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ARTICLE

1D iron(II)-1,2,4-triazolic chains with spin crossover assembled from discrete polynuclear complexes

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We report on a molecular cationic iron(II) complex with a 4-amino-1,2,4-triazole ligand and a tetraiodomercurate anion exhibiting an incomplete spin crossover (SCO). The complex exhibits an unusual disordered structure with a linear arrangement of ligand and water molecules that can potentially accommodate up to four iron atoms, but both terminal metal positions have half chemical occupancies, while occupancies of all ligands are full. This corresponds to the crystallisation of disordered trinuclear complexes arranged into 1D supramolecular chains. Iron cations have different N_6 or N_3O_3 coordination environments, leading to the thermally induced SCO in two thirds of the metal centres. This SCO behaviour was characterised by magnetic susceptibility measurements and Mössbauer spectroscopy.

Introduction

Spin crossover (SCO) complexes are an interesting class of materials with molecular bistability resulting from their ability to exist in two different spin states and to switch between them in response to an external stimulus.¹ This phenomenon is known for certain $3d^4$ – $3d^7$ metal complexes, but the majority of SCO research has been dedicated to the study of octahedral Fe^{II} ($3d^6$) compounds. Ferrous complexes with 1,2,4-triazoles constitute one of the most important and largest classes of SCO materials.² An Fe^{II} ion coordinated by six N atoms of six triazole rings will – apart from a few exceptions – exhibit a temperature and/or pressure induced spin transition due to the favourable ligand field strength.

For Fe^{II} and other first-row transition metals mononuclear triazole complexes are extremely rare. As a rule, bridging coordination of the triazole ring by N1 and N2 atoms occurs, provided that there are no steric constraints.³ However, mononuclear ferrous complexes with SCO, in which one of N1/N2 atoms remains idle, can be obtained with 4-R-1,2,4-triazoles ($R = N$ -salicylidene-4-amine or 2,4,6-trimethylpyridinium) (Fig. 1a).⁴

Trinuclear ferrous complexes $[Fe_3(trz)_6(Solv)_6]A_6$ ($Solv = H_2O, MeOH, EtOH$) can be obtained (Fig. 1b) with a ligand-to-metal ratio of 2:1 and with certain 4-substituted triazoles ($R =$ ethyl, isopropyl, nitrophenyl, furanylidene, etc.).⁵ In these compounds, the central Fe is hexakis-triazole coordinated (FeN_6) and usually shows spin transition. Two terminal Fe atoms are coordinated by three triazole rings and three solvent molecules each (e.g., FeN_3O_3) and remain high-spin (HS). Thus there are no strong interactions between the SCO centres, and the trinuclear complexes typically exhibit a gradual, non-cooperative transition. Alternatively, discrete triazolic complexes can be obtained starting from a chelating ligand, e.g. (1,2,4-triazol-1-yl)borate (Fig. 1c).⁶ Although formally mononuclear, the resulting complexes resemble trinuclear species, in which the two terminal metal ions are substituted by boron atoms.

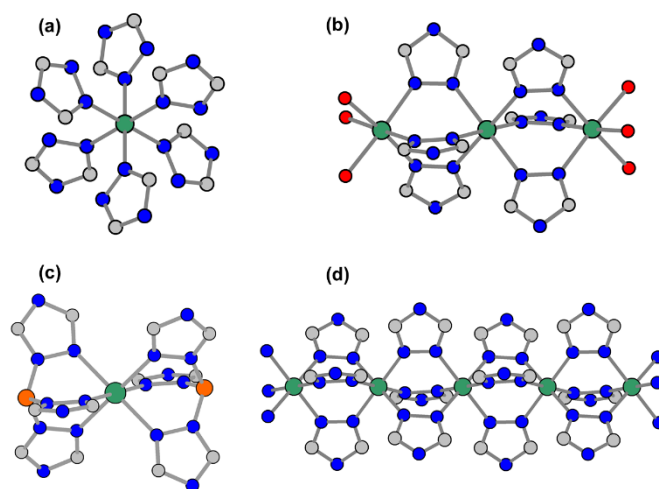


Fig. 1. Common types of ferrous complexes with 1,2,4-triazole exhibiting SCO: (a) mononuclear, (b) trinuclear, (c) scorpionate, (d) trinuclear.

