High-Field EPR on $Fe(mtz)_6$, a Spin-Crossover Complex and Single-Molecule Magnet

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Introduction

Magnetic bistability can be used for, e.g. spintronics, quantum information processing and sensor applications. To realize these potential applications on the molecular scale either molecules displaying slow relaxation of the magnetization (single molecule magnets, SMMs) or molecules showing spin-crossover are most promising. The latter are characterized by a reversible transition between a low- and high-spin state. The transition can be driven by temperature, pressure, magnetic field or irradiation. $[Fe(mtz)_6](CF_3SO_3)_2$ (mtz = 1-methyltetrazole, $Fe(mtz)_6$ in short) displays a rather rich phase diagram as function of temperature. In the low-temperature phase high-spin Fe^{II} (S = 2) are present and they can be reversible converted to low-spin (S = 0) by irradiation (inverse LIESST effect). Further, it was found that the high-spin Fe^{II} ions in this phase do display slow-relaxation of the magnetization and that this is preserved after reversed transformation to low-spin.[1]

These experiments aim to determine the magnetic parameters, which determine the SMM properties, of $Fe(mtz)_6$ in the low-temperature phase. For molecules with significant anisotropy and integer spin, like $Fe(mtz)_6$, high microwave frequencies ν_{MW} and magnetic fields B_0 are required.

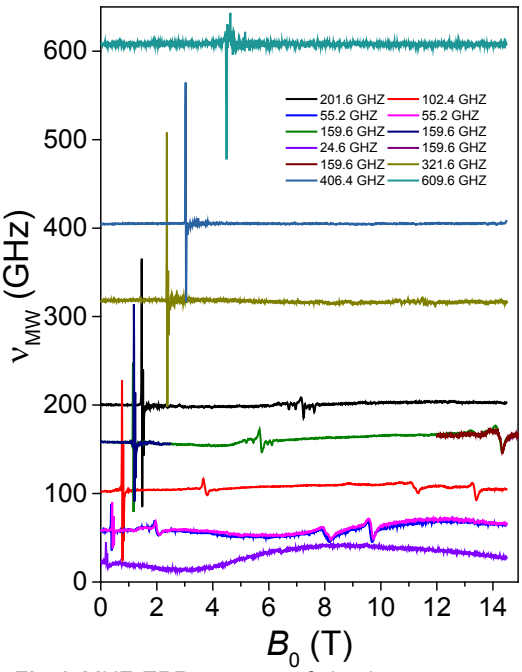

Fig.1 MHF-EPR spectra of the low-temperature high-spin phase of $Fe(mtz)_6$. Spectra were recorded at a temperature of 5 K and the indicated ν_{MW}. They are rescaled and offset according to ν_{MW}.

Experimental

Experiments were done at the EMR facility using the transmission spectrometer and a 15/17 T superconducting magnet. Finely ground powder of $Fe(mtz)_6$, immobilized with mineral oil was investigated at various frequencies between 25 and 630 GHz at a temperature of 5 K. Rapid cooling can quench the transitions in the phase diagram. Experiments aimed at studying the high-temperature phase were done by rapidly cooling down the sample. Conversely, very slow cooling was required to reach high conversion to the low-temperature phase.

Results and Discussion

Spectra of the high temperature phase (not shown) are dominated by an EPR line around g_{eff} = 9 ($h\nu_{MW} = \mu_B g_{eff} B_0$, with the Planck constant h and the Bohr magneton μ_B). Spectra of the low-temperature phase are shown in **Fig.1**. The remaining g_{eff} = 9 signal was assigned to molecules remaining in the high-temperature phase, as its intensity varied between cooling cycles. Further, a line around g_{eff} = 2 was assigned to a side product of the synthesis. The additional lines at high fields and low frequencies, which do not follow a linear field-frequency relationship, were assigned to the low-temperature phase.
Although we could observe clear differences in the EPR spectra between the high- and low-temperature phases, the experimental results do not allow assigning clear-cut magnetic parameters.

Conclusions and Outlook

The experiments presented here revealed clear differences in the magnetic properties between the high- and low-temperature phase. In conjunction with recently elsewhere performed frequency-domain EPR experiments we should be able to assign the magnetic parameters of $Fe(mtz)_6$.

In future experiments we plan to follow the inverse LIESST effect in an EPR experiment. The sample will be irradiated with light at the proper wavelength. Such a population of the low-temperature, high-spin phase can be altered and, hence, the intensity of the corresponding EPR signals should vary.

Acknowledgements

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References

[1] Urtizberea, A., *et al.*, Chem. Sci, **8**, 2290-2295 (2017).