Anion driven modulation of magnetic intermolecular interactions and spin crossover properties in an isomorphous series of mononuclear iron(III) complexes with a hexadentate Schiff base ligand†

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A series of spin crossover iron(III) complexes with the general composition \([\text{Fe}(4\text{OH-L6})]\text{X}\) (H\(_2\)-4OH-L\(_6\) = 1,8-bis(4-hydroxy-salicylaldiminate)-3,6-diazaocotane; \(X = \text{Cl}, \text{Ia}; \text{Br}, \text{Ib}; \text{I}, \text{Ic}\)) was prepared. A combination of the results following the single crystal X-ray analysis, infrared and EPR spectroscopy, and temperature dependent magnetic experiments revealed that the Fe(III) atoms occur in the low-spin state below room temperature and the crystal structures of the complexes involve rich networks of non-covalent intermolecular contacts resulting in two-dimensional supramolecular structures. Alterations in the halide anions influence the strength of the non-covalent contacts and affect the magnetic properties of the studied complexes. The antiferromagnetic exchange interaction between the non-covalently bound cations is the most obvious in the case of \(\text{Ia}\) and it weakens with the growing anionic volume of \(X\). The 1D and 2D spin Hamiltonian models were applied to quantitatively extract the information about the intermolecular magnetic exchange (fit on 1D infinite chain gives \(J(\text{Ia}) = -2.86 \text{ cm}^{-1}\), \(J(\text{Ib}) = -2.02 \text{ cm}^{-1}\), \(J(\text{Ic}) = -1.16 \text{ cm}^{-1}\)). Furthermore, gradual spin crossover behaviour for all of the compounds of the series was observed above room temperature in the solid state. Spin crossover accompanied by thermochromism was also demonstrated by EPR experiments in solution.

Introduction

The coordination compounds exhibiting spin crossover (SCO) phenomena have been the subject of research for almost 80 years from their discovery. SCO is considered to be an entropy driven, unimolecular reaction (resp. transition) between the low-spin (LS) and high-spin (HS) states of the 3d\(^6\)-3d\(^3\) coordination compounds exposed to an external perturbation such as temperature, pressure, a magnetic field change, and light irradiation. The iron (II) and iron(III) complexes are the most widely and thoroughly explored SCO compounds, especially the iron(II) compounds such as \([\text{Fe}^{\text{II}}(\text{bpy})_2(\text{NCS})_2]\) or \([\text{Fe}^{\text{II}}(\text{phen})_2(\text{NCS})_2]\) (bpy = 2,2’-bipyridine, phen = 1,10’-phenanthroline).

One of the most studied series of iron(III) SCO compounds is represented by the complexes with the hexadentate Schiff-base ligand H\(_2\)-L\(_6\) resulting from the reactions of variously substituted aromatic 2-hydroxy-aldehydes with triethylenetetramine. (H\(_2\)-L\(_6\) = N,N‘-Bis[2-(salicylideneamino)ethyl]ethane-1,2-diamine, see Fig. 1). Common abbreviations found in the literature are H\(_2\)saltrien, H\(_2\)saltrien, herein, the abbreviation X-L\(_6\) will be used, where X marks the substitution of the aromatic rings.

Concerning the SCO phenomenon, several interesting results

† Electronic supplementary information (ESI) available: ORTEP graphics of the title compounds, thermogravimetric data, and details of the magnetic and EPR data analysis. CCDC reference numbers 884404–884406. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce25862e

![Fig. 1 Drawings of H\(_2\)-L\(_6\) (left) and H\(_2\)-4OH-L\(_6\) (right).](Image 320x64 to 538x145)
were achieved within this series. The compound of [Fe(L6)][Ni(dmit)2] \( (\text{dmit}^2 = 2\text{-thioxo-1,3-dithiole-4,5-dithiolate}) \) exhibits abrupt SCO with wide thermal hysteresis (30 K wide)\(^{6}\) which is accompanied with a large reorganization within the crystal structure. Generally speaking, such compounds may serve as precursors for the preparation of hybrid materials combining the SCO and electrical conductivity properties.\(^{5}\) Another interesting combination of physical properties was achieved by insertion of the [Fe(L6)]\(^{+}\) cation between the ferromagnetic bimetallic oxalate layers.\(^{7}\) Both magnetic phenomena are observed, though the spin transition is of a gradual character. The [Fe(3MeO-L6)]\(^{+}\) derivative was intercalated within the MnPS\(_3\) layered magnet and the observed spin transition is gradual when the sample is untreated. After the removal of co-intercalated water molecules, magnetic behaviour is affected significantly, i.e. a broad hysteresis appears.\(^{8}\)

