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Relationship between strength of hydrogen bonding and spin crossover behaviour in a series of iron(III) Schiff base complexes

Ivan Nemec, a Radovan Herchel, a and Zdeněk Trávníček b,c*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

X-ray crystal structures and magnetic properties of an isostructural series of iron(III) Schiff base complexes with the general formula [Fe(L5)(NCX)]·Solv (where H2L5 = N,N'-bis(2-hydroxy-naphthylidene)-1,6-diamino-4-azahexane, X = S, Solv = tetrahydrofuran, 1a; X = S, Solv = methanol and 0.5 pyrazine, 1b; X = S, Solv = butanone, 1c; Solv = N,N'-dimethylformamide, X = S (1d) or X = Se (1d'); X = S, Solv = dimethyl sulfoxide, 1e) are reported. In the crystals, the individual [Fe(L5)(NCX)] molecules are connected through weak C–H···O hydrogen bonding that stabilizes the Fe(III) complexes and the presence of the guest molecules in the crystal lattice of the SCO compound. The N–H···O hydrogen bonds connecting the Solv oxygen atom with the amine group of the [Fe(L5)(NCX)]·Solv molecule tune the electronic structure and affect the occurrence and tuning of spin crossover (SCO) in the complexes.

Introduction

The spin crossover (SCO) phenomenon, as a well-known example of molecular bistability, attracts attention of material chemists due to its potential applications in molecular switches, memories, displays or hybrid materials.1 It represents the spin transition between the low-spin (LS, in the case of Fe III octahedral complexes, S = 1/2, 2Tg) and high-spin (HS) states (S = 5/2, 6A1g) upon external perturbations such as thermal and/or pressure changes or light irradiation.2 Such a dramatic change in the electronic structure is accompanied by changes in the magnetic and structural properties, which can be detected and monitored by basic experimental techniques such as magnetometry, various kinds of spectroscopy or X-ray structural analysis.3 The SCO phenomenon is very sensitive to the environment of the SCO molecule. In isolated systems, the spin state conversion follows the Maxwell-Boltzmann statistics in most cases,4 but when cooperative interactions (represented by non-covalent contacts such as hydrogen bonding and/or n–π stacking interactions) come into play, the transition might be very abrupt (within the interval of a few Kelvins). Furthermore, if these interactions are able to propagate large changes in the crystal structure upon SCO, then thermal hysteresis may appear.4

In general, the role of solvent molecules of crystallization (Solv) in the SCO process is still not clear, because there are several opposed examples describing the solvent influence. The presence of the guest molecules in the crystal lattice of the SCO compound can dramatically affect their magnetic behaviour by changing the cooperative interactions with respect to the parent compound and therefore the lattice phonon distribution is affected.2 It can be also rationalized that non-covalent interactions, such as hydrogen bonds, may affect a charge distribution on the ligands and therefore, consecutively, the change in the ligand field strength can occur.5 The stabilization of the LS state is usually observed for the solvated samples and there are many examples of a downward shift of T1/2 (or just occurrence of SCO in the formerly LS-only solvated compounds) upon desolvation of the sample.6

Scheme 1 Schematic representation of the H2L5 ligand

In accord with these observations, the solvation of a sample usually tends to increase T1/2. Alternatively, upon guest molecule exchange, the variation in T1/2 and in steepness of the transition is observed, as has been reported recently in the remarkable single-
crystal-to-single-crystal transformation studies. Rational tuning of the SCO behaviour by the lattice solvent exchange was reported firstly for the nanoporous metal-organic frameworks (MOFs) built by [Fe(Hapy)(NCS)₂] molecules (Hapy = trans-4,4’-azopyridine) in 2002 by Kept et al., and then, other similar studies have followed. The vapour and gas adsorption studies on [{Fe(PY2)Ni(CN)₃}] Hoffmann-type metal-organic frameworks (MOFs) revealed the relationship between the guest size and T₁/₂ (PY = pyrazine) and similar relationships were reported also for 0D supramolecular systems such as [Fe(4ditz)(PF₆)]₂·Solv (4ditz = 1,4-Bis(tetrazole-1-yl)butane, Solv = CH₃OH, CH₃CH₂OH) or [Fe(bdpt)₂]·Solv (Hbdpt = 3-(5-bromo-2-pyridyl)-5-(4-pyridyl)-1,2,4-triazole), Solv = CH₃OH, CH₃CH₂OH). Another possible Solv-SCO relationship was found in MOFs such as [Fe(bpdb)₂(NCS)]·Solv (bpbd = 2,3-bis(4’-pyridyl)-2,3-butadiol, Solv = CH₃CN, CH₃CH₂OH, CH₃CH₂OH), CH₃CH₂OH (CH₃CO) and it was outlined that lower values of the Solv dielectric constants (ε) result in the LS state being more stabilized. The solvent-SCO relationship was documented also for Fe(III) SCO compounds several times but the systematic study is still missing.

