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An Iron(II) Spin-Crossover Complex with a 70 K Wide Thermal Hysteresis Loop**

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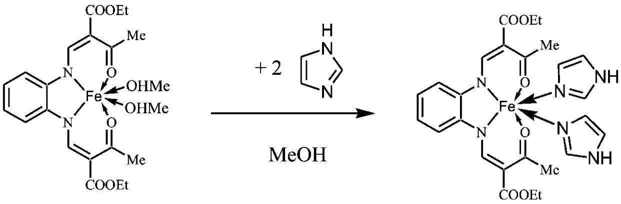
Spin-crossover (SCO) complexes are a fascinating class of molecules that can be switched on the molecular level by the use of temperature, pressure, or light.[1] For potential applications, these compounds should exhibit a cooperative spin transition with a wide thermal hysteresis loop that is centered at room temperature.[2] In the past few years, several strategies were discussed as to how geometry changes occurring during the spin transition can be transmitted effectively through the crystal lattice, as these cooperative interactions are the key factor for the appearance of wide thermal hysteresis loops. One promising strategy is the use of covalent linkers to form coordination polymers, as suggested by Kahn et al.[2a,3] However, no real breakthrough has occurred in the last decade. This is not surprising considering that we could demonstrate for the bridging ligand 4,4′-bipyridine that different SCO properties are not based on the covalent linker but are due to interactions (e.g. van der Waals forces) between the polymer chains.[4]

Over the last few years, we have investigated the properties of several SCO complexes with N_4O_2 coordination spheres.[5,6] The properties of the spin transition curve correlate well with the number and intensity of the intermolecular contacts, and thermal hysteresis loops up to 18 K wide could be obtained, owing to a 3D network of short van der Waals contacts.[4] The widest hysteresis loops observed to date for a structurally characterized SCO complex are about 40 K.[7] In both examples, this hysteresis arises from π–π interactions between ligands with extended aromatic structures.[7] In other compounds with thermal hysteresis loops 70 K wide[8] or up to 92 K[9] wide, π stacking is also considered to play a central role; however, no X-ray structure analyses are available for these compounds. To date, we have not succeed in applying this strategy to our N_4O_2 ligand system.[10] Therefore, we decided to use hydrogen bonds as intermolecular contacts, as these should be stronger than van der Waals contacts but more flexible than covalent linkers. Although the possibility to transmit cooperative interactions through H bonds has not been drawn into questioned, to date relatively few examples of H-bond-linked SCO complexes are known.[11] Recently, indications were found that the 35 K wide thermal hysteresis loop in the SCO coordination polymer $[Fe(NH_2trz)_3](NO_3)_2$ (trz = 4-amino-1,2,4-triazole) is due to a network of hydrogen bonds.[12]

The reaction of imidazole with the iron complex $[FeL(MeOH)_2]$ (Scheme 1) in methanol was first investigated by Müller et al.[13] and resulted in the formation of an iron complex with the composition $[FeL(HIm)_{1.80}]$ that was reported to display an incomplete spin transition ($\gamma_{HS} = 0.1$) with a 4 K wide thermal hysteresis loop above room temperature.[13] A hydrogen-bond network between the NH hydrogen atom of the imidazole unit and the *O*COEt oxygen atom of the equatorial ligand is made responsible for the cooperative interactions; however, no further details are given, and the composition of the powder sample differs between literature references.[13,14]



$[FeL(MeOH)_2]$ imidazole (HIm) $[FeL(HIm)_2]$ (**1**)

Scheme 1. Synthesis of compound **1** and the abbreviations used.

We therefore decided to investigate the reaction of $[FeL(MeOH)_2]$ with imidazole in more detail. The general route for the synthesis of **1** is given in Scheme 1 with the abbreviations used. In contrast to the results from the literature, a fine crystalline precipitate with the formula $[FeL(HIm)_2]$ (**1**) was obtained.

