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Communication

A New Family of Spin-Crossover Complexes Based on a $Fe^{II}(Tetrazolyl)_4(MeCN)_2$-Type Core

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A bitopic ligand 2-hydroxy-1-(tetrazol-1-yl)-3-(tetrazol-2-yl)propane (12pbtzOH) was synthesized and reacted with $Fe(ClO_4)_2 \cdot 6H_2O$, giving a 1D coordination polymer $\{[Fe(12pbtzOH)_2(CH_3CN)_2](ClO_4)_2 \cdot 2CH_3CN\}_\infty$ that exhibits a high-spin to low-spin transition ($T_{1/2}{\downarrow} = T_{1/2}{\uparrow} \cong 104$ K). This is an unprecedented example of an iron(II) complex containing $Fe(tetrazolyl)_4(MeCN)_2$ cores.

Since 1982, 1-alkyltetrazoles[1,2] and their halogenated derivatives[3,4] (1Rtz) have been intensively investigated as ligands for the preparation of iron(II) complexes exhibiting thermally induced spin-crossover (SCO).[5] In such compounds, iron(II) ions are octahedrally surrounded by 1-substituted tetrazoles, which coordinate through N4 nitrogen atom.[2,4,6] Thus, the $Fe(tetrazolyl)_6$ core is a characteristic feature of this class of complexes. Examples of the SCO compounds based on other monodentately coordinating azoles such as isoxazoles,[7] 1-substituted-1,2,3-triazoles,[8] and 2-substituted tetrazoles[9] are relatively scarce. In these complexes, iron(II) ions are also bonded to six azole rings. Recently, studies concerning the SCO phenomenon have been extended on polymeric systems,[10] and 1D,[11] 2D,[8] and 3D[9,12] coordination polymers of bis(azolyl)alkanes were synthesized. The successful preparation of SCO polymeric systems has been an encouragement to the design and synthesis of novel bi- and tridentate ligands containing azole donors.[13,14] In the above-mentioned polymeric SCO systems, as well as in monomeric $[Fe(1Rtz)_6]X_2$ ($X = ClO_4^-$, BF_4^-, and $CF_3SO_3^-$) complexes, iron(II) ions are octahedrally coordinated with azole rings.

Continuing our investigations concerning the application of azole-based ligands that may be useful in the preparation of iron(II) SCO coordination polymers,[8,9] we have decided

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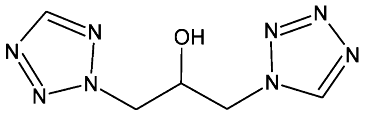
Chart 1



to carry out modifications of bis(azolyl)alkanes in two ways. First, following Kahn and Martinez idea,[15] we have designed a bitopic ligand containing two kinds of monodentately coordinating azole donors. Each of these two donors is able to form iron(II) SCO complexes. Second, as suggested by Kepert et al.,[16] we have also modified an alkyl spacer. Taking into account the above-mentioned conceptions, we have synthesized 2-hydroxy-1-(tetrazol-1-yl)-3-(tetrazol-2-yl)propane (**1**)—a bitopic ligand containing 1-substituted and 2-substituted tetrazole rings tethered by a propylene spacer which was functionalized by the incorporation of the hydroxyl group (Chart 1).

While preparing **1**, we have utilized the fact that the alkylation of tetrazoles usually leads to the formation of comparable amounts of 1- and 2-substituted derivatives.[17] The reaction of sodium tetrazolate with 1,3-dibromo-2-hydroxypropane yielded three bistetrazole isomers: 2-hydroxy-1-(tetrazol-1-yl)-3-(tetrazol-2-yl)propane (**1**), 2-hydroxy-1,3-di(tetrazol-1-yl)-3-propane (**2**), and 2-hydroxy-1,3-di(tetrazol-2-yl)-3-propane (**3**).[18] **1** was isolated as colorless crystals[19] with a 41% yield. Recently, a 2D SCO complex of iron(II) with **2** was synthesized.[20] In this case, the iron(II) ions are also surrounded by six tetrazole rings.

Successful formation of the complex of **1** was achieved when applying an excess of iron(II) salt. Thus, synthesis performed in acetonitrile at a 1:1 molar ratio of $Fe(ClO_4)_2 \cdot 6H_2O$ to **1** gave colorless crystals of [Fe(**1**)$_2$(CH_3CN)$_2$](ClO_4)$_2 \cdot 2CH_3CN$ (**4**) with a 19% yield.[21] The complex is unstable during storage, and crystals started to become cloudy about 10 days after removal from the mother liquor. The stoichiometry of **4** suggests an absence of the six tetrazoles surrounding the iron(II) ion. However, we have noticed that the crystals turned purple during sample cooling to the liquid nitrogen temperature. This thermochromic effect indicates the capability of **4** to undergo the thermally induced high-spin to low-spin transition.

