Experimental report

18/12/2019

Proposal: **5-12-346**

Council: 4/2019

Title: A proton-displacive phase transition encompassing spin crossover in hydrogen-bonded iron(II) complexes

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Francisco ROMERO**

Experimental team: Laura CANADILLAS DELGADO
Francisco ROMERO
Veronica JORNET MOLLA

Local contacts: Laura CANADILLAS DELGADO

Samples: C40H41FeN13O14

Instrument	Requested days	Allocated days	From	To
D19	16	12	24/06/2019	08/07/2019

Abstract:

The iron(II) complex [Fe(bpp)2](isonicNO)2·HisocNO·5H2O (bpp = 2,6-bis(pyrazol-3-yl)pyridine; isonicNO = isonicotinate N-oxide anion) crystallizes in a triclinic phase with 100% of Fe2+ cations in their high-spin state state. It undergoes a partial spin crossover with symmetry breaking at T1 = 167 K to a mixed-spin phase (50% high-spin (HS), 50% low-spin(LS)) that is metastable below T2 = 116 K. Annealing the compound at lower temperatures results in a 100% LS phase that differs from the initial HS phase in the formation of a hydrogen bond between two water molecules of crystallisation and the transfer of a proton between two isonicNO anions. Both phenomena can also be detected by X-ray diffraction of the mixed-spin phase and could be explained in terms of H-bond cooperativity. The aim of this proposal is to characterize these two proton-displacive phase transitions that unusually take place along with spin crossover by locating more precisely the position of H atoms. Three different temperature points (240 K, 120 K and 95 K) will be collected. Considering the small crystal size and the number of experiments, we estimate that 16 days will be needed to complete the characterization.

A proton displacive phase-transition encompassing spin crossover in hydrogen-bonded iron(II) complexes

Objective

Spin crossover (SCO) metal complexes are well-known bistable materials that are able to interconvert between different spin states under an external perturbation, such as light irradiation, temperature change or application of pressure.

Among the different compounds exhibiting SCO behaviour, we turned our attention to $[Fe(bpp)_2]^{2+}$ complexes (bpp = 2,6-bis(pyrazol-3-yl)pyridine, Chart 1). The main reason is that they have four pyrazolyl N–H moieties that can act as hydrogen-bond donors towards polytopic anionic hydrogen-bond acceptors. The high directionality and strength of hydrogen bonds allow for designing SCO salts with the desired properties.

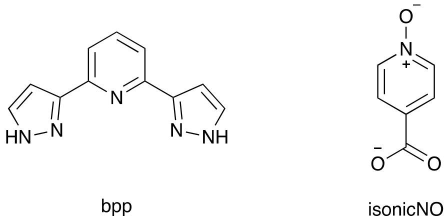

Chart 1. Molecular structures of bpp and isonicNO anion.

Our study focuses on the crystalline salt $[Fe(bpp)_2](isonicNO)_2 \cdot HisonicNO \cdot 5H_2O$ (**1**) comprising a SCO complex and isonicotinic acid N-oxide (isonicNO, Chart 1), present in its free and deprotonated forms.

Magnetic, calorimetric and structural (single-crystal XRD) studies had shown that **1** exhibits three different crystal phases (space group *P*–1): *phase I*, stable at $T > 167$ K, contains 100% of Fe^{2+} cations in their HS states; *phase II*, stable in the thermal range 116 K < T < 167 K, is a mixed-spin phase containing 50% HS and 50% LS cations that results from *phase I* by a thermal transition; *phase III* is a 100% LS reentrant phase and can be obtained by annealing the metastable *phase II* at lower temperatures.

Besides the differences in the ground spin state of the Fe^{2+} cations, other important aspects emerged from the comparison of the X-ray crystal structures of *phase I* and *phase III*, the most important being a proton transfer between two isonicNO anions involved in a short-strong hydrogen bond. Both features were also present around the LS “sublattice” of *phase II*.

The aim of this proposal was to confirm unambiguously by neutron diffraction that SCO in **1** is accompanied by a proton migration across the short-strong hydrogen bond (SSHB) in two steps, with breaking of symmetry and formation of a metastable high-spin/low-spin (HS/LS) pair.

Methodology

Confirmation of the existence of the three crystal phases and their corresponding ranges of stability was obtained from preliminary measurements in CYCLOPS Laue diffractometer. We could also discard in this way the presence of incommensurate structures. We could also follow the annealing of the metastable *phase II* at 95 K to give *phase III*. It was found that an anneling time of ca. 4 h was needed in order to observe the reentrant phase.

For a complete characterization of the different crystal phases, a single crystal of **1** was measured at D19 at three different temperature points using the 4-circle cryostat. The wavelengths used were 1.455 Å and 0.950 Å, provided by a flat Cu monochromator using the 220 and 331 reflections, respectively, at $2\theta_M = 69.91°$ take-off angle. Similar results were obtained with both wavelengths and, accordingly, only the 1.455 Å-data are discussed here. The sample was cooled up to 240 K, 120 K and 95 K with 2K/min cooling rate. In the last case, in order to achieve the relaxation of the compound, temperature was kept at 95 K for 4 hours. Once the transition took place, the data collection started. The measurement strategy consisted on 25 omega (ω) scans with steps of 0.07° at different χ

and φ positions. These omega scans cover either 79° or 64° depending on the χ angle, in order to avoid collisions with the sample environment.

The NOMAD software from ILL was used for data collection. Unit cell determination was done by using PFIND and DIRAX programs, and processing of the raw data was applied using RETREAT and RAFD19 programs. Absorption correction was applied using D19ABS program.