Recently, we have reported on the SCO phenomenon observed in a series of [Fe(L₅)(NCS)₂]·Solv compounds (Scheme 1, H₂L₅ = N,N’-bis(2-hydroxy-naphthylidene)-1,6-diamino-4-azahexane, L stands for pseudoaloidal ligands). The thiocyanate and selenocyanate complexes from the mentioned series, [Fe(L₃)(NCN)]·CH₃CN and [Fe(L₅)(NCN)]·CH₃CO, (X = S, Se), exhibited magnetic behaviour dependent on the presence of a solvent molecule incorporated in the crystal structure: the acetonitrile solvate showed SCO while the latter compound stayed in the HS state down to 2 K. In both cases, the solvent molecule is connected with the donor nitrogen amine atom from the L ligand via a hydrogen bond (the nitrogen/oxygen atom from the Solv molecules serves as an acceptor). In order to explore the influence of the co-crystallized Solv molecules on SCO in greater details, we decided to investigate the properties of the aforementioned system utilizing various Solv molecules. In this work, we report on the crystal structures and magnetic properties of an isostructural (for bond lengths and selected structural parameters see Table 1, for crystallographic data see Parts of the crystal structures of the complexes 1a–d, with the guest molecules highlighted in the space-fill model (left). Selected hydrogen atoms of the complex molecules were omitted for clarity, except for those involved in the selected non-covalent contacts. The lengths of the non-covalent contacts (in Å): 1a, d(C1…O1) = 3.475(2), d(C8…S1) = 3.753(2); 1b, d(C1…O1) = 3.507(3), d(C8…S1) = 3.818(3); 1c, d(C1…O1) = 3.623(2), d(C8…S1) = 3.826(2); 1d, 298 K, d(C1…O1) = 3.546(5), d(C8…S1) = 3.816(4); 1d, 150 K, d(C1…O1) = 3.456(2), d(C8…S1) = 3.819(2); 1d, 308 K, d(C1…O1) = 3.552(5), d(C8…S1) = 3.914(4); 1d, 150 K, d(C1…O1) = 3.468(6), d(C8…S1) = 3.882(5); 1e, d(C1…O1) = 3.448(3), d(C8…S1) = 3.801(3); 1f, Fe1, d(C21…O1) = 3.475(2), d(C8…S1) = 3.754(2); 1f, Fe2, d(C48…O3) = 3.519(3), d(C8…S1) = 3.796(3); 1g, d(C21…O1) = 3.474(3), d(C8…S1) = 3.843(2).

Table 2) series of [Fe(L₅)(NCX)]·Solv complexes, where X = S, Solv = tetrahydrofuran (THF), (1a); X = S, Solv = methanol (MeOH) and 0.5 pyrazine (PYZ), (1b); X = S, Solv = butanone (MEK), (1c); X = S, Solv = N,N’-dimethylformamide (DMF, 1d); X = Se, Solv = DMF, (1d’); X = S, Solv = dimethyl sulfoxide (DMSO, 1e). Moreover, previously published compounds (X = S, Solv = 0.5 MeOH and 0.5 MEK) and 1g (X = S, Solv = acetone) were included into the discussion for comparative purposes. Apparently, the use of PYZ as a guest molecule deviates from the series because PYZ can potentially form N–H···N hydrogen bond, while the other guests from the series are O-acceptors of hydrogen bonding. However, the use of this guest allowed us to study the influence of a methanol molecule on magnetic behaviour of the [Fe(L₅)(NCX)] molecule (vide infra), since the preparation of the pure methanol solvate is impossible by a direct synthesis in methanol. The previously reported [Fe(L₅)(NCX)]·CH₃CN compounds were not included because they are not isostructural with compounds 1a-1g.

The presented series of the [Fe(L₅)(NCX)]·Solv compounds is unique due to very similar structural frameworks of constitutive [Fe(L₅)(NCX)] molecules (Fig.1, see ESI, Fig. S1-S7). Due to only very tiny structural differences (both at the molecular and supramolecular level) between the particular members of the series, the [Fe(L₅)(NCX)] framework cannot be responsible for the differences in their magnetic behaviours, but the properties of the Solv molecules must be considered as the main perturbative term responsible for the (non)occurrence and characteristics of SCO.

### Results

#### Synthesis and infrared spectroscopy

The synthesis of compounds 1a-1e is uncomplicated and it can be performed in two consecutive steps: (1) the preparation of the [Fe(L₅)Cl] precursor complex; (2) the reaction between the precursor and potassium pseudohalide in methanol in the presence of the Solv molecules.
Infrared spectra of 1a-1e are very similar for all the compounds in the series. The only differences between them originate from the presence of the different guest molecules of crystallization (in cm$^{-1}$, $\nu$(C=O) = 1699 in 1c, 1663 in 1d, 1665 in 1d', $\nu$(O–H) = 3272 in 1b). The differences in the frequency of the $\nu$(N–H) vibrations were also observed (between 3163 and 3242 cm$^{-1}$). This should reflect different strength of N–H···N hydrogen bonds within the present series (vide infra), but the obtained results are not very informative (see ESI, Fig. S8), probably due to the broadness of the observed bands, which prevented us to perform a deeper study.

