High-Field EPR Studies on Polynuclear Transition Metal Complexes

Andrzej Ożarowski

National High Magnetic Field Laboratory, Florida State University, 1800 E Paul Dirac Dr, Tallahassee, Florida 32310, United States

Some of the most interesting phenomena encountered in the dimeric and polymeric transition metal complexes are related to the metal-metal interactions. These interactions in general have a substantial isotropic exchange part which is described by the Heisenberg-Dirac-Van Vleck Hamiltonian $\hat{\mathbf{H}}=J\mathbf{S}_1\mathbf{S}_2$. In a binuclear complex of two transition ions with spins S_1 and S_2, this interaction creates a series of coupled spin states with the total spin S_T ranging from $|S_1-S_2|$ to S_1+S_2. The energies of the S_T states are

$$E(S_T)=\frac{J}{2}\{S_T(S_T+1)-S_1(S_1+1)-S_2(S_2+1)\}$$

This isotropic exchange interaction affects the magnetic susceptibility of a dimeric or in general a polymeric complex so that the Curie law is no longer valid. Depending on the sign of the exchange integral J, a complex may be ferromagnetic ($J<0$) or antiferromagnetic ($J>0$).

The much smaller anisotropic metal-metal interactions split the total spin states into their M_S substates (this is the so-called Zero-Field Splitting, ZFS), thus in principle allowing application of the Electron Paramagnetic Resonance spectroscopy to study such coupled systems. However, the splittings between the M_S states are often quite large and the microwave quantum energy of the commonly used X-Band (9.5 GHz) or even Q-Band (35 GHz) may be insufficient to bring about transitions between these M_S levels. The High-Field, High-Frequency EPR (HFEPR), which became widely available towards the end of the past century, has solved this problem. The EPR instruments available at the EMR facility of the NHMFL allow everyday operation at frequencies up to 900 GHz (30 cm^{-1}) and at a magnetic field up to 16 Tesla. HFEPR is also able to resolve very close g values in metal complexes and in the free radicals.

Some binuclear and trinuclear copper complexes, binuclear oxygen-bridged iron(III) complexes and an interesting hexanuclear Mn(III)/Mn(IV) system with a ground spin state $S_T=11$ will be discussed.