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

X-ray crystallography is an experimental technique that exploits the fact that X-rays are diffracted by crystals. The phenomenon of diffraction occurs when electromagnetic waves interact with a regular repeating structure whose repeat distance is about the same as their wavelength. X-rays have wavelengths of the order of a few Ångstroms (1Å = 10^{-10} m), the same as typical interatomic distances in crystalline solids. When certain geometric requirements are fulfilled, X-rays scattered from a crystalline solid can constructively interfere, producing a diffracted beam. The diffracted radiation can be recorded using proper detectors and these data provide information about the crystal structure of the material concerned. Therefore it is not surprising that crystallographic methods and techniques are employed in many fields of physics, chemistry, materials science, geology, pharmacy and molecular biology in which crystals occur. In this first chapter a brief introduction will be given to X-rays, the main tool of X-ray crystallography, the basic elements of crystallography and diffraction theory, the basic concept of the derivation of the three-dimensional structure from diffraction data, a short introduction to powder diffraction and the scope of this thesis.

1.2. X-rays

X-rays, discovered by Röntgen in 1895, are electromagnetic waves whose wavelength \( \lambda \) ranges from about 0.1 to 100 Å and their energy \( E \) is so high that they can penetrate objects that are opaque to ordinary light. When fast moving electrons impinge on matter, X-rays result from two general types of interaction of the electrons with the atoms of the target material. The first one occurs when a high-speed electron removes an electron from an innermost shell, thereby
ionizing the atom. Then, an electron from an outer shell may fill the vacant position resulting in the emission of an X-ray photon characteristic of the atom involved. The other manner in which a high-speed electron interacts with matter is manifested by its deceleration when passing through the strong electric field near the nucleus of an atom. The decrease in energy $\Delta E$ of the electron appears as an X-ray photon of frequency $\nu$ as given by Einstein’s equation $\hbar \nu = \Delta E$, in which $\hbar$ is Planck’s constant. X-ray radiation produced in this manner is independent of the nature of the atoms of the target material and appears as a continuous band of wavelengths, which depend on the energy of the bombarding electrons (white radiation).

1.2.1. Laboratory X-rays

In a crystallography laboratory, X-rays are produced in X-ray tubes. In an X-ray tube, a very high voltage is applied between the electrodes at the two ends of the high-vacuum tube. The electrons generated in the cathode (one of the two electrodes) are accelerated between the two electrodes and strike the metal target, for example copper, molybdenum etc. This causes the emission of X-rays according to the mechanisms explained above, the former creating sharp intensity peaks that are called characteristic lines. In laboratory practice usually monochromatic characteristic X-ray radiation, depending on the material of the target, is used while all other wavelengths are filtered out.

1.2.2. Synchrotron Radiation

Synchrotron radiation is produced when charged particles, in particular electrons or positrons, are forced to move in a circular orbit. At relativistic velocities the photons are emitted in a narrow cone in the forward direction, at a tangent to the orbit. In synchrotron radiation stations, in which high-energy electrons or positrons are available, the emitted photons range from low energy (infrared) photons to high energy (short wavelength) X-rays. Synchrotron radiation is extremely intense (around a billion times more brilliant than conventional X-ray tubes), highly collimated and it is emitted with a wide range of energies.

In a synchrotron radiation experimental station, electrons are emitted by an electron gun being first accelerated in a linear accelerator (linac) and then transmitted to a circular accelerator (booster synchrotron) where they are accelerated to reach a high energy level, e.g. 6 GeV at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) and 8 GeV at the SPring8 of the Japan Synchrotron Radiation Research Institute (JASRI, Hyogo, Japan). These high-energy electrons are then injected into a large storage ring where they circulate in a vacuum, at a constant energy for many hours [Fig. 1.2.1 (left)]. As they travel round the ring, the electrons pass through different types of magnets, e.g. bending magnets or insertion devices, the latter being comprised of rows of magnets of alternating polarity. [Fig. 1.2.1 (right)]. When the electrons pass through such a device, they are deflected from their straight path by several degrees and this change in direction causes them to emit synchrotron radiation.
The synchrotron beams emitted by the electrons are directed towards the "beamlines" which surround the storage ring in the experimental hall. Each beamline is designed for use with a specific technique or for a specific type of research.

Third-generation facilities are optimised to use insertion devices and a synchrotron radiation facility is considered to be of large-scale when it has more than 5 GeV electron energy, and is capable of delivering X-rays from undulators (a type of insertion devices). Currently three third-generation large-scale synchrotron radiation facilities exist in the world, SPring8, ESRF and APS (Advanced Photon Source, Argonne, USA). The experiments to be discussed in this thesis have been carried out at the ESRF and SPring8.