Fig.2. Perspective view of non-covalent interactions of the Solv molecule with [Fe(L$_5^\cdot$(NCS))] in 1a-f. Most of hydrogen atoms were omitted for clarity, except for those involved in hydrogen bonding and non-covalent contacts (black dashed lines). The lengths of selected non-covalent contacts (in Å): 1a, $d$(N2···O1S) = 3.295(2), $d$(C1S···O2) = 3.120(2), $d$(C12···O1S) = 3.591(2); 1b, $d$(N2···O1S) = 3.110(3), $d$(O1S···N1S) = 2.839(4); 1c, $d$(N2···O1S) = 3.705(6), $d$(C3SA···O2) = 3.448(3); 1d, $d$(N2···O1S) = 2.944(5), $d$(C2S···O2) = 3.965(8), $d$(C12···O1S) = 3.512(6); 1d', $d$(N2···O1S) = 3.524(6); 1e, $d$(N2···O1S) = 2.921(6), $d$(C3SA···O2) = 3.623(7), $d$(C12···O1S) = 3.576(3); 1f, $d$(N2···O1S) = 3.57(3), $d$(O1S···O4) = 2.771(3), $d$(N6···O1S) = 3.264(4), $d$(C39···O1S) = 3.493(4), $d$(C29···O2) = 3.499(4), $d$(C12···S2) = 3.797(3), $d$(C2S···O2) = 3.526(5), $d$(C12···O2S) = 3.357(4), $d$(O1S···O4) = 2.771(3) Å; 1f A, $d$(N6···O1S) = 3.264(4) Å, $d$(C39···O1S) = 3.493(4) Å.
General description of molecular and crystal structures

The molecular structure of the \([\text{Fe}(L^5)(\text{NCX})]\)-type complexes was well-described in our previous work\(^{15}\) and therefore it is discussed only briefly and the main attention is focused on the tiny differences in the molecular geometry between the particular members of the 1a-1g series and in the case of the SCO compounds, on the LS vs. HS molecular structure distinctions. Doubly deprotonated pentadentate ligand \(L^5\) provides an \(\text{N}_2\text{O}_2\) donor set to the iron(III) central atom and the remaining coordination site is occupied by the nitrogen atom from the anionic NCX ligand. The pentadentate ligand coordinates to the iron(III) atom through the oxygen atoms in the \(\text{cis}\) position as is typical for this group of compounds with the propyl-ethyl aliphatic part of the pentadentate ligand.\(^{15,18,19}\) The chromophore consists of the \(\text{Fe}^3\text{N}_5\text{O}_6\text{Solv}\) core with the \(\text{L}^5\) ligand at the axial positions. The LS structures were determined only for compounds 1d and 1d'. Both compounds possess very similar bond lengths and selected structural parameters (Table 1), which correspond well with the values found for the purely LS cyanido complexes reported previously.\(^{15,19,20}\)

The crystal structures of 1a-1g are very similar. They are composed of the \([\text{Fe}(L^5)(\text{NCX})]\) and Solv molecules which form a three-dimensional framework via C–H⋯O and C–H⋯π weak interactions. The essential part of the framework consists of a centrosymmetric dimer of two adjacent \([\text{Fe}(L^5)(\text{NCX})]\) molecules interconnected by a rather weak C–H⋯O non-contact between the CH group of the naphthalene ring and the phenolic oxygen atom (Fig.1). Further small stabilization within the dimer is provided by an offset ring-ring stacking interaction of the naphthalene rings. The interconnections between the adjacent dimeric units, lying in the same layer, are provided by very weak C–H⋯π and C–H⋯S non-contact contacts. The cavities with the Solv molecules are placed between the dimeric units (Fig.1).

Each cavity is occupied by two same guest molecules in most of the cases, but two exceptions can be found within the present series: two \(\text{CH}_3\text{OH}\) and one PYZ molecules in 1b, MEK and \(\text{CH}_3\text{OH}\) in 1f. The Solv guests from the cavity are hydrogen bonded to the amine groups of the \([\text{Fe}(L^5)(\text{NCX})]\) molecules from the upper, or lower \([\text{Fe}(L^5)(\text{NCX})]\) layer. The cavities are of similar size with the volumes ranging from 224.4 Å\(^3\) in 1b to 295 Å\(^3\) in 1d'. The contraction of the framework induced by SCO is documented also by a change in the cavity size by approximately 13 % (1d, 247.3 at 150 K vs. 283.3 Å\(^3\) at 298 K) and 16 % (1d', 247.0 Å\(^3\) at 150 K vs. 294.8 Å\(^3\) at 308 K). Additional stabilization of the Solv molecule is provided by weak contacts such as C–H⋯O and C–H⋯π interactions. Especially the C–H⋯O contact between the CH group from Solv and the phenolic oxygen atom from the \([\text{Fe}(L^5)(\text{NCX})]\) molecule is of importance, because together with N–H⋯O hydrogen bond, these two contacts form ring synthons (Fig.2): \(R_2^2(6)\) in 1b and 1f (\(\text{CH}_3\text{OH}\) molecules), \(R_3^2(8)\) in 1e, 1f (MEK molecule), 1e and 1g, \(R_3^2(9)\) in 1d and 1d'. It must be noted that the aliphatic chain (in most of the cases the C–H⋯O contact provided by the carbon atom C12, Fig.2) from the L5 ligand is also interacting with the solvent oxygen atom. Besides these dominant contacts other weak non-contact C–H⋯O, C–H⋯S and C–H⋯π interactions can be found in the crystal structures of 1a-g.

The Fe–O bond lengths are the shortest adopting values close to 1.94 Å.

Fig.3 Temperature dependence of effective magnetic moment for compounds 1e, 1d, 1d' and 1e (top left). Plot of possible \(T_{1/2}\) dependence on the length of the hydrogen bond between the amine group and the acceptor atom from guest solvent molecule (top right). The \(T_{1/2}\) values for the purely HS compounds were set to zero and highlighted by a red rectangle. Detailed view of the thermal hysteresis in 1e and 1d (below).
Magnetic properties

The compounds of the presented series can be divided into two subgroups according to their magnetic behaviour, i.e. purely HS compounds and SCO compounds.

