

[Fe(3DITZ)₃](BF₄)₂: A RARE EXAMPLE OF A STRONGLY COOPERATIVE SPIN TRANSITION BEHAVIOUR OF A 1D-CHAIN-TYPE COORDINATION POLYMER USING A *PER SE* FLEXIBLE LIGAND

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Synthesis and Crystal Structure

A modified phase-transfer catalyst assisted synthetic pathway has been developed thus widening the pool of accessible 1-substituted tetrazoles as possible ligands for iron(II) spin crossover compounds.^[1] Within the family of α,ω -bis-(tetrazol-1-yl)-alkanes a series of ligands and their respective iron(II) spin crossover compounds have been synthesized, structurally and spectroscopically characterized in the past.^[2-4] The classical route to prepare these ligands is based on the respective amino-precursors^[5] hence limiting the pool of compounds by commercially or synthetically available α,ω -bis-amino-alkanes. As this alternative protocol allows the start from bromo-precursor molecules rather than amino-precursor molecules the so far inaccessible 1,3-bis-(tetrazol-1-yl)propane [3ditz] was prepared for the first time (see Figure 1). Upon complexation with Fe(II) 1D chain-type coordination polymers are formed (see Figure 2).

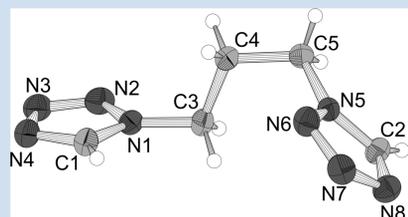


Figure 1: Ellipsoid plot of the molecular structure of [3ditz]. C and N atoms are represented by light and dark grey ellipsoids drawn at 75% probability levels. H are represented by white spheres of arbitrary radius.

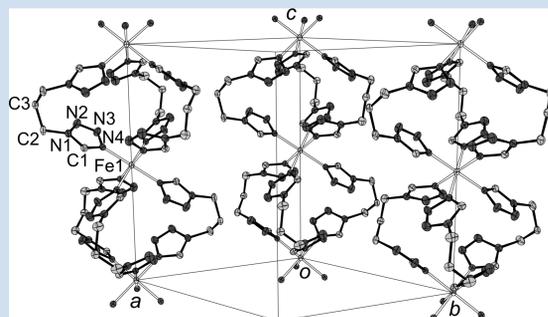


Figure 2: Perspective projection of [Fe(3ditz)₃](BF₄)₂ showing the one-dimensional chain-structure. Colour codes as in Fig. 1, Fe²⁺-ions are white. Ellipsoids indicate 50% probability levels. H-atoms and disorder of the ligands have been omitted for clarity.

Surprisingly, owing to a more corrugated conformation of the [3ditz] ligand in comparison with shorter 1,2-bis(tetrazol-1-yl)ethane [2ditz] and 1,2-bis(tetrazol-1-yl)propane [btzp], the Fe²⁺—Fe²⁺-distances along the cationic chains are significantly shorter in the complex of the former (7.1325(11) vs. 7.293(4) and 7.273(1) Å at 100 K), which translates to a shorter lattice parameter $c=2d(\text{Fe}^{2+}\text{—Fe}^{2+})$. The additional space needed for the extra methylene group in [3ditz] is provided by a less dense packing of the cationic chains than in the [2ditz] complex and in consequence an increase of the lattice parameters $a=b$ (10.9153(4) vs. 10.178(2) Å) (see Figure 3).

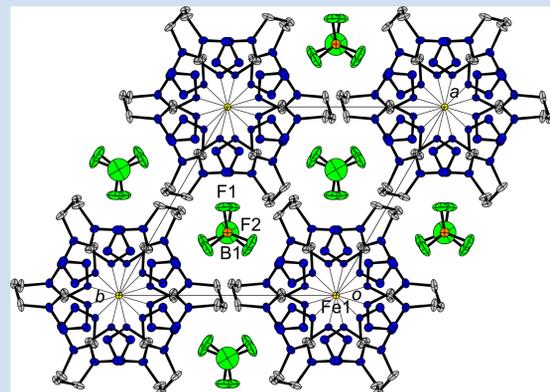


Figure 3: Crystal structure of [Fe(3ditz)₃](BF₄)₂ viewed down [001]. Atom colour codes: Fe, C, N, B and F. H-atoms and disorder of the ligands has been omitted for clarity.