As was reported in 2008,\(^{9}\) the various magnetic behaviours of the [Fe(X-L6)]\(^{+}\) analogues can be explained on the basis of the molecular shape flexibility (a conformation of the coordinated ligand), especially the varying angle between the least square planes of the phenolate rings (\(\alpha\), usually lying in the range of 60–125°), which seems to be an important and useful parameter. Despite a few exceptions, it can be generalized that the LS compounds adopt the ligand conformation with the \(\alpha\) angle of 60–70° approximately, while the L\(^{6-}\) ligand is structurally more variable in the HS compounds and adopts the conformation with the \(\alpha\) angle bigger than 90°. Compounds with the value of the \(\alpha\) angle close to 90° are likely to undergo SCO. The intermolecular interactions present in the crystal structure cause cooperative behaviour, which is responsible for the abruptness of the transitions, or even for the occurrence of thermal hysteresis.\(^{2,10}\)

In order to achieve systems rich in hydrogen bonding,\(^{11}\) we decided to prepare the 4-hydroxy derivative of L\(^{6-}\) \( (4\text{OH-L6 dianion}) \) and to use it as a ligand (Fig. 1).

Herein, we report the synthesis, X-ray structures, magnetic and spectroscopic properties of a series of isostructural compounds with the general formula [Fe(4OH-L6)X \( (X = \text{Cl}^-, \text{Br}^-, \text{I}^-) \)]. Physical properties are discussed with respect to the alteration of the size and hydrogen bonding acceptor properties of the halide anion.

### Results and discussion

#### Crystal structures

The compounds involved into the studied series are isomorphous and crystallize in the \( P2/c \) space group. Crystal data and structure refinements can be found in Table 1. The crystallographically independent parts of the structures consist of half of the [Fe(4OH-L6)]\(^{+}\) cations and half of the halide anions of Cl\(^-\) \( (1\text{a}), \text{Br}^- \) \( (1\text{b}) \) or I\(^-\) \( (1\text{c}) \) (ORTEP plots of \( 1\text{a–c} \) are provided in ESI† Fig. S1). The iron(III) atoms as well as the halogen atoms lie in the special positions on the two-fold axis and are constrained with the occupation factors equal to 0.5. The bond lengths within the FeN\(_2\)O\(_2\) chromophore as well as the shape of the cation parameterized by \( z \) (Table 2, \( z \ (1\text{a–c}) = 62.3–62.7 \))\(^{9}\) correspond to the low spin character of the iron centre. The observed \( z \) values are similar to those which were found in the previously reported [Fe(L6)]\(^{+}\) compounds purely in the LS state.\(^{12}\)

The crystal structures of the polymorphs (Fig. 2) are formed by the layers of supramolecular one-dimensional zig-zag chains of the \( (\{\text{Fe}(4\text{OH-L6})\})_n \) cations stacked by the

### Table 1

<table>
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<tr>
<th>Crystal system</th>
<th>1a</th>
<th>1b</th>
<th>1c</th>
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<td>( c/\AA )</td>
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<td>13.7350(7)</td>
<td>13.871(4)</td>
</tr>
<tr>
<td>( \beta/\AA^3 )</td>
<td>13.590(12)</td>
<td>13.7350(7)</td>
<td>13.871(4)</td>
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<td>( T/K )</td>
<td>298</td>
<td>160</td>
<td>298</td>
</tr>
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### Table 2

<table>
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<th>T/K</th>
<th>( d(\text{Fe–N})_{\text{am}} )</th>
<th>( d(\text{Fe–N})_{\text{bm}} )</th>
<th>( d(\text{Fe–O}) )</th>
<th>( d(\text{N}_2\cdot\cdot\cdot\text{O}_2) )</th>
<th>( d(\text{O}_2\cdot\cdot\cdot\text{X}) )</th>
<th>( d(\pi\cdot\cdot\cdot\sigma) )</th>
<th>( \Sigma j^{ab} )</th>
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<td>1a</td>
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<td>1b</td>
<td>298</td>
<td>2.016 (2)</td>
<td>1.924 (2)</td>
<td>1.877 (2)</td>
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<td>3.188 (3)</td>
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<tr>
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<td>160</td>
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<td>1.881 (4)</td>
<td>2.973 (6)</td>
<td>3.344 (8)</td>
<td>4.046 (6)</td>
</tr>
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</table>

\( ^{a} \) Centroid–centroid distance. \( ^{b} \) Octahedral distortion calculated as \( \Sigma j = 12 \phi - z_\Delta \), where \( z_\Delta \) stands for 12 \( \phi \) angles of the coordination polyhedron.
N2–H(NH)…O2i [Symmetry code: (i) x − 1, −y − 1, z − 1/2] hydrogen bonds between the amino nitrogen atoms (N2, donor) and peripheral hydroxy oxygen atoms (O2) with the $d(N2…O2i)$ distances in the range of 2.96–3.00 Å (Table 2). The hydrogen-bonding angles, $\{N2–H(NH)–O2i\}$, are in the narrow range of 170–179°. The pair of the N2–H(NH)…O2i hydrogen bonds link two neighbouring $[\text{Fe}(4\text{OH-L6})]^+$ cations into the $R_2^2(16)$ ring structure, thus creating the infinite zig-zag chains. 13 The chain structure is supported by the offset $\pi$-stacked $\pi$–$\pi$ stacking interactions14 between the phenyl rings of the adjacent cations. The plane–plane distances are found to be in the range of 3.36–3.52 Å, and the centroid–centroid distances in the range of 3.74–4.07 Å (Table 2). These values are in agreement with the parameters reported for the offset $\pi$-stacked interactions.14

