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Synthesis and Characterization of Fe(II) Spin Crossover Complexes with asymmetric ditetrazole bridging ligands

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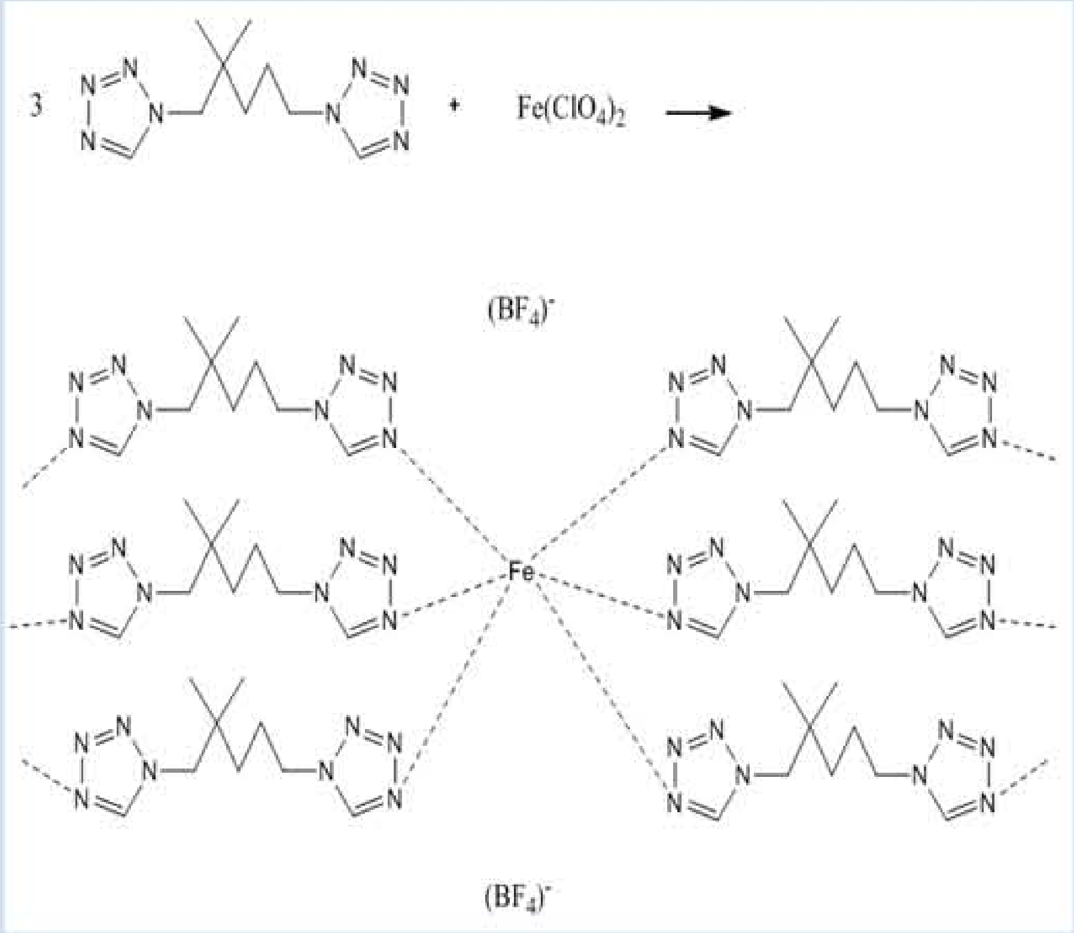
Introduction

Based on literature [1] proving that asymmetric tetrazolic bridging ligands in an iron(II) complex can facilitate a complete and abrupt spin crossover behavior, the aim of this work was to prepare homologous ligands. The envisaged new ligands should fit in a series of ditetrazoles [nditz] with n=2 to n=12 where n is the number of carbon atoms between the two tetrazole moieties. These new prepared ligands will be complexed with iron(II) salts yielding novel spin crossover compounds.
Recent work [2] showed that short bridging ligands with n = 2 - 4 give the complexes a certain rigidity which leads to a good crystallization of the respective complexes. For a longer spacer between the coordinating tetrazole moieties or longer substituents of terminal ligands it was shown that these spacer chains have due to their high degree of flexibility a rather poor crystallinity, probably due to the fact they can curl up. So far only asymmetric bridging ditetrazole ligands are known having not more than the 3 C atoms in the spacer. Therefore, a ligand with a spacer with n=4 was envisaged but turned out to be impossible to synthesize. Unexpectedly, it was possible to prepare the next homologue bridging ligand with n=5. Its complexation with iron(II) salts with BF_4^- and ClO_4^- as counter anions yielded the desired products.

