A reversible metal–ligand bond break associated to a spin-crossover

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The [$Fe^{II}L(CN)_2$]·H_2O complex, dicyano[2,13-dimethyl-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene]iron(II) monohydrate, exhibits a thermal induced metal–ligand bond break reversible in the solid state and associated to a spin crossover that corresponds to an unprecedented structurally characterized modification of the coordination metal environment from a hepta-coordinate high spin state to a hexa-coordinate low spin state.

With about forty years of study, the spin-crossover phenomenon attracts more and more scientists of all fields—from theoretical to experimental physicists, chemists and physical-chemists.[1] One of the reasons is probably that industrial applications—*molecular electronics, optical devices*…—appear almost near-at-hand. The paradox however is that from the consequent increasing amount of data coming out in the literature, the scientific community realizes that there are many efforts still to design in a rational way spin-crossover materials with properties required for these applications. Within this context the light-induced spin-state trapping, namely LIESST,[2,3] effect is particularly promising since it allows a spin state control through light irradiation. Indeed, it has been very recently proved that room-temperature photo-induced spin crossovers are achievable in certain cases.[4] However, the control of the features of the spin conversion in the solid state—in terms of lifetime, kinetics and hysteresis—is still a major challenge. For example, the design of materials showing ultra-rapid spin conversion is probably one of the major goals. In addition, only spin crossover solids with large reversible volume modification will be eligible as photo-switches. Consequently, the mechanism of propagation of the spin conversion within the solid is one of the essential characteristics requiring elucidation, with the determination of the structural properties by single-crystal X-ray diffraction being one of the key approaches.

In view of getting relevant materials for photo-switches, we have previously shown using in parallel a photomagnetic database[5,6] and a structural data base[7] that one of the possible roads is to design high denticity materials together with potentially high distortion of the metal coordination sphere at the spin crossover. Looking into the literature we notably focused on one already known iron(II) compound described 20 years ago and of potential relevance. Indeed, this complex, namely [$Fe^{II}L(CN)_2$]·H_2O (Fig. 1), has been suspected through preliminary magnetic and powder X-ray diffraction studies to exhibit a photo-induced spin crossover at a relatively high temperature[8,9] and to undergo a large modification of the iron environment with a solid state transition corresponding probably to a change of coordination.[10] Neither experimental proof of the latter nor a full description of the magnetic behaviour was however available. The detailed magnetic and photo-magnetic phase diagram has only been recently described.[11] This material shows a phase diagram in which thermal history, time and light conditions are intricate and exhibits a relatively high temperature LIESST effect characterized by a *T*(LIESST) of 135 K that indeed is the highest for an iron mononuclear complex.[12] Elsewhere, DFT calculations[13] and considerations on the crystal structure of the **A** phase[14] have recently indicated that a change of metal coordination is highly probable for this material. The present work describes the single-crystal X-ray diffraction study of this unusual transition.†

[$Fe^{II}L(CN)_2$]·H_2O undergoes a thermal spin crossover at 155 K by cooling but, depending on the experimental protocol, different phases and different levels of conversion can be achieved (Fig. 1). We focus here on the full spin crossover corresponding to the transition from a pure high spin, HS, namely phase **A**, to a pure low spin state, LS, namely phase **B**. From an experimental point of view, this **A** to **B** phase transition is observed after a cooling time from room temperature, **A**, to low temperature, **B**, of about 2 h. We note that slower cooling modes lead to partial spin crossover and a different structural phase, namely C, still under investigation.