The zig-zag chains are interconnected by the O2–H(OH)…X1ii hydrogen bonds [symmetry code: (ii) x, y, z] between the hydroxy groups and halide anions, which form the $R_6^4(22)$ ring.13 With the growing volume of the halide anion, the significant changes in the lengths of intermolecular contacts (Fig. 3, middle) are observed. The centroid–centroid distances of the stacked aromatic rings, as well as the lengths of the hydrogen bonds between the peripheral hydroxy groups and the halide anions, grow significantly with the anion substitution. These changes can be explained on the basis of the growing anion volume and lowering of the electronegativity in a series from chloride to iodide. Due to these reasons the big iodide anion is a much weaker acceptor of a hydrogen bond in comparison with the smaller and more electronegative chloride anion. Therefore, the iodide anion provides weaker and longer hydrogen bonds (Cl: $d(O2…Cl1) = 3.029(3)$ Å at 100 K, I: $d(O2…I1) = 3.351(4)$ Å).15 The hydrogen-bonding angles $\{O2–H(OH)–X1\}$ are in the range of 166–171°, which are typical for moderate and weak O–H…X hydrogen bonds.16

The length of the centroid–centroid distance grows with the increasing ionic radius of the halide anions much more significantly than the plane–plane distance (the distance between the least-square planes of the stacked aromatic rings). Thus, it is obvious that the present offset is dependent on the steric influence of the halide anions (Fig. 3, left).

**Infrared spectroscopy**

The formation of hydrogen bonds affects the vibrational properties of the donor group significantly and usually leads to the observation of a redshift in the frequency of the donor stretching vibration upon the hydrogen bond formation. The frequency of the donor stretching vibration also lowers with the strengthening of the hydrogen bond and thus it can be expected in the series of the isostructural complexes 1a–c that the compounds with shorter hydrogen bond lengths tend to show lower vibrational frequencies of the appropriate groups.15

As was discussed above, the amino and hydroxy donor groups are involved in hydrogen bonding and therefore the attention has to be focused on the wavelength range of 2000–4000 cm$^{-1}$, where their stretching vibrations can be found. The largest wavelength shift is observed due to the anion substitution for the ν(O–H) vibration. The hydrogen bonded hydroxy group provides
superposed peaks broader more than 150 cm\(^{-1}\) at the base lines in the spectra of all the compounds (Fig. 3). The largest red shift of the peak maximum is observed in the spectrum of the chloride compound 1a; \(v_{\text{max}}(\text{O-H, 1a}) \approx 3020\) cm\(^{-1}\), which is in agreement with the shortest distance of the OH···X hydrogen bond found in 1a (Table 2) and with the reported correlations between hydrogen bond parameters and vibrational properties.\(^\text{17}\)

On the contrary, the wavelength of \(v_{\text{max}}(\text{O-H, 1c})\) is observed at a significantly higher frequency, at ca. 3180 cm\(^{-1}\). Such a big difference in the maxima of this vibration confirms a large variation in the hydrogen bond strength found between the compounds 1a and 1c. The stretching vibration of the amine group is approximately at the same position in all the samples, which is consistent with the structural data, where the length of this contact changes only very slightly upon the anion substitution. All the other vibrations found in the range of 400–2000 cm\(^{-1}\) are practically identical, which confirms the isostructurality of the compounds 1a–c.

**EPR spectroscopy**

The powder X-band EPR spectra of 1a–c were recorded at liquid nitrogen and also at room temperature. At \(T = 77\) K, the LS Fe(III) configuration with \(S = 1/2\) is expected by taking into account the Fe–N and Fe–O bond distances (Table 2). In this case, the LS Fe(III) \(^2T_{2g}\) term splitting due to spin–orbit coupling and symmetry of the chromophore can be described by the axial (\(\Delta\lambda\)) and tetragonal (\(V\lambda\)) splitting parameters, respectively, where \(\lambda\) is the spin–orbit splitting parameter within the crystal-field term.\(^\text{18}\) The linear combinations of \(d_{yz}\), \(d_{xz}\) and \(d_{xy}\) orbitals

\[
|\pm\rangle = \pm \alpha |d_{yz}\rangle - ib |d_{xz}\rangle - c |d_{xy}\rangle
\]

(1)

are used to describe the ground state with the pure spin Hamiltonian formalism for \(S = 1/2\). As EPR does not provide the information about the signs of \(g\)-factors, Taylors’ equations were used to determine the components of \(g\)-tensor and subsequently also the splitting parameters \(\Delta\lambda\) and \(V\lambda\).\(^\text{19}\) A representative spectrum of 1c is depicted in Fig. 4. The spectrum is almost axial, with a small rhombic distortion. The EasySpin package\(^\text{20}\) was used to simulate all spectra of 1a–c with three \(g\)-factors. The resulting parameters are summarized in Table 3. The own-written program was used to analyse these \(g\)-factors by Taylors’ equations and to extract the information about the splitting of the \(d_{yz}\), \(d_{xz}\) and \(d_{xy}\) orbitals (see ESI, Table S1 for more details).

