Light induced modulated structure of the spin crossover compound \{Fe(abpt)\_2[N(CN)\_2]\_2\}

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Abstract. \{Fe(abpt)\_2[N(CN)\_2]\_2\} is an intriguing spin crossover system which crystallizes in two separate phases. Phase A has already been investigated; its crystal structure consists of a single molecule sitting on a center of symmetry. Phase B is the subject of the present structural analysis and presents two independent molecules in the asymmetric unit. We have observed a unique order-disorder phase transition at very low temperature induced either by laser light irradiation or through rapid thermal quenching from room temperature. The corresponding metastable phase exhibits an incommensurate modulation of the crystal structure, disappearing at the HS to LS relaxation temperature (52 K). This modulation is most probably related to a particular ordering of the dicyanamide ligands.

1. Introduction

It is well documented that the characteristics of solid-state spin transitions are intimately related to the cooperativity of the molecular crystal lattice. In several cases the spin transition occurs jointly with a structural phase transition, like order-disorder phase transition, where correlations between short range interactions and long range ordering may yield interesting structural phenomena. For instance, the two step spin transition of [Fe(2-pic)\_3]Cl\_2EtOH has been attributed to the onset of an intermediate superstructure phase, coupled to two successive order-disorder phase transitions [1,2]. It is clear that such behaviors originate from the large molecular volume change between high spin (HS) and low spin (LS) species and from long range elastic interactions in the solid. A better understanding of the coupling between spin transition characteristics and structural properties is still required. We have given some crystallographic evidences of the formation of spin-like domains during the thermal and photoinduced LIESTT spin transitions of Fe(btr)\_2(NCS)\_2H\_2O, a highly bidimensional cooperative system [3].

\{Fe(abpt)\_2[N(CN)\_2]\_2\} is a spin crossover system which has been first investigated by Moliner et al. [4]. Magnetic measurements indicate an incomplete HS to LS thermal transition with an anomaly at T\_1/2 = 86 K at which 50 % of the conversion takes place. The residual trapped HS fraction at low temperature (below 50 K) is nearly 37 %.

By thermal quenching from room temperature to 5 K (100 K mm\(^{-1}\) rate), a residual HS fraction of nearly 50 % was achieved. From relaxation kinetics study, a thermal relaxation temperature of 52 K has been derived for this quenched metastable state. In
addition, an almost quantitative LIEST effect (“Light Induced Excited Spin State Trapping”) has been induced by irradiation at 5 K with a Xe lamp (λ = 550 nm, P = 2 mW cm⁻²) for 90 min.

By careful observation with an optical microscope of the crystals obtained during the crystallization process, it appeared that two phases coexist: phase A in majority, the structure of which has been determined at room temperature [4] and a new phase called B hereafter. We report here on the structural properties of this new phase B of [Fe(abpt)₂[N(CN)₂]₂]. We believe the magnetic measurements performed by Moliner et al. correspond to a mixture of both phases. We give here a comparison of four crystal structures in particular measurement conditions (temperature, laser excitation) corresponding to the different spin states: room temperature HS state, close to the step in the thermal transition at T = 91 K, 15 K thermally quenched and 15 K photo-induced. A unique order-disorder phase transition involving a modulation of the crystal structure has been observed for the first time in spin transition compounds.

2. X-ray diffraction measurements

[Fe(abpt)₂[N(CN)₂]₂] has been synthesized as previously reported [4], single crystals suited for an X-ray diffraction experiment were grown by slow diffusion methods. The obtained single crystals exhibited two distinct crystallographic phases. Several samples of phase B have been selected according to their slightly different crystal habitus with respect to phase A. Cell parameters and crystal structure differences confirmed the presence of the two phases (see below). X-ray diffraction measurements have been performed using graphite-monochromated Mo K radiation on an Oxford Diffraction Xcalibur diffractometer equipped with a bidimensional CCD detector. Low temperatures were reached using an N₂ gas flow cryosystem (for 91 K measurements) and a He open flow cryojet system (for 15-55 K measurements); the temperatures were calibrated with a thermocouple and the tetragonal to orthorhombic phase transition of DyVO₄ (T = 14K) respectively. Diffraction data have been collected on phase B in the different spin states: room temperature HS state, close to the step in the thermal transition at T = 91 K, 15 K thermally quenched and 15 K photo-induced.

