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Structural Characterization of a Photoinduced Molecular Switch

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In iron (II) molecular complexes, the so-called spin-crossover phenomenon derives from the possible existence of two different electronic configurations for the iron ion corresponding to different spin states, high-spin (HS, $S = 2$) and low-spin (LS, $S = 0$). The transition from one electronic state to the other is accompanied by a modification of the magnetic behavior, from a paramagnetic (HS) to a diamagnetic (LS) state. At the molecular scale, the driving force of the spin conversion is the entropy due to the metal−ligand bond length changes. In solid state, the presence of short- and long-range interactions may lead to cooperative first-order spin transition (ST). The ST may be induced by temperature, pressure, or light-irradiation effects. This phenomenon and its associated thermodynamics has been widely studied over the past 35 years[1] and is still under investigation, strongly encouraged by industrial interests.[2] One of the most promising features of the ST is the possibility to reversibly address some information by light irradiation according to the well-known LIESST effect[3] (light-induced excited spin state trapping) and reverse-LIESST effect[4] in solid state without any fatigue of the material. The weak point, however, is that trapping the system in the metastable HS state requires very low temperatures. Until now, the HS → LS relaxation process is known to be influenced by the cooperativity, the octahedral distortion, and the metal−ligand bond lengths associated with the ST. A determination of the crystal structure for the light-induced metastable high-spin state (HS-2) and the comparison with the thermal form (HS-1) is of fundamental interest not only to study the LIESST effect but also, more generally, to understand the effect of light on molecular materials. We focus here on one of the most studied iron (II) complexes, $[Fe(phen)_2(NCS)_2]$ (phen = 1,10-phenanthroline)[5] (Scheme 1).

It undergoes an extremely abrupt thermal ST at 176 K,[6] and "the switch" may also occur at room temperature by applying pressure[7] or at low temperature upon irradiation.[8] The only structural study upon irradiation of this complex in the HS-2 state concerns local information obtained by X-ray absorption (EXAFS).[9] Here we report the crystal structure in the HS-2 state at 30 K as well as in the LS crystal structure at the same temperature and the comparison with the crystal structure in the stable room-temperature HS state,[10] HS-1, as obtained by single-crystal X-ray diffraction.

Single crystals were synthesized following the slow-diffusion method.[11] X-ray diffraction at 30 K on a suitable sample gave the LS crystal structure. The same sample has been irradiated with a He/Ne laser ($\lambda = 647$ nm, 5 mW/cm^2) for 1 h, before switching the laser OFF, and immediately redetermining the crystal structure.[12] The features of the magnetic transition upon light irradiation were also investigated at 30 K on a sample made of a few single crystals[13]

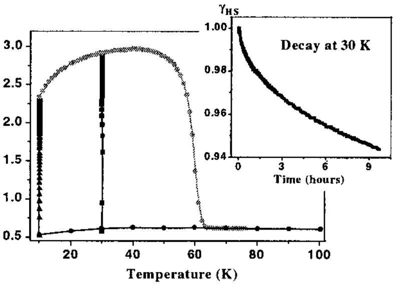
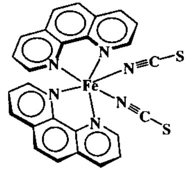


Figure 1. Low-temperature magnetic properties of $[Fe(phen)_2(NCS)_2]$. (a) $\chi_m T$ versus T, plot showing the LIESST effect: a LS to HS conversion is obtained by irradiating the crystal at 10 K (the experiment at 30 K is also shown). Solid black squares and triangles correspond to the irradiation ON, black circles to the baseline, and gray circles to the irradiation OFF. (b) Decay at 30 K: the HS molar fraction, γ_{HS}, versus time at 30 K once the irradiation is OFF, showing that the relaxation to the LS state as a function of time is long enough to allow a complete X-ray diffraction investigation (9 h data collection).

Scheme 1. $[Fe(phen)_2(NCS)_2]$ (phen = 1,10-Phenanthroline)



Clearly, the photoinduced HS → LS relaxation process is slow enough at 30 K to allow a single-crystal X-ray diffraction experiment to be carried out using a diffractometer equipped with an area detector (Figure 1).

As expected, the coordination environment of the iron atom (Table 1 and Figure 2) is strongly dependent upon the spin state; that is, the Fe−N bond lengths are much shorter and the distortion parameter is lower in the LS state than in the HS state. This clearly shows that the crystal structure obtained after light irradiation corresponds to HS-2 and is similar to HS-1. For instance, the distortion parameter Σ[14] as well as the other geometrical parameters of the octahedron appear identical for HS-1 and HS-2 as they are identical for LS at 130 K and LS at 30 K. The main distinction between HS-2 and HS-1 seems to concern the decrease of the Fe−N bond lengths after irradiation. Indeed, the difference between average values for the HS and LS Fe−N bond-lengths is not the same for the photoinduced spin transition, from LS to HS-2 at 30 K, and for the thermal spin transition, from LS at 130 K to HS-1 at 293 K: 0.139(5) Å and 0.164(5) Å, respectively. Thus, the use of the X-ray data from the thermally induced ST may only represent a crude estimation of the Fe−N change induced by light. Such a result is in agreement with the previously reported EXAFS measurements.