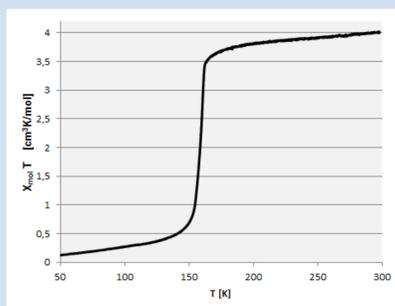


Figure 4: Molar magnetic susceptibility of [Fe(3ditz)₃](BF₄)₂ between 50 K and 300 K at an external field strength of $H = 1$ T.

X-ray powder diffraction (XRPD)

As all spectroscopic and magnetic investigations have been performed on powder samples of the title compound we verified that the powder samples of the complex are identical to the single crystals sample used for structure determination (see Figure 5).

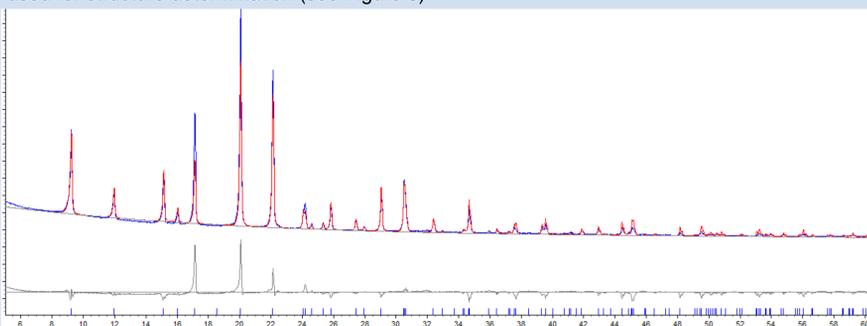


Figure 5: XRPD of [Fe(3ditz)₃](BF₄)₂ in comparison to a calculated XRPD pattern using data of the single crystal XRD measurement (only calculated, NOT refined data)

Magnetic and spectroscopic characterisation of [Fe(3ditz)₃](BF₄)₂

The magnetic susceptibility of [Fe(3ditz)₃](BF₄)₂ was measured between 50 K and 300 K revealing an almost complete and abrupt spin transition behaviour at $T_{1/2} = 159$ K (see Figure 4).

The results of the magnetic measurements are supported by independent spectroscopic measurements using variable temperature FIR (see Figure 6), MIR (see Figure 7), UV-VIS-NIR spectroscopy (see Figure 8) and ⁵⁷Fe-Mössbauer spectroscopy (see Figure 9).