1.3. Elements of Crystallography

The majority of the solids can be classified into crystalline and non-crystalline (amorphous) forms based on the internal arrangement of their atoms or molecules. For simplicity, the special cases of incommensurate compounds and quasi-crystals will not be discussed. Non-crystalline solids, such as plastics or glasses, have only a local atomic order but crystalline solids have a consistent, three-dimensional periodic long-range order. If this periodicity extends throughout the material to a size (in each direction) of at least 0.1 mm, it is called a single crystal. A polycrystalline material is an agglomeration of very small crystals, so called crystallites (~ 0.1μm).

A crystal can be considered as a repetition of identical units and in order to describe it, the concept of the space lattice is used, which is a collection of lattice points in a periodic arrangement. Theoretically a lattice is infinite in extent, all its lattice points are identically surrounded and mathematically it can be described by a set of translation vectors. A parallelepiped formed by eight connected lattice points is called the unit cell, which can be considered as a building block that can be periodically repeated to result in the crystal lattice. Several ways exist to connect adjacent lattice points, so in principle allowing for a large number of possible unit cells, but in practice the smallest unit cell in accordance with the three-dimensional (3D) symmetry elements present in the structure is chosen. The unit cell is defined by the length of the basic vectors \(\mathbf{a}, \mathbf{b}\) and \(\mathbf{c}\) (a, b and c) along its edges and the three interaxial angles \(\alpha\) (between \(\mathbf{b}\) and \(\mathbf{c}\)), \(\beta\) (between \(\mathbf{a}\) and \(\mathbf{c}\)) and \(\gamma\) (between \(\mathbf{a}\) and \(\mathbf{b}\)). Any crystal belongs to one of seven crystal systems (Table 1.1), the symmetry of which limits the possible values of the
unit cell parameters. There are 230 possible arrangements of symmetry elements that lead to a 3D periodic stacking at the atomic level, called space groups, and each crystal belongs to one (and only one) of these space groups.

**TABLE 1.1. The seven crystal systems**

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Axis</th>
<th>Interaxial angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>a ≠ b ≠ c</td>
<td>α ≠ β ≠ γ</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>a ≠ b ≠ c</td>
<td>α = γ = 90°, β ≠ 90°</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>a ≠ b ≠ c</td>
<td>α = β = γ = 90°</td>
</tr>
<tr>
<td>Trigonal/Rhombohedral</td>
<td>a = b = c</td>
<td>α = β = γ ≠ 90°</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>a = b ≠ c</td>
<td>α = β = 90°, γ = 120°</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>a = b ≠ c</td>
<td>α = β = γ = 90°</td>
</tr>
<tr>
<td>Cubic</td>
<td>a = b = c</td>
<td>α = β = γ = 90°</td>
</tr>
</tbody>
</table>

In order to solve the atomic 3D structure of a (periodic) crystal, it is only necessary to solve the 3D structure of the asymmetric part of the unit cell, because the rest of the crystal can be generated by the application of the symmetry operations and by periodic translations of the unit cell in the three lattice directions. To describe crystallographic directions and interatomic distances in the unit cell, the concept of parallel equispaced lattice planes intersecting the unit cell edges is used. The Miller indices (hkl) associated with a stack of parallel equispaced lattice planes denote the interceptions of the three axes of a unit cell at the points a/h, b/k, c/l, where a, b and c are the unit cell axes (h, k and l are integral). The interplane distance of a set of parallel Miller planes (hkl) is called d(hkl)-spacing.

Ewald (1921) devised the concept of the reciprocal lattice, a geometrical construction that consists of the normals to all possible (lattice) planes whose indices are (hkl). The normals have a common origin (0, 0, 0 in the unit cell) and the length of each normal is proportional to the reciprocal of the d(hkl)-spacing. The reciprocal lattice is commonly described by a set of vectors a*, b* and c*, being normal to b and c, c and a, a and b respectively. Then, in the reciprocal lattice, each family of (hkl) planes is described by only one point, the end point of the vector H,

\[ H = h a^*+k b^*+l c^* \]  

(1.1)

### 1.4. X-ray diffraction

X-ray diffraction, the scattering of X-rays by the regularly spaced atoms in a crystal, is most simply explained using Bragg’s law (Bragg and Bragg, 1913). Bragg explained X-ray diffraction in term of reflection from a stack of parallel lattice planes, although not to be confused with the phenomenon of surface reflection. When a beam of X-rays strikes an extended crystal face and is reflected, the same happens at an effectively infinite stack of equispaced atomic planes parallel to the face because X-rays penetrate to a depth of several million layers before being appreciably absorbed. At each lattice plane a minute portion of the beam may be considered to be reflected.

