A Novel Dinuclear Fe^{II} Spin-Crossover Complex Based on a 2,2-Bipyrimidine Bridge Ligand: $[Fe(CH_3bipy)(NCS)_2]_2bpym$

Ana B. Gaspar,[a] Vadim Ksenofontov,[a] Víctor Martinez,[c] M. Carmen Muñoz,[b] José A. Real,*[c] and Philipp Gütlich*[a]

Keywords: Spin crossover / Iron(II) bpym-bridged dinuclear compounds / Pressure-induced spin transition / Mössbauer spectroscopy

The dinuclear iron(II) complex $\{[Fe(CH_3bipy)(NCS)_2]_2bpym\}$ has been synthesised and its crystal structure determined at 293 K. The magnetic properties display intramolecular antiferromagnetic coupling at 1 bar ($J = -4.2$ cm^{-1}), and the onset of a pressure-induced spin conversion is observed at 11 kbar. Magnetic field Mössbauer measurements have been carried out at 4.2 K, and indicate that the HS species correspond to [HS-HS] pairs.

Introduction

Spin crossover (SCO) materials present magnetic and optical bistability due to a high-spin (HS) to low-spin (LS) cooperative spin transition driven by an external perturbation such as a change in temperature and/or pressure or irradiation with light.[1] Many publications stress the potential for applications of such compounds in information storage, as sensors, or as molecular switches.[2] The characteristics of this class of bistable compounds, for example, transition temperatures, hysteresis, thermochromism, photochromism as well as thermodynamic and kinetic properties, depend on the interplay between the ligand-field strength at the transition-metal ion and the interactions between the metal complex, the counterions, and solvate molecules as governed by crystal packing. In comparison with monomers, a little is known on cooperativity in small clusters or extended coordination polymers of Fe^{II}. Understanding the cooperativity between clusters and the synergy, if any, between intracluster magnetic exchange coupling and the SCO phenomenon has been the subject of investigation,[3] and continues to present other fundamental challenges.

Dinuclear iron(II) complexes of the type $\{[Fe(L)(NCX)_2]_2bpym\}$ (L: 2,2′-bipyrimidine, 2,2′-bithiazoline, 2,2′-dipyridylamine, X: S, Se) and $\{[Fe(phdia)(NCS)_2]_2(phdia)\}$ (phdia: 4,7-phenanthroline-5,6-diamine) provide a first step in the research line aimed at combining magnetic exchange and SCO phenomena in a molecule or polymeric network.[4] Extensive research has led to the conclusion that the plateau of the spin-transition curve, a special feature of this class of compounds, is constituted mainly of [HS−LS] pairs. This result confirmed that the spin conversion in these dinuclear entities proceeds through [HS-HS] ⇄ [HS−LS] ⇄ [LS−LS] pairs. The appearance of [HS−LS] species should be interpreted in terms of a synergy between intramolecular and intermolecular cooperative interactions (short- and long range) that energetically stabilises the mixed pairs, gives rise to the plateau region of a two-step transition curve and determines its width. Further, a form of synergy between spin-crossover and magnetic-coupling phenomena has been observed under the application of hydrostatic pressure or by light irradiation. Presently, the question is posed as to whether all dinuclear compounds will exhibit this two-step behaviour and/or synergy between electronic properties. In this respect, a very gradual SCO behaviour without a plateau has been observed in the $\{[Fe(dpa)(NCS)_2]_2bpym\}$ derivative,[5] the lack of such a plateau being ascribed to interdimer interactions. Murray[6] and Kaizaki[7] and their groups have reported new dinuclear iron(II) SCO systems based on pyrazolate bridges in which the conversion takes place through [HS−HS] ⇄ [LS−LS] pairs.

Here we report on the synthesis and characterisation by means of X-ray, magnetic and Mössbauer spectroscopic studies of a novel dinuclear SCO system $\{[Fe(CH_3bipy)(NCS)_2]_2bpym\}$ (**1**), where CH_3bipy = 6-methyl-2,2′-bipyridine.

