

This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Mémoire / Full paper

Above room temperature spin transition in a series of iron(II) bis(pyrazolyl)pyridine compounds

N.T. Madhu, Ivan Salitros, Frank Schramm, Svetlana Klyatskaya,
Olaf Fuhr, Mario Ruben*

Institute of Nanotechnology, Forschungszentrum Karlsruhe GmbH, P.O. Box 3640, 76012 Karlsruhe, Germany

Received 8 April 2008; accepted after revision 30 June 2008

Available online 22 August 2008

Abstract

We report on the synthesis of a series of iron(II) compounds of the general composition $[\text{Fe}^{\text{II}}(\text{L})_2](\text{ClO}_4)_2 \cdot n\text{CH}_3\text{CN}$ (where **L** is 4-iodo-2,6-bis(pyrazol-1-yl)pyridine (**L**¹), 4-(4'-hydroxyphenyl)-2,6-bis(pyrazol-1-yl)-pyridine (**L**²), 4-(4'-trimethylsilylethynyl)-2,6-bis(pyrazol-1-yl)pyridine (**L**³), and 4-ethynyl-2,6-bis(pyrazol-1-yl)pyridine (**L**⁴)). The compounds $[\text{Fe}^{\text{II}}(\text{L})_2](\text{ClO}_4)_2 \cdot n\text{CH}_3\text{CN}$ (**1**–**4**; $n = 0$ for **1**, **2**, and **4**; $n = 2$ for **3**) were characterised by single crystal X-ray diffraction studies, MALDI-TOF mass spectrometry and elemental analysis. Temperature-dependent magnetic studies reveal different types of spin transition behaviour. Compounds $[\text{Fe}^{\text{II}}(\text{L}^1)_2](\text{ClO}_4)_2$ (**1**) and $[\text{Fe}^{\text{II}}(\text{L}^2)_2](\text{ClO}_4)_2$ (**2**) show above or near room temperature spin transition with $T_{1/2} = 333$ and 281 K. The investigations of compound $[\text{Fe}^{\text{II}}(\text{L}^3)_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$ (**3**) elucidate a more complex magnetic behaviour with spin transition of half of the involved iron(II) centres at temperatures above 140 K and ferromagnetic exchange coupling of the remaining high-spin centres below 125 K. Finally, compound $[\text{Fe}^{\text{II}}(\text{L}^4)_2](\text{ClO}_4)_2$ (**4**) is completely blocked in the diamagnetic low-spin state in the temperature range from 5 to 380 K. **To cite this article: N.T. Madhu et al., C. R. Chimie 11 (2008).**

© 2008 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Keywords: Iron(II); Bispyrazolylpyridine ligands; Spin transition

1. Introduction

The design of molecules which could be utilised for information processing and data storage is one of the main challenges in present material science. Molecules suitable for information technology applications should ideally exhibit bistability, which may be defined as a property of a molecular system that allows it to exist in two different electronic states over a certain range of external perturbation. Among potentially

suitable classes of molecules, spin transition (ST) iron(II) complexes have been studied extensively, in particular because of their well-differentiable magnetic signal discriminating the diamagnetic low-spin (LS; $S = 0$) and the paramagnetic high-spin (HS; $S = 2$) states. The ST event can be driven by external triggers such as temperature, pressure or light irradiation [1]; external parameters which are of interest for applications. Thus, iron(II) ST compounds possessing high transition temperatures ($T_{1/2}$), ideally around room temperature, have drawn much attention due to their potential as active components in molecular devices [2,3]. The potential of ST systems for data storage

* Corresponding author.

E-mail address: Mario.Ruben@int.fzk.de (M. Ruben).

has been emphasised by several reports [2]. For successful implementation of ST compounds into information processing devices, a thermally induced spin state transition should occur (i) at or around room temperature, (ii) with a high degree of abruptness and (iii) with a large magnetic hysteresis loop [2]. Recently, it has been shown how targeted substitution in the 4-position of the bispyrazolylpyridine motif can steer the spin transition of the respective Fe(II) complexes to regions above room temperature exhibiting a good degree of steepness [4] and acceptable widths of the magnetic hysteresis loops [5].

In continuation of this work and in view of the continuing interest in room temperature ST in iron(II) compounds [4–7], we report herein on the synthesis, structural and magnetic characterisation of a series of four iron(II) bispyrazolylpyridine compounds of the general formula $[\text{Fe}^{\text{II}}(\text{L}^{1-4})_2](\text{ClO}_4)_2 \cdot n\text{CH}_3\text{CN}$ (**1–4**) with **L** being 4-iodo-2,6-bis(pyrazol-1-yl)pyridine (**L**¹), 4-(4'-hydroxyphenyl)-2,6-bis(pyrazol-1-yl)-pyridine (**L**²), 4-(4'-trimethylsilylethynyl)-2,6-bis(pyrazol-1-yl)pyridine (**L**³) and 4-ethynyl-2,6-bis(pyrazol-1-yl)pyridine (**L**⁴); $n = 0$ for **1**, **2**, and **4**; $n = 2$ for **3**.

2. Experimental

2.1. General

All chemicals were purchased and used as received. The solvents diisopropyl ether, acetonitrile, hexane, ethyl acetate were used without any further purification. ¹H and ¹³C NMR spectra were recorded in a Bruker DPX 300 spectrometer with solvent protons as an internal standard. Elemental analyses were carried out on a Vario MICRO cube. MALDI-TOF MS data were acquired on a Voyager-DE PRO Bio spectrometry workstation.

2.2. Magnetic susceptibility measurement

Temperature dependent static susceptibilities of the complexes (15–20 mg) were recorded for cooling and heating cycles (2 K min⁻¹) using a MPMS-5S (Quantum Design) SQUID magnetometer over a temperature range 4.5–380 K in a homogeneous 0.1 Tesla external magnetic field. Gelatine capsules were used as sample containers for measurements. The very small diamagnetic contribution of the gelatine capsule had a negligible contribution to the overall magnetisation, which was dominated by the sample. The diamagnetic corrections of the molar magnetic susceptibilities were applied using Pascal's constants.

2.3. Single crystal diffraction

Single crystal X-ray diffraction data were collected on a STOE IPDS II diffractometer with graphite monochromated Mo K α radiation (0.71073 Å). The structures were solved by direct methods (SHELX-97). Refinement was performed with anisotropic temperature factors for all non-hydrogen atoms (disordered atoms were refined isotropically) [12,13].

