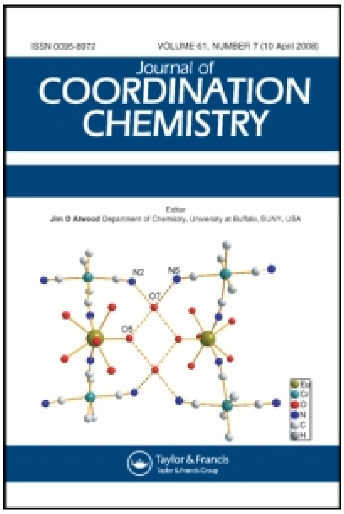

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Physical properties of a new iron(III) complex, $[3\text{-pmH}\bullet 3\text{-pm}][Fe(NCS)_4(3\text{-pm})_2]$

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The iron(III) compound of formula $[3\text{-pmH}\cdot 3\text{-pm}][Fe(NCS)_4(3\text{-pm})_2]$ (3-pm = 3-(hydroxymethyl)pyridine) has been prepared by reaction between iron(III) thiocyanate and 3-(hydroxymethyl)pyridine in ethanol. The characterization was based on elemental analysis, infrared spectra and magnetic measurements. Single crystal X-ray diffraction methods show the monoclinic $P2(1)/c$ space group with unit cell parameters: $a = 12.295(3)$ Å, $b = 15.854(3)$ Å, $c = 16.880(3)$ Å, $\beta = 100.12(3)^\circ$ and $Z = 4$. The asymmetric unit of the title compound consists of $[3\text{-pmH}\cdot 3\text{-pm}]^+$ and $[Fe(NCS)_4(3\text{-pm})_2]^-$ held together by ionic interaction and a hydrogen bond interaction (O(68)–H(68) $\cdots$ O(78)). The central metal ion is octahedrally coordinated by six nitrogens, four from NCS^- form the equatorial plane and two from two 3-(hydroxymethyl)pyridines occupy axial positions. Magnetic susceptibility data in the temperature range 1.8–300 K show that iron(III) is high-spin $S = 5/2(^5T_{2g})$. Structural parameters and IR spectra of similar complexes are compared and discussed.

Keywords: Iron(III) thiocyanato-complexes; 3-(Hydroxymethyl)pyridine; Thiocyanate; Crystal structure; Spectra; Magnetism

1. Introduction

Iron thiocyanato-complexes have been extensively investigated and the relationships between the structure, reactivity, catalytic and biochemical activity have major importance [1, 2]. In coordination compounds a linear thiocyanate group can act as anion NCS^- or ligand; thiocyanato ligand possesses good coordination ability and various bonding possibilities, coordinating unidentate through sulphur (usually to second- and third-row transition metals) or nitrogen (first-row transition metals), and as a bridging ligand through both S and N [3, 4].

We prepared and characterized iron(III) thiocyanate and 3-(hydroxymethyl)pyridine. The crystal structure analysis confirms that the asymmetric unit of the compound is built from cation $[3\text{-pmH}\cdot 3\text{-pm}]^+$ and anion $[Fe(NCS)_4(3\text{-pm})_2]^-$ held together by ionic interaction and an additional hydrogen bond (O(68)–H(68) $\cdots$ O(78)).

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The cation [3-pmH · 3-pm]$^+$ consists of one 3-pm and one protonated 3-pm (3-pmH) linked by a (N(7)–H(7) ··· N(8)) hydrogen bond. For protonated 3-pmH, formation of hydrogen bonds is characteristic. One crystal structure of salt with 3-(hydroxymethyl)-pyridinium and 1,1′-binaphthyl-8,8′-dicarboxylic acid, where amide H atom of [3-pmH]$^+$ cations and O atom of anions of carboxylic acids are interconnected through N–H ··· O hydrogen bonds [5]. There is also a N–H ··· Cl hydrogen bond between the amide H atom of [3-pmH]$^+$ and Cl$^-$ in 3-(hydroxymethyl)pyridinium hydrochloride [6].

This article is a continuation of our reported studies on spectral and thermal properties of Fe(III) complexes with derivatives of pyridine [7–9]. Here we describe synthesis, spectral and magnetic properties as well as the crystal and molecular structure of the new iron(III) coordination compound [3-pmH · 3-pm][Fe(NCS)$_4$(3-pm)$_2$] containing thiocyanate groups and 3-(hydroxymethyl)pyridine as ligands in the anion. (Note: In the literature many synonyms for 3-(hydroxymethyl)pyridine occur; e.g. ronicol, 3-pyridinyl methanol, 3-pyridinemethanol, pyridine-3-carbinol, beta-pyridylcarbinol, beta-pyridi necarbinol, pyridyl-3-methanol, roniacol, pyridyl-3-carbinol, 3-pyridylcarbinol).