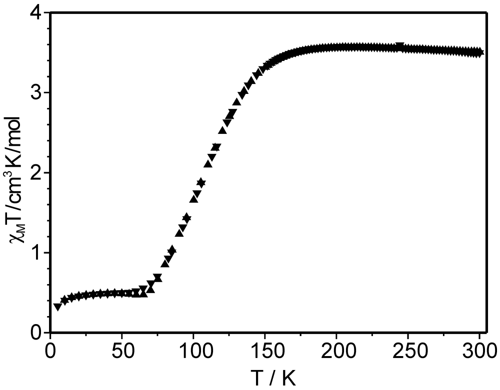


Figure 1. The $\chi_M T(T)$ plot for **4** in cooling (▼) and warming (▲) modes.

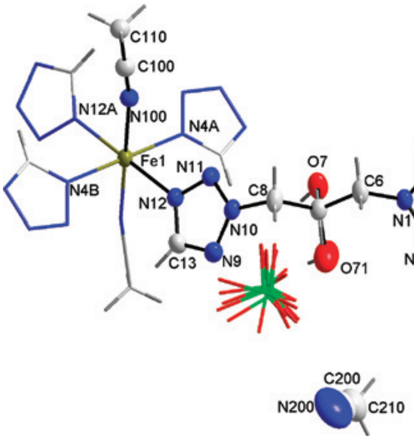


Figure 2. A coordination environment of Fe(II) in **4**.

In order to characterize the spin transition, the temperature-dependent magnetic susceptibility measurements were performed over a 5−300 K range on a freshly prepared sample of the solvate **4** (Figure 1). The value of $\chi_M T$ at 300 K is equal to 3.50 cm^{3}K/mol and is characteristic for a high-spin iron(II) ion. Upon cooling, the $\chi_M T$ value remains almost constant until 180 K. Below this temperature, a gradual decrease is observed. At approximately 50 K, it reaches a value of 0.50 cm^{3}K/mol. This behavior points toward the spin-state change of iron(II) ions.

Below 50 K, the $\chi_M T(T)$ dependency reaches a plateau. Further lowering of the $\chi_M T$ value observed below 10 K may be attributed to the zero-field splitting of the residual high-spin iron(II) sites. In the warming mode, the course of $\chi_M T(T)$ dependency is the same as was observed in the cooling mode. **4** displays the gradual spin transition, and ca. 90% of the iron(II) ions change the spin state.

X-ray measurements of **4** were performed at 293 and 100 K.[19] In **4**, the nearest surrounding of the iron(II) ion consists of two trans-positioned 1-substituted tetrazole rings and two 2-substituted tetrazole rings which form the basal plane of the coordination octahedron (Figure 2). Two axial positions are occupied by acetonitrile molecules. As a consequence, the constitution of the Fe(II) spin crossover center in **4** differs

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[18] 1,3-Dibromo-2-hydroxypropane (0.040 mol, 8.72 g) dissolved in acetonitrile (50 mL) was added to the sodium tetrazolate (0.090 mol, 8.28 g) suspended in acetonitrile (100 mL). The reaction mixture was stirred and refluxed for 48 h. Then, the precipitated NaBr was filtered off and the MeCN was evaporated under reduced pressure. From the obtained residue, **3** ($R_f = 0.7$), **1** ($R_f = 0.5$), and **2** ($R_f = 0.3$) were isolated by column chromatography on silica gel eluting with a mixture of CH_2Cl_2/MeCN/MeOH, 6:2:0.4 (v/v). **3**, **1**, and **2** were obtained with yields of 19.4% (1.52 g), 41.0% (3.22 g), and 14.6% (1.15 g), respectively. Anal. Calcd for **1** ($C_5H_8N_8O$, $M_w = 196.17$): C, 30.6; H, 4.1; N, 57.1. Found: C, 30.9; H, 4.1; N, 56.9%. ^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ: 8.89 (s, 1H, C*H* of tetrazol-1-yl), 8.64 (s, 1H, C*H* of tetrazol-2-yl), 5.71 (d, 1H, O*H*, $^3J = 5.8$ Hz), 4.88 (dd, 1H, −CH*H*-tetrazol-2-yl, $^2J = 13.7$ Hz, $^3J = 3.8$ Hz), 4.67−4.77 (two overlapped dd, 1H of −CH*H*-tetrazol-2-yl and 1H of −CH*H*-tetrazol-1-yl), 4.51 (dd, 1H, −CH*H*-tetrazol-1-yl, $^2J = 13.4$ Hz, $^3J = 8.2$ Hz), 4.37−4.48 (m, 1H, −C*H*(OH)−). ^{13}C NMR (300 MHz, DMSO-*d*$_6$): δ 153.3 (tetrazol-2-yl), 144.7 (tetrazol-1-yl), 67.3 (−*C*H(OH)−), 55.7 (−*C*H$_2$-tetrazol-2-yl), 50.9 (−*C*H$_2$-tetrazol-1-yl). ESI-MS: *m*/*z* 197.1 (LH$^+$). The analytical characteristics of **2** and **3** were deposited as Supporting Information.