A schematic representation of Bragg’s law is shown in Fig. 1.4.1 and it states that for a given d spacing between the lattice planes and for a given wavelength \( \lambda \) of the X-ray radiation,
the various orders $n$ of reflection occur only at those values of angle $\theta$ which satisfy the following equation

$$n\lambda = 2d \sin \theta \quad (1.2)$$

The angle $\theta$ is called the Bragg angle. The above law is easily derived by imposing the condition that for a constructive interference of all elastically reflected beams by the parallel lattice planes, their path difference within the crystal must be an integer multiple of the wavelength $\lambda$, so that they interfere in phase, i.e. $AP + PC = n\lambda$, and from trigonometry it is easy to derive that $AP = PC = OP\sin\theta = d\sin\theta$. The integer $n$ is called the order of reflection. Because of the condition of constructive interference, all planes in the stack that are not too deep in the crystal will contribute to the reflection and if this number of planes is large enough, theoretically at no other angles than Bragg angles a diffracted beam can be observed.

![Figure 1.4.1. Schematic representation of Bragg’s law.](image)

### 1.5. Structure determination using X-ray diffraction data

From a physical point of view, X-rays are electromagnetic waves that are scattered by the electrons of the atoms. As a result, the intensity of the reflected beam will be proportional to the intensity of the incident beam and to the 3D periodic electron density $\rho(x,y,z)$ ($e/V^3$). The structure factor $F_{hkl}$ of an X-ray reflection (diffracted beam) $hkl$, the quantity that represents the resultant amplitude of the waves scattered by the electron density of one unit cell in the direction $H$, is the primary quantity necessary for the derivation of the three-dimensional distribution of electron density. The structure factor can be expressed by

$$F_{hkl} = \sum_{j=1}^{N} f_j \exp[2\pi i(hx_j + ky_j + lz_j)] = |F_H| \exp(i\varphi_H) \quad (1.3)$$

with the sum taken over the $N$ atoms in the unit cell, $f_j$ being the atomic scattering factor expressing the scattering amplitude of an atom, $h$, $k$ and $l$ the Miller indices and $x$, $y$ and $z$ the fractional coordinates of each atom with respect to the unit cell vectors $a$, $b$ and $c$ respectively.
Because of its periodicity, the electron density can be expressed as a Fourier series with the structure factors \( F_{hk\ell} \) being the Fourier coefficients.

\[
\rho(x, y, z) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l} F_{hk\ell} \exp[-2\pi i (hx + ky + lz)]
\]  

(1.4)

In principle, the summation should go from \(-\infty\) to \(+\infty\) for all \( h, k, l \), but because of practical limitations, the amount of observable diffraction data is finite, the synthesis will always be an approximation.

The intensity \( I_H \) of a diffracted beam is proportional to \( |F_H|^2 \) but, unfortunately, there is no method available yet for observing the phase \( \varphi_H \) of each structure factor. The absence of all phases that are necessary to construct an image of the structure via (1.4), constitutes the so-called phase problem in crystallography. A crystal-structure determination therefore consists of applying some technique to obtain approximate phase values for at least some of the X-ray reflections. After the first construction of \( \rho(x,y,z) \) via (1.4) and its interpretation in terms of atomic coordinates, a preliminary structural model is available. In the subsequent process of structure completion and refinement, gradually phase values are obtained for all observed reflections.

Since the phases cannot be compared with any observable quantities, the validity of the proposed structure can be judged only by comparing the calculated structure factor magnitudes \( |F_c| \) \( [= F_{hk\ell}(\text{calc})] \) with the observed magnitudes \( |F_0| \) \( [= F_{hk\ell}(\text{obs})] \). A quantity commonly used for this purpose is the reliability index or \( R \) factor defined as

\[
R = \frac{\sum |F_c| - |F_0|}{\sum |F_0|}
\]  

(1.5)

with the summation taken over all the observed reflections. Because of random errors in the observed structure factors \( |F_0| \), and approximations made in the model on which the calculated structure factors are based, it is never possible to obtain a set of \( |F_c| \) which reproduces exactly the \( |F_0| \), so structure refinement never reduces \( R \) to zero.