2.4. Synthesis of the ligands

The ligands 4-iodo-2,6-bis(pyrazol-1-yl)pyridine (**L**¹), 4-(4'-trimethylsilylethynyl)-2,6-bis(pyrazol-1-yl)pyridine (**L**³) and 4-ethynyl-2,6-bis(pyrazol-1-yl)pyridine (**L**⁴) were synthesised following reported protocols [4,6].

2.4.1. Synthesis of 4-(4'-hydroxyphenyl)-2,6-bis(pyrazol-1-yl)-pyridine (**L**²)

4-Iodo-2,6-bis(pyrazol-1-yl)pyridine (**L**¹) (0.67 g, 2 mmol) and 4-hydroxy phenyl boronic acid (0.29 g, 2.1 mmol) and Pd(0)(PPh₃)₄ (10 mol.%) were suspended in N₂ bubbled solvents of methanol and toluene (1:1, 100 ml) and 2 M Na₂CO₃ (8 ml). The mixture was heated to 70 °C for 2 days under nitrogen atmosphere. The crude reaction mixture was poured into ice water (500 ml) and extracted with dichloromethane. The separated organic layer was dried over MgSO₄ and the solvent removed. The solid residue was purified by column chromatography on silica gel with hexane/ethyl acetate (10:1) as the eluent obtaining the ligand (**L**²) as a white powder 0.41 g (68% yield). ¹H NMR (DMSO-*d*₆; δ): 9.27 (s, 1H, OH); 8.34 (d, 2H, Pz-H₅, $J = 4$ Hz); 7.71 (s, 2H, Py); 7.46 (m, 2H, Pz-H₄); 7.38 (d, 2H, H_{ar}, $J = 9$ Hz); 6.64 (d, 2H, H_{ar}, $J = 9$ Hz); 6.22 (d, 2H, -H₃, $J = 5$ Hz). ¹³C NMR (DMSO-*d*₆; δ): 159.25; 153.51; 142.34; 128.31; 127.49; 126.94; 116.48; 108.14; 106.09. MALDI-TOF (matrix 2,5-dihydroxybenzoic-acid) *m/z*: found 303.80 (M⁺, 100%), calcd. for C₁₇H₁₃N₅O (M⁺) 303.11. Elemental analysis: calcd. for C₁₇H₁₃N₅O: C 67.32%; H 4.32%; N23.09%, found: C 67.39%; H4.53%; N23.00%.

2.5. Synthesis of the compounds **1–4**

All the compounds **1–4** were prepared by using the following general method. In a 100 ml Schlenk tube, a solution of the ligand **L** (0.33 mmol) and Fe(ClO₄)₂·6H₂O (0.165 mmol) in acetonitrile (60 ml) was heated at 80 °C for about 5 h under N₂. The

reaction mixture was cooled and filtered. The single crystals were grown by diffusing diisopropyl ether to the above solution under N_2 at room temperature in several days.

Caution. Although we have experienced no difficulties in handling these complexes, metal-organic perchlorates are potentially explosive and should be handled with care in small quantities.

2.5.1. Compound 1

Calcd. for $C_{22}H_{16}Cl_2FeI_2N_{10}O_8$: C 28.44%; H 1.74%; N 15.08%. Found: C 28.41%; H 1.82%; N 15.02%. Yield = 79%, formula weight = 929.00, MALDI-TOF (matrix glycerol anhydrous) m/z : found 727.90 ($[Fe^{II}(L^1)_2]^{2+}$, 20%), calculated for $C_{22}H_{16}FeI_2N_{10}$, 730.1, crystal colour: brown, $T/K = 180$, crystal system: orthorhombic, space group: $Pbcn$, $a/\text{Å} = 16.988(3)$, $b/\text{Å} = 11.010(2)$, $c/\text{Å} = 15.999(3)$, $V/\text{Å}^3 = 2992.5(10)$, Z ; $\rho_{\text{calc}}/\text{g cm}^{-3} = 4$; 2.062, $\mu(\text{Mo K}\alpha)/\text{mm}^{-1} = 2.810$, $F(000) = 1792$, crystal size/mm = $0.34 \times 0.33 \times 0.30$, θ range for the data collection/ $^\circ = 2.20$ – 25.68 , final R indices [$I > 2\sigma(I)$]: $R1 = 0.0273$; $wR2 = 0.0669$, R indices (all data): $R1 = 0.0287$; $wR2 = 0.0678$, extinction coefficient = 0.0053(3), GOF on $F^2 = 1.139$, CCDC reference number: 682057.

2.5.2. Compound 2

Calcd. for $C_{34}H_{26}Cl_2FeN_{10}O_{10}$: C 47.41%; H 3.04%; N 16.26%. Found: C 47.14%; H 3.27%; N 16.05%. Yield = 85%, formula weight = 861.40, MALDI-TOF (matrix glycerol anhydrous) m/z : found 660.61 ($[Fe^{II}(L^2)_2]^{2+}$, 90%), calculated for $C_{34}H_{26}FeN_{10}O_{10}$, 662.5, crystal colour: brown, $T/K = 180$, crystal system: orthorhombic, space group: $Pcca$, $a/\text{Å} = 22.345(5)$, $b/\text{Å} = 10.753(2)$, $c/\text{Å} = 14.579(3)$, $V/\text{Å}^3 = 3503.1(12)$, Z ; $\rho_{\text{calc}}/\text{g cm}^{-3} = 4$; 1.633, $\mu(\text{Mo K}\alpha)/\text{mm}^{-1} = 0.659$, $F(000) = 1760$, crystal size/mm = $0.37 \times 0.36 \times 0.24$, θ range for the data collection/ $^\circ = 2.52$ – 25.65 , final R indices [$I > 2\sigma(I)$]: $R1 = 0.0456$; $wR2 = 0.1136$, R indices (all data): $R1 = 0.0475$; $wR2 = 0.1149$, extinction coefficient = 0.0106(16), GOF on $F^2 = 1.105$; the perchlorate anions are disordered, CCDC reference number: 682058.

2.5.3. Compound 3

Calcd. for $C_{36}H_{40}Cl_2FeN_{12}O_8Si_2$: C 45.92%; H 4.58%; N 17.37%. Found: C 45.24%; H 4.27%; N 17.31%. Yield = 75%, formula weight = 951.73, crystal colour: dark orange, $T/K = 180$, crystal system: monoclinic, space group: $C2/c$, $a/\text{Å} = 23.575(5)$, $b/\text{Å} = 12.106(2)$, $c/\text{Å} = 17.743(4)$, $\beta/^\circ = 115.68(39)$, $V/\text{Å}^3 = 4563.8(16)$, Z ; $\rho_{\text{calc}}/\text{g cm}^{-3} = 4$; 1.385, $\mu(\text{Mo K}\alpha)/\text{mm}^{-1} = 0.561$,

$F(000) = 1968$, crystal size/mm = $0.40 \times 0.38 \times 0.35$, θ range for the data collection/ $^\circ = 2.54$ – 25.63 , final R indices [$I > 2\sigma(I)$]: $R1 = 0.0629$; $wR2 = 0.1553$, R indices (all data): $R1 = 0.0680$; $wR2 = 0.1591$, extinction coefficient = 0.0036(12), GOF on $F^2 = 1.043$, the perchlorate anions and the acetonitrile molecules are disordered, CCDC reference number: 682059.

