Structure determination of Fe(II) spin-crossover complexes from powder diffraction data with direct-space methods
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Summary

Spin crossover is the phenomenon that external influences (temperature, light or pressure) can change the spin state [high-spin (HS) ↔ low-spin (LS)] of an atom, thereby changing the total magnetic moment of the compound. Spin-crossover compounds can be used for storage of information or display devices, which are important aspects of molecular electronics.

In this thesis, structural studies at various temperatures of five spin-transition complexes of the form [Fe(teeX)_6]A_2 (teeX = halo-ethyltetrazole, X = Cl, I, Br, F, and A = BF_4^- or ClO_4^-) are reported. These complexes show a remarkable variety of gradual spin-crossover behaviours: a complete spin transition in [Fe(teei)_6](BF_4)_2 and [Fe(teeb)_6](BF_4)_2, a 50% incomplete in [Fe(teec)_6](ClO_4)_2, a two-step complete in [Fe(teec)_6](BF_4)_2, and an incomplete and possibly two-step in [Fe(tefe)_6](BF_4)_2. All structures have been determined using X-ray powder-diffraction data with various direct-space methods, as no single-crystal could be prepared while their structure was thought to be important in order to interpret their observed spin-crossover behaviour.

Chapter 1 presents a brief introduction to X-rays, the basic elements of crystallography and diffraction theory, the basic concept of the derivation of the three-dimensional structure from diffraction data and a short introduction to powder diffraction.

In Chapter 2 a review is given of the techniques being used nowadays for the structure determination from powder diffraction data, focusing to a number of direct-space methods, namely Grid Search (GS), Genetic Algorithm (GA) and Parallel Tempering (PT) that have been used for structure determination in this thesis.

Chapter 3 discusses several elements of the Rietveld refinement method, which has been applied at the structure refinement stage of all compounds.

Chapter 4 contains the experimental work having been carried out and the obtained results. Diffraction data have been collected with Guinier camera and at synchrotron radiation facilities, namely the ESRF (Grenoble, France) and the SPring8 (Hyogo, Japan). Two types of temperature-dependent diffraction data have been collected at the latter, the first during the so-called scan experiments (5 min data collection time) at temperatures 300K and from 250 to 90K in steps of 10K, and the second during the long-term experiments (50-60 min data collection time) at several selected temperatures.

In the first section 4.1, an introduction to the spin-crossover phenomenon is given with a main emphasis on the Fe(II) compounds exhibiting this property, as well as some possible applications of these compounds.

In section 4.2, the crystal structures of [Fe(teec)_6](BF_4)_2 at room temperature (RT) and at 90 K are presented, solved using both Guinier and synchrotron radiation data (long-term) and applying the GS and PT techniques. A remarkable result was the different unit-cell parameters determined from the scan and long-term experiments at the same temperature. The unit-cell contraction along the axes during both the scan and the long-term measurements was anisotropic along different directions in each case. Anisotropic changes in lattice parameters that depend on
the cooling rate do not seem to have been reported previously. No significant structural phase transition has taken place from 300 K→90 K.

Section 4.3 discusses the results for [Fe(teec)₆](ClO₄)₂ that exhibits a 50% incomplete spin crossover. Crystal structures at 300 and 90 K were solved with GA and PT techniques. In the scan-experiment diffraction patterns as function of temperature it was observed that two distinguishable lattices occur, suggested to belong to the HS and LS states, whose quantities vary with the temperature, a behaviour suggesting a structural phase transition. This observation supports the theory that domains with the same spin can be formed during the spin crossover. The lattice-parameter contractions of [Fe(teec)₆](ClO₄)₂ relative to the values at 300 K show a remarkable anisotropy along the a-axis.

Section 4.4 presents the crystal structure of [Fe(teei)₆](BF₄)₂, a compound that exhibits a complete single-step spin crossover. The structure has been solved at RT and 90 K with GS, GA and PT techniques. Visual inspection of the scan diffraction patterns and the corresponding patterns of the long-term measurements did not reveal any significant differences, in contrast to the cases of [Fe(teec)₆](BF₄)₂ and [Fe(teec)₆](ClO₄)₂. It was concluded that the spin-crossover behaviour of [Fe(teei)₆](BF₄)₂ seems to be more consistent with the regular solution theory, according to which both the electronic and structural changes evolve gradually and smoothly.