The quenched metastable state has been trapped at 15 K by flash cooling the single crystal sample directly in the He flux on the diffractometer. Under such conditions, thermal equilibrium is reached in less than a second for typical molecular solids of hundred micrometers in thickness. This means that this procedure is far more rapid than performed by Moliner et al for their magnetic measurements (≈ 100 K min⁻¹).

For the photocrystallographic experiments, a low temperature LS state has to be reached as a first step. According to the magnetic measurements, the only possibility to get such a LS state is by quenching the system to very low temperature and then to increase it till the HS to LS relaxation occurs. Indeed, a slow temperature decrease from room temperature leads only to an incomplete HS to LS transition. Therefore, the crystal was first quenched to 15 K, the temperature was subsequently increased till the HS to LS relaxation occurs. The sample was maintained at this temperature for 3 hours to ensure a complete relaxation while checking the global spin state through the determination of the cell parameters versus time. The temperature was further decreased to 15 K and the crystal exposed to the 534 nm line of an Ar-Kr gas laser (P = 40 mW) for 4 minutes.

For all four data collections, the diffraction frames were integrated using CRYSSALIS, numerical absorption corrections were applied based on the indexed crystal faces (μ = 0.582 mm⁻¹). Reflections were merged in the P-1 space group using SORTAV [5].

The structures were solved by direct methods and refined by the full-matrix least squares method against F² using SHELXS and SHELXL respectively [6]. All non hydrogen atoms were refined anisotropically, H atoms were located by Fourier difference synthesis and refined isotropically. At all temperatures, the dicyanamide ligand presents more or less severe disorder; restraints have been applied on the anisotropic displacement parameters of the dicyanamide atoms when necessary. More details on data collections and crystallographic parameters are given in table 1.
Table 1. Data collection and crystallographic details.

| Measurement temperature | Phase A [4] | Phase B          |
|-------------------------|-------------|------------------|
| 298 K                   | 298 K       | 91 K (quenched) |
| 15 K (light induced)    |             |                  |
| Crystal system / space group | triclinic / P-1 | triclinic / P-1 |
| Unit-cell parameters    |             |                  |
| \(a\), \(b\), \(c\), \(\alpha\), \(\beta\), \(\gamma\) (Å, °) | 8.4618(5)   | 9.5993(9)       |
|                         | 9.6086(3)   | 9.9878(9)       |
|                         | 9.6381(7)   | 10.019(1)       |
|                         | 83.661(4)   | 16.041(2)       |
|                         | 86.642(5)   | 96.498(9)       |
|                         | 65.821(4)   | 100.932(9)      |
| Cell volume (Å³)        | 710.44(7)   | 1491.6(3)       |
|                         | 1434.4(4)   | 1434.5(4)       |
|                         |             | 1441.1(4)       |
| \(Z\)                  | 1           | 2                |
|                         | 2           | 2                |
|                         | 2           | 2                |
| sin(θ)/λ max (Å⁻¹)     | /           | 0.73             |
|                         | /           | 0.73             |
|                         | /           | 0.76             |
|                         | /           | 0.70             |
| Measured reflections    | /           | 14028            |
|                         | /           | 13440            |
|                         | /           | 12515            |
|                         | /           | 8101             |
| Average redundancy      | /           | 1.7              |
|                         | /           | 1.6              |
|                         | /           | 1.8              |
|                         | /           | 1.1              |
| Indep. reflections      | /           | 8489             |
|                         | /           | 8180             |
|                         | /           | 7132             |
|                         | /           | 7126             |
| Completeness (%)        | /           | 86.3             |
|                         | /           | 86.6             |
|                         | /           | 67.3             |
|                         | /           | 85.4             |
| Rint                   | /           | 0.071            |
|                         | /           | 0.079            |
|                         | /           | 0.049            |
|                         | /           | 0.096            |
| \(R_1\) (Shelx, I>4\(\sigma(I)\)) | /           | 0.073            |
|                         | /           | 0.068            |
|                         | /           | 0.080            |
|                         | /           | 0.079            |

