HFEPR Studies on Octahedral Mononuclear Ni(II) Complexes of Novel Chelating Ligands Based on 1,2,3-Triazoles

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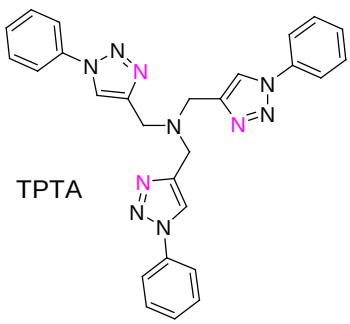
Introduction

Several bidentate and tripodal ligands have been synthesized via "click" chemistry. These include TPTA (tris[(1-phenyl-1H-1,2,3-triazol-4-yl)methyl]amine), TBTA (tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine), TDTA (tris[(1-(2,6-diisopropyl-phenyl)-*1H*-1,2,3-triazol-4-yl)methyl]amine) and PYTA (1-(2,6-diisopropylphenyl)-4-(2-pyridyl)-1,2,3-triazole)).[1,2] These ligands form a number of mononuclear transition metal complexes. We have used HFEPR to understand the electronic structures of these compounds. A series of high-spin octahedral Ni(II) complexes, with two or three of these ligands $[Ni(TP(B/D)TA)_2]^{2+}$ (**1**-**3**) and $[Ni(PYTA)_3]^{2+}$ (**4**) were investigated. Our aim in the present project is to see the influence of ligand donor strength and denticity on the zero-field splitting parameters of such nickel complexes.



Experimental

HFEPR spectra were recorded at the EMR Facility of the NHMFL using a 15/17-T superconducting magnet. Powder samples were used.

Results and Discussion

The complexes gave excellent HFEPR spectra which could be simulated to get accurate spin Hamiltonian parameters (**Figure 1**). The spin Hamiltonian parameters obtained from these measurements are summarized in **Table 1**. The data clearly indicate that changing the denticity of the "click" ligands has a large influence on the values of the axial zero-field splitting parameter, *D*. Complexes of the tripodal ligands display a larger anisotropy compared to the bidentate ligands.

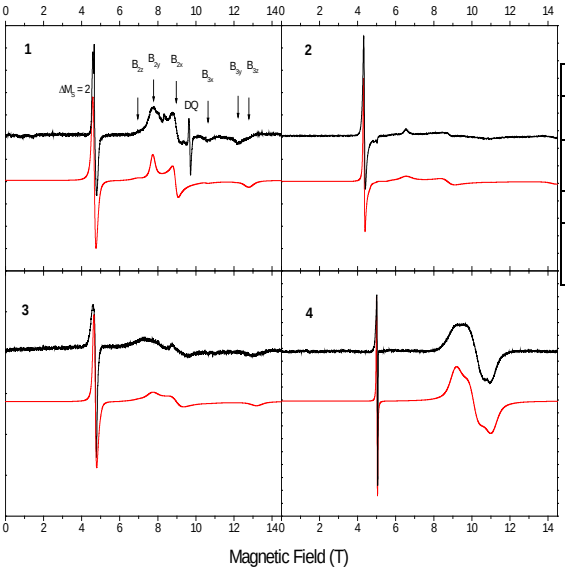


Figure 1. Experimental (black) and simulated (red) HFEPR spectra for complexes **1** - **4**.

Table 1. *S* = 1 Spin Hamiltonian parameters obtained from HFEPR measurements.

Complex	D (cm^{-1})	E (cm^{-1})	g_x	g_y	g_z
1	2.92(2)	0.45(1)	2.135(5)	2.108(6)	2.138(6)
2	4.35(2)	0.738(4)	2.143(7)	2.178(6)	2.150(6)
3	2.91(3)	0.50(3)	2.18(1)	2.120(15)	2.130(6)
4	0.992(3)	0.284(3)	2.146(3)	2.169(3)	2.15 (fixed)

Conclusions

Results obtained from HFEPR experiments have been used to obtain the full set of *S* = 1spin Hamiltonian parameters, and these have been used in elucidating the electronic structures of the investigated complexes. The results discussed here display the subtle differences induced at the metal centers on changing the properties of the coordinating ligands, and the utility of HFEPR spectroscopy in investigating such effects.

Acknowledgements

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References

[1] Schweinfurth, D., *et al.*, Inorg. Chem., **51**, 7592-7597 (2011).
[2] Schweinfurth, D., *et al.*, Dalton Trans., **41**, 12984-12990 (2012).