The magnetic data for the purely HS compounds, 1a-c, 1f, are shown in ESI, Fig. S9-S11, Table S1. The magnetic behaviours observed for 1a-c, 1f and 1g are essentially similar. The effective magnetic moment at room temperature adopts little bit higher values (\( \mu_{\text{eff}} = 6.0-6.1 \mu_B \)) than is the spin-only value calculated for \( S = 5/2 \) and \( g = 2.0 (5.92 \mu_B) \). The \( \mu_{\text{eff}} \) values stay almost constant down to 20 K, where the zero-field splitting (ZFS) and/or weak magnetic interactions mediated through the non-covalent interactions start to dominate the magnetic behaviour and this is observed as an abrupt drop in the \( \mu_{\text{eff}} \) values down to ca. 5 \( \mu_B \). The magnetic data were analysed using the following equation (1),

\[
\hat{H} = D(S_z^2 - S^2/3) - g\xi \langle S_z \rangle S_z + \mu_B B g S_z
\]

comprising the spin Zeeman term, ZFS term and the molecular field correction term for the parallel (\( a = z \)) and perpendicular (\( a = x, y \)) directions. The obtained results can be found in ESI, Fig. S11. The magnetic data for the SCO compounds (1c, 1d, 1d', 1e) are shown in Fig.3. In accord with the previous observations for this group of compounds, the typical \( \mu_{\text{eff}} \) value for the LS state is higher (2.0 - 2.1 \( \mu_B \)) than the spin-only value (1.73 \( \mu_B \)) calculated for \( g = 2.0 \) and \( S = 1/2 \). This is due to the orbital angular momentum present in the \( \tilde{T}_{1g} \) electronic state for the octahedral coordination environment. The presented SCO behaviours are of a cooperative character which is especially apparent in the case of the DMF and DMSO solvates, where the spin transition is accompanied by thermal hysteresis (1d, 1d' = 232 K, 1e, 1g = 235 K and 1e, 1g = 127 K 1d' = 138 K). Less cooperative SCO behaviours are observed for 1d' (1d' = 244 K) and in particular for 1e (1e = 84 K), which has a considerably incomplete transition with \( \mu_{\text{eff}}(20 \text{ K}) = 3.80 \mu_B \) (Fig.3).

Discussion

Magnetic-structural relationship

When looking for the reason for such a striking difference in the magnetic behaviours found in this isostructural series, the attention must be focused on the role of the guest solvent molecules, which are the major variable within the present series. If one inspects the relationship between the length of the N-H-\( \cdot \cdot \cdot \)O contact and occurrence of SCO, or even more, its correlation with \( T_{1/2} \), a possible association can be found. The donor-acceptor (D-\( \cdot \cdot \cdot \)A) distances of the N-H-\( \cdot \cdot \cdot \)O hydrogen bonds are summarized in Table 3, together with the values of \( T_{1/2} \) of the SCO compounds and several basic properties of the guest molecules. It is apparent that SCO occurs only in the compounds with the D-\( \cdot \cdot \cdot \)A distance shorter than \( ca \ 3.0 \) Å and moreover, the compounds with the shortest D-\( \cdot \cdot \cdot \)A distance have the highest \( T_{1/2} \) (1d, 1d'). Comparison between the crystal structure and magnetic properties of the compounds 1e and 1f might serve as a good example of such a relationship. Both compounds have the MEK guest molecules and 1f has additional CH\( _3 \)OH molecules in the cavities. In 1f (purely HS) the D-\( \cdot \cdot \cdot \)A distance is 3.154(4) Å, while this distance is significantly shorter in 1e (SCO, Fig.3): 2.988(2) Å. From the magnetic and structural data presented for compounds 1a-1g, the relationship between \( T_{1/2} \) and hydrogen bonding might seem to be straightforward. However, as it is well established, the \( T_{1/2} \) value is thermodynamically defined as the ratio of the enthalpy and entropy of SCO. Especially, the entropy originates in the molecular and lattice vibrations which cannot be purposely modulated but they can be easily influenced by chemical modifications (such as ligand substitution, different lattice solvent etc.). Therefore, the rational tuning of the SCO phenomenon is always a challenging task which involves simultaneous changes of entropy and enthalpy.
Table 2 Crystallographic data and structure refinement details.

