

Room temperature switching of a neutral molecular iron(II) complex†

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Abrupt room temperature switching ($T_c = 295$ K with a 5 K hysteresis) was achieved in a neutral Fe^{II} complex based on a 2-(1*H*-pyrazol-1-yl)-6-(1*H*-tetrazol-5-yl)pyridine ligand. Structural characterization and spin crossover study (via SQUID magnetometry, photoexcitation and X-ray absorption spectroscopy) in the solid state are described.

Spin-crossover (SCO) complexes can switch their intrinsic spin state between the high spin (HS) state and the low spin (LS) state. This is caused by external stimuli such as temperature, pressure, light, electric or magnetic fields or charge flow.¹ Most of the known SCO compounds are transition-metal complexes, especially with 3d⁴–3d⁷ metal ions in (distorted) octahedral coordination geometry. A majority is based on Fe^{II} stabilized in a coordination environment of six nitrogen atoms of the ligand backbone. Molecular magnetic switches have been intensely investigated and discussed, especially in view of potential applications in devices for information storage and processing.² Assemblies of such SCO complexes have been synthesized and characterized in bulk, nanoscale, and surface phases. Typical methods for preparing the latter include *e.g.* Langmuir–Blodgett techniques, spin coating, and vacuum deposition, leading to multi-, mono- or sub-monolayer coverage of the substrate.³ The change in the spin state can steer the physical and chemical properties of the surface phase and can be monitored by a wide variety of methods, for example, IR, Mössbauer, NMR, Raman, UV/vis, and X-ray absorption

spectroscopies (XAS), conductometry, dielectrometry, diffractometry, refractometry, and magnetometry.^{4–10} For the preparation of functional devices it has to be considered that SCO complexes have to be brought into contact with metal surfaces directly leading to a partial loss of the switching properties.^{10,11} That is why the SCO molecules have to be decoupled from the underlying metallic surface, either by a thin insulator¹⁰ such as Cu₂N,¹² or by at least one sacrificial layer of molecules.^{10,11}

However, in order to process the SCO compounds into functional devices it is required that the material shows an abrupt and complete spin transition together with a wide thermal hysteresis behaviour at around room temperature.^{13,14} In recent years considerable effort has been undertaken to develop SCO complexes matching these requirements, but compounds with $T_{1/2}$ around room temperature are still scarce.¹⁵ Up to now it is still a great challenge to design and realize systems that can be switched at room temperature.

In this communication, we report for the first time a newly designed ligand **LH** (2-(1*H*-pyrazol-1-yl)-6-(1*H*-tetrazol-5-yl)pyridine) and the unprecedented neutral Fe^{II} complex **1**, [Fe(**LH**)₂], Scheme 1. We report the synthesis, the structural determination, and the characterisation of the spectral and magnetic properties of complex **1**. Magnetic studies of **1** revealed abrupt spin transition at room temperature ($T_{1/2} = 295$ K) with a hysteresis of 5 K which was characterised by susceptibility measurements. The room temperature character of the spin crossover was further studied by XAS.

The synthesis of **LH** was accomplished within four steps from commercially available starting materials in a yield of

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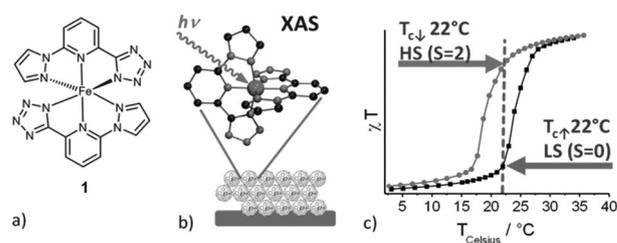
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Scheme 1 (a) Structural formula of **1**, (b) illustration of a layer of **1** investigated by SQUID magnetometry, photoexcitation, and XAS, (c) χT product as a function of temperature measured by SQUID magnetometry.

