On the role of intermolecular interactions on structural and spin-crossover properties of 2D coordination networks $[Fe(bbtr)_3]A_2$ (bbtr = 1,4-bis(1,2,3-triazol-1-yl)butane; A = ClO_4^-, BF_4^-).

Autorzy

Joachim Kusz

Robert Bronisz

Maciej Zubko

G. Bednarek

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Streszczenie

A series of complexes [M(bbtr)(3)]A(2) (M=Fe(II), Zn(II); bbtr=1,4-bis(1,2,3-triazol-1-yl)butane; A=ClO(4)(-), BF(4)(-)) and [Fe(x)Zn(1-x)(bbtr)(3)](ClO(4))(2) (0<x<1) dilute systems was synthesized and characterized. Earlier studies on [Fe(bbtr)(3)](ClO(4))(2) (1·ClO(4)), which crystallizes in space group P3, revealed an abrupt spin transition with T(1/2)↓ ≈101 K and T(1/2)↑ ≈109 K. Variable-temperature measurements of the lattice parameters and change in Bragg peaks profiles of 1·ClO(4) showed a structural phase transition at 125 K leading to space group P1. Single-crystal X-ray diffraction studies allowed structures of the quenched high-spin phase and then a low-symmetry low-spin phase of 1·ClO(4) to be determined. We established that tetrafluoroborate analogue 1·BF(4) remains in the high-spin form in the temperature range 5-300 K. Contrary to 1·ClO(4), structural investigations did not reveal the presence of a structural phase transition in 1·BF(4). Analogous to 1·ClO(4), [Zn(bbtr)(3)](ClO(4))(2) (2·ClO(4)) undergoes a structural transition at 151 K, whereas at low-temperature [Zn(bbtr)(3)](BF(4))(2) (2·BF(4)) remains in space group P3. The structural phase transitions in both perchlorates are accompanied by similar reorganization of the intermolecular contacts, which leads to a shift of 2D layers. In effect, compression of the unit cell takes place, favouring the appearance of the spin transition in 1·ClO(4) in relation to 1·BF(4). The metal ion determines the temperature of the structural phase transition in 1·ClO(4) and 2·ClO(4). This property was exploited to separate the non-magnetic structural transformation and spin transition in 1·ClO(4). The spin and structural transitions in the [Fe(x)Zn(1-x)(bbtr)(3)](ClO(4))(2) systems take place at different temperatures, and the temperature difference between them increases with increasing zinc(II) content. This means that structural phase transition is necessary for appearance of the spin transition, but this transformation does not trigger directly the spin transition in 1·ClO(4).

Słowa kluczowe

magnetic properties, Iron, N ligands, phase transition, Spin crossover