2. Experimental

2.1. *Reagents*

Ethanol was purified before use by standard methods. All other chemicals were purchased commercially and used without further purification.

2.2. *Preparation of [3-pmH • 3-pm][Fe(NCS)$_4$(3-pm)$_2$]*

First ethanol solutions of Fe(NCS)$_3$ were prepared by mixing ethanol solution of FeCl$_3$ · 6H$_2$O with ethanol solution of KSCN in molar ratio 1 : 3. The resulting mixture was chilled and the insoluble KCl formed during the reaction was filtered off. The prepared ethanol solution (30 cm^3) of iron(III) thiocyanate (2 mmol) and ethanol solution (5 cm^3) of 3-(hydroxymethyl)pyridine (0.6 cm^3, 6 mmol) were mixed and stirred for 15 min at ambient temperature. Then the solution was diluted with ethanol to 300 cm^3. The diluted solution was left standing for several days, which led to formation of red crystals. Anal. Calcd for [3-pmH · 3-pm][Fe(NCS)$_4$(3-pm)$_2$] (%): C, 45.77; H, 4.51; N, 13.94; Fe, 9.26. Found: C, 45.42; H, 3.95; N, 14.39; Fe, 9.63.

2.3. *Crystallographic studies*

All single crystal X-ray experiments were performed on a KUMA KM4 CCD κ-geometry diffractometer [graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å); ω scans] equipped with an Oxford Cryosystems open flow cryostat. One crystal specimen of dimension $0.20 \times 0.25 \times 0.35$ mm^3 was used for the 100 K data sets. Data collection and cell refinement were carried out using Kuma KM4 diffractometer software [10]. Intensity data were corrected for Lorentz and polarization factors. The structure was solved by the heavy atom method with SHELXS-86 [11] and subsequent Fourier synthesis using SHELXL-97. Geometrical analysis was performed using SHELXL-97 [12]. Details of the crystal parameters, data collection and refinement are listed in table 1 and selected bond distances and angles are given in table 2. Relevant hydrogen bonds and angles are summarized in table 3.

2.4. *Other measurements*

Elemental analyses (carbon, hydrogen, sulphur and nitrogen) were carried out on a CHNSO FlashEA 1112 (ThermoFinnigan) elemental analyzer. The Fe content was determined chelatometrically with Chelaton 3 using sulphosalicylic acid.

Table 1. Crystal data and structure refinement for [3-pmH·3-pm][Fe(NCS)$_4$(3-pm)$_2$] (Å and °).

Empirical formula	$C_{28}H_{29}FeN_8O_4S_4$
Formula weight	725.68
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cells and dimensions (Å, °)	
a	12.295(3)
b	15.854(3)
c	16.880(4)
β	100.12(3)
V (Å^3)	3239.1(1)
Z	4
D_{Calcd} (Mg m^{-3})	1.488
Absorption coefficient (mm^{-1})	0.771
$F(000)$	1500
Crystal size (mm^3)	$0.2 \times 0.25 \times 0.35$
Theta range for data collection (°)	3.21 to 30.06
Limiting indices	$-17 \le h \le 17$, $-22 \le k \le 22$, $-23 \le l \le 23$
Reflections collected/unique	57247/9456 [$R_{(\mathrm{int})} = 0.0814$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9456/8/470
Goodness-of-fit on F^2	1.125
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0606$, $wR_2 = 0.0919$
R indices (all data)	$R_1 = 0.1146$, $wR_2 = 0.1062$

Table 2. Selected bond lenghts (Å) and angles (°) for [3-pmH·3-pm][Fe(NCS)$_4$(3-pm)$_2$].