The crystal structure determination on **1** was performed at 293 K. The structure of **1** consists of centrosymmetric

---

[a] Institut für Anorganische und Analystiche Chemie, Johannes Gutenberg Universität,
Staudinger Weg 9, 55099 Mainz, Germany
[b] Departament de Física Aplicada, Universitat Politécnica de València,
Camí de Vera s/n, 46071 València, Spain
[c] Institut de Ciéncia Molecular, Universitat de València,
Doctor Moliner 50, 46100 Burjassot, València, Spain

DOI: 10.1002/ejic.200400586

discrete dinuclear molecules, in which two iron(II) ions are bridged by a bpym ligand in a bis-bidentate fashion. A perspective view of the molecule with the labeling of the atoms is shown in Figure 1. The Fe···Fe intramolecular distance is 6.052(5) Å. Each iron atom is bound to six nitrogen atoms that belong to two NCS$^-$ groups in a *cis*-position, one CH$_3$bipy ligand, which occupies the terminal positions in the iron surrounding, and one bridging bpym ligand. The Fe−N bond lengths involving NCS$^-$ [2.060(16) and 2.148(10) Å] are much shorter than those involving the CH$_3$bipy and bpym ligands [from 2.144(8) to 2.222(9) Å,] (Table 1). The [FeN$_6$] chromophore is rather distorted with Fe−N bond lengths characteristic for an iron(II) ion in the HS state. Whereas the N−C−S groups are quasi-linear, the Fe−*N*−C(S) linkages are significantly bent [Fe−N3−C5 = 156.3(11)° and Fe−N4−C6 = 159.2(11)°]. There is no π−π stacking between dimers. The shortest intermolecular Fe···Fe separation is 8.250(4) Å (*i* = *x*, 1 − *y*, *z*).

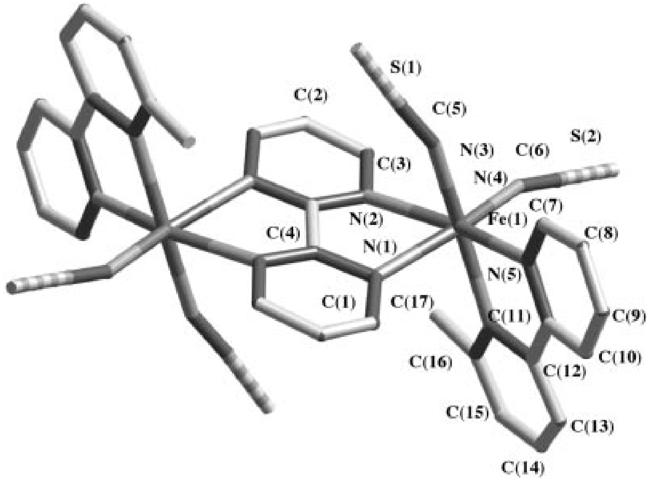


Figure 1. Molecular structure of {[Fe(CH$_3$bipy)(NCS)$_2$]$_2$bpym} (**1**) solved at 293 K with the corresponding atom numbering scheme; thermal ellipsoids are shown at 40% probability levels

Table 1. Selected bond lengths [Å] and angles [°] for **1**

Fe−N(1)	2.292(13)	N(1)−Fe−N(2)	69.6(4)
Fe−N(2)	2.272(9)	N(1)−Fe−N(3)	85.2(5)
Fe−N(3)	2.148(10)	N(3)−Fe−N(6)	164.9(4)
Fe−N(4)	2.060(16)	N(6)−Fe−N(5)	75.6(4)
Fe−N(5)	2.144(8)	N(5)−Fe−N(4)	105.3(5)
Fe−N(6)	2.222(9)	N(4)−Fe−N(2)	93.8(5)