Two physically reasonable solutions were found when \(g_x = -g_1\), \(g_y = g_2\) and \(g_z = -g_3\) or \(g_x = -g_2\), \(g_y = g_1\) and \(g_z = -g_3\). Resulting negative values of \(\Delta\lambda \approx -10.2\) for 1a–c signify that the ground state involves the electronic configuration corresponding to \((d_{yz}, d_{xz}, d_{xy})\). Similar values of the axial splitting parameter were found in other analogous Schiff-base iron(III) LS complexes.\(^\text{21}\) The relatively small values of \(|V/\lambda|\) are in agreement with the presence of the slightly elongated tetragonal bipyramid of the \([\text{FeN}_4\text{O}_2]\) chromophore. In contrast to the liquid nitrogen spectra, the room temperature EPR spectra of 1a–c are purely axial (Fig. 4), and only the information about \(g^+\) (\(g_1 = g_2\)) and \(g_3\) were determined, see Table 3. Nevertheless, the value of the orbital splitting parameter \(\Delta\lambda \approx -10.1\) is practically the same for all the compounds and for both temperatures. Moreover, the methanolic solutions of 1a–c were studied by X-band EPR at the same temperatures as powder samples. By dissolving 1a–c, dark brown solutions were formed at room temperature and on cooling them with liquid nitrogen, a conspicuous change of colour to bright blue occurred, see Fig. 4.

This process was found to be fully reversible and suggests that the spin crossover phenomenon accompanied by thermochromism takes place within the temperature interval of 77–300 K, as reported previously for a group of the \([\text{Fe}(\text{X}-\text{L6})]^+\) compounds.\(^\text{22}\)

Indeed, the frozen solution spectra of 1a–c were typical for \(S = 1/2\) and they resembled the powder EPR spectra of the solid samples, see Fig. 4. Utilizing the same procedure as explained above, we were able to extract the information about three \(g\)-factors and consequently the information about the energy
level splitting of the $\text{^2T}_2g$ term, see Table 3 (see also Table S2, ESI†). It can be concluded that the geometry of the octahedral FeN$_4$O$_2$ chromophore is more symmetrical as deduced from the experimental data (gray line) and calculated data (black lines) with the parameters given in Table 3 (up). The thermochromism for the methanolic solution of compound 1c (below right, room temperature, below left, cooled down closely to the freezing point of the solution).

Table 3 The X-band powder and solution EPR parameters for 1a–c

| $T$/K | $g_1$ | $g_2$ | $g_3$ | $\text{lwpp}^a$ | $|V/L|$ | $\Delta L$ | $|V/A|$ |
|------|------|------|------|---------------|--------|----------|--------|
| 77   | 2.208| 2.172| 1.965| 2.70          | 1.73   | −10.3    | 0.169  |
| 77   | 2.208| 2.173| 1.964| 2.41          | 1.66   | −10.2    | 0.163  |
| 77   | 2.207| 2.177| 1.967| 1.96          | 1.44   | −10.2    | 0.141  |
| 300  | 2.191| 1.965| 5.75  | 10.1          |        |          |        |
| 300  | 2.192| 1.967| 6.48  | 10.2          |        |          |        |
| 300  | 2.187| 1.963| 5.87  | 10.2          |        |          |        |

$^a$ Line widths for isotropic magnetic-field domain broadening (PP, peak-to-peak, in mT); the Lorentzian broadening was used for powder samples, while the Gaussian broadening was used for methanolic solutions.

The advantage of this approach is that in addition to the susceptibility data, the magnetization data set can also be
temperature dependence of the magnetization measured at temperature dependence of the effective magnetic moment. Inset: Ising-like model, dashed lines—the Brillouin functions for non-interact-
g
dvia

data

tensor operators. 24 Moreover, the C 2 symmetry of the spin

a

S

, using the irreducible

j

energy levels is

N

= (2S + 1)19 = 524 288. To be able to treat this

problem, the coupled spin basis set labelled as |zSM S>, where z represents the intermediate quantum numbers denoting the coupling path, can be efficiently utilized. In the case of the isotropic exchange and only when all local g-factors are equal, the whole interaction matrix can be factorized in accordance with the final spin S. Moreover, it is also sufficient to calculate the zero-field levels only, labelled as |zS>, using the irreducible tensor operators. 24 Moreover, the C 2 symmetry of the spin