Fe–N(1)	2.037(2)	Fe–N(6)	2.152(2)
Fe–N(2)	2.026(2)	N(7)–H(7)	1.00(4)
Fe–N(3)	2.031(2)	H(68)–O(68)	0.860(2)
Fe–N(4)	2.047(2)	O(58)–H(58)	0.860(2)
Fe–N(5)	2.155(2)	O(88)–H(88)	0.860(2)
N(2)–Fe–N(1)	90.37(9)	N(2)–Fe–N(4)	90.83(1)
N(3)–Fe–N(1)	90.07(9)	N(3)–Fe–N(4)	88.74(1)
N(1)–Fe–N(4)	178.71(8)	N(5)–Fe–N(6)	178.15(1)
N(1)–Fe–N(5)	91.22(8)	N(5)–Fe–N(1)	91.22(1)
N(1)–Fe–N(6)	89.87(8)	N(6)–Fe–N(4)	89.65(1)
N(2)–Fe–N(3)	178.94(8)	N(6)–Fe–N(2)	89.63(1)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z$.

Table 3. Parameters in (Å) and (°) of hydrogen bonds for [3-pmH·3-pm][Fe(NCS)$_4$(3-pm)$_2$].

D–H···A	d(D–H)	d(H···A)	d(D···A)	d(D···A)
N(7)–H(7)···N(8)	1.00(4)	1.68(4)	2.675(3)	175.4(4)
O(68)–H(68)···O(78)	0.860(2)	1.86(1)	2.710(3)	170(6)

Infrared spectra in the region 4000–100 cm^{-1} were measured with a Nicolet Magna 750 IR spectrometer using KBr pellets from 4000–400 cm^{-1} and polyethylene pellets from 400–100 cm^{-1}. Electronic spectra (190–1100 nm) of the complex were measured in ethanol at room temperature with a SPECORD 200 (Carl Zeiss Jena) spectrophotometer.

The DSC studies were carried out on a Perkin–Elmer DSC-7 calorimeter with cooling/heating rates of 10 K min^{-1}. The measurements were performed between 120 K and 300 K. Magnetic susceptibility data for powdered samples were collected in the temperature range 1.8–300 K with a Quantum Design SQUID Magnetometer MPMS XL-5. The superconducting magnet was generally operated at a field strength ranging from 0 to 5 T. Measurements of compound were made at magnetic field 0.5 T. The SQUID magnetometer was calibrated with a palladium rod sample. Corrections are based on subtracting the sample-holder signal and contribution χ_D estimated from the Pascal constants and equal -421×10^{-6} cm^3 mol^{-1}. The effective magnetic moment was calculated from the equation, $\mu_{\text{eff}} = 2.83(\chi_M T)^{1/2}$(B.M.), where χ_M is the molar magnetic susceptibility.

3. Results and discussion

Reaction of 3-pm with iron(III) thiocyanate in ethanol led to [3-pmH · 3-pm][Fe(NCS)$_4$(3-pm)$_2$] (3-pm = 3-(hydroxymethyl)pyridine) as a red, air-stable crystalline product.

An ORTEP diagram of [3-pmH · 3-pm][Fe(NCS)$_4$(3-pm)$_2$] is shown in figure 1 and a view of two [3-pmH · 3-pm]$^+$ cations and two [Fe(NCS)$_4$(3-pm)$_2$]$^-$ anions illustrating the hydrogen-bonding network is presented in figure 2. The asymmetric unit is built from [3-pmH · 3-pm]$^+$ and [Fe(NCS)$_4$(3-pm)$_2$]$^-$ held together by ionic interaction and a hydrogen bond interaction (O(68)–H(68) ··· O(78)). The hydrogen bond interaction is formed by H atom of –CH$_2$OH in the anion and O of –CH$_2$OH group in the cation. Cation [3-pmH · 3-pm]$^+$ consists of one 3-pm and one protonated 3-pm (3-pmH) linked by a hydrogen bond, N(7)–H(7) ··· N(8). Analogously protonated 4-methylpyridine (pic), i.e. 4-methylpyridinium (picH) serves as a cation in a Fe(II) complex (picH)$_2$[Fe(NCS)$_4$(pic)$_2$] · 2pic [13].

The Fe(III) in the anion of [3-pmH · 3-pm][Fe(NCS)$_4$(3-pm)$_2$] is octahedrally coordinated by six nitrogens; four from NCS$^-$ forming the equatorial plane and two from two 3-pyridylmethanols occupying axial positions. The Fe–N (of NCS) distances are slightly shorter (av. 2.0353(2) Å) than the Fe–N (of 3-pyridylmethanol) distances (av. 2.154(2) Å), hence FeN$_6$ octahedron is axially distorted. Similar distortion of FeN$_6$ octahedron was observed for (bdhtip)[Fe(NCS)$_4$(isoq)$_2$] [where isoq is isoquinoline; bdhtip is 2,5-*bis*(1,3-dithiolato-2-ylidene)1,3,4,6-tetrathiapentalene(1+)] [14] and for

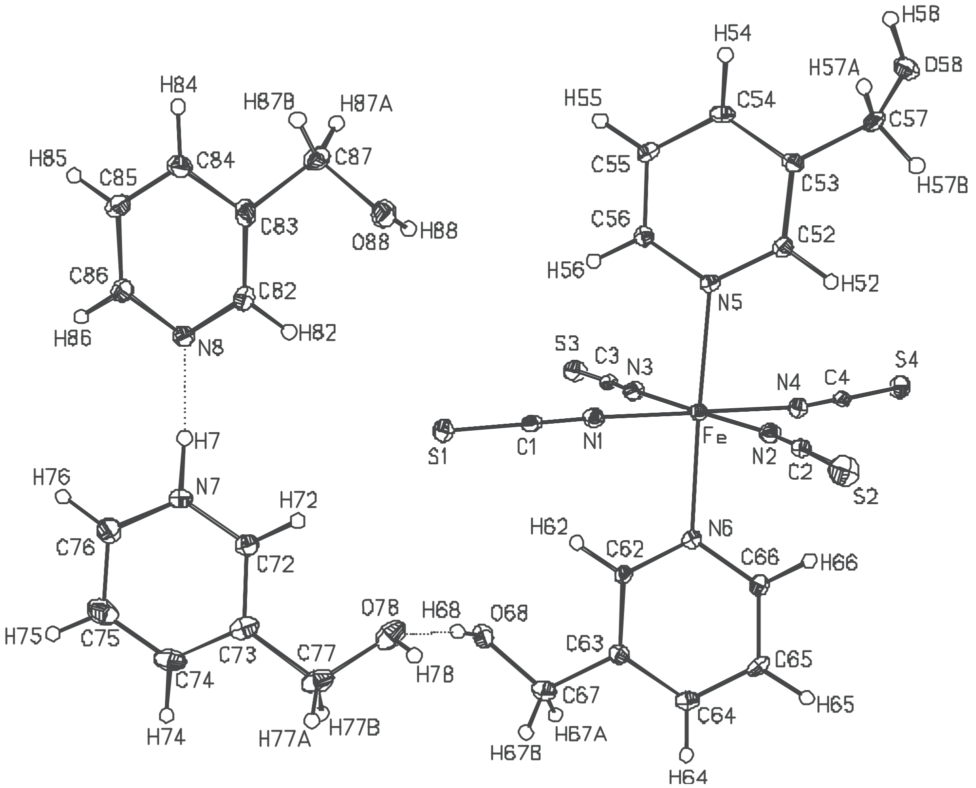

Figure 1. An ORTEP plot of [3-pmH·3-pm][Fe(NCS)$_4$(3-pm)$_2$].

(picH)$_2$[Fe(NCS)$_4$(pic)$_2$] · 2pic [13]. The Fe–N(NCS) distances of 2.026(2)–2.047(2) Å in our compound are similar to that of high spin ferric coordination compounds, (bdhtip)[Fe(NCS)$_4$(isoq)$_2$] (2.025(3) and 2.037(3) Å), [Fe(NCS)(oep)(py)] (2.031(2) Å) [15], [Fe(NCS)(py)(smts)] (2.026(4) Å) [16] and [Fe(NCS)$_3$(OPPh$_3$)$_3$] (2.010(3)–2.032(3) Å) [2] (where oep is octaethylporphyrinate(2-), smts is S-methylisothiosemicarbazide(2-), py is pyridine and OPPh$_3$ is triphenylphosphine oxide).

The IR spectrum shows (table 4) the stretching vibrations ν(CN), ν(CS) and δ(NCS) occur in the regions accepted for terminally N-bonded thiocyanate. It has been suggested [17, 18] for Fe—NCS complexes, the C—N stretch lies below 2100 cm^{-1}, the C—S stretch in the 780–860 cm^{-1} region and the NCS stretch in the 460–490 cm^{-1} region. Another band at about 300 cm^{-1} may be assigned as ν(Fe—N) of N-bonded NCS [19]. Bands in the range 1593–1615 cm^{-1} in the title compound suggest bond formation of the metal with the nitrogen atom of pyridine, increasing the dipolar contribution of C=N$^+$ in the heterocyclic ring.

The electronic spectrum exhibits one very broad and symmetrical band at $\lambda = 506$ nm, attributed to ligand-to-metal charge transfer (LMCT) N(2p) → Fe(3d), and ultraviolet bands in the region 210–290 and 300–360 nm to the intraligand transitions IL($\pi \rightarrow \pi^*$) localized predominantly on the pyridine ring and C=N fragments of the ligands. The band positions are similar for Fe(III) complexes with derivatives of pyridine [20].

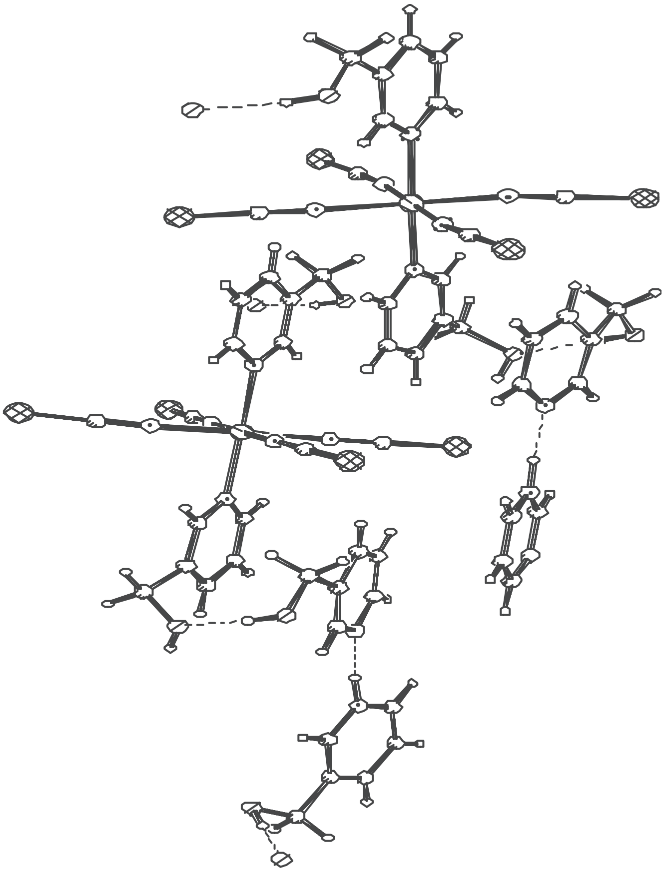

Figure 2. A view of two $[3\text{-pmH}\cdot 3\text{-pm}]^+$ cations and two $[Fe(NCS)_4(3\text{-pm})_2]^-$ anions illustrating the hydrogen-bonding.

Table 4. Comparison data on IR spectra (cm^{-1}) for iron(III) isothiocyanato-complexes and KNCS.

Complex	ν(CN)	ν(CS)	δ(NCS)	Ref.
$[3\text{-pmH}\cdot 3\text{-pm}][Fe(NCS)_4(3\text{-pm})_2]$	2094sh 2052vs	829m	484m 476m	This work
[Fe(NCS)(oep)(py)]	2038s	n	n	[14]
[Fe(NCS)(py)(smts)]	2055	n	n	[15]
$(NEt_4)_3[Fe(NCS)_6]$	2098sh 2052s	822w	479m	[21]
$(NMe_4)_3[Fe(NCS)_6]$	2075s 2057s	828w	n	[22]
$[Fe(NCS)_3(OPPh_3)_3]$	2081vs 2041vs	856w	476m	[16]
KNCS	2053s	748	471m 486m	[21]

s = strong, vs = very strong, m = medium, w = weak, sh = shoulder, n = not given.

Magnetic properties of [3-pmH $\cdot$ 3-pm][Fe(NCS)$_4$(3-pm)$_2$] were determined over the temperature range 1.8–300 K. Plot of molar magnetic susceptibility $-\chi_{\mathrm{M}}$ and $\chi_{\mathrm{M}}T$ *versus* temperature $-T$ is shown in figure 3. Magnetic data were fitted using the susceptibility equation (1). To elucidate the significance of exchange between iron ions in the crystal lattice, a molar field correction term has also been included in equation (2),

$$\chi_{\mathrm{M}} = \frac{N\beta^2 g^2}{3kT} S(S+1) \tag{1}$$

$$\chi_{\mathrm{M}}^{\mathrm{corr}} = \frac{\chi_{\mathrm{M}}}{1 - (2zJ'/N\beta^2 g^2) \cdot \chi_{\mathrm{M}}} \tag{2}$$

where N is Avogadro's number, g is the spectroscopic splitting factor, β is the intermolecular exchange parameter and z is the number of nearest Fe(III) magnetic centers. The criterion used for the determination of the best fit was based on minimalization of the sum of squares of the deviation (3).