3. Diffraction pattern and reciprocal lattice of the 15 K high spin metastable states

The diffraction pattern corresponding to the room temperature and 91 K crystal structures can be indexed with three reciprocal vectors \((\vec{a}^*, \vec{b}^*, \vec{c}^*)\). The precession image of the (hk0) layer for the 91 K case has been reconstructed from the diffraction frames using CRYSTALIS and is given on figure 1. The diffraction patterns of the metastable 15 K quenched and light induced states exhibit additional diffraction peaks that cannot be indexed with the reciprocal vectors \((\vec{a}^*, \vec{b}^*, \vec{c}^*)\). Based on the superspace formalism introduced by deWolff, Janner and Janssen [7], these satellites have been indexed using four dimension basis vectors \((\vec{q}^*, \vec{b}^*, \vec{c}^*, \vec{q})\) using program NADA [8]; only first order satellites are observable on the diffraction frames. The coordinates of \(\vec{q}\) have been refined on 1048 observed satellite reflections (15 K HS quenched state) by least squares: \(\vec{q} = 0.340(2)\vec{a}^* + 0.558(2)\vec{b}^* - 0.048(3)\vec{c}^*\), which is incommensurate with the reciprocal lattice vectors \((\vec{a}^*, \vec{b}^*, \vec{c}^*)\). Similar coordinates have been obtained for the 15 K photo induced state. Following this description, the superspace group is P-1(αβγ). The \(\vec{q}\) vector, which gives the direction of the modulation propagation vector, is nearly lying in the \((\vec{a}^* \vec{b}^*)\) plane. We have no indication on the modulation type, displacive, occupational or both.
The evolution of the diffraction pattern has been followed on increasing the temperature from 15 K to 50 K. The satellite reflections are present on the whole temperature range, and disappear around \( T = 50 \) K. Figure 2 illustrates this behavior for the \((-5 4 -3)\) Bragg peak and its first order satellite. In parallel, the evolution of the corresponding cell parameters indicates that the HS to LS thermally activated relaxation occurs around 50-55 K, in agreement with the magnetic measurements \( T_{LIESST} = 52 \) K. The temperature at which the modulation disappears corresponds therefore exactly to the LIESST relaxation temperature, the modulated crystal structure is directly related to the HS metastable phase.

4. Crystal structure analysis

In this preliminary report, for the 15 K quenched and photo induced states, we discuss only the mean structures of \( \{\text{Fe(abpt)}_2[\text{N(CN)}_2]\}_2 \) refined against the main reflections, the satellite reflections have not been taken into account at that point.

The molecular structure at room temperature is very similar to the molecular structure of phase A. The Fe\(^{II}\) ion is located in a distorted octahedral FeN\(_6\) environment of two nitrogen atoms of the pyridyl groups, two nitrogen atoms of triazole rings and completed by two dicyanamide ligands in trans position (see figure 3). The Fe-N bond distances at room temperature are consistent with both iron sites in the HS electronic configuration, with distances differing significantly from the phase A values (table 2). The asymmetric unit consists of two independent \( \{\text{Fe(abpt)}_2[\text{N(CN)}_2]\}_2 \) molecules (Fe1 and Fe2), contrary to phase A where a single iron site is present. Even though the space group is identical, P-1 in both phases, the crystal packing is radically different, phase B does not results from a symmetry breaking of phase A. In phase B alternated layers of Fe1 and Fe2 molecules are stacked along the \( c \) crystallographic axis (figure 3).
On decreasing temperature, a gradual conversion from purely HS to an intermediate spin state at $T = 86$ K has been observed in magnetic measurements. The 91 K crystal structure is as close as possible to this intermediate state and shows that the Fe1 site has been totally converted to the LS state whereas the Fe2 site remains in the HS state. The thermal spin transition is therefore site specific. This situation is analogous to several other spin crossover materials presenting a two-step spin transition attributed to the HS to LS conversion of the two iron sites at slightly different temperatures [9].