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and (d) 1D coordination polymers. Colour code: Fe, green; N, blue; C, gray; O, red; B, orange.

With a higher ligand-to-metal ratio, 4-substituted triazoles and Fe^{II} salts yield coordination polymers of composition $[\text{Fe}(\text{Rtrz})_3]\text{A}_n$ ($n = 1-2$).² They have been in the spotlight after early works of Haasnoot and Lavrenova,⁷ with the major developments made by the groups of Kahn and Gütlich and later by Bousseksou, Letard, and Garcia.⁸ For a few decades, crystal structures of the polymeric complexes remained unavailable, as they could only be obtained as micro-crystalline powders. The first single crystal structure of $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2$ ($\text{NH}_2\text{trz} = 4\text{-amino-1,2,4-triazole}$) with SCO, in which Fe^{II} ions form 1D chains triple bridged by triazole rings (Fig. 1d), was reported by Guionneau et al. in 2011.^{9a} Since then, the structures of $[\text{Fe}(\text{Htrz})_2(\text{trz})]\text{BF}_4$,^{9b} $[\text{Fe}(\text{benzyl-trz})_3]\text{Pt}(\text{CN})_4$,^{9c} and $[\text{Fe}(\text{NH}_2\text{trz})_3]\text{SO}_4$ ^{9d} have been reported. Nowadays, these polymeric SCO systems appear to have the greatest potential for technological applications, for example in microthermometry,¹⁰ molecular electronics,¹¹ chemical sensors,¹² microwave absorbers,¹³ actuators,¹⁴ composite switchable materials,¹⁵ chiral switches,¹⁶ or switchable catalysis.¹⁷

Various studies on SCO materials in conjunction with using different ligand-to-metal ratios have illustrated that variation of the counterion is a powerful tool to tune the properties of Fe^{II} complexes with triazole ligands.¹⁸ Both cationic and anionic trinuclear complexes have been reported with different magnetic behaviour.¹⁹ One example of a neutral molecular complex with SCO has emerged.²⁰ Here we report the use of the tetraiodomercurate anion with the aim to isolate a Fe^{II} complex with NH_2trz , as a heavy anion may facilitate crystallisation of an uncommon species. In this way, we have obtained a molecular complex with an unprecedented composition and nuclearity exhibiting a SCO in two thirds of Fe^{II} centres at room temperature.

Results and discussion

The title complex (**1**) with the formal composition $[\text{Fe}_3(\text{NH}_2\text{trz})_9(\text{H}_2\text{O})_6](\text{HgI}_4)_3$ was prepared using a slow diffusion technique from $\text{Fe}(\text{ClO}_4)_2$, NH_2trz and K_2HgI_4 in a water-ethanol solution (see ESI† for details). X-ray diffraction analysis performed at 173 K showed that **1** crystallizes in the trigonal space group $R\bar{3}c$ with 6 formula units per cell. Its asymmetric unit contains two Fe centres, with Fe1 coordinated by six triazole rings and Fe2 coordinated by three triazole rings and three water molecules. By symmetry, two other positions (Fe1i and Fe2i) complete the apparent tetranuclear unit of the title complex (Fig. 2). Specifically, inner Fe^{II} ions show octahedral FeN_6 coordination, while the coordination environment of the Fe^{II} ions in the terminal positions is FeN_3O_3 . Average Fe–N bond distances for inner and outer metal ions are 2.029(12) and 2.178(15) Å respectively, suggesting that FeN_6 centres are low-spin (LS), and FeN_3O_3 are HS at 173 K.