Hamiltonian (the closed ring of spins) can be employed and the symmetry-adapted spin function can be generated using the projection operator method. 26 The classification of the new spin functions is listed in ESI† (Table S3). Now, the largest dimension of the sub-matrix is 12 618 for \( S = 3/2 \) and \( \Gamma_1 = \Lambda \). Next, the magnetic levels are calculated as 

\[ \epsilon_j (\Gamma_1, xS) = \epsilon_{0j} (\Gamma_1, xS) + \mu_B g M_\beta B. \]

The resulting energy levels were then used to calculate the molar magnetization as

\[ M_{\text{mol}} = N_A \mu_B B \frac{\sum_j M_j \exp \left[ -\frac{\epsilon_j (\Gamma_1, xS) B}{kT} \right]}{\sum_j \exp \left[ -\frac{\epsilon_j (\Gamma_1, xS) B}{kT} \right]} \] (3)

The concurrent fitting of both temperature and field dependent datasets resulted in the isotropic exchange parameter

\[ J = -2.86 \text{ cm}^{-1} \]

g and \( g = 2.19 \) for \( 1a \)—see ESI† (Fig. S3). It is obvious that a quite large intermolecular magnetic interaction of the antiferromagnetic nature is present. The g-value is very similar to the arithmetic average obtained by powder EPR, which is equal to \( g = (2g^+ + g^z) = 2.12 \) for \( 1a \). The application of the same fitting procedure for other two compounds \( 1a–c \) was not so successful: (i) the isothermal magnetization data cannot be fitted so well (ii) the g-factors were too high in comparison with the EPR data. These facts inspired us to include the HS (\( S = 5/2 \)) impurity fraction (a residual HS fraction), which might originate from the defects in the solid, into the fitting procedure. In order to avoid overparametrization, the LS g-factors were fixed to \( g_{LS} = 2.12 \) for \( 1b \) and \( 1c \) as deduced from the EPR data, and the HS g-factors were fixed to \( g_{HS} = 2.0 \), which is the expected value for the 3d electronic configuration within the pseudo-octahedral geometry. Now, the fitting procedure was successful and resulted in the parameters listed in Table 4 (see also ESI† Fig. S3). The strength of the antiferromagnetic exchange increases from the iodido-complex \( 1c \) to chlorido-complex \( 1a \), which is in agreement with the structural observations.

Secondly, a two-dimensional network model was tested to evaluate the intermolecular interactions. It was simulated by a finite-size closed \( 4 \times 4 \) grid of spins (see ESI† Scheme S1) according to the following spin Hamiltonian:

Fig. 5 Magnetic data for \( 1a \) (top), \( 1b \) (middle) and \( 1c \) (bottom). Left: temperature dependence of the effective magnetic moment. Inset: temperature dependence of the magnetization measured at \( B = 0.1 \) T. Right: field dependence of magnetization at \( T = 2.0 \) and 4.6 K. Empty circles—experimental data; full lines—the best fits to the experimental data via the 2D network model (eqn. (5)), dotted lines—the best fits using Ising-like model, dashed lines—the Brillouin functions for non-interacting system. The calculation parameters are listed in Table 4.

| Table 4 | The summary of the magnetic parameters for \( 1a–c \) |
|---------|---------|---------|
| Model   | \( 1a \) | \( 1b \) | \( 1c \) |
| 1D chain\( ^b \) | \( J = -2.86 \) | \( J = -2.02 \) | \( J = -1.16 \) |
| \( g = 2.19 \) | \( g = 2.12^e \) | \( g = 2.12^e \) |
| 2D network\( ^c \) | \( J = -1.79 \) | \( J = -1.21 \) | \( J = -0.68 \) |
| \( g = 2.21 \) | \( g = 2.12^e \) | \( g = 2.12^e \) |
| Iising-like\( ^d \) | \( \Delta = 2720 \) | \( \Delta = 2616 \) | \( \Delta = 2682 \) |
| \( r_{\text{eff}} = 17.8 \) | \( r_{\text{eff}} = 32.7 \) | \( r_{\text{eff}} = 210, \gamma = 209 \) |

\( ^a \) Values of the exchange parameter \( J \) are in cm\(^{-1}\), values of \( \Delta \) and \( r_{\text{eff}} \) in K. \( r_{\text{eff}} \) is dimensionless; the best temperature-independent parameter \( J_{\text{TIP}} \) values were found as: 5.2 (\( 1a \)), 2.8 (\( 1b \)) and 1.7 (\( 1c \)) m\(^2\)mol\(^{-1}\) (SI units). 2D 1D chain according to eqn. (2). 2D 2D network according to eqn. (4). Spin crossover model—see ESI† for more details. \( ^d \) g-value fixed was based on EPR analysis. 26
\[
\begin{align*}
\mathcal{H} &= -J \left( S_1 \left( S_2 + S_4 + S_5 + S_{15} \right) + S_2 \left( S_3 + S_6 + S_{14} \right) \\
&+ S_3 \left( S_4 + S_7 + S_{15} \right) + S_4 \left( S_5 + S_{16} \right) \\
&+ S_5 \left( S_6 + S_3 + S_4 \right) + S_6 \left( S_7 + S_{10} \right) + S_7 \left( S_8 + S_{11} \right) \\
&+ S_8 \left( S_{12} + S_9 \right) \left( S_{10} + S_{12} + S_{13} \right) + S_{10} \left( S_{11} + S_{14} \right) \\
&+ S_{11} \left( S_{12} + S_{15} \right) \left( S_{12} + S_{16} + S_{13} \right) \left( S_{14} + S_{16} \right) \\
&+ S_{14} \left( S_{15} + S_{16} \right) \right) \end{align*}
\]

\[+ \mu_B S^2 \sum_{i=1}^{16} S_{z,i} \]

