

New thiocyanato iron(II) complex with 3,5-bis(3-pyridyl)-1,2,4-thiadiazole: Synthesis, structure, magnetic and spectral properties



Róbert Uhrecký^{a,*}, Iveta Ondrejčovičová^a, Darina Lacková^a, Zuzana Fáberová^a, Jerzy Mroziński^b, Božena Kalińska^b, Zdeňka Padělková^c, Marian Koman^a

^a Institute of Inorganic Chemistry, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia

^b Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

^c Department of General and Inorganic Chemistry, University of Pardubice, 532 10 Pardubice, Czech Republic

ARTICLE INFO

Article history:

Received 23 May 2013

Received in revised form 22 January 2014

Accepted 23 January 2014

Available online 31 January 2014

Keywords:

Iron(II) complex

Thiocyanate complex

3,5-Bis(3-pyridyl)-1,2,4-thiadiazole

Crystal structure

Infrared spectra

Magnetic properties

ABSTRACT

The new iron(II) complex $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$ (bpta = 3,5-bis(3-pyridyl)-1,2,4-thiadiazole) has been prepared by refluxing $\text{Fe}(\text{NCS})_3$ or $\text{Fe}(\text{NCS})_2$ with thionicotinamide in methanol solution. It is supposed that the bpta ligand is generated in situ by the oxidative dimerization of thionicotinamide. The complex was characterized by X-ray structural analysis at 150 and 293 K, elemental analysis, spectral and magnetic measurements. The compound crystallizes in the monoclinic $P2_1$ space group, with unit cell parameters at 293 K: $a = 7.869(2)$, $b = 17.056(3)$, $c = 12.637(3)$ Å, $\beta = 102.88(1)^\circ$. The crystal structure analysis showed that the iron atom has a distorted octahedral environment with FeN_4O_2 chromophore. Iron atom is coordinated by two nitrogen atoms from NCS^- ions, by two oxygen atoms from methanol molecules in the equatorial plane and by two nitrogen atoms of pyridine rings from dpta ligands in axial positions. The crystal lattice forms 2D supramolecular network which is stabilized by a system of hydrogen bonds and π - π stacking interactions. Variable-temperature magnetic susceptibility data in the temperature range 1.8–300 K show that the octahedral iron(II) is high-spin $S = 2(^5T_{2g})$ and as a result effects due to zero-field splitting are anticipated at low temperatures. Structural parameters and infrared spectra of similar complexes are compared and discussed.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Thiadiazoles constitute an important class of five membered nitrogen-sulfur heterocycles exhibiting a large variety of biological activities [1,2]. Moreover, the derivatives of thiadiazoles and their metal complexes have attracted increasing attention because of their potential applications in pharmaceutical, agricultural, industrial, coordination and polymer chemistry [3–11].

Thiadiazoles with two substituted pyridyl groups, i.e. bis(*n*-pyridyl)-thiadiazoles ($n = 2, 3$ or 4) occur in different isomeric forms such as 4,5-bis(*n*-pyridyl)-1,2,3-thiadiazoles, 3,5-bis(*n*-pyridyl)-1,2,4-thiadiazoles, 2,5-bis(*n*-pyridyl)-1,3,4-thiadiazoles and 3,4-bis(*n*-pyridyl)-1,2,5-thiadiazoles. In the literature there is much information on the 1,3,4-thiadiazole derivatives and their coordination compounds.

Recently we reviewed the structural data of 83 metal complexes with bis(*n*-pyridyl)-thiadiazoles ($n = 2, 3$ or 4) and analyzed their coordination modes [12]. Thiadiazoles act as mono- to tetra-dentate ligands without involving the sulfur atom. The ligands have four potential donor sites, viz. two N atoms of the pyridine rings and two N atoms of the thiadiazole ring. The most numerous group form complexes with 2,5-bis(*n*-pyridyl)-1,3,4-thiadiazoles (81 examples). There are 50 examples of 4-pyridyl, 26 examples of 2-pyridyl and 5 with 3-pyridyl derivatives. There are only four iron complexes with 2,5-bis(2-pyridyl)-1,3,4-thiadiazole (L) of the composition $[\text{Fe}(\text{L})_2(\text{X})_2]$ ($\text{X} = \text{NCS}, \text{NCSe}, \text{B}(\text{CN})_4, \text{NCBH}_3$) [4,5]. The bidentate thiadiazole ligands L are coordinated to the Fe(II) atom forming five membered chelate rings. There are known also two complexes with 3,4-bis(2-pyridyl)-1,2,5-thiadiazole [6]. According to our best knowledge, complexes with 4,5-bis(*n*-pyridyl)-1,2,3-thiadiazoles and 3,5-bis(*n*-pyridyl)-1,2,4-thiadiazoles have not yet been characterized by X-ray structural analysis [12].

This paper is a continuation of our previously reported studies on iron complexes with pyridine derivatives [13–16]. During

* Corresponding author. Tel.: +421 2593 25 184; fax: +421 2524 93 198.