Importantly, the site occupancies of two terminal Fe2 atoms are 0.5 each. However, all water molecules crystallised around the

Fe2 positions and the triazole ligands triply bridging Fe1 and Fe2 are fully occupied. The positive charge of the iron-triazolic chains is compensated by the HgI_4^{2-} anions, which occupy scarce voids between the chains. Because HgI_4^{2-} is bulky, only three anions can be crystallised per one cationic complex, which leads to crystallisation of only three Fe^{2+} ions into four potential metal sites.

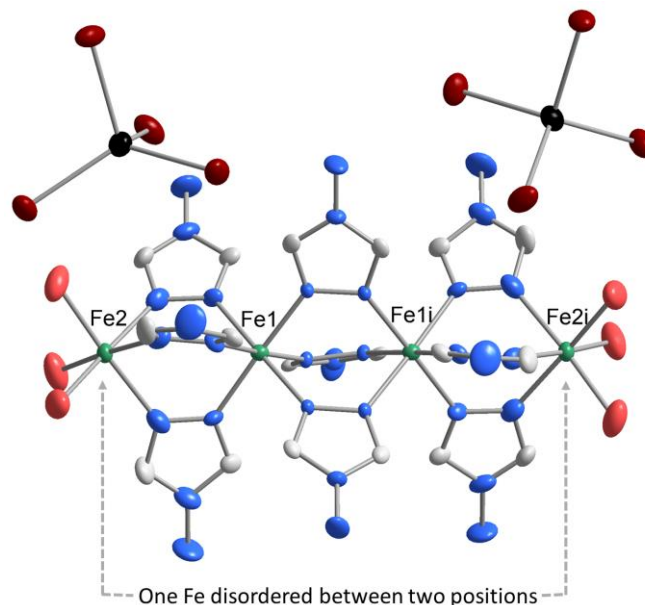


Fig. 2. Fragment of the crystal structure of **1** with atomic displacement parameters drawn at 50% probability. Occupancies of the Fe2 positions are 0.5, the disorder of anions is not shown. H atoms are omitted for clarity. Colour code: Fe, green; N, blue; O, red; C, gray; Hg, black; I, brown.

The linear disordered trinuclear complexes form infinite supramolecular 1D chains *via* hydrogen bonds. The H atoms of the water molecules were placed disordered between two positions with equal occupations to satisfy all possible options for hydrogen bonding. Each O atom of the water molecules coordinated to Fe2 acts as donor for a water molecule from a neighbouring complex with O–H...O distances of 2.82(2) Å (Fig. 3). When the Fe2 position is not filled due to a crystallographic disorder, water O atoms act as donors for the vacant N atoms of triazole rings with O–H...N distances of 3.07(3) Å. Careful analysis of the system of these contacts supports the assumption that a filled Fe2 position of each unit is oriented toward an Fe2 vacancy of the neighbouring unit. Statistically, however, the other alternatives with two vacant Fe2 positions or two occupied Fe2 positions placed side by side are also possible (Fig. S1, ESI†). The remaining H atoms of water molecules form weak O–H...I contacts (3.54(2)–3.79(2) Å) with the $(\text{HgI}_4)^{2-}$ anions. In addition, each I atom forms two weak N–H...I contacts (3.61(3)–3.87(3) Å and 3.38(2)–3.73(2) Å) with two amino groups of NH_2trz ligands. Iodine atoms of the $(\text{HgI}_4)^{2-}$ anions are disordered between two positions with occupancies 0.5 each, while occupancies of all Hg are full (Fig. S2, ESI†). Overall, this combination of intermolecular contacts leads to the stabilisation of the densely packed framework of **1** (Fig. S3,

ESI[†]). The general structure of **1** mimics to some extent the classic structure of 1D Fe-triazolic complexes $[\text{Fe}(\text{Rtrz})_3]\text{A}_n$, while displaying metal deficiency at certain metal centres and having water clusters instead of some organic ligands.⁹ In this regard, the inner core (Fe1 and Fe1i) resembles dinuclear iron-triazolic complexes with SCO, in which both metal cations exhibit FeN_6 coordination environment.²¹

