

1,4-Di(1,2,3-triazol-1-yl)butane as Building Block for the Preparation of the Iron(II) Spin-Crossover 2D Coordination Polymer

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The novel bidentate ligand 1,4-di(1,2,3-triazol-1-yl)butane (btr) reacts with $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ to form the 2D coordination polymer with (3,6) network topology. The $\{[\text{Fe}(\text{btr})_3](\text{ClO}_4)_2\}_\infty$ represents an example of spin-crossover material based on 1,2,3-triazole as donor group, and displays an abrupt spin transition accompanied by a thermal hysteresis loop ($T_{1/2}^\downarrow = 101 \text{ K}$ and $T_{1/2}^\uparrow = 109 \text{ K}$).

An advance in investigations of self-assembly processes resulted in synthesis of coordination polymers possessing interesting features originating from the combination of their structure and physicochemical properties of building blocks.¹ An incorporation of the iron(II) spin-crossover (SCO) centers allows changing of the optical, magnetic, and dielectric properties of the compound by the application of external perturbation such as light irradiation, change of temperature, and/or change of pressure.² Hence, such complexes are regarded as potential materials for applications as molecular switches, data displays, memory devices, and intelligent contrast agents.³ The majority of those applications require complexes exhibiting an abrupt SCO accompanied by a hysteresis loop.⁴ One of the methods of preparation of such materials depends on enhancing the cooperativity of the spin transition through the direct connection of the iron(II) SCO centers.⁵ The first experimental result supporting this approach was provided by the 2D SCO complex $[\text{Fe}(\text{btrz})_2-$

$(\text{NCS})_2] \cdot \text{H}_2\text{O}$ (where btrz = 4,4'-bis-1,2,4-triazole).⁶ This conception of increasing efficiency of the information transmission about the structural changes upon the SCO is actually realized by the construction of the spin crossover 1D, 2D, and 3D coordination polymers.⁷

Among the complexes based on bis(polyazoly)alkane ligands^{8–10} there are only a few examples of 1D and 3D iron(II) SCO coordination polymers.¹¹ The strong influence of the polyazole on the architecture and properties of the coordination polymers points to the necessity of exploration of new polyazole based ligands. Presently there is a shortage of structurally characterized complexes of 1-substituted-1,2,3-triazoles. This polyazole ring, possessing the *exo* located nitrogen donor atom N3 and simultaneously more sterically hindered *endo* nitrogen atom N2, can be regarded as the potentially monodentate and nonbridged donor group. Hence, di- and polypodal ligand systems based on the 1,2,3-triazole ring as the donor group should be particularly suitable for

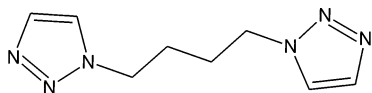
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the preparation of coordination polymers. For the investigation of coordination properties of 1-substituted-1,2,3-triazoles and aiming especially at iron(II) coordination polymers a novel potentially bidentate and nonchelating ligand—1,4-di(1,2,3-triazol-1-yl)butane (Chart 1, bbtr)—was selected and synthesized.

Chart 1



Bbtr, isolated as colorless needles, was obtained in the reaction of sodium 1,2,3-triazolate with 1,4-dichlorobutane.¹² A lack of regioselectivity of alkylation of 1H,2,3-triazole involves a formation of other bistriazoles i.e., 1-(1,2,3-triazol-1-yl)-4-(1,2,3-triazol-2-yl)butane and 1,4-di(1,2,3-triazol-2-yl)butane which leads to the lowering of the bbtr synthesis yield. The coordination properties of bbtr have been studied in the reaction with $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. The synthesis performed in the molar ratio of bbtr/Fe(II) = 3:1 in acetonitrile afforded the complex of formula $\{[\text{Fe}(\text{bbtr})_3](\text{ClO}_4)_2\}_\infty$ (**1**).¹³ **1** crystallizes with 55% yield as colorless, hexagonal plates, stable in air. No formation of other products in such performed syntheses was observed.