E-mail address: robert.uhrecky@stuba.sk (R. Uhrecký).

attempts to prepare iron(III) complexes with thionicotinamide, there was observed reduction of Fe(III) to Fe(II) and formation of the title complex. Herein, we report the syntheses, crystal and molecular structure, magnetic and spectral properties of the Fe(II) complex, $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$ where bpta is 3,5-bis(3-pyridyl)-1,2,4-thiadiazole. The compound has been prepared by the reaction of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and KSCN with thionicotinamide in methanol and also when was used $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ instead of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. This complex represents the first example of metal complex with the 1,2,4-thiadiazole ligand.

2. Experimental

2.1. Materials and general methods

All the chemicals and solvents were purchased commercially and used without further purification. Elemental analysis (C, H, N and S) was carried out by means of a Flash EA 1112 analyzer. The content of Fe was determined spectrophotometrically with 1,10-phenanthroline. The presence of gaseous sulfane released during the reaction was proven with $\text{Pb}(\text{NO}_3)_2$. The infrared spectrum ($4000\text{--}100\text{ cm}^{-1}$) was measured by solid-state KBr technique and recorded on Nicolet 5700 FTIR spectrophotometer.

EPR spectra were recorded at room temperature and 77 K on a Bruker Elexsys E 500 spectrometer operating at the X-band equipped with an NMR teslameter (ER 036TM) and frequency counter (E 41 FC). Variable-temperature magnetic measurements of polycrystalline sample were carried out with a Quantum Design SQUID magnetometer (MPMSXL-5-type) at a magnetic field of 0.5 T over the temperature range 1.8–300 K. Corrections are based on subtracting the sample-holder signal and contribution χ_{Dia} corrections for iron(II) compound estimated from Pascal constants [17] and equal $-394 \times 10^{-6}\text{ cm}^3\text{ mol}^{-1}$. The effective magnetic moment was calculated from the equation $\mu_{\text{eff}} = 2.83(\chi_{\text{M}}T)^{1/2}$ (B.M.). Magnetization versus magnetic field measurements were carried out at 2 K in the magnetic field range 0–5 T.

2.2. Synthesis of the complex

The title compound was prepared by two similar ways differing by using starting iron compound. Firstly was used $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (method A) and in the second case was used $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (method B).

2.2.1. Method A

Solid thionicotinamide (0.276 g, 2.0 mmol) was added into a solution of $\text{Fe}(\text{NCS})_3$, under stirring, which was prepared from KSCN (0.145 g, 1.5 mmol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.135 g, 0.5 mmol) in methanol (50 ml). The reaction mixture was refluxed for 2 h. Then the mixture was chilled and the insoluble KCl formed during the reaction was filtered off. The dark-red filtrate was allowed to stand at room temperature. After a few days, well-formed orange crystals of the title compound, suitable for X-ray analysis, were obtained. Yield: 0.614 g; 85.6 %.

2.2.2. Method B

Solid thionicotinamide (0.276 g, 2.0 mmol) was added to a solution of $\text{Fe}(\text{NCS})_2$, under stirring, which was prepared from KSCN (0.097 g, 1.0 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.100 g, 0.5 mmol) in methanol (50 ml). The reaction mixture was refluxed for 2 h. Then the mixture was chilled and the insoluble KCl was filtered off. The orange filtrate was allowed to stand at room temperature. Orange crystals were obtained by similar way as by method A.

Anal. Calc. for $\text{C}_{28}\text{H}_{24}\text{N}_{10}\text{O}_2\text{S}_4\text{Fe}$: C, 46.93; H, 3.35; N, 19.54; S, 17.90; Fe, 7.79. Found (method A): C, 46.07; H, 3.27; N, 19.17; S,

17.68; Fe, 7.79%; found (method B): C, 46.20; H, 3.37; N, 19.22; S, 17.74; Fe, 7.79%.

The title compound has been also obtained from the reaction mixtures containing a (2–6): 1 M mix of thionicotinamide and $\text{Fe}(\text{NCS})_3$ in methanol.

2.3. Single-crystal X-ray diffraction measurements

Intensity data for $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$ prepared by method A were obtained using Oxford Cryostream low-temperature device on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at 150 K. Absorption correction was applied using the program SADABS [18]. Data reductions were performed with EvalCCD [19]. Intensity data for the same compound at 293 K were collected using a Siemens P4 diffractometer with graphite monochromated Mo $\text{K}\alpha$ radiation [20]. The diffraction intensities were corrected for Lorentz and polarization effects with XSCANS [21]. Absorption correction was applied using the program XEMP [21]. The structures were solved by direct methods using the program SIR-2011 [22] and refined by the full-matrix least-squares method on all F^2 data using the program SHELXL-2013 [23]. Geometrical analysis was performed using SHELXL-2013. The structures were drawn by ORTEP-3 [24] and Mercury [25] software. The single crystal suite WINGX was used as integrated system for all crystallographic programs and software for preparing the material for publication [26].