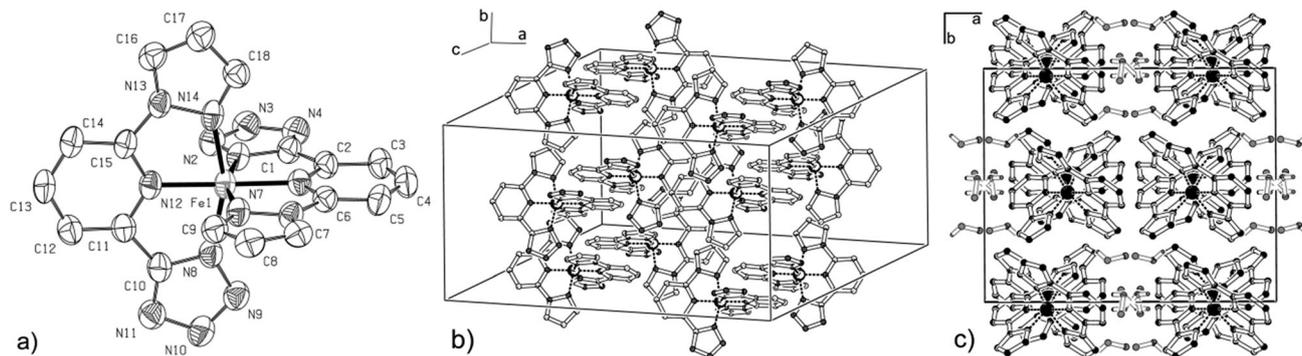


Fig. 1 (a) Molecular structure of **1**; crystal packing in the unit cell of **1**, (b) H atoms and solvent molecules omitted, (c) with lattice-CH₃OH in red.

about 37%. The substitution of the central pyridine moiety in **2** and **6** positions with a pyrazolyl and a tetrazolyl ring yields a ligand of asymmetric nature. The potassium salt of **L** was formed *in situ* by reacting the tetrazolyl NH function of **LH** with KO^tBu. This salt chelated the Fe^{II} ions to form a neutral uncharged complex without any counter ions, Scheme 1.

The reaction solution was allowed to evaporate slowly and single crystals suitable for X-ray diffraction were isolated after a few days. The yellow block-shaped crystals changed their colour to red after being removed from the mother solution. The molecular structure of **1** is shown in Fig. 1 (Fig. S1 and Tables S1 and S2, ESI[†]).

The unit cell of **1** contains eight complex units [Fe(L)₂] and ten molecules of methanol. Six nitrogen atoms of two ligands coordinate one Fe atom in a distorted octahedral way. At 180 K the Fe–N bond lengths have typical values for an LS Fe(II) ion of 1.916(3)–1.971(4) Å. Other indicators of the spin state in related Fe^{II}-bis(pyrazol-1-yl)pyridine complexes are the N_{pyrazole}–Fe–N_{pyrazole} angles (*ca.* 160° for LS and 145° for HS) and the Σ parameter (*ca.* 90° for LS and 160° for HS).^{16,17} According to the determined N–Fe–N angles of N(7)–Fe(1)–N(1) 160.04(14)°, N(14)–Fe(1)–N(8) 159.83(14)° and the calculated Σ = 87.1° one may conclude that compound **1** is in the LS state at 180 K. A detailed inspection of the crystal lattice of **1** shows two types of intermolecular interactions of neighbouring complexes: (A) a π-stacking between two pyrazolyl units, and (B) an edge-to-face π-stacking between a pyrazolyl ring and a tetrazolyl ring (Fig. 1 and Fig. S2–S4, ESI[†]). A more detailed description of both types of intermolecular interactions is given under point 4 of ESI.[†]

The conformational change of **1** due to the transition of the LS state to the HS state and *vice versa* induces a change of these intermolecular π–π interactions which propagate over the complete crystal lattice. Such weak intermolecular π–π interactions between the complexes in the crystal lattice are the reason for a cooperativity effect which is parental for the observed hysteresis behaviour (*vide infra*). The mono-anionic nature of **L** gives rise to the uncharged character of **1**.

The temperature-dependent investigation of the magnetic properties in the thermal range of 4–371 K revealed a room temperature SCO of complex **1** (Fig. 2a). The measurement shows abrupt and complete thermal SCO centred at 294.5 K from the HS state ($\chi T = 3.15 \text{ cm}^3 \text{ K mol}^{-1}$) to the LS state ($\chi T < 0.2 \text{ cm}^3 \text{ K mol}^{-1}$). Three subsequent cooling–heating cycles revealed the presence of a stable thermal hysteresis loop with 5 K width ($T_{1/2\downarrow} = 292 \text{ K}$, $T_{1/2\uparrow} = 297 \text{ K}$) whereby 80% of iron(II) atoms convert within 24 K upon cooling and within 21 K upon heating respectively.