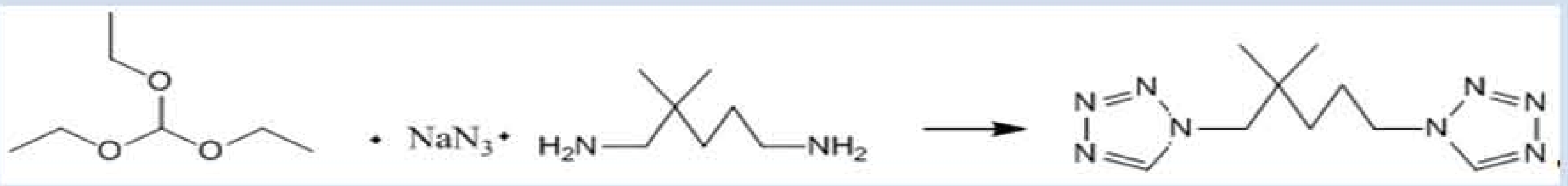


Complexation

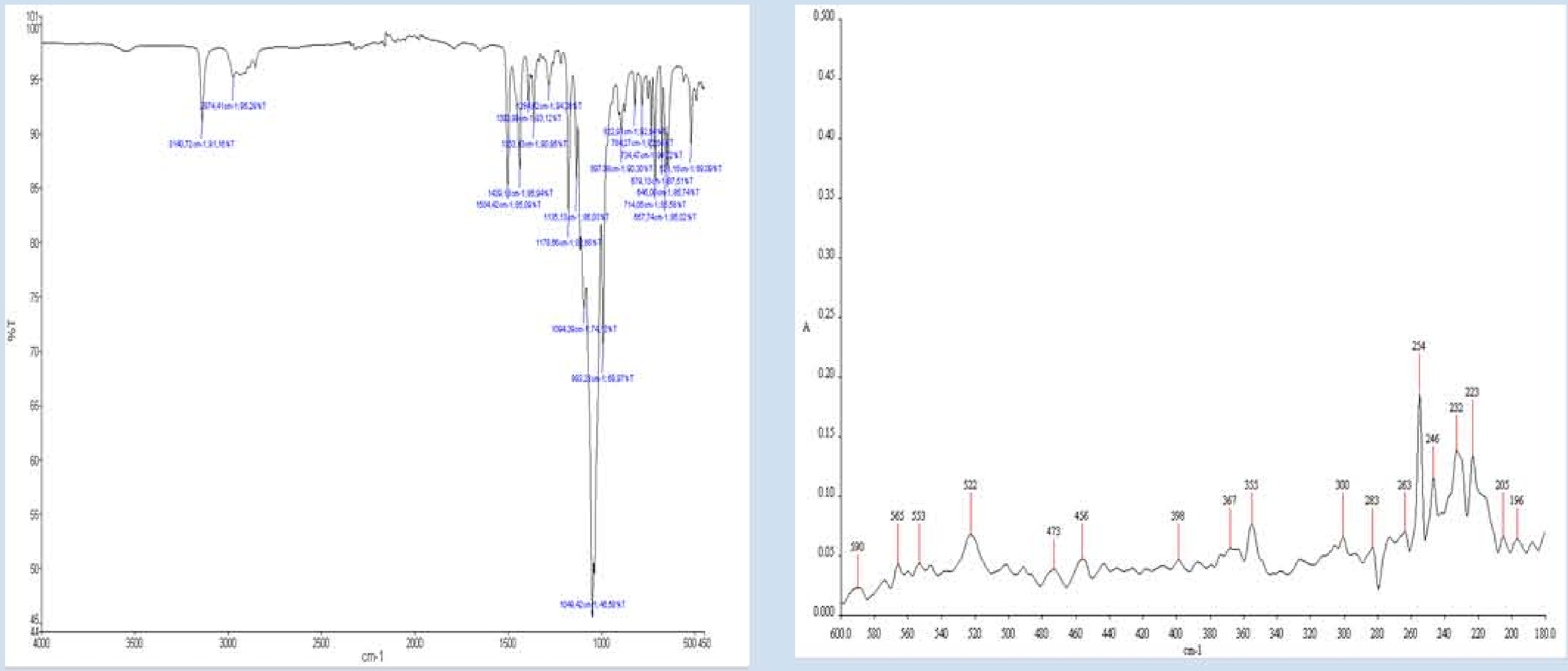
For the complexation the iron(II) salts with weak coordinating anions like BF_4^- and ClO_4^- were used. In a Schlenk-tube with a reverse frit the viscous liquid ligand was provided. The Schlenk-tube was repeatedly set under vacuo and refilled with argon for three times. Under a constant flow of argon degassed ethanol and the iron (II) salt were added. These educts were stirred and kept for 24 hours at 40°C. Finally, the ethanol was filtered off and the complex was washed with degassed ethanol. White powder of product was isolated and charactierized.

