

On the role of intermolecular interactions on structural and spin-crossover properties of 2D coordination networks $[\text{Fe}(\text{bbtr})_3]\text{A}_2$ (bbtr = 1,4-bis(1,2,3-triazol-1-yl)butane; A = ClO_4^- , BF_4^-).

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Rok wydania

2011

Czasopismo

Chemistry-A European
Journal

Numer woluminu

17

Strony

6807-6820

DOI

10.1002/chem.201100394

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

A series of complexes $[M(\text{bbtr})(3)]A(2)$ ($M=\text{Fe(II)}$, Zn(II) ; $\text{bbtr}=1,4\text{-bis}(1,2,3\text{-triazol-1-yl})\text{butane}$; $A=\text{ClO}(4)(-)$, $\text{BF}(4)(-)$) and $[\text{Fe}(x)\text{Zn}(1-x)(\text{bbtr})(3)](\text{ClO}(4))(2)$ ($0 < x < 1$) dilute systems was synthesized and characterized. Earlier studies on $[\text{Fe}(\text{bbtr})(3)](\text{ClO}(4))(2)$ ($1 \cdot \text{ClO}(4)$), which crystallizes in space group $P3$, revealed an abrupt spin transition with $T(1/2)_{\downarrow} \approx 101$ K and $T(1/2)_{\uparrow} \approx 109$ K. Variable-temperature measurements of the lattice parameters and change in Bragg peaks profiles of $1 \cdot \text{ClO}(4)$ 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 $1 \cdot \text{ClO}(4)$ to be determined. We established that tetrafluoroborate analogue $1 \cdot \text{BF}(4)$ remains in the high-spin form in the temperature range 5-300 K. Contrary to $1 \cdot \text{ClO}(4)$, structural investigations did not reveal the presence of a structural phase transition in $1 \cdot \text{BF}(4)$. Analogous to $1 \cdot \text{ClO}(4)$, $[\text{Zn}(\text{bbtr})(3)](\text{ClO}(4))(2)$ ($2 \cdot \text{ClO}(4)$) undergoes a structural transition at 151 K, whereas at low-temperature $[\text{Zn}(\text{bbtr})(3)](\text{BF}(4))(2)$ ($2 \cdot \text{BF}(4)$) 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 $1 \cdot \text{ClO}(4)$ in relation to $1 \cdot \text{BF}(4)$. The metal ion determines the temperature of the structural phase transition in $1 \cdot \text{ClO}(4)$ and $2 \cdot \text{ClO}(4)$. This property was exploited to separate the non-magnetic structural transformation and spin transition in $1 \cdot \text{ClO}(4)$. The spin and structural transitions in the $[\text{Fe}(x)\text{Zn}(1-x)(\text{bbtr})(3)](\text{ClO}(4))(2)$ 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 $1 \cdot \text{ClO}(4)$.

Słowa kluczowe

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

Adres publiczny

<http://dx.doi.org/10.1002/chem.201100394>

Strona internetowa wydawcy

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Plik został wygenerowany dnia 2026-06-29 09:38:39

Adres w repozytorium https://old.chem.uni.wroc.pl/pl/repozytorium/2_meC-3.