HFEPR Studies on Mononuclear High-Spin Co(II) Complexes of Tripodal Ligands Based on Tris(Triazole)Amines

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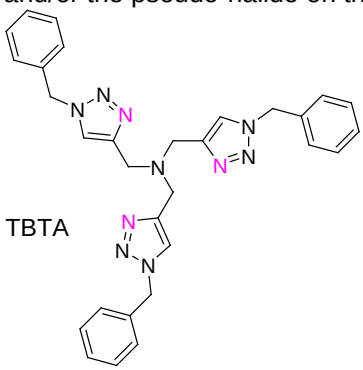
Introduction

Pseudo-tetrahedrally coordinated Co(II) complexes based on "click" derived tripodal ligands have found recent use as catalysts for olefin polymerization.[1] In this project, the electronic properties of such 4+1 coordinated high spin Co(II) complexes of the form $[Co(TBTA)X]^+$ and $[Co(TPTA)X]^+$, where TBTA = (tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine) and TPTA = (tris[(1-phenyl-1H-1,2,3-triazol-4-yl)methyl]amine), X = Cl^- or SCN^- were investigated with HFEPR spectroscopy. The aim was to investigate the effect of changing the tripodal ligands and/or the pseudo-halide on the electronic structures of these complexes.



TBTA

Experimental

HFEPR spectra were recorded at the DC Facility of the NHMFL using the 25 T resistive (Keck) magnet and at the EMR facility. Powder samples were used.

Results and Discussion

Spectra of excellent quality could be obtained for most of the cases. A representative spectrum together with its simulation is shown in Figure 1. Simulations of the HFEPR spectra delivered the magnitude and the sign of the *D* parameter with high accuracy for three of the four cases that were investigated. A comparison of the data obtained for the four complexes shows that the absolute value and the sign of *D* can be varied by changing the substituents on the tripodal ligands or the pseudo-halide ligand. For example, a change from –9.02 cm^{-1} to +8.29 cm^{-1} for the *D* parameter was observed on changing the X ligand from Cl^- to SCN^- while keeping the tripodal ligand constant (TPTA).

Table 1: Spin Hamiltonian parameters of the investigated complexes

Complex	D (cm^{-1})	$\|E\|$ (cm^{-1})	g_x	g_y	g_z
$[Co(TBTA)Cl](BF_4)_2$	(–)5.20(5)	0.75(6)	2.30(4)	2.15(4)	2.41(8)
$[Co(TBTA)SCN](BF_4)_2$	–4.41(3)	0.13(5)	2.29(38)	2.160(15)	2.18(3)
$[Co(TPTA)Cl](BF_4)_2$	–9.02(4)	1.64(2)	2.324(14)	2.42(2)	2.22(2)
$[Co(TPTA)SCN](BF_4)_2$	+8.29(1)	0.445(12)	2.25(1)	2.24(1)	2.138(2)

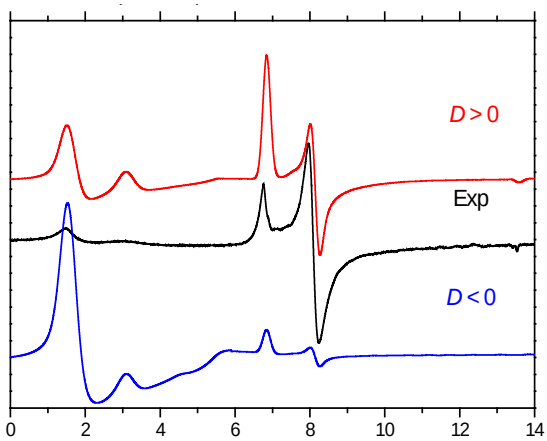


Figure 1. HFEPR Spectra of $[Co(tpta)SCN]^+$ at 406 GHz and 10 K together with simulatiosn using parameters as in Table 1; $D > 0$, red trace; $D < 0$, blue trace.

Conclusions

The magnitude and sign of *D* were determined accurately for most cases in a series of 4+1 coordinated HS Co(II) complexes. This parameter is likely to contribute to the rate of magnetic relaxation in these complexes, as has been recently shown for similar cases.[2] Investigations in that direction are currently underway.

Acknowledgements

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References

[1] Schweinfurth, D., *et al.*, Inorg. Chem., **51**, 7592-7597 (2012).
[2] Zadrozny, J.M., *et al.*, Chem. Commun., **48**, 3897-4020(2012).