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# Structural Diversity on a New Series of Halogenated Quinolyl Salicylaldimides-Based Felll Complexes Showing Solid-State Halogen-Bonding/Halogen---Halogen Interactions

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# Structural Diversity on a New Series of Halogenated Quinolyl Salicylaldimides-Based Fe<sup>III</sup> Complexes Showing Solid-State Halogen-Bonding/Halogen…Halogen Interactions

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# ABSTRACT

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A new series of tridentate N-8-quinolyl-salicylaldimine ligands, Hqsal-5,7- $X_2$  [X = Cl(1), Br(2), I(3)], halo-substituted at the 5,7 position of the aminoquinoline moiety and their corresponding complexes with Fe<sup>III</sup> were synthesized and formulated as [Fe(qsal-5,7-X<sub>2</sub>)(NCS)(MeO)]<sub>2</sub>·solv. (X = Cl (1a), Br (2a), I (3a, solv =  $\frac{1}{2}$  MeOH), [Fe<sub>4</sub>(qsal-5,7-X<sub>2</sub>)<sub>4</sub>(NCS)<sub>2</sub>(MeO)<sub>2</sub>]·solv. (X = Br (2b), I (**3b**; solv =  $4CH_2Cl_2$ ) by single-crystal X-ray diffraction analysis. **1a** and **2a** are isostructural dimers where each Fe<sup>III</sup> metal ion, showing a distorted octahedral environment, is bound by a N,N,O tridentate  $(qsal-5,7-X_2)^-$  (X = Cl and Br) ligand, a N-coordinated SCN<sup>-</sup> anion, and a bridging methanolate anion. 2b and 3b are centrosymmetric tetramers where each Fe<sup>III</sup> is bound by three nitrogen atoms and three oxygen atoms deriving from a tridentate  $(qsal-5,7-X_2)^-$  (X = Br and I), a SCN<sup>-</sup>, a bridging methanolate anions and a bridging  $\mu^2$ -oxo moiety. In **3b**, the iodine atoms dominate the packing interactions through the establishment of a halogen-bonding network. The magnetic behavior of 1a-3a dimers and 2b-3b tetramers indicate the presence of strong antiferromagnetic interactions between Fe<sup>III</sup> centers (S = 5/2), mediated by the alkoxy bridges. Experimental data can be modeled with an isotropic Hamiltonian,  $H = -2J(S_1 \cdot S_2)$ for dimers  $(J = -15 \text{ cm}^{-1})$  and  $H = -2J(S_2 \cdot S_3) - 2J'(S_1 \cdot S_2 + S_3 \cdot S_4)$ , for tetramers (J = -24) $cm^{-1}$ ,  $J' = -11 cm^{-1}$ ). The magnetic behavior of **1a-3a** dimers, indicate the presence of strong antiferromagnetic interactions between Fe<sup>III</sup> centers (S = 5/2), mediated by the alkoxy bridges. **2b** 

and **3b** show the same magnetic behavior since they contains analogous bridges between paramagnetic centers, but for a linear tetramer. DFT Calculations, based on hybrid functional mPW1PW paralleled by the Def2SVP all-electron split-valence basis sets, support the experimental results, showing that monomers could possibly show a SCO behavior, even though the formation of complexes with an even number of metal ions results in the strong anti ferromagnetic interactions. Accordingly, Broken Symmetry DFT calculations carried out on **1a** clearly show that the antiferromagnetic coupling of the two HS Fe<sup>III</sup> centers results in the lowest energy electron configuration of the complex.