The magnetic properties of **1** were determined by temperature-dependent susceptibility measurements using a SQUID magnetometer at two different field strengths (0.02 and 0.05 T). Figure 1 gives the temperature dependence of the magnetic properties of **1** ($\chi_M T$ vs. T) analyzed in the temperature range 200–350 K. The room-temperature value of $\chi_M T = 3.26\ cm^3\,K\,mol^{-1}$ (295 K) is characteristic for an iron(II) complex in the high-spin (HS) state. Upon cooling, this value remains constant down to 250 K, where an abrupt transition to the low-spin (LS) state is observed that is centered at 244 K with a remaining magnetic moment of $\chi_M T = 0.15\ cm^3\,K\,mol^{-1}$ at 200 K. Upon heating, $\chi_M T$ remains

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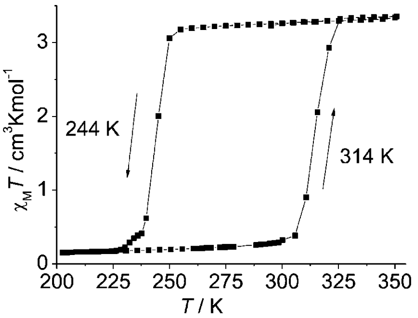

Figure 1. Thermal variation of $\chi_M T$ of compound **1**. The hysteresis loop remains unchanged after being repeated three times.

constant up to 300 K ($\chi_M T = 0.31$ cm^3 K mol^{-1}), where it increases abruptly to $\chi_M T = 3.32$ cm^3 K mol^{-1} at 325 K. A spin transition with a 70 K wide thermal hysteresis loop is observed that can be repeated several times. Furthermore, the SCO properties are resistant with regard to grinding effects. This aspect is of great importance for potential applications.

Crystals suitable for X-ray structure analysis were obtained from the same sample used for the magnetic measurements, and the molecular structure was determined at 275 K. An ORTEP drawing of the asymmetric unit is given in Figure 2. Selected bond lengths and angles are summarized in Table 1. The average bond lengths of the inner coordination sphere (2.08 Å (Fe–N_{eq}), 2.03 Å (Fe–O_{eq}), 2.22 Å (Fe–N_{ax})) are in the region reported for similar HS iron(II) complexes—in full agreement with the results of the susceptibility measurements.[4–6] The observed O-Fe-O angle (108°), the so-called bite angle of the ligand, is also in the region typical for iron(II) HS complexes of this ligand type.[4–6] The determination of the X-ray structure of the LS state was not possible, as the crystals crumbled upon cooling.

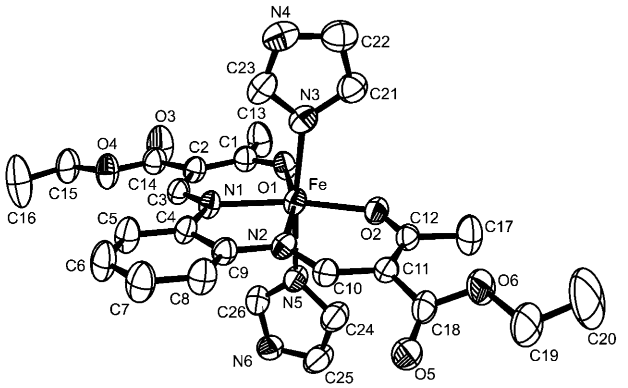

Figure 2. ORTEP drawing of the asymmetric unit of compound **1** at 275 K.

Table 1: Selected bond lengths [Å] and angles [°] of **1** within the first coordination sphere at 275 K.

Fe–N1/2	Fe–O1/2	Fe–N3/5	O1-Fe-O2	N3-Fe-N5
2.088(3)	2.011(3)	2.198(4)	108.04(11)	173.92(12)
2.078(3)	2.048(3)	2.239(4)		

The intermolecular interactions are of great significance for an understanding of the magnetic properties of compound **1**. The packing of the molecules in the crystals (Figure 3) reveals two different hydrogen bonds between neighboring molecules. One involves the NH hydrogen atom (H66) of the imidazole unit and the *O*COEt oxygen atom (O5) of the equatorial ligand, as discussed previously,[13] while the second one connects the NH hydrogen atom of the second imidazole ligand (H4) with the coordinated carbonyl oxygen atom (O1) of the equatorial ligand. The combination of the two hydrogen-bond types leads to an infinite two-dimensional layer of linked molecules along the (10−1) plane. Furthermore, weak contacts between an imidazole CH (H22) and a second OC*O*Et oxygen atom (O4) of the equatorial ligand increase the number of contacts between the molecules in the layer. The single layers are linked by additional short contacts between two aromatic CH hydrogen atoms of the phenylene bridge and the *O*COEt oxygen atom O3, leading in total to a 3D network of linked molecules. The details for all intermolecular contacts are given in Table 2.

