

Extremely Slow Thermally-Induced Spin Crossover in the Two-Dimensional Network [Fe(bbtr)₃](BF₄)₂

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Rok wydania

2024

Czasopismo

Chemistry-A European
Journal

Numer woluminu

30

Strony

e202302887/1-
e202302887/14

DOI

10.1002/chem.202302887

Kolekcja

Naukowa

Język

Angielski

Streszczenie

Cooling [Fe(bbtr)₃](BF₄)₂ (bbtr=1,4-di(1,2,3-triazol-1-yl)butane) triggers very slow spin crossover below 80 K ($T_{1/2}^{\downarrow}=76$ K). The spin crossover (SCO) is accompanied by a hysteresis loop ($T_{1/2}^{\uparrow}=89$ K). In contrast to isostructural perchlorate analogue [Fe(bbtr)₃](ClO₄)₂ in which spin crossover during cooling is preceded by phase transition at $T_{PT}=126$ K in tetrafluoroborate phase transition does not occur to the beginning of spin crossover (80 K). Studies of mixed crystals [Fe(bbtr)₃](BF₄)_{2(1-x)}(ClO₄)_{2x} (0.5≤x≤0.9) showed that a phase transition precedes spin crossover, however, for x≅0.46 intersection of $T_{1/2}(x)$ and $T_{PT}(x)$ dependencies takes place. The application of pressure of 1 GPa shifts the spin crossover in [Fe(bbtr)₃](BF₄)₂ to a temperature above 270 K. High-pressure studies of neat tetrafluoroborate and perchlorate, as well as mixed crystals [Fe(bbtr)₃](BF₄)_{2(1-x)}(ClO₄)_{2x} (0.1≤x≤0.9), revealed that at 295 K $P_{1/2}$ value changes linearly with x indicating similar mechanism of spin crossover under elevated pressure in all systems under investigation. Variable pressure single crystal X-ray diffraction studies confirmed that in contrast to thermally induced spin crossover undergoing differently in tetrafluoroborate and perchlorate an application of high pressure removes this differentiation leading to a similar mechanism depending at first on start spin crossover and then P-3→P-1 phase transition occurs. In this report we have shown that 2D coordination polymer [Fe(bbtr)₃](BF₄)₂ (bbtr=1,4-di(1,2,3-triazol-1-yl)butane) treated to date as spin crossover silent shows thermally induced spin crossover phenomenon. Spin crossover in tetrafluoroborate is extremely slow. Determination of the spin crossover curve required carrying measurement in the settle mode-cooling from 85 to 70 K took about 600 h (average velocity of change of temperature ca. 0.0004 K/min).

Typ publikacji

Artykuł

Słowa kluczowe

coordination polymers, high pressure studies, phase transition, spin crossover, 1,2,3-triazole

Adres publiczny

<http://dx.doi.org/10.1002/chem.202302887>

Strona internetowa wydawcy

onlinelibrary.wiley.com

Plik został wygenerowany dnia 2026-08-24 03:25:54

Adres w repozytorium <https://old.chem.uni.wroc.pl/pl/repozytorium/e4VHGB9>.