A High-Spin Square-Planar Fe(II) Complex Stabilized by a Trianionic Pincer-Type Ligand and Conclusive Evidence for Retention of Geometry and Spin State in Solution

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Introduction

Square-planar high-spin Fe(II) molecular compounds are rare and the only three non-macrocyclic or sterically-driven examples reported share a common FeO_4 core. Using a pincer-ligand, we synthesized the first compound of this type that breaks the FeO_4 motif and present the first evidence that geometry and spin state persist in solution. Extensive characterization includes the first high-field EPR and variable field/temperature Mössbauer spectra for this class of compounds, revealing a large and positive zero-field splitting tensor.

Experimental

High-frequency EPR spectra were recorded using a home-built spectrometer at the EMR facility of NHMFL. The instrument is a transmission-type device in which waves are propagated in cylindrical lightpipes. The microwaves were generated by a phase-locked oscillator (Virginia Diodes) operating at a frequency of 13 ± 1 GHz and generating its harmonics, of which the 4th, 8th, 16th, 24th and 32nd were available. A superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T was employed. Mössbauer spectra were recorded using an instrument fitted with a helium-flow Janis 8DT Super Varitemp cryostat that had a built in 8 T, American Magnetics superconducting magnet. The spectrometer was operated in a constant acceleration mode and used a 100 mCi ^{57}Co(Rh) source. This spectrometer allowed for recording variable-temperature spectra from 4.2 to 250 K in applied fields parallel to the incident γ-radiation from 0 to 8 T.

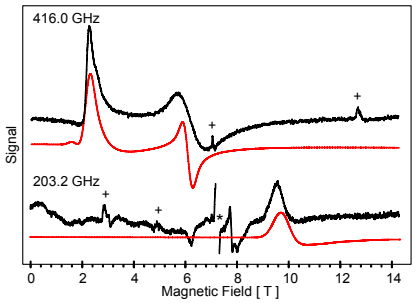

Figure 1. High-field EPR spectra recorded at 5K and 416.0 (top) or 203.2 GHz (bottom). The solid red traces are simulations.

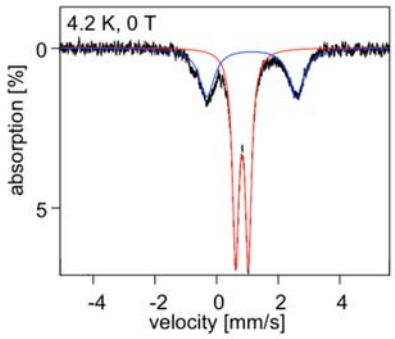

Figure 2. Zero-field ^{57}Fe Mossbauer spectra recorded at 4.2 K. The solid red lines are simulations

Results and Discussion

High-field EPR measurements on powder samples were analyzed in the framework of a standard $S = 2$ spin-Hamiltonian. Using $g_x = 2.19$, $g_y = 2.18$, $g_z = 2.04$, $D = 17.4$ cm^{-1} and $E/D = 0.14$ it is possible to not only simulate the individual spectra (Figure 1), but also reproduce the field and frequency-dependent behaviour of the observed resonances. In agreement with the results of the crystallographic investigation, Mössbauer data and the EPR spectra recorded exhibit two distinct spectral components. At 4.2 K, the zero-field Mössbauer spectrum consists of a sharp quadrupole doublet with an isomer shift δ = 0.83(1) mm/s and quadrupole splitting ΔE_Q = -0.45(1) mm/s. The uniquely small ΔE_Q offers an opportunity to examine if the square-planar geometry and spin state are retained in solution. The zero-field spectrum recorded at 4.2 K for a ^{57}Fe enriched toluene solution revealed that more than 70 % of the iron exhibits a quadrupole doublet that is essentially identical to that observed in the solid state.

Conclusions

This work extends the set of known Fe(II) square-planar high-spin compounds beyond the limited FeO_4 motif, and presents the first high-field EPR and variable field/temperature Mössbauer characterization of this class of compounds. Moreover, the ^{57}Fe enriched solution phase Mössbauer confirms for the first time that the square planar geometry is retained in solution.

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