$T/K = 298$, crystal colour: light orange, $\lambda/\text{Å} = 0.71073$, crystal system: monoclinic, space group: $C2/c$, $a/\text{Å} = 23.629(5)$, $b/\text{Å} = 12.322(3)$, $c/\text{Å} = 17.845(4)$, $\beta/^\circ = 115.15(3)$, $V/\text{Å}^3 = 4703.3(16)$, Z ; $\rho_{\text{calc}}/\text{g cm}^{-3} = 4$; 1.344, $\mu(\text{Mo K}\alpha)/\text{mm}^{-1} = 0.544$, $F(000) = 1968$, crystal size/mm = $0.38 \times 0.12 \times 0.10$, θ range for the data collection/ $^\circ = 1.90$ – 25.63 , final R indices [$I > 2\sigma(I)$]: $R1 = 0.0558$; $wR2 = 0.1660$, R indices (all data): $R1 = 0.0656$; $wR2 = 0.1733$, GOF on $F^2 = 1.042$.

2.5.4. Compound 4

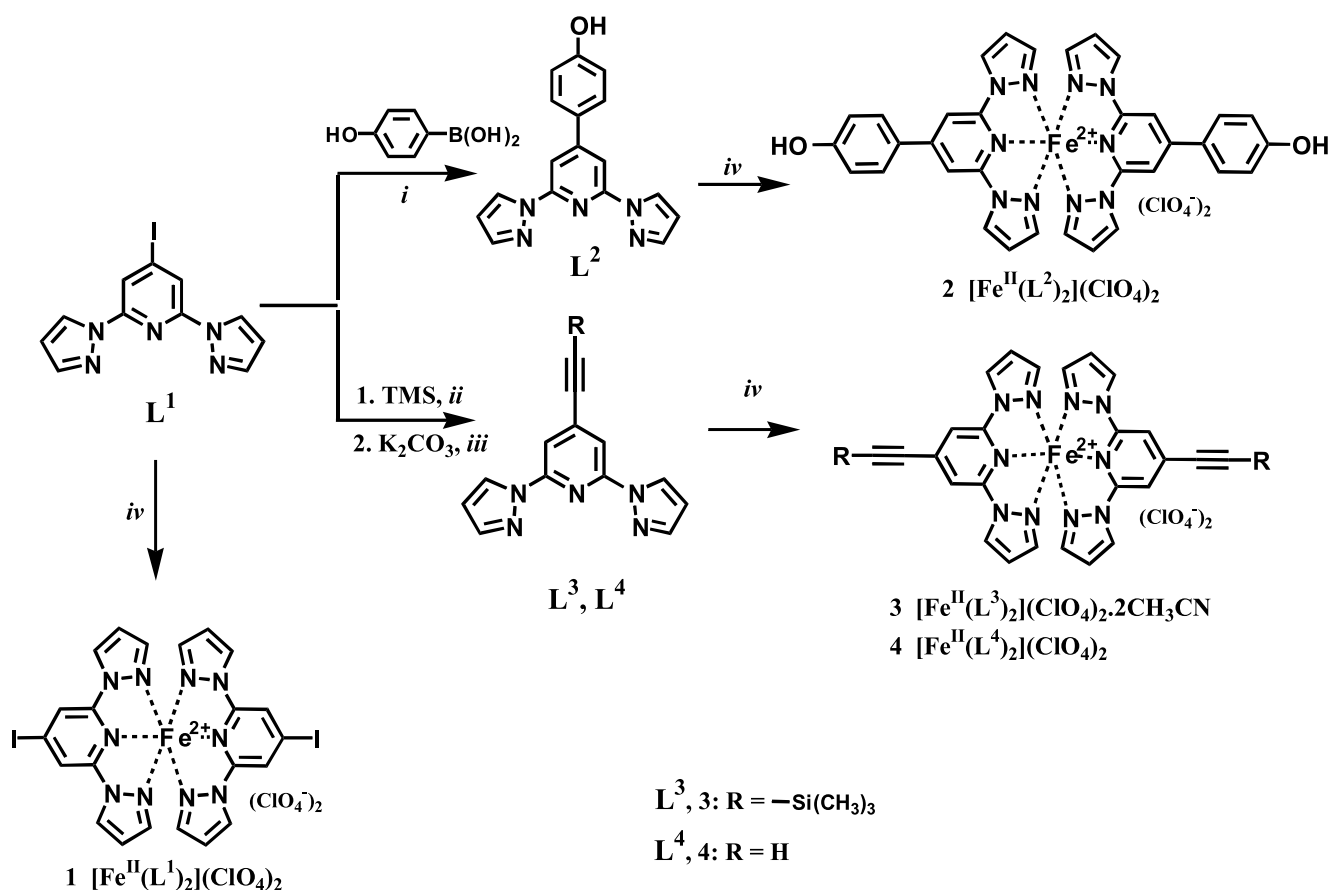
Calcd. for $C_{26}H_{18}Cl_2FeN_{10}O_8$: C 43.06%; H 2.05%; N 19.31%. Found: C 43.19%; H 2.5%; N 19.24%. Yield = 80%, formula weight = 725.23, MALDI-TOF (matrix glycerol anhydrous) m/z : found 623.82 ($[Fe^{II}(L^1)_2]^+(\text{ClO}_4)$, 15%), calculated for $C_{26}H_{18}ClFeN_{10}O_4$, 625.78, crystal colour: red, $T/K = 180$, crystal system: tetragonal, space group: $I4_1/a$, $a/\text{Å} = b/\text{Å} = 9.6248(14)$, $c/\text{Å} = 29.593(6)$, $V/\text{Å}^3 = 2741.4(8)$, Z ; $\rho_{\text{calc}}/\text{g cm}^{-3} = 4$; 1.757, $\mu(\text{Mo K}\alpha)/\text{mm}^{-1} = 0.819$, $F(000) = 1472$, crystal size/mm = $0.25 \times 0.22 \times 0.20$, θ range for the data collection/ $^\circ = 2.23$ – 25.63 , final R indices [$I > 2\sigma(I)$]: $R1 = 0.0558$; $wR2 = 0.1660$, R indices (all data): $R1 = 0.0558$; $wR2 = 0.1660$, extinction coefficient = 0.0026(6), GOF on $F^2 = 1.120$, CCDC reference number 682060.

