Photoinduced *HS* state in the first spin-crossover chain containing a cyanocarbanion as bridging ligand†

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A new polymeric approach, based on cyanocarbanion ligands, for the design of spin crossover (SCO) compounds led us to the compound $[Fe(abpt)_2(tcpd)]$ (1) $(tcpd^{2-} = (C[C(CN)_2]_3)^{2-}$, abpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole) which has been characterised as the first SCO molecular chain involving a cyanocarbanion as bridging ligand.
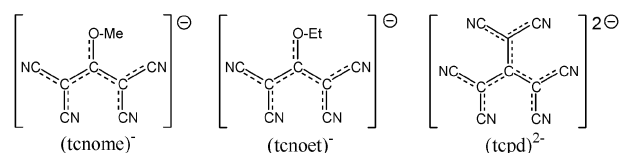
The design of new molecular compounds exhibiting the spin crossover phenomenon (SCO) is one of the most relevant and challenging questions in the field of magnetic molecular materials.[1–4] Iron(II) metal complexes involving the octahedral coordination sphere $[FeN_6]$ are the most studied SCO compounds. In such materials, the intermolecular interactions (π-stacking, hydrogen bonding and van der Waals interactions) play a crucial role to transmit the transition.[5] Albeit, the lack of control of these non-covalent interactions hardens their organization in the crystal. To better explore the cooperative effect between the active metal sites, Kahn *et al.*,[2] and others,[3,4] introduced an interesting and alternative approach based on the use of neutral suitable bridging ligands to covalently connect the metal centres. This resulted in the synthesis of several Fe^{II} SCO coordination polymers exhibiting rich and fascinating structural features coupled to their magnetic behaviours. However, these studies concern a limited number of neutral ligands and deal essentially with 4-substituted-1,2,4-triazole and poly-N-donating heterocyclic ligands.[2–4] In this context, our strategy is to extend this polymeric approach to anionic ligands involving several potentially donating nitrogen atoms (Scheme 1).

In our ongoing work on the new potentially bridging cyanocarbanion ligands, we have shown in the last few years that their structural and electronic characteristics (original coordination modes and high electronic delocalization) can be tuned by slight chemical or electrochemical modifications such as substitution of functional groups or variation of the

negative charge.[6] In this context, we have directed our efforts to the preparation of new SCO polymeric systems based on such bridging anions, for which the magnetic properties are essentially governed by subtle structural changes and therefore by the nature of the cyanocarbanion ligand.

Recently we have reported the first SCO series based on the tcm^- ($[C(CN)_3]^-$), $tcnome^-$ and $tcnoet^-$ ligands and abpt co-ligand (Scheme 1).[5] In this series, the single charge on the anion induces a terminal coordination mode for the polynitrile unit, resulting in neutral discrete SCO complexes. A further step in this direction would be the preparation of original extended SCO networks bearing the Fe^{II}-abpt complexes by using covalent bonds. Here we show how the use of potentially bridging dianionic ligands bearing different coordination sites constitute a very good and simple method to perform this task. We report herein the first SCO iron(II) molecular neutral chain $[Fe(abpt)_2(tcpd)]$ (1) involving an anion as bridging ligand. To the best of our knowledge, only two SCO molecular chains involving bridging anions have been reported. The first one, based on the triazolato anion, has not been fully structurally characterized,[7a] the second one is based on dicyanamide anion (aza-cyanocarbanion).[7b]