The $\chi_M T$ vs. T curve for **1** at ambient pressure shows that the iron(II) centres of the dinuclear entities are antiferromagnetically coupled with a typical value for the magnetic coupling constant[3,4] $J = -4.2\ \mathrm{cm}^{-1}$ and $g = 2.21$ [$\hat{H} = -J\hat{S}_a\hat{S}_b + g\beta(\hat{S}_a + \hat{S}_b)H$ (Figure 2)]. The maximum of the χ_M vs. T curve is centred at $T_c = 15$ K. Up to applied pressures of about 7 kbar, the magnetic properties of **1** remain practically unaltered. Further increase in the pressure up to 11 kbar induces a very incomplete spin transition around 100 K that involves 10% of the metal ions, the rest are antiferromagnetically coupled. Zero-field Mössbauer measurements of compound **1** have been carried out at 4.2 K (see a in Figure 3). At this temperature, the spectra consist of one doublet corresponding to the $S = 2$ high-spin state characterised by a quadrupole splitting of $\Delta E_Q(\mathrm{HS}) = 2.91(3)$ mm s^{-1} and an isomer shift of $\delta(\mathrm{HS}) = 0.87(1)$ mm s^{-1} (relative to α-Fe). The application of an external magnetic field of 50 kOe at 4.2 K causes only a broadening of the paramagnetic doublet lines of the HS species, which indicates that the HS species of **1** correspond to the [HS−HS] pairs[4] (see b in Figure 3). The effective magnetic field at the iron nuclei may be estimated by using the expression $H_{\mathrm{eff}} \approx H_{\mathrm{ext}} - [220 - 600(g - 2)] <S>$ (1). The effective field felt by the iron nuclei, H_{eff}, estimated from the spectrum was 14 kOe. To explain this value, one must consider the electronic levels of a dinuclear unit in the presence of antiferromagnetic coupling.[3−4] Admixture of upper levels of higher multiplicity with $S \geq 1$ to the singlet ground state $S = 0$ of the antiferromagnetically coupled pair caused by temperature and magnetic field splitting leads to a non-zero expectation value of $<S>$.