#### INTRODUCTION

One of the most powerful strategies to design halogen-bonded systems is based on the use of tectons, in particular metallotectons, namely metal complexes bearing peripheral halogen atoms, able to be involved in well identified non-covalent intermolecular interactions, such as halogen bonds. Over the last decade halogen bonding (XB), a strong, specific and highly directional non-covalent interaction, has gained great interest among the known non-covalent bonds, for the construction of one dimensional (1D), 2D, 3D self-assembled supramolecular architectures<sup>1-4</sup>. This interaction plays a role as crucial as hydrogen bonding (HB)<sup>5</sup> in driving highly specific crystal packing patterns and several applications of XB are reported<sup>[11]</sup> in various research areas such as materials science and synthetic chemistry. Halogen…halogen (XX) interactions are also a peculiar class of halogens bonds interactions, that although weak, play a key role in the formation of supramolecular networks ranging from 1-3D materials to self-assembled monolayers, and can be considered as a reliable supramolecular tool in molecular self-assembly.<sup>6-9</sup> In this context the combination of halo-substituted anilates, the 3,6-dihalo

derivatives of 2,5-dihydroxybenzoquinone (H<sub>4</sub>C<sub>6</sub>O<sub>4</sub>),  $X_2An^{2-}$  (X = Cl, Br, I), with paramagnetic metals has been shown to be particularly successful.<sup>10–15</sup> In the search of novel halo-substituted tectons where the halogen atoms can play a role on the crystalline packing pattern and/or physical properties, we focused our attention on the tridentate N-8-quinolyl-5-Xsalicylaldiminate (X = H, Hqsal) ligand and its halo-substituted derivatives on the 5salicylaldiminate moiety (gsal-X) (X = F, Cl, Br, I), because of the interesting spin crossover (SCO) properties shown by their Fe<sup>III</sup>/Fe<sup>II</sup> complexes. <sup>16–21</sup> Temperature-induced spin transition in fact was observed in [Fe(qsal)<sub>2</sub>]NCS and [Fe(qsal)<sub>2</sub>]NCSe<sup>22-25</sup> with wide thermal hysteresis loop of 140 K and 180 K respectively, while switching spin state upon exposure to light (LIESST effect) was also found.<sup>24</sup> Halogen effects on the SCO behavior was reported in  $[Fe^{III}(qsal-X)_2]NCS \cdot solvent$  (X = F, Cl, Br; solvent=  $1/4CH_2Cl_2 \cdot 1/2MeOH$ ) complexes, as the spin transition temperature was found to increase on going from F to Br.<sup>17,26–31</sup> Very recently, an abrupt two-step SCO above room temperature<sup>32,33</sup> was observed in the [Fe<sup>II</sup>(qsal-Cl)<sub>2</sub>] complex due to the halogen substitution on the salicylaldiminate moiety of the ligand that has the potential to improve the SCO properties within Fe<sup>II</sup>-SCO systems. Therefore, the introduction of halogen atoms at certain key positions of the metal complexes influences significantly their physical properties, although keeping their structure unaltered. In this work we investigate the influence of the halogen substitution on the quinolyl moiety of the Hqsal ligand, which has never been studied so far, with the aim to highlight how a simple change in the positions of the halogen atoms in the same ligand can dramatically change the crystal structure and physical properties of the related metal complexes. We report herein the synthesis and structural characterization of the novel class of halo-substituted Hqsal-5,7- $X_2$  ligands (X = Cl, 1, Br, 2, I, 3), shown in Chart 1, and their Fe<sup>III</sup> complexes: [Fe(qsal-Cl<sub>2</sub>)(NCS)(MeO)]<sub>2</sub> (1a), [Fe(qsal-5,7-Br<sub>2</sub>)(NCS)(MeO)]<sub>2</sub>

(2a),  $[Fe_4(qsal-5,7-Br)_4(NCS)_2(MeO)_2]$  (2b),  $[Fe(qsal-5,7-I_2)(NCS)(MeO)]_2$ ,  $(3a, \frac{1}{2}MeOH)$  and  $[Fe_4(qsal-5,7-I_2)_4(NCS)_2(MeO)_2]$  (3b,  $\frac{1}{4}CH_2CI_2$ ). The magnetic properties of the 1a–3a, 2b–3b complexes are also reported.



 $\begin{array}{c} N-(8-quinolyl) 5, 7-X_2-salicylaldimine \\ Hqsal-(5,7)-X_2 \end{array}$ 

Chart 1: Structure of Hqsal-5,7- $X_2$  ligand. X = Cl(1), Br(2), I(3).