3. Results

3.1. Synthesis

The ligands L^1 , L^3 and L^4 were synthesised following literature procedures [4,6]. Ligand L^2 , 4-(4'-hydroxyphenyl)-2,6-bis(pyrazol-1-yl)-pyridine was obtained as a white powder in 68% yield via a Pd-catalyzed Suzuki cross-coupling reaction from ligand L^1 , 4-iodo-2,6-bis(pyrazol-1-yl)pyridine, with 4-hydroxyphenyl boronic acid (Scheme 1).

The compounds (**1–4**) were prepared by the reaction of two equivalents of the respective ligand L with one equivalent of iron(II) perchlorate in acetonitrile at 80°C under inert atmosphere of N_2 . Single crystals suitable for X-ray diffractions were grown by diffusing diisopropyl ether into the acetonitrile solution of the complexes under N_2 at room temperature for



Scheme 1. Reagents and conditions: (i) $\text{Pd}(0)(\text{PPh}_3)_4$, 2 M Na_2CO_3 , toluene, MeOH; (ii) $\text{Pd}(0)(\text{PPh}_3)_4$, CuI, Et_2NH ; (iii) K_2CO_3 , MeOH; (iv) $\text{Fe}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$, CH_3CN .

several days. Compounds **1** and **2** crystallise as brown blocks while the colour of compound **3** is light orange. The compound **4** crystallises as dark red blocks. All the crystals were found to be stable at room temperature without decomposition and loss of solvent molecules.

3.2. Solid state structures of the compounds 1–4

Selected Fe–N bond lengths of the complex dications in (**1–4**) at different temperatures are given in Table 1. The X-ray diffraction studies of single crystals of $[\text{Fe}^{\text{II}}(\text{L}^1)_2](\text{ClO}_4)_2$ (**1**) reveal the orthorhombic space group *Pbcn* exhibiting a unit cell volume of $2992.5(10) \text{ \AA}^3$ ($a = 16.988(3) \text{ \AA}$, $b = 11.010(2) \text{ \AA}$ and $c = 15.999(3) \text{ \AA}$). Four formula units are included in

the unit cell and no solvent molecules are present in the crystal lattice. Fig. 1a shows the molecular structure of the dication $[\text{Fe}^{\text{II}}(\text{L}^1)_2]^{2+}$ in **1**. The coordination environment in the iron(II) metal ion can be described as a distorted octahedron. The complex exhibits at 180 K Fe(II)–N bond lengths varying from 1.899(2) to 1.968(2) Å (Table 1).

X-ray diffraction studies on single crystals of $[\text{Fe}^{\text{II}}(\text{L}^2)_2](\text{ClO}_4)_2$ (**2**) at 180 K show the orthorhombic group *Pcca* symmetry exhibiting a unit cell volume of $3503.1(12) \text{ \AA}^3$ ($a = 22.345(5) \text{ \AA}$, $b = 10.753(2) \text{ \AA}$ and $c = 14.579(3) \text{ \AA}$). Four formula units can be found within the unit cell. The molecular structure of the dication $[\text{Fe}^{\text{II}}(\text{L}^2)_2]^{2+}$ is shown in Fig. 1b. The hydroxyl group is protonated, but the respective OH groups do

Table 1
Selected bond distances and angles of the coordination polyhedra of the complex dications in **1–4**

	1		3		4
	180 K	180 K	180 K	298 K	
Fe1–N1	1.968(2)	1.964(2)	2.106(3)	2.176(3)	1.972(15)
Fe1–N3	1.899(2)	1.900(2)	2.054(3)	2.123(2)	1.881(2)
Fe1–N5	1.962(2)	1.976(2)	2.104(3)	2.176(3)	–

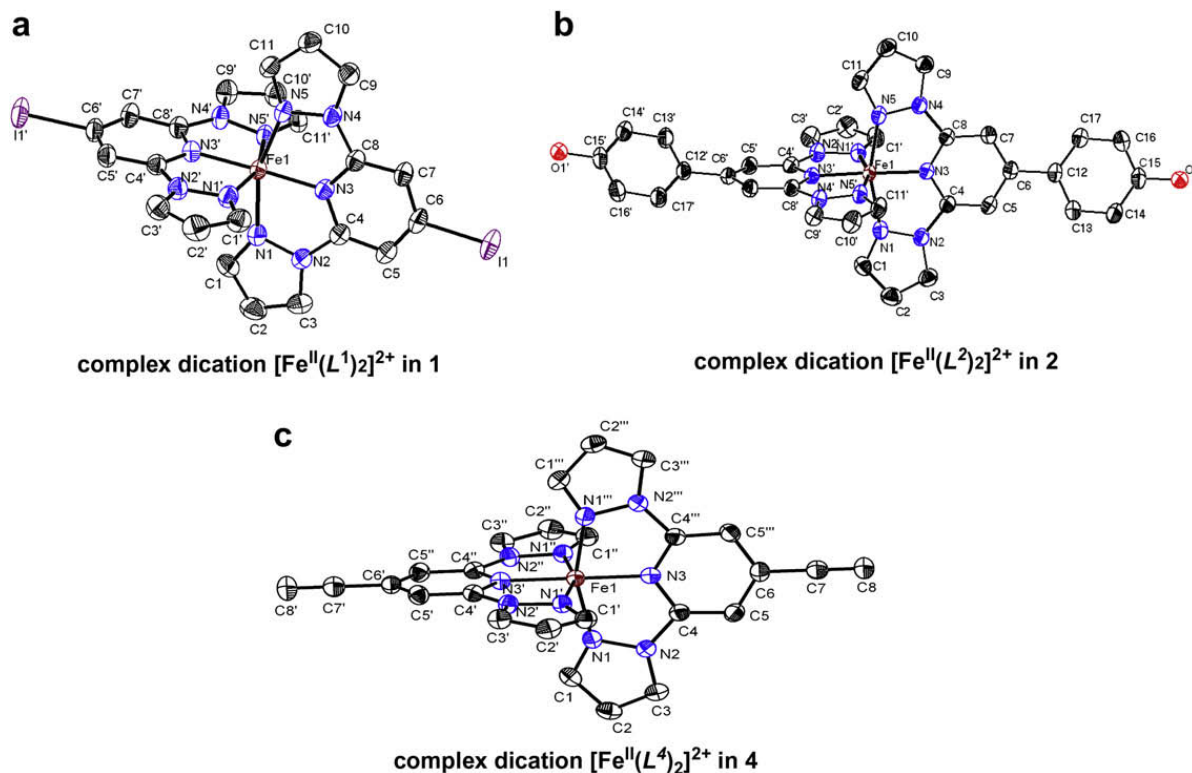


Fig. 1. (a–c) Representation of the ORTEP views of the dications $[\text{Fe}^{\text{II}}(\text{L}^x)_2]^{2+}$ in **1**, **2** and **4**. The thermal ellipsoids represent the 50% probability level. All molecular structures were determined at 180 K. Anions and hydrogen atoms were omitted by clarity.