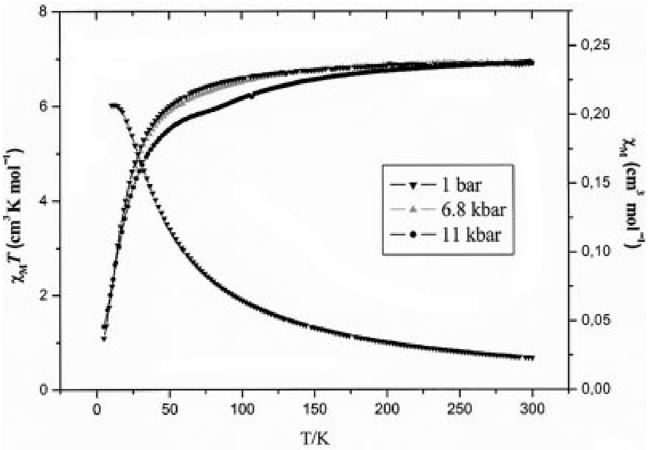
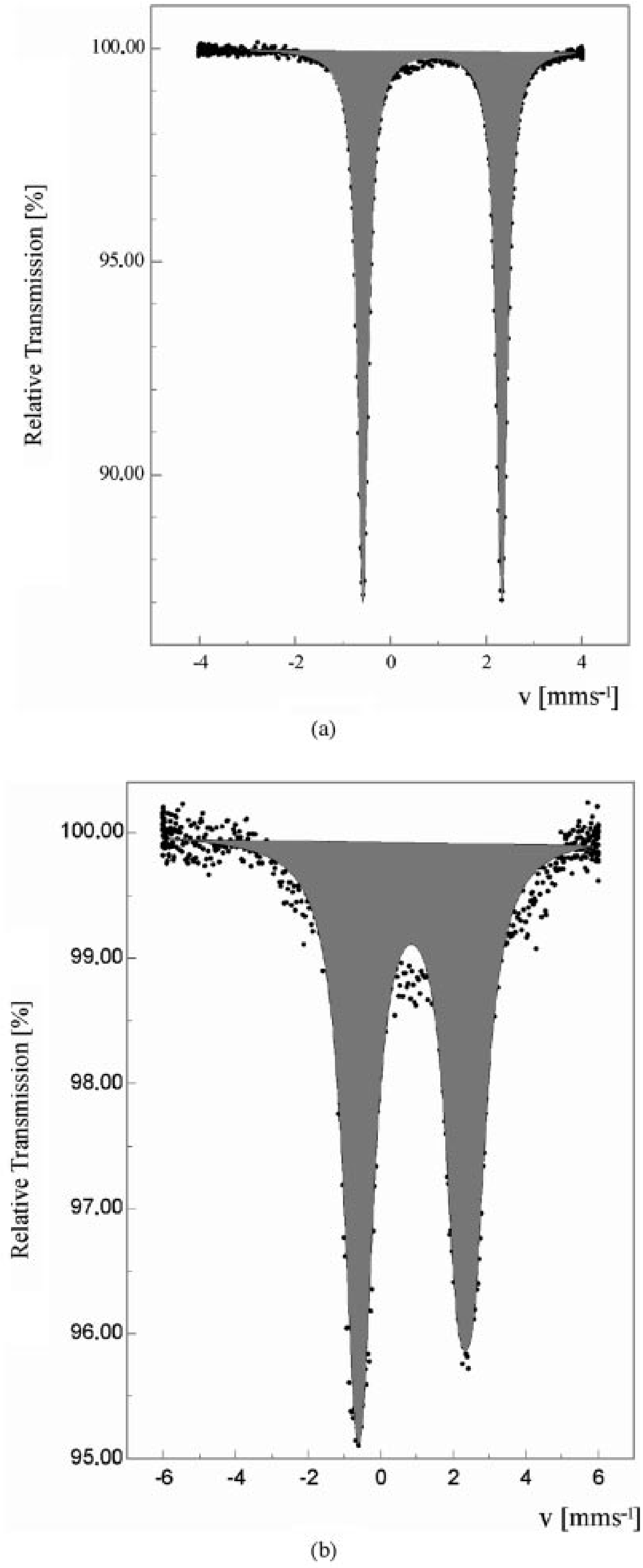


Figure 2. $\chi_M T$ and χ_M vs. T curves for {[Fe(CH$_3$bipy)(NCS)$_2$]$_2$-bpym} (**1**) at different pressures, 1 bar, 6.8 kbar, 11 kbar

The significantly higher pressures required to trigger the spin transition in **1** than the analogous dinuclear system {[Fe(bpym)(NCS)$_2$]$_2$bpym}[3,4] is not surprising despite the fact that the molecular structures of both compounds are similar. At ambient pressure, the complex {[Fe(bpym)-(NCS)$_2$]$_2$bpym} is paramagnetic in the temperature region 4−300 K and shows the intramolecular antiferromagnetic interaction. At $p = 9$ kbar, {[Fe(bpym)(NCS)$_2$]$_2$bpym} undergoes spin transition at $T_{1/2} \approx 150$ K involving 50% of iron atoms and ultimately causing the disappearance of antiferromagnetic coupling. The average Fe−N bond lengths are 2.188 Å and 2.180 Å for **1** and {[Fe(bpym)(NCS)$_2$]$_2$bpym}, respectively. Hence, the strength of the ligand field is expected to be weaker for **1** than for {[Fe(bpym)(NCS)$_2$]$_2$bpym}, which should be the



(a)

(b)

Figure 3. (a) Mössbauer spectra of {[Fe(CH_3bipy)$(NCS)_2$]$_2$bpym} (**1**) at 4.2 K; (b) at 4.2 K and $H = 50$ kOe

reason for the difference in sensitivity to pressure-induced spin conversion.

Further dinuclear iron(II) examples of the present and related types are being sought.

