



## Search for New Single-Molecule Magnets: High-Field EPR Studies on High-Spin Complexes of d-Electron Metals – Co(II)

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### Introduction

The main goal of our project is to construct new magnetic molecular materials which possess high magnetic anisotropy in conjunction with long relaxation times and exhibit spontaneous magnetization below the blocking temperature. Along these lines, three pentacoordinate  $[\text{Co}(\text{pypz})\text{X}_2]$  complexes were synthesized (where pypz is a tridentate ligand 2,6-bis(pyrazol-1-yl)pyridine and  $\text{X} = \text{Cl}^-$ ,  $\text{NCS}^-$  and  $\text{NCO}^-$ , for complexes **1**, **2** and **3**, respectively), and were characterized by single-crystal X-ray crystallography as well as by magnetic and EPR studies.

### Experimental

Far-infrared magnetic spectroscopy (FIRMS) studies were performed at the National High Magnetic Field Laboratory in a 17 T vertical-bore superconducting magnet using a Fourier-transform infrared spectrometer Bruker Vertex 80v. High-Field EPR spectra were recorded on the 17 T transmission spectrometer of the EMR facility. Variable-temperature (2–300 K) direct current (DC) magnetic susceptibility measurements under applied field BDC = 0.1 T (below 20 K) and 1.0 T (above 20 K) and variable-field (0–7 T) magnetization measurements at low temperatures in the range 2–7 K were carried out with Quantum Design SQUID magnetometer (Faculty of Chemistry, University of Wrocław). Variable-temperature (2 – 8 K) alternating current (AC) magnetic susceptibility measurements under different applied static fields in the range of BDC = 0 – 0.5 T were carried out with Quantum Design Physical Property Measurement System (PPMS). Raw magnetic susceptibility data were corrected for the underlying diamagnetism and the sample holder. Magnetic measurements were carried out by crushing the crystals and restraining the sample in order to prevent any displacement due to its magnetic anisotropy.

### Results and Discussion

The DC magnetic data show a sizable magnetic anisotropy, which was confirmed by high-field EPR measurement together with FIRMS method. The AC susceptibility data present a slow magnetic relaxation under a small applied DC field with two relaxation modes. The low frequency mode at  $T = 2.0$  K is as slow as  $\tau_{\text{LF}} = 0.72(6)$  s,  $1.9(4)$  s, and  $0.69(27)$  s, respectively (BDC = 0.35, 0.40, and 0.20 T).

Well-resolved high-field EPR spectra of high spin cobalt (II) were observed over the microwave frequency range 100–650 GHz. The zero-field splitting in our compounds is very large and even with frequencies as high as 600 GHz no transitions between the Kramer's doublets could be observed. Only the transitions within the lower Kramer's doublet are seen, from which the spin Hamiltonian parameters  $g$ , as well as the  $E/D$  ratios were estimated. The higher  $E/D$  ratio of 0.295 in for **2** compared to 0.078 in **3** is associated with the lower symmetry of **2**, as it is lacking the twofold axis. To determine the exact  $D$  value for **2** ( $38.4 \text{ cm}^{-1}$ ) and **3** ( $40.92 \text{ cm}^{-1}$ ), the FIRMS method was applied. In FIRMS, zero-field transitions were observed at  $84 \text{ cm}^{-1}$  for **2**,  $81.5 \text{ cm}^{-1}$  for **3** (Fig.1) and  $\sim 158 \text{ cm}^{-1}$  for **1**.

### Conclusions

Knowledge of the zero field splitting parameters and their signs is crucial for interpretation of the SMM (Single-Molecule Magnet) or SChM (Single-Chain Magnet) behavior. There is growing evidence for the SMM behavior in compounds with  $D > 0$ , provided that a positive  $D$  is accompanied by a sizable rhombic component  $E$ . A negative  $D$  associated with the easy-axis of magnetization is thus no longer an ultimate demand for the SIM (Single-Ion Magnet) behavior. The result obtained here for complex **1**, **2** and **3** fully confirm this hypothesis. The results of this research have been recently published [1].

### Acknowledgements

A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1644779 and the State of Florida.

### References

[1] Świtlicka, A., *et al.*, *Inorg. Chem.*, **57**, 12740–12755 (2018).

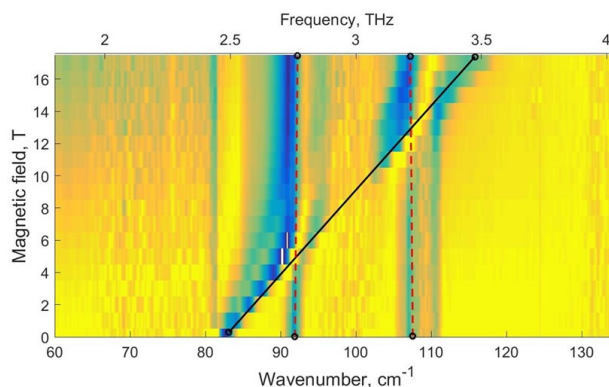


Fig.1 A FIRMS spectrum observed for **3** at 5 K showing a zero-field transition at  $81.5 \text{ cm}^{-1}$ .