1.5.1. Single-crystal diffraction

In case of a single crystal all \( I_H \) can be observed individually by an appropriate re-orientation of the crystal (planes \( H \)) with respect to the incident beam. Several techniques have been developed allowing the structure determination from single-crystal data to be considered as routine, mainly because the amount of data \( (I_H) \) generally largely exceeds the amount of structural parameters to be determined.

1.5.2. Powder diffraction

In some cases, a single crystal cannot be obtained or used for specific research reasons, and only a polycrystalline material (crystallites \( \sim 1-10 \) \( \mu \)m) is available. The diffracted beams of such a sample form continuous cones (Fig. 1.5.1). A detector can be used to record the diffraction pattern, e.g. a film in the shown figure. Each cone intersects the film giving diffraction lines. The lines are seen as arcs on the film.
The basic disadvantage of using a polycrystalline sample is that the collected data are condensed into one dimension as a result of the random orientation distribution of the crystallites comprising the polycrystalline sample. Thus, important information concerning the direction of the reflection is lost and needs to be recovered first, which is not easy if independent directions and associated intensities overlap.

Powder diffraction plays an important role in structural physics and chemistry because the one-dimensional diffraction pattern (Intensity versus $2\theta$) characterizes the solid material. When a single crystal of a material is not available and it is of interest to determine its structure, powder diffraction data may be used instead but certainly not in a routine way because the amount of accurately known intensity data is much less than in single-crystal diffraction. Crystal structures determined by both techniques show that although the accuracy of the structure obtained by powder diffraction is lower than that obtained by single crystal data, the former can be considered reliable (e.g. Kaduk, 2002; Dova et al, 2001; Goubitz et al, 2001; Kaduk & Partenheimer, 1997).

For more details about problems encountered in powder diffraction and methods for the structure solution from powder diffraction data, the reader is referred to Chapter 2.

### 1.6. Scope of the thesis

Spin-crossover complexes are metal-organic compounds of which the magnetic moment can be changed by several physical phenomena, e.g. temperature, pressure. The specific Fe(II) spin-crossover complexes studied in this thesis could not be crystallized as single crystals while their structure was thought to be important in order to interpret their observed spin-crossover behaviour.

In the framework of this thesis, crystal-structure determinations have been carried out of five Fe(II) spin-crossover complexes with halo-ethyltetrazole ligands, using laboratory Guinier camera and high-resolution powder diffraction data, the latter being collected at two synchrotron
radiation facilities (ESRF and SPring8). At the latter facility various temperature-dependent X-ray diffraction data were collected for those complexes.

In Chapter 2 a review is given of the techniques being used nowadays for the structure determination from powder diffraction data. Special attention is given to a number of direct-space methods for structure solution from powder diffraction data, namely Grid Search, Genetic Algorithm and Parallel Tempering, 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. 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(teecc)_6](BF_4)_2 at room temperature (RT) and at 90 K are presented, solved using both Guinier and Synchrotron radiation data and applying the Grid Search and Parallel Tempering techniques. The two-step spin crossover of [Fe(teecc)_6](BF_4)_2 is discussed.

Section 4.3 discussed the results for [Fe(teecc)_6](ClO_4)_2 that exhibits a 50% incomplete spin crossover. The crystal structures of [Fe(teecc)_6](ClO_4)_2 at 300 and 90 K were solved by Genetic Algorithm and Parallel Tempering techniques.

Section 4.4 presents the crystal structure of [Fe(teei)_6](BF_4)_2, a compound that exhibits a complete single-step spin crossover. The structure has been solved at RT and 90 K with Grid Search, Genetic Algorithm and Parallel Tempering techniques.

Section 4.5 discusses the crystal structure determination of [Fe(teeb)_6](BF_4)_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.

Section 4.6 focuses on the crystal structure of [Fe(teef)_6](BF_4)_2 at RT as determined by Genetic Algorithm techniques. This is the only compound of this series crystallizing in Pabal, while all the previous complexes crystallize in P2_1/c. [Fe(teef)_6](BF_4)_2 exhibits an interesting incomplete and two-stepped spin crossover.

In each of the sections 4.2 – 4.4 and 4.6, the diffraction and crystal structure results will be discussed in view of existing theories of the spin-crossover behaviour.

On the basis of the crystal structures of all complexes and 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 particular, it will be shown that in case of two-step or incomplete spin transitions, diffraction data should be collected in special way.

Finally, in Chapter 5, the experience gained with the various structure determination and refinement methodologies applied in this thesis will be discussed and suggestions for future improvements are given.
References


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Bibliography