Experimental Section

General Remarks: All reactions were carried out under Ar using standard Schlenk techniques. The ligand 6-methyl-2,2′-bipyridine (CH_3bipy) was synthesised according to a procedure described previously.[1] 2,2′-Bipyrimidine (Lancaster), $FeSO_4\cdot 7H_2O$ (Panreac), and KNCS (Aldrich) were used as received.

{[Fe(CH_3bipy)$(NCS)_2$]$_2$bpym} (1): To a solution of $FeSO_4\cdot 7H_2O$ (0.25 mmol) in methanol (15 mL) was added a methanol solution (15 mL) of KNCS (0.5 mmol). The solution was stirred for 15 min, and the resulting precipitate (K_2SO_4) was filtered. The colourless solution containing Fe/NCS^- (1:2) was mixed with a solution of CH_3bipy (0.5 mmol) in methanol (25 mL), and the colour of the solution changed to orange. To this solution was added dropwise bpym (0.25 mmol) dissolved in methanol (15 mL). The final dark red solution was filtered and allowed to evaporate for a week, giving cubic black crystals of {[Fe(CH_3bipy)$(NCS)_2$]$_2$bpym} (**1**) suitable for X-ray studies. Yield: 70%. $C_{34}H_{26}Fe_2N_{12}S_4$ (842.6): calcd. C 48.47, H 3.11, N 19.95; found C 48.16, H 3.15, N 19.18.

X-ray Crystallographic Study: Diffraction data for {[Fe(CH_3bipy)$(NCS)_2$]$_2$bpym} was collected at room temperature with an Enraf−Nonius CAD-4 diffractometer by using graphite-monochromated Mo-K_α radiation with the ω-2θ scan method. The unit cell parameters were determined from least-squares refinement on the setting angles from 25 centered reflections in the range 12° $< \theta <$ 20°. No significant fluctuations were observed in the intensities of three standard reflections monitored periodically throughout data collections. The structure of {[Fe(CH_3bipy)-$(NCS)_2$]$_2$bpym} was solved by standard Patterson methods and refined by the full-matrix least-squares method on F^2. The computations were performed using SHELXS-86 and SHELXL-93.[8] All non-hydrogen atoms were refined anisotropically. Details are listed in Table 2. CCDC-239827 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystal data of compound **1**

Empirical formula	$C_{34}H_{26}Fe_2N_{12}S_4$
M	842.61
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	14.048(8)
b [Å]	18.250(3)
c [Å]	17.357(7)
β [°]	113.78(3)
V [Å^{3}9	1840.9(14)
Z	2
D_c [mg·cm^{-3}]	1.520
F(000)	860
μ (Mo-K_α) [mm^{-1}]	1.059
Crystal size [mm]	0.04 × 0.06 × 0.08
Temperature [K]	293(2)
No. of total reflections	2425
No. of independent reflections	1272
No. of parameters	237
R_1	0.0715
wR_2	0.0950
S	0.922

Magnetic Susceptibility Measurements under Hydrostatic Pressure: The variable-temperature magnetic susceptibility measurements were performed on small single crystals by using a Quantum Design MPMS2 SQUID susceptometer equipped with a 5.5 T magnet and operating at 1 T and 1.8−375 K, the PAR 151 Foner-type magnetometer, equipped with a cryostat operating in the temperature range 2−300 K. The hydrostatic pressure cell made of hardened beryllium bronze with silicon oil as the pressure-transmitting medium operates in the pressure range 1 bar $< p <$ 13 kbar Cylindrically shaped powder sample holders with dimensions of 1 mm in diameter and 5−7 mm in length were used. The pressure was measured by using the pressure dependence of the superconducting transition temperature a of built-in pressure sensor made of high purity tin.[9] Experimental data were corrected for diamagnetism using Pascal's constants.

Mössbauer Spectroscopy: ^{57}Fe Mössbauer spectra were recorded with a constant-acceleration conventional spectrometer and helium bath cryostat. A superconducting magnet was applied to create a magnetic field directed parallel to the wave vector of the γ-quanta. The sample and the Mössbauer source ^{57}Co/Rh were immersed in liquid helium. About 40 mg of microcrystalline powder were placed in a 16 mm diameter absorber holder made of polished transparent acryl. The Recoil 1.03a Mössbauer Analysis Software was used to fit the experimental spectra.

