High-Field EPR and Magnetic Studies on a Binuclear Nickel(II) Complex

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Introduction

Thiosemicarbazones (TSCs) are known as versatile ligands for various metals [1]. Especially, their complex chemistry with first row transition metals e.g. Fe(II), Cu(II), Ni(II), Zn(II), Fe(III) is well developed. A special feature of TSCs and their metal complexes is their broad biological activity including antiviral, antibacterial, antimalarial, antifungal and anticancer activity [2-5]. A series of new water-soluble thiosemicarbazone-proline conjugates and their copper(II), nickel(II) and zinc(II) complexes was synthesized as possible anticancer agents [6]. Since the nickel(II) complexes proved to be thiolato-bridged dimers with a central Ni(μ-S)$_2$Ni core in the solid state, it was of interest to study the magnetic properties of these new compounds.

Experimental

High-field EPR spectra were recorded on the transmission instrument of the EMR facility and its 15/17 T superconducting magnet. Magnetic susceptibility data (2–300 K) were collected on powdered samples using a SQUID magnetometer (Quantum Design MPMS-XL) at 0.1 T.

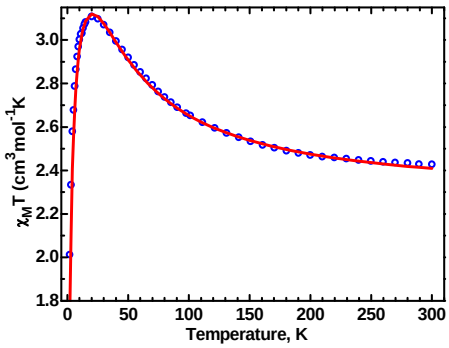

Fig. 1. Temperature dependence of the product χT for the Ni(μ-S)$_2$Ni complex.

Results and Discussion

The temperature dependence of the magnetic susceptibility for dinuclear nickel(II) complex (Fig. 1) was analyzed according to the Hamiltonian

$$\hat{H} = -2J\, \hat{S}_1 \cdot \hat{S}_2 + \mu_B \mathbf{B}\, \{g_1\}\, \hat{S}_1 + \hat{S}_1\, \{D_1\}\, \hat{S}_1 + \mu_B \mathbf{B}\, \{g_2\}\, \hat{S}_2 + \hat{S}_2\, \{D_2\}\, \hat{S}_2 + \hat{S}_1\, \{D_{12}\}\, \hat{S}_2 \qquad [1]$$

The complex was found to be ferromagnetic with J = +10.5(3) cm^{-1}. HF EPR spectra (Fig. 2) due to the ground state with S = 2 were interpreted in terms of the "giant spin" Hamiltonian

$$\hat{H}_{S=2} = \mu_B \mathbf{B} \cdot \{g_S\} \cdot \hat{S} + D[\hat{S}_z^2 - S(S+1)/3] + E(\hat{S}_x^2 - \hat{S}_y^2) \qquad [2]$$

D = +2.11 cm^{-1} and E = +0.52 cm^{-1} were found. With the help of Density Functional Theory (DFT) calculations, correlation between the parameters of equations [1] and [2] was established [5].

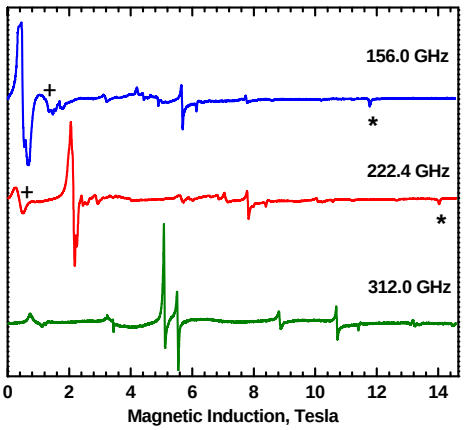

Fig. 2. HF EPR spectra recorded at 3 K. The resonances marked with + and * were used to determine the spin Hamiltonian parameters for S = 2 (formula [2]).

Conclusions

The "broken symmetry" DFT calculations reproduced the experimental J magnitude and were helpful in determining the directions of the zero-field splitting tensor components. In the interpretation of the magnetic data, advantage was taken of that information as well as of the EPR parameters $\mathbf{g}$, D and E. The results of this work were published [5].

Acknowledgements

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References

[1] Casas, J. S., *et al.*, Coord. Chem. Rev., **209**, 197−261 (2000).
[2] Beraldo, H., *et al.,* Mini-Rev. Med. Chem., **4**, 31−39 (2004).
[3] Rodríguez-Argüelles, M.C., *et al.,* J. Inorg. Chem., **99**, 2231−2239 (2005).
[4] Quenelle, D.C., *et al.,* Antiviral Res., **71**, 24−30 (2006).
[5] Bacher, F., *et al.,* Inorg. Chem., **53**, 12595-12609 (2014).
[6] Bacher, F., *et al.,* Inorg. Chem., **52**, 8895-8908 (2013).