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<td>wR_f/a (all data)</td>
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<td>0.0620/0.0976</td>
<td>0.0367/0.0814</td>
<td>0.0438/0.0895</td>
<td>0.0802/0.1500</td>
<td>0.0839/0.1588</td>
<td>0.0853/0.1201</td>
<td>0.0533/0.1195</td>
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<td>R_f/a (I&gt;2σ(I))</td>
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<td>0.0396/0.0929</td>
<td>0.0298/0.0789</td>
<td>0.0328/0.0931</td>
<td>0.0522/0.1416</td>
<td>0.0616/0.1523</td>
<td>0.0467/0.1127</td>
<td>0.0412/0.1156</td>
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<td>CCDC number</td>
<td>943181</td>
<td>943182</td>
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<td>943184</td>
<td>1030135</td>
<td>943185</td>
<td>1030136</td>
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* R_f = \( \sum |F_o| - |F_c| \)/ \( \sum |F_o| \)^1/2
  \( wR_f = \left( \sum [w(F_o^2 - F_c^2)^2] \right)^{1/2} \)
For example, any prediction fails in the case of the isosctructural series, where the SCO complexes [Fe(pa)]Cl₂·Solv (pa = 2-picolylamine)⁵ have very similar surroundings of the [Fe(pa)]²⁺ cation consisting of relatively strong N–H···Cl hydrogen bonds, and different Solv guests are involved in the supramolecular system only by weak non-covalent contacts. However, the difference between the aforementioned system and the present series must be emphasized. On the contrary to the [Fe(pa)]Cl₂·Solv series, the 1a-1g compounds have the complex framework built by weak non-covalent contacts and the strongest contact is formed between the solvent molecule and the amine group, which is directly involved in the coordination of the metal centre. Therefore, a dominant role of this contact in influencing the ligand field strength might be expected due to the charge transfer of the electron density from the acceptor to hydrogen bonding donor upon formation of the hydrogen bond.²³

Finally, it should be pointed out that each solvent molecule has different intrinsic properties such as electron density distribution, vibrational states, basicity, polarity etc., which might affect the SCO behaviour or Solv···SCO complex interaction. Therefore, the accurate Tc predicion based only on D···A distance is not expected and this can be also documented within the 1a-g series in which 1e has longer D···A distance but higher Tc/2 than 1e (Table 3).

Abruptness of SCO

We proposed previously,¹⁵ inspired by findings reported by Halcrow et al.,²⁶ that the dihedral angle between the least-square planes of the aromatic rings (α)²⁵ could be a valuable structural parameter to characterize the cooperativeness of the spin transition in this group of compounds. By comparison of the LS and HS values, one can expect larger differences (Δα) for the compounds with more abrupt transitions. In the case of 1d and 1d’, a larger α(LS) – α(HS) difference is found for 1d (Δα = 2.1°) than for 1d’ (Δα = 1.3°) and from Fig.3 it is apparent that the spin transition is indeed more abrupt for 1d. Another parameter (δxyz) which might be useful in the characterization of the structural changes observed upon spin transition can be defined as a sum of the absolute values of LS and HS coordinate differences (x, y, z), only non-hydrogen atoms) divided by the number of the atoms (N) involved in the calculation:

\[
\delta_{xyz} = \frac{\sum |x_{LS} - x_{HS}| + |y_{LS} - y_{HS}| + |z_{LS} - z_{HS}|}{N}
\]  

(2)

This parameter literally measures the difference between the LS and HS crystal structure of the SCO compound. It could be expected that the compounds exhibiting cooperative SCO behaviours might have the changes in the crystal structure more pronounced (and the δxyz values higher) than those exhibiting gradual transitions. This can be understood on the basis of the elastic interaction model developed by Spiering et al.²⁶ where the cooperativity is defined as the interaction between the LS and HS species in the SCO solids, which are expected to be stronger for molecules capable to form a “larger” point defect in the crystal lattice upon spin transition. Furthermore, it can be expected that the use of this parameter should be valid for the compounds consisting of the SCO molecules with a similar second coordination sphere, i.e. with non-covalent interactions of similar strength, which is, as it was mentioned above, the case of the herein studied series of compounds. The LS and HS structures are available for two compounds in this work: 1d and 1d’. The δxyz values calculated for these compounds differ significantly: 0.0526 (1d) and 0.0463 (1d’). Only one SCO compound with determined LS and HS structures belonging to the group of [Fe(L5)(NCX)] compounds was reported previously: [Fe(L5)(NCSe)]·CH₃CN.¹⁵ The δxyz value calculated for this compound is equal to 0.0300.

Again, as in the case of the α parameter, the largest δxyz value is found for the most abrupt transition in 1d. In order to compare these values properly, it is necessary to define abruptness of SCO. This can be done by utilizing a modification of the previously published SCO smoothness equation:²⁷ \( T_c = T_{TSHS} = 0.9) - T_{TSHS} = 0.1); Km(1d) = 24 K, Tm(1d’) = 45 K and Tm([Fe(L5)(NCSe)]·CH₃CN) = 76 K. The Tm values found for 1d, 1d’ and [Fe(L5)(NCSe)]·CH₃CN agree with expected changes of abruptness in above mentioned compounds.

Table 3 The N–O (donor–acceptor) hydrogen bond distances in 1a-1f, critical temperatures of the SCO transition (Tc), and solvent of crystallization molecular volumes (Vmol) and their relative permittivity (εr).