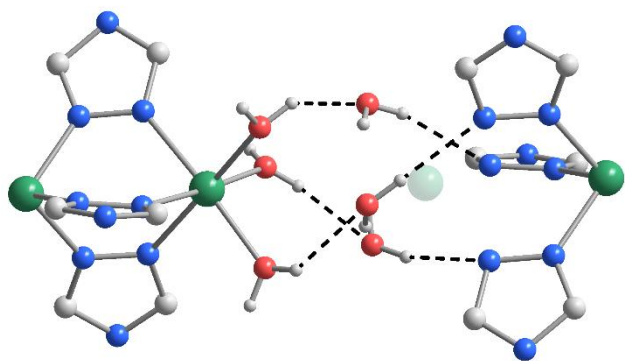


Fig. 3. System of hydrogen bonds linking the disordered trinuclear units into infinite 1D chains. Colour code: Fe, green; N, blue; O, red; H, gray. The non-filled due to crystallographic disordering Fe2 position is shown as transparent.

The magnetic properties of crystals of **1** recorded in the cooling and warming regimes are shown in Fig. 4. The product of the molar magnetic susceptibility with temperature, $\chi_{\text{M}}T$, as a function of temperature reveals a one-step spin transition. It is $9.9 \text{ cm}^3 \text{ K mol}^{-1}$ at 350 K, which is consistent with three Fe^{II} ions in the HS state. Upon cooling, $\chi_{\text{M}}T$ decreases gradually and reaches a value of $3.9 \text{ cm}^3 \text{ K mol}^{-1}$ below 100 K. This behaviour can be interpreted as a spin crossover of two thirds of Fe^{II} ions in **1**, while the other third remains HS. $\chi_{\text{M}}T$ is constant during further cooling, as expected on the basis of Curie's law for the paramagnetic species. An abrupt drop of the susceptibility below 20 K appears due to zero-field splitting, which is caused by residual HS Fe^{II} sites. The temperature dependence of the susceptibility was completely reversible when the sample was heated in the magnetic field, indicating the absence of hysteresis with $T_{1/2}$ (the temperature at which half of the SCO centres transited) of 280 K. The SCO behaviour of **1** was successfully reproduced in the subsequent cycle of cooling and heating (Fig. S4, ESI[†]). The first and second thermal cycles are virtually identical, because the structure of **1** does not contain any guest molecules and is thermally stable within the operated temperature region.

The incomplete character of SCO in **1** originates from the existence of two types of Fe^{II} with different first coordination spheres. Two inner Fe^{II} ions coordinated by six bridging triazole rings each apparently undergo a spin transition. This is consistent with their LS state at 173 K determined from the crystal structure. Two outer Fe^{II} sites with crystallographic occupancies of 0.5 constitute together one third of total iron content in **1** and exist in the HS state over the whole temperature range. By contrast, in classic trinuclear complexes

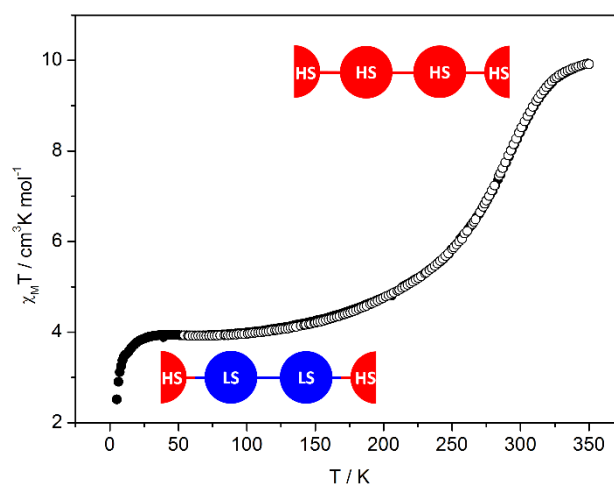


Fig. 4. Magnetic properties of powdered single crystals of **1** in the form of $\chi_{\text{M}}T$ versus T recorded in cooling (filled circles) and warming modes (open circles). The $\text{Fe}^{\text{II}}\text{N}_6$ centres exhibit SCO, while the $\text{Fe}^{\text{II}}\text{N}_3\text{O}_3$ centres with half occupancies remain HS over the whole temperature range.

