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Spin-crossover in the complex of iron(II) nitrate with tris(3,5-dimethylpyrazol-1-yl)methane

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ABSTRACT

Novel coordination compound $[Fe(HC(3,5\text{-}Mepz)_3)_2](NO_3)_2$ is obtained by a reaction of $Fe(NO_3)_2$ with tris(3,5-dimethylpyrazol-1-yl)methane. The compound is characterized with magnetic susceptibility method, electronic (diffuse reflection) and IR spectroscopy and powder diffraction. According to temperature dependence $\mu_{eff}(T)$ the compound possesses spin-crossover $^1A_1 \Leftrightarrow {}^5T_2$ with hysteresis ($T_c\uparrow = 231$, $T_c\downarrow = 227$ K) accompanied by thermochromism (pink ⇔ colorless). A crystal structure of the compound was determined just before ($T = 240$ K, Fe^{HS}–N 2.14–2.18 Å) and after ($T = 123$ K, Fe^{LS}–N 1.97–1.99 Å) spin phase transition.

1. Introduction

Last years a close attention has been focused on octahedral complexes of 3d metals with d^4–d^7 electronic configuration and specific ligand field that possess spin-crossover (SCO) in the crystalline state [1–9]. Search for new compounds that can exist both in high- (HS) and low- (LS) spin state with a lasting lifetime is important either for the further development of spin transition theory, or for various applications in molecular-based materials (e.g., triggers in electronic devices such as displays), in data recording technology [6,10,11]. Spin multiplicity is known to be changed under external conditions like temperature, pressure or light irradiation of a certain wavelength.

Complexes of iron(II) with poly-nitrogen heterocyclic ligands, and particularly 1,2,4-triazoles, are of special interest owing to thermochromism that accompanies SCO [5–9]. This property expands the use of iron(II) complexes to temperature sensors or hardware components [6]. Previously we synthesized and characterized iron(II) complexes with 1,2,4-triazoles [5,12–14], most of which demonstrate $^1A_1 \Leftrightarrow {}^5T_2$ SCO accompanied by thermochromism (pink ⇔ colorless).

Tris(pyrazol-1-yl)methane (**HC(pz)$_3$**) and its derivatives are another perspective class of nitrogen-containing ligands for synthesis of new iron(II) complexes possessing SCO [15–17]. In 1970, these ligands were first shown to coordinate iron(II) mostly in tridentate-cyclic manner using three N^2 atoms of pyrazole rings [15]. Thereafter, a full magnetochemical investigation was carried out only for $[Fe\{HC(pz)_3\}_2](BF_4)_2$ [16] that revealed gradual SCO at relatively high temperature ~470 K. We prepared series of compounds with common formula $[Fe\{HC(pz)_3\}_2]A_2{\cdot}nH_2O$, $A = Cl^-$, Br^-, I^-, $½SO_4^{2-}$, $n = 0$–7 [17] and showed them all possessing high temperature SCO without hysteresis on $\mu_{eff}(T)$ curves. Depending on the nature of anion the temperature of SCO (T_c) varies from 400 to 445 K.

Thorough investigation of a new compound that possesses SCO requires a combination of magnetic and structural study of both HS and LS modification (see Supporting information). The latter faces various problems [18–23]. First of all, a single crystal must chemically and structurally fit the bulky product. Chemical fit makes problem when so-called solvatomorphs (or pseudopolymorphs) appear [18]. Structural fit can be broken by polymorphism, since different (pseudo)polymorphs can possess different SCO characteristics, as in the case of $Fe\{HC(3,5\text{-}Me_2pz)_3\}\{HC(pz)_3\}](BF_4)_2$ [19,20]. Even if these problems have been overcome, the structural investigation of the single crystal at different temperatures is still a challenge. The structural changes during SCO lead often to an internal stress and cracking of the single crystal, which in most cases twins or even shatters. Note that thermo-induced SCO of complex Fe(II) with $HC(pz)_3$ [16,17], occurs at high