<table>
<thead>
<tr>
<th>Compound</th>
<th>d(N–O)/Å</th>
<th>Tc/K</th>
<th>Vmol/Å³</th>
<th>εr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>3.295(2)</td>
<td>HS</td>
<td>78.0</td>
<td>7.5</td>
</tr>
<tr>
<td>1b</td>
<td>3.110(3)</td>
<td>HS</td>
<td>73.2</td>
<td>33.0</td>
</tr>
<tr>
<td>1c</td>
<td>2.988(2)</td>
<td>84</td>
<td>81.5</td>
<td>18.6</td>
</tr>
<tr>
<td>1d 308 K</td>
<td>2.941(2)</td>
<td>232²</td>
<td>77.5</td>
<td>38.3</td>
</tr>
<tr>
<td>1d 150 K</td>
<td>2.944(4)</td>
<td>156²</td>
<td>77.5</td>
<td>38.3</td>
</tr>
<tr>
<td>1d’ 308 K</td>
<td>2.935(5)</td>
<td>244</td>
<td>77.5</td>
<td>38.3</td>
</tr>
<tr>
<td>1d’ 150 K</td>
<td>2.921(6)</td>
<td>127²</td>
<td>71.4</td>
<td>47.2</td>
</tr>
<tr>
<td>1f Fe1</td>
<td>3.272(4)</td>
<td>CH₃OH</td>
<td>37.2</td>
<td>33.0</td>
</tr>
<tr>
<td>1f Fe2</td>
<td>3.154(4)</td>
<td>MEK</td>
<td>81.5</td>
<td>18.6</td>
</tr>
<tr>
<td>1g</td>
<td>3.134(3)</td>
<td>HS</td>
<td>64.7</td>
<td>21.0</td>
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</table>

* Molecular volumes calculated by the Molinspiration program predictions,²⁸ according to the reference²⁹

Theoretical insight into intermolecular interactions

With the aim to quantitatively analyse the impact of the N–H···O contact on the SCO behaviour, or more precisely, on critical temperature Tc, we analysed bonding properties between [Fe(L⁵)(NCX)] and the solvent molecule in ([Fe(L⁵)(NCX)]···Solv) moieties. All the calculations were based on geometries following from the experimental X-ray structures, but all the hydrogen atom positions were optimized using the B3LYP functional together with the atom-pairwise dispersion correction to the DFT energy with Becke-Johnson damping (D3BJ) using ORCA 3.0.1. The polarized triple-ζ quality basis set, def2-TZVP(-f), was used for iron, nitrogen, sulphur and selenium atoms, while the def2-SVP basis set was used for carbon and hydrogen atoms. The calculations also utilized the RI
Fig. 4 Left: (a) Non-covalent interaction (NCI) analysis of SCO compounds (1c-e). (b) NCI analysis of HS compounds (1a, 1b, 1f, 1g). (c) plot of NCI isosurface ($s = 0.3$) coloured according to the RGB scheme over the range of $-0.03 < \text{sign} (\lambda_2) \rho < 0.01$ for $\{\text{Fe(L5)(NCS)}\} \cdots \text{DMF}$. Red indicates strong attraction; green indicates very weak interaction and blue indicates weak repulsion. (d) NCI analysis of SCO compounds (1c-e) zoomed to N–H–O contact region.

First, non-covalent interaction (NCI) index was utilized to visualize both attractive (hydrogen bonding, van der Waals) and repulsive (steric) interactions based on the properties of the electron density using program NCIPLOT. The method is based on the analysis of the reduced gradient of density $s$, defined as

$$s = \frac{1}{2^{3/2} \pi^{3/2}} \frac{\sqrt{\rho}}{\sqrt{\rho}}$$

where $\rho$ is electron density. Weak intermolecular or intramolecular interaction causes a radical change in the reduced gradient of density $s$ between the interacting atoms resulting in density critical points between interacting fragments. These critical points are represented with troughs in 2D plots of $s$ vs. $\rho$. In order to judge whether non-covalent interaction is attractive or repulsive, the sign of an eigenvalue $\lambda_2$ of the electron density Hessian matrix, $\nabla^2 \rho = \lambda_1 \nabla^2 + \lambda_2 \nabla$, ($\lambda_1 < \lambda_2 < \lambda_3$) can be utilized. The $\lambda_2$ is negative in the case of bonding interactions (e.g. hydrogen bonds), which characterized by an accumulation of electron density perpendicular to the bond. On the contrary, positive $\lambda_2$ means that there are non-bonded interactions (e.g. steric repulsions), which result in electron density depletion. In summary, the troughs of reduced gradient of density $s$ are used to identify non-covalent contacts, and at point where $s$ is approaching zero, the quantity $\text{sign} (\lambda_2) \rho$ defines their strength (the larger the value, the stronger the interaction) and nature (negative sign – attractive interaction vs. positive sign – repulsive interaction).

In order to accomplish our intention, the NCIPLOT was used to calculate the NCI index for all available $\{\text{Fe(L5)(NCS)}\} \cdots \text{Solv}$ moieties 1a-g, utilizing their HS experimental single-crystal X-ray structures with optimized hydrogen atom positions. The keyword LIGAND was used to address only NCI between complex and solvent requiring the use of promolecular densities. The results are divided into two groups, purely HS compounds (1a, 1b, 1f, 1g) and SCO compounds (1c-e) – Fig. 4. As an example of NCI calculation, the molecular structure of $\{\text{Fe(L5)(NCS)}\} \cdots \text{DMF}$ (1d) is shown in Fig. 4c, together with NCI isosurfaces coloured according to the nature and strength of these interactions showing the N–H–O contact (orange-red approximation with the decontracted auxiliary def2-TZV/C and def2-SVPC Coulomb fitting basis sets and the chain-of-spheres (RIJCOSX) approximation to exact exchange as implemented in ORCA.
colour), C–H–O and C–H–π contacts (green-blue colour) and O–lone-pair–O–lone-pair contact (blue colour). This 3D plot of NCI then can be transformed to 2D plot, in which the above mentioned NCIs are represented by troughs (Fig. 4, a-b). The troughs found approximately in the region of -0.015 < sign(Δρ) < +0.015 represents weak interactions. In the group of SCO compounds, the strongest and attractive interactions belonging to the N–H–O contact are found in the region of -0.027 < sign(Δρ) < -0.024 (Fig. 4, d). Furthermore, the sign(Δρ) values of these troughs, corresponding to the strength of the N–H–O contact, nicely correlates with $T_{1/2}$ (Fig. 5).

