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Thermal and Photoinduced Spin Crossover in a Mononuclear Iron(II) Complex with a Bis(pyrazolyl)pyridine Type of Ligand



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A mononuclear iron(II) compound 1 of the general formula $[Fe(L)_2](ClO_4)_2$ {L = 4-[2,6-bis(pyrazol-1-yl)pyridin-4-yl]benzaldehyde} was prepared and structurally characterised. Single-crystal X-ray structure analysis revealed the presence of a complex dication $[Fe(L)_2]^{2+}$ and two ${\rm ClO}_4^-$ counteranions within the unit cell. The bond lengths and angles within the coordination polyhedron FeN₆ indicate the low-spin state of the central iron(II) metal ion at T = 180 K. Magnetic investigations elucidate spin crossover with $T_{1/2}$ = 285 K. The experimental magnetic susceptibility data could be satisfactorily

Introduction

Projections of information technology well into the twenty-first century express a strong need for molecular switches.^[1,2] Among the multitude of molecular materials that exhibit switching between two stable states,^[3] Fe^{II} spincrossover (SCO) complexes present a class of compounds in which the low-spin (LS) \leftrightarrow high-spin (HS) reversible transformation can be found in solution as well as in the solid state.^[4] However, the outstanding position of SCO materials is also based on the large number of different external stimuli by which the change of the spin state can be performed. Up to now, the LS \leftrightarrow HS conversion was ob-

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fitted with the Curie law in combination with the Ising-like model. The room-temperature character of the spin crossover was further studied by variable-temperature far-IR, Vis and Mössbauer spectroscopy. Laser irradiation of 1 carried out at 10 K gives rise to a complete low-spin to high-spin photoconversion. A subsequent temperature-dependent investigation revealed the existence of a photoexcited metastable HS state up to T_{LIESST} = 70 K (LIESST = light-induced excited-spinstate trapping) as well as the presence of a light-induced thermal hysteresis loop with a width of 10 K.

served by temperature,^[5] pressure,^[6] magnetic^[7] or electric field^[8,9] and by electromagnetic irradiation in the Vis/near-IR^[10] or even X-ray^[11] range. This variability of external stimuli in conjunction with the pronounced physical property changes of SCO material (variation of magnetic, electric or spectral parameters and so on) promote the use of SCO compounds in data storage devices,^[12] as magnetic resonance imaging (MRI) contrast agents^[13] or for display technology.[14]

So far, the idea of possible utilisation of SCO switchers was mostly based on the change of bulk physical properties like abrupt and room-temperature transitions accompanied by a wide thermal hysteresis width ($\Delta T \approx 50$ K); only recently the exploitation of SCO at the single-molecule level was achieved.^[15,16] The iron(II) complexes based on tridentate ligands derived from bis(pyrazol-*n*-yl)pyridine (bpp; *n* = 1 or 3) are promising candidates in view of the required technological terms.^[15-19] Their synthesis as well as the study of their physical properties are the subject of ongoing interest and are under continuous investigation.^[20-34] The efforts of directed and systematic modification of either the pyrazole^[18-20] or pyridine^[21-31] part of the bpp moiety culminated in a plentiful collection of room-temperature SCO compounds. The tuning of the transition parameters $(T_{1/2})$ temperature, abruptness or presence of the thermal hysteresis loop) was also achieved by counteranion variation and/ or control of the lattice solvents in the crystal structure.^[26-28] The investigation of the polymorphism eluci-



dated the influence of the strong sensitivity of SCO behaviour on structural effects, deployment of SCO molecules within the crystal lattice as well as intermolecular cooperativity.^[31,32] From the point of view of possible applications, one of the pivotal challenges in research of SCO compounds is to discover new photoactive materials, whereby the LS \leftrightarrow HS conversion will be activated by means of controlled photoirradiation through light-induced excited-spinstate trapping (LIESST) at possibly high temperatures. Such scientific effort is focussed on the understanding of the relations between the T_{LIESST} temperature and thermal SCO properties^[35] and/or on the structural aspects,^[36,37] which might influence the existence and lifetimes of the photoexcited metastable HS state. With respect to this, the iron(II)-bpp spin-crossover compounds exhibit one of the highest range of reported T_{LIESST} temperatures.^[38,39]

Herein we report the synthesis, structural, magnetic, photomagnetic and spectral characterisation of the novel iron(II) SCO compound 1, which contains two tridentate bpp-type ligands L {4-[2,6-bis(pyrazol-1-yl)pyridin-4-yl]benzaldehyde}.^[40] Single-crystal X-ray diffraction studies revealed one defined complex [Fe(L)₂]²⁺ cation and two perchlorate counteranions per unit cell of 1. Temperaturedependent magnetic measurements show spin crossover with $T_{1/2} = 285$ K. The magnetic susceptibility was successfully fitted by combination of the Curie law and the Isinglike model with nonzero cooperativity.

The spin-crossover behaviour was also investigated by variable-temperature absorption (far-IR, Vis) and Mössbauer spectroscopy. The photomagnetic experiments reveal the existence of a metastable photoinduced high-spin state up to $T_{\text{LIESST}} = 70$ K, and the investigation of light-induced thermal hysteresis confirms a significant presence of intermolecular cooperativity in the crystal lattice of the photoactivated high-spin state of compound 1.

