HFEPR Studies on Nickel(II) Complexes with a Novel Carbene "Scorpionate" Ligand

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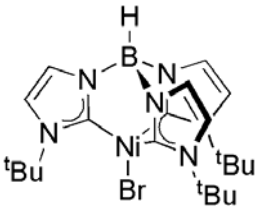
Introduction

Four-coordinate, non-planar, "high-spin" ($3d^8$, $S = 1$) Ni(II) complexes have been previously successfully investigated by HFEPR at NHMFL. Based on these successes, we are extending the range of complexes studied to a novel and unusual four-coordinate Ni(II) complex, HB(*t*-BuIm)$_3$NiBr, in which HB(*t*-BuIm)$_3$ is a tris(imidazol-2-ylidene)borate ligand with bulky *t*-butyl protecting groups (as shown at left).[1,2] This complex resembles the well-known tris(1-pyrazolyl)borate, "scorpionate", complexes studied previously, but differs significantly in that the ligand is a C_3 donor (formally a carbene), rather than N_3. The electronic effects of C rather than N as a ligand to paramagnetic transition metal complexes have hitherto not been much studied, due to a lack of suitable complexes. Computational studies using density functional theory (DFT) will complement the experimental results from HFEPR and allow the development of biomimetic complexes for nickel hydrogenase enzymes.



Experimental

The NHMFL Mm- and Sub-mm Wave Facility with the resistive ("Keck") 25-T magnet, and the EMR Facility with the superconducting 17-T magnet were used to study a polycrystalline sample of HB(*t*-BuIm)$_3$NiBr, prepared as described.[2]

Results and Discussion

HB(*t*-BuIm)$_3$NiBr afforded remarkably high quality HFEPR spectra over an extremely wide range of frequencies (Fig. 1). A 2-D map of the field-frequency dependencies confirms the triplet ($S = 1$) ground spin state with all turning points within the triplet powder pattern apparent. A computer fit of the entire dataset provided the following complete set of spin Hamiltonian parameters: $D = +2.49(4)$ cm^{-1}, $E = +0.54$ cm^{-1}, $g_{iso} = 2.22(1)$.

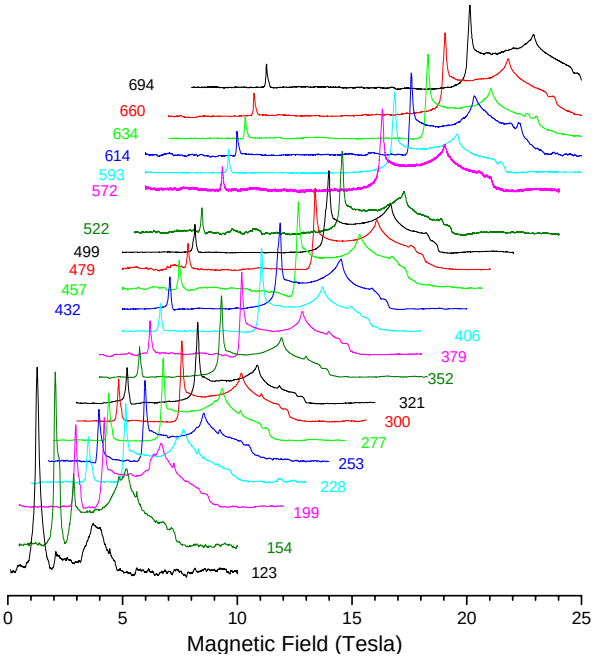


Figure 1. Multi-frequency HFEPR spectra of poly-crystalline HB(*t*-BuIm)$_3$NiBr at 4.2 K; the frequencies (in GHz) are indicated next to each spectrum.

Conclusions

This study demonstrates again the utility of HFEPR in characterizing paramagnetic Ni(II) coordination complexes. The obtained data, together with structural and optical experimental results and in combination with DFT computational studies[1] will allow the full understanding of the electronic structure of Ni(II) in the unusual coordination environment provided by the studied complex.

Acknowledgements

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References

[1] Cowley, R.E., *et al.*, Inorg. Chem. **45**, 9771-9779 (2006).
[2] Nieto, I., *et al.*, Chem. Commun., 3811-3813 (2005).