not form any intermolecular contact with neighboring hydrogen bond acceptors or donors. The coordination environment in the iron(II) metal ion can be described as a tetragonally distorted octahedron. The complex cation exhibits Fe(II)–N bond lengths varying from 1.900(2) to 1.976(2) Å at 180 K (Table 1).

For $[\text{Fe}^{\text{II}}(\text{L}^3)_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$ (**3**), X-ray diffraction data were collected at both 298 K as well as 180 K using two different crystals. In both cases, single crystal X-ray structure analysis reveals the monoclinic space group $C2/c$. At 180 K compound **3** contains two non-bonded CH_3CN solvent molecules per complex molecule, which were also detected in the crystal lattice at 293 K. The cell volume and unit cell dimensions show slight variations at the two different temperatures. At 180 K, the cell volume is $4563.8(16) \text{ \AA}^3$ and increases to $4703.3(16) \text{ \AA}^3$ at 298 K. The corresponding unit cell parameters are $a = 23.575(5) \text{ \AA}$, $b = 12.106(2) \text{ \AA}$, and $c = 17.743(4) \text{ \AA}$ at 180 K and $a = 23.629(5) \text{ \AA}$, $b = 12.322(3) \text{ \AA}$, and $c = 17.845(4) \text{ \AA}$ at 298 K. Fig. 2a depicts the molecular structure of the dication $[\text{Fe}(\text{L}^3)_2]^{2+}$ in **3**. At 180 K, the Fe(II)–N bond lengths range from 2.054(3) to 2.106(3) Å, while at room temperature the Fe(II)–N bond lengths range from 2.123(2) to 2.176(3) Å (Table 1). At both temperatures, the coordination environment in the iron(II) metal ion can be

described as a distorted octahedron. Moreover, the temperature dependence of the colour change of one crystal of complex **3** was investigated by decreasing the temperature slowly from 298 to 180 K, the initially light orange colour of a crystal of complex **3** changes successively to dark orange without losing crystallinity (Fig. 2b).

The single crystals of $[\text{Fe}^{\text{II}}(\text{L}^4)_2](\text{ClO}_4)_2$ (**4**) are red and the X-ray diffraction studies reveal the tetragonal space group $I4_1/a$ at 180 K. The compound shows a unit cell volume of $2741.4(8) \text{ \AA}^3$ ($a = b = 9.6248(14) \text{ \AA}$, and $c = 29.593(6) \text{ \AA}$) including four formula units per unit cell. No solvent molecules were detected in the crystal lattice. Fig. 1c shows the molecular structure of the complex dication $[\text{Fe}^{\text{II}}(\text{L}^4)_2]^{2+}$ in **4**. The coordination environment in the iron(II) metal ion can be described as a distorted octahedron. The complex exhibits Fe(II)–N bond lengths varying from 1.881(2) to 1.972(15) Å at 180 K (Table 1).

3.3. Temperature dependent magnetic properties

The temperature dependent magnetic susceptibilities of the compounds **1–4** were performed for both heating (\uparrow) and cooling cycles (\downarrow) in the temperature range 4.5–380 K. Field dependent magnetisation measurement was also carried out for complex **3**.

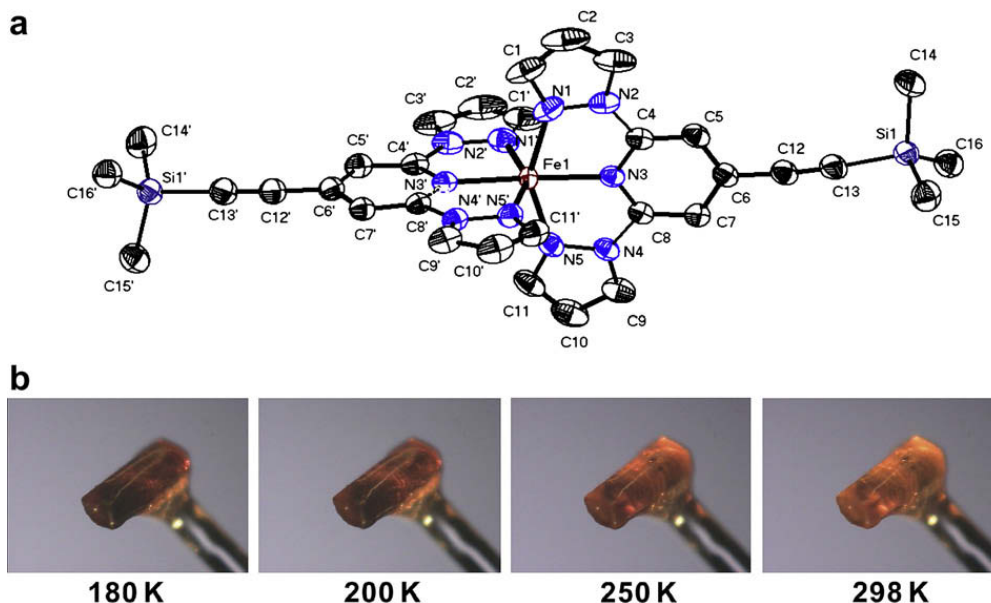


Fig. 2. (a) ORTEP plot of the complex dication $[\text{Fe}^{\text{II}}(\text{L}^3)_2]^{2+}$ in $3 \cdot 2\text{CH}_3\text{CN}$ at 180 K (50% probability ellipsoids). The molecular structure was determined at 180 K. Anions, solvent molecules and hydrogen atoms were omitted for clarity. (b) Photographs of a single crystal of complex $3 \cdot 2\text{CH}_3\text{CN}$ showing its thermochromism at four different temperatures.