Section 4.5 discusses the crystal structure determination of [Fe(teei)₆](BF₄)₂ that also exhibits a complete single-step spin transition. Because of the lower crystallinity of the sample, only the main structural characteristics could be determined and not the complete structure. Small structural changes are expected in view of the diffraction patterns of the scan measurements in which no remarkable appearance of new intensity peaks or fading of existing ones can be observed. It seems that also the spin crossover behaviour of [Fe(teei)₆](BF₄)₂ is more consistent with the regular solution theory.

Section 4.6 focuses on the crystal structure of [Fe(teei)₆](BF₄)₂ at RT as determined by GA techniques. [Fe(teei)₆](BF₄)₂ exhibits an interesting incomplete and two-stepped spin crossover. After inspection of the long-term and the scan measurements at every temperature, it could be concluded that the diffraction patterns of both scan and long-term measurements exhibit remarkable differences at those temperatures at which spin changes occur. However, distinguishable (supposedly HS and LS) lattices, as in case of [Fe(teec)₆](ClO₄)₂, have not been observed, at least not at the time scale at which the scan measurements were carried out.

On the basis of the crystal structures of all complexes, the observed temperature-dependent X-ray data, their spin-crossover behaviour versus temperature is discussed and several conclusions are drawn in section 4.7. In spite of the large variety in the spin-crossover behaviour of those complexes, the structures of the first four complexes appear to be quite similar, at least in view of the space group (P2₁/c, Z = 2) and the centrosymmetric molecules with Fe(II) at a special position. Only the last complex (teef) crystallized in P1 (Z = 2), the molecule is not centrosymmetric and Fe(II) is at a general position. These results point out that space group and Fe(II) positions are not sufficient to explain the spin-crossover behaviour.

From all the structural characteristics of the Fe(teeX)₆[(A)₂ complexes discussed in this thesis, it could be concluded that prominent structural changes seem to be related to a peculiar (i.e. two-step or incomplete) spin-crossover behaviour while smooth and small structural changes
hint most probably at a gradual single-step complete spin transition. Also, it could be observed that in the cases of the more *peculiar* spin-crossover behaviour the lattice contraction along a certain direction (almost perpendicular to the structural layers for the teec’s and along the b-axis for the teef) was facilitated after the first spin crossover.

The differences observed between scan and long-term experiments in case of a peculiar spin crossover point out that the magnetic susceptibility data should not be interpreted on the basis of long-term crystal structure data alone. The scan experiments have shown that in the cases of a single-step spin crossover (teei and teeb) the paths of the structural changes that are induced by a decrease of temperature and spin crossover are different from those of a *peculiar* spin crossover (both the teec’s and the teef).

Finally, in Chapter 5, the experience gained with the various structure determinations and refinement methodologies applied in this thesis is discussed and suggestions for future improvements are given. It is pointed out that sample preparation is very important factor in order to obtain good data quality. The data resolution, the quality of the initial search model and the definition of its degrees-of-freedom (DOF) are key points in the direct-space methods. Theoretically, an exhaustive search procedure like the GS may be preferable but because of the very long computational times often required it is not always realistic to apply this method. The sophisticated methods (GA and PT) have been successfully used in this thesis but it cannot be stated that one algorithm performed more efficiently than the other. It is also stressed out that systematic work should be carried out towards the definition of general rules and criteria that both the application of geometrical restraints and the texture correction methods during the structure refinement should obey. Finally, the structure quality, both in the structure solution and in the refinement stage, should not be assessed only on the basis of the values of the used criteria-of-fit but also on the chemical correctness of the structure.

The work carried out in the framework of this thesis has pointed out that availability of X-ray diffraction data and knowledge of the (crystal) structure are fundamental (among other information) to evaluate the theories on spin-transition phenomena that have been proposed. Moreover, temperature-dependent X-ray powder diffraction data has proven to be a powerful tool and the means for important observations concerning structural changes possibly correlated with the spin crossover mechanism. Finally, it is pointed out that the structure determination from powder diffraction data cannot be carried out on a routine basis yet.