Synthesis of the 2,2-dimethyl-pentanditetrazole ligand [*22dime5ditz*]

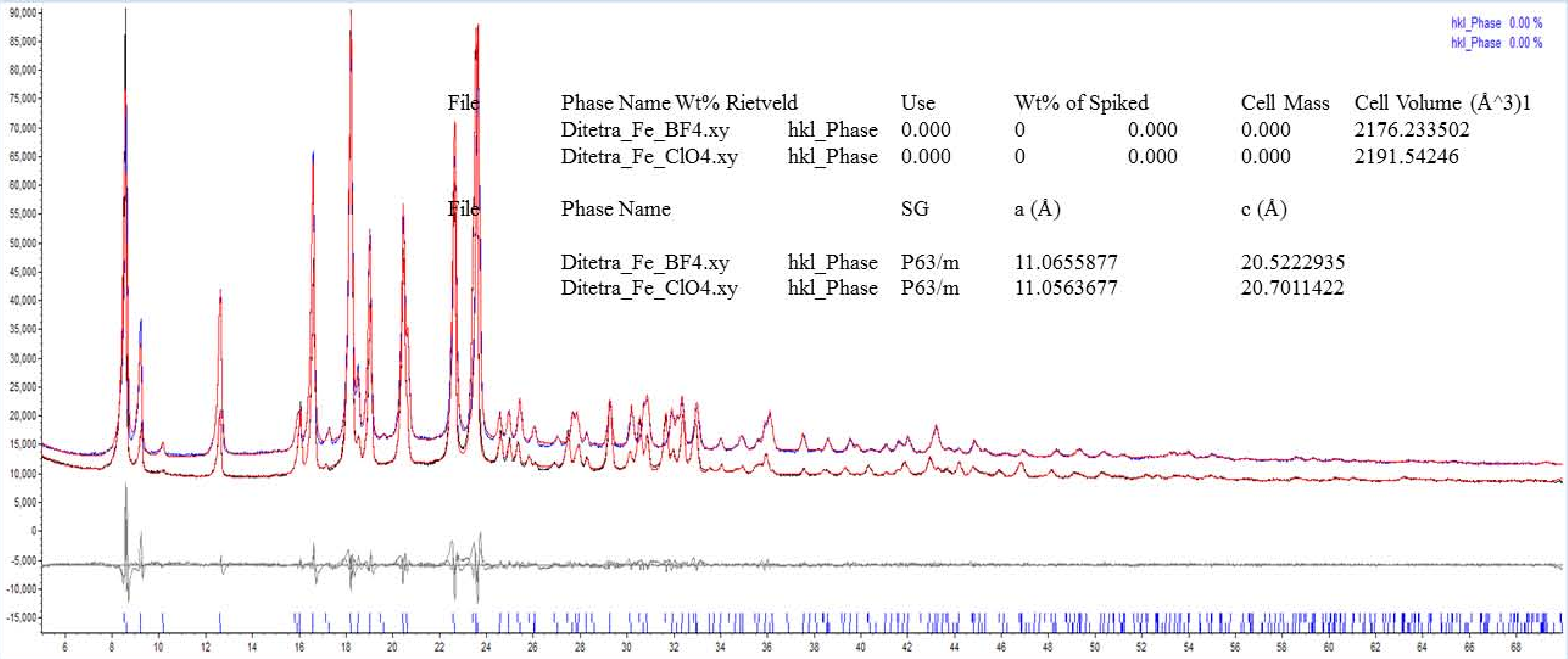
For this synthesis the 2,2-dimethyl-pentandiamine was used as precursor. To prepare the respective tetrazole the Franke synthesis [3] was applied directly. A 250ml flask was used to dissolve the educts in acetic acid. The reaction mixture was heated to 80°C for 60 hours. After this HCl was added and the isolated salts were washed with $NaHCO_3$ dissolved in ethyl acetate. The pH of the solution was adjusted to pH = 8. Raw product was isolated in high yield and further purification was necessary.