The theoretical magnetization was calculated analogously as in the previous case, but now, the symmetry-adapted spin function formation was not necessary. Again, both the experimental datasets were analyzed simultaneously and the fitted parameters are summarized in Table 4. Fixing of \( g_{LS} \) and \( g_{HS} \) for 1b and 1c was done in the same way as in the previous calculations. By scaling up to the 2D model, the decrease of the isotropic exchange constants was observed. Again, the good agreement between the experimental and calculated data was achieved (Fig. 5). Therefore, we might conclude that both 1D and 2D model analyses fitted experimental data very well, which unfortunately, does not allow us to decide whether both types of the intermolecular interactions forming the quasi 2D network are magnetically important. The fitted \( J \) values could serve as minimal and maximal estimates of the primary magnetic interactions in 1a–c.

Furthermore, the experimental magnetic data above 250 K, showing the spin crossover phenomenon, were analyzed using the Ising-like model,\(^{27}\) where free parameters are: \( \Delta \)—the energy difference between the HS and LS states, \( \gamma \)—the cooperativeness and \( r_{\text{eff}} \)—the effective degeneracy ratio of the HS and LS states (see details in ESI\(^+\)). In the case of compounds 1a and 1b, only two parameters \( \Delta \) and \( r_{\text{eff}} \) were sufficient to properly describe the increase of the effective magnetic moment up to 450 K. For the latter compound, it was necessary to incorporate also the \( \gamma \) parameter—Table 4. Because none of the compounds reached the 100% HS limit up to 450 K, the found parameters may be considered as roughly estimated only. Nevertheless, the decrease in the calculated critical temperatures \( T_c = 945, 750 \) and 502 K \( (\chi_{HS} = 0.5) \) for 1a–c, is in agreement with the observed trend of the effective magnetic moments, see Fig. 5.

**DFT calculations**

Density functional theory (DFT) calculations were performed in order to optimize the molecular geometry of the \([\text{Fe}(4\text{OH-L6})]^+\) cation in vacuum with the aim to evaluate the molecular geometry of the complex cation non-affected by intramolecular non-covalent contacts in both the HS and LS state. As already mentioned above, the spin-state of \([\text{Fe}(X-L6)]^+\) seems to be dependent on the geometry of the cation.\(^9,28\) The optimization procedures provided the results which are in agreement with the following hypothesis: the LS structure of the \([\text{Fe}(4\text{OH-L6})]^+\) cation has a “tighter” ligand conformation with \( z \) parameter at value (65.3°) typical for the LS compounds, while the HS cation was optimized to have a more distorted geometry having \( z = 80.8^\circ \) (Table 5). The metal–ligand bond lengths are similar to those observed in the solid state.

With the aim to compare the DFT obtained chromophore bond lengths, the Crystallographic Structural Database (CSD, version 1.14, 2011) was used to extract information about the \([\text{Fe}(X-L6)]^+\) complexes. Only the X-ray structures of pure LS and HS compounds were included into the analysis in order to avoid a contamination of the data set with bond lengths affected by the presence of a residual different spin-state fraction possibly present in SCO compounds. The analysis resulted in average values of the Fe–Nim, Fe–Nim, Fe–O bond lengths either in the LS or HS state, which are shown in Table 5 and the details of the calculation, can be found in ESI.\(^+\)

Both HS and LS DFT-optimized geometry possesses slightly longer Fe–Nim and Fe–Nim bond lengths than found in the solid state—the discrepancy is about \( 0.05 \) Å (LS) and \( 0.06 \) Å (HS) for the Fe–Nim bonds; \( 0.03 \) Å (LS) and \( 0.01 \) Å (HS) for the Fe–Nim bonds. The Fe–O bond lengths show the smallest difference—below 0.01 Å in both spin states. The angular distortion of the octahedron \( \Sigma \) is slightly higher than the solid state average in the optimized geometry of the LS form, contrary to the HS form, where the \( \Sigma \) parameter from the optimized geometry is significantly lower with respect to the solid state average (Table 5). Both values of the \( \Sigma \) parameter originating from the calculation fall into the ranges typical for the LS or HS geometries of the \([\text{Fe}(X-L6)]^+\) compounds, even if they are at the upper (LS) or lower (HS) border (see ESI,\(^+\) Table S4 and ref. 9 and 28).