All non-hydrogen atoms of the title compound were refined anisotropically as independent atoms. Hydrogen atoms were calculated into idealized positions. Crystal data and conditions of data collection and refinement are reported in Table 1, bonds lengths and bonds angles are reported in Table 2 and hydrogen bonds parameters are reported in Table 3.

Discrete positional disorder of the thiadiazole ring [C10A, C11A, N5A, N6A, S3A] and [C10B, C11B, N5B, N6B, S3B] is observed in the title compound with site occupancy factor of 0.760(6) and 0.240(6) for (1), and 0.603(5) and 0.397(5) for (2). The sulfur atom of thiocyanate group [N1, C1, S1A] and [N1, C1, S1B] is localized in two positions with site occupancy factor of 0.83(2) and 0.17(2) for (1), and 0.74(1) and 0.26(1) for (2). Results of measurements at 293 K showed that carbon atom of methanol molecule [C3A, C3B] is also localized in two positions with site occupancy factor of 0.18(7) and 0.82(7), respectively. All disordered groups were restrained using SADI and EADP commands of SHELXL-2013 program.

3. Results and discussion

3.1. Synthesis

The title iron(II) complex has been prepared by two ways; by a reaction of thionicotinamide with of $\text{Fe}(\text{NCS})_3$ (method A) or $\text{Fe}(\text{NCS})_2$ (method B) in methanol. It is believed that the bpta ligand is generated in situ by the oxidative dimerization of thionicotinamide (Scheme 1) and then is coordinated to Fe(II). In the first case (method A) during the reaction iron(III) atom is reduced to iron(II). We suppose that there can be oxidized NCS^- anion to $(\text{SCN})_2$ [27]. The quantity of $(\text{SCN})_2$ that would have been produced in the reaction would have been too small to observe. Also, any $(\text{SCN})_2$ produced would have undergone hydrolysis [27]. Simultaneously can also take place oxidation of methanol to methanal [28]. Formed gaseous H_2S was detected by smell and by a reaction with $\text{Pb}(\text{NO}_3)_2$, too. Oxidative dimerization of thioamides (including thionicotinamide) is one of methods for preparation of 3,5-disubstituted 1,2,4-thiadiazoles [10,29,30].

Table 1

The crystal data, X-ray measurements and structure determination summary for $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$ at 150 and 293 K.

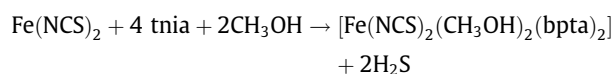
	150 K	293 K
Chemical formula	$\text{C}_{28}\text{H}_{24}\text{N}_{10}\text{O}_2\text{S}_4\text{Fe}$	
Formula weight	716.66	
Crystal color, habit	dark orange, needle	
Crystal system, space group	monoclinic, $P2_1$	
<i>a</i> (Å)	7.749(2)	7.869(2)
<i>b</i> (Å)	16.780(3)	17.056(3)
<i>c</i> (Å)	12.534(3)	12.637(3)
β (°)	102.36(3)	102.88(1)
<i>V</i> (Å ³)	1592.0(6)	1653.4(6)
<i>Z</i>	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.495	1.440
Radiation type	Mo K α	Mo K α
μ (mm ⁻¹)	0.78	0.75
Crystal size (mm)	$0.47 \times 0.28 \times 0.23$	$0.52 \times 0.31 \times 0.26$
Diffractometer	Bruker-Nonius KappaCCD	Siemens P4
Absorption correction	multi-scan, SADABS	Ψ -scan, XEMP
<i>T</i> _{min} , <i>T</i> _{max}	0.710, 0.841	0.696, 0.829
<i>S</i>	1.03	1.02
<i>R</i> _{int}	0.060	0.068
<i>R</i> ₁ [<i>I</i> ² > 2 σ (<i>I</i> ²)], <i>wR</i> ₂ (<i>I</i> ²)	0.051, 0.078	0.049, 0.114
No. of reflections	6013	3657
No. of parameters	429	432
No. of restraints	21	23
Δ _{max} , Δ _{min} (e Å ⁻³)	0.32, -0.30	0.26, -0.32
CCDC No.	889109	889110

Table 2

Selected geometric parameters (Å, °) for $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$.