As evidenced by large anisotropic displacement parameters, the room temperature and intermediate 91 K crystal structures exhibit some disorder on the dicyanamide ligands of both Fe1 and Fe2 molecules. Such disordering effect is not surprising as is often observed for thiocyanate ligands in other spin crossover materials.

The 15 K metastable crystal structures are far more complicated than the room temperature and 91 K ones owing to the presence of the modulation. The main reflections correspond to the mean crystal structure whereas the satellite reflections are related to an additional incommensurate periodicity of the structure. The mean structure of the 15K quenched and photo-induced phases have been solved in a first step using only main reflections using SHELXL [6]; the obtained Fe1-N and Fe2-N bond lengths are characteristics of HS states. We can notice slightly shorter values for the quenched state than the photo-induced one. Such a difference could result from a small relaxation during the quenching procedure. This is of importance since both Fe1-N and Fe2-N distances are shorter, contrary to the site-specific thermal transition. We can conclude that the two structural HS to LS phase transitions (during the LIESST relaxation and the thermal transition) behave in different ways. This point need however to be further investigated.

By comparison with the room temperature and 91 K crystal structures, the disorder of the dicyanamide groups only affects Fe2 in the metastable state. We believe the modulation of the crystal structure has something to do with an ordering of the dicyanamide ligand. A clear structural model including main and satellite reflections is under way.
5. Conclusion

\{Fe(abpt)₂[N(CN)₂]₂\} presents two different crystal phases with specific behaviors. Phase A, as described by Moliner et al. [4], consists of single molecular species. On the contrary, in phase B, two independent molecular entities coexist which forms alternated layers along the crystallographic c axis. At room temperature, both sites are in the HS state, whereas decreasing temperature induces first the HS to LS conversion of site Fe1. By light irradiation or thermal quenching, a metastable state has been reached at very low temperature whose crystal structure is characterized by the two Fe sites in the HS state. The presence of satellite reflections on the diffraction pattern indicates a modulation of the crystal structure whose propagation vector is almost lying in the \((a^*, b^*)\) plane.

\[ \vec{q} = 0.340(2)a^* + 0.558(2)b^* - 0.048(3)c^* \]. Starting from the 15 K metastable state and on increasing temperature, the modulation persists till the HS to LS relaxation temperature, indicating that the HS metastable state and the modulation of the crystal structure are closely related to each other. The physical mechanism of the light induced modulation of the crystal structure is not clear at the moment; a crystal structure model describing the intensity of the satellite reflections is being further investigated.

### Table 2. Selected bond distances (Å).

| Measurement temperature | Phase A | Phase B |
|-------------------------|---------|---------|
| 298 K                   | 298 K   | 91 K    | 15 K (quenched) | 15 K (light induced) |
| Fe1-N(pyridyl)          | 2.216(2)| 2.203(3)| 2.014(2)        | 2.173(3)             |
| Fe1-N(triazole)         | 2.121(2)| 2.137(4)| 1.978(2)        | 2.107(3)             |
| Fe1-N(dicyanamide)      | 2.160(3)| 2.131(4)| 1.963(2)        | 2.125(3)             |
| Fe2-N(pyridyl)          | 2.202(3)| 2.195(2)| 2.178(3)        | 2.197(3)             |
| Fe2-N(triazole)         | 2.142(3)| 2.141(2)| 2.137(3)        | 2.143(3)             |
| Fe2-N(dicyanamide)      | 2.120(4)| 2.107(2)| 2.108(4)        | 2.142(4)             |

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