Results and discussion:

For the three crystal phases (*I* (240 K), *II* (120 K) and *III* (95 K)), similar cell parameters to those obtained from the X-ray study were obtained. Non-hydrogen atomic coordinates were practically the same in all cases but the positions of the H atoms change significantly. As expected, N–H distances obtained from X-ray data refinement are shorter by 0.1-0.2 Å with respect to neutron data. In turn, H···O distances are overestimated by the same amount. In any case, neutron diffraction data clearly confirm that hydrogen bonds involving the second coordination sphere of $[Fe(bpp)_2]^{2+}$ cations are shorter for the LS species. Thus, the mean NH···O distance decreases from 1.744 Å at 240 K to 1.694 Å at 95 K, whereas in the mixed-spin phase the mean NH···O distances are 1.737 Å and 1.693 Å for the HS and LS centers, respectively.

Other important hydrogen-bonding parameters to discuss are the N–H···O bond angles (θ), which can be accurately determined from neutron diffraction and can differ from the estimated XRD values. It was found that the N–H···O bond angles in the second coordination sphere are lower for the LS species. They decrease from an average value of 170° at 240 K to a value of 164° at 95 K. This is striking, as in most cases shorter H bonds tend to be more linear. The depart from linearity on going from the HS to the LS state can be ascribed to the change of the bpp bite angle below the phase transition.

The most remarkable observation concerns the SSHB interaction O1···O5 (Figure 1). In the HS phase at 240 K, the H1O proton is located halfway between the two oxygen atoms (O1···H1O: 1.203(7) Å; H1O···O5: 1.206(7) Å), in qualitative agreement with the XRD study. In the mixed-spin phase at 120 K, this contact is split into two. While the O1A···H1OA···O5B interaction keeps the proton in the middle of the H bond (O1A···H1OA: 1.216(7) Å; H1OA···O5B: 1.213(7) Å), in the O1B···H1OB···O5A interaction the proton separates slightly from O1B (O1B···H1OB: 1.221(7) Å; H1OB ···O5A: 1.198(7) Å). In the reentrant LS phase at 95 K, the symmetry is restored but the H1O proton still deviates from the center of the H bond (O1···H1O: 1.222(6) Å; H1O···O5: 1.200(6) Å). Since in all cases the nuclear density of the H atom is well localized, these results clearly confirm a genuine proton migration. SSHBs with O···O distances smaller than 2.45 Å are expected to show broad single-well potentials suitable for this process. Normally, the proton is located halfway between the heteroatoms at high temperature and becomes off-centred as temperature decreases, as it is observed in this work. This can be due either to an asymmetric potential energy well; or to a change of the potential energy surface with temperature. The latter seems to apply in our case, given the rather symmetric environment of the H atom. The similar behaviour of the LS phase and the LS sublattice of the mixed-spin phase confirms that the modulation of the potential energy surface and the subsequent proton migration is a consequence of the SCO process. The shift in the proton position is small but significant (5 times the experimental error) and compares well with similar shifts observed in H-bonded ferroelectrics.

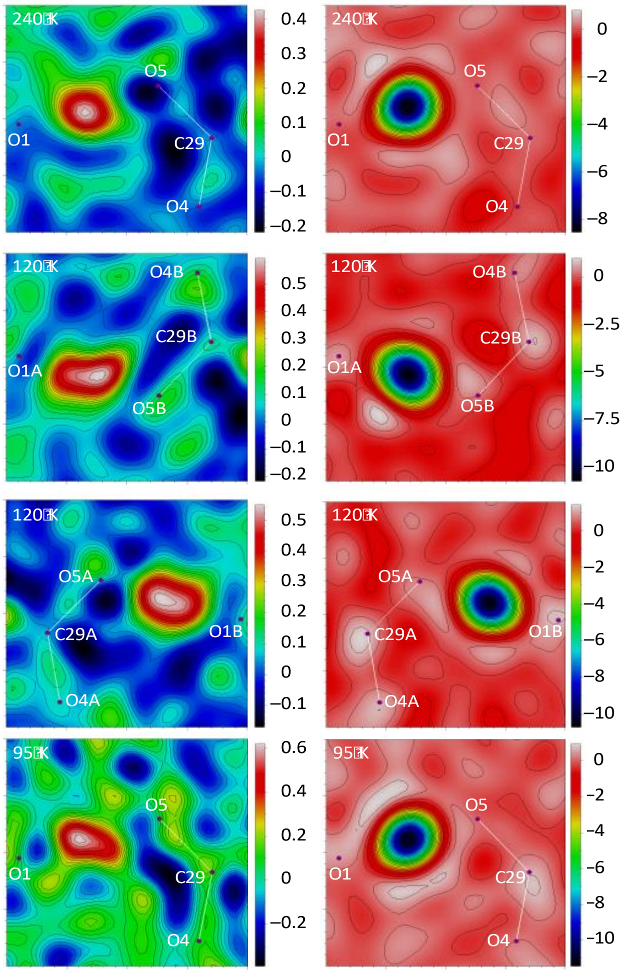

Figure 1. X-ray (left) and neutron (right) Fourier difference maps ($F_o - F_c$) for **1** at different temperatures showing, respectively, the electronic and nuclear density corresponding to the H atom involved in the short-strong H-bond. Images (2×2 Å^2) were calculated on a plane defined by atoms O1, O5 and C29. Note that at 120 K the interaction is split into two due to symmetry breaking. Hydrogen peaks are negative in the neutron images due to the sign of the neutron scattering length.