High-Field EPR and Mössbauer Studies on Tetranuclear $Cu_2^{II}Fe_2^{III}$ Complexes Exhibiting Catalytic Activity

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Introduction

Two closely related heterometallic complexes containing a tetranuclear core $[Cu_2Fe_2(HL)_2(H_2L)_2]$, arranged into a chain Cu-Fe-Fe-Cu, were prepared in an one-pot reaction of copper powder, iron(II) chloride and DMSO or DMF solution of the polydentate Schiff base ligand H_4L, formed *in situ* from derivatives of salicylaldehyde and tris-(hydroxymethyl)-aminomethane. Metal atoms in the four-membered chain are joined by μ-O bridges of the deprotonated ligands. Magnetic susceptibility is indicative of antiferromagnetic coupling, $J_{Cu\text{-}Fe}$~9 cm^{-1}, $J_{Fe\text{-}Fe}$~16 cm^{-1}. Both compounds exhibit exceptionally high catalytic activity towards oxidation of cyclohexane by hydrogen peroxide under mild conditions.

Experimental

The 15/17 T transmission EPR system and the zero-field Mössbauer spectrometer of the EMR facility were used. Spectra were recorded over the temperature range 3 K - 300 K.

Results and Discussion

Interpretation of the EPR spectra of the Cu_2Fe_2 system consisting of 144 closely spaced energy levels is very challenging. With the exchange integrals $J_{Cu\text{-}Fe}$~9 cm^{-1}, $J_{Fe\text{-}Fe}$~16 cm^{-1} as found from the magnetic susceptibility, a spin singlet S = 0 is the ground state and the first excited state is a triplet, S = 1. A triplet state EPR spectrum was indeed recognized at very low temperatures (**Figure 1**) showing the zero-field splitting parameters D and E of ca. 2.7 cm^{-1} and 0.4 cm^{-1}, respectively. Because of weak exchange interactions, the 'giant spin model' cannot be applied for interpretation of the magnetic properties and EPR spectra [1].

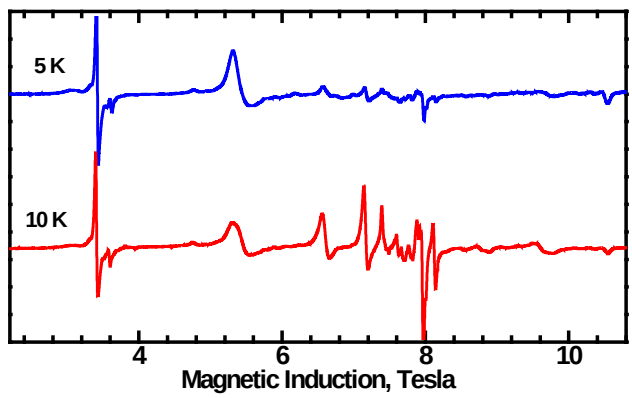

Figure 1. 216 GHz EPR spectra of $[Cu_2Fe_2(HL)_2(H_2L)_2]\cdot 2DMF$ at 5 K and at 10 K showing increasing thermal population of the spin states lying above the lowest triplet.

Small isomer shift (*IS*) and quadrupole splitting (*QS*) observed in the room-temperature Mössbauer spectra (**Figure 2**) confirm the presence of alkoxo-bridges (rather than oxo) between the Fe^{3+} ions [2].

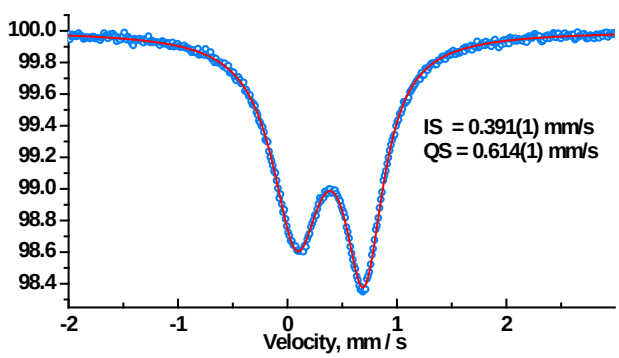

Figure 2. Blue: Room-temperature Mössbauer spectrum of $[Cu_2Fe_2(HL)_2(H_2L)_2]\cdot 2DMF$. Red: simulated with parameters shown.

Conclusions

This research is still in progress. Interpretation of the EPR spectra using a spin Hamiltonian expressed in spin operators of individual ions is being attempted.

Acknowledgements

This work was supported by the FCT (Portugal), project SFRH/BPD/63710/2009), Slovak VEGA projects 1/0052/11 and 1/0233/12, and NSF Cooperative Agreement DMR-0654118, the State of Florida and the DOE. The Mössbauer instrument was funded by UCGP grant 5064 (AO).

References

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[2] Kurtz Jr., D.M., Chem. Rev., **90**, 585 (1990).