# **RESULTS AND DISCUSSIONS**

# Synthesis of Hqsal-5,7-X<sub>2</sub> ligands and their Fe<sup>III</sup> complexes

An overview of the synthetic procedure of the Hqsal-5,7-X<sub>2</sub> ligands is shown in Scheme 1.

Scheme 1. Overview of the synthetic procedure of Hqsal-5,7-X<sub>2</sub> ligands.

The halo-substituted Hqsal-5,7- $X_2$  ligands were prepared in good yields (48% to 89%) by treating 5,7-dihalo-8-aminoquinoline in EtOH with salicylaldehyde and glacial acetic acid. The synthesis of the Hqsal-5,7- $X_2$  ligands was performed according to the synthetic pathway shown in Scheme S1 in Supporting Information (SI). The first stage of the process is a simple formation of an imine, starting from amine and aldehyde, at room temperature and with good yields despite of the substituents used. The reaction is carried out in ethanol and in the presence of acetic acid. Acetic acid was used both for increasing the electrophilicity of the carbonyl aldehyde group, given the low nucleophilicity of the aromatic amine, and for favoring the water elimination in the second stage. The reagents and the products are poorly soluble in ethyl alcohol, therefore reaction times of almost 24 hours are required for the complete disappearance of the amines as reported in Scheme S2 in SI. More details on the synthesis <sup>34-37</sup> are given in SI.

The Fe<sup>III</sup> complexes, **1a–3a**, **2b–3b**, were synthesized according to the general synthetic strategy recently reported for analogous complexes<sup>20</sup> (Scheme 2).



Scheme 2. General synthetic scheme for 1a-3a, 2b-3b complexes; X = Cl(1), Br(2), I(3);

**a**=dimer; **b**=tetramer.

These complexes were obtained by carefully layering the ligands **1–3** with Et<sub>3</sub>N in CH<sub>2</sub>Cl<sub>2</sub> and on top FeCl<sub>3</sub>·6H<sub>2</sub>O and NaSCN in 1:1 ratio, dissolved in MeOH. ESI-MS spectra recorded on freshly prepared CHCl<sub>3</sub>/MeOH solutions, in the 100-2000 m/z mass range, showed only the molecular ions, which can be assigned to [Fe(qsal-5,7-X<sub>2</sub>)<sub>2</sub>]<sup>+</sup> monomeric species [X = Cl (**1c**<sup>+</sup>), Br (**2c**<sup>+</sup>), and I (**3c**<sup>+</sup>)]. Mass spectra recorded on solutions with concentration values at the upper solubility limit (10 mg/mL) and lower values of needle voltage of 4500 V did not show dimeric forms (*vide infra*). Therefore, to improve peak resolution, spectra were recorded in 100-1000 m/z mass range. The isotopic patterns of the ligands **1–3** and of the monomeric species **1c**<sup>+</sup>, **2c**<sup>+</sup> and **3c**<sup>+</sup> are reported in SI (Figure S1-S2).

### **Structural Studies**

Among the ligands, only single crystals of **3** could be obtained by recrystallization of the crude product in dichloromethane, confirming the expected composition (Figure S3).

Single crystals of the iron complexes were obtained by slow diffusion of ligand in dichloromethane and Fe<sup>III</sup> salt with NaSCN in methanol. The X-ray diffraction analysis unexpectedly established the complexes to be dimers or tetramers according to Scheme 3 and Table 1.

Table 1: Summary of the obtained Fe<sup>III</sup> complexes.

	$FeCl_3 \cdot 6H_2O + NaSCN$		
	X = Cl	Br	Ι
[Fe(qsal-5,7-X <sub>2</sub> )(NCS)(MeO)] <sub>2</sub> dimer	1a	2a	3a <sup>a</sup>
$[Fe_4(qsal-5,7-X_2)_4(NCS)_2(MeO)_2] tetramer$	_	2b	3b <sup>b</sup>

<sup>a</sup> Structurally characterized in **3a**<sup>1</sup>/<sub>2</sub>MeOH. <sup>b</sup> Structurally characterized in **3b**<sup>4</sup>CH<sub>2</sub>Cl<sub>2</sub>.