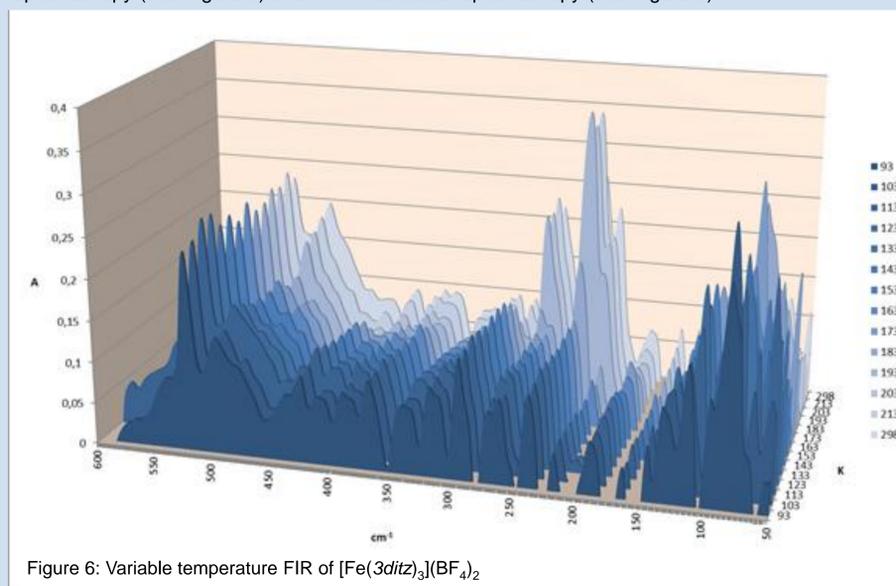


Figure 6: Variable temperature FIR of [Fe(3ditz)₃](BF₄)₂

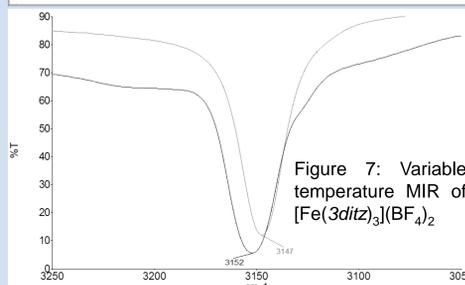


Figure 7: Variable temperature MIR of [Fe(3ditz)₃](BF₄)₂

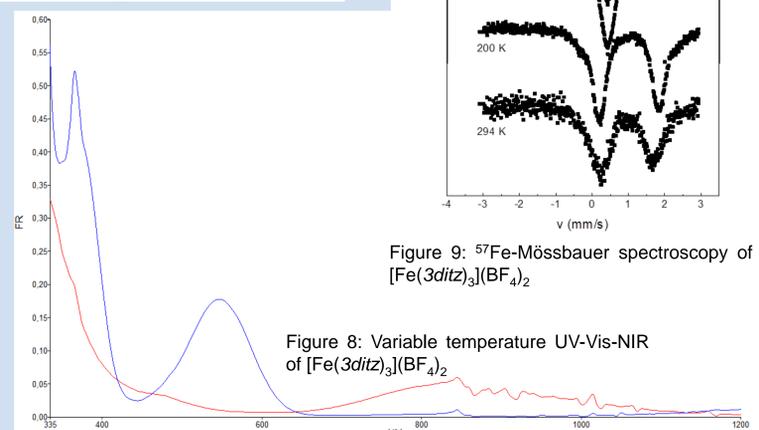


Figure 8: Variable temperature UV-Vis-NIR of [Fe(3ditz)₃](BF₄)₂

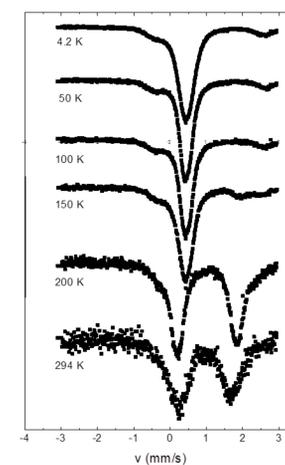


Figure 9: ⁵⁷Fe-Mössbauer spectroscopy of [Fe(3ditz)₃](BF₄)₂

Conclusions

The astonishing abruptness of the spin transition due to a strong cooperative effect among the spin switching iron(II) coordination centres can be explained by the significant shorter Fe(II) – Fe(II) distance alongside the 1D chain-type coordination polymer in comparison to the homologous [Fe(2ditz)₃](BF₄)₂ compound, *i.e.* 7.13 Å vs. 7.29 Å at 100 K.^[2] Furthermore, the three helically twisted bridging [3ditz] ligands form a stiffer packing motif than the shorter [2ditz] ligands in the corresponding [Fe(2ditz)₃](BF₄)₂ compound thus preventing a kind of shock-absorber effect of the bridging ligand, which impairs the cooperativity of the iron(II) centres in the [Fe(2ditz)₃](BF₄)₂ compound.

Therefore, the title complex is a rare example for spin crossover compounds with *per se* flexible ligands that yield abrupt spin transition behaviour mainly due to packing effects rather than the stiffness of the ligand itself.

Acknowledgements

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