How nonequivalency of the flexibility of the ligand bridges leads to anisotropy of perturbation transmission in a 3D spin-crossover coordination network.

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Rok wydania

2013

Czasopismo

European Journal of Inorganic Chemistry

Strony

875-883

DOI

10.1002/ejic.201200645

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The role of the covalent connections of iron(II) spin-crossover centres in the transmission of perturbation produced by the HS ↔ LS transition has been investigated for the new 3D coordination polymer $\{[Fe(qbtr)_3](ClO_4)_2\}_\infty$ [qbtr = 1,5-di(1,2,3-triazol-1-yl)pentane]. In this complex, a sequence of structural phase transitions occurs. A Ph1 (HS,HS) → Ph2 (HS,HS,HS) transition precedes spin crossover and is associated with an increased number of crystallographically unique iron(II) ions, whereas the change of spin state Ph2 (HS,HS,HS) → Ph3 (HS,LS) triggers another structural phase transition accompanied by a reduction in the number of the unique iron(II) sites. Iron(II) ions occupying two crystallographically unique Fe1 and Fe2 sites form the nodes of a coordination network in the Ph1 phase. The characteristic feature of the polymeric skeleton is the presence of three kinds of ligand bridges tethering the Fe1···Fe1, Fe1···Fe2 and Fe2···Fe2 sites. The ligand linkages differ from each other in rigidity, and the diversification of their properties arises from the susceptibility of the ligand molecules to undergo conformational changes. The high rigidity of the bridge established in the Ph2 phase between iron(II) ions occupying Fe2 sites allows for the propagation of the perturbation produced by the HS (Fe2) → LS (Fe2) transition through the crystal lattice. A strong compression along the Fe2···Fe2 bridging direction occurs. In contrast, the ligand molecules that form the two remaining types of bridge are disordered in the Ph2 phase and the change of spin state for the iron(II) ions occupying Fe2 sites induces their ordering, which leads to an increase in the separation between donor atoms. In effect, perturbation cannot be effectively transmitted along the Fe1···Fe1 and Fe1···Fe2 linkage directions because the “elongation” of conformationally labile ligand molecules compensates for the shortening of the Fe2–N bond lengths.

Słowa kluczowe

Iron, N ligands, conformational analysis, Spin crossover, coordination network, symmetry breaking

Adres publiczny

http://dx.doi.org/10.1002/ejic.201200645

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