Two stages in one step spin crossover in $[Fe(bbtr)_3](CF_3SO_3)_2$

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Spin crossover occurs in octahedral coordination compounds of the $3d^4$-$3d^7$ electronic configuration of metal ions. The most spectacular changes are observed in Fe(II) complexes, where the HS→LS (HS – high spin, LS – low spin) transition is associated with shortening of Fe-N distance at about 0.2 Å. Although an ability to change of spin state is an intrinsic feature of the metal ion, the spin crossover properties of bulky, crystalline samples depend on the crystal structure of the coordination compound. Thus, different compositions of first coordination spheres of metal ions or presence in the crystal lattice crystallography unique molecules can result in the complex course of $\gamma_{HS}(T)$ dependence ($\gamma_{HS}(T)$ – the molecular ratio of molecules in HS form). Most often, a two-step spin crossover can be observed in such a situation. Our studies on iron(II) coordination polymers based on 1,4-di(1,2,3-triazol-1-yl)butane (bbtr) and its derivatives revealed a variety of spin crossover behaviours. $[Fe(bbtr)_3](ClO_4)_2$ exhibits abrupt spin crossover accompanied by hysteresis loop ($T_{1/2}^{\downarrow}$ = 112 K, $T_{1/2}^{\uparrow}$ = 141 K)[1]. Importantly spin crossover in this complex is accompanied by structural phase transition P-3→P-1 depending on the shift of neighbouring polymeric layers. The structural phase transition has not been found in the tetrafluoroborate analogue, and the complex $[Fe(bbtr)_3](BF_4)_2$ remains in the HS form in the range 10-300 K[2]. The importance of structural changes on spin crossover properties showed our further studies using bbtr derivatives. An application of 1,4-di(5-ethyl-1,2,3-triazol-1-yl)butane (ebbtr) leads to the formation of two-dimensional coordination polymers exhibiting unique spin crossover: "double"[3] and "normal and reverse"[4] transitions. The occurrence of uncommon spin transitions in these complexes is associated with significant structural changes. An application of regioisomeric ligand bbtre leads to forming a three-dimensional coordination network in which the multi-way spin crossover is strongly related to conformational changes of the bridging ligands[5].

Studies of bbtr-based coordination polymers revealed the importance of counterion. Therefore, we have expanded our studies on the application of triflate derivatives. Synthesis performed between $Fe(CF_3SO_3)_2 \cdot 6H_2O$ and bbtr leads to forming a two-dimensional coordination polymer. The complex crystallizes in R-3 space group. The characteristic feature is the ordering of the half of bbtr bridging molecules and the presence of two crystallographically unique Fe(II) ions. Spin crossover is gradual and complete. Careful analysis of change of Fe-N distances revealed interesting phenomena. Namely, despite one-step spin crossover, both crystallographically unique Fe(II) ions change the spin state in different temperature ranges. Moreover, we have established the occurrence of very slow structural phase transition R-3→ $P6_3$. This structural transformation is associated with the vanishing of ligand disorder. Details concerning crystal structures of complexes before and after R-3→ $P6_3$ transformations on the poster.

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