HIGH-FREQUENCY AND -FIELD ELECTRON PARAMAGNETIC RESONANCE INVESTIGATION OF A SQUARE HETERONUCLEAR Co(II) - Mn(II) COMPLEX

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Introduction

Among the class of self-assembled clusters of metal ions the form of molecular square is favored both enthalpically and entropically. Some of us have prepared a heteronuclear complex based on square pyramidal Co(II) and tetrahedral Mn(II): $[\{Mn^{II}Cl_2\}_2\{Co^{II}(triphos)(CN)_2\}_2]$ (complex **1**, Fig. 1) [1]. Magnetometric measurements point at a high-spin (S = 4) ground state for this complex. We used HFEPR to further investigate magnetic properties of this species.

Experimental

Polycrystalline sample of complex **1** was investigated using the multi-frequency transmission spectrometer of the EMR facility, and the 17-T superconducting magnet, in a 54 – 310 GHz frequency, and 3.8 – 80 K temperature range.

Results and Discussion

Richly structured HFEPR spectra were obtained at any applied frequency (Fig. 2, blue trace). The structure is nearly frequency-independent, which indicates that it originates from zero-field splitting (zfs) of a high-spin state, with the axial zfs component being on the order of ~ 0.2 cm^{-1}. More detailed information on the spin Hamiltonian parameters of the ground spin state of complex **1** was yielded by spectral simulations assuming a powder-like distribution of crystallites in the magnetic field (Fig. 2, red trace). Thus, S = 4, D = –0.22 cm^{-1}, E = –0.009 cm^{-1}, $g_{x,y}$ = 1.995, g_z = 2.00.

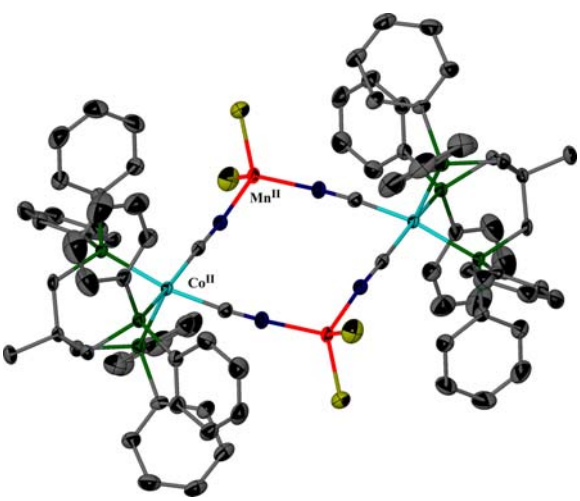

Figure 1. Molecular structure of complex **1**.

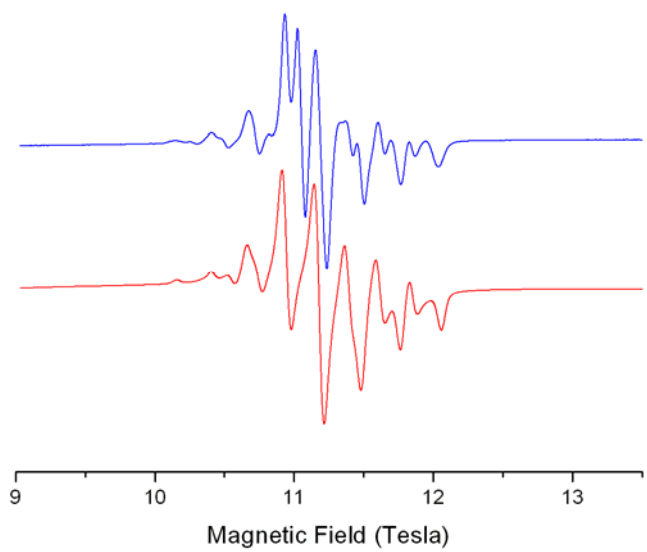

Figure 2. EPR spectrum of complex **1** recorded at 309.6 GHz and 40 K (blue trace), and its simulation using parameters as in text (red trace). A mononuclear Mn(II) signal appearing at 11.05 T (g = 2.00) is not simulated.

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References

[1] Karadas, F., *et al*., Chem. Commun., 1414-1416 (2005).