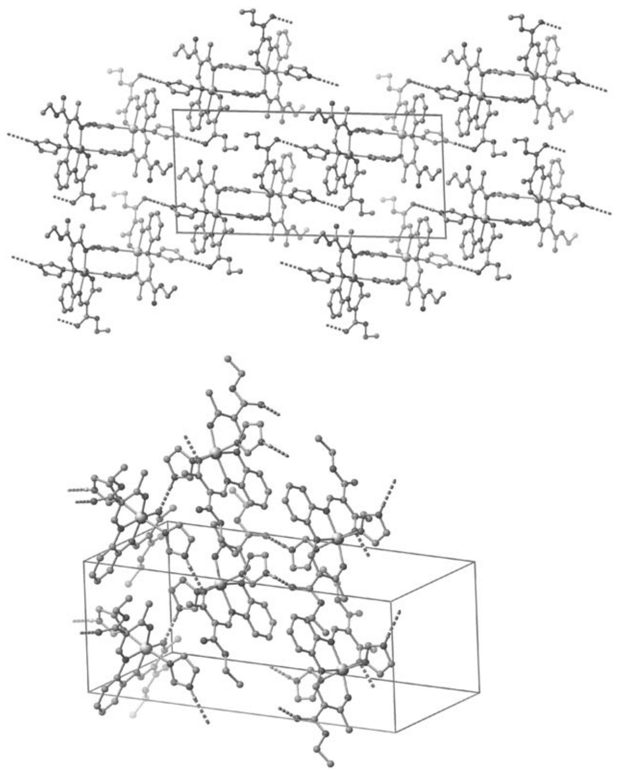

Figure 3. Packing of compound **1** in the crystal at 275 K. Top: view along [010]; bottom: excerpt of the 2D layer of hydrogen-bond-linked complex molecules.

The described network, especially the 2D hydrogen-bond network, is clearly responsible for the highly cooperative interactions during the spin transition observed in compound **1**. This thermal hysteresis loop is by far the widest in a structurally characterized compound, and the transition even takes place around room temperature. As a consequence, the importance, or alternatively the very good suitability, of

Table 2: Selected intermolecular distances [Å] of compound **1** at 275 K resulting in an infinite 2D hydrogen-bond network with the base vectors [010] and [101] along the plane (10−1) with additional weak contacts between the planes.

	D−H[a]	H···A	A···D	DH···A
N4−H4···O1[b]	0.860	2.000	2.829(5)	161.6
N6−H66···O5[c]	0.858	1.984	2.841(5)	176.1
C22−H22···O4[b]	0.93	2.686	3.54	
O3···H7−C7[d]	0.93	2.664	3.29	
O3···H8−C8[d]	0.93	2.698	3.31	

[a] D = donor; A = acceptor. [b] 3/2−*x*, 1/2+*y*, 3/2−*z*. [c] 1−*x*, −*y*, 1−*z*. [d] 1+*x*, *y*, *z*.

hydrogen bonds for transmitting cooperative interactions in SCO compounds must be reconsidered.

One last question to be addressed is the appearance of the 4 K wide hysteresis loop described by Müller et al.[13] The corresponding compound appears to be a second modification of complex **1**, which we were able to obtain if the complex precipitates not at room temperature but at 4 °C. Results from elemental analysis indicate a higher content of imidazole than for **1**—in agreement with results from Leibeling,[14] but in contrast to the results of Müller et al.[13] Both possibilities (more or less imidazole in the crystals) would partially destroy the H-bond network and thereby reduce the cooperative interactions.

Herein, we have presented an SCO complex with the widest known thermal hysteresis loop for a structurally characterized complex around room temperature. The results emphasize the high potential of H-bonds for transmitting cooperative interactions during a spin transition.

Experimental Section

All syntheses were carried out under argon using standard Schlenk techniques. Methanol was purified and distilled under argon before use. [FeL(MeOH)$_2$] was prepared as described in the literature.[15] Imidazole was purchased from Alfa Aesar and used as received.