$[\text{Fe}_3(\text{trz})_6(\text{H}_2\text{O})_6]\text{A}_6$ only one third of the Fe^{II} atoms undergoes SCO, while two thirds (*i.e.*, terminal Fe ions) remain always HS.⁵ The only exception is the molecular complex $[\text{Fe}_3(\text{bntrz})_6(\text{tcnset})_6]$ (bntrz = 4-(benzyl)-1,2,4-triazole; tcnset = tetracyano-2-thioethylpropenide), which exhibits a complete spin transition above room temperature, because all metal centres have FeN_6 ligation.²²

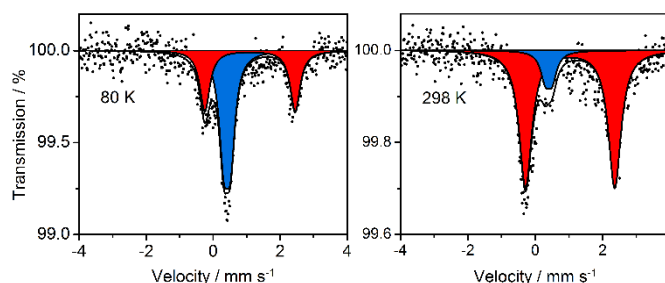


Fig. 5. ^{57}Fe Mössbauer spectra of **1** recorded at 80 K and 298 K. The quadrupole doublets attributed to the LS and HS Fe^{II} are shown in blue and red, respectively.

The spin crossover in **1** was investigated by ^{57}Fe Mössbauer spectroscopy, which allowed to monitor the molar fractions of different spin forms with temperature. The spectrum acquired at 80 K (Fig. 5) shows the co-existence of HS and LS Fe^{II} with a relative intensity 1:2. The outer two lines correspond to the quadrupole doublet arising from the terminal Fe^{II} ions. Its hyperfine parameters, isomer shift $\delta = 1.12(1) \text{ mm s}^{-1}$ and quadrupole splitting $\Delta E_{\text{Q}} = 2.85(2) \text{ mm s}^{-1}$, indicate the HS state of divalent iron. The signal in the middle represents the narrow doublet of the inner Fe^{II} ions in the LS state, with the parameters $\delta = 0.41(1) \text{ mm s}^{-1}$ and $\Delta E_{\text{Q}} = 0.2(1) \text{ mm s}^{-1}$. Upon heating the sample to 298 K, the relative intensity of the HS doublet ($\delta = 1.04(1) \text{ mm s}^{-1}$, $\Delta E_{\text{Q}} = 2.55(3) \text{ mm s}^{-1}$) increases up to 85% due to the LS to HS transition of the inner Fe^{II} ions. Correspondingly,

the LS doublet ($\delta = 0.4(1) \text{ mm s}^{-1}$, $\Delta E_Q = 0.2(1) \text{ mm s}^{-1}$) constitutes only 15% of the spectral intensity at 298 K in accordance with the magnetic susceptibility data. Investigation of **1** by Mössbauer spectroscopy was challenging, because of the HgI_4^{2-} anions with strong nonresonant γ -ray absorbance. This resulted in poorly resolved Mössbauer signals, especially at room temperature. Therefore, quadrupole doublets of the inner and terminal Fe^{II} ions in the HS state cannot be distinguished, although they are expected to have similar hyperfine parameters and overlap in the spectrum.^{5b}