$$R = \sqrt{\frac{\sum_{i=1}^{n} \left[\left(\chi_{\mathrm{M}}^{\mathrm{exp}}\right)_i - \left(\chi_{\mathrm{M}}^{\mathrm{calc}}\right)_i\right]^2 / \left(\chi_{\mathrm{M}}^{\mathrm{exp}}\right)_i^2}{\sum_{i=1}^{n} 1/\left(\chi_{\mathrm{M}}^{\mathrm{exp}}\right)_i^2}} \tag{3}$$

The best fit parameters: zJ', g and the agreement factor over the temperature range 1.8–300 K give $zJ' = -0.22\,\mathrm{cm}^{-1}$, $g = 1.90$, and $R = 7.24 \times 10^{-4}$. Values of the Curie and Weiss constants determined from the linear relation $\chi_{\mathrm{M}}^{-1} = f(T)$ over the temperature range 50–300 K are $C = 4.15\,\mathrm{cm}^3\,\mathrm{K\,mol}^{-1}$ and $\Theta = -6.37\,\mathrm{K}$. Negative values of the Weiss constant and intermolecular exchange parameter, $-0.2\,\mathrm{cm}^{-1}$, confirm the occurrence of weak antiferromagnetic interactions between iron centers in the crystal lattice. Variation of the magnetization M *versus* magnetic field H at 2 K (figure 4)

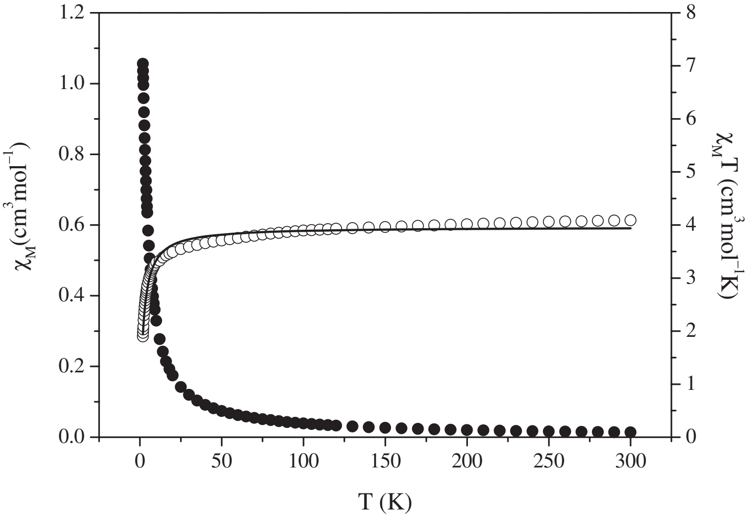

Figure 3. Thermal dependence of χ_{M} (●) and χ_{M}T (○) for [3-pmH·3-pm][Fe(NCS)$_4$(3-pm)$_2$]. The solid line is the calculated curve.

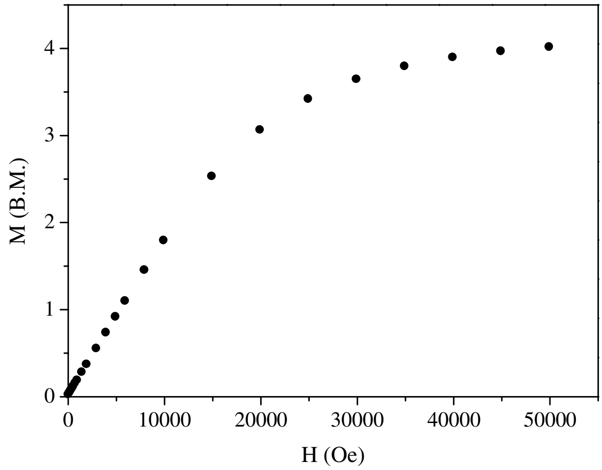

Figure 4. Magnetization *vs* magnetic field for [3-pmH·3-pm][Fe(NCS)$_4$(3-pm)$_2$].

clearly supports the occurrence of a weak magnetic interaction. As magnetic field increases, the *M versus H* curve is linear up to ~1.5 T and afterwards shows a sinusoidal variation up to 5 Tesla with $M = 4.00$ B.M. without saturation [21].

Supplementary data

CCDC-666909 contains the supplementary crystallographic data for this article. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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