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temperatures, while modern single crystal diffractometers are usually equipped with low temperature devices that cannot provide temperature above 100 °C. Moreover, in many cases grinding of the sample can seriously affect the SCO characteristics [21,22]. For this reason a crystal structure made from powder diffraction might not reveal structural changes during SCO. Thus, it is not surprising that there are only two iron(II) complexes with $HC(3,5\text{-}Me_2pz)_3$ ligand for which both HS and LS forms were structurally investigated with a single crystal [23] (see below). Here we report synthesis, single crystal X-ray diffraction and magnetochemical study for $[Fe(HC(3,5\text{-}Me_2pz)_3)_2](NO_3)_2$ (**1**), where $HC(3,5\text{-}Me_2pz)_3$ = tris(3,5-dimethylpyrazol-1-yl)methane.

2. Experimental

2.1. Physical measurements

2.1.1. Elemental analysis

Elemental analysis was performed at the analytical laboratory of the Institute of Inorganic Chemistry, Siberian Division of the RAS on EURO EA 3000 instrument (Euro Vector, Italy). The metal in the complexes was quantified by trilon titration after sample digestion in a mixture of concentrated H_2SO_4 and $HClO_4$ (1:2) with heating.

2.1.2. Spectroscopy

IR spectrum of **1** was recorded on Scimitar FTS 2000 spectrometer in the range of 400–4000 cm^{-1} at resolution 4 cm^{-1}. The samples were prepared as mineral and fluorinated oil mulls. The diffuse reflectance spectrum was measured on a UV-3101 PC Shimadzu scanning spectrometer at room temperature.

2.2. Synthesis

For synthesis, we used $FeSO_4 \cdot 7H_2O$ (‘p’ grade), freshly re-crystallized from acidic water solution, ascorbic acid (medical grade). $Ba(NO_3)_2$ was of commercial quality and used as purchased. Tris(3,5-dimethylpyrazol-1-yl)methane is prepared according to slightly developed technique [24].

2.2.1. $[Fe\{HC(3,5\text{-}Me_2pz)_3\}_2](NO_3)_2$ (**1**)

$FeSO_4 \cdot 7H_2O$ (0.56 g, 2 mmol) and ascorbic acid (0.2 g) was dissolved at heating in 5 mL of water with 1 drop of concentrated HNO_3. Ascorbic acid was used as an oxidation inhibitor of Fe(II) and soft acidifying agent. $Ba(NO_3)_2$ (0.52 g, 2 mmol) was dissolved at heating in water (5–7 mL) and then was added with stirring to hot solution of $FeSO_4$. Precipitate of $BaSO_4$ was filtered out. $HC(3,5\text{-}Me_2pz)_3$ (1.79 g, 6 mmol) was dissolved at heating on a water bath in acetone (10 mL). The resulted solution was quickly added to hot solution of $Fe(NO_3)_2$. Resulted brown solution was boiled down to minimal volume on a water bath, cooled under ice and then cold acetone (5 mL) was added. Resulted colorless precipitate was filtered out, washed twice with acetone and then dried on air (0.44 g, 28%). Elemental analysis (in %) Calc. for $C_{32}H_{44}FeN_{14}O_6$ (776.66): C, 49.5; H, 5.7; N, 22.5; Fe, 7.2. Found: C, 49.4; H, 5.8; N, 24.4; Fe, 7.3.

2.3. Magnetic susceptibility measurements

The static magnetic susceptibility of polycrystalline sample was measured by a Faraday method in the temperature range of 78–300 K at an external magnetic field strength of up to 5 kOe. The effective magnetic moments were calculated as $\mu_{\text{eff}} = (8\chi'_{\text{M}})^{1/2}$, where χ'_{M} is the molar magnetic susceptibility corrected for diamagnetism. The heating (cooling) rate in the field of spin-crossover was 0.5 K/min.