The product of the molar magnetic susceptibility and temperature (χT) of the complex $[\text{Fe}^{\text{II}}(\text{L}^1)_2](\text{ClO}_4)_2$ (**1**) is $3.49 \text{ emu K mol}^{-1}$ at 380 K, which is slightly higher than the value expected for a HS state ($S = 2$) of an iron(II) ion (Fig. 3a). On cooling, χT starts to decrease very abruptly at 340 K and reaches a plateau at 260 K approaching a low temperature value of $0.045 \text{ emu K mol}^{-1}$. This value can be attributed to the iron(II) LS ($S = 0$) state. Measurements were performed in both heating (\uparrow) and cooling (\downarrow) cycles. It is interesting to note that the compound **1** is one rare example of Fe(II) complexes exhibiting spin transition above room temperature with a $T_{1/2}$ of 333 K [5a].

The temperature dependent magnetic measurement of complex $[\text{Fe}^{\text{II}}(\text{L}^2)_2](\text{ClO}_4)_2$ (**2**) is shown in Fig. 3b. At 380 K, the value of χT is $3.01 \text{ emu K mol}^{-1}$, which is in accordance with the value for a high-spin ($S = 2$) state iron(II) metal ion. On cooling, χT starts to decrease at 360 K relatively smoothly before reaching at 200 K a plateau close to zero a value which corresponds to the LS state ($S = 0$) of an iron(II) metal ion. Meanwhile, the measurements performed in both heating (\uparrow) and cooling (\downarrow) cycles have revealed that there is no indication of hysteresis as a result of intermolecular cooperativity in the solid state. In this case also, it is interesting to note that the ST temperature is close to room temperature [8] with a $T_{1/2} = 281 \text{ K}$.

For the complex $[\text{Fe}^{\text{II}}(\text{L}^3)_2](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$ (**3**), the product of the molar magnetic susceptibility and temperature (χT) is $3.03 \text{ emu K mol}^{-1}$ at 380 K

(Fig. 4a), which is in accordance to the value expected for a HS state ($S = 2$) of an iron(II) ion. On cooling the χT value remains constant at this value over the temperature range from 380 to 300 K. Spin transition occurs between 300 and 125 K reaching a second plateau of $1.76 \text{ emu K mol}^{-1}$ around 140 K. This value coincides with a situation where half of the iron(II) centres in the crystal lattice have undergone spin transition, while the other half remain in the paramagnetic HS state. Field dependent magnetisation measurements at 4.2 K exhibit magnetic saturation at around $2 \mu_{\text{B}} \text{ mol}^{-1}$ (Fig. 4b). The χT in temperature range 120–5 K reveals a strong increase, in particular below 50 K. Below 10 K, χT versus T plot drops strongly due to the zero field splitting of Fe(II) HS metal ions. Measurements were performed in both heating (\uparrow) and cooling (\downarrow) cycles and have revealed that there is no evidence for thermal hysteresis. It is also interesting to note that the compound does not seem to lose any solvent molecules in the lattice even at 380 K unlike other compounds of the iron(II) bispyrazolopyridine family [5b].

In the case of complex $[\text{Fe}^{\text{II}}(\text{L}^4)_2](\text{ClO}_4)_2$ (**4**), variable temperature magnetic susceptibility measurements show that the complex remains completely low spin in the whole temperature range from 5 to 380 K. This is surprising, since the structurally very close compounds **3** and **4** are only distinguished by the replacement of the trimethylsilyl group by the less bulky proton.

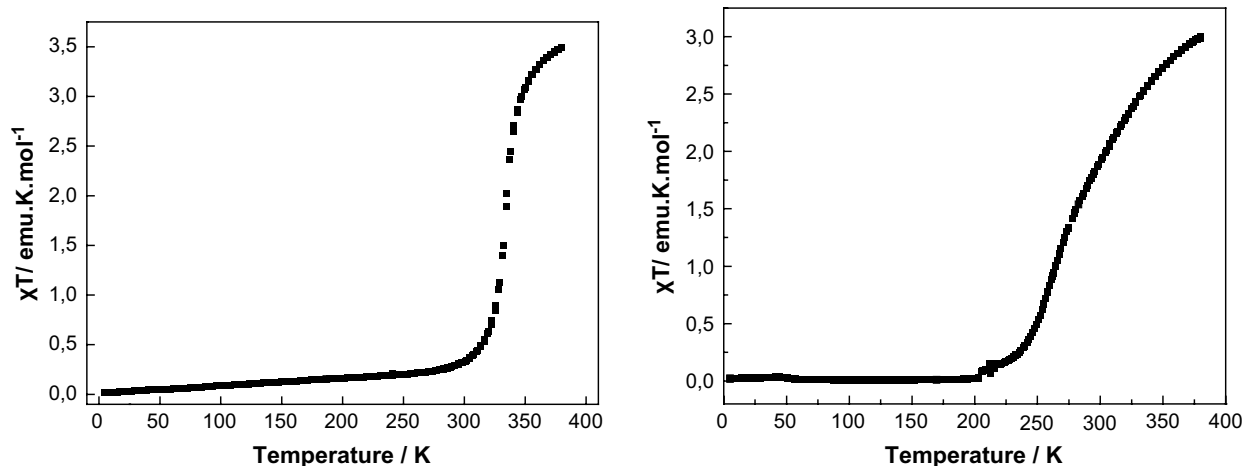


Fig. 3. The solid state χT vs. T plots of compound **1** (left) and compound **2** (right) exhibiting $T_{1/2}$ value above room temperature.

4. Discussion

The single crystal diffraction and magnetic studies of compounds **1** and **2** reveal for both compounds very similar structural and magnetic behaviour. At 180 K, the averaged Fe(II)–N bond lengths are close to 1.90 Å for the central pyridine rings and between 1.96 and 1.98 Å for the peripheral pyrazolyl rings (Table 1). Such bond length values are typical for iron(II) metal ions in the LS state, [1b] which is also confirmed by the magnetic investigations with χT values close to 0 emu K mol⁻¹ below 180 K. Both complexes exhibit drastic changes of χT with increasing temperatures: While compound **2** reveals a smooth, almost gradual transition between 200 and 380 K, compound **1** exhibits a relatively steep increase of χT between 330 and 370 K. At 380 K, both complexes reach magnetic saturation of the χT at values typical for the HS state with

$S = 2$. Noticeably, both compounds show spin transition above room temperature, a region extremely interesting for applications.