Characterisation



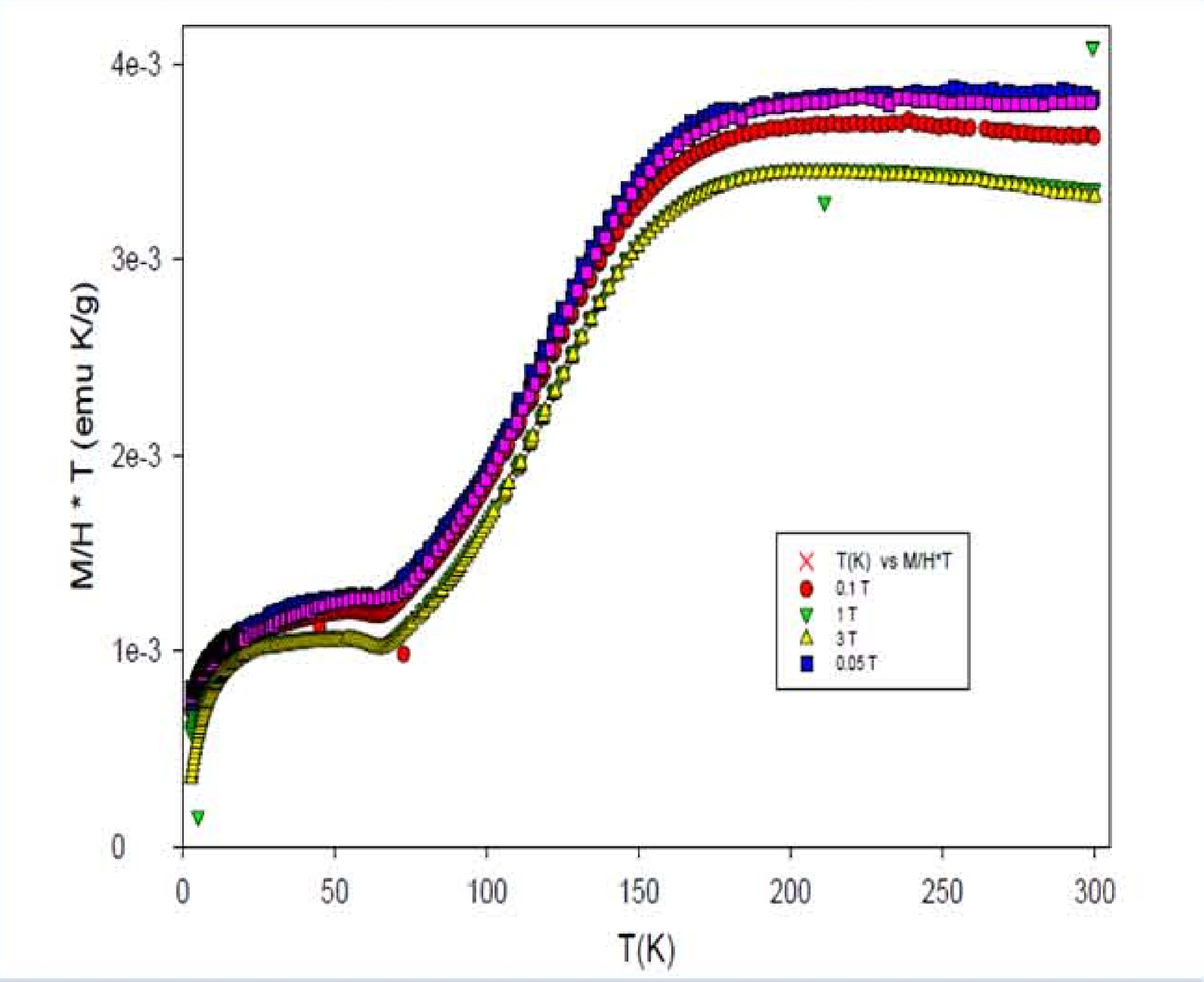
MIR (left) and FIR (right) of [Fe(*22dime5ditz*)$_3$](BF$_4$)$_2$



File	Phase Name	Wt% Rietveld	Use	Wt% of Spiked	Cell Mass	Cell Volume (Å^3)1
Ditetra_Fe_BF4.xy	hkl_Phase	0.000	0	0.000	0.000	2176.233502
Ditetra_Fe_ClO4.xy	hkl_Phase	0.000	0	0.000	0.000	2191.54246

File	Phase Name	SG	a (Å)	c (Å)
Ditetra_Fe_BF4.xy	hkl_Phase	P63/m	11.0655877	20.5222935
Ditetra_Fe_ClO4.xy	hkl_Phase	P63/m	11.0563677	20.7011422

PXRD of [Fe(*22dime5ditz*)$_3$](BF$_4$)$_2$ (upper diffractogram) and [Fe(*22dime5ditz*)$_3$](ClO$_4$)$_2$ (lower diffractogram)



molar magnetic susceptibility *vs.* temperature of Fe(*22dime5ditz*)$_3$](BF$_4$)$_2$

References:
[1] M. Quesada, H. Kooijman, P. Gamez, J. Sanchez Costa, P.J. van Koningsbruggen, P. Weinberger, M. Reissner, A.L. Spek, J.G. Haasnoot, J. Reedijk, *Dalton Trans.* 46 (2007) 5434-5440.
[2] D. Müller, C. Knoll, B. Stöger, W. Artner, M. Reissner and P. Weinberger, *Eur. J. Inorg. Chem.* (2012) http://dx.doi.org/10.1002/ejic.201201062.
[3] P.L. Franke, J.G. Haasnoot, A.P. Zuur, *Inorg. Chim. Acta*, 5 (1982) 59.