In the case of the photomagnetic experiments, the sample was slowly cooled down to 10 K which results in the LS state of **1** and an external magnetic field of 0.1 T was applied. The subsequent irradiation of **1** using green laser light ($\lambda = 532 \text{ nm}$, laser intensity was adjusted to 10 mW cm^{-2}) caused a significant increase of the magnetic moment (Fig. 2a, blue triangles). After about 40 minutes of irradiation, the χT product function reached saturation at $1.6 \text{ cm}^3 \text{ K mol}^{-1}$ and the irradiation was turned off. The heating of the photoexcited sample caused an increase of χT up to $1.76 \text{ cm}^3 \text{ K mol}^{-1}$ (at 25 K; Fig. 2a, pink squares), which

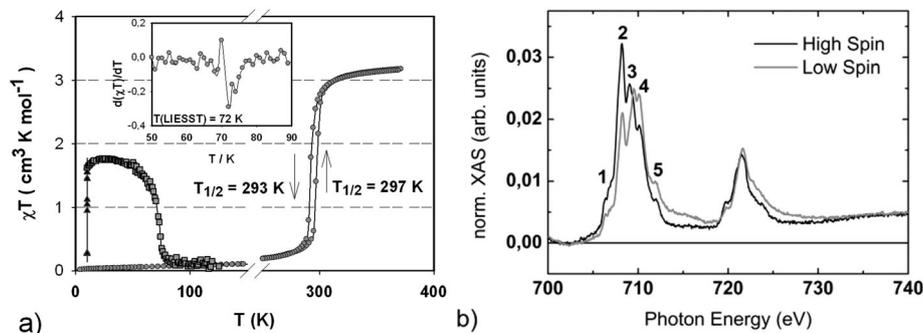


Fig. 2 (a) Magnetic properties of **1** ($B = 0.1 \text{ T}$). Temperature dependence of the χT product (red circles) in darkness; laser excitation ($\lambda = 532 \text{ nm}$) at 10 K (blue triangles); data recorded in the warming mode after irradiation (pink squares). Inset: temperature dependence of the first derivative of the χT product vs. temperature; (b) X-ray absorption spectra at the Fe L_{2,3} edge of **1** (red: LS state at $T = 5 \text{ K}$, black: HS state at 300 K).

corresponds to 56% of HS iron(II) ions. An increase of the product function between 10 and 25 K is attributed to the zero-field splitting of the metastable $S = 2$ state. The further increase of the temperature above 25 K results in a decreased χT product which finally undergoes a complete thermal relaxation in the LS ground spin state. The $T(\text{LIESST})$ value, calculated from the minimum in the $\partial(\chi T)/\partial T$ vs. T curve, is 72 K (inset of Fig. 2a).

The two spin states of **1** were also investigated by X-ray absorption spectroscopy (XAS) of a 150 μm layer deposited on the UHV tape. Fig. 2b shows the absorption spectra at the Fe $L_{2,3}$ edges of **1** at $T = 300$ K (black line) and $T = 5$ K (red line). The spectrum at 300 K belongs to the first measurement after transferring the sample to the UHV chamber, so the molecules had no history concerning higher or lower temperatures. Afterwards the sample was cooled down to 5 K and the red spectrum was recorded. In steps of 50 K we performed the X-ray absorption measurements until we reached 300 K again. Up to 300 K the spectra were identical to the one recorded at 5 K. After heating the sample to 340 K the spectrum revealed the same structures as that of the initial one. With this temperature dependent XAS measurement we confirm the high spin–low spin transition with a sharp transition temperature in the region of 300 K and a small thermal hysteresis. This results in different spin states at 300 K depending on the history of the sample, whether the molecules were cooled before or not. The Fe L_3 edge of the molecules shows several features, consecutively numbered from lower to higher energies (Fig. 2b). These spectral differences appear clearly and permit distinguishing between the LS state and the HS state of **1** at the respective temperatures. The shoulders 1 and 5 change their intensities, absolutely as well as relatively to each other. Even more obvious are the differences of the features 2, 3 and 4 of both spin states. While 2 is clearly the highest peak in the HS state, it is lower in intensity than 3 and 4 which are of similar intensity in the LS state. These spectral changes originate from the rearrangement and reoccupation of the Fe 3d-states along the HS–LS transition. In the HS state peak 3 is not only clearly more intense than 4, compared to the low spin state it is also shifted in energy. Typically, the low energy peak (2) is the highest in intensity in a HS state and decreases strongly in the LS state.^{9,10,18}

In conclusion, we have synthesized a neutral uncharged mononuclear SCO complex which completely and abruptly switches its spin state exactly at room temperature. To the best of our knowledge this is the first example of an uncharged tridentate pyridine based complex abstaining from charge-balancing counter ions. The weak intermolecular π – π interactions determined in the crystal lattice give rise to cooperativity of the investigated crystalline material culminating in a small hysteresis of 5 K. The uncharged molecular character of **1** makes it especially interesting for the sublimation process and the future integration of SCO compounds into functional devices for information storage, sensors and switchers which is currently in progress.¹⁹

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