NOVEL APPROACH TO ZERO-FIELD SPLITTING TREATMENT OF BINUCLEAR COMPLEXES OF Ni(II)

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Introduction

Polynuclear clusters of Ni(II) have been of interest because of their potential role as molecular nanomagnets. Understanding the nature of magnetic coupling between the metal ions is thus of paramount importance. Some of us have recently developed a novel approach to calculate the zero-field splitting (zfs) occurring in ferromagnetically-coupled binuclear species [1-2]. This approach requires possibly accurate experimental observables. We thus submitted the following complex: $[\{Ni(en)_2\}_2(\mu\text{-}Cl)_2]Cl_2$ where en=ethylenediamine (complex **1**, Fig. 1) to high-frequency and -field EPR experiments in order to determine the spin Hamiltonian parameters of its ground state.

Experimental

Polycrystalline complex **1** was investigated in a 150 – 700 GHz frequency range using the Mm and Sub-mm Wave Facility and the 25-T resistive "Keck" magnet. Preliminary HFEPR spectra were obtained using the EMR facility and the 17-T superconducting magnet.

Results and Discussion

Fig. 2 shows frequency dependencies of the experimentally observed EPR resonances in **1** at 4.2 K. These dependencies were simulated using the following spin Hamiltonian parameters: $S = 2$, $|D| = 1.7$ cm^{-1}, $E = 0$, $g_{iso} = 2.25$, which describe the ground (quintet) state of the complex and agree well with previous magnetometric results. The presence of the next excited spin state ($S = 1$) could not be observed experimentally, presumably due to very large zfs in this state, on the order of D ~ 24 cm^{-1} as estimated by magnetometry. The obtained parameters will be used in calculating magnetic interactions within complex **1**.

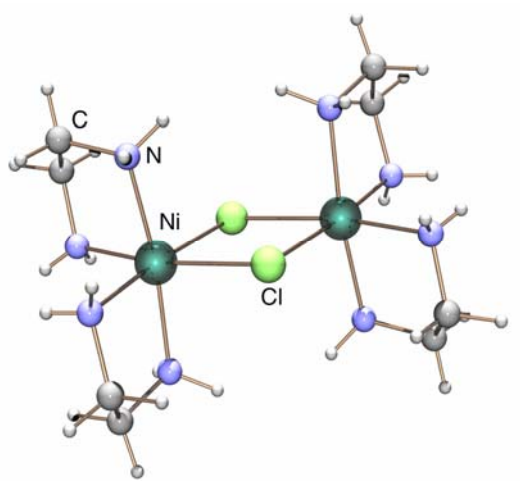

Figure 1. Molecular structure of complex **1**.

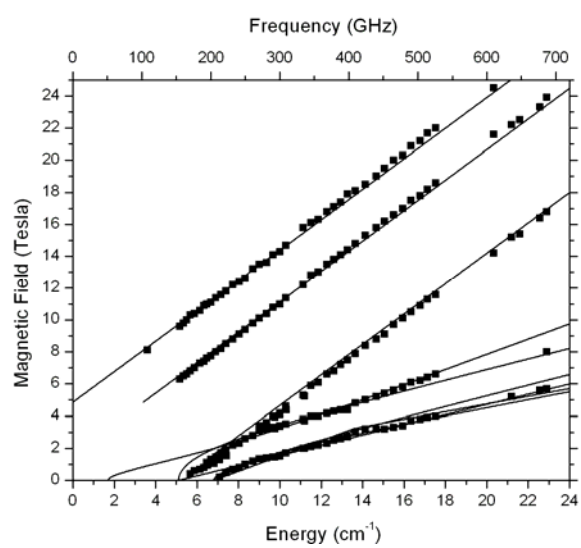

Figure 2. Frequency dependence of EPR resonances in complex **1** (squares) and their simulation using parameters as in text (curves).

References

[1] Boča, R., Theoretical Foundations of Molecular Magnetism. Elsevier, Amsterdam (1999).
[2] Herchel, R., Ph.D. thesis, Slovak University of Technology, Bratislava (2005).