X-ray diffraction studies for **1** were carried out for 293(1), 135(1), and 130(1) K.¹⁴ At 293(1) K complex **1** crystallizes in the $P\bar{3}$ space group. The coordination environment of the Fe(II) (which lies on the 3-fold axis) is composed of six 1,2,3-triazole rings with N3 nitrogen donor atoms located at a distance of 2.198(2) Å in the corners of an almost perfect octahedron. The bbtr molecule, which comprises monodentately coordinating 1,2,3-triazole moieties, bridges

- (12) 1,4-Dichlorobutane (0.045 mol, 5.72 g) was added to the sodium 1,2,3-triazolate (0.10 mol, 9.10 g) suspended in MeCN (200 mL) and the obtained reaction mixture was stirred and refluxed for 48 h. Then the precipitated NaCl was filtered off and the MeCN was evaporated under reduced pressure. The resulted yellow oil was extracted with boiling diethyl ether (6 × 25 mL) and next with hot ethyl acetate (6 × 25 mL). The bbtr crystallized during the evaporation of the ethyl acetate and was purified by the recrystallisation from the MeCN/ethyl acetate (10 mL, 1:1, V/V) mixture. Yield 8.4% (0.73 g). Anal. calcd for $\text{C}_8\text{H}_{12}\text{N}_6$: C, 50.0; H, 6.29; N, 43.7. Found: C, 50.0; H, 6.30; N, 43.5%. ¹H NMR (300 MHz, CD_3CN) δ 7.73 (s, 2H), 7.62 (s, 2H), 4.37 (m, 4H), 1.83 (m, 4H) ppm. ¹³C NMR (300 MHz, CD_3CN) δ 134.2, 125.0, 49.8, 27.9 ppm. ESI-MS: m/z 193.0 (LH+).
- (13) Synthesis of **1** was performed under nitrogen atmosphere using standard Schlenk technique. The bbtr (0.12 mmol, 23.1 mg) dissolved in MeCN (2.0 ml) was added to the solution of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.04 mmol, 14.5 mg) in MeCN (1.0 mL) and the resulted clear reaction mixture was left in the closed Schlenk flask. After 24 h the colorless crystals of **1** were filtered off and dried in the nitrogen atmosphere. Yield 18.9 mg (55%). Anal. calcd for $\text{FeC}_{24}\text{H}_{36}\text{N}_{18}\text{Cl}_2\text{O}_8$: C, 34.7; H, 4.36; N, 30.3. Found: C, 34.9; H, 4.28; N, 30.5%.
- (14) Crystal data for **1**: $\text{C}_{24}\text{H}_{36}\text{Cl}_2\text{FeN}_{18}\text{O}_8$, $M_w = 831.46$, trigonal, space group $P\bar{3}$ (no. 147). At 293(1) K: $a = 11.7190(9)$ Å, $c = 7.8041(8)$ Å, $V = 928.2(2)$ Å³, $Z = 1$, $D_{\text{calc}} = 1.487$ g/cm³, $\mu = 0.620$ mm⁻¹, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, 11 859 reflections collected, 1484 independent reflections [$R_{\text{int}} = 0.0494$], $R_1 = 0.0567$, $wR_2 = 0.1048$ (with $I > 2\sigma(I)$). At 130(1) K (heating mode): $a = 11.6562(12)$ Å, $c = 7.7453(9)$ Å, $V = 911.3(2)$ Å³, $Z = 1$, $D_{\text{calc}} = 1.515$ g/cm³, $\mu = 0.632$ mm⁻¹, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, 11 624 reflections collected, 1466 independent reflections [$R_{\text{int}} = 0.1007$], $R_1 = 0.0690$, $wR_2 = 0.1077$ (with $I > 2\sigma(I)$). At 135(1) K (cooling mode, second crystal sample): $a = 11.6138(9)$ Å, $c = 7.7724(10)$ Å, $V = 907.9(2)$ Å³, $Z = 1$, $D_{\text{calc}} = 1.521$ g/cm³, $\mu = 0.634$ mm⁻¹, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, 11 540 reflections collected, 1451 independent reflections [$R_{\text{int}} = 0.0803$], $R_1 = 0.0808$, $wR_2 = 0.1050$ (with $I > 2\sigma(I)$).