Results and Discussion

Synthesis and Crystallisation

The tridentate N-donor ligand L was obtained as a white powder from Suzuki coupling reaction of 4-iodo-2,6-bis-(pyrazol-1-yl)pyridine^[25,23] with (4-formylphenyl)boronic acid, catalysed by $[Pd^{0}(PPh_{3})_{4}]$ in deoxygenated tetrahydrofuran solvent in 85% yield. Then the obtained ligand L was coordinated by the Fe(ClO₄)₂·xH₂O salt in acetonitrile, and single crystals of compound 1 were obtained by diffusion of diethyl ether into the solution.

Structural Investigation

The result of the single-crystal X-ray studies on complex **1** is depicted in Figure 1a. This single-crystal X-ray structural investigation of **1** was carried out at 180 K and revealed a monoclinic $P_{2_1/c}$ space group with unit-cell parameters a = 17.162(3) Å, b = 14.827(3) Å, c = 15.012(3) Å, $\beta = 107.81(3)^\circ$, and V = 3636.9(13) Å³ (Table 3). The asym-

metric unit of 1 contains one complex dication $[Fe(L)_2]^{2+}$ and two corresponding ClO_4^- counteranions. There is no solvent molecule present in the crystal structure, and four $[Fe(L)_2](ClO_4)_2$ molecular species can be found within the unit cell (Figure 1b). At the temperature of measurement, the Fe–N bond lengths acquire values typical for the LS iron(II) central atom [1.890(4)-1.977(5) Å]. On the basis of the plasticity of the FeN₆ coordination polyhedron, other structural indicators of the spin state in the iron(II)–bpp complexes are the N_{pyrazole}–Fe–N_{pyrazole} angle (ca. 160° for LS and 145° for HS)^[30] and the Σ parameter^[41] (ca. 90° for LS and 160° for HS).^[30] Thus, the crystal structure of **1** shows N–Fe–N angles, according to which at 180 K those two parameters indicate the LS state of the complex (N1– Fe–N5 159.5°, N6–Fe–N10 160.0°, $\Sigma = 87.7°$).

Detailed inspection of the crystal structure of **1** revealed hydrogen bonding between the carbaldehyde oxygen atoms and CH groups of the ligand moieties, which vary in the range 3.175-3.449 Å. Another type of hydrogen bonding was found between the oxygen atoms of the perchlorate counteranion and hydrogen atoms of the aldehyde group as well as between the aldehyde hydrogen atom and oxygen atoms of perchlorate counteranions (Cl–O···C_{ald} 2.972–3.438 Å).

Magnetic and Photomagnetic Investigations

Magnetic measurements of compound 1 revealed roomtemperature SCO (Figure 2a, red circles). In the thermal range of 5-200 K, the compound exhibits typical diamagnetic LS (S = 0) behaviour. The product function of the molar magnetic susceptibility and temperature (γT) adopts constant and positive values close to zero (ca. $0.17 \,\mathrm{cm^3 K \, mol^{-1}}$), which can be attributed either to the presence of a small amount of paramagnetic impurities or to the small portion of remnant high-spin molecules. Above 200 K, SCO takes place: the (χT) product function starts to increase, and at 330 K it reaches a plateau value of 3.3 cm³K mol⁻¹, which is in the expected range for the HS state of an iron(II) mononuclear system. The conversion of the spin is situated exactly in the room-temperature region and centred at $T_{1/2}$ = 285 K. When the sample was further heated to 370 K, its magnetic behaviour obeyed Curie's law, and the χT product function remained constant (at a value of approximately $3.3 \text{ cm}^3 \text{ K mol}^{-1}$). Variable-temperature magnetic measurements were carried out in heating as well as in cooling mode but did not reveal the presence of a thermal hysteresis.

The values of the SCO parameters that resulted from the best fit of experimental magnetic susceptibility (R = 5.4%) are collected in Table 1. The reconstructed curve is displayed in Figure 2a. The lower values of the susceptibility product between 280 and 320 K cannot be described in the context of the model employed. Indeed, the susceptibility curve is affected by the sample quality,^[42–44] which is hard to quantify, and one should also consider that the approach of Curie's paramagnet might be oversimplified for the non-octahedral coordination environment of **1**.^[41]







Figure 1. (a) Crystal structure of compound 1 { $[Fe(L)_2](ClO_4)_2$ }. At 180 K, bond lengths [Å] of the coordination polyhedron are: Fel-N8 1.890(4), Fel-N3 1.900(4), Fel-N6 1.954(6), Fel-N10 1.968(6), Fel-N5 1.971(5), Fel-N1 1.977(5) Å. (b) View of the unit cell of 1 along the *a*-*c* plane.

Table 1. Fitting parameters extracted from the reconstructed SCO curve for compound 1.

$g_{\rm HS}$	$x_{\rm PI}$	$(\Delta_{\rm eff}/k_{\rm B})$ [K]	$(J/k_{\rm B})$ [K]	$T_{1/2}$ [K]
2.17	0.04	1833	243.2	284.5

For photomagnetic experiments, the sample was slowly cooled down to 10 K, which resulted in the switching of 1 into the LS state, and an external magnetic field of 0.1 T was applied. The subsequent irradiation of 1 by using green laser light ($\lambda = 532$ nm, laser intensity was adjusted to

10 mW cm⁻²) caused a significant increase in the magnetic moment (Figure 2b, blue triangles). After about 60 min of irradiation, the χT product function reached saturation at 2 cm³ K mol⁻¹ and then the irradiation was turned off. The photoexcitation of the sample caused an increase in χT up to 3.17 cm³ K mol⁻¹ (at 55 K), which is very similar to the HS value observed above 330 K in the case of thermally induced SCO (standard magnetic measurement in the dark). The increase in the product function between 10 and 55 K can be attributed to the zero-field splitting of the metastable S = 2 state. The rise in the temperature above