Compound 1 was obtained by diffusion of a methanolic solution containing $FeCl_2·4H_2O$ and abpt in an aqueous solution of $K_2(tcpd)$[8] in a silica gel (see S1 in ESI†). Single-crystal X-ray diffraction data of 1 were collected at 293, 100 and 10 K (flash cooled and light induced states).‡ The structure of 1 is built from one iron Fe^{II} ion, one $tcpd^{2-}$ anion presenting an orientation disorder (both located on inversion centers) and one chelating abpt ligand located on a general position. As shown in Fig. 1, the Fe^{II} ion adopts a FeN_4N_2 distorted octahedral geometry with four equatorial nitrogen atoms from two abpt chelating ligands (N1, N2, N1[(a)] and N2[(a)]) and two axial nitrogen atoms (N3 and N3[(a)]) from the $tcpd^{2-}$ ligand. The cyanocarbanion ligand adopts a $μ_2$-bridging mode *via* two nitrogen atoms of two different $C(CN)_2$ wings leading to a chain structure as depicted in Fig. 1. It is important to note that the disordered $tcpd^{2-}$ bridging ligand implies a more complicated local structure.

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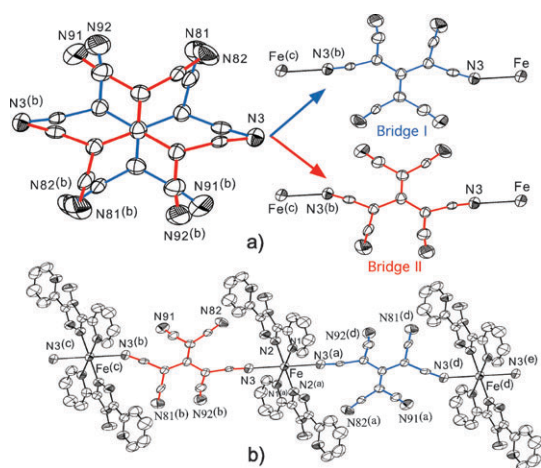

Scheme 1 Some examples of cyanocabanions.

Fig. 1 (a) ORTEP structure of the disordered bridging tcpd^{2-} anion; (b) ORTEP perspective view of a possible portion of the 1-D structure of **1** at 293 K. Code of equivalent positions: (a) $1 - x, 2 - y, -z$; (b) $2 - x, 2 - y, -z$; (c) $1 + x, y, z$; (d) $-1 + x, y, z$; (e) $-x, 2 - y, -z$.

Thus, the overall crystal structure may be pictured as formed by chains presenting statistically two different orientations of the tcpd^{2-} ligand as shown in Fig. 1(a) (see also Fig. S2 in ESI†). This observation is in good agreement with the crystallographic data since all attempts to solve the crystal structure in the corresponding non-centrosymmetric space group (Pn, $P2_1$ and $P1$) failed.

As can be seen in Table 1, strong modifications of the iron coordination sphere are observed in the temperature range 293–10 K. Such behaviour is in agreement with the presence of a SCO transition from HS to LS in **1**. The average Fe–N distances at room temperature and at 10 K "flash cooled" are in the range expected for 100% and 50% of the HS iron(II), respectively.[9] This observation is consistent with the presence of a metastable HS state at low temperatures as magnetic data indicate only *ca.* 30% remaining HS Fe^{II} at low temperature. Flash cooling results therefore in nearly 50% trapped HS species. When a single crystal is irradiated at 10 K, the average Fe–N distance increases to 2.156(3) Å, very close to the corresponding value observed at room temperature (2.159(2) Å).

This unusual behaviour is the structural signature of the presence of a photo-induced HS state in **1**, in agreement with the magnetic properties of this complex (see below).

The thermal dependence of the product of the molar magnetic susceptibility and the temperature ($\chi_m T$) for **1** shows a room-temperature value of 3.35 cm^3 K mol^{-1} that remains constant down to *ca.* 170 K (Fig. 2). This value, slightly higher than the spin-only value calculated for an isolated metal ion

Table 1 Selected bond distances (Å) for **1**

| | | | $T = 10$ K | |
| | | | Flash cooled | Light induced |
	$T = 293$ K	$T = 100$ K		
Fe1–N1	2.187(2)	2.114(2)	2.091(3)	2.179(3)
Fe1–N2	2.113(2)	2.060(2)	2.047(3)	2.113(3)
Fe1–N3	2.176(2)	2.075(2)	2.056(3)	2.175(3)
$<$Fe–N$>$	2.159(2)	2.083(2)	2.065(3)	2.156(3)