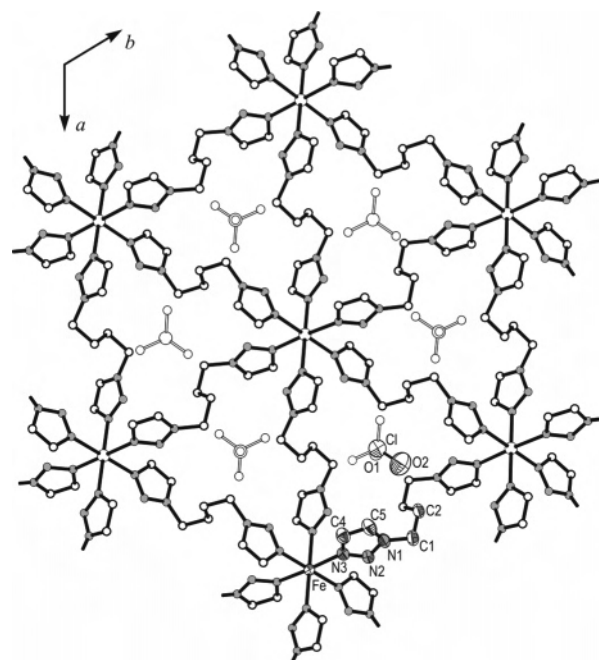


Figure 1. Perspective view of the 2D polymeric layer of **1** along c axis. Thermal ellipsoids are at 50% probability level. Hydrogen atoms were omitted for clarity.

two neighbored metal ions separated at a distance of 11.719(1) Å. Simultaneously each metal atom is linked via bbtr molecules to six other ones gathered in a common plane. This bridging mode is propagated in three directions ([010], [100], and [110]). It leads to formation of 2D polymeric layers with triangular pattern, situated parallel to the crystallographic ab plane (Figure 1). **1** represents the rare example of the coordination polymer with (3,6) network topology.¹⁵ Fe–N3 bonds of adjacent octahedra are oriented in the same directions but they are not collinear. Such a relative orientation of neighbored octahedra excludes the formation of 3D coordination polymers in case of application of linear rigid ligand molecules. In this event, the ligand flexibility enables accommodation to the shift between Fe–N3 bonds (ca. 6.8 Å) of adjacent octahedra. Namely, the location of the inversion center in the middle of the bbtr molecule and the value of the torsion angle N1–C1–C2–C2a of $-61.6(4)^\circ$ involve a *GTG* conformation of the 1,4-butylene spacer. Consequently, trans orientation of triazole rings in the bbtr molecule allows bridging of the neighbored metal centers. Parallel arrangement of the adjacent polymeric layers afforded the formation of the triangular channels. The shortest distance between iron atoms from neighboring polymeric layers is equal to 7.804(1) Å. Noncoordinated perchlorate anions are gathered in the periphery of the polymeric layers *vis-à-vis* the triangular holes. They are arranged in pillars perpendicularly oriented to the polymeric sheets. Anions are engaged in C–H \cdots O(Cl) contacts tethering the 2D polymeric layers.

The characteristic feature of spin-crossover iron(II) complexes is the thermochromic effect observed during the HS–

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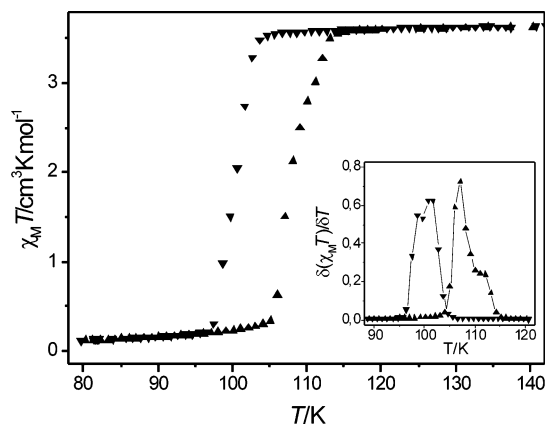


Figure 2. The $\chi_M T$ vs. T plot for **1** in cooling (\blacktriangledown) and warming (\blacktriangle) modes.

($S = 2$) \rightarrow LS($S = 0$) conversion as the result of the spin-allowed $^1A_1 \rightarrow ^1T_1$ d–d transition in the low spin form of the complex.³ In the case of **1** the cooling of the sample is accompanied by a pronounced change of color from white to purple indicating the occurrence of the HS \rightarrow LS transition.

