High-Field EPR and Magnetic Study of $[Ni(L\text{-}Tyr)_2(bpy)] \cdot 1.5H_2O \cdot 0.5CH_3OH$

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Introduction

The pseudo-octahedral *cis*-$[Ni(\text{-tyr})_2(bpy)]\cdot 1.5\cdot H_2O\cdot 0.5\cdot CH_3OH$ complex was synthesized and characterized by X-ray, HFEPR and magnetic methods. In crystals, the neighboring $[Ni(L\text{-}Tyr)_2(bpy)]$ units are joined via weak hydrogen bonds, which create a helical polymeric chain. Relations between the structure and magnetic parameters as well as antibacterial and antifungal activity of the complex were studied in this work.

Experimental

High-field, high-frequency EPR spectra at temperatures ranging from ca. 6 K to 290 K were recorded on the transmission spectrometer at the EMR facility of the NHMFL. The magnetic measurements were performed at the Institute of Low Temperatures and Structural Research in Wroclaw.

Results and Discussion

The triplet-state (S = 1) EPR spectra (**Figure 1**) were interpreted using the standard spin Hamiltonian (Eq 1).

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

which gave a set of spectroscopic parameters : $g_x = 2.14$, $g_y = 2.16$, $g_z = 2.19$, $D = -3.26$ cm^{-1}, $E = -0.11$ cm^{-1}. The high-field "Z" resonance and the low-field "X" and "Y" resonances are suppressed when the temperature is lowered, while the intensity of the low-field "Z" and of the high-field "X" and "Y" resonances increases. This is well seen in the bottom part of Figure 1, and is diagnostic of the negative sign of *D*. These spin Hamiltonian parameters, together with a weak intramolecular antiferromagnetic exchange parameter $J = -0.48$ cm^{-1}, allowed us to reproduce the powder magnetic susceptibility and field-dependent magnetization of the complex. **Figure 2** shows the magnetization at 1.72 K simulated with and without the intramolecular exchange.

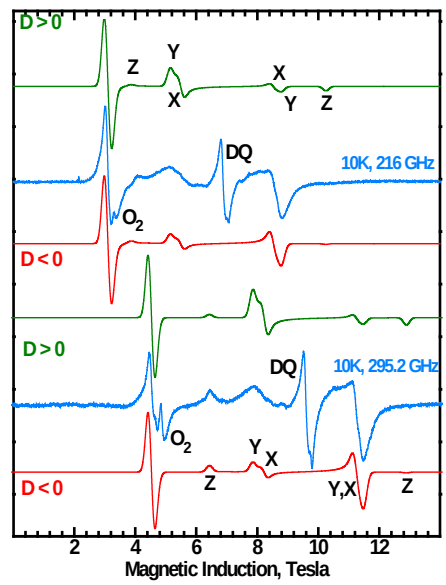

Figure 1. High-field EPR spectra measured at 10 K with the microwave frequencies as marked. Simulations used spin S = 1 and parameters given in the text. Simulations with positive *D* and *E* are also shown for comparison. Resonances marked with O_2 are due to oxygen adsorbed on the powder sample. DQ marks the 'double quantum transition'.

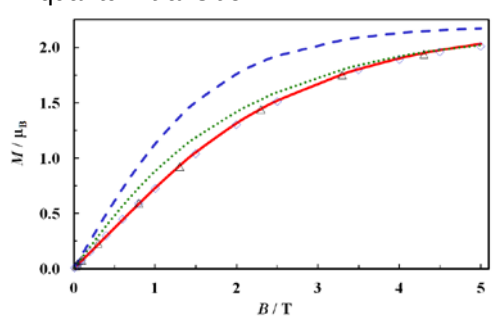

Figure 2. Magnetization at 1.72 K. ◇: increasing field, Δ : decreasing field. Dashed line: Brillouin function for *S*=1 and *g*=2.20. Dotted line: magnetization calculated with the HFEPR parameters. Solid line: intramolecular with $J = -0.48$ cm^{-1} taken into account.

Conclusions

The zfs parameters derived from HFEPR experiments yielded satisfactory agreement between the measured and calculated magnetization after taking into account a weak antiferromagnetic exchange interaction transmitted through helical polymeric chain based on the hydrogen bonds between Ni^{2+} ions.

Acknowledgements

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