The indispensable role of this N–H–O contact is further demonstrated in Fig. 4b for purely HS compounds, in which there are no troughs in the region of -0.027 < sign(Δρ) < -0.024, which means that there are no strong enough N–H–O contacts. We can only observe the strong and attractive O–H–O contact in 1f between MeOH and phenolic oxygen atom. This contact should act in an opposite direction (than N–H–O contact) in charge transfer due to hydrogen bonding because the solvent molecule acts as hydrogen bond donor. The strongest N–H–O contact is found in 1b, sign(Δρ) = -0.020, but evidently the strength of this contact is not sufficient to induce the SCO behaviour.

To push further our effort to substantiate the role of the N–H–O contact on the SCO behaviour within the presented series of complexes, we used another approach based on topological analysis using the total molecular electronic density $ρ(r)$ and Laplacian of $ρ(r)$ ($V^2ρ(r)$) based on atom in molecule (AIM) calculations. The single point energy DFT calculations on [[Fe(L5)(NCX)]·Solv] moieties resulted in the geometry-basis-wavefunction (GBW) files, which were then transformed to the MOLDEN format and analysed in a program Multiwfn 3.3.5 (A Multifunctional Wavefunction Analyzer). The so-called bond critical points (BCP) of the type (3,-1) were located in the N–H–O contacts and in these points, the potential energy density $V(r)$ was calculated, because it was shown that the energy of hydrogen bonds ($E_{HB}$) can be approximated as $E_{HB} = V(r)/2$. The results depicted in Fig. 5 (right) proved that the energy of the N–H–O hydrogen bonds within the series of SCO compounds correlates with $T_{1/2}$, showing that the stronger N–H–O hydrogen bond in the HS X-ray structure is formed, the higher $T_{1/2}$ is observed.

![Fig. 5](image)

To summarize, both theoretical approaches based on ab initio calculations identified the N–H–O hydrogen bond strength (energy) as the key driving force for observing SCO in the isostructural series of the [Fe(L5)(NCX)]·Solv complexes.

**Conclusions**

In this article the crystal structures and magnetic properties of the compounds belonging to an isostructural series of iron(III) Schiff base complexes were reported. From the magnetic and structural data, a possible relationship between the occurrence of SCO (and its critical temperature) and strength of hydrogen bonding between the guest solvent molecules and amine group from the [Fe(L5)(NCX)] molecules was outlined. Remarkably, there is no apparent correlation of the SCO behaviour with the other parameters such as the size of the host cavity, the guest volume or its dielectric constant (Table 3) and that the guest molecule substitution affects $T_{1/2}$ much more significantly than the substitution in the monodentate NCX ligand, as was documented on compounds 1d and 1d’. The N–H–O hydrogen bonding in 1a-f compounds was studied by combined DFT and Bader charge analysis calculations in greater details and these calculations identified a correlation between the strength of the N–H–O hydrogen bond and $T_{1/2}$ in the SCO compounds of this series. More concretely, the stronger N–H–O hydrogen bond (i.e. the shorter distance) implies higher value of $T_{1/2}$. This hypothesis can be supported also by previous works where similar relationship was observed for solution studies of anion binding Fe(II) SCO cations. However, further research involving a preparation of the [Fe(L5)(NCX)]·Solv compounds with a different type of the guest Solv molecules is inevitable in order to prove this hypothesis.

Furthermore, the group of the [Fe(L5)(NCX)]·Solv compounds is interesting not only for the above mentioned relationship in host-guest system. These compounds are perspective also due to the capability of the host [Fe(L5)(NCX)] framework to propagate cooperative interactions resulting in occurrence of abrupt SCO with thermal hysteresis (1d, $ΔT = 3 \text{ K}$, 1e, $ΔT = 11 \text{ K}$). This, along with the possibility to exploit the Solv guests as $T_{1/2}$ tuners, gives an opportunity to prepare cooperative SCO compounds with $T_{1/2}$ at ambient temperature.

**Acknowledgement**

We acknowledge the financial support from the Grant Agency of the Czech Republic (GAČR P207/11/0841) and the National Programme of Sustainability I (LO1305) of the Ministry of Education, Youth and Sports of the Czech Republic. We also would like to thank Mr. Pavel Zoufalý for the help with the preparation of compound 1e.

**Experimental**

All reagents and solvents were purchased from commercial sources (Sigma Aldrich, Acros Organics) and used as received.

The complex 1a was prepared by the reaction of [Fe(L5)Cl]$^{17+}$ (100 mg, 0.186 mmol) with KCNS (20 mg, 0.206 mmol) in tetrahydrofuran (10 cm$^3$) and methanol (20 cm$^3$). This solution was stirred and heated for 10 minutes. Then it was filtered through a paper filter and left to crystallize for several days. Yield (based on [Fe(L5)Cl]) = 74 %.
The complex 1b was prepared by the reaction of [Fe(L5)Cl] (100 mg) with KCNS (20 mg, 0.206 mmol) in methanol (25 cm³) and 4g of pyrazine was added afterwards. This solution was stirred and heated for 10 minutes. Then it was filtered through a paper filter and left to crystallize for several days. Yield (based on [Fe(L5)Cl] = 12 %.