	150 K	293 K
Bonds		
Fe1–N1	2.095 (5)	2.105 (6)
Fe1–N2	2.089 (6)	2.110 (6)
Fe1–N3	2.226 (6)	2.273 (5)
Fe1–N4	2.242 (5)	2.257 (6)
Fe1–O1S	2.124 (5)	2.166 (5)
Fe1–O2S	2.117 (5)	2.122 (5)
Angles		
N1–Fe1–N2	178.7 (3)	178.5 (3)
N1–Fe1–N3	89.7 (2)	89.4 (2)
N1–Fe1–N4	90.0 (2)	89.9 (2)
N1–Fe1–O1S	90.9 (2)	90.8 (2)
N1–Fe1–O2S	88.7 (2)	89.2 (2)
N2–Fe1–N3	90.4 (2)	89.9 (2)
N2–Fe1–N4	89.9 (2)	90.7 (2)
N2–Fe1–O1S	87.8 (2)	87.9 (2)
N2–Fe1–O2S	92.5 (2)	92.1 (2)
N3–Fe1–N4	178.7 (2)	178.6 (2)
N3–Fe1–O1S	87.8 (2)	87.4 (2)
N3–Fe1–O2S	90.5 (2)	91.0 (2)
N4–Fe1–O1S	91.0 (2)	91.4 (2)
N4–Fe1–O2S	90.8 (2)	90.2 (2)
O1S–Fe1–O2S	178.2 (2)	178.4 (2)
N1–C1–S1(A);(B)	173.9 (7); 160 (1)	172.5 (8); 158 (1)
N2–C2–S2	178.5 (6)	178.9 (6)

Formation of the title complex from $\text{Fe}(\text{NCS})_2$ and tnia (method B) can be described by following equation:



3.2. Structure description

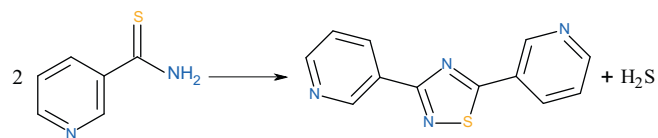
The complex $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$ crystallizes in the monoclinic system with space group $P2_1$. The molecular structure of the neutral mononuclear complex is displayed in Fig. 1. The iron

Table 3

Selected hydrogen-bond parameters for $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$.

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
150 K				
O1S–H1S...N10 ⁱ	0.84	1.90	2.731 (7)	170
O2S–H2S...N7 ⁱⁱ	0.84	1.91	2.721 (6)	162
293 K				
O1S–H1S...N10 ⁱ	0.82	1.95	2.759 (7)	171
O2S–H2S...N7 ⁱⁱ	0.82	1.94	2.751 (7)	170

Symmetry code(s): (i) $x + 1, y, z + 1$; (ii) $x - 1, y, z - 1$.



Scheme 1. Formation of bpta by oxidative dimerization of thionicotinamide.

n(II) atom is six coordinated by two nitrogen atoms from two thiocyanate anions and two oxygen atoms from methanol molecules in the equatorial plane, and two nitrogen atoms of pyridine rings from two bpta ligands in the axial positions. The data indicate that all the Fe–N and Fe–O distances are in the range 2.089(6)–2.273(5) Å, typical for high-spin iron(II) compounds. However, Fe–N(bpta) distances are longer than the Fe–N(NCS) and Fe–O(CH₃OH) distances where Fe–N(NCS) = 2.095(5) and 2.089(6) Å for (**1**); Fe–N(NCS) = 2.105(6) and 2.110(6) Å for (**2**); Fe–O(CH₃OH) = 2.124(5) and 2.117(5) Å for (**1**); Fe–O(CH₃OH) = 2.166(5) and 2.122(5) Å for (**2**); (Fe–N(bpta) = 2.226(6) and 2.242(5) Å for (**1**); Fe–N(bpta) = 2.273(5) and 2.257(6) Å for (**2**). These bond distances are comparable with those reported for $[\text{Fe}(\text{4-acpy})_2(\text{H}_2\text{O})_2(\text{NCS})_2]$ (4-acpy = 4-acetylpyridine) [31], $[\text{Fe}(\text{NCS})_2(\text{bipy})(\text{CH}_3\text{OH})_2] \cdot \text{bipy}_n$ (bipy = 4,4'-bipyridine) [32] and $[\text{Fe}(\text{NCS})_2(\text{3-bpo})_2(\text{H}_2\text{O})_2]$ (3-bpo = 2,5-di-3-pyridyl-1,3,4-oxadiazole) [33]. The thiocyanate anions, bpta and methanol molecules are coordinated to iron(II) in a monodentate terminal mode in mutually *trans*-position. The unidirectional thiocyanate anions [N2, C2, S2] are almost linear with the angles of 178.5(6)° for (**1**) and 178.9(6)° for (**2**). Disordered thiocyanate anions are deviated from the linear alignment with values of angles in the range from 160(1)° to 173.9(7)° at 150 K and 158(1)° to 172.5(8)° at 293 K. In the title complex the uncoordinated nitrogen atoms of pyridine rings from bpta ligands and hydrogen atoms from the methanol molecules are joined through O1S–H1S...N10 and O2S–H2S...N7 hydrogen bonds [length *d*(D...A) and angle <(D–H...A) vary from 2.721(6) to 2.731(7) Å and 162–170° for (**1**), and 2.751(7) to 2.759(7) Å and 170–171° for (**2**)] into 1D polymeric chain (Fig. 2A, Table 3). Moreover, the thiadiazole rings of the bpta ligands [N5, N6, C10, C11, S3; N8, N9, C22, C23, S4] are involved in the face-to-face aromatic π - π stacking interactions with the centroid to centroid distance of 3.489 Å (Fig. 2B) for (**1**) and 3.579 Å for (**2**). Furthermore, these 1D chains are stacked parallel to form a 2D sheet through the inter-chain aromatic interaction between the thiadiazole rings. Therefore, in the complex the hydrogen bonds and π - π stacking interactions play an influential role in expanding the mononuclear units to 2D supramolecular network (Fig. 2C).

