

## Effect of coordinated radical ligands on the rate of spin crossover processes in iron(II) complexes

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Spin crossover (SCO) processes are entropy-driven redistributions of electrons among the d-orbitals of metal ions induced by a change in temperature or pressure or by light irradiation. The most intensively studied SCO complexes contain iron(II) ions. Among the various physical methods to study the SCO transition in these complexes, especially Mössbauer spectroscopy is a very valuable tool. SCO processes of iron(II) complexes below 250 K are generally slower than the time scale of the Mössbauer experiment.

We are interested in SCO complexes in which the metal ion is coordinated to radical ligands. [1,2] As part of this study we prepared iron(II) complexes containing the tetradentate N,N'-dimethyl-2,11-diaza[3.3](2,6)pyridinophane and radical anions of N,N'-diphenyl-acenaphthene-1,2-diimine derivatives as ligands. Characterization of the resulting octahedral iron(II) radical complexes by structural (Fig. 1a), magnetochemical and spectroscopic methods reveal that spin crossover equilibria occur between an  $S = 1/2$  ground state and an  $S = 3/2$  excited spin state. Using Mössbauer spectroscopy (Fig. 1b) it can be shown that the spin interconversion rate at the iron(II) site is considerably enhanced by the presence of a coordinated radical.

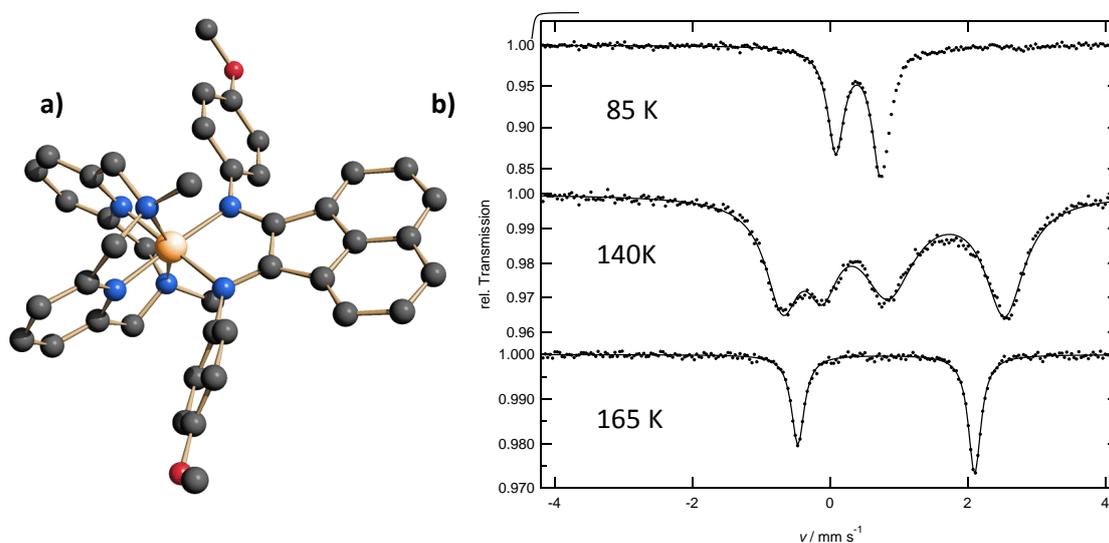


Figure 1: a) Perspective view of the complex cation in SCO the iron(II) radical complex.  
b) Mössbauer spectra at different temperatures.

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### References

- [1] a) M. Graf, G. Wolmershäuser, H. Kelm, S. Demeschko, F. Meyer, H.-J. Krüger, *Angew Chem Int Ed* 49, 950-953 (2010); b) M. Schmitz, M. Seibel, H. Kelm, S. Demeschko, F. Meyer, H.-J. Krüger, *Angew Chem Int Ed* 53, 5988-5992 (2014).