The presence of halogen atoms on the ligands periphery expands the types of interactions that can be exchanged by the iron complexes.<sup>38,39</sup> Here, we will analyze the influence of the halogen substitution (Cl, Br, I) on the second coordination sphere and crystal packing.

The complexes **1a** and **2a** crystallize in the triclinic space group *P*-1; **2b** crystallizes in monoclinic space group  $P2_1/c$ . The molecular structure of **1a** is reported in Figure S4. The molecular structure of **2a**, **3a**, **2b**, **3b** are reported in Figures 1-3. A summary of X-ray crystallographic data for **3**, **1a-3a**, **2b-3b** are reported in Table S1, and selected bond distances (Å) and angles (°) for **1a-3a**, **2b-3b** are reported in Table S2-S7.



Figure 1. Molecular structure of **2a** (symmetry code ' = -x; 1-y; 1-z). and **3a** (symmetry code ' = 2-x; 1-y; -z, '' = 1-x; -y; 1-z). Thermal ellipsoids are drawn at the 30% probability level. Color code: C = grey, Cl = green, Br = brown, O = red, S = yellow, Fe = orange, N = blue, H = white.

Compounds **1a** and **2a** are isostructural and their molecular features can therefore be described together. Both complexes lie on an inversion center and half dimer represents the asymmetric unit. The Fe<sup>III</sup> metal is in a distorted octahedral environment and it is bound by a N,N,O tridentate ligand, a SCN<sup>-</sup> anion, and a bridging methanolate anion. For the tridentate ligand, the Fe-N bond distances are significantly longer (0.13-0.25 Å) than the remaining bond distances, and the shortest distance is that between the metal and the phenolate moiety, Table S2 in SI. The SCN<sup>-</sup> anion is bound to the metal center through the nitrogen atom, and consistently, it exhibits a linear coordination geometry. The asymmetric unit of compound **3a** comprises two half dimeric units and one methanol molecule of crystallization (Figure 1). The overall structural arrangement is nevertheless similar to that of **1a** and **2a**, since the presence of the iodine on the periphery of the aromatic rings has a negligible influence on the iron coordination environment. The methyl alcohol molecule forms a hydrogen bond with the oxygen atom of the phenolate moiety, O(11).

In **1a-3a**, the metal-metal distance is approximately 3.15 Å. The crystal packing of **1a** and **2a** is reported in Figure S5. Adjacent molecules exchange different types of interactions, namely, C1···C1 (3.39 Å) and Br···Br (3.51 Å) with symmetry related halogen atoms, CH···S with the aromatic ring and the SCN<sup>-</sup> anion and  $\pi$ - $\pi$  stacks with adjacent bromo-quinoline rings. The crystal packing of **3a** is more complex due to the presence of two different molecular entities and the solvent of crystallization. In this system, the presence of the iodine atom with respect to the bromine and chlorine in **1a** and **2a**, expands the possible types of interactions that can be formed between adjacent molecules. In fact, I(22) and I(21) both interacts with S(1T) of the thiocyanate group. The geometry of the I(22)···S(1T) interaction (3.49 Å) is consistent with the presence of a halogen bond, whereas the geometry of the I(21)···S(1T) interaction (3.56 Å) presumably occurs through the negatively charged corona on iodine towards the terminal sulphur consistent with the presence of a chalcogenide bond.<sup>1,4,40</sup>



Figure 2. Portion of the crystal packing of **2a** (**a** and **b**) and **3a** (**c**), with the methanol molecule of crystallization highlighted. Dashed lines represent short interactions between symmetry related molecules. Selected weak interaction distances are indicated in Å.

**2b** and **3b** are centrosymmetric tetramers where the two outermost metal have a different coordination environment than the two innermost metals (Figure 3).



**2b** 

3b

Figure 3. Molecular structure of **2b** (left) and **3b** (right), with thermal ellipsoids drawn at the 30% probability level. Solvent molecules and hydrogen atoms were removed for clarity. Symmetry code ' = 1-x; 1-y; 1-z. Color code C = grey, Br = brown, I= violet, O = red, S= yellow, Fe = orange, N = blue, H = white.