Figure 2. Magnetic and photomagnetic properties of **1** recorded at B = 0.1 T. (a) Variable-temperature dependence of the χT product (red circles) in the dark; reconstruction of the ST curve according to the Ising-like model (black solid line); laser excitation ($\lambda = 532$ nm) at 10 K (blue triangles); data recorded in the warming mode after the irradiation (pink squares). The inset graph presents the temperature dependence of the χT product (red circles) in the dark; laser excitation ($\lambda = 532$ nm) at 10 K (blue triangles); data recorded in the χT product with respect to the temperature. (b) Variable-temperature dependence of the χT product (red circles) in the dark; laser excitation ($\lambda = 532$ nm) at 10 K (blue triangles); the heating and the subsequent cooling mode of the light-induced thermal hysteresis (LITH) experiment were recorded while the sample was permanently irradiated by the laser (brown circles).

55 K results in a decrease in the χT product, which ultimately undergoes a complete thermal relaxation to the LS ground spin state. The T_{LIESST} value, calculated from the minimum in the $\partial(\chi T)/\partial T$ versus T curve, was determined to be 70 K. The result of the thermal quenching of the photo excited HS fraction in compound 1 is a new entry to the $T_{\rm LIESST}$ database proposed by Létard et al. In this study, the authors compared and investigated the relation between the experimental $T_{1/2}$ and T_{LIESST} temperatures for the several families of iron(II) spin-crossover complexes. For the iron(II)-bis(pyrazol-n-yl)pyridine^[35] complexes (for which n = 1 or 3), the empirical formula $T_{\text{LIESST}} = 150 - 0.3T_{1/2}$ has been proposed. Thus, we can conclude that the spincrossover parameters of compound 1 reported herein are consistent with the linear dependence T_{LIESST} versus $T_{1/2}$ being close to the calculated T_{LIESST} temperature of 64.5 K.

To learn more about the bistability of the photoexcited HS state of 1, the light-induced thermal hysteresis (LITH) was investigated (Figure 2b). The sample was irradiated at 10 K until saturation of the magnetic signal was reached, then the temperature was slowly elevated up to 100 K under permanent irradiation and subsequently cooled again to 10 K. According to the calculated x_{HS} fraction, 50% of photoexcited HS molecules exist at 72 K in the heating and at 62 K in the cooling mode. Thus, the experiment reveals a width of around 10 K of light-induced thermal hysteresis, thereby proving that the phototrapped HS phase displays a considerable degree of cooperativity.

Temperature-Dependent Spectroscopic Investigation

The change in the Fe–N bond strength due to the SCO can be monitored by using variable-temperature far-IR

spectroscopy. The far-IR spectra of compound 1 were recorded within the spectral range of 550 and 200 cm⁻¹ between 173 and 321 K (Figure 3). The prominent N-Fe-N mode of the LS iron(II) ion at around 400 cm^{-1} and the HS iron(II) ion at around 200 cm⁻¹ can be used as a verification of the spin-crossover behaviour obtained by magnetic measurements and additionally for the comparison of several vibrational modes that are significant for the respective molecule within the measured temperature range.^[45] In a series of far-IR spectra measured as a function of temperature, the vibrations at 247, 255 and 303 cm^{-1} that belong to the HS species can be readily recognised as those that increase in intensity with elevation of the temperature. The high-spin molar fraction was calculated from the integrated area of three particular vibrational bands that show a consistent temperature dependence of $x_{\rm HS}$ (Figure 5, at 247 cm⁻¹ black triangles, at 255 cm⁻¹ green triangles, at 303 cm⁻¹ pink hexagons; see also the Supporting Information). The transition temperatures determined by far-IR spectroscopy are in very good agreement with those obtained from the magnetic measurements (see above) and possess values of 280 (for the 247 cm^{-1} band), 282 (for the 255 cm⁻¹ band) and 283 K (for the 303 K band). The presence of HS vibrational bands at 173 K can be explained by a small amount of remnant or frozen high-spin fraction. The absence of thermally activated LS vibrational bands with decreasing intensities expected around 400 cm⁻¹ can most probably be explained by the fact that they are hidden behind skeletal vibrations with stronger intensities.

The thermal SCO properties of compound 1 were also monitored by variable-temperature Vis absorption spectroscopy. The Vis spectra, measured by diffuse reflectance as a function of the temperature in the range 209–373 K,



Figure 3. Variable-temperature far-IR spectra recorded in the thermal region of the spin crossover of compound 1. The labelled vibrational bands at 247, 255 and 303 cm⁻¹ show increasing absorbance with the elevation of temperature.

were recorded in the spectral range 12000–24000 cm⁻¹. Figure 4a presents the spectral changes for compound 1 measured along its thermal spin crossover. The band around 12000 cm⁻¹ (833 nm) corresponds to a d-d transition (${}^{5}T_{2}$ \rightarrow ⁵E) of the high-spin iron(II) centre, whereas the absorption in the 15000–20000 cm⁻¹ (666–500 nm) range can be attributed to both the d-d and metal-to-ligand chargetransfer (MLCT) transition of the low-spin state. At the lowest temperature of measurement (209 K), the shoulder centred at 18666 cm⁻¹ (535 nm) possesses the strongest intensity and decreases with elevation of temperature, thus indicating an increase of high-spin-state value. At 373 K the low-spin band has vanished completely. The resulting absorption bands of 1 at about 20000 cm⁻¹ show only HS character. To extract the high-spin molar fraction from the temperature-dependent spectroscopic data set, the spectrum

of the high-spin compound recorded at 373 K was subtracted from all measured spectra, which caused apparition of a clear low-spin ${}^{1}A_{1}-{}^{1}T_{1}$ band (Figure 4b) centred at 17222 cm⁻¹ (581 nm). Then, the values of maximum absorbance were used for calculation of the high-spin molar fraction (Figure 5 blue squares; see also the Supporting Information), and the determined transition temperature $T_{1/2}$ = 288 K is situated very close to the value observed in the case of the magnetic investigation ($T_{1/2}$ = 285 K; see above).

