Far-Infrared Magnetic Spectroscopy of a Novel Ni(II) Pincer Complex

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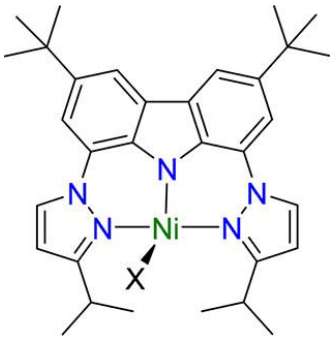

Fig.1 Structure of Ni(II) complex of NNN pincer ligand, X = Cl, Br, I.

Introduction

The "pincer" ligand type is a key platform in inorganic chemistry, in which three chelating donor atoms enforce approximate planar geometry, [(EE′E″)ML], where E, E′, E″ = C, N, O, P, S (in various combinations) and L = ancillary ligand, so the complex has approximate C_{2v} symmetry. The Lee group is currently developing novel pincer ligands, such as one with E, E′, E″ = N, as shown in **Fig.1**. A Ni(II) ($3d^8$) complex of this ligand has been very recently reported, in which the Ni(II) ion is paramagnetic (S = 1 ground state, solely by Evans NMR method at room temperature) [1]. The variation in halido ligand (X) will allow the electronic structure to be probed systematically, as was done in TpNiX (Tp = the tripodal hydridotrispyrazolylborate ligand) [2,3].

Experimental

The three halido complexes, Ni(NNN)X, X = Cl, Br, I, were synthesized as previously described [1]. These are all air stable complexes and were studied as microcrystalline powders. Each was investigated by HFEPR at the EMR Facility using the 15/17 T SC magnet, and by FIRMS at the DC Field Facility using the SCM3 magnet.

Results and Discussion

HFEPR of each of the complexes was unsuccessful due to the large magnitude zero-field splitting (zfs). However, the chlorido and bromido complexes both gave informative FIRMS spectra. A representative field-frequency map for Ni(NNN)Br is shown in **Fig.2**. A single zf transition is observed at ca. 35.2 cm^{-1}, which suggests the zfs tensor is axial, with the transition energy equal to zfs parameter $|D|$. The chlorido complex showed a similar single transition at ca. 33.3 cm^{-1} (not shown). A FIRMS experiment on Ni(NNN)I under the same experimental conditions was unsuccessful.

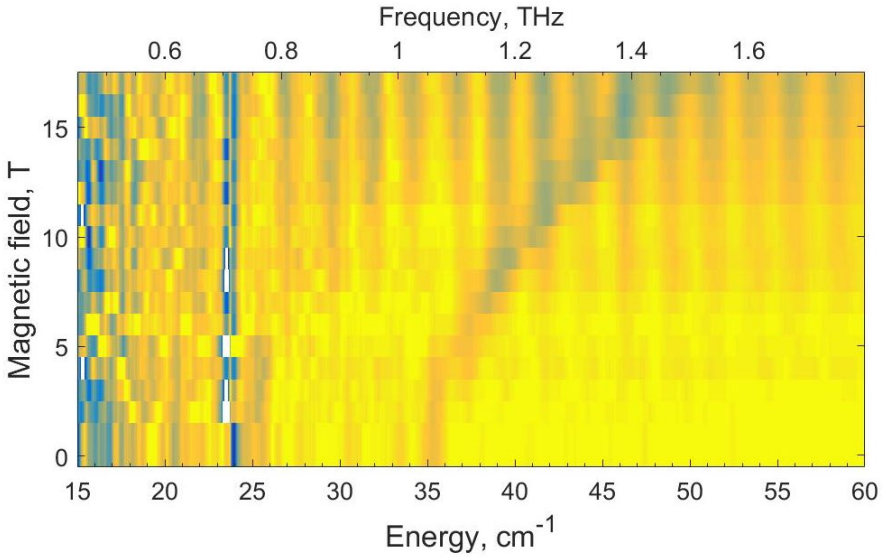

Fig.2 FIRMS field vs. frequency false-color map of Ni(NNN)Br at 5 K.

Conclusions

A well-defined series of novel Ni(II) pincer complexes has been studied by field- and frequency-domain methods (HFEPR and FIRMS) and shown to have large magnitude zfs. This observation will lead to undertaking a more detailed study of the electronic structure of these compounds.

Acknowledgements

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References

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