The room-temperature crystal structure, **A**, adopts the monoclinic *C*2/*c* space group. The iron(II) ion is in a pentagonal bipyramidal environment and lies on a twofold axis. The Fe–O bonds are geometrically strictly identical by symmetry. The ion is

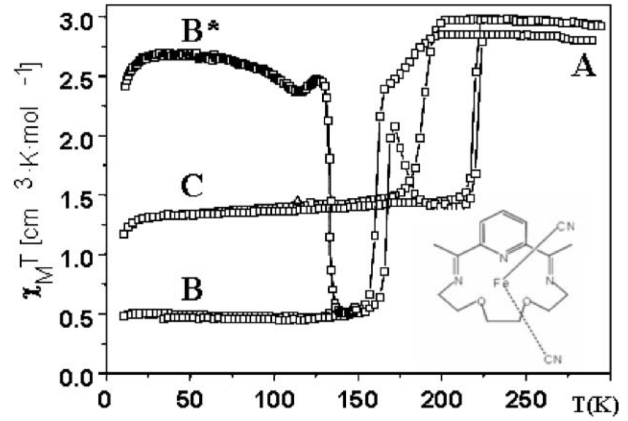

Fig. 1 Magnetic property diagram for [$FeL(CN)_2$]·H_2O from previously reported SQUID measurements.[11] Depending on the method of cooling the conversion levels appear different. The present paper deals with the **A** to **B** solid state transition, where **B*** corresponds to the photo-induced HS phase obtained after light irradiation of the sample in **B**.

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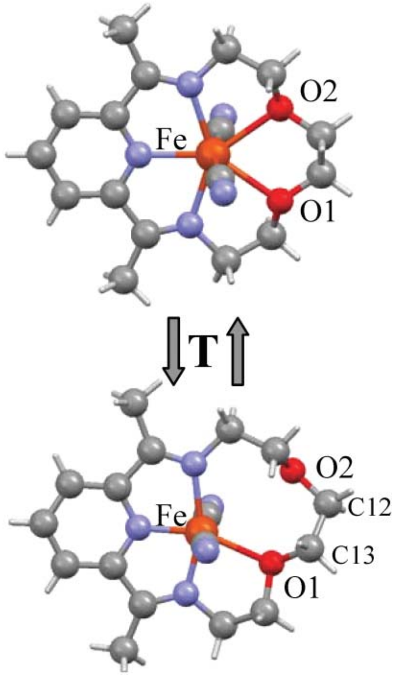

Fig. 2 View of the two X-ray diffraction molecular structures of $[FeL(CN)_2]$ in HS **A** (top) and LS **B** (bottom) showing the reversible transition from a hepta-coordinate high spin state (HS-7, $FeN_3C_2O_2$) to a hexa-coordinate low spin state (LS-6, FeN_3C_2O) for $[Fe(L)(CN)_2]\cdot H_20$ in the solid state.

hepta-coordinate and the metal–ligand bond lengths characterize a HS state. Structural modifications from **A** to **B** are drastic (Fig. 2). The low-temperature crystal structure, **B**, adopts the monoclinic $P2_1/c$ space group, with loss of the twofold axis. The iron(II) ion is thus on a general position in the **B** phase. This symmetry breaking corresponds to the differentiation of the Fe···O distances. The latter split from 2.334(1) Å in **A** to 2.243(1) Å for Fe–O_1 and 3.202(1) Å for Fe–O_2 in **B**. The Fe–O_2 bond in **A** is thus broken in **B**. The iron(II) changes from an hepta- to an hexa-coordination environment from **A** to **B**, going from a $FeN_3C_2O_2$ to a FeN_3C_2O polyhedron. Moreover, the Fe–N distances unambiguously show the complexes are in the LS state in **B**. To summarize, the transition from **A** to **B** corresponds to a transition from a hepta-coordinate HS state, HS-7, to a hexa-coordinate LS state, LS-6. The present results thus experimentally confirm the hypothesis made by Nelson *et al.*[8] Note that the full reversibility of this structural transition has been checked.

