Mössbauer Studies on Binuclear Oxygen-Bridged Iron(III) Complexes

A. Ozarowski (NHMFL); J. Jezierska (Wroclaw U., Poland, Chemistry)

Introduction

Iron(III) forms a large family of binuclear, oxygen-bridged complexes which have important implications in biology [1]. Antiferromagnetic exchange coupling in these systems (J ~ 200 cm^{-1} for $\hat{\mathbf{H}} = J\hat{S}_1\hat{S}_2$ [1, 2]) leads to formation of the coupled-spin states with a total spin S = 0 through 5. An interesting subgroup is formed by complexes of 2,2'-bipyridine (bipy) and 1,10-phenathroline (phen). Complexes with stoichiometry Fe: Ligand = 1:2 [1] and 1:1 [2, 3] have been synthesized, where Ligand = bipy or phen. Room-temperature Mössbauer measurements on a series of such complexes have been performed.

Experimental

The Mössbauer spectra (examples in Fig. 1) were recorded on a See-Co instrument of the EMR facility at the NHMFL in constant acceleration mode using a ^{57}Co (embedded in Rh) gamma source.

Results and Discussion

The isomer shift (IS) parameters, which do not exhibit significant variation among different compounds in this group of complexes indicate similar electron density on iron, independent even of the stoichiometry (Fe:Ligand = 1:1 or 1:2). The quadrupole splitting (QS) for the 1:2 complex (C in Fig. 1) is consistent with the literature data. [1, 4, 5] No literature data for the 1:1 systems are available. The large difference in QS between the isomeric 1:1 species A and B in Fig. 1 can be attributed to significantly lower symmetry of the Fe^{3+} environment in the latter.

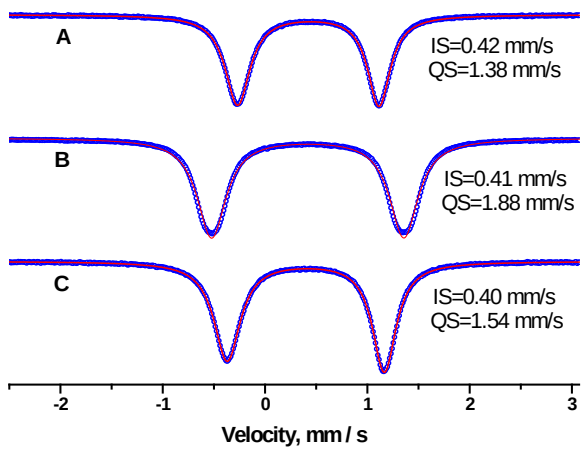

Figure 1. Room-temperature Mössbauer spectra of complexes containing the binuclear entities $[Fe(phen)(H_2O)_2]_2O^{4+}$ (A), $[Fe(phen)(H_2O)(SO_4)_2]_2O$ (B) and $[Fe(phen)_2]_2O^{4+}$ (C). Blue circles: experimental, red lines: calculated with the isomer shift (IS) and quadrupole splitting (QS) as shown.

Conclusions

This is work in progress. A correlation between the QS in species A and B with the spin Hamiltonian parameter E determined for the triplet spin state from the high-field Electron Paramagnetic Resonance experiments is observed.

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