The Mössbauer spectroscopy on a powdered and ⁵⁷Feenriched sample of compound 1 was carried out at 14, 47, 98, 151, 200, 260, 276, 285 and 297 K. The spectroscopic parameters obtained by the least-squares fitting of the experimental data are given in Table 2. The spectra measured in the temperature range of 14–200 K are composed of two components and are similar to each other. The isomer shift



Figure 4. (a) Variable-temperature absorption spectra of compound 1. (b) The subtraction of all recorded Vis spectra with the spectrum of 1 in HS (at 373 K) reveals a low-spin d–d absorption band centred at 17222 cm⁻¹, the intensities of which decrease with elevation of the temperature.



Figure 5. Comparison of the temperature-dependent high-spin molar fraction calculated from the magnetic measurements (red circles) with those from variable-temperature Mössbauer (green diamonds), Vis (blue squares) and far-IR (vibration at 247 cm⁻¹ black triangles, at 255 cm⁻¹ green triangles, at 303 cm⁻¹ pink hexagons) spectroscopy.

and quadrupole splitting of the major doublet vary in the range 0.405–0.369 mm s⁻¹ (δ) and 0.725–0.687 mm s⁻¹ ($E_{\rm O}$), respectively, with typical values for Fe^{II}-bis(pyrazol-1-yl)pyridine compounds in the low-spin state.^[26,27,30] The parameters of the second minor doublet collected in the temperature range of 14–200 K ($\delta = 1.124-0.878 \text{ mm s}^{-1}$; $E_{\Omega} =$ $2.872-2.079 \text{ mm s}^{-1}$) allow to conclude that the second fraction belongs to the HS Fe^{II} ions. The ratio of LS and HS molar fractions is approximately 87:13. The presence of about 13% remaining HS $\mathrm{Fe^{II}}$ fraction below 200 K is in disagreement with the magnetic measurements, which has shown an almost complete $LS \leftrightarrow HS$ transition and can be explained by the inconsistency between the Debye-Waller factors of iron(II) in LS and in HS.^[46] Upon subsequent heating, the LS doublet loses intensity in favour of the HS doublet, thus indicating unambiguously the occurrence of spin conversion. The HS mole ratio calculated from Mössbauer spectra increases in good accord with the HS molar fraction obtained from the magnetic measurements (Figure 3). At 297 K, the LS and HS states are observed in populations of 26 and 74%, respectively.

Table 2. Mössbauer spectra parameters for compound 1.

T [K]		Fe ^{II} LS			Fe ^{II} HS	
	$\delta [{ m mms^{-1}}]$	$E_{\rm Q} [{\rm mms^{-1}}]$	A [%]	$\delta [{ m mms^{-1}}]$	$E_{\rm Q} [{\rm mms^{-1}}]$	A [%]
14	0.4050	0.7250	82	1.1240	2.8720	18
47	0.3990	0.7070	84	1.0880	2.7100	14
98	0.3860	0.6730	88	1.0110	2.3840	12
151	0.3840	0.6860	90	0.9240	2.2170	10
200	0.3690	0.6870	90	0.8780	2.0790	10
260	0.3220	0.7300	79	1.0040	1.7430	10
276	0.3200	0.7130	58	0.9930	1.6480	42
285	0.3200	0.7010	48	0.9870	1.6590	52
297	0.3130	0.5320	26	0.9700	1.6470	74

Conclusion

The presented study explores a novel photoswitchable spin-crossover coordination compound. We have successfully synthesised and structurally investigated the thermally and photoswitchable iron(II) compound 1 of the formula $[Fe(L)_2](ClO_4)_2$. Importantly, the investigation of the magnetic properties reveals that the complex displays reversible $LS \leftrightarrow HS$ transition at about room temperature. The magnetic susceptibility can be satisfactorily modelled by the combination of the Curie law and an Ising-like approach that includes a weak cooperativeness. Furthermore, variable-temperature spectroscopic investigations allowed us to validate the room-temperature spin-state conversion of compound 1. Far-IR spectra indicate three different HS vibrational bands. Their intensity increased upon elevation of the temperature. Absorption spectroscopy in the Vis spectral range allows the monitoring of spin crossover according to the LS d-d electronic transition. The intensity of this transition decreases with increasing temperature. Mössbauer spectroscopy was focused on the low-temperature region and revealed a small remnant fraction of HS iron(II). The transition temperatures extracted from the spectroscopy investigations are highly consistent with the value of $T_{1/2}$ that was concluded from the magnetic investigation. The LS \rightarrow HS photoinduced spin conversion was measured at low temperature and revealed the existence of a metastable photoactivated paramagnetic HS state almost up to the boiling temperature of liquid nitrogen. Moreover, the temperature dependence of a permanently irradiated sample shows a wide light-induced thermal hysteresis loop for compound 1. These results set the stage for implementing photoswitchable SCO compounds in device environments under near-surface conditions^[47] to enable single-molecule experiments.^[48]

