic parameter, $|E|$ = 0.15 cm^{-1} [see Fig. 1(b)].

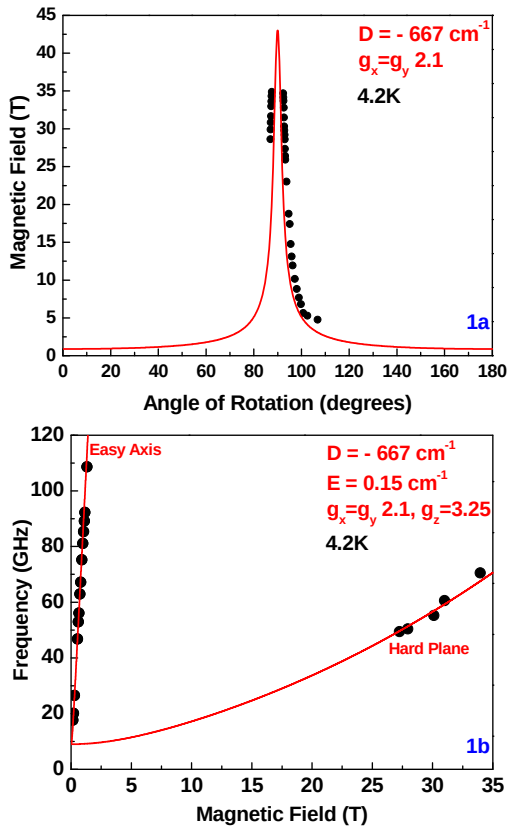

Fig. 1 (a) Angle dependence plots of the EPR peak position at 81 GHz for [$NiCl_3$(Me-dabco)$_2$]. (b) Frequency vs field plot, with the field in the molecular hard plane (high field data) and parallel to the easy-axis (low field data).

Conclusions

High-field EPR measurements provide very strong spectroscopic evidence for a huge easy-axis anisotropy in the TBP [$Ni^{II}Cl_3$(Me-dabco)$_2$] complex, which maintains an orbitally degenerate ground state. These studies are important in terms of realizing the ultimate goal of molecular Ni^{II} nanomagnets with increased magnetic anisotropies and, therefore, higher blocking temperatures.

Acknowledgements

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References

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