

HIGH-FIELD HIGH-FREQUENCY EPR STUDIES ON METAL-METAL INTERACTIONS IN BINUCLEAR OXYGEN-BRIDGED IRON(III) COMPOUNDS

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Introduction

Strong antiferromagnetic exchange interactions between two high-spin Iron(III) ions in the title compounds give rise to the spin states of the binuclear system that are characterized by the total spin quantum numbers S ranging from 0 to 5 with the singlet state ($S=0$) being the ground state.¹⁻³ Higher spin states, triplet, $S=1$, quintet, $S=2$ and septet, $S=3$, are thermally accessible at the room temperature. EPR studies on such compounds are extremely rare.¹⁻³

Experimental

We report here the measurements performed on the 15/17 Tesla instrument at the frequencies between 95 and 380 GHz on two isomeric compounds with a formula $[\text{Fe}(\text{phen})_2\text{O}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$ where phen is 1,10-phenanthroline. The sensitivity of the high-frequency instrument that employs no resonance cavity was sufficient for recording spectra due to both the triplet states and the weakly populated quintet states (the latter appears as a group of strong lines around 7.9 T in Fig. 1).

Results and Discussion

Table 1: Spin Hamiltonian parameters

Compound	g_x, g_y, g_z	D (cm^{-1})	E (cm^{-1})
green $[\text{Fe}(\text{phen})_2\text{O}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$	2.010, 2.008, 2.015	4.15	0.677
orange $[\text{Fe}(\text{phen})_2\text{O}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$	2.012, 2.012, 2.00	4.86	0.262

The spin Hamiltonian parameters for $S=1$ were determined for each of complex (Table 1). The magnitudes of the D and E parameters indicate that the low-frequency EPR is clearly not suitable to study the triplet states in this important class of compounds. The work on interpretation of the $S=2$ state spectrum is still in progress.

Conclusions

- (1) Triplet state EPR spectra in binuclear iron (III) complexes can be observed at very high frequencies and very high magnetic fields.
- (2) Anisotropic metal-metal exchange interactions must contribute to the zero-field splitting.
- (3) Assumption of the isotropic $g = 2$ that is satisfactory in X or Q Band must be abandoned in high-field EPR.

Acknowledgements

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References

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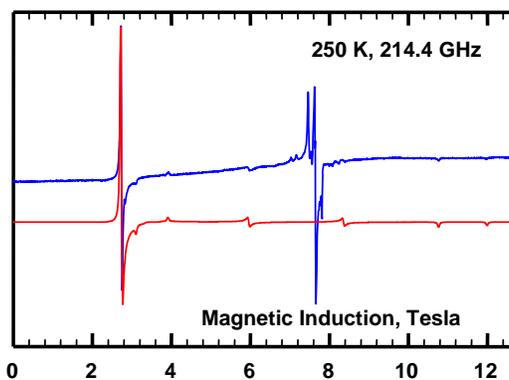


Fig. 1. The EPR spectrum of the green form of $[\text{Fe}(\text{phen})_2\text{O}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$. Blue: experimental, Red: simulated for a triplet state with parameters in Table 1.