Experimental Section

General: Purchased chemicals {(4-formylphenyl)boronic acid, [Pd⁰(PPh₃)₄], Fe(ClO₄)₂·xH₂O, Na₂CO₃} were used as received. 4-Iodo-2,6-bis(pyrazol-1-yl)pyridine was prepared as described previously.^[21,25] Tetrahydrofuran, dichloromethane, methanol, acetonitrile and diethyl ether solvents were used without any further purification. ¹H and ¹³C NMR spectra were recorded with a Bruker DPX 300 spectrometer with solvent proton and carbon atoms as internal standards. MALDI-TOF mass spectrometric analytical data were acquired with a Voyager-DE PRO Bio spectrometry workstation. Electrospray ionisation time-of-flight (ESI-TOF) mass spectrometric analytical data were acquired with a Bruker microOTOF-Q II. FTIR spectra were measured in KBr pellets (Magna FTIR 750, Nicolet) in the 4000–400 cm⁻¹ region. Elemental analyses of carbon, hydrogen, and nitrogen were carried out with a Vario Micro Cube.

Ligand Preparation: 4-Iodo-2,6-bis(pyrazol-1-yl)pyridine was prepared according a reported procedure^[25,23] in 80% yield as a white powder. Ligand L was prepared similarly to the already reported procedure:^[40] 4-iodo-2,6-dipyrazolylpyridine (1.348 g, 4 mmol), (4formylphenyl)boronic acid (0.6 g, 4 mmol) and $[Pd^0(PPh_3)_4]$ (0.46 g, 0.4 mmol, 10%) were suspended in a solution of tetra-



Table 3. Crystal data for compound 1 $[Fe(L)_2](ClO_4)_2$.

ring, a deoxygenated solution of Na_2CO_3 (10 cm ³ , 2 M) in water
was added, and the mixture was heated to reflux at 80 °C under
nitrogen for 24 h. Then the mixtures of solvents were removed with
a rotary evaporator, and the remaining residue was treated with
water and extracted with CH ₂ Cl ₂ . The separated organic layers
were dried with MgSO ₄ , and the solvent was removed by evapora-
tion. The solid residue was at first column-chromatographed on
silica with CH ₂ Cl ₂ /methanol (25:1; $R_{\rm f} = 0.84$) as eluent. The com-
bined colourless solutions upon evaporation yielded a white pow-
der of L (1 g, yield 85%). ¹ H NMR (300 MHz, CD ₂ Cl ₂ , 25 °C): δ
= 10.07 (s, 1 H, C-H _{ald}), 8.62 (dd, 2 H, pyrazole), 8.13 (s, 2 H,
pyridine), 8.00 (dd, 4 H, 1.4-phenylene), 7.76 (dd, 2 H, pyrazole),
6.50 (td, ${}^{3}J$ = 2.7 Hz, ${}^{4}J$ = 0.6 Hz, 2 H, pyrazole) ppm. ${}^{13}C$ NMR
(75 MHz, CDCl ₃ , 25 °C): <i>δ</i> = 191.93 (C=O), 152.97, 151.06, 143.47,
142.91, 137.21, 130.67, 128.27, 127.58, 108.54, 107.77 ppm.
MALDI-TOF: experiment: <i>m</i> / <i>z</i> (%) = 316.78 (100), 317.77 (22),
318.77 (5); simulation: m/z (%) = 315.11 (100), 316.11 (21), 317.12
(4). FTIR: \tilde{v} = 3152, 3123, 3107, 3095 (C _{ar} –H); 1615 (HC=O); 1561
$(C_{ar}-C_{ar})$ cm ⁻¹ . $C_{18}H_{13}N_5O$ (315.33): calcd. 68.56, H 4.16, N 22.21;
found C 68.21, H 4 33, N 21.23.

hydrofuran into which N_2 gas was bubbled. After 30 min of stir-

Synthesis of Compound 1: Ligand L (100 mg, 0.317 mmol) was dissolved in CH₃CN (100 cm³) and stirred under N₂ at 70 °C for 30 min. Then $Fe(ClO_4)_2 \cdot 6H_2O$ (57 mg (0.158 mmol) as a solid was added. The complexation of the ligand occurred immediately and exhibited a colour change of the solution to red-orange. The reaction mixture was stirred for a further 4 h (70 °C, N₂), cooled, filtered and left for crystallisation by diffusion of diethyl ether under N2. After two weeks, orange crystals were collected, washed in a small amount of acetonitrile, rinsed with diethyl ether and dried under N₂. Yield: 80%. ¹H NMR (300 MHz, CD₃CN, 25 °C): δ = 62.37 (pyrazole), 55.05 (4-pyridine), 37.51 (pyrazole), 35.94 (s, pyrazole), 10.13 (1 H, HC=O), 8.04 (dd, 4 H, phenyl) ppm. ESI-TOF MS: calcd. for $C_{36}H_{26}FeN_{10}O_2$ [Fe(L)₂]²⁺ 343.08; found 343.08; calcd for C₃₆H₂₆ClFeN₁₀O₆ [Fe(L)₂(ClO₄)]¹⁺ 785.11; found 785.12. FTIR (KBr pellet): $\tilde{v} = 3146$, 3118, 3053, 3034 (C_{ar}-H); 1687 (HC=O); 1631 (C_{ar} - C_{ar}) cm⁻¹. $C_{36}H_{26}Cl_2FeN_{10}O_8$ (885.42): calcd. 48.83, H 2.96, N 15.82; found C 48.44, H 3.10, N 15.68.

Single-Crystal Diffraction: Single-crystal X-ray diffraction data (Table 3) were collected with a STOE IPDS II diffractometer with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). 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).^[40,49,50] CCDC-899972 (1) 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.