The magnetic susceptibility of the iron(II) complex was determined over the 5–300 K range. The magnetic behavior of **1** is shown in Figure 2 in the form of the $\chi_M T$ vs T dependency (χ_M = molar susceptibility, T = temperature). The $\chi_M T$ equal to 3.60 cm³K/mol at 293 K corresponds to the expected value for the high-spin form of Fe(II). The variable temperature magnetic susceptibility measurement showed that in the range from 293 to 130 K the $\chi_M T$ value remains almost constant, ranging from 3.60 to 3.75 cm³K/mol, respectively. Further lowering of the temperature involves first gradual and then a very abrupt decrease of the $\chi_M T$ value with $T_{1/2}^\dagger$ at 101 K, which confirms the HS \rightarrow LS conversion. In the range of 5 K, i.e., from 102 K (here the molar fraction of high spin form γ_{HS} is equal to 0.85) to 97 K ($\gamma_{HS} = 0.05$) 80% of the spin transition takes place. Below 96 K the $\chi_M T$ decreases more gradually reaching at 75 K the value of ca. 0.09 cm³K/mol which points to the complete spin transition. In the warming mode the abrupt spin transition is centered around $T_{1/2}^\dagger = 109$ K indicating the presence of a thermal hysteresis loop of width 8 K.

The differential scanning calorimetry (DSC) measurement carried out for **1** in the cooling mode showed the presence of one exothermic peak with maximum at 103 K (Figure 3).¹⁶ In the warming mode the endothermic peak positioned at 116 K is accompanied by the poorly resolved second one. This singularity observed in the DSC curve is also reflected in the $\chi_M T$ vs T dependency as the change of the slope of the $\chi_M T$ curve (see insert in Figure 2).

The variable temperature X-ray diffraction investigations of **1** exhibited that lowering of the temperature from 293 to 135 K is accompanied only by the contraction of the lattice parameters. There is no change in the space group ($P\bar{3}$) at these temperatures. Determination of the crystal structure of the high-spin form at 135(1) K did not reveal any significant

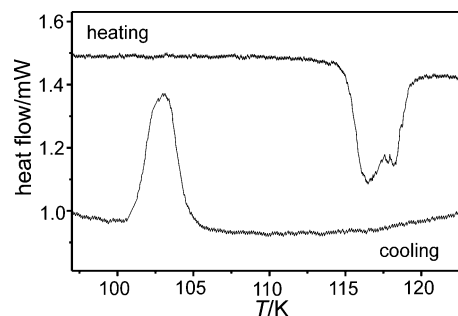


Figure 3. DSC curves for **1** in cooling and heating modes.

differences for Fe(1,2,3-triazole)₆ core, polymeric backbone, and structure of anions in relation to the structure of **1** determined at 293(1) K. The kind and number of contacts were also unchanged. However, below 130 K, it was not possible to evaluate the accurate lattice parameters. Unfortunately, despite many attempts, determination of the low-spin form crystal structure performed at 80(1) K (for several sample crystals of **1**) failed too. After cooling to 80 K the single crystal of **1** was warmed to 130(1) K and then the crystal structure of the high spin form was successfully determined. No differences in the structures of the polymeric network and anions in relation to the crystal structure of the high-spin form determined at 135 K (cooling mode) were observed. Experiments to further explain the structural aspects accompanied by the SCO in **1** are in progress.

In summary, we report on the iron(II) SCO complex based on 1,2,3-triazole ring as donor group. **1** represents the unprecedented example of the 2D SCO coordination polymer composed of the homoleptic surrounded iron(II) centers covalently linked via bidentate ligand molecules. **1** exhibits the abrupt spin transition accompanied by a thermal hysteresis loop. The presented result shows that an application of bis(1,2,3-triazol-1-yl)alkanes significantly expands a possibility of preparation of SCO complexes differing from each other both in their topology and dimensionality but with preservation of the same surrounding of the central atom. Construction of such materials creates the conditions for investigation of the influence of the coordination polymers architecture on the physical and chemical properties of the complexes.

Taking into account a successful application of bis(1,2,3-triazol-1-yl)alkane ligand to the construction of SCO coordination polymers, the current efforts are directed to synthesis of new di- and poly podal 1,2,3-triazole based ligands, with various length, stiffness, and composition of the spacer, suitable for construction of polymeric functional materials.

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Supporting Information Available: Crystallographic information files (CIFs). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(16) Sample weight 7.666 mg. Scanning rate (heating and cooling) 1 K/min.