

**MS23-P8** Single crystal X - ray structure analysis of the complex  $[\text{Fe}(\text{bbtr})_3](\text{ClO}_4)_y(\text{BF}_4)_{2-y}$ . Joachim Kusz,<sup>a</sup> Robert Bronisz,<sup>b</sup> Gabriela Bednarek,<sup>a</sup> Maria Nowak,<sup>a</sup> <sup>a</sup>*Institute of Physics, University of Silesia, Katowice, Poland*, <sup>b</sup>*Faculty of Chemistry, University of Wrocław, Wrocław, Poland*  
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Spin crossover (SCO) phenomenon is connected with the switching process of electronic configuration of iron(II) ion by a change of temperature [1], pressure [2], magnetic field [3] or after light irradiation [4]. The result of such transition is not only the change of metal – ligand bond lengths but also cooperative interactions with other SCO centers. The cooperative effect can be strengthened for example by connecting Fe(II) centers using covalent bonds which belong to bridging ligands [5].

$[\text{M}(\text{bbtr})_3]\text{A}_2$  (M = Fe, Zn, bbtr = 1,4-bis(1,2,3-triazol-1-yl)butane, A =  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ) complexes create coordination networks [6]. Single crystal X – ray measurements revealed that these compounds crystallize in  $P\bar{3}$  space group. In  $[\text{Fe}(\text{bbtr})_3](\text{ClO}_4)_2$  spin transition is observed at 101 K (cooling mode) and 109 K (heating mode). What is interesting, analogue complex  $[\text{Fe}(\text{bbtr})_3](\text{BF}_4)_2$  remains in high spin form in whole temperature range [7]. Lately it has been shown that this compound can be switched to the low spin form by irradiating with red laser light [8]. Therefore it is very important to analyze in a detailed way the crystal structure during SCO both for pure Fe(II) complexes as well as systems doped with zinc(II).

A structural phase transition is observed for  $[\text{M}(\text{bbtr})_3](\text{ClO}_4)_2$  from  $P\bar{3}$  to  $P\bar{1}$  space group (for M = Fe at 125 K, for M = Zn at 151 K). It is assumed that this effect is connected with reorganization of intermolecular interactions.

Accurate structural measurements of the doped systems  $[\text{Fe}_x\text{Zn}_{1-x}(\text{bbtr})_3](\text{ClO}_4)_2$  (x = 0.86, 0.60, 0.43, 0.34, 0.26) revealed that with lowering of the temperature at first there is structural phase transition from trigonal phase ( $P\bar{3}$ ) to triclinic phase ( $P\bar{1}$ ) and next the SCO occurs in the low – symmetric phase [7].

For both tetrafluoroborate derivatives  $[\text{M}(\text{bbtr})_3](\text{BF}_4)_2$  (M = Fe, Zn) no change of space group is observed with temperature lowering therefore  $[\text{Fe}(\text{bbtr})_3](\text{BF}_4)_2$  does not exhibit SCO [7]. The synchrotron measurements show that reversible switching between spin states in  $[\text{Fe}(\text{bbtr})_3](\text{BF}_4)_2$  is possible and leads to lowering of the symmetry from  $P\bar{3}$  to  $P\bar{1}$  (in the low spin state) [8].

In the presented work there is shown detailed structural analysis of iron(II) complex with mixed counteranions  $[\text{Fe}(\text{bbtr})_3](\text{ClO}_4)_y(\text{BF}_4)_{2-y}$ .

- [1] Gütlich, P., Goodwin, H. A. (2004). *Top. Curr. Chem.* **233**, 1–47.
- [2] Ksenofontov, V., Gaspar, A., B., Gütlich, P. (2004). *Top. Curr. Chem.* **235**, 39–66.
- [3] Bousseksou, A., Varret, F., Goiran, M., Boukheddaden, K., Tuchagues, J. P. (2004). *Top. Curr. Chem.* **235**, 309–329.
- [4] Gütlich, P., Hauser, A., Spiering, H. (2003). *Angew. Chem. Int. Ed.* **33**, 2024–2054.
- [5] Kahn, O., Martinez, C. J. (1995). *Science* **279**, 44–48.
- [6] Bronisz, R. (2005). *Inorg. Chem.* **44**, 4463–4465.
- [7] Kusz, J., Bronisz, R., Zubko, M., Bednarek, G. (2011). *Chem. Eur. J.* **17**, 6807–6820.
- [8] Chakraborty, P., Bronisz, R., Besnard, C., Guénee, L., Pattison, P., Hauser, A. (2012). *J. Am. Chem. Soc.* **134**, 4049–4052.