In **3b**, four dichloromethane molecules of crystallization per tetrameric complex are present. In both systems Fe(1) is bound by three nitrogen atoms and three oxygen atoms deriving from a N,N,O tridentate ligand, a SCN<sup>-</sup> anion a bridging methanolate and a bridging oxo moiety. Differently, Fe(2) is bound by two nitrogen atoms and four oxygen atoms deriving from a N,N,O tridentate ligand, two bridging oxo moieties and a bridging methanolate anion. In both compounds, the Fe(1)-Fe(2) and Fe(2)-Fe(2)' bond distances are 3.07 and 2.96 Å, respectively. The crystal packing of **2b** is reported in Figure 4. Ideally, the molecules form layers by means of  $\pi$ - $\pi$  stacks, CH···S and CH····C/N interactions between the aromatic ring and the SCN<sup>-</sup> anion.

These layers interacts by forming halogen bonds (Br(3) $\cdots$ Br(4), 3.62 Å) and CH $\cdots$ Br (3.77 Å) interactions between symmetry related molecules.



Figure 4. Portion of the crystal packing of **2b**. Dashed lines represent short interactions between symmetry related molecules. Selected weak interaction distances are indicated in Å.

In **3b**, the iodine atoms dominate the packing interactions, as shown in Figure 5. According to the geometries of the interactions, the negative corona of I(1) interacts with the  $\sigma$ -hole of I(4) of a symmetry related molecule. Likewise, the lone pair distribution of S(1) interacts with the  $\sigma$ -hole of I(3).<sup>1,4,40</sup> Hence, I(3) acts as XB donor with respect to the carbon atom of an adjacent SCN<sup>-</sup> anion. Hence I(2), I(3) and I(4) acts as XB donor whereas acts as XB acceptor. Dichloromethane molecules of crystallization are also involved in weak interactions among adjacent complex molecules.



Figure 5. Highlights on the interaction exchanged by the iodine atoms in **3b**. Dashed lines represent short interactions between symmetry related molecules, distances are indicated in Å.

Different views of the crystal packing of **3b** are reported in Figure S6. In all ligand systems, the aromatic moieties linked by the imino group are not coplanar since they form a dihedral angle in the 31-41° range. In **2b** and **3b**, the tridentate ligands positioned on the same side with

#### Crystal Growth & Design

respect to the Fe<sub>4</sub>O<sub>4</sub> core, form  $\pi$ - $\pi$  stacks with the quinoline and phenolate residues. The shortest contact is between the aromatic rings of the phenolate groups (3.4-3.5 Å range), whereas the distances between the quinoline groups is approximately 3.6 Å for **2b** and greater than 3.7 Å for **3b**.

## **Magnetic Measurements**

In these series, compounds type **a** (dimers) and **b** (tetramers) are magnetically identical, if we consider the intermolecular magnetic interactions as negligible. Indeed, their magnetic behavior is indistinguishable within experimental error. Therefore, we only describe the magnetic properties of **1a** and **2b**, as representatives of these two magnetic structures.

The  $\chi T$  product for **1a** at room temperature is 5.01 emu K mol<sup>-1</sup>, lower than the expected value for the spin-only contribution of two high spin (HS) Fe<sup>III</sup> S = 5/2 centers ( $\chi T_{\text{HS}} \approx 8.750$  emu K mol<sup>-1</sup>), but significantly higher than the spin-only contribution of two low spin (LS) Fe<sup>III</sup> S = 1/2centers ( $\chi T_{\text{LS.}} \approx 0.750$  emu K mol<sup>-1</sup>). This confirms the HS state of the Fe<sup>III</sup> centers and suggests the presence of strong antiferromagnetic interactions between them, mediated by the alkoxo bridges. In the 2–300 K range,  $\chi T$  decreases with temperature (Figure 6, left), reaching values close to zero at very low temperatures. The experimental data can be fitted to the Hamiltonian:

$$H = -2J(S_1 \cdot S_2)$$

where  $S_1 = S_2 = 5/2$ . The best fit (Figure 6, left) was found for g = 2.09, J = -21 K (-14.6 cm<sup>-1</sup>), with the addition of a small paramagnetic impurity, equivalent to  $\approx 2\%$  of the total spin carriers.