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Table 1. X-ray Diffraction FeN_6 Octahedron Geometry versus Spin State[a]

spin state	experimental conditions	Fe–N1 (Å)	Fe–N2 (Å)	Fe–N3 (Å)	Σ (deg)	d_{Fe-G} (Å)	V_p (Å^3)
LS	30 K	1.990	2.007	1.953	35	0.05	10.3
LS	130 K[10]	2.014	2.005	1.958	36	0.05	10.5
LS	1.0 GPa[7b]	1.975	2.003	1.954	35	0.05	10.0
HS-2	30 K	2.177	2.184	2.006	64	0.18	12.7
HS-1	293 K[10]	2.199	2.213	2.057	64	0.18	13.0

[a] Σ is defined as the sum of the absolute values of the deviation from 90° of the 12 cis angles in the coordination sphere. Standard deviations are inferior to 0.005 Å on Fe−N bond lengths and estimated to 2° on the distortion parameter Σ. d_{Fe-G} is the distance between the ion and the center of the octahedron, and V_p is the volume of the octahedron.

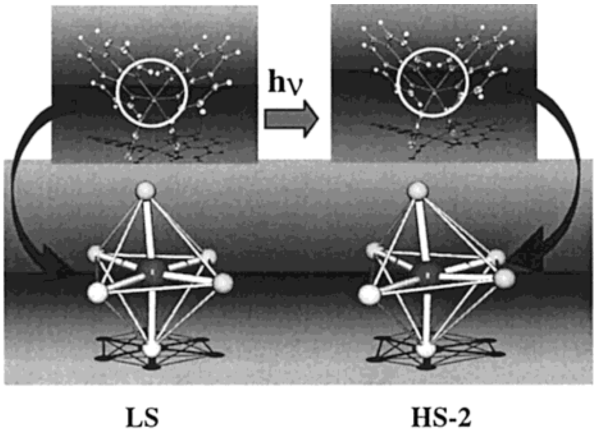

Figure 2. Effect of light irradiation at 30 K: expansion and deformation of the FeN_6 octahedron and consequently of the molecule induced by light at 30 K from LS to HS-2.

An important feature of the LIESST process concerns the absence of any fatigability and the exceptional switching activity in solid state. Our X-ray data demonstrate that the LS → HS-2 unit cell volume variation is, in fact, very small (24 Å^3) and corresponds to an increase of the crystal volume of 1.1%. The modification at 30 K is only due to light irradiation and corresponds to the exact amplitude of the ST dilatation, while the volume variation (97 Å^3) between the HS-1 and the HS-2 unit cells gives the amplitude of the contraction from 293 to 30 K due to thermal effect only. The X-ray studies of photoinduced states already reported[15] concern tetrazole-built complexes, $[Fe(ptz)_6](BF_4)$ and $[Fe(mtz)_6](PF_6)$, with structural properties very different from the $Fe(phen)_2(NCS)_2]$ ones. In these two cases, the volume modifications due to either the thermal effect or to the light effect are larger than those found in our study.

Let us now consider the cooperativity parameter responsible for instance of the light-induced thermal hysteresis and of the sigmoidal relaxation process. In $[Fe(phen)_2(NCS)_2]$ the cooperativity is linked to the intermolecular interactions network, governed by hydrogen-bond-like contacts between sulfur atoms and carbon atoms of the neighboring entity along c and by π-stacking along b. Variations of the shortest sulfur−carbon distance as well as the three shortest carbon−carbon intermolecular distances are representative of the global modification of the intermolecular interaction topology.[16] Briefly, from HS-1 to HS-2 all the intermolecular contacts systematically decrease due to the thermal unit cell contraction while retaining a similar molecular volume. Therefore, from this point of view, the HS-2 crystal structure corresponds to a more cooperative network by far than the HS-1 crystal structure. Consequently, the direct comparison with thermal ST cooperativity, as commonly used in theoretical approach to interpret the photomagnetic properties, may be not adequate.

The present results, which show the crystal structures in both irradiated and nonirradiated states of a photoinduced molecular switch based on the spin-crossover phenomenon, bring relevant information not only in the study of the LIESST effect but also in the field of the general study of photoexcited states in the context of the design of materials for electronic molecular devices.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Data collections at 30 K were performed using an Oxford Cryosystems Helix open flow He gas cryostat combined with a Bruker SMART-CCD area detector diffractometer using the Mo Kα radiation. The diffraction frames were integrated using the SAINT package.[17] The structures were solved and refined with SHELXL-97.[18] Data for the LS crystal structure at 30 K: $a = 12.781(5)$ Å, $b = 10.073(4)$ Å, $c = 17.227$(Å), $V = 2217(1)$ Å^3, orthorhombic space group *Pbcn*. 1829 unique observed reflections were used to refine 191 atomic parameters and gave a final R factor of 0.046. Data for the HS-2 crystal structure at 30 K: $a = 13.121(3)$ Å, $b = 9.954(3)$ Å, $c = 17.163(4)$ (Å), $V = 2241(1)$ Å^3, orthorhombic space group *Pbcn*. 1592 unique observed reflections were used to refine 191 atomic parameters and gave a final R factor of 0.060.
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(16) The shortest S···C intermolecular distance and the three shortest C···C intermolecular distances (Å) are respectively: 3.353 (1), 3.502 (1), 3.537 (1), and 3.546 (1) in LS at 30 K; 3.266 (1), 3.368 (1), 3.543 (1), and 3.546 (1) in HS-2 at 30 K; 3.357 (1), 3.530 (1), 3.617 (1), and 3.580(1) in HS-1 at 293 K.
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