3.3. Magnetic properties

The magnetic properties of the title complex prepared by method A were determined over the temperature range 1.8–300 K. Plots of magnetic susceptibility of χ_M and the χ_M^{-1} versus *T* are given in Fig. 3.

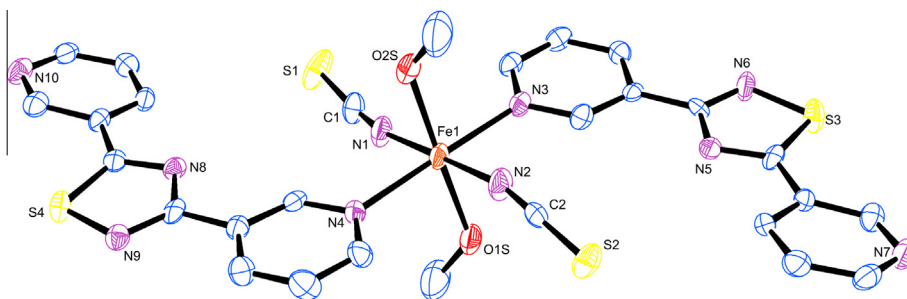


Fig. 1. ORTEP structure of the $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$, at 150 K showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

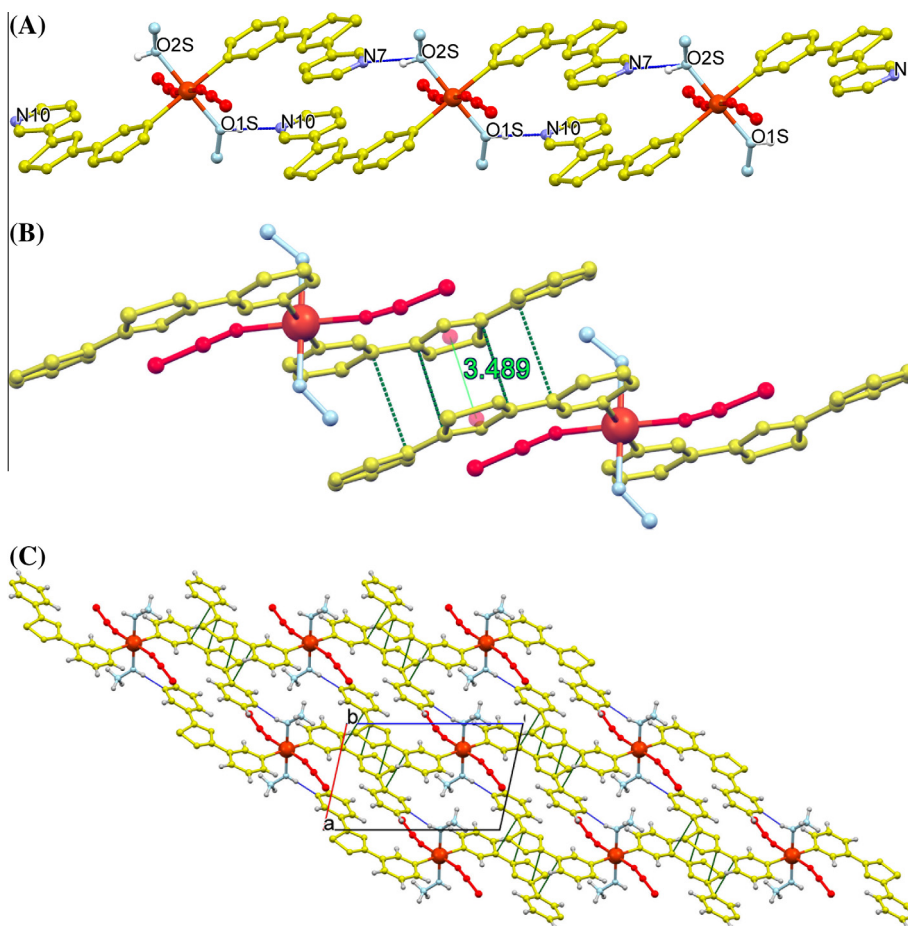


Fig. 2. (A) A view of the 1D chains of $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$ formed by N–H...O hydrogen bonds (blue lines). Irrelevant hydrogen atoms are omitted for clarity. (B) Schematic representation of π – π stacking interactions (green lines) in $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$. Hydrogen atoms are omitted for clarity. (C) Packing diagram along *b* axis in $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$ showing 2D supramolecular network. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The variation of the magnetization (*M*) versus magnetic field (*H*) at temperature 2 K indicates a linear variation up to *M* = 0.7 T and then relations agree with Brillouin function up to *M* = 2.72 B.M. at 5 T (Fig. 4).