from all known iron(II) SCO systems based on monofunctional tetrazoles.

The tetrazole rings are coordinated to iron(II) ions through the N4 nitrogen atoms. At 295 K, the Fe−N4(tetrazol-1-yl) and Fe−N12(tetrazol-2-yl) bond lengths are equal to 2.179(2) and 2.203(2) Å, respectively, whereas the nitrogen atom of acetonitrile molecules is placed at a distance of 2.164(2)Å (Fe−N100). Thus, the complex possesses an Fe(tetrazol-1-yl-κN^4)$_2$(tetrazol-2-yl-κN^4)$_2$(CH_3CN)$_2$ core, and the values of Fe−N bond lengths are characteristic for the high-spin form of iron(II). Molecules of **1** contain both 1-substituted and 2-substituted tetrazole rings that are linked by a propylene chain adopting a *TT* conformation. The oxygen atom of the ligand molecule is crystallographically disordered over two positions. Two crystallographically related ligand molecules bridge Fe(II) ions, which are separated by 11.435(3) Å. This bridging mode is propagated along the [001] direction, leading to the formation of 1D macrocations (Figure 3a). The 1D polymeric chains gathered in the *bc* plane form parallel oriented layers (Figure 3b). The shortest interchain Fe···Fe distance within the layer is equal to 10.205(4) Å. Highly disordered perchlorate anions (over four positions) and acetonitrile molecules are placed between the layers (Figure 3b). Anions are involved in (CH)OH···O(Cl) hydrogen-bond interactions, while the noncoordinated acetonitrile molecules are not engaged in any hydrogen-bond formation. The shortest distances, between iron atoms from neighboring layers, are equal to 8.968(2) ([100] direction) and 10.128(5) Å ($[1\bar{1}0]$ direction).

The cooling of **4** to 100 K leads to significant changes in the crystal structure. At this temperature, the Fe−N bonds lengths are equal to 2.065(3) for Fe−N4(tetrazol-1-yl), 2.080(3) for Fe−N12(tetrazol-2-yl), and 2.038(3) for Fe−N100(CH_3CN). Complete SCO in the tetrazole-based iron(II) complexes usually involves shortening of the Fe−N bond lengths by 0.16 to 0.20 Å. Here, the observed average shortening of the Fe−N4, Fe−N12, and Fe−N100 bond lengths at 0.11, 0.12, and 0.13Å, respectively, correlates well with the magnetic susceptibility measurements, indicating that approximately 50% of the iron(II) ions change their spin state at 100 K. A temperature change from 293 to 100 K results in a distance decrease between the ligand-bridged iron(II) ions to 11.257(4)Å. This shortening is accompanied by the formation of the intrachain C5−H5···O1(Cl) (−*x*, −*y*, 1 − *z*) hydrogen bond. Furthermore, the separation between iron atoms from neighboring chains gathered in the *bc* plane is reduced to 9.904(3)Å. The interchain Fe···Fe separation in the [100] direction decreases to 8.801(2) Å, whereas the distance between iron(II) ions in the $[1\bar{1}0]$ direction is shortened to 9.973(5) Å. At 100 K, perchlorates remain disordered.

