ESR Study of a Family of *S* = 1 Ni(II) Coordination Complexes Featuring Poly-HF Ligands

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Introduction

The three-dimensional coordination polymer $[Ni(HF_2)(pyz)_2]SbF_6$ (pyz = pyrazine) is illustrated in Fig. 1 and contains NiF_2N_4 sites and two types of bridging ligands leading to vastly different exchange pathways; Ni-FHF-Ni (J_{FHF}) and Ni-pyz-Ni (J_{pyz}).[1] From density-functional theory it was found that J_{FHF} exceeded J_{pyz} by a factor of ~4. Simultaneous presence of zero-field splitting (*D*), as expected in six-coordinate Ni(II) complexes, rendered it difficult to experimentally determine any of these parameters with any certainty. Angular-overlap modeling of electronic spectra for the polymer gave *D* = +11.2 K which agreed with the DFT-computed value. To gain experimental confirmation of *D*, we designed a family of *S* = 1 molecules that contain the same NiF_2N_4 core but with pyz being replaced by non-bridging ligands such as 3,5-lutidine (lut), 3-chloropyridine (Clpy), and 4-picoline (pic).[2] In particular, $Ni(HF_2)_2(lut)_4$ shares tetragonal symmetry with the 3D polymer, whereby the F-Ni-F axis lies along the *c*-axis. Herein, we describe the results of the ESR study performed on molecular $Ni(HF_2)_2(lut)_4$.

Experimental

High-field, high-frequency EPR spectra were collected at the EMR facility of the NHMFL using powdered samples (≈ 30 mg). A continuous-flow He cryostat (3 K ≤ *T* ≤ 20 K) was used to conduct experiments on a home-built spectrometer (203 GHz ≤ *f* ≤ 425 GHz) equipped with a 15/17 T superconducting magnet.

Results and Discussion

A representative ESR spectrum of $Ni(HF_2)_2(lut)_4$ measured at 20 K and 322 GHz is shown in the main plot of Fig. 2. A view of its molecular structure is shown in the inset of Fig.2 (*c*-axis is vertical). The experimental data are well reproduced by the simulated spectrum for $g_x = g_y = 2.217$, $g_z = 2.165$, *D* = +11 K, and *E* = 0. The fitted *D*-value is consistent with the *D* obtained from electronic structure calculations for the 3D polymer. The Clpy and pic derivatives show additional rhombic distortions (*E*/*D* = 0.16) which is consistent with their monoclinic symmetries.

Conclusions

ESR has proven to be an invaluable asset to our study of molecular and polymeric magnetism. For the Ni(II) coordination polymers, which have *S* = 1 ground states, the zero-field splitting competes with the exchange interaction making it difficult to deconvolute them. By eliminating *J*, we could directly measure *D* and found that this parameter can be as large as +11 K for highly symmetry NiF_2N_4 cores.

Acknowledgements

This work was supported by the NSF under grant no. DMR-1306158.

References

[1] Manson, J.L., *et al*., Inorg. Chem, **50**, 5990-6009 (2011).
[2] Manson, J.L., unpublished results.

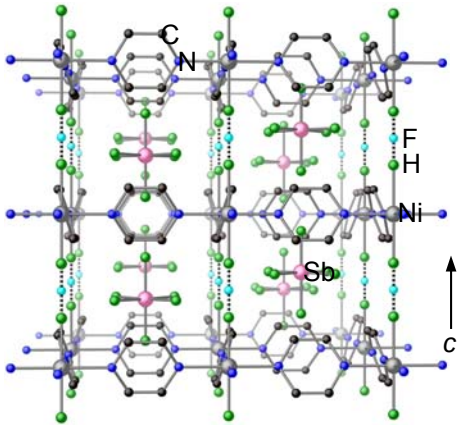

Fig.1. Crystal structure of polymeric $[Ni(HF_2)(pyz)_2]SbF_6$.

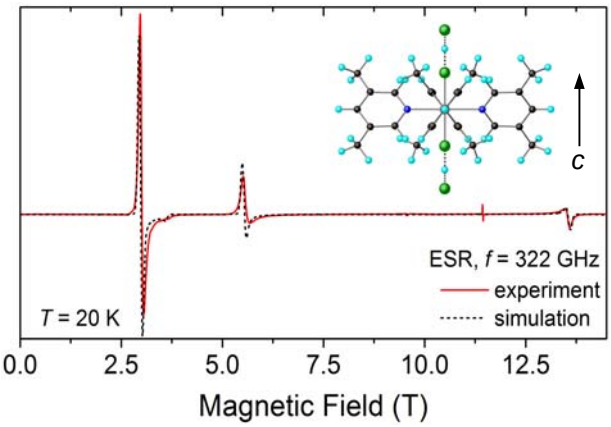

Fig.2. Inset: molecular structure of $Ni(HF_2)_2(lut)_4$. Main plot: Derivative ESR plot taken at 20 K and a frequency of 322 GHz.