HF-EPR Studies on a Linearly Bridged Nickel(II) Complex $\{[Ni(L\text{-}Tyr)_2(\mu\text{-}4,4'\text{-}bpy)]\cdot 4H_2O\}_\infty$

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Introduction

A novel and rare Ni^{2+} ions complex with L-tyrosine of formula $\{[Ni(L\text{-}Tyr)_2(\mu\text{-}4,4'\text{-}bpy)]\cdot 4H_2O\}_\infty$ (**1**) was synthesized and its X–ray crystal structure determined. Ni^{2+} ions are difficult to study by conventional X-band EPR due to the effects of large zero-field splitting, therefore high-field EPR was applied.

Experimental

High-field, high-frequency EPR spectra at temperatures ranging from ca. 5 K to 30 K were recorded on a home-built spectrometer at the EMR facility of the NHMFL (frequency range ~100 to 420 GHz) using a 15/17 T SC magnet. The magnetic susceptibility in the temperature range from 1.79 to 300 K in a field of 500 mT and magnetization up to 5 T were measured with a Quantum Design SQUID magnetometer at the Wroclaw University.

Results and Discussion

The high-field, high-frequency EPR spectra were interpreted using the spin Hamiltonian for S = 1:

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

The spin Hamiltonian parameters g_x = 2.162(3), g_y = 2.157(3), g_z = 2.190(5), D = -5.74(2) cm^{-1}, E = -0.429(7) cm^{-1} were obtained by simulations of the powder spectra recorded at 30 K (Fig. 1). The parameters are slightly temperature dependent and the set g_x = 2.178(5), g_y = 2.156(4), g_z = 2.19(1), D = -5.76(2) cm^{-1}, E = -0.41(1) cm^{-1} was found at 5 K. The sign of D and E could be determined thanks to the Zeeman splitting being comparable to or even larger than kT, which is achievable in high-field EPR at low temperatures (Fig. 2).

Conclusions

The magnetic susceptibility fitting resulted in D = –5.74 cm^{-1}, E = –0.429 cm^{-1} (HFEPR values), g_x = 2.139, g_y = 2.132, g_z = 2.166, and the temperature independent susceptibility $N\alpha = 41\cdot 10^{-6}$ in a reasonable agreement with the corresponding HFEPR values.

Acknowledgements

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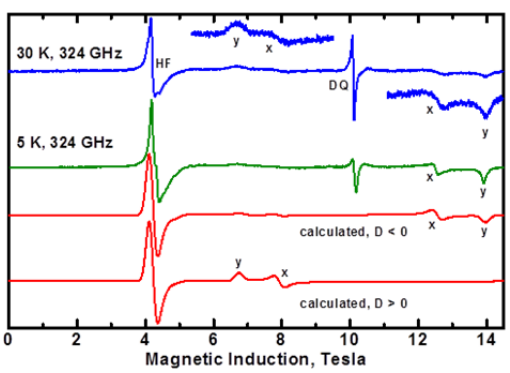

Fig.1 324 GHz EPR spectra recorded at temperatures indicated. The molecular orientations for respective transitions are marked with X, Y and Z.

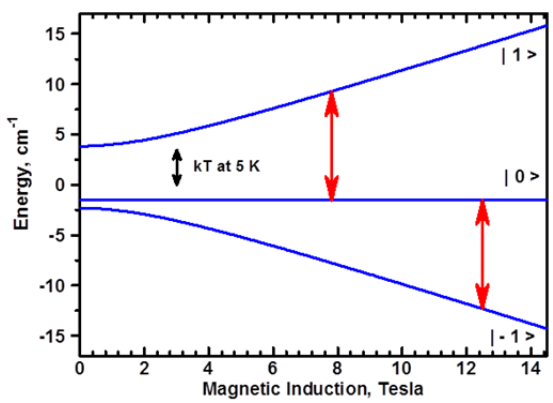

Fig.2. Energy of the spin states in magnetic field at the "X" orientation, calculated with the spin Hamiltonian parameters of **1** (negative D and E). Red arrows represent the microwave quantum energy of 10.8 cm^{-1} (324 GHz). kT at 5 K equals 3.475 cm^{-1}. The transition occurring at the higher magnetic field starts from the lowest energy state, while the transition at lower field starts from a thermally depopulated state and will be frozen out. With a positive D, these relations would be inverted.