2.4. Crystal structure determination

Single crystals of **1** were prepared by slow evaporation of ethanol solution. Crystal structure of $\mathbf{1^{HS}}$ and $\mathbf{1^{LS}}$ were obtained from different single crystals (Table 1S). Crystal structure of $\mathbf{1^{HS}}$ was measured at 240 K at *Bruker X8 Apex* (Mo Kα, graphite monochromator, combined ω- and φ-scans of 0.5° frames). Semi-empirical absorption corrections from equivalents were applied [25]. Structure was solved by direct methods and refined by full-matrix least-squares method using SHELX program set [26].

When cooled down, the single crystal cracked right after the color change form colorless to pink. Our attempts to define twin components using CELL_NOW program from *Bruker X8 Apex* software package [25] failed. Since quite big crystals cannot overcome magnetic phase transition due to high strain, and smaller crystals showed too weak diffraction pattern for the measurement, we found an opportunity to measure small crystal using *Oxford Diffraction Gemini R Ultra* equipped with intensive Cu Kα Enhance Ultra X-ray source. In the case of twinning using Cu Kα radiation with bigger weave length would give a chance at least to separate the twin components on extended diffraction pattern. Thus, crystal structure of $\mathbf{1^{LS}}$ was studied from smaller single crystal that luckily survived during the phase transition followed by cooling down to T = 123 K. Before low temperature measurement we checked the unit cell and quality of crystal at 237 K and found the cell constants to be similar to $\mathbf{1^{HS}}$ measured previously. After slow (~1.5°/min) cooling to 123 K we found no traces of twinning on diffraction pattern. Structure of $\mathbf{1^{LS}}$ was refined using starting model for cation in $\mathbf{1^{HS}}$. Semi-empirical absorption corrections from equivalents (multi-scan) were applied [27]. Hydrogen atoms in both cases were refined in rigid body approximation. Anion that was disordered in $\mathbf{1^{HS}}$ over three positions with 0.41/0.26/0.33 occupation factors appeared to be ordered in $\mathbf{1^{LS}}$.

Topological motifs of cationic packing were analyzed with TOPOS 4.0 Professional program suit for crystal chemical analysis [28] as described in Refs. [29,30].

2.4.1. X-ray powder diffraction analysis

Powder diffraction pattern was recorded on Philips PW1700 diffractometer using graphite monochromated Cu Kα radiation ($\theta/2\theta$-scan in 2θ range of 3–30°, 0.03° steps, 10 s/step) with Si as external standard. Theoretical pattern was calculated from $\mathbf{1^{HS}}$ single crystal data using Mercury 2.4 program [31].

3. Results and discussion

Compound **1** was isolated from water–acetone solution upon the reaction of freshly prepared iron(II) nitrate and $HC(3,5\text{-}Me_2pz)_3$ in 1:2 or 1:3 molar ratio. Excess of the ligand resulted in higher yield. At room temperature the compound is colorless that points to HS state of Fe^{2+}. Analytical data agree with the formula $[Fe(HC(3,5\text{-}Me_2pz)_3)_2](NO_3)_2$ established by X-ray structural analysis. Powder diffraction data (Fig. 2 in Supporting information) are in good agreement with calculated from crystal structure.

According to X-ray diffraction data, **1** is an ionic complex compound. $HC(3,5\text{-}Me_2pz)_3$ ligand is coordinated to Fe(II) atom in tridentate-cyclic manner resulting in $[Fe(HC(3,5\text{-}Me_2pz)_3)_2]^{2+}$ cation with three six-membered FeNNCNN chelate rings with two common vertices, Fe(II) ion and methine group (Fig. 1). Nitrate ion is in outer sphere being disordered over three close positions. Ligand-to-metal ratio of 2:1 results in six nitrogen octahedral coordination of Fe^{2+}. Spin state of Fe^{2+} can be revealed either directly from Fe–N distances ($d^{HS} > 2.1$ and $d^{LS} < 2.0$ Å), or integral magnitudes F and Σ showing the degree of distortion for FeN_6 octahedron [32]: