An iron(II) incomplete spin-crossover compound: pressure effects and Mössbauer spectroscopy study†

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A one-dimensional iron(II) spin-crossover compound $[Fe(3py\text{-}im)_2(NCS)_2]\cdot 7H_2O$ (**1**) (3py-im = 2,4,5-tris(4-pyridyl)-imidazole) has been solvothermally synthesized and structurally characterized. Compound **1** crystallizes in the monoclinic space group $P2/c$ with $a = 11.9078(2)$, $b = 9.9474(1)$, $c = 17.7290(3)$ and $\beta = 102.361(2)°$ at 105 K. Studies on the variable-temperature magnetic susceptibilities and Mössbauer spectra suggest that compound **1** undergoes incomplete spin transition behaviour. Pressure effects on the transition behaviour have also been investigated, the thermal-induced spin transition becomes more gradual and the critical temperature shifts towards slightly higher temperature range when external pressure increases. However, the spin transition can not be completed by applying external pressure even as high as 0.79 GPa.

Introduction

The search of bistable systems, which are promising materials for applications as memory or display devices,[1] is a great challenge in the field of advanced materials. Undoubtedly, metal–organic compounds with reversible transitions between the low-spin (LS) and high-spin (HS) states, usually triggered by external perturbations, such as heat, pressure and light,[2] are a class of potential candidates. Therefore, synthesis and study of new spin-crossover systems have been a hot topic in recent years. So far, the iron(II) spin-crossover compounds are mostly studied, in which the iron(II) ion usually locates in a $[FeN_6]$ octahedron and the coordination sphere varies along with the spin transitions, for example, the average iron(II)-to-ligand bond length is typically 0.2 Å longer in the HS state.[3] Thus, structural information is essential in identifying spin-crossover behaviours. These structural changes could be transmitted from one metal site to another one through intermolecular interactions (π–π interaction, hydrogen bonding, van der Waals interaction) as well as covalent bonds, and the ability of the crystal lattice to efficiently transmit the structural changes is what defines the cooperativity, which is the most important factor to control the steepness and hysteresis width of the transition. However, the non-covalent interactions (π–π interaction, hydrogen bonding, van der Waals interaction) and the extent of their transmission through the crystal is difficult to control. Kahn *et al.* firstly introduced the idea that strong direct links of the active spin-crossover metal sites through organic ligands could improve cooperativity in polymeric compounds as compared to mononuclear ones,[4] since then syntheses of multi-dimensional spin-crossover compounds with diverse topologies have attracted wide attention.

On the other hand, intermolecular interactions in the spin-crossover compounds, the so-called 'chemical pressure', partially contribute to the coordination field strength and are sensitive to external pressure, which consequently plays an important role in tuning the spin states. For example, a spin transition may occur when pressure is applied on a compound that originally remains in HS state in the whole temperature range.[5] And what is more, enhancing pressure may cause the critical temperature of spin transition shifts to higher temperature range, the slope turns horizontal and/or the incomplete transition becomes complete.[5,6]

Up to now, numerous spin-crossover compounds with 0D to 3D structures and diverse transition behaviours have been reported, in which the widely used ligands are nitrogen-containing ligands, such as triazoles, tetrazoles and pyridyls.[1,2] Nevertheless, among the 1D spin-crossover compounds, the most investigated ligands are the family of Rtrz (4-R-1,2,4-triazole), which triply bridge iron(II) atoms by the nitrogen atoms occupying the 1- and 2-positions and defining a linear chain.[7] Most of these compounds show very abrupt spin transitions close to room temperature and with wide thermal hysteresis, for example, the transition temperatures of $[Fe(NH_2trz)_3][NO_3]_2$[8] and $[Fe(Htrz)_2(trz)]BF_4$[9,10] center at 330 and 344 K, and hysteresis widths reach 35 and 38 K, respectively. It is believed that very strong short-range Fe(II)-ligands-Fe(II) interactions along the chains together with overall long-range interactions are necessary to reproduce these features.

In our efforts to synthesize new spin-crossover compounds, we notice that a rigid ligand, 2,4,5-tris(4-pyridyl)-imidazole (3py-im), possesses three pyridine groups centered on a imidazole core (Scheme 1) that can be viewed as an expanded triazole ligand, and thus may be a good candidate to achieve one-dimensional spin-crossover compounds. However, the reaction of 3py-im with Fe(II) salts did not result in a triply bridged chain structure, instead a doubly bridged chain was obtained when $Fe(SCN)_2$

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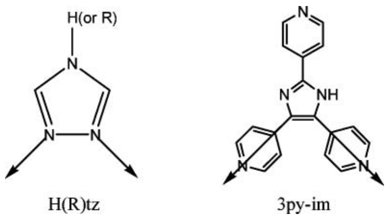

Scheme 1

was used. Here, we report the synthesis, crystal structure and magnetic properties of the new 1D spin-crossover compound, namely [Fe(3py-im)$_2$(NCS)$_2$]·7H$_2$O(**1**). Studies of the magnetic susceptibilities and Mössbauer spectra reveal that compound **1** exhibits incomplete spin transition behaviour, the pressure effect on the spin transition behaviour has also been investigated.

Experimental

All chemicals, unless otherwise stated, were commercially available and used as received. The ligand 3py-im·H$_2$O (2,4,5-tris(4-pyridyl)-imidazole) was prepared by literature method.[11] Solvents were analytically pure and were deoxygenated prior to use. IR spectra were collected on KBr pellets with a Nicolet Avatar 360 FT-IR spectrophotometer under ambient temperature. Elemental analyses were performed with a Vario EL III analyzer.

Synthesis of [Fe(3py-im)$_2$(NCS)$_2$]·7H$_2$O (1)

Fe(ClO$_4$)$_2$·6H$_2$O (364 mg, 1.0 mmol) and ascorbic acid (30 mg) were slowly added to a 10 mL ethanol solution of KSCN (196 mg, 2.0 mmol) with stirring, the resulting solution was filtered to discard the white precipitate KClO$_4$. Then 1 mL filtrate and 9 mL aqueous solution of 3py-im·H$_2$O (32 mg, 0.1 mmol) were mixed and stirred for 1 h, the solution was then sealed in a 23 mL Teflon-lined autoclave and heated at 150 °C for 36 h to give light-red block crystals of **1**, which were collected by filtration, washed with ethanol and dried in air. The amount of lattice water molecules in the unit cell is estimated from elemental analysis results.

IR (ν/cm^{-1}): 3415 (br), 2364 (w), 2080 (s), 1609 (s), 1508 (m), 1489 (m), 1426 (m), 1383 (m), 1216 (m), 1064 (m), 1012 (m), 838 (m), 749 (w), 690 (w), 615 (w), 538 (w). CHNS calcd for $C_{38}H_{40}N_{12}O_7S_2Fe$ (found): C 50.90% (50.91%); N 18.74% (18.49%); H 4.50% (4.13%); S 7.15% (7.26%).

Caution! Perchlorate salts are potentially explosive, only small quantities should be used and handled with care.

Magnetic data

Magnetic susceptibility measurements were carried out at 1 K min^{-1} sweeping rate in the temperature range of 2-300 K on Quantum Design MPMS XL-7 SQUID magnetometer equipped with 7 T magnet. The magnetic measurements under pressure were performed by using a hydrostatic pressure cell, which is specially designed for the MPMS set up and made of hardened beryllium bronze with silicon oil as pressure transmitting medium. The applied pressure was measured by using the pressure dependence of the superconducting transition temperature of a built-in pressure sensor made of high-purity tin. Magnetic data were calibrated with the sample holder and the diamagnetic contributions.

Table 1 Crystallographic data of **1** at 105 K

Formula	$C_{38}H_{40}N_{12}O_7S_2Fe$
M	896.78
Crystal system	Monoclinic
Space group	$P2/c$
a/Å	11.9078(2)
b/Å	9.9474 (1)
c/Å	17.7290(3)
β/°	102.361(2)
V/Å^3	2051.35(5)
Z	2
D_c/g cm^{-3}	1.452
λ/Å	1.54178
μ/mm^{-1}	4.445
F(000)	932
θ range/°	3.80–62.22
Data collected/unique	9679/3240
Parameters	240
S	1.120
R_1($I > 2\sigma(I)$)	0.0641
wR_2 ($I > 2\sigma(I)$)	0.1890

Note: the solvent water molecules are excluded and the data were calculated with PLATON SQUEEZE. The S1 atom is highly disordered. Checkcif reports 301 Å^3 voids, which is attributed to the exclusion of unidentified solvent water molecules. Checkcif also reports a lower than usual U(eq) value for C19. This is probably due to reason that it is able to move about its position slightly.

X-Ray crystallography

X-Ray diffraction data at 105 K were collected on an Oxford diffractometer with the Cu Kα radiation (λ = 1.54178 Å). The structures were solved by direct methods and refined by the full-matrix least-squares calculations based on F^2 using the SHELXL97 software package.[12] All non-hydrogen atoms were refined anisotropically. Solvent water molecules were excluded and the data were calculated by using PLATON SQUEEZE software.[13]

Results and discussion

Crystal structure

Single-crystal X-ray diffraction data of **1** were collected at 105 K and shown in Table 1. Structural analysis reveals that the asymmetric unit contains one 3py-im ligand, one Fe(II) ion (half occupied), one thiocyanate ion and three or four solvated water molecules. The slightly distorted coordination sphere of the Fe(II) atom is formed by six nitrogen atoms, four of which are pyridine nitrogen atoms from different 3py-im ligands and the other two are from two thiocyanate ions (Fig. 1). The 3py-im ligands use their two-third pyridine groups to link adjacent Fe(II) ions into a chain structure with the residual pyridine groups uncoordinated, the thiocyanate ions are coordinated in *trans* positions that are almost perpendicular to the chain plane, as shown in Fig. 2. Selected bond lengths and angles are presented in Table 2.

At 105 K, the Fe–N bond distances are in the range of 1.989 to 2.099 Å (average 2.062 Å), the *cis* N–Fe–N bond angles are in the range 88.6 to 91.5° and Σ equals to 15.1°, indicating stronger crystal field and thus LS state (Σ is defined as the sum of the deviations from 90° of the *cis* N–Fe–N angles).[14]

The three-dimensional supramolecular structure of **1** is similar to its Cd analogue (Fig. 3).[15] The polymeric chains run along

Table 2 Selected bond lengths (Å) and angles (°) for **1** at 105 K

Fe1–N1	2.099(3)	N6–Fe1–N1	89.4(1)
Fe1–N2B	2.099(3)	N2B–Fe1–N1	177.9(1)
Fe1–N6	1.989(4)	N2C–Fe1–N1	88.7(1)
N6–Fe1–N6A	179.9(2)	N6A–Fe1–N1	90.6(1)
N6–Fe1–N2B	91.5(2)	N1–Fe1–N1A	91.3(2)
N6A–Fe1–N2B	88.6(1)	N2B–Fe1–N2C	91.2(2)

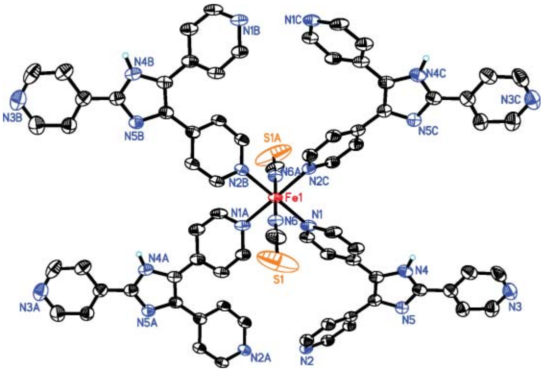

Fig. 1 Perspective view of the coordination environment of the iron(II) atom in **1**. Solvent water molecules were omitted for clarity. Symmetry codes: (A) $-x + 1, y, -z + 3/2$; (B) $-x + 1, y - 1, -z + 3/2$; (C) $x, y - 1, z$.

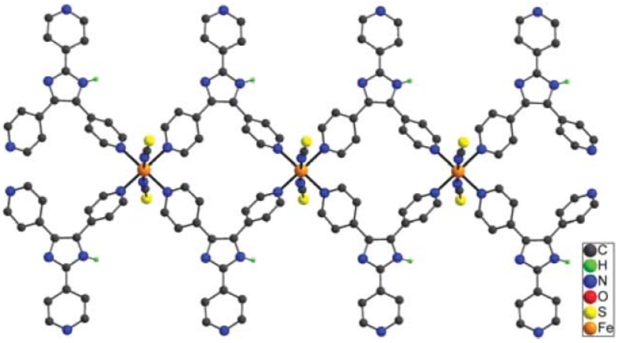

Fig. 2 Perspective view of the polymeric chain structure of **1**.

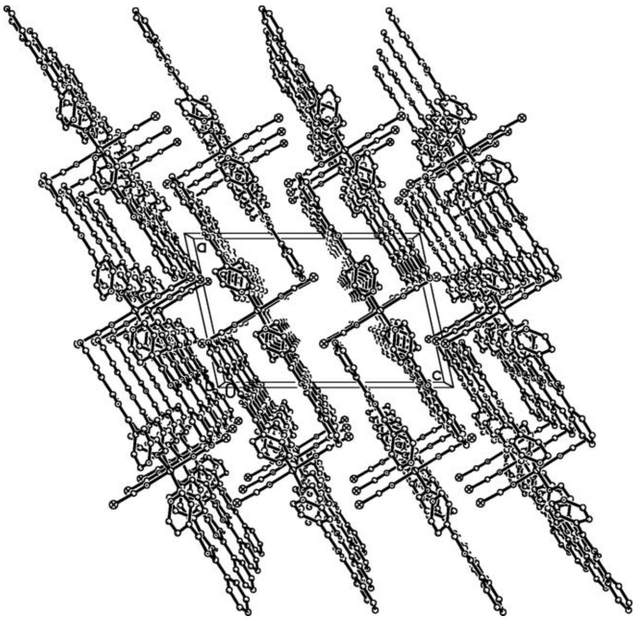

Fig. 3 View of the 3D structure of compound **1** along the *b* axis.

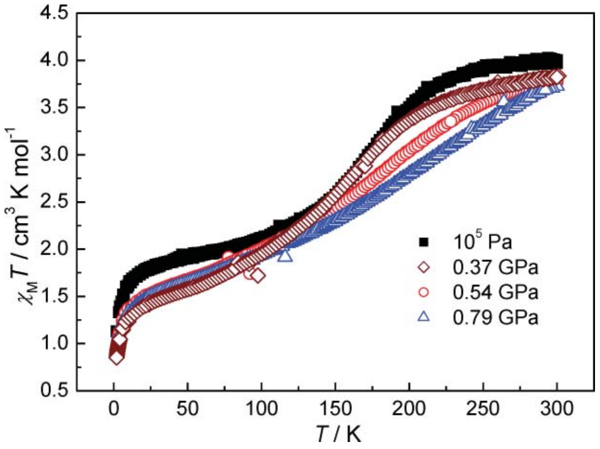

Fig. 4 $\chi_M T$ *vs.* T plots for **1** at a field of 5 kOe under variable pressures.

the *b* axis to form sheets, which then are packed in the *ac* plane alternately to form layers possessing the thickness of two sheets. At 105 K, the shortest inter-chain Fe–Fe distance is 11.908 Å and that of intra-chain is 9.947 Å, respectively.

Magnetic properties

The $\chi_M T$ *vs.* T plots of compound **1** under various pressures are represented in Fig. 4. Under atmospheric pressure (black blocks), the $\chi_M T$ value is 3.97 cm^3 K mol^{-1} at room temperature, higher than the expected one for a spin-only high-spin iron(II) ion, which is likely the results of an orbital contribution to the paramagnetic susceptibility. $\chi_M T$ value decreases gradually on cooling to 250 K and then descends more rapidly to attain a value of 2.11 cm^3 K mol^{-1} at 100 K. Between this temperature and 20 K (1.78 cm^3 K mol^{-1}) there exists an inclined plateau. As temperature further decreases, it decreases abruptly reaching a value of 1.13 cm^3 K mol^{-1} at 2 K. The plots between 300 and 100 K evidently indicate the occurrence of a continuous and thermally dependent incomplete spin transition, the critical temperature of this incomplete spin transition is 172 K. The sudden decrease of $\chi_M T$ from 20 to 2 K is most likely due to the zero-field splitting effects of the remaining high-spin iron(II) ions. Undoubtedly, especially at very low temperature, intramolecular antiferromagnetic exchange coupling between the iron(II) ions mediated by the bridging ligands may also play an important role in causing the sudden decrease, and which may be the reason that there is a subtle disagreement between the variable temperature magnetic susceptibility data and the amount of low-spin isomer predicted at low temperature from the Mössbauer spectra (see below). This situation of incomplete spin transition and zero-field splitting was also observed in a 3D spin-crossover iron(II)-N(CN)$_2$ compound[5b] and a pressure-induced spin-crossover dinuclear iron(II) compound.[16] It is well-known that the incomplete transition is a consequence of low temperature at which the rate of the process HS → LS becomes slow enough to quench the spin transition.

Mössbauer spectroscopy

In order to further confirm the incomplete spin-crossover properties of compound **1**, ^{57}Fe Mössbauer spectra were measured

Table 3 Parameters of Mössbauer spectra for compound **1**[a]

T/K	δ/mm s^{-1}	ΔE_Q/mm s^{-1}	Γ/mm s^{-1}	Relative area (%)	States
300 K	0.87	2.19	0.44	93.1	HS
	0.34		0.58	6.9	LS
200 K	0.96	2.50	0.58	73.5	HS
	0.34		0.58	26.5	LS
100 K	1.01	2.83	0.68	63.5	HS
	0.33		0.58	36.5	LS
25 K	1.01	2.84	0.62	62.7	HS
	0.31		0.48	37.3	LS
9 K	0.99	2.89	0.56	58.4	HS
	0.32		0.48	41.6	LS

[a] δ: isomer shift (with reference to metallic iron at 293 K), ΔE_Q: quadrupole splitting, Γ: half-height width.

and shown in Fig. 5. The hyperfine parameters were obtained by least-square fitting to the Lorentzian lines. The values of main Mössbauer parameters over the whole temperature range are listed in Table 3.

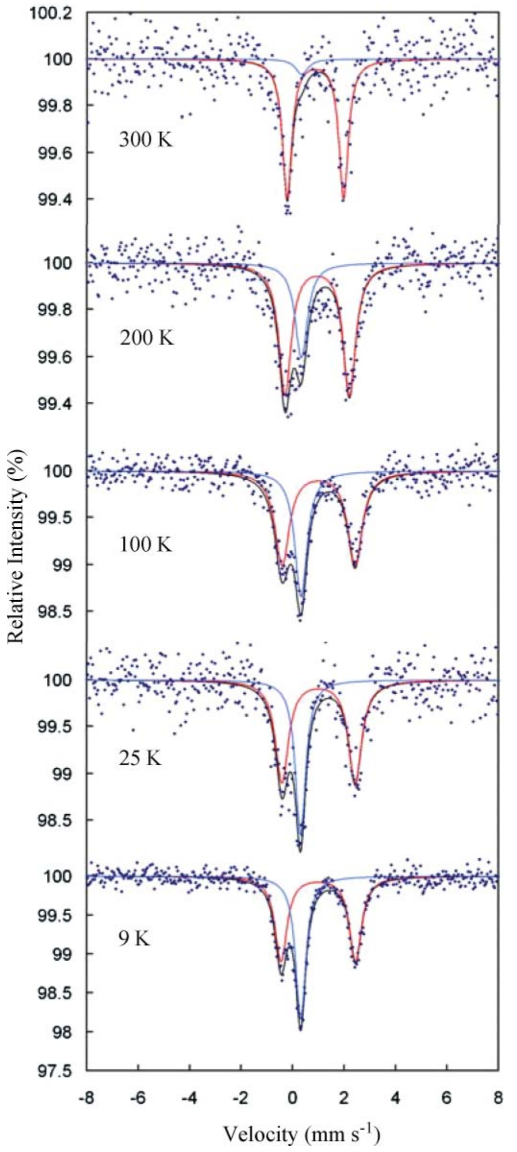

Fig. 5 Mössbauer spectra of [Fe(3py-im)$_2$(NCS)$_2$]·7H$_2$O.

As shown in the crystal structure, all Fe(II) centers in **1** are equivalent with a [FeN$_6$] octahedral geometry, so there are only two doublets at 300 K. The main doublet (red line) can be characterized by the quadrupole splitting with $\Delta E_Q = 2.19$ mm s^{-1} and isomer shift $\delta = 0.87$ mm s^{-1}, corresponding to the high-spin state of Fe(II) ($S = 2$) state.[17] The presence of the quadrupole splitting in this case stems from asymmetric electronic distribution around the Fe nucleus and is connected to the lattice distortions to much lesser extent. A poorly resolved doublet (blue line) of relative area 6.9% appears with isomer shift value of 0.34 mm s^{-1} is assigned to low-spin Fe(II) ($S = 0$), indicating the existence of low-spin population even at room temperature. On lowering the temperature, the resonance lines start to broaden and the intensity of the LS doublet increases at the expense of HS doublet, confirming thermally induced HS → LS conversion for a single Fe(II) site. At 100 K, the LS fraction reaches a value of 36.5% (area), slightly lower than that estimated from magnetic susceptibility. When the temperature decreases to 9 K, the magnitude of LS fraction increases a little and reaches a value of 41.6%, which confirms the gradual and incomplete nature of the spin transition as found through the magnetic susceptibilities.

Pressure effect

We anticipated that the spin transition in compound **1** would be sensitive to increased pressure, which is the case for a large number of spin-crossover complexes that have been studied in this regard.[5,6,16] First of all, at room temperature the high-spin populations under any pressure are almost the same as that under atmospheric pressure, which is unexpected because in most spin-crossover compounds additional pressure favours low-spin states and reduces high-spin populations.[18] Secondly, the spin-crossover incompleteness maintains intact even at 0.79 GPa and the percentage of high-spin state deduced from the susceptibility values at 60 K is about 58%. Finally, primary changes under pressure mainly arise in the high temperature range (160–260 K), where the critical temperature shifts to higher temperature range with increasing pressure, and the slopes turn to more gradual. It should also be mentioned that the kinetic effect responsible for the incomplete HS → LS conversion below 70 K still exerts its influence and does not alter under any applied pressure.

Generally, flexible ligands can distort to compensate the decrease of the Fe–N distances and thus show notable pressure effects on the spin transition behaviour. In contrast, the 3py-im ligand is rigid, which is hard to distort to compensate and consequently the spin transition behaviour is not highly sensitive to the application of pressure.

Conclusions

A one-dimensional iron(II) compound has been synthesized. Both variable-temperature magnetic susceptibilities and Mössbauer spectra reveal incomplete spin-crossover property in the temperature range 2–300 K. Unexpectedly, this incomplete spin transition behaviour is not highly sensitive to the application of pressure, which may be due to the rigid one-dimensional structure that is hardly affected by pressure and/or due to the lack of "pressure-transmittable" inter-chain interactions.

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