In the cases of hexa-coordinated iron(II) complexes, it has been shown that the volume of the coordination sphere, calculated from the atomic positions, decreases from 13.0(5) Å^3 in HS to 10.0(5) Å^3 in LS.[15] In the present case, the volume of the coordination sphere decreases from 17.0(1) Å^3 to 10.0(1) Å^3, more than the double the standard case. As a general matter of fact, the mechanism of propagation of the spin crossover along a solid starts with modification of the volume of the coordination sphere geometry, which then acts on the molecular entity, generally through ligand torsion and then extends to the solid through the modification of the crystal packing, for instance shown by the unit cell variations. The latter reflect, by definition, the modification of the macroscopic solid. The spin crossover propagation is thus strongly dependent on the topology of the intermolecular space. Consequently, the amplitude of the macroscopic modifications is in general not of the same order of magnitude as the initial ion environment change and it appears different from one compound to another. Examination of the literature shows that in the case of the hexa-coordinate complexes, the 3 Å^3, *i.e.* about 25%, of the coordination sphere volume change corresponds to 1 to 5% of the unit cell, and thus macroscopic, volume change. The final amplitude of the volume change effectively depends also on the nature of the ligand and on the nature of the complex (mononuclear, dinuclear or polymeric). The solid volume modification is of importance since it is implicated in the HS to LS crossover process.[16] An accurate knowledge of the volume changes at the different scales—coordination sphere, molecular entity, unit cell and macroscopic—is also crucial in the perspective of the use of spin crossover materials for molecular motors, *i.e.* molecular materials with reversible significant modifications of length induced by controlled stimuli. In the present case of the HS-7 to LS-6 transition, the modification of 7.0 Å^3 of the coordination sphere, *i.e.* more than 40%, does not correspond to a larger unit cell and macroscopic change of the solid volume. Indeed, the unit cell volume decreases by 103 Å^3 from 293 to 120 K, *i.e.* about 5.4%, but the contraction due to pure thermal effects must be subtracted. The latter is typically 2–3% in this kind of materials for this temperature range.[15] Consequently, the unit cell and macroscopic volume variations due to the sole spin crossover lie in the range of usual values, despite the huge modification of the coordination sphere volume. This is due to the remoteness of the oxygen atom from the iron ion that increases the volume of the whole molecular entity.

Another noteworthy change of the molecular structure from HS-7 to LS-6 concerns the inversion of the O–CH_2–CH_2–O ethylene ring conformation (Fig. 2). The change of conformation is for instance evidenced by the distance of the two carbon atoms of the ethylene group, C12 and C13, from the plane defined by the two oxygen atoms and the iron atom. In HS-7, for symmetry reasons, the distances from C12 and C13 to the plane are identical and these atoms are not located on the same side of the plane (+0.353 Å for C13 and −0.353 Å for C12). On the contrary, in LS-6, C12 and C13 are located on the same side of the plane at different distances to the plane (+0,872 Å for C13 and +0.303 Å for C12). The inversion of the ethylene conformation and the transformation of the coordination sphere induce significant modifications of the intermolecular interactions. Indeed, the crystal packing is also strongly affected by the symmetry breaking since the loss of the twofold axis in LS-6 allows a dissymmetry of the intermolecular contacts around the molecular entity though they are strictly identical in HS-7 (Fig. 3). The shortest distance between iron ions slightly decreases from 7.652 Å in HS-7 to 7.348 Å in LS-6. However, the main modifications of the intermolecular interactions topology concerns hydrogen like bonds. First, if in HS-7 the two oxygen atoms involved in the coordination sphere do not participate to any intermolecular interaction due to their internal position, in LS-6 the oxygen atom that leaves the coordination sphere, O2, is involved in the crystal packing and a hydrogen bond is formed with a methyl group of the neighbouring complex (O2···H–C (x, ½ − x, ½ + z): O···C = 3.226(1) Å, O···H = 2.33 Å, OCH = 154°). Elsewhere, the hydrogen bonds involving the water of solvation are also affected.