**Conclusions**

A series of three isomorphous \([\text{Fe}(4\text{OH-L6})][X (X = CL^-, 1a, Br^-, 1b, I^-, 1c)]\) complexes is reported. The crystal structure of these compounds is rich on non-covalent contacts (hydrogen bonding, \( \pi-\pi \) interaction) between the discrete mononuclear cations and halide anions. The anion substitution and subsequently, the changes in the anionic volume, electronegativity and polarizability of the anions resulted in prolonging of these contacts with the increasing anionic volume (Table 2, Fig. 3).

Magnetic properties were studied in order to clarify the impact of the intermolecular interactions on the magnetic behaviour of SCO compounds. In the temperature range of 2–300 K no

<table>
<thead>
<tr>
<th>Compound</th>
<th>Fe–Nim (Å)</th>
<th>Fe–Nim (Å)</th>
<th>Fe–O (Å)</th>
<th>( \chi )</th>
<th>( \Sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS</td>
<td>2.057</td>
<td>1.964</td>
<td>1.875</td>
<td>65.3</td>
<td>48.1</td>
</tr>
<tr>
<td>HS</td>
<td>2.268</td>
<td>2.136</td>
<td>1.910</td>
<td>80.8</td>
<td>50.2</td>
</tr>
</tbody>
</table>

\( \Sigma \) Octahedral distortion calculated as \( \frac{1}{2} \sum_{i=1}^{12} |d_i - a| \), where \( a \) stands for 12 \( \theta \) angles of the coordination polyhedron. \( \chi \) Average bond length values for each bond pair typical for the LS \([\text{Fe}(X-L6)]^+\) compounds. Average bond length values for each bond pair typical for the HS \([\text{Fe}(X-L6)]^+\) compounds.
obvious signs of the SCO phenomena were detected. At low temperatures significant deviations from Curie-Weiss law and Brillouin function in magnetic behaviour was observed. These deviations from the ideal paramagnetic behaviour originated from the presence of the antiferromagnetic exchange interaction and they cannot be explained on the standard basis, using a molecular field correction parameter. With no present covalent exchange pathway, it has to be concluded that the magnetic exchange interaction is mediated by intermolecular non-covalent contacts. Nevertheless, with all available data and used analytical and theoretical methods we are not able to judge which contact, with respect to the overall magnetic exchange interaction, dominates. However, there are some remarks, which must be taken into account:

a) the results of the 1D closed ring model and 2D 4 × 4 grid model are more or less the same and the magnetic dimensionality of the system cannot be distinguished

b) the antiferromagnetic interaction found in compounds 1a–c is not constant, the |J| value decreases in the sequence of 1a (Cl−) > 1b (Br−) > 1c (I−) (Table 4)

c) remarkably, the centroid–centroid distances of the ring–ring stacking interactions and donor–acceptor distances of the OH···X hydrogen bonds show a similar variance and both contacts prolong (Fig. 3, Table 2) in the same sequence as J.

Therefore, it might be expected that both contacts are predominantly responsible for the mediation of the exchange interaction. This assumption can be supported by several literature references. Mediation of the magnetic exchange interaction via the ring–ring stacking interaction has been evaluated for organic radicals mostly, but also this kind of the exchange interaction has been found for polynuclear complexes. The hydrogen bonds are well known mediators of intermolecular magnetic interactions, especially in molecule-based magnets with long-range ordering and their role can be accentuated in molecular magnetic sponges.

d) SCO was for the very first time observed in the group of the [Fe(X-L6)]⁺ derivatives with the “tight” geometry of the hexadentate ligand (σ1a-c = 62–63°) and the transition occurs above room temperature in all three cases. This suggests that such a ligand conformation favours the LS state and along with the rigid system of hydrogen bonds leads to the increase of the SCO enthalpy causing a consequent shift of Tc to higher temperatures. The preference of the 4OH-L6 ligand tight geometry in the LS [Fe(4OH-L6)]⁺ compounds was also supported by the DFT optimization of the molecular geometry in vacuum (Table 5).

e) the transition SCO temperature decrease in the series of 1a–c with the increasing volume of the anion (Cl−–Br−–I−) which was also observed for other SCO systems. Despite the thorough quantitative analysis of the intermolecular interactions in 1a–c, the detailed investigation of their impact on spin crossover properties, especially on the cooperativeness, is hindered by incompleteness of SCO.

Experimental

All reagents and solvents were purchased from commercial sources (Sigma Aldrich) and used as received. Elemental analysis was carried out on a Flash EA 1112, ThermoFinnigan. FTIR spectra were measured with an ATR setup (Magna FTIR 750, Nicolet) in the 4000–400 cm⁻¹ region. EPR spectra were recorded on a MiniScope MS200 spectrometer (Magnettech) at liquid nitrogen (~77 K) and at room temperature; DPPH (2,2-diphenyl-1-picrylhydrazyl) was used as a standard.

