HIGH-FIELD EPR STUDIES ON AN ISOMERIC PAIR OF BINUCLEAR IRON(III) COMPLEXES: THE RED AND GREEN \([\text{Fe(1,10-PHENANTHROLINE)}]_2\text{O(SO}_4\text{)}_2\cdot6\text{H}_2\text{O}\)

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Introduction

Two isomeric compounds, the red and the green \([\text{Fe(phen)}]_2\text{O(SO}_4\text{)}_2\cdot6\text{H}_2\text{O}\) and an analogous green 2,2'-bipyridine compound \([\text{Fe(bipy)}]_2\text{O(SO}_4\text{)}_2\cdot6\text{H}_2\text{O}\) were prepared. The X-Ray structures of the green phen and of the bipy complex were determined in this work, while the structure of the red phen compound has been reported earlier\(^1\). All three complexes were studied by the magnetic susceptibility measurements, IR and UV-VIS spectroscopy as well as by the High-Field, High-Frequency EPR.

Experimental

High-frequency EPR spectra were recorded on the transmission spectrometer at the EMR facility of NHMFL. Magnetic susceptibility data of a powdered sample were measured with a SQUID magnetometer (Quantum Design MPMSXL-5) over the temperature range 1.8–300 K at the magnetic induction of 0.5 T.

Results and Discussion

The X-Ray structures revealed that both the green phen and the bipy complex contain two iron(III) ions joined by one \(\mu\)-oxo bridge and two \(\mu\)-sulfato bridges, opposite to the red phen complex that only has a single \(\mu\)-oxo bridge (Fig. 1). The results of the magnetic susceptibility measurements were interpreted in terms of the Hamiltonian \(H = JS_1S_2\). All three complexes exhibited very similar exchange integral values, covering the range \(J=225\pm7\ \text{cm}^{-1}\). While the X-Band EPR spectra showed only the presence of the quintet spin states in the three systems, the triplet spin states could be observed in high-frequency spectra. For all three complexes, the spin Hamiltonian parameters for both \(S=1\) and \(S=2\) states were determined, for example in the bipy complex \(D_{S=1}=3.820\ \text{cm}^{-1}, E_{S=1}=0.865\ \text{cm}^{-1}, D_{S=2}=0.148\ \text{cm}^{-1}, E_{S=2}=0.0342\ \text{cm}^{-1}\). The bipy complex was doped with gallium(III) in order to free iron atoms from the exchange coupling and determine the zero-field splitting for the \(S=5/2\) state on single iron ions. Values of \(D = + 0.50\ \text{cm}^{-1}, E = + 0.090\ \text{cm}^{-1}\) were obtained. An attempt to extract the contributions to \(D\) and \(E\) due to the magnetic dipolar interactions, anisotropic exchange, and to the zfs on separate iron ions was only partially successful, as the tensors of these interactions are diagonal in different systems of coordinates.

Conclusions

An unprecedented case of isomerism among the binuclear iron(III) complexes was identified. Single-crystal EPR studies at high frequencies are needed to fully correlate the EPR parameters with the molecular structures.

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References