**Keywords:** spin crossover; coordination network; symmetry breaking

**MS23-P9** Contribution of weak S-H...X hydrogen bonds to phase transitions in crystals of cysteine, its salts and derivatives under high pressures and low temperatures. Vasily Minkov,<sup>ab</sup> Elena Boldyreva,<sup>ab</sup> <sup>a</sup>*Institute of Solid State Chemistry and Mechanochemistry SB RAS, Russian Federation*, <sup>b</sup>*REC-008 Novosibirsk State University, Russian Federation*  
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Cysteine is a very important naturally occurring amino acid. Owing to the presence of thiol group in its side-chain residue, cysteine is prone to form S-H...X hydrogen bonds and participates in formation of protein secondary structures. Cysteine also plays a very important role in stabilizing the conformation of protein active site in zinc fingers and iron-sulfur proteins due to high affinity of thiol group to bind with metal. In addition -SH group can be easily oxidized providing cysteine with a covalent disulfide bridge often found in secreted proteins like insulin and trypsin. Besides, cysteine and its derivatives are used as drugs. In crystals cysteine can adopt different conformations since its side chain may easily rotate along C-C bond providing three general types of its orientation characterized by the value of N-C-C-S torsion angle: *gauche+*, *gauche-* and *trans*. Investigations of L- and DL-cysteine on variation of temperature and pressure have revealed many phase transitions<sup>[1-6]</sup>. On cooling the orthorhombic L-cysteine its side chain becomes ordered, in monoclinic L-cysteine a subtle phase transition is detected. Increasing pressure leads to series of phase transitions accompanied by changes in intramolecular geometry and hydrogen bonds in both polymorphs. It is remarkable that high-pressure phases are not the same for these two modifications of L-cysteine. DL-cysteine also undergoes phase transitions on cooling and increasing pressure. Even on slow cooling crystals split into several fragments and as recently has been shown fragmentation is caused by breaking the weak S-H...S hydrogen bonds between layers in crystal structure. More phase transitions in DL-cysteine are observed on increasing pressure but only the first high-pressure phase is similar to the low-temperature phase. Very recently we have shown that reducing or suppressing completely the mobility of the side chain results in the crystal structure stabilization with respect to phase transitions. It was found that chemical modification of H-bonded groups (N-acetyl-L-cysteine) as well as introducing a potentially stronger acceptor or donor for hydrogen bonding in the structure (oxalates of DL-cysteine 1:1 and 1:2) considerably increases the stability of the crystal structures with respect to phase transitions on increasing pressure. In the present work we report that contribution of weak hydrogen bonds formed by the side-chain of cysteine in temperature- and pressure- induced phase transitions is crucial in such system.

- [1] Minkov, V. S., Krylov, A. S., Boldyreva, E. V., Goryainov, S. V., Bizyaev, S. N., Vtyurin, A. N. (2008). *J. Phys. Chem. B*, **112**, 8851–8854.
- [2] Kolesov, B. A., Minkov, V. S., Boldyreva, E. V., Drebushchak, T. N. (2008). *J. Phys. Chem. B*, **112**, 12827–12839.
- [3] Minkov, V. S., Tumanov, N. A., Kolesov, B. A., Boldyreva, E. V., Bizyaev, S. N. (2009). *J. Phys. Chem. B*, **113**, 5262–5272.
- [4] Minkov, V. S., Goryainov, S. V., Boldyreva, E. V., Görbitz, C. H. (2010). *J. Raman Spectrosc.*, **41**, 1748–1758.
- [5] Minkov, V. S., Tumanov, N. A., Boldyreva, E. V., Cabrera, R. Q. (2010). *CrystEngComm*, **12**, 2551–2560.
- [6] Bordallo, H. N., Boldyreva, E. V., Fischer, J., Koza, M. M., Seydel, T., Minkov, V. S., Drebushchak, V. A., Kyriakopoulos, A. (2010). *Biophys. Chem.*, **148**, 34–41.

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