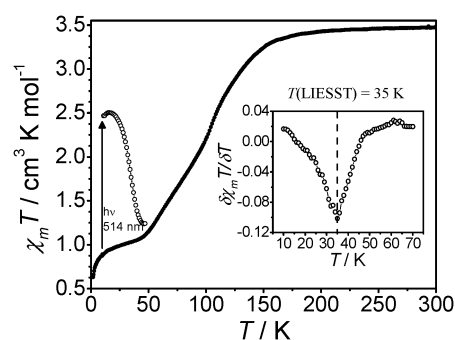**Fig. 2** Thermal variation of the $\chi_m T$ product (●), light irradiation at 10 K ($\lambda = 514$ nm) and thermal variation of the $\chi_m T$ product for **1** after irradiation (○). Inset: derivative of the thermal variation of the $\chi_m T$ product on increasing temperature after irradiation showing the T(LIESST) value.

with $S = 2$ (3.0 cm^3 K mol^{-1}), indicates that compound **1** is essentially paramagnetic and the Fe^{II} ions present the high spin ($S = 2$) configuration in that temperature range.

Below 170 K the $\chi_m T$ product decreases continuously down to 45 K and then reaches a plateau with a value close to 1.0 cm^3 K mol^{-1}. These features reveal an incomplete HS–LS conversion of about 70%. Below 10 K, $\chi_m T$ presents a sharp decrease to reach a value of 0.8 cm^3 K mol^{-1} at 2 K that is probably due to the presence of a zero-field splitting in the remaining HS molecules and/or to a weak antiferromagnetic coupling of the remaining HS molecules. The heating scan shows an identical behaviour within the experimental error. Careful examination of the $\chi_m T$ product in the temperature range 170–45 K reveals an unexpected thermal behaviour with a slight change in the slope around 100 K and maxima at *ca.* 60 and 105 K in the derivative of $\chi_m T$ (Fig. S3A, ESI†). This observation is in agreement with the crystal structure of **1** since the two statistical orientations of the tcpd^{2-} ligand (see crystal structure description) imply at least two Fe^{II} environments. Such atypical feature may be explained by the contraction, just below 170 K, of the Fe^{II} coordination sphere due to the HS–LS transition leading to an increase of the energy gap between HS and LS levels of one or two neighbouring Fe^{II} ions along the chain. Such a phenomenon is somewhat similar to that observed for some Fe^{II} dinuclear complexes and for the 1-D chain [Fe(NCSe)$_2$(bdpp)], for which their SCO transitions are of the two-step character.[10,11] In the case of the title compound, the situation is much more complicated since its overall structure presents two statistically different orientations of the tcpd^{2-}, and then the SCO transition may be viewed as a multi-step process operating statistically within the crystal. This assumption is emphasized by the presence of two statistically different orientations of the bridging tcpd^{2-} anion and by the incomplete HS–LS conversion observed below 45 K. Fig. 2 also shows the photomagnetic properties performed with a SQUID magnetometer coupled to a mixed krypton–argon laser, using a reported standardised procedure.[12] Irradiation at 10 K with green laser light ($\lambda = 514$ nm, 5 mW cm^{-2}) resulted in a large increase of the magnetic signal. After 1 h of irradiation, the light was switched off and the temperature increased at a rate of 0.3 K min^{-1}, corresponding to the measurement of the T(LIESST) temperature.[12] Based