Magnetic Susceptibility Measurements: All magnetic measurements reported herein were performed with a SQUID magnetometer (MPMS-XL7, Quantum Design). For standard magnetic as well as for photomagnetic experiments, the temperature-dependent magnetisation was recorded at B = 0.1 T as an external magnetic field. The temperature-sweeping rate was 1 K min⁻¹ (standard measurements in the dark) or 0.3 K min⁻¹ (photomagnetic experiments), and it was the same for the cooling and for the heating mode. Gelatine capsules were used as sample containers for the standard measurement in the temperature range $5 \leftrightarrow 370$ K. The very small diamagnetic signal 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 by using Pascal's constants.^[51,52] The photo-

Empirical formula	C ₃₆ H ₂₆ Cl ₂ FeN ₁₀ O ₁₀
$M_r [gmol^{-1}]$	885.42
Crystal colour	dark orange
T[K]	180(2)
λ[Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	17.162(3)
b [Å]	14.827(3)
c [Å]	15.012(3)
β [°]	107.81(3)
$V[Å^3]$	3636.9(13)
Z	4
$\rho_{\text{calcd.}} [\text{g cm}^{-3}]$	1.617
μ (Mo- K_{α}) [mm ⁻¹]	0.638
F(000)	1808
Crystal size [mm]	$0.18 \times 0.15 \times 0.05$
θ range for data collection [°]	2.07-23.31
Final <i>R</i> indices $[I > 2\sigma(I)]^{[a]}$	$R_1 = 0.0708, wR_2 = 0.1012$
<i>R</i> indices (all data) ^[a]	$R_1 = 0.1553, wR_2 = 0.1219$
GoF on F^2	0.937

[a] $R1 = \Sigma(F_{o} - F_{c})/\Sigma(F_{o}); wR2 = \{\Sigma[w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma[w(F_{c}^{2})^{2}]\}^{1/2}.$

magnetic measurements were performed with a diode-pumped solid-state laser (DPSS) Kvant ($\lambda = 532 \text{ nm}$, 300 mW) coupled through an optical fibre to the cavity of the MPMS SQUID instrument, and the power at the sample surface was adjusted to 10 mW cm⁻². For the photomagnetic experiments, the mixture of sample and low-temperature grease was filled into a small quartz glass jar and mounted in the sample holder. The weight of compound 1 (ca. 0.45 mg) was obtained by weighing in the quartz glass jar at first and then verified by comparison of the thermal SCO curve with that of a more accurately weighed sample of the same compound. After slowly cooling to 10 K, the sample, now in the low-spin state, was irradiated and the change in magnetisation followed. When the saturation point was reached (after ca. 70 min), the light was switched off, the temperature was increased at a rate of 0.3 K min-1, and the magnetisation was measured at 1 K intervals. T_{LIESST} was determined from the minimum of the $\partial(\chi_M T)/\partial T$ versus T curve for the relaxation process. For the detection of lightinduced thermal hysteresis (LITH), the sample was slowly cooled to 10 K again, and then the light and magnetic field (0.1 T) were switched on. Next, the temperature dependence of magnetisation of the material under permanent irradiation was monitored during thermal cycling up to 100 K and back down to 10 K at a rate of 0.3 K min⁻¹. Since we have observed that the quartz glass jar filled with low-temperature grease only (in the absence of sample) exhibits a very small paramagnetic signal that is rather stable with temperature (ca. 1.0×10^{-5} cm³), all magnetic data were corrected for this background value and then processed into the (χT) product function.

Theoretical Approach: From the monitored spin-crossover quantities, the magnetic susceptibility possesses the highest accuracy (see above), therefore we fitted this data set. The total susceptibility was calculated as Equation (1):

$$\chi = (x_{\rm LS} \cdot \chi_{\rm LS} + x_{\rm HS} \cdot \chi_{\rm HS}) \cdot (1 - x_{\rm PI}) + \chi_{\rm PI} \cdot x_{\rm PI}$$
(1)

in which x_{LS} , x_{HS} and x_{PI} indicate the molar fractions of the lowspin centres, high-spin centres and a paramagnetic impurity, respectively. The HS fraction was calculated with the Ising-like model^[42] in a slightly modified form [Equation (2)]:

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$$x_{\rm HS} = \frac{1}{1 + \exp\left[\frac{(\Delta_{\rm eff} + 2J) - 4Jx_{\rm HS}}{k_{\rm B}T} - \frac{\Delta_{\rm eff}}{k_{\rm B}T_{\rm 1/2}}\right]}$$
(2)

in which the effective degeneracy ratio $r_{\rm eff}$ was transformed to that of $T_{1/2}$ since this quantity can be easily retrieved from the experimental curve in our case. The relationship between $r_{\rm eff}$ and $T_{1/2}$ in the frame of the used model is shown in Equation (3):

$$T_{1/2} = \frac{\Delta_{\text{eff}}}{k_{\text{B}} \ln r_{\text{eff}}}$$
(3)

A nonzero value of the cooperativity parameter *J* has to be taken into account to reconstruct the shape of the transition curve sufficiently. Consequently, an iterative procedure has to be applied to reach the value of x_{HS} . The ratio of paramagnetic impurity does not affect the iteration process. For corresponding individual susceptibilities, the Curie law is considered to be a sufficient approximation, so that it is fulfilled by Equation (4):

$$\chi_{S} = \frac{N_{A}\mu_{0}\mu_{B}^{2}}{k_{B}T}\frac{g_{S}^{2}S(S+1)}{3}$$
(4)

in which all symbols adopt their usual meaning. We suppose the paramagnetic impurity is a high-spin Fe^{III} system (i.e., S = 5/2) with fixed $g_{\rm PI} = 2.00$. The transition temperature was fixed to 284.5 K. Finally, we are left with four free parameters: $x_{\rm PI}$, $\Delta_{\rm eff}$, J and $g_{\rm HS}$, which are to be obtained by fitting the experimental susceptibility data after their correction to the underlying diamagnetism.