Acknowledgments

A. B. G. thanks the Alexander von Humboldt Foundation for financial assistance. We also acknowledge the Deutsche Forschungsgemeinschaft (Priority Program SPPU37 "Molecular Magnetism"), the Fonds der Chemischen Industrie and the Materialwissenschaftliches Forschungszentrum der Universität Mainz for financial help. M. C. M. and J. A. R. thank the Ministerio Español de Ciencia y Tecnología (project BQU 2001−2928).

---

[1] P. Gütlich, A. Hauser, H. Spiering, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2024; P. Gütlich, *Struc. Bonding* **1981**, *44*, 83; P. Gütlich, Y. Garcia, H. A. Goodwin, *Chem. Soc., Rev.* **2000**, *29*, 419; J. A. Real, A. B. Gaspar, V. Niel, M. C. Muñoz, *Coord. Chem. Rev. Ed.* **2003**, *236*, 121.

[2] O. Kahn, C. J. Martinez, *Science* **1998**, *279*, 44; O. Kahn, C. Kröber, *Adv. Mater.* **1992**, *4*, 367; J. A. Real, E. Andrés, M. C. Muñoz, M. Julve, T. Trainer, A. Bousseksou, *Science* **1995**, *268*, 265; G. J. Halder, C. J. Kepert, B. Mourabaki, K. S. Murray, J. D. Cashion, *Science* **2002**, *298*, 1762.

[3] J. A. Real, A. B. Gaspar, M. C. Muñoz, P. Gütlich, V. Ksenofontov, H. Spiering, *Top. Curr. Chem.* **2004**, *233*; S. Brooker, P. G. Plieger, B. Moubaraki, K. Murray, *Angew. Chem. Int. Ed.* **1999**, *38*, 408.

[4] J. A. Real, H. Bolvin, A. Bousseksou, A. Dworkin, O. Kahn, F. Varret, J. Zarembowitch, *J. Am. Chem. Soc.* **1992**, *114*, 4650; V. Ksenofontov, A. B. Gaspar, J. A. Real, P. Gütlich, *J. Chem. Phys. B.* **2001**, *105*, 12266; A. B. Gaspar, V. Ksenofontov, H. Spiering, S. Reiman, J. A. Real, P. Gütlich, *Hyp. Interact.* **2002**, 144/145, 297; V. Ksenofontov, H. Spiering, S. Reiman, Y. Garcia, A. B. Gaspar, N. Moliner, J. A. Real, P. Gütlich, *Chem. Phys. Lett.* **2001**, *348*, 381; V. Ksenofontov, H. Spiering, S. Reiman, Y. Garcia, A. B. Gaspar, N. Moliner, J. A. Real, P. Gütlich, *Hyper. Inter.* **2001**, *141*/*142*, 47; V. Ksenofontov, A. B. Gaspar, S. Reiman, V. Niel, J. A. Real, P. Gütlich, *Chem. Eur. J.* **2004**, *10*, 1291.

[5] A. B. Gaspar, V. Ksenofontov, J. A. Real, P. Gütlich, *Chem. Phys. Lett.* **2003**, *373*, 385.

[6] B. A. Leita, B. Moubaraki, K. Murray, J. P. Smith, J. D. Cashion, *Chem. Commun.* **2004**, 156.

[7] K. Nakano, N. Suemura, S. Kawata, A. Fuyuhiro, T. Yagi, S. Nasu, S. Morimoto, S. Kaizaki, *Dalton Trans.* **2004**, 982.

[8] G. M. Sheldrick, SHELX97, *Program for Crystal Structure Determination*, University of Göttingen, Germany, **1997**.

[9] M. Baran, G. G. Levchenko, V. P. Dyakonov, G. Shymchak G, *Physica C* **1995**, *241*, 383.

Received July 6, 2004