Mössbauer Spectroscopic Observation of a Very Large Internal Hyperfine Field in Bis(2,2,6,6-Tetramethylpiperidido)Iron(II)

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Introduction

Two-coordinate iron(II) compounds display the largest internal hyperfine fields, H_{INT}, of any iron compounds in any oxidation states [1-3]. The orbital contribution, H_L, dominates H_{INT} in these high-spin d^6 compounds, and arises from degeneracy of the lowest-lying xy and x^2-y^2 d-orbitals. This degeneracy and the resulting orbital angular momentum are larger for compounds with linear ligand-iron-ligand geometries [3]. An open question is whether the important feature generating large orbital angular momentum is a molecular rotation axis relating the xy and x^2-y^2 d-orbitals (i.e., high local symmetry), or merely a small energy difference between these d-orbitals. Because the xy and x^2-y^2 d-orbitals are essentially non-bonding, the energies of these orbitals must be relatively unperturbed by small bending distortions, whereas the local C_∞ axis relating these orbitals is destroyed by any bending; a slightly bent compound could thus distinguish between the two hypotheses. We have recently isolated the new two-coordinate compound bis(2,2,6,6-tetramethylpiperidido)iron(II), $Fe(tmp)_2$, which has an N-Fe-N angle of 173°.

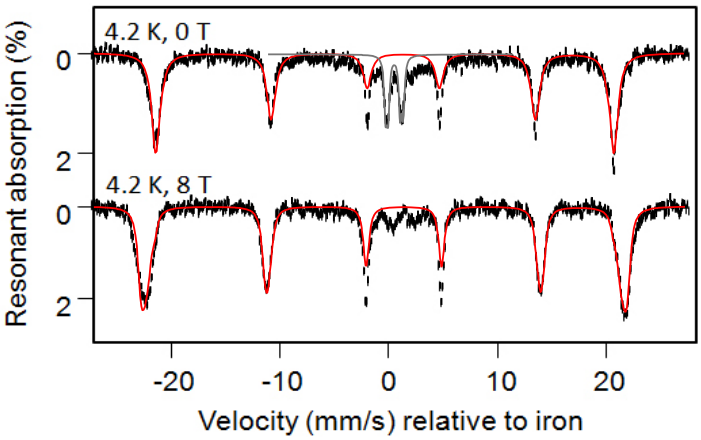

Figure 1. Mössbauer spectra of $Fe(tmp)_2$ at 4.2 K in zero field (top) and an 8 T applied field (bottom).

Experimental

Crystalline samples of $Fe(tmp)_2$ were prepared at Illinois and loaded as a neat powder and as a Krytox mull. Low-temperature, zero- and applied-field Mössbauer spectra were collected at the EMR facility of the NHMFL.

Results and Discussion

The zero-field Mössbauer spectrum of $Fe(tmp)_2$ at 4.2 K (Fig. 1, top) shows magnetic hyperfine splitting (the outermost six lines) of ca. 42 mm/s, corresponding to H_{INT} =136 T. Some sites in the lattice are thus in the slow relaxation limit even in zero field; this feature is unusual among two-coordinate iron(II) compounds, and previously observed only for $Fe[C(SiMe_3)_3]_2$ [1]. The central two lines represent a fast-relaxing quadrupole doublet with δ = 0.5-0.6 mm/s and ΔE_Q = 1.3-1.7 mm/s, similar to the quadrupole doublet observed at zero field and 77 or 293 K. In an applied field of 8 T at 4.2 K (Fig. 1, bottom), the slow relaxation limit is induced for nearly all of these sites, and the effective field (which is the sum of the applied and internal fields) increases to ca. 44 mm/s. This increase demonstrates that H_{INT} is positive, confirming that H_L dominates H_{INT} [2, 3]. H_L can be estimated to be 187 T, ca. 30 T larger than that observed in the closely related linear compound $Fe[N(t\text{-}Bu)_2]_2$ [2]. This observation cannot be explained by the local symmetry of the compounds, and instead appears to result from weak Fe···H-C interactions splitting the xy and x^2-y^2 d-orbital energies less in $Fe(tmp)_2$ than in $Fe[N(t\text{-}Bu)_2]$ [2].

Conclusions

The measured H_{INT} = 136 T is among the largest ever reported [1-3]. Because $Fe(tmp)_2$ is bent, this result supports an understanding of orbital angular momentum as arising from degeneracy rather than local symmetry.

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References

[1] Reiff, W.M., *et al.*, J. Am. Chem. Soc., **126**, 10206-10207 (2004).
[2] Reiff, W.M., *et al.*, J. Am. Chem. Soc., **131**, 404-405 (2009).
[3] Merrill, W.A., *et al.*, J. Am. Chem. Soc., **131**, 12693-12702 (2009).