[FeL(HIm)$_2$] **1**: A solution of [FeL(MeOH)$_2$] (0.56 g, 1.11 mmol) and imidazole (3.8 g, 0.056 mol) in methanol (20 mL) was heated at reflux for 5 min. After cooling, the fine crystalline black precipitate was filtered off, washed with methanol (2 × 5 mL), and dried in vacuum. Yield: 0.43 g (67 %). Elemental analysis (%) calcd for $C_{26}H_{30}N_6O_6Fe$ (578.40): C 53.99, H 5.23, N 14.53; found: C 53.23, H 5.09, N 15.07. IR (nujol): $\tilde{\nu}_{C=O} = 1703, 1672, 1620\ \text{cm}^{-1}$. MS (DEI$^+$): *m*/*z*: 68 (HIm$^+$, 100 %), 442 ([FeL]$^+$, 64 %). DTG (difference thermogravimetry): up to 150 °C: −1.1 % = loss of HIm in the crystal; up to 220 °C: −12.6 % = loss of 1 HIm (theory: 11.7 %); at 240 °C: decomposition.

Magnetic measurements were performed on a Quantum Design MPMSR-XL SQUID magnetometer in a temperature range from 5 to 295 K at 0.02 and 0.05 T in the settle mode. Data corrections were made using tabulated Pascal's constants. Reflection intensities of **1** were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo$_{K\alpha}$ radiation. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (Sir 97[16]) and refined by full-matrix least-square techniques against F_o^2 (SHELXL-97[17]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. Cell parameters and refinement results are summarized in Table S1 in the Supporting Information.[18] ORTEP-III was used for structure representation.[19]

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[1] a) H. A. Goodwin, *Coord. Chem. Rev.* **1976**, *18*, 293; b) P. Gütlich, *Struct. Bonding (Berlin)* **1981**, *44*, 83; c) E. König, *Prog. Inorg. Chem.* **1987**, *35*, 527; d) P. Gütlich, A. Hauser, *Coord. Chem. Rev.* **1990**, *97*, 1; e) E. König, *Struct. Bonding (Berlin)* **1991**, *76*, 51; f) P. Gütlich, A. Hauser, H. Spiering, *Angew. Chem.* **1994**, *106*, 2109; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2024; g) "Molecular Magnetism: From Molecular Assemblies to the Devices:": P. Gütlich, J. Jung, H. Goodwin, *NATO ASI Ser. E* **1996**, *321*, 327; h) "Spin Crossover in Transition Metal Compounds I–III": *Topics in Current Chemistry* (Eds:. P. Gütlich, H. A. Goodwin), Springer, Berlin, **2004**; i) J. A. Real, A. B. Gaspar, M. C. Munoz, *Dalton Trans.* **2005**, 2062; j) O. Sato, J. Tao, Y.-Z. Zhang, *Angew. Chem.* **2007**, *119*, 2200 – 2236; *Angew. Chem. Int. Ed.* **2007**, *46*, 2152 – 2187.

[2] a) O. Kahn, C. Jay Martinez, *Science* **1998**, *279*, 44 – 48; b) O. Kahn, C. Jay, J. Kröber, R. Claude, F. Grolière, Patent EP0666561, **1995**; c) J.-F. Létard, O. Nguyen, N. Daro, Patent FR0512476, **2005**; d) J.-F. Létard, P. Guionneau, L. Goux-Capes, *Topics in Current Chemistry* (Eds.: P. Gütlich, H. A. Goodwin), Springer, Vienna, **2004**, p. 221; e) A. Galet, A. B. Gaspar, M. C. Munoz, G. V. Bukin, G. Levchenko, J. A. Real, *Adv. Mater.* **2005**, *17*, 2949 – 2953.

[3] a) O. Kahn, E. Codjovi, *Philos. Trans. R. Soc. London Ser. A* **1996**, *354*, 359; b) O. Kahn, Y. Garcia, J.-F. Létard, C. Mathonière, *NATO ASI Ser. Ser. C* **1998**, *518*, 127.

[4] a) B. Weber, R. Tandon, D. Himsl, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1159 – 1162; b) B. Weber, E. S. Kaps, C. Desplanches, J.-F. Létard, *Eur. J. Inorg. Chem.* **2008**, 2963 – 2966.