on this experiment several remarks can be made. The small decrease of the magnetic signal recorded below 25 K can be attributed either to the zero-field splitting of the individual photo-induced HS state and/or to a small antiferromagnetic coupling between the Fe^{II} HS states in the 1-D chain, as reported with a larger magnitude for Fe^{II} dinuclear complexes and for some chain complexes with the same bridging $tcpd^{2-}$ ligand.[13] The comparison between the maxima of the T(LIESST) curves and the magnetic value of the thermal high-spin state argues in favour with a photoconversion of about 70% in bulk material. Along these lines, upon increasing the intensity and/or changing the wavelength of excitation, it was not possible to reach a quantitative photo-excitation. As the colour of the sample is basically not so deep, a problem of penetration depth can be ruled out, this effect can rather be attributed to a competition between excitation and an efficient HS–LS relaxation process, also illustrated by the relatively small T(LIESST) temperature of 35 K. The last comment concerns the trapped HS state which relaxes back to the original thermal spin transition curve, rather than to a fully low-spin state. This confirms that the incompleteness of the spin-crossover in this compound may not be caused by kinetic trapping of a high-spin fraction of the sample at low temperatures, as was recently reported for the $[FeL_2][BF_4]_2 \cdot xH_2O$ complex (L = 2,6-bis{3-methylpyrazol-1-yl}pyridine; $x = 0-\frac{1}{3}$).[14] However, further studies such as solving the crystal structure at 10 K after slow cooling should provide more information about the origin of this residual HS fraction.

In summary, we have reported the synthesis, structural characterisations and magnetic properties of the complex $[Fe(abpt)_2(tcpd)]$ (**1**) which is the first SCO neutral molecular chain containing a cyanocarbanion as bridging ligand. Magnetic and photomagnetic studies show a gradual LS–HS conversion and photoinduced effects (T_{LIESST} = 35 K), in agreement with the crystallographic and photo-crystallographic results. In a synthetic perspective, this result confirms the ability of the cyanacarbanions to act as bridging ligands to generate new SCO complexes exhibiting original extended arrangements.

Notes and references

‡ *Crystal data for* **1**: $C_{34}H_{20}N_{18}Fe$, M = 736.53, monoclinic, space group $P2_1/n$, Z = 2, T = 293 K: yellow; a = 11.3762(3), b = 12.4222(3), c = 11.8683(3) Å, β = 92.031(2)°, V = 1676.14(7) Å^3, D_c = 1.459 cm^{-3}, 18 122 collected reflections, 2390 unique (R_{int} = 0.0275), final GOF = 1.112 (all data), R1 = 0.0353, wR2 = 0.0747, R indices based on 1858 reflections with $I > 2\sigma(I)$, 333 parameters. T = 100 K: red; a = 11.2359(3), b = 12.2079(2), c = 11.8655(2) Å, β = 91.703(2)°, V = 1626.83(6) Å^3, D_c = 1.504 g cm^{-3}, 21 459 collected reflections, 3234 unique (R_{int} = 0.0311), final GOF = 1.110 (all data), R1 = 0.0417, wR2 = 0.0839, R indices based on 2353 reflections with $I > 2\sigma(I)$, 323 parameters. T = 10 K, "flash cooled": red; a = 11.2071(8), b = 12.1518(6), c = 11.8916(5) Å, β = 91.495(5)°, V = 1618.9(2) Å^3, D_c = 1.511 g cm^{-3}, 7010 collected reflections, 2474 unique (R_{int} = 0.0457), final GOF = 1.040 (all data), R1 = 0.0485, wR2 = 0.0810, R indices based on 1514 reflections with $I > 2\sigma(I)$, 298 parameters. T = 10 K, light induced: yellow; a = 11.3894(8), b = 12.1165(4), c = 11.8384(4) Å, β = 92.832(4)°, V = 1631.70(14) Å^3, D_c = 1.499 g cm^{-3}, 6258 collected reflections, 2337 unique (R_{int} = 0.0267), final GOF = 1.144 (all data), R1 = 0.0483, wR2 = 0.0892, R indices based on 1747 reflections with $I > 2\sigma(I)$, 289 parameters (see S2 in ESI† for details).

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