

MS16-P06**Structural studies of HS↔LS transition triggered by temperature or laser light irradiation in the [Fe(ebtz)₂(RCN)₂](BF₄)₂ complexes**

Joachim Kusz¹, Marcin Kaźmierczak², Maria Książek¹, Miłosz Siczek², Robert Bronisz², Aleksandra Tołoczko², Marek Weselski²

1. Institute of Physics, University of Silesia, Katowice, Poland

2. Faculty of Chemistry, University of Wrocław, Wrocław, Poland

email: kusz@us.edu.pl

Spin crossover in the complexes of 3d⁴-3d⁷ metal ions is associated with the change of magnetic, optical and structural properties.¹ In iron(II) complexes the HS↔LS transition is accompanied by shortening of Fe-ligand distance at about 0.2Å. This alteration becomes an origin of perturbation influencing on neighbored molecules as well as spreading through intermolecular interactions on the whole crystal lattice. It can lead to appearance of cooperative behaviours resulting in occurrence of spin crossover in narrow temperature range.

1,2-di(tetrazol-2-yl)ethane (ebtz) creates with iron(II) perchlorate one-dimensional (1D) coordination polymer [Fe(ebtz)₂(C₂H₅CN)₂](ClO₄)₂ exhibiting abrupt spin crossover accompanied by wide hysteresis loop (T_{1/2}[↑] ≈ 112K, T_{1/2}[↓] ≈ 141K).² The characteristic feature of this complex is uncommon orientation of axially coordinated propionitrile molecules because Fe-N-C(nitrile) angle adopt at 250K value of 149.1(3)°. What is interesting the HS↔LS transition is connected with reorientation of nitrile molecules and in the LS form Fe-N-C(nitrile) angle increases to 162.9(2)°. In order to elucidate a mechanism of spin crossover in [Fe(ebtz)₂(RCN)₂](BF₄)₂ polymers, we have carried out systematic studies changing coordinated nitrile molecules (R = -CH₃, -C₂H₅, -C₃H₅, -C₃H₇, -CH₂Cl). It was established that the novel complexes crystallize as 1D coordination polymers in which two ebtz molecules link neighbouring Fe(II) ions and axial positions in coordination octahedron are occupied by nitriles. In the complexes containing coordinated molecules of butyro-, allylo- or chloroacetonitrile the HS↔LS transition is accompanied by shortening of the Fe-N distances at about 0.2Å, however, values of Fe-N-C(nitrile) angles remain very similar in both spin forms. In acetonitrile based system the difference becomes more visible. In the HS form Fe-N-C(acetonitrile) angle adopts value of 167.4(2)° (230K), whereas it increases to 171.6(2)° (120K) in the LS form. Unfortunately propionitrile derivative remains in the HS form up to 80 K upon cooling. Therefore in order to determine the crystal structure of the LS form and find the value of Fe-N-C(nitrile) angle we have performed the HS↔LS switching at 15K using laser light irradiation (808nm). We have established that similarly to [Fe(ebtz)₂(C₂H₅CN)₂](ClO₄)₂ formation of the LS form in tetrafluoroborate analogue is associated with reorientation of propionitrile molecule. Detailed results of single crystal X-ray diffraction studies of [Fe(ebtz)₂(RCN)₂](BF₄)₂ (R = -CH₃, -C₂H₅, -C₃H₅, -C₃H₇, -CH₂Cl) complexes in HS and LS forms, generated by change of temperature or as a result of laser light irradiation, will be presented.

This work was supported by the Polish National Sciences Centre Grant No. DEC-2014/15/B/ST5/04771.

References:

[1] M. A. Halcrow, *Spin-Crossover Materials: Properties and Applications*, Wiley (2013).

[2] A. Białońska, R. Bronisz, *Inorg. Chem.* (2012). 51, 12630 - 12637.

Keywords: spin crossover, Fe(II) complexes