[5] a) B. Weber, E. Kaps, J. Weigand, C. Carbonera, J.-F. Letard, K. Achterhold, F.-G. Parak, *Inorg. Chem.* **2008**, *47*, 487 – 496; b) B. Weber, E. S. Kaps, J. Obel, W. Bauer, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1421 – 1426; c) B. Weber, C. Carbonera, C. Desplanches, J.-F. Létard, *Eur. J. Inorg. Chem.* **2008**, 1589 – 1598.

[6] a) B. Weber, E. Kaps, *Heteroat. Chem.* **2005**, *16*, 391 – 397; b) B. Weber, F.-A. Walker, *Inorg. Chem.* **2007**, *46*, 6794 – 6803; c) B. Weber, E. S. Kaps, J. Obel, K. Achterhold, F. G. Parak, *Inorg. Chem.* **2008**, *47*, 10779 – 10787.

[7] a) J.-F. Létard, P. Guionneau, E. Codjovi, O. Lavastre, G. Bravic, D. Chasseau, O. Kahn, *J. Am. Chem. Soc.* **1997**, *119*, 10861 – 10862; b) Z. J. Zhong, J.-Q. Tao, Z. Yu, C.-Y. Dun, Y.-J. Lui, X.-Z. You, *J. Chem. Soc. Dalton Trans.* **1998**, 327 – 328.

[8] S. Hayami, Z.-z. Gu, H. Yoshiki, A. Fujishima, O. Sato, *J. Am. Chem. Soc.* **2001**, *123*, 11644 – 11650.

[9] a) J.-F. Létard, L. Capes, G. Chastanet, N. Moliner, S. Létard, J.-A. Real, O. Kahn, *Chem. Phys. Lett.* **1999**, *313*, 115 – 120; b) H. Daubric, C. Cantin, C. Thomas, J. Kliava, J.-F. Létard, O. Kahn, *Chem. Phys.* **1999**, *244*, 75 – 88.

[10] B. Weber, E. S. Kaps, C. Desplanches, J.-F. Létard, K. Achterhold, F. G. Parak, *Eur. J. Inorg. Chem.* **2008**, 4891 – 4898.

[11] a) H. Hagiwara, S. Hashimoto, N. Matsumoto, S. Iijima, *Inorg. Chem.* **2007**, *46*, 3136 – 3143; b) S. M. Neville, B. Moubaraki, K. S. Murray, C. J. Kepert, *Angew. Chem.* **2007**, *119*, 2105 – 2108; *Angew. Chem. Int. Ed.* **2007**, *46*, 2059 – 2062; c) D. Boinnard, A. Bousseksou, A. Dworkin, J.-M. Savariault, F. Varret, J.-P. Tuchagues, *Inorg. Chem.* **1994**, *33*, 271 – 281; d) A. Galet, A. B. Gaspar, M. C. Munoz, J. A. Real, *Inorg. Chem.* **2006**, *45*, 4413 – 4422.

[12] Y. Garcia, S. J. Campbell, J. S. Lord, Y. Boland, V. Ksenofontov, P. Gütlich, *J. Phys. Chem. B* **2007**, *111*, 11111 – 11119.

[13] B. R. Müller, G. Leibeling, E.-G. Jäger, *Chem. Phys. Lett.* **2000**, *319*, 368 – 374.

[14] a) G. Leibeling, Ph. D. Thesis, Universiy of Jena, Germany, **2003**; b) E.-G. Jäger in *Chemistry at the Beginning of the Third Millenium* (Eds.: L. Fabbrizzi, A. Poggi), Springer, Berlin, **2000**, pp. 103 – 138.

[15] E.-G. Jäger, E. Häussler, M. Rudolph, M. Rost, *Z. Anorg. Allg. Chem.* **1985**, 525, 67.

[16] A. Altomare, M. C. Burla, G. M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, “SIR 97”, Campus Universitario Bari, **1997**; (*J. Appl. Crystallogr.* **1999**, *32*, 115).

[17] G. M. Sheldrick, “SHELXL 97”, University of Göttingen, Germany, **1993**.

[18] CCDC-691362 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[19] C. K. Johnson, M. N. Burnett, “ORTEP-III”, Oak-Ridge National Laboratory, Oak-Ridge **1996**; L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.