Variable-Temperature Spectroscopy Investigation: The temperaturedependent far-IR spectra were measured in the 550-200 cm⁻¹ region with a Perkin-Elmer 2000 far-FTIR spectrometer. The polyethylene pellets of the sample were mounted in a thermostatable sample holder with silicon windows between 173 and 321 K. To obtain a reasonable signal-to-noise ratio, 800 scans were totalled for each spectrum. The sample was thermostatted 10 min for each measurement. The area of LS vibrational bands, which were chosen for the analysis of spin-crossover properties, was integrated by using the Origin 8.0 software.^[53] Electronic spectra of the powder samples were measured with a Perkin-Elmer Lambda 900 UV/Vis/ NIR spectrometer equipped with a thermostable powder sample holder in diffuse reflection geometry (Praying MantisTM) between 12000 and 24000 cm⁻¹ in the temperature range of 209-373 K. The Mössbauer spectral absorber contained approximately 80 mg cm⁻² of compound 1 and the spectra were measured from 14 K to room temperature on a constant-acceleration spectrometer that utilised a ⁵⁷Co source in a rhodium matrix and was calibrated at room temperature with an α -Fe foil.

Supporting Information (see footnote on the first page of this article): Far-IR and Vis absorption spectroscopy of 1; Mössbauer spectra of compound 1.

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- R. Vincent, S. Klyatskaya, M. Ruben, W. Wernsdorfer, F. Balestro, *Nature* 2012, 488, 367.
- [2] H. van der Zant, Nat. Nanotechnol. 2012, 7, 555.
- [3] *Molecular Switches* (Ed.: B. L. Feringa), Wiley-VCH, Weinheim, **2001**.
- [4] E. Breuning, M. Ruben, J. M. Lehn, F. Renz, Y. Garcia, V. Ksenofontov, P. Güttlich, E. Wegelius, K. Rissanen, Angew. Chem. 2000, 112, 2563; Angew. Chem. Int. Ed. 2000, 39, 2504.
- [5] I. Nemec, R. Herchel, R. Boča, Z. Trávníček, I. Svoboda, H. Fuess, W. Linert, *Dalton Trans.* 2011, 40, 10090.
- [6] V. Ksenofontov, A. B. Gaspar, P. Gütlich, Top. Curr. Chem. 2004, 235, 23.
- [7] A. Bousseksou, F. Varret, M. Goiran, K. Boukheddaden, J. P. Tuchagues, *Top. Curr. Chem.* 2004, 235, 65.
- [8] V. Meded, A. Bagrets, K. Fink, R. Chandrasekar, M. Ruben, F. Evers, A. Bernand-Mantel, J. S. Seldenthuis, A. Beukman, H. S. J. van der Zant, *Phys. Rev. B* 2011, *83*, 245415.
- [9] F. Prins, M. Monrabal-Capilla, E. A. Osorio, E. Coronado, H. S. J. van der Zant, Adv. Mater. 2011, 23, 1545.
- [10] A. Hauser, Top. Curr. Chem. 2004, 234, 155.
- [11] D. Collison, C. D. Garner, C. M. McGrath, J. F. W. Mosselmans, M. D. Roper, J. M. W. Seddon, E. Sinn, N. A. Young, J. *Chem. Soc., Dalton Trans.* 1997, 4371.
- [12] O. Kahn, C. Jay-Martinez, Science 1998, 279, 44.
- [13] R. N. Muller, E. L. Vander, S. Laurent, J. Am. Chem. Soc. 2003, 125, 8405–8407.
- [14] J.-F. Létard, P. Guionneau, L. Goux-Capes, *Top. Curr. Chem.* 2004, 235, 221.
- [15] T. Miyamachi, M. Gruber, V. Davesne, M. Bowen, S. Boukari, L. Joly, F. Scheurer, G. Rogez, T. K. Yamada, P. Ohresser, E. Beaurepaire, W. Wulfhekel, *Nature Commun.* 2012, DOI: 10.1038/ncomms1940.
- [16] T. G. Gopakumar, F. Matino, H. Naggert, A. Bannwarth, F. Tuczek, R. Berndt, Angew. Chem. 2012, 124, 6367; Angew. Chem. Int. Ed. 2012, 51, 6262–6266.
- [17] I. Šalitroš, N. T. Madhu, R. Boča, J. Pavlik, M. Ruben, Monatsh. Chem. 2009, 140, 695.
- [18] M. A. Halcrow, Coord. Chem. Rev. 2005, 249, 2880.
- [19] C. A. Kilner, M. A. Halcrow, Polyhedron 2006, 25, 235.
- [20] J. Elhaïk, D. J. Evans, C. A. Kilner, M. A. Halcrow, *Dalton Trans.* 2005, 1693.
- [21] J. Elhaïk, V. A. Money, S. A. Barrett, C. A. Kilner, I. R. Evans, M. A. Halcrow, *Dalton Trans.* 2003, 2053.
- [22] J. M. Holland, J. A. McAllister, C. A. Kilner, M. Thornton-Pett, A. J. Bridgeman, M. A. Halcrow, J. Chem. Soc., Dalton Trans. 2002, 548.
- [23] N. T. Madhu, I. Salitros, F. Schramm, S. Klyatskaya, O. Fuhr, M. Ruben, C. R. Chim. 2008, 11, 1166.
- [24] R. Gonzalez-Prieto, B. Fleury, F. Schramm, G. Zoppellaro, R. Chandrasekar, O. Fuhr, S. Lebedkin, M. Kappes, M. Ruben, *Dalton Trans.* 2011, 40, 7564.
- [25] R. Chandrasekar, F. Schramm, O. Fuhr, M. Ruben, Eur. J. Inorg. Chem. 2008, 2649.
- [26] C. Rajadurai, O. Fuhr, R. Kruk, M. Ghafari, H. Hahn, M. Ruben, *Chem. Commun.* 2007, 2636.
- [27] C. Rajadurai, F. Schramm, S. Brink, O. Fuhr, M. Ghafari, R. Kruk, M. Ruben, *Inorg. Chem.* 2006, 45, 10019.
- [28] M. Clemente-León, E. Coronado, M. C. Giménez-López, F. M. Romero, *Inorg. Chem.* 2007, 46, 11266.
- [29] C. Rajadurai, Z. Qu, O. Fuhr, B. Gopalan, R. Kruk, M. Ghafari, M. Ruben, *Dalton Trans.* 2007, 3531.
- [30] I. Šalitros, J. Pavlik, R. Boča, O. Fuhr, C. Rajadurai, M. Ruben, *CrystEngComm* 2010, 12, 2361.
- [31] M. Haryono, F. W. Heinemann, K. Petukhov, K. Gieb, P. Müller, A. Grohmann, *Eur. J. Inorg. Chem.* 2009, 2136.
- [32] I. Šalitroš, O. Fuhr, A. Eichhöfer, R. Kruk, J. Pavlik, L. Dlháň, R. Boča, M. Ruben, *Dalton Trans.* 2012, 41, 5163.
- [33] M. A. Halcrow, Coord. Chem. Rev. 2009, 253, 2493.
- [34] J. Olguin, S. Brooker, Coord. Chem. Rev. 2011, 255, 203.