The value of effective magnetic moment at room temperature is equal to 5.38 B.M. and it is higher than the predicted value 4.90 B.M. for *S* = 2 as usually observed for high-spin iron(II) complexes.

The value of $\chi_M T$ product is stable up to 50 K and its lowering is observed at the lowest temperatures. The more evident decrease in its value, reaching $\chi_M T = 2.37 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and $\mu_{\text{eff}} = 4.36 \text{ B.M.}$ at 1.8 K.

The values of the Curie and Weiss constants determined from the relation $\chi_M^{-1} = f(T)$ over the temperature range 1.8–300 K are equal to $C = 3.66 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and $\Theta = -0.98 \text{ K}$ for iron(II)

complex. The decrease of the value of $\chi_M T$ in the lowest temperature range is caused by occurrence of zero-field splitting parameter *D* and weak antiferromagnetic coupling between Fe(II) centers. High-spin octahedral Fe(II) (*S* = 2) possesses a ${}^5T_{2g}$ ground state and as a result due to zero-field splitting are anticipated at low temperatures [34]. The parameter *D* was determined by fitting Eq. (1) (using the Hamiltonian, $H = DS_z^2 + g\beta HS$) to the magnetic data [35,36]:

$$\mu^2 = \frac{6g^2(e^{-D/T} + 4e^{-4D/T})}{1 + 2e^{-D/T} + 2e^{-4D/T}} + \frac{2g^2 k_B T (18 - 14e^{-D/T} - 4e^{-4D/T})}{D(1 + 2e^{-D/T} + 2e^{-4D/T})} \quad (1)$$

where *D* = zero field splitting parameter (ZFS), *g* = spectroscopic splitting factor and *k* = Boltzmann's constant.

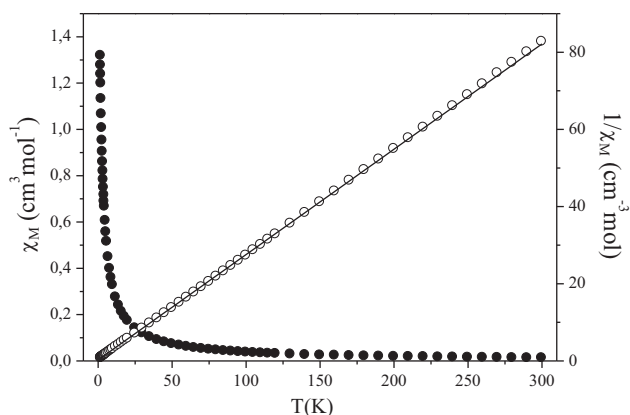


Fig. 3. Experimental magnetic data plotted as χ_M (○) and χ_M^{-1} (●) vs. T for the title complex $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$. Solid line concern theoretical relation $\chi_M^{-1} = f(T)$.

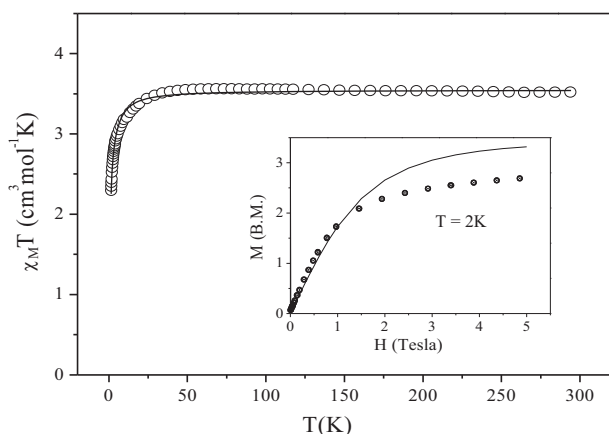


Fig. 4. Experimental magnetic data plotted as $\chi_M T$ (○) vs. T for the title complex $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$. Solid line concerns the best fit parameters. The inset showing variation of the magnetization M vs. the magnetic field H for investigated complex (●) and continuous line corresponds to Brillouin function for an isolated $S = 2$ with $g = 2.0$.

Table 4
EPR data at solid state of $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$.

Temperature (K)	Factors g			
293	$g_1 = 4.50$	$g_2 = 3.32$	$g_3 = 2.78$	$g_4 = 2.06$
77	$g_1 = 4.20$	$g_2 = 3.26$	$g_3 = 3.11$	$g_4 = 2.11$

The magnetic data was fitted with a molecular field correction Eq. (2) [37]:

$$\chi_M^{\text{corr}} = \frac{\chi_M}{1 - \frac{2zJ'}{Ng^2\mu_B} \cdot \chi_M} \quad (2)$$

where χ_M is molar magnetic susceptibility of Fe(II) center, N = Avogadro's number, μ_B = Bohr magneton, zJ' = intermolecular exchange parameter and z is the number of nearest neighbor Fe(II) centers.