The complexes 1c, 1d, 1d' were prepared in the very same way. The precursor complex [Fe(L5)Cl] (100 mg, 0.186 mmol) was reacted with K2C2H3Fe2N3O3S2; Found: C, 62.9; H, 5.5; N, 9.1 %, requires C, 63.1; H, 5.5; N, 9.2 %. IR mid (in cm⁻¹): ν(C–N) = 3166, (w), ν(C–H) = 2924, 2861 (m), ν(C=O) = 1699, (w), ν(C=N) = 1603, 1536, 1506 (vs); 1b: Mw = 609.52, C₂H₁₂Fe₂N₂O₃S₂; Found: C, 61.3; H, 5.2; N, 11.5 %, requires C, 61.1; H, 5.1; N, 11.5 %, IR mid (in cm⁻¹): ν(O–H) = 3272, (w), ν(N–H) = 3204, (w), ν(C–N) = 3103, (w), ν(C=O) = 1699, (w), ν(C=N) = 1603, 1536, 1506 (vs); 1c, Mw = 609.53, C₂H₁₂Fe₂N₂O₃S₂; Found: C, 61.3; H, 5.1; N, 11.5 %, requires C, 61.1; H, 5.1; N, 11.5 %, IR mid (in cm⁻¹): ν(O–H) = 3272, (w), ν(N–H) = 3204, (w), ν(C–N) = 3103, (w), ν(C=O) = 1699, (w), ν(C=N) = 1603, 1536, 1506 (vs); 1d': Mw = 657.42, C₃H₁₃Fe₂N₂O₃S₂; Found: C, 56.7; H, 5.0; N, 10.5, requires C, 56.6; H, 4.9; N, 10.7 %, IR mid (in cm⁻¹): ν(C–S) = 3103, (w), ν(C–H) = 3051 (w), ν(C–H) = 2967, 2924, 2861 (m), ν(C–O) = 1663, (s), ν(C=C) = 1605, 1537, 1506 (s); 1d: Mw = 610.53, C₂H₁₂Fe₂N₂O₃S₂; Found: C, 61.1; H, 5.2; N, 11.4, requires C, 61.0; H, 5.3; N, 11.5 %, IR mid (in cm⁻¹): ν(N–H) = 3166, (s), ν(C–S) = 3046 (w), ν(C–H) = 2967, 2926, 2859 (m), ν(C=O) = 1663, (s), ν(C=O) = 1605, 1539, 1506 (s); 1c: Mw = 568.64, C₂H₁₂Fe₂N₂O₃S₂; Found: C, 58.6; H, 5.1; N, 9.9, requires C, 58.5; H, 5.1; N, 9.1 %, IR mid (in cm⁻¹): ν(N–H) = 3167, (s), ν(C–S) = 3049 (w), ν(C–H) = 2969, 2925, 2867 (m), ν(C=O) = 1665, (s), ν(C–C) = 1603, 1537, 1506 (s).

Equipment, measurements and software
Elemental analysis (CHN) was performed on a FLASH 2000 CHNS Analyzer (ThermoFisher Scientific). Magnetic data were measured on powdered samples pressed into the pellets using an MPMS XL-7 Quantum Design SQUID magnetometer. The experimental data were corrected for the diamagnetism of the constituent atoms using Pascal’s constants. Magnetic susceptibility and magnetization measurements were done using a SQUID magnetometer (MPMS, Quantum Design) from T = 2 K at B = 0.1 T. The magnetization data were taken at T = 2.0 and 4.6 K. The effective magnetic moment was calculated as usual: \( \mu_{eff,\text{B}} = 798(2) \) when SI units are employed. Analysis of magnetic data was done with the package POLYMAGNET. The visualization of non-covalent interactions based on NCI PLOT calculation was done with the help of a VMD program.

Single crystal X-ray diffraction data were collected using an Oxford diffraction Xcalibur2 CCD diffractometer with a Sapphire CCD detector installed in a fine-focus sealed tube (Mo-Kα radiation, λ = 0.71073 Å) and equipped with an Oxford Cryosystems nitrogen gas-flow apparatus. All structures were solved by direct methods using SHELXL9744 and SIR-9245 incorporated into the WinGX program package. For each structure, its space group was checked by the ADSYM procedure of the PLATON45 software. All structures were refined using full-matrix least-squares on \( F^2 \). Some parts (carbon atoms) of the solvent molecules in the compounds 1c, 1d and 1d' are disordered over two positions: 1c, C1S/A/B, C2S/A/B, C3S/A/B, C4S/A/B (occupancy factors, A, B = 0.51:0.49).

Notes and references
1 Regional Centre of Advanced Technologies and Materials, Department of Inorganic Chemistry, Faculty of Science, Palacky University, Tř. 17, 50014 Olomouc, Czech Republic. E-mail: zdenek.travnick@upol.cz
2 Electronic Supplementary Information (ESI) available: results of magnetic data analysis for the HS compounds, detailed crystal structure information for compounds 1a-1e. See DOI: 10.1039/b000000x/
The magnetic (spin crossover) properties of the complexes were tuned by the different crystal solvent molecules.