Synthesis of [Fe(4OH-L6)]Cl (1a) and [Fe(4OH-L6)]Br (1b)

Both complexes were prepared in a similar way: 2.8 g of 4-hydroxy-salicylaldehyde was mixed with 1.5 g of triethylentetramine in 50 ml of methanol. Immediate formation of a yellow precipitate was observed. After 5 min of stirring, 2.7 g of FeCl₃.6H₂O (1a), or 3 g of FeBr₃ in 30 ml of methanol, was added to the ligand suspension. The reaction mixture was refluxed for 2 h (the yellow precipitate in the reaction mixture could be observed for the first 60 min). Then the solution was filtered through a paper filter and left to cool down and to evaporate slowly. After approximately one day the dark blue microcrystalline product was isolated (yields: 85% for 1a, 81% for 1b). Single-crystals suitable for X-ray diffraction experiments were obtained by the slow diffusion of diethyl ether into the methanolic solution of complexes. 1a: Found: C, 50.2; H, 5.2; N, 11.7. C₂₀Cl₁Fe₁H₂₆N₄O₄ (M = 475.73) requires C, 50.5; H, 5.1; N, 11.7%. IR mid: v(N–H) = 3207 cm⁻¹ (m), v(O–H) = 3023 cm⁻¹ (broad, m), v(C–H)aliphatic = 2979, 2932, 2907, 2861 cm⁻¹ (w), v(C=C) and v(C=C) = 1595, 1548 cm⁻¹ (vs). (1b): Found: C, 46.0; H, 4.8; N, 10.6. Br₁C₂₀Fe₁H₂₆N₄O₄ (M = 520.18) requires C, 46.2; H, 4.7; N, 10.8%. IR mid: v(N–H) = 3208 cm⁻¹ (w), v(O–H) = 3099 cm⁻¹ (broad, m) v(C–H)aliphatic = 2977, 2929, 2906, 2851 cm⁻¹ (m), v(C=N) and v(C=C) = 1593, 1547 cm⁻¹

Synthesis of [Fe(4OH-L6)]I (1c)

This compound was prepared by the anion substitution of 1a: 0.4 g of 1a was dissolved in 50 ml of methanol and 0.16 g of KI was added to the reaction mixture, which was refluxed for 20 min. Then the solution was filtered through a paper filter and left to cool down and to evaporate slowly. After approximately one day the brown crystalline product was isolated (yield: 44%). The product is dark blue when ground. (Found: C, 42.2; H, 4.3; N, 9.8. C₂₀Cl₁Fe₁I₂₆N₄O₄ (M = 567.18) requires C, 42.4; H, 4.4; N, 9.9%). IR mid: v(O–H) = 3177 cm⁻¹ (broad, m), v(N–H) = 3222 cm⁻¹ (m), v(C–H)aliphatic = 3017 cm⁻¹ (w), v(C–H)aromatic = 2976, 2925, 2905, 2859 cm⁻¹ (w), v(C=N) and v(C=C) = 1596, 1548 cm⁻¹ (vs)

Magnetic data

Magnetic susceptibility and magnetization measurements were done using a SQUID magnetometer (MPMS, Quantum Design) from T = 2 K at B = 0.1 T (temperature dependance). The magnetization data were taken at T = 2.0 and 4.6 K, respectively (field dependence from 0 to 7 T). The effective magnetic moment was calculated as usual: µₑff/µB = 798(γ/T)¹/² when SI units are employed.

In the case of high temperature magnetic measurements (300–450 K), the experiment was carried out on an MPMS SQUID magnetometer (Quantum Design, model MPMS-XL-5) with installed special heating setup. A high temperature sample holder consisted of a quartz glass tube and Teflon filler. The very small
diamagnetic contribution of the gelatine capsule and high temperature sample holder had a negligible contribution to the overall magnetization, which was dominated by the sample. The diamagnetic corrections of the molar magnetic susceptibilities were applied using Pascal’s constants. Analysis of magnetic data was done with the package POLYMAGNET.

X-ray crystallography

Single crystal X-ray diffraction data were collected on an Oxford diffractometer Xcalibur2 with the Sapphire CCD detector and fine-focused sealed tube (Mo Kα radiation, λ = 0.71073 Å) source and equipped with an Oxford Cryosystem nitrogen gas-flow apparatus. All structures were solved by direct methods using SHELEX97 incorporated into the WinGX program package. For each structure its space group was checked by the ADSYM procedure of the PLATON software. All structures were refined using full-matrix least-squares on F₀ with the package POLYMAGNET.

Theoretical calculation

Density functional calculations were performed using the Spartan software package (Spartan10, Ver. 1.1.0) The geometries of the [Fe(4OH-L6)]⁺ complex cation were optimized both at the Hartree-Fock level of theory. Theoretical foundation of molecular magnetism

Acknowledgements

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References

All of the LS [Fe(X-L6)]+ derivatives not exhibiting SCO which were reported so far had small counter anions (halido, nitrato). These create hydrogen bonds of significant strength with the amine groups of the coordinated ligand, or with an assistance of the water molecules.


Spartan10, Ver. 1.1.0, Wavefunction, Inc., 2010.