- [35] J.-F. Létard, P. Guionneau, O. Nguyen, J. Sanchez Costa, S. Marcén, G. Chastanet, M. Marchivie, L. Goux-Capes, *Chem. Eur. J.* 2005, 11, 4582.
- [36] V. A. Money, I. R. Evans, M. A. Halcrow, A. E. Goeta, J. A. K. Howard, *Chem. Commun.* 2003, 158.
- [37] E. Collet, N. Moisan, C. Baldé, R. Bertoni, E. Trzop, C. Laulhé, M. Lorenc, M. Servol, H. Cailleau, A. Tissot, M. L. Boillot, T. Graber, R. Henning, P. Coppens, M. Buron-Le Cointe, *Phys. Chem. Chem. Phys.* **2012**, *14*, 6192.
- [38] C. Carbonera, J. S. Costa, V. A. Money, J. Elhaïk, J. A. K. Howard, M. A. Halcrow, J. F. Létard, *Dalton Trans.* 2006, 3058–3066.
- [39] S. Marcén, L. Lecren, L. Capes, H. A. Goodwin, J. F. Létard, *Chem. Phys. Lett.* 2002, 358, 87.
- [40] P. Hui, K. M. Arif, R. Chandrasekar, Org. Biomol. Chem. 2012, 10, 2439.
- ^[41] $\Sigma = \sum_{i=1}^{12} (|\phi_i 90|)$; in which ϕ_i is the value of the N–Fe–N octahedron angle.
- [42] F. Varret, S. A. Salunke, K. Boukheddaden, A. Bousseksou, É. Codjovi, C. Enachescu, J. Linares, C. R. Chim. 2003, 6, 385.
- [43] M. S. Haddad, W. D. Federer, M. W. Lynch, D. N. Hendrickson, *Inorg. Chem.* 1981, 20, 131.
- [44] E. W. Muller, H. Spiering, P. Gütlich, Chem. Phys. Lett. 1982, 93, 567.

- [45] R. Boča, M. Boča, L. Dlháň, K. Falk, H. Fuess, W. Haase, R. Jaroščiak, B. Papánková, F. Renz, M. Vrbová, R. Werner, *Inorg. Chem.* 2001, 40, 3025.
- [46] J. A. Real, H. Bolvin, A. Bousseksou, A. Dworkin, O. Kahn, F. Varret, J. Zarembowitch, J. Am. Chem. Soc. 1992, 114, 4650.
- [47] M. Ruben, Angew. Chem. 2005, 117, 1620; Angew. Chem. Int. Ed. 2005, 44, 1594.
- [48] a) N. Lin, S. Stepanov, F. Vidal, K. Kern, M. S. Alam, S. Strömsdörfer, V. Dremov, P. Müller, A. Landa, M. Ruben, *Dalton Trans.* 2006, 2794; b) E. A. Osorio, T. Bjornholm, J.-M. Lehn, M. Ruben, H. S. J. van der Zant, *J. Phys. Condens. Matter* 2008, 20, 374121.
- [49] G. M. Sheldrick, Acta Crystallogr., Sect. A 1990, 46, 467.
- [50] G. M. Sheldrick, SHELXL-97 Program for the refinement of Crystal Structures, Release 97-2, University of Göttingen, Germany, 1997.
- [51] O. Kahn, Molecular Magnetism, VCH, New York, 1993.
- [52] R. Boča, *Theoretical Foundations of Molecular Magnetism*, Elsevier, Amsterdam, **1999**.
- [53] Origin, Version 8.0, OriginLab Corporation, One Roundhause Plaza, Northampton, MA 01060, USA, 2007.

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