Poster

X-ray diffraction study of bis(tetrazolyl)alkane-based Fe(II) coordination polymers

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Reactions between 1,2-di(tetrazol-2-yl)ethane (ebtz), 1,6-di(tetrazol-2-yl)hexane (hbtz) or 1,1'-di(tetrazol-1-yl)methane (1ditz) and $Fe(BF_4)_2$ in presence of adiponitrile (AND), glutaronitrile (GLN) or suberonitrile (SUN) resulted in the formation of coordination polymers $[Fe(\mu\text{-ebtz})_2(\mu\text{-ADN})](BF_4)_2$ (**1**), $[Fe(\mu\text{-hbtz})_2(\mu\text{-ADN})](BF_4)_2$ (**2**), $[Fe(\mu\text{-1ditz})_2(GLN)_2](BF_4)_2\cdot GLN$ (**3**) and $[Fe(\mu\text{-1ditz})_2(\mu\text{- SUN})](BF_4)_2\cdot SUN$ (**4**). The intentional selection of bis(tetrazoles) and dinitriles as building blocks has led, as expected, to obtaining systems with the structure of the first coordination sphere consisting of four tetrazole rings and two axially coordinated nitrile molecules. It created the conditions required for the occurrence of thermally induced spin crossover.

Magnetic measurements and single crystal X-ray diffraction studies were used for the characterization of spin crossover properties of **1**–**4** [1]. The complexes exhibited diverse properties. The $\chi_M T(T)$ dependence in **1** indicated gradual and incomplete spin crossover. In **2** and **4**, quite abrupt and complete spin crossover occurred. In **3**, however, the spin crossover was incomplete and $\chi_M T(T)$ dependence was irregular. It was established that each of the four crystallographically independent Fe(II) ions in **3** changed the spin state in different temperature ranges and the completeness of spin crossover at 80 K for each Fe(II) ion was also different. The tendency to shift the spin crossover temperature to the higher values with an increase of Fe-N-C(nitrile) angle can be addressed as a dominant effect for Fe(II) ions occupying Fe2 and Fe4 sites. Whereas in the case of the second pair i.e. Fe1 and Fe3 simple dependence seemed to be disturbed by differentiation of intermolecular interactions of coordinated nitriles linked with Fe(II) ions occupying these sites [1].

Both 1- and 2-substituted tetrazoles may be a convenient building component allowing for the control of the structure of the coordination compound. 1D and 2D polymeric subunits based on 1,2-di(tetrazol-2-yl)ethane (ebtz) and 1,6-di(tetrazol-2-yl)hexane (hbtz), can serve as “polymeric tectons” enabling the manipulation of the structure of coordination networks. The use of ebtz or hbtz molecules, known for creating 1D or 2D coordination polymers in the presence of mononitriles, leads to an increase of the dimensionality of networks to 2D and 3D, respectively, when using adiponitrile (AND) as a coligand. Ebtz and hbtz based “polymeric tectons” also show stability in relation to neutral dinitrile coligands.

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