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The Influence of the Spin Crossover on the Crystal Structure of the [Fe$_3$(hyetrz)$_6$(H$_2$O)$_6$](CF$_3$SO$_3$)$_6$ Complex Compound

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[Fe$_3$(hyetrz)$_6$(H$_2$O)$_6$](CF$_3$SO$_3$)$_6$ (where hyetrz = 4-(2'-hydroxyethyl)-1,2,4-triazole) is an interesting linear, trinuclear iron(II) compound with incomplete spin crossover. We reinvestigated crystal structure of this compound in the wide temperature range because the knowledge only about the crystal structure in the initial and final phases is not sufficient to establish correlations between the structural and magnetic properties of the spin crossover system. The complex [Zn$_3$(hyetrz)$_6$(H$_2$O)$_6$](CF$_3$SO$_3$)$_6$ was used for comparison because it does not exhibit spin crossover phenomenon and it is isostructural with a high spin phase of Fe(II).

1. Introduction

The spin crossover (SCO) in iron(II) systems brings a lot of attention due to the possibility of switching between high (HS, $S = 2$) and low (LS, $S = 0$) spin state using different stimuli like temperature, pressure, alternating magnetic field or light. The SCO phenomenon is usually accompanied by change of other properties like magnetic, optical, structural, dielectric, etc. In particular, it is connected with the step change of the Fe-ligand bond lengths. During incomplete SCO only some part of the Fe(II) changes its spin state. The structural distortions caused by the modification of structural parameters of chromophore FeN$_6$ propagates further, changing also the second coordination sphere. The spread of the deformation on the whole crystal leads to the appearance of the cooperative effects, including structural bistability, which is a basis for the potential applications in molecular electronics [1].

Till now the multitemperature studies for the trinuclear iron(II) compounds with incomplete SCO were not performed. Such research will increase the understanding of propagation processes of the structural distortion and as a result allow to rationally design new materials.

2. Experimental

Single crystals of [Fe$_3$(hyetrz)$_6$(H$_2$O)$_6$](CF$_3$SO$_3$)$_6$ and the isostructural complex with Zn were obtained as it was previously described by Garcia et al. [2]. The structural measurements for both compounds were performed using the four circle X-ray Xcalibur diffractometer (Oxford Diffraction) and Oxford Cryosystem low temperature cooler in the range 100–320 K for 12 temperatures. CCDC 1445224–1445247 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

3. Results and discussion

Complex [Fe$_3$(hyetrz)$_6$(H$_2$O)$_6$](CF$_3$SO$_3$)$_6$ and the isostructural compound with Zn crystallize in the trigonal crystal system. The $R\bar{3}$ space group does not change

with the change of temperature. It also remains unchanged during the SCO which occurs for the Fe(II) complex. It is in accordance to the previous work [2]. Figure 1 presents the molecule of the title compound with numbering scheme.
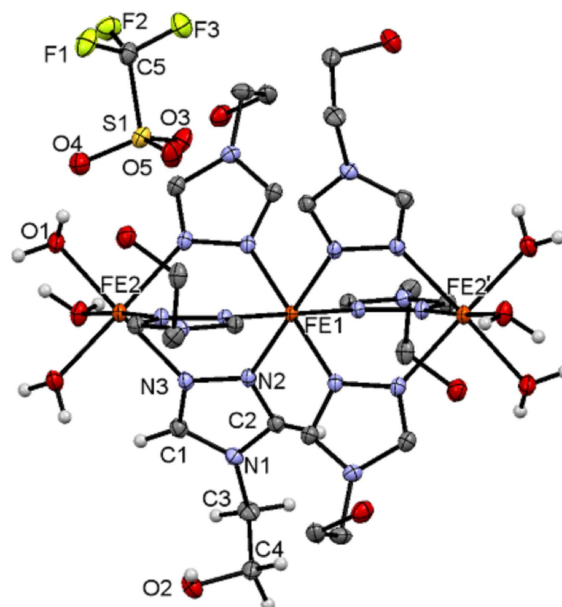

Fig. 1. The molecule of the compound [Fe$_3$(hyetrz)$_6$(H$_2$O)$_6$](CF$_3$SO$_3$)$_6$ at 100 K with 50% probability displacement ellipsoids. For the sake of clarity only the H atoms from the asymmetric unit are shown.

In the studied Fe(II) complex compound only the central Fe(II) ion changes its spin state thus the SCO causes changes in the first coordination sphere of the central Fe1 ion (Fig. 2). Therefore there has been observed only significant change of the Fe1–N2 bond length (about 0.16 Å) with decreasing temperature. Such change leads also to the significant change of the volume of the Fe1N$_6$ chromophore (Fig. 2). The crystal structure of the Zn(II) complex in all temperatures is similar to the HS form of

the Fe(II) compound. The intramolecular bond lengths and the volume of the octahedrons ZnL_6 (L = N, O) for the Zn(II) complex do not change with temperature (Fig. 2).
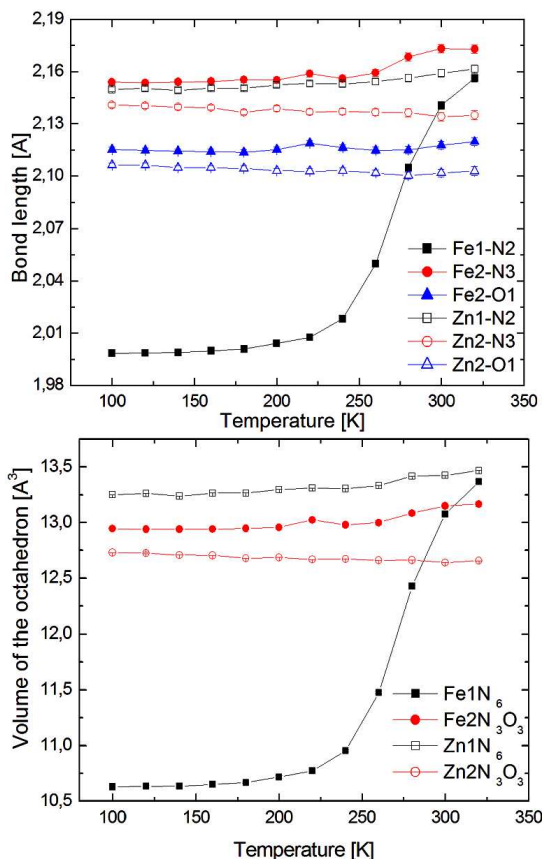