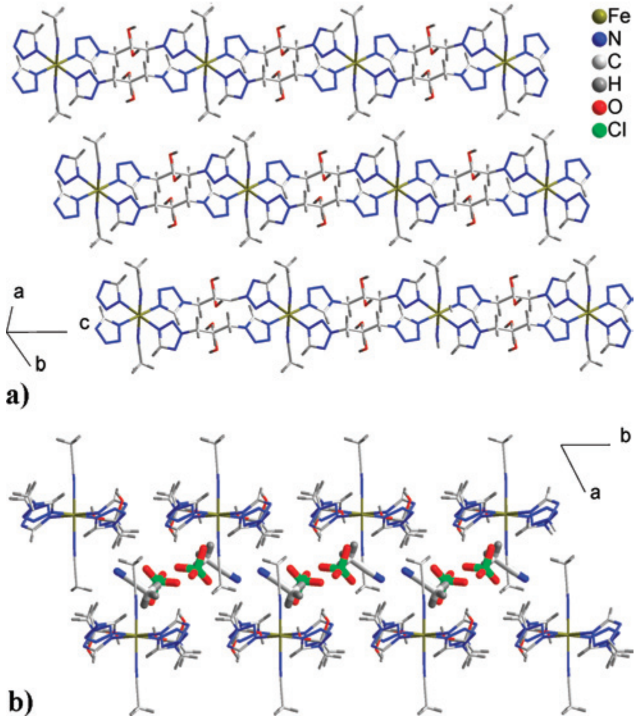

Figure 3. Drawing showing (a) 1D chains (perchlorates and noncoordinated CH_3CN molecules were omitted for clarity) and (b) the layered arrangement of 1D chains in **4** (a view along the *c* axis).

In summary, this communication reports on a first example of an SCO system based on monofunctional tetrazole donors in which iron(II) ions are coordinated only by four tetrazole rings. Thus, in the 1D coordination polymer {[Fe(**1**)$_2$(CH_3CN)$_2$](ClO_4)$_2$·2CH_3CN}$_\infty$, 1- and 2-substituted tetrazole rings of bitopic ligand 2-hydroxy-1-(tetrazol-1-yl)-3-(tetrazol-2-yl)-propane (**1**) form the basal plane of the coordination octahedron, whereas the axial positions are occupied by acetonitrile molecules. It is worth adding that the presented result opens new possibilities to the design and construction of SCO networks based on bitopic ligands containing tetrazoles, as well as organic nitriles.

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Supporting Information Available: Crystallographic information files (CIFs) for **1** and **4**, analytical characteristics for **2** and **3**, and a plot of $\chi_M T$ vs *T* dependency (1st and 2nd temperature cycle) for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Crystal data for **1** at 100 K: $C_5H_8N_8O$, $\lambda = 0.71073$ Å, monoclinic, $P2_1/c$, $a = 8.508(2)$ Å, $b = 11.454(3)$ Å, $c = 9.485(3)$ Å, $\beta = 113.36(3)°$, $V = 848.6(4)$ Å^3, R1 = 0.0464, wR2 = 0.1007 (for 2834 reflections with $I > 2\theta(I)$). Crystal data for **4** at 293 K: $[Fe(C_5H_8N_8)_2(CH_3CN)_2](ClO_4)_2 \cdot 2(CH_3CN)$, $\lambda = 0.71073$ Å, triclinic, $P\bar{1}$, $a = 8.968(2)$ Å, $b = 10.205(4)$ Å, $c = 11.435(3)$ Å, $\alpha = 68.05(3)°$, $\beta = 85.64(2)°$, $\gamma = 63.39(3)°$, $V = 862.5(5)$ Å^3, R1 = 0.0460, wR2 = 0.1218 (for 3632 reflections with $I > 2\theta(I)$). Crystal data for **4** at 100 K: $[Fe(C_5H_8N_8)_2(CH_3CN)_2](ClO_4)_2 \cdot 2(CH_3CN)$, $\lambda = 0.71073$ Å, triclinic, $P\bar{1}$, $a = 8.801(2)$ Å, $b = 9.904(3)$ Å, $c = 11.257(4)$ Å, $\alpha = 68.91(3)°$, $\beta = 85.37(2)°$, $\gamma = 64.12(3)°$, $V = 820.3(4)$ Å^3, R1 = 0.0395, wR2 = 0.0992 (for 2989 reflections with $I > 2\theta(I)$).

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(21) Synthesis of the complex was performed under a nitrogen atmosphere. **1** (0.15 mmol, 29.4 mg) dissolved in CH_3CN (4 mL) was added to the solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (0.15 mmol, 54.4 mg) in CH_3CN (4 mL). The resulting clear solution was left in the closed Schlenk flask. After 10 days, the colorless crystals of the complex were filtered off and dried in a stream of nitrogen. Yield: 11.8 mg (19.4%). Anal. Calcd for $FeC_{18}H_{28}N_{20}Cl_2O_{10}$: C, 26.6; H, 3.5; N, 34.5. Found: C, 26.7; H, 3.2; N, 34.4%.