The best fit parameters are $D = 3.19 \text{ cm}^{-1}$, $zJ' = -0.04 \text{ cm}^{-1}$ and $g = 2.47$, as indicated by the solid curve in Fig. 4. The agreement factor R is equal $R = 3.47 \times 10^{-4}$.

The criterion used in determination of the best fit was based on minimalization of the sum squares of the deviation:

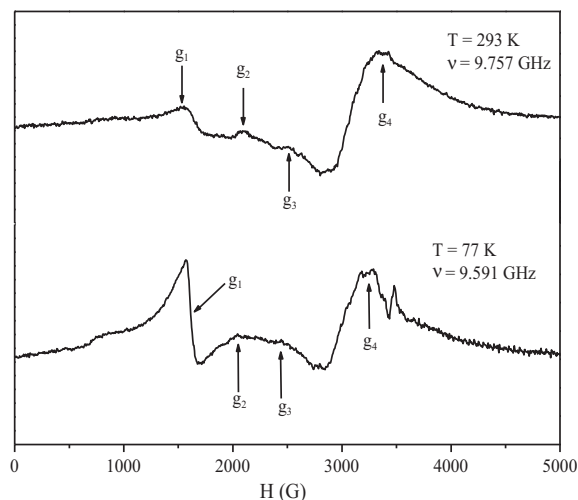


Fig. 5. EPR spectra of $[\text{Fe}(\text{NCS})_2(\text{CH}_3\text{OH})_2(\text{bpta})_2]$ at solid state.

$$R = \sqrt{\frac{\sum_{i=1}^n \frac{1}{(\chi_i^{\text{exp}})^2} (\chi_i^{\text{exp}} - \chi_i^{\text{calc}})^2}{\sum_{i=1}^n \frac{1}{(\chi_i^{\text{exp}})^2}}}$$

The g values in excess of 2.0 are expected for Fe(II) ion as a result of the ${}^5T_{2g}$ electronic state and the value of D is well within the range expected for six-coordinate high-spin Fe(II) complexes.

3.4. EPR and IR spectra

EPR spectra of the iron complex were taken at room and liquid nitrogen temperatures indicated few weak lines (Table 4 and Fig. 5).

The infrared spectrum for the title compound shows typical bands for N-bonded thiocyanate complexes [14,38]. It is evident from two peaks at 2053(s) and 816(m) cm^{-1} which are allotted to $\nu(\text{C-N})$ and $\nu(\text{C-S})$ vibrations. The peak at 478(w) cm^{-1} is attributed to the stretch $\nu(\text{NCS})$. The spectrum shows also characteristic bands of bpta ($\nu_{\text{max}}/\text{cm}^{-1}$: 1595(s), 1590(sh), 1477(m), 1400(s), 1339(s), 1302(m), 1035(s) and 729(s)) which are very close to the published data for free bpta [29]. The presence of methanol molecules in the complex can be indicated by bands at 1102(w) and 1047(m) cm^{-1} ($\nu(\text{C-O})$), 2775(w) cm^{-1} ($\nu(\text{O-H})$), 3040(m) cm^{-1} ($\nu_a(\text{CH}_3)$), 1453(m) and 1410(m) cm^{-1} ($\delta_d(\text{CH}_3)$) [38]. In the far infrared area are important stretches; $\nu(\text{Fe-N})$ (N is from pyridine ring) exhibits peak at 255 cm^{-1} and stretch $\nu(\text{Fe-N})$ (N is from NCS group) exhibits sharp peak at 295 cm^{-1} . Band assigned to $\nu(\text{Fe-O})$ is observed at 410 cm^{-1} [14,16].

4. Conclusion

We have successfully prepared first metal complex with 3,5-bis(3-pyridyl)-1,2,4-thiadiazole ligand by two ways. It is interesting that the thiadiazole ligand is formed in situ by the oxidative dimerization of thionicotinamide. The X-ray structural analysis shows that the system of N-H...O hydrogen bonds and π - π stacking interactions stabilized crystal lattice to 2D supramolecular network. Measurements at two different temperatures showed small changes in the lattice parameters. Variable-temperature magnetic susceptibility data in the temperature range 1.8–300 K show that the octahedral iron(II) is high-spin $S = 2$ (${}^5T_{2g}$) and as a result effects due to zero-field splitting are anticipated at low temperatures. The molecular structure is in good agreement with the observed infrared spectra.

Acknowledgements

This work was supported by the Slovak Grant Agency (VEGA 1/0056/13 and APVV-0014-11) and by the National Science Centre (Poland) under grant No 2011/01/B/ST5/01624.

Appendix A. Supplementary material

CCDC 889109–889110 contain the crystallographic data for title complex at two different temperatures. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2014.01.032>.