Conclusions

In conclusion, we report a temperature-induced spin crossover in an unprecedentedly disordered trinuclear cationic Fe^{II} complex with 4-amino-1,2,4-triazole and tetraiodomercurate as a counteranion, which mimics a tetranuclear species. The triazole and water molecules build a robust linear coordination set for four metal centres. Two inner metal positions are formed by six triazole molecules, and two terminal positions are surrounded by three triazole and three water molecules each. One would expect this to lead to the genuine tetranuclear complex with four Fe^{II} ions in the metal pockets and corresponding number of anions around. However, probably due to steric hindrance, only three bulky $(\text{HgI}_4)^{2-}$ anions can be crystallised per one complex molecule leading to the availability of only three Fe^{II} ions to fill four positions. On the other hand, the triazole rings and water molecules are fully occupied, presumably due to the $\text{O} \cdots \text{H} \cdots \text{N}$ hydrogen bonds emerging in lieu of coordination bonds. Interestingly, the two inner metal positions (FeN_6) are always occupied, while two terminal pockets (FeN_3O_3) have only half occupancy. The complex exhibits an incomplete spin crossover with $T_{1/2} = 280 \text{ K}$, because only the inner metal positions have a hexakis-triazole environment favourable for SCO.

Experimental

Synthesis of $[\text{Fe}_3(\text{NH}_2\text{trz})_9(\text{H}_2\text{O})_6](\text{HgI}_4)_3$ (**1**)

All reagents and solvents were purchased from commercial sources and used without further purification. Single crystals of **1** were obtained by slow diffusion within three layers in a 10 mL test tube. A total of 1 mL of an aqueous solution containing K_2HgI_4 (0.2 mmol) and 4-amino-1,2,4-triazole (0.3 mmol) was poured on the bottom of the tube. Then 2 mL of a water-ethanol mixture (1:1) was gently layered on top. The third layer was a solution (1 mL) of $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol) in ethanol. In 2 weeks, this yielded pink crystals in the second layer; they were collected and used for X-ray diffraction experiments, magnetic susceptibility measurements, Mössbauer spectroscopy, and elemental analysis (Calcd for $\text{Fe}_3\text{C}_{18}\text{H}_{48}\text{N}_{36}\text{O}_6\text{Hg}_3\text{I}_{12}$: C, 6.85; H, 1.53; N, 15.97. Found: C, 6.77; H, 1.59; N, 16.03).

X-ray Diffraction

Single-crystal X-ray diffraction data for **1** were collected on a Bruker SMART diffractometer at 173 K, using $\text{Mo K}\alpha$ radiation. The structure was solved with ShelXS using direct methods and

refined with ShelXL using least-squares minimisation.²³ Olex2 was used as an interface to the ShelX programs.²⁴ Occupancies of two terminal iron atoms ($\text{Fe}2$) were found to be 0.5. Iodine atoms of the $(\text{HgI}_4)^{2-}$ anions were found to be disordered between two positions with occupancies of 0.5 each. Hydrogen atoms were placed at calculated positions and refined using a riding model.

Magnetic susceptibility measurements

Temperature-dependent magnetic susceptibility measurements on powdered single crystals of **1** were carried out using a Quantum Design MPMS-XL-5 SQUID magnetometer equipped with a 5 T magnet over the temperature range 5–350 K with a heating/cooling rate of 1 K min^{-1} and a magnetic field of 0.5 T. Diamagnetic correction for the molecule was derived from Pascal's constants.

Mössbauer Spectroscopy

^{57}Fe Mössbauer spectra were recorded in transmission geometry using a constant-acceleration Mössbauer spectrometer Wissel equipped with a liquid-nitrogen gas-flow cryostat. ^{57}Co embedded in a rhodium matrix was used as a Mössbauer source. The absorber was prepared by placing the powdered single crystals of **1** in a poly(methyl methacrylate) sample holder. Due to the poor resonant absorption, each spectrum was collected for 14 days. Fitting of the experimental data was performed with the Recoil software.²⁵ Hyperfine parameter uncertainties were evaluated from the covariance matrix of the fit. Isomer shifts are given relative to α -Fe at room temperature.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

‡ X-ray diffraction temperature is slightly above the LS region found in the magnetic experiment. Notably, this may lead to some elevated Fe-N bond lengths compared to the expected LS values.

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