Fig. 2. The temperature dependence of the bond length (upper) and volume of the octahedrons (lower) for the complexes $[M_3(hyetrz)_6(H_2O)_6](CF_3SO_3)_6$, where M = Fe, Zn. The error bars are within symbol size.
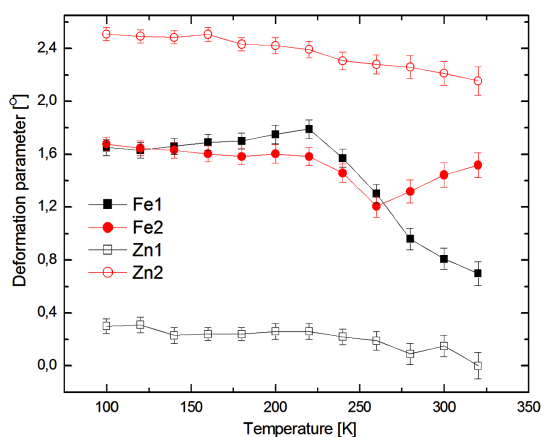
Fig. 3. The temperature dependence of the deformation parameter Σ for the complexes $[M_3(hyetrz)_6(H_2O)_6](CF_3SO_3)_6$, where M = Fe, Zn.

Apart from the changes of the bond length and volume of the octahedron during SCO there has been also observed the distortion of the FeL_6 (where L = N, O) octahedra. It is visible as the change of the L–Fe–L angles (Fig. 3). Such distortion can be described using Σ parameter [3]. It is equal to the sum of the deviation from $90°$ of twelve L–Fe–L angles in the octahedron FeL_6:

$$\Sigma = \sum_{i=1}^{12} (|\phi_i - 90|). \tag{1}$$

For a perfect octahedron the value of Σ parameter is equal to 0. The more distorted the octahedron, the greater value of this parameter. There is no dependence between Σ parameter and Fe–L bond length. Therefore these two parameters are complementary in the analysis of the structural modifications which are caused by SCO.

The spin transition in the central octahedron $Fe1L_6$ also causes the partial deformations of the $Fe2L_6$ octahedra (Fig. 3). It has not been observed for the volumes of these octahedra (Fig. 2).

Interestingly, the changes in the coordination sphere of the central Fe1(II) ion also cause change of the distance to the other Fe2(II) ions (Fig. 4). It reflects the temperature dependence of the $\chi_M(T)$ [2].
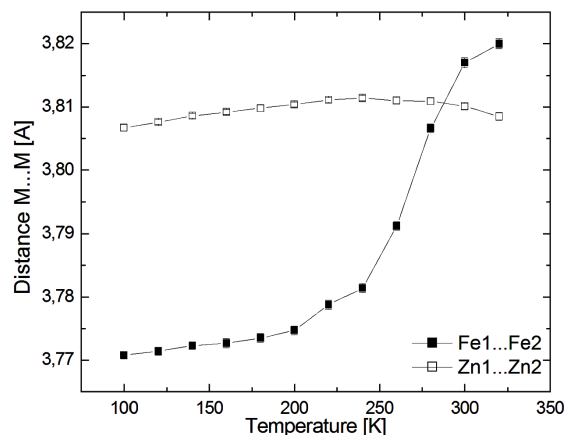

Fig. 4. The temperature dependence of the distances between coordination centers for the complexes $[M_3(hyetrz)_6 (H_2O)_6](CF_3SO_3)_6$, where M = Fe, Zn. The error bars are within symbol size.

All water molecules in Fe(II) and Zn(II) complexes are coordinated to the peripheral central ions and they take part in the hydrogen bonding. The distances of such bonds for Fe(II) and Zn(II) complexes are within 2.65–2.85 Åand they do not vary between each other. It means that the SCO does not have a significant influence on the hydrogen bonding.

4. Conclusions

The multitemperature detailed inspection of the diffraction data provides that only one of the three Fe(II) ions in the studied molecule exhibit SCO which

is in accordance with previous magnetic measurements. The bond lengths of the central Fe1 ion and the volume of the octahedron Fe1N$_6$ reflect the temperature dependence of the $\chi_M(T)$ [2]. The peripheral Fe2 ions in this linear, trinuclear compound which are also surrounded by three water molecules do not change their bond lengths and the volumes of the octahedrons with the change of temperature.

Performed studies confirmed that [Fe$_3$(hyetrz)$_6$ (H$_2$O)$_6$](CF$_3$SO$_3$)$_6$ complex does not reveal structural phase transition. It is described by trigonal $R\bar{3}$ space group in the whole temperature range. The changes of the bond length between Fe(II) ion and ligands show that the spin transition is complete for the central metal ion. The other two, peripheral Fe(II) ions in this complex do not undergo spin crossover. It is worth to note that the changes of the volume of the central octahedron and the distances between coordination centers exactly reflect the SCO curve as it was shown for the first time for the [Fe(ptz$_6$)](BF$_4$)$_2$ complex [4, 5].

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