HFEPR Studies of the *S* = 1 Octahedral *Trans*-[Ni$^{(II)}${(OPPh$_2$)(SPPh$_2$)N}$_2$(dmso)$_2$] Complex

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Introduction

With an aim of probing magnetostructural correlations in a family of pseudo-octahedral *S* = 1 Ni(II) complexes, the magnetic and electronic properties of *trans*-[Ni{(OPPh$_2$)(EPPh$_2$)N}$_2$(sol)$_2$], E = S, Se; sol = dmf, thf, have been recently investigated by magnetometry, High -Frequency and -Field EPR (HFEPR) and quantum chemistry [1,2]. These complexes exhibit subtle and well defined structural differences, due to the nature of the coordinated solvent molecules and E donor atoms. The scope of this work is currently being extended to include additional solvent adduct complexes of the above type (sol = dmso, pyridine, pyrazine). In the work presented herein, HFEPR spectroscopy was employed to investigate the electronic properties of *trans*-[Ni{(OPPh$_2$)(SPPh$_2$)N}$_2$(dmso)$_2$] (**1**) (dmso = dimethysulfoxide). The three-dimensional structure of **1** was determined by X-ray crystallography (Fig. 1).

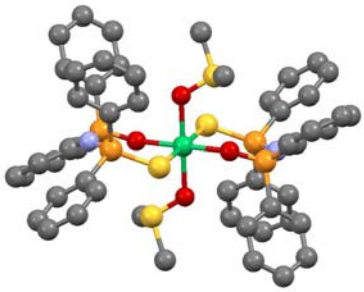

Fig. 1 X-ray crystal structure of **1**. Color coding: Ni green, O red, S yellow, C gray.

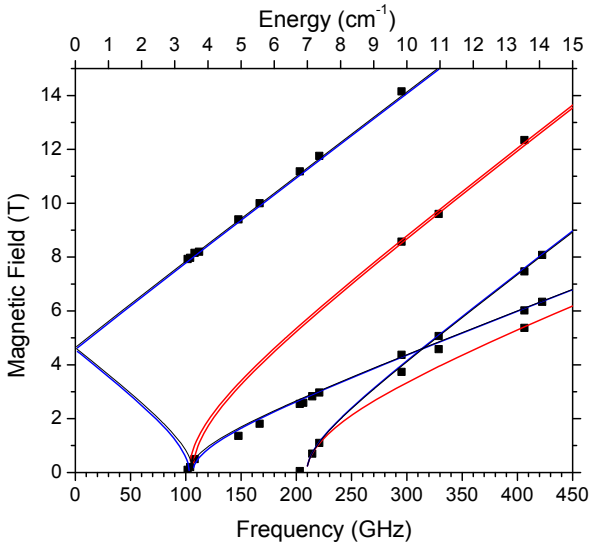

Fig. 2. 2D field vs. frequency map of observed resonances in **1** at 5 K. Squares are experimental points; lines were drawn using the best-fitted spin Hamiltonian parameters as in the text. Red lines: B_0 || *x*, blue lines: B_0 || *y*, black lines: B_0 || *z*.

Experimental

The pseudo-tetrahedral complex [Ni{(OPPh$_2$)(SPPh$_2$)N}$_2$] was converted to pseudo-octahedral **1** by recrystallization from the coordinating solvent dmso. The EPR experiments were performed using the EMR Facility and in particular its15/17 T superconducting magnet.

Results and Discussion

The spectra of **1** showed two very broad zero-field transitions near 105±5 GHz and 210±10 GHz, implying a near-maximum rhombicity of the zero-field splitting tensor. Based on the full 2D field vs. frequency map of observed resonances (Fig. 2), a least-square computer fit of the spin Hamiltonian parameters to the experimental resonances yielded the following values: D = 5.29(5) cm^{-1}, E = 1.74(1) cm^{-1} (E/D = 0.33), g_{iso} = 2.29(2).

Conclusions

Complex **1** is characterized by an extremely rhombic zfs tensor, which could be attributed to its highly distorted metal coordination sphere (Fig. 1). In future work, additional complexes of the same type, namely *trans*-[Ni{(OPPh$_2$)(SePPh$_2$)N}$_2$(dmso)$_2$] and *trans*-[Ni{(OPPh$_2$)(EPPh$_2$)N}$_2$(sol)$_2$], E = S, Se; sol = pyridine, are planned to be investigated by HFEPR and other physicochemical or computational methods. These studies will provide additional information concerning the electronic structure of such *S* = 1 systems.

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References

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[2] Maganas, D. *et al*., Inorg. Chem., **51**, 7218-7231 (2012).