References

- [1] K.A. Kumar, G.V. Kumar, N. Renuka, *Int. J. PharmTech Res.* 5 (2013) 239.
- [2] N. Siddiqui, P. Ahuja, W. Ahsan, S.N. Pandeya, M.S. Alam, *J. Chem. Pharm. Res.* 1 (2009) 19.
- [3] R. Leung-Toung, J. Wodzinska, W. Li, J. Lowrie, R. Kukreja, D. Desilets, K. Karimian, T.F. Tam, *Bioorg. Med. Chem.* 11 (2003) 5529.
- [4] J. Klingele, D. Kaase, J. Hilgert, G. Steinfeld, M.H. Klingele, J. Lach, *J. Chem. Soc., Dalton Trans.* (2010) 4495.
- [5] J. Klingele, D. Kaase, M.H. Klingele, J. Lach, *J. Chem. Soc., Dalton Trans.* (2012) 1397.
- [6] C. Richardson, P.J. Steel, D.M. D'Alessandro, P.C. Junk, F.R. Keene, *J. Chem. Soc., Dalton Trans.* (2002) 2775.
- [7] C.-Y. Niu, B.-L. Wu, X.-F. Zheng, H.-Y. Zhang, H.-W. Hou, Y.-Y. Niu, Z.-J. Li, *Cryst. Growth Des.* 8 (2008) 1566.
- [8] J.-Q. Liu, Y.-Y. Wang, S.R. Batten, H. Sakiyama, D.-Y. Ma, *Inorg. Chem. Commun.* 19 (2012) 27.
- [9] U. Heinemann, R. Tieman, H.W. Dehne, United States Patent Number 5,633, 267, 1997.
- [10] H.Z. Boeini, *J. Iran. Chem. Soc.* 6 (2009) 547.
- [11] F. Bentiss, M. Lebrini, H. Vezin, M. Lagrenée, *Mat. Chem. Phys.* 87 (2004) 18.
- [12] F.H. Allen, *Acta Crystallogr., Sect. B38* (2002) 380 (The Cambridge Structural Database, Version 5.34 of 2012).
- [13] A. Fargašová, I. Ondrejková, Z. Kramarová, Z. Fáberová, *Bioresour. Technol.* 101 (2010) 6410.
- [14] I. Ondrejková, S. Galková, J. Mroziński, J. Kłak, T. Lis, Z. Olejnik, *Inorg. Chim. Acta* 361 (2008) 2483.
- [15] I. Ondrejková, M. Wrzecion, M. Nahorska, J. Mroziński, *Polish J. Chem.* 83 (2009) 1547.
- [16] S. Štefánková, I. Ondrejková, M. Koman, T. Lis, J. Mroziński, M. Wrzecion, *J. Coord. Chem.* 61 (2008) 3895.
- [17] E. König, *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds*, Springer, Berlin, 1966.
- [18] G.M. Sheldrick, *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, 2003.
- [19] A.J.M. Duisenberg, L.M.J. Kroon-Batenburg, A.M.M. Schreurs, *J. Appl. Crystallogr.* 36 (2003) 220.
- [20] Siemens, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA 1990.
- [21] Siemens XSCANS and XEMP, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1994.
- [22] M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 45 (2012) 357.
- [23] G.M. Sheldrick, *Acta Crystallogr., Sect. A64* (2008) 112.
- [24] L.J. Farrugia, *J. Appl. Crystallogr.* 30 (1997) 565.
- [25] C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Crystallogr.* 39 (2006) 453.
- [26] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [27] K.A. Crouse, M. Badri, *J. Sci. Technol.* 1 (1993) 159.
- [28] H. Adkins, W.R. Peterson, *J. Am. Chem. Soc.* 53 (1931) 1512.
- [29] P.C. Patil, D.S. Bhalerao, P.S. Dangate, K.G. Akamanchi, *Tetrahedron Lett.* 50 (2009) 5820.
- [30] Y. Takikawa, K. Shimada, K. Sato, S. Sato, S. Takiyawa, *Bull. Chem. Soc. Jpn.* 58 (1985) 995.
- [31] G.J. Long, G. Galeazzi, U. Russo, G. Valle, S. Calogero, *Inorg. Chem.* 22 (1983) 507.
- [32] M. Wriedt, C. Näther, *Z. Anorg. Allg. Chem.* 1061 (2010) 636.
- [33] X.-J. Zhao, J.-H. Guo, M. Du, *Acta Crystallogr., Sect. E61* (2005) m913.
- [34] R.L. Carlin, *Magnetochemistry*, Springer, Berlin, 1986.
- [35] D.V. Behereand, S. Mitra, *Inorg. Chem.* 19 (1980) 992.
- [36] J.L. Manson, A.M. Arif, J.S. Miller, *J. Mater. Chem.* 9 (1999) 979.
- [37] J. Samuel Smart, *Effective Field Theories of Magnetism*, W.B. Saunders Comp., Philadelphia and London, 1966.
- [38] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds; Part A: Theory and Applications in Inorganic Chemistry*, Wiley, 2009.