On comparing the electronic effects of the substituents in the 4-position of the bispyrazolylpyridine moiety, the iodo group of compound **1** exercises a slightly negative, while the hydroxyl phenyl group a slightly positive inductive effect. Interestingly, the analogous, in the 4-position unsubstituted bispyrazolylpyridine iron(II) perchlorate compound remains fully high-spin between 300 and 5 K [10]. Although comparability is given by the same type of counteranions and the absence of lattice solvent molecules, the scattering of these results is not fully explicable on the only base of ligand field strength discussions. It has been previously shown for the class of iron(II) bispyrazolylpyridine compounds that slight packing effects in the crystal lattice, varying positions and

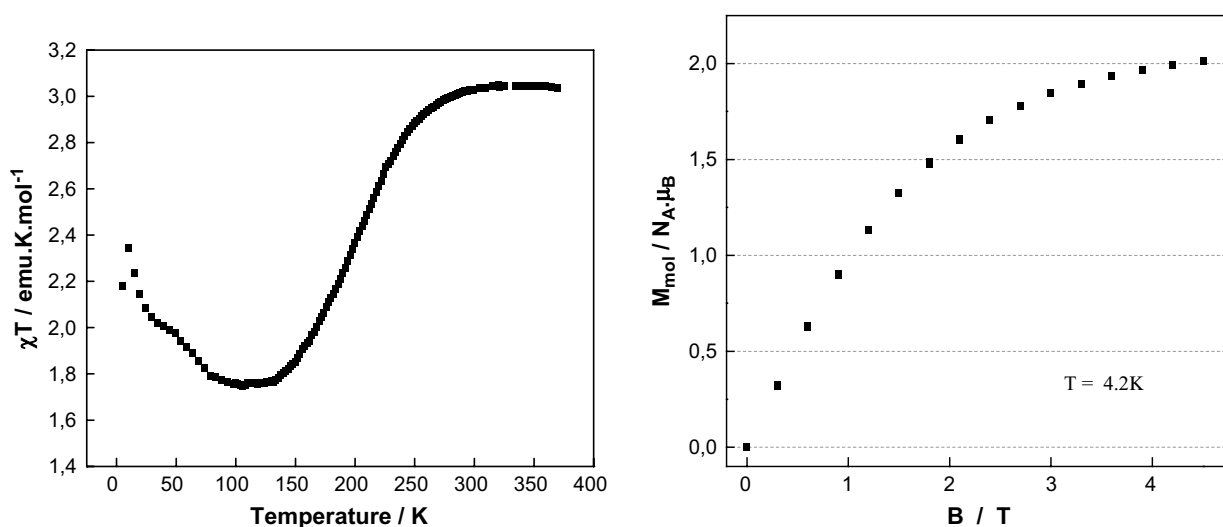


Fig. 4. (a) The solid state χT vs. T plot and (b) field vs. magnetisation plot (right) of compound **3**.

even different disordered schemes of anions are strong enough to alter considerably the ST behaviour [5b]. In accordance with the absence of intermolecular contacts in the X-ray diffraction studies, no hysteresis was observed in the solid state magnetic studies of **1** and **2**. The importance of such contacts for the evolution of intermolecular cooperativity, expressed by the appearance of hysteresis loops with up to 8 K width, has been shown previously for further members of the bispyrazolopyridine iron(II) compound family [4,5a].

The spin transition behaviour of compound **3** turned out to be more complex. The presence of a spin transition above 180 K was evidenced by the distinct thermochromism going from dark to pale orange on heating to 298 K (Fig. 3b). At 298 and 180 K, the X-ray single crystal structure of compound **3** shows the inclusion of two acetonitrile solvent molecules into the crystal lattice. The averaged Fe–N bond distances correspond with 2.12 Å for the central pyridine and 2.18 Å for the pyrazol groups of the ligand **L**³ indicate HS state character of the coordinated iron(II) metal ion at 298 K. This result is confirmed by the magnetic studies showing a χT value close to 3 emu K mol⁻¹, which is in accordance to the value expected for an all HS situation at 298 K and higher temperatures (Fig. 4a). However, the χT value starts to decrease drastically at temperatures below 260 K in order to reach a plateau between 140 and 125 K with a χT value of 1.76 emu K mol⁻¹. This value can only be interpreted by a magnetic situation where only half of the involved iron(II) metal ions have undergone transition into the LS ($S = 0$) state, while the remaining iron(II) centres are supposed to be kept in the HS state ($S = 2$). Such 50%/50% HS/LS situation at low temperatures was further confirmed by field dependent magnetisation measurements at 4.2 K where saturation shows up at around 2 μ_B mol⁻¹; half of the value expected for four electrons per molecule (Fig. 4b). Accordingly, the X-ray diffraction studies at 180 K reveal in terms of Fe(II)–N bond lengths a situation ($d(\text{Fe}-\text{N}_{\text{pyridine}}) = 2.05$ Å; $d(\text{Fe}-\text{N}_{\text{pyrazol}}) = 2.11$ Å), which can be also attributed to an admixture of LS and HS bond lengths. Below 125 K the χT value shows first a slight increase, and then a strongly pronounced increase in the temperature range 50–5K, which can be attributed to a successive inset of weak ferromagnetic coupling of the remaining iron(II) HS centres. Cohabitation of spin transition and ferromagnetic coupling is rather unusual, but was recently reported [9]. Below 10 K, χT drops strongly due to the zero field splitting of Fe(II) HS metal ions. Magnetic

measurements performed in both heating (\uparrow) and cooling (\downarrow) cycles revealed absence of magnetic hysteresis so demonstrating absence of intermolecular cooperativity in the solid state.

Compound **4** does not show any evidence for spin transition and the iron(II) centres and remains completely diamagnetic in the temperature range of 5–380 K. In accordance, the crystal structure at 180 K exhibits Fe–N bond distances typical for the iron(II) LS state (Fig. 1, Table 1). In comparison with compound **3**, not only the steric bulk of the trimethylsilyl group but also the inclusion of solvent molecules leads obviously to this drastically changed ST behaviour; proving high sensitivity of the spin transition to subtle changes in the molecular environment.

5. Conclusions

We have characterised structurally and magnetically four iron(II) bispyrazolopyridine compounds bearing different substituents in the 4-position. Variable temperature magnetic studies reveal that the substituents in the 4-position of the bispyrazolopyridine ligand have a pronounced effect on the ST properties of the complexes. In view of applications, the access to spin transition iron(II) complexes showing transition temperatures close to ambient temperature is of pivotal importance for their use as active units in device architectures [11]. Out of the four studied compounds herein, two show spin transition above or close to room temperature, which shows how controlled molecular design can achieve attractive working parameters. The still missing hysteretic behaviour can be reintroduced by increasing the cooperativity between the ST centres, e.g. by incorporating additional interlinking paramagnetic centres using polydentate ligands or by favoring weak hydrogen or π – π bonds in the crystal lattices. The construction of such multinuclear ST architectures is under progress [4,5].

