High-Field EPR and Magnetic Studies on Cr-Cr Interactions in a New Heterometallic Tetranuclear Complex

V. N. Kokozay, V.V. Semenaka (National Taras Shevchenko U., Chemistry), J. Jezierska, (Wroclaw U., Chemistry), A. Ozarowski, (NHMFL)

Introduction

A new heterometallic complex \([\text{Zn}_2\text{Cr}_2(\text{NCS})_4(\text{L})_2(\text{HL})_2]\cdot2\text{CH}_3\text{CN}\), where \(\text{L}\) is the dianion of diethanolamine, was synthesized and investigated by means of X-Ray crystallography, infrared spectroscopy and magnetic susceptibility. The complex is a weak antiferromagnet with an exchange integral between the \(\text{Cr}^{3+}\) ions (equal to the singlet-triplet splitting) of 15 \(\text{cm}^{-1}\). No interpretable EPR spectra were observed at X-Band.

Experimental

High-field and frequency EPR spectra over the frequency range ca. 100-416 GHz were recorded on the transmission instrument at the NHMFL EMR facility.

Results and Discussion

The ground state of the binuclear \(\text{Cr}^{3+}-\text{Cr}^{3+}\) system is a singlet with \(S=0\). At high microwave frequencies spectra due to all three excited states, \(S=1\), \(S=2\) and \(S=3\) were observed and the spin Hamiltonian parameters were determined. \(g\) was essentially isotropic and equal to 1.982. ZFS parameters \(D\) and \(E\) were +0.794 cm\(^{-1}\), +0.230 cm\(^{-1}\) for \(S=1\), -0.105 cm\(^{-1}\), -0.0187 cm\(^{-1}\) for \(S=2\) and -0.168 cm\(^{-1}\), -0.014 cm\(^{-1}\) for \(S=3\). The zero-field splitting parameters for separate \(\text{Cr}^{3+}\) ions, \(D_c = +0.387 \text{ cm}^{-1}\) and \(E_c = +0.045 \text{ cm}^{-1}\) were found from the above parameters of the coupled \(\text{Cr}^{3+}-\text{Cr}^{3+}\) system by using relations given in ref. 1.

Conclusions

The observation and interpretation of the EPR spectra in this dichromium system was possible only under the high-field and frequency conditions due to the large zero-field splitting in the triplet \((S=1)\) and septet \((S=3)\) spin states. Preliminary DFT calculations resulted in a correct sign and order of magnitude of the \(D_c\) parameter (see above).

Acknowledgements

This work was supported in part by the Fundamental Researches State Fund of Ukraine (Project 14.3/005) and by the NHMFL. The NHMFL is funded by the NSF through the Cooperative Agreement No. DMR-0654118, by the State of Florida and by the DOE.

References