The EPR Silence of Bis(2,2,6,6-tetramethylpiperidido)iron(II) Indicates the Presence of a Near-Degenerate Ground $M_S = \pm 2$ Quasi-Doublet

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Introduction

Two-coordinate iron(II) compounds have been found to exhibit magnetic moments that are much larger than the expected spin-only values for high-spin d^6 configurations, as well as unusually large magnetic hyperfine splittings.[1-4] These properties have been rationalized on the basis of the strong spin-orbit coupling of two nearly degenerate orbital states for which either the *xy* or the x^2-y^2 d-orbital is doubly occupied. Interestingly, this situation leads to a ground state for which the two lowest $M_S = \pm 2$ magnetic sublevels are nearly degenerate and are characterized by an effective *g* tensor such that $g_z >> g_x \approx g_y$.[1-3] Consequently the EPR behavior of these complexes offers a direct measure of the orbital degeneracy and of the spin-orbit interactions present. Recently we have shown that $Fe(tmp)_2$ (**1**), despite having a bent N-Fe-N angle, displays a larger hyperfine splitting and effective magnetic moment than the related linear compound $Fe[N(t\text{-}Bu)_2]_2$ (**2**).[4] Thus, we sought to explore the EPR behavior of $Fe(tmp)_2$ and establish whether its *g* value is also larger than that determined for $Fe[N(t\text{-}Bu)_2]_2$.

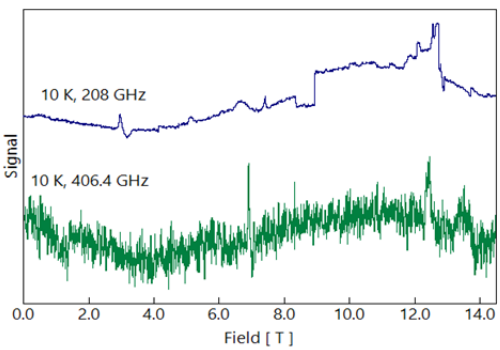

Fig. 1. HFEPR spectra recorded for **1**.

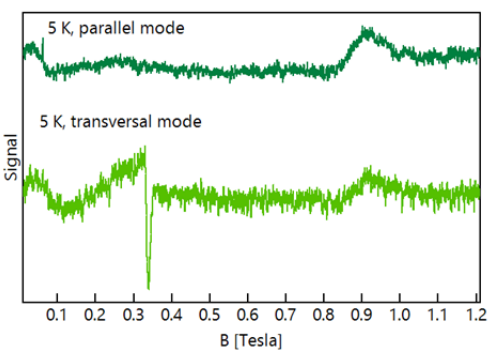

Fig. 2. X-band EPR spectra recorded for **1**.

Experimental

Crystalline samples of $Fe(tmp)_2$ were prepared at Illinois and flame-sealed in an EPR tube or loaded in a HFEPR cup as a neat powder (fixed by a drop of Krytox oil). A 1:1 pentane:toluene solution was flame-sealed in a second EPR tube. A sample dissolved in eicosane was prepared for Mössbauer. X-band EPR, HFEPR, and Mössbauer spectra were collected at the EMR facility of NHMFL.

Results and Discussion

The EPR spectra recorded for $Fe(tmp)_2$ showed no resonances that could be associated with this complex (Fig.1-2). This contrasts with $Fe[N(t\text{-}Bu)_2]_2$, which displays an X-band resonance corresponding to $g_{eff} \sim 10.3$.[1] As the M_S sublevels approach strict degeneracy, g_{eff} approaches 12 and the EPR transition probability correspondingly approaches 0. Thus, the present observations suggest that modestly bent $Fe(tmp)_2$ has a more axial ground state than linear $Fe[N(t\text{-}Bu)_2]_2$. This conclusion is consistent with the larger orbital field and magnetic moment observed for $Fe(tmp)_2$.[4]

Conclusions

No X-band or high-field EPR signal can be observed for $Fe(tmp)_2$. Owing to the bent N-Fe-N angle, this result provides further support for the idea that the electronic structures of two-coordinate iron(II) centers are more sensitive to changes in the close approach of the ligand periphery than in the primary coordination geometry (L-M-L angle).

Acknowledgements

This research was supported by the National Science Foundation under grant CHE-1112360 (to GSG). A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by NSF Cooperative Agreement No. DMR-1157490, the State of Florida, and the U.S. Department of Energy. The Mössbauer instrument was funded by UCGP-5064 (to A. Ozarowski).

References

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