Acknowledgements

The authors thank the Deutsche Forschungsgemeinschaft (DFG) for financial support under CFN (Center for Functional Nanostructures – Project E3). We are also thankful to Prof. Horst Hahn for providing the necessary instrumental facilities.

References

- [1] (a) P. Gülich, J. Jung, H.A. Goodwin, *Nato ASI Ser. E. Appl. Sci.* 321 (1996);

- (b) P. Gütllich, A. Hauser, H. Spiering, *Angew. Chem., Int. Ed.* 33 (1994) 2024;
(c) A. Hauser, *Coord. Chem. Rev.* 111 (1991) 275;
(d) P. Gütllich, A. Hauser, *Coord. Chem. Rev.* 97 (1990) 1.
- [2] (a) I. Sanner, E. Meissner, H. Köppen, H. Spiering, *Chem. Phys.* 86 (1984) 227;
(b) J.A. Real, E. Andres, M.C. Munoz, M. Julve, T. Granier, A. Bousseksou, F. Varret, *Science* 268 (1995) 265;
(c) O. Kahn, C. Jay Martinez, *Science* 279 (1998) 44;
(d) A. Galet, A.B. Gasper, M.C. Munoz, G.V. Bukin, G. Levchenko, J.A. Real, *Adv. Mater.* 17 (2005) 2949;
(e) O. Kahn, J. Kröber, C. Jay, *Adv. Mater.* 4 (1992) 718;
(f) D. Gatteschi, *Adv. Mater.* 6 (1994) 635.
- [3] (a) M. Ruben, F.J. Rojo, J. Romero-Salguero, L.H. Uppadine, J.-M. Lehn, *Angew. Chem., Int. Ed.* 43 (2004) 3644;
(b) M. Ruben, U. Ziener, J.-M. Lehn, V. Ksenofontov, P. Gütllich, G.B.M. Vaughan, *Chem.—Eur. J.* 11 (2005) 94;
(c) M. Ruben, E. Breuning, J.-M. Lehn, V. Ksenofontov, F. Renz, P. Gütllich, G.B.M. Vaughan, *Chem.—Eur. J.* 9 (2003) 4422;
(d) E. Breuning, M. Ruben, F. Renz, J.-M. Lehn, Y. Garcia, V. Ksenofontov, P. Gütllich, E. Wegelius, K. Rissanen, *Angew. Chem., Int. Ed.* 39 (2000) 2504.
- [4] C. Rajadurai, F. Schramm, S. Brink, O. Fuhr, M. Ghafari, R. Kruk, M. Ruben, *Inorg. Chem.* 45 (2006) 10019.
- [5] (a) C. Rajadurai, O. Fuhr, R. Kruk, M. Ghafari, H. Hahn, M. Ruben, *Chem. Comm.* (2007) 2636;
(b) C. Rajadurai, Z. Qu, O. Fuhr, B. Gopaln, R. Kruk, M. Ghafari, M. Ruben, *Dalton Trans.* (2007) 3531.
- [6] C. Rajadurai, F. Schramm, O. Fuhr, M. Ruben, *Eur. J. Inorg. Chem.* 17 (2008) 2649.
- [7] (a) R. Mukherjee, *Coord. Chem. Rev.* 203 (2000) 151;
(b) C. Enachescu, F. Varret, E. Codjovi, J. Linares, S. Floquet, P. Manikandan, P.T. Manoharan, *J. Phys. Chem. B* 110 (2006) 5883;
(c) C. Enachescu, J. Linares, F. Varret, K. Boukhehdaden, E. Codjovi, S.G. Salunke, R. Mukherjee, *Inorg. Chem.* 43 (2004) 4880;
- (d) S. Mahapatra, N. Gupta, R. Mukherjee, *J. Chem. Soc., Dalton Trans.* (1991) 2911;
(e) S. Mahapatra, R.J. Butcher, R. Mukherjee, *J. Chem. Soc., Dalton Trans.* (1993) 3723;
(f) V.A. Money, J.S. Costa, S. Marcen, G. Chastanet, J. Elhaik, M.A. Halcrow, J.A.K. Howard, J.-F. Letard, *Chem. Phys. Lett.* 391 (2004) 273;
(g) J.M. Holland, S.A. Barrett, C.A. Kilner, M.A. Halcrow, *Inorg. Chem. Comm.* 5 (2002) 328;
(h) J. Elhaik, C.A. Kilner, M.A. Halcrow, *Dalton Trans.* (2006) 823;
(i) C. Carbonera, J.S. Costa, V.A. Money, J. Elhaik, J.A.K. Howard, M.A. Halcrow, J.-F. Letard, *Dalton Trans.* (2006) 3058;
(j) C. Carbonera, C.A. Kilner, J.-F. Letard, M.A. Halcrow, *Dalton Trans.* (2007) 1284;
(k) M.A. Halcrow, *Polyhedron* 26 (2007) 3523;
(l) M.A. Halcrow, *Chem. Soc. Rev.* 37 (2008) 278.
- [8] (a) J. Kröber, E. Codjovi, O. Kahn, F. Groliere, C. Jay, *J. Am. Chem. Soc.* 115 (1993) 9810;
(b) C. Cantin, H. Daubric, J. Kliava, Y. Servant, L. Sommier, O. Kahn, *J. Phys. Condens. Matter* 10 (1998) 7057;
(c) Y. Garcia, O. Kahn, L. Rabardel, B. Chansou, L. Salmon, J.P. Tuchagues, *Inorg. Chem.* 38 (1999) 4663;
(d) S. Bonhommeau, G. Molnar, A. Galet, A. Zwick, J.-A. Real, J.J. McGarvey, A. Bousseksou, *Angew. Chem., Int. Ed.* 44 (2005) 4069;
(e) S. Cobo, G. Molnar, J.-A. Real, A. Bousseksou, *Angew. Chem., Int. Ed.* 45 (2006) 5786.
- [9] K.S. Min, K. Swierczek, A.G. DiPasquale, A.L. Rheingold, W.M. Reiff, A.M. Arif, J.S. Miller, *Chem. Comm.* (2008) 317.
- [10] J. Elhaik, D.J. Evans, C.A. Kilner, M.A. Halcrow, *Dalton Trans.* (2005) 1693.
- [11] O. Kahn, *Molecular Magnetism*, Wiley-VCH, August 1993.
- [12] G.M. Sheldrick, *Acta Crystallogr., Sect. A* 660 (1990) 467.
- [13] G.M. Sheldrick, *SHELXL-97 (Release 97-2) Program for the Refinement of Crystal Structures*, University of Göttingen, Germany.