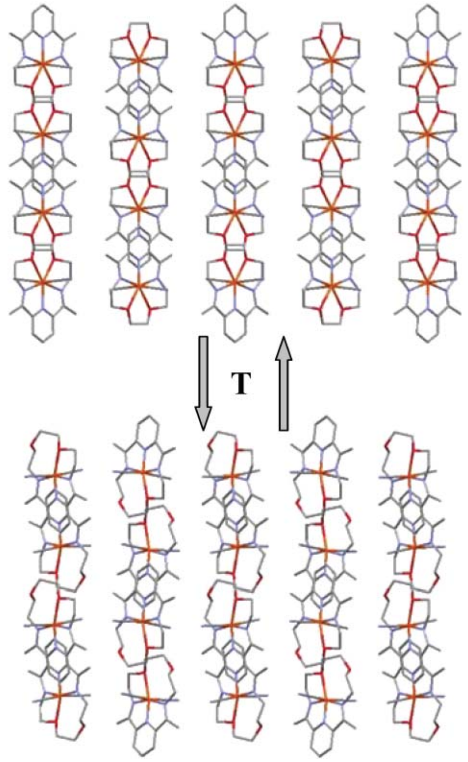

Fig. 3 Temperature dependence of the crystal packing of $[Fe(L)(CN)_2]\cdot H_2O$ from HS-7 **A**, $C2/c$ (top) to LS-6 **B**, $P2_1/c$, (bottom) showing the modification of the ion network and the symmetry breaking due to the change of the coordination metal environment.

The two hydrogen bonds formed between the hydrogen atom of the water molecule and the nitrogen atoms of cyanide groups are only slightly affected while the hydrogen bond formed between the oxygen atom and a methyl group of the neighbouring molecule appears strongly reinforced in the LS-6 crystal structure as shown by the bond parameter changes from HS-7 (O···C = 3.550(1) Å, O···H = 2.67 Å, OCH = 152°) to LS-6 (O···C = 3.423(1) Å, O···H = 2.49 Å, OCH = 163°). Finally, the above described change of the conformation of the ethylene induces drastic modifications of the corresponding intermolecular contacts. In HS-7, the shortest intermolecular distance involving C12 concerns a contact with one nitrogen atom of a cyanide group (C···N = 3.786(1) Å, C–H···N = 2.89 Å, CHN = 154°) and the intermolecular contacts involving C13 are strictly identical by symmetry to those involving C12. On the contrary, in LS-6, intermolecular contacts involving C12 and C13 are totally different from each other since C12 moves towards the nitrogen atom (C···N = 3.664(1) Å, C–H···N = 2.71 Å, CHN = 167°) while C13 moves away from any contact with the nitrogen atom (C···N = 4.501(1) Å, C–H···N = 4.65 Å, CHN = 75°) and does not form any short intermolecular contact.

All the above significant modifications of the intermolecular contacts are noteworthy since hydrogen bonds play a paramount role in the propagation of the spin crossover along the solid.

To summarize, given that reversible high distortion of the solid during the spin crossover is a requirement for potential applications, the modification of the metal coordination number associated to a spin crossover, explicitly a HS-7 to LS-6 transition, unambiguously evidenced here by structural determination, appears of interest since it corresponds to a reversible molecular volume change of around 40% accompanied by a modification of the ligand conformation. However, this huge molecular alteration has no remarkable repercussion at the macroscopic level since the unit cell volume modification matches the usual value of about 3%.[15]

To conclude, the non-destructive reversible metal–ligand bond break described here appears of fundamental importance in the general context of the investigation of solid-state phase transitions.

Notes and references

† *Crystal structure* at 120 K: phase **B**, after a cooling from room temperature at a fixed rate of 90 K h^{-1}: monoclinic, $P2_1/c$, a = 10.624(1), b = 11.916(1), c = 14.676(1) Å, β = 105.08(1)°, V = 1793.9(1) $Å^3$, 4123 independent reflections, R_{int} = 0.02, refinement on F^2, 244 parameters, S = 1.17, R = 0.038, $wR2$ = 0.083, $R1$(all) = 0.042. ⟨Fe–N⟩: 2.171(1) Å in HS-7 and 1.936(1) Å in LS-6. ⟨Fe–C⟩: 2.163(1) Å in HS-7 and 1.958(1) Å in LS-6. Fe–O1: 2.334(1) Å in HS-7 and 2.243(1) Å in LS-6. Fe···O2: 2.334(1) Å in HS-7 and 3.202(1) Å in LS-6.

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The crystal structure was re-determined after warming and matches perfectly the **A** crystal structure previously obtained.[14] Room-temperature crystal structure: monoclinic, $C2/c$, a = 17.326(5), b = 12.054(5), c = 10.125(5) Å, β = 116.27(1)°, V = 1896.2(13) $Å^3$, R = 0.038.

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