The magnetic behavior for **2b** is similar, since it contains analogous bridges between paramagnetic centers, but now in a linear tetramer. The room temperature  $\chi T$  product is 8.50 emu K mol<sup>-1</sup>. This value can only be assigned to four HS Fe<sup>III</sup> centers, antiferromagnetically coupled

 $(\chi T_{\rm HS} \approx 17.50 \text{ emu K mol}^{-1}, \chi T_{\rm LS} \approx 1.50 \text{ emu K mol}^{-1})$ . In this case, the appropriate phenomenological Hamiltonian is:

$$H = -2J(S_2 \cdot S_3) - 2J'(S_1 \cdot S_2 + S_3 \cdot S_4)$$

where  $S_1 = S_2 = S_3 = S_4 = 5/2$ . The temperature dependence of the  $\chi T$  product was satisfactorily reproduced with parameters: g = 2.03, J = -35 K (24.3 cm<sup>-1</sup>), J' = -16 K (11.1 cm<sup>-1</sup>), and a paramagnetic impurity equivalent to  $\approx 2.5$  % of the total spin carriers. (Figure 6, right). It is particularly significant the fact that the shape of the curve can be reproduced only if J > J'. We found a ratio of 2 between both exchange parameters as optimum to reproduce the data. This can be rationalize if we look into the Fe–O–Fe angles. Whereas the Fe1–O–Fe2 bridging angles are asymetric ( $\approx 98^\circ$  and 105°), the two Fe2–O–Fe2 angles are almost identical, forming a perfect square. This permits a better overlap between the magnetic orbitals, and a stronger antiferromagnetic superexchange in the central bridge.



Figure 6. Thermal variation of  $\chi_M T$  versus T plots for **1a** (left) and **2b** (right). In red, the fitting obtained with the following parameters: g = 2.09, J = -21 K (-14.6 cm<sup>-1</sup>) (**1a**) and g = 2.03, J = -35 K (24.3 cm<sup>-1</sup>), J' = -16 K (11.1 cm<sup>-1</sup>), (**2b**).

# **DFT Calculations**

In order to investigate the electronic structure and reactivity of the ligands 1-3 and the relevant iron(III) complexes, Quantum-Mechanical (QM) calculations were carried out at the Density Functional Theory level.<sup>41</sup> Previous theoretical investigations showed that the correct modeling of high/low spin equilibria at DFT level depends dramatically on the choice of the functional.<sup>42</sup> which can unevenly favor one of the two spin states. In particular, it was observed that the pure functionals PW91<sup>43,44</sup> and BLYP<sup>45</sup> favor the LS state, while the paradigmatic hybrid functional B3LYP.<sup>46-48</sup> featuring a 20% Hartree-Fock (HF) exchange, favors the HS state.<sup>[37]</sup> Kepp comparatively examined twelve different functionals and demonstrated that the B3LYP\* hybrid functional (HF exchange 15%)<sup>49,50</sup> provide an accurate evaluation of the HS-LS energy gap for 30 different SCO iron complexes.<sup>51</sup> This notwithstanding, in the peculiar case of gsal-X<sup>-</sup> (gsal- $X^{-}$  = monosubstituted quinolylsalicylaldiminate; X = H, OMe, F, Cl, Br, I) Fe<sup>III</sup> tris-complexes, the B3LYP\* functional was recently proved to overestimate the HS-LS enthalpy difference  $\Delta H_{\rm SCO.}$ <sup>52</sup> In this work, based on the very good results achieved in the past on a variety of both organic<sup>53-55</sup> and inorganic systems,<sup>56-58</sup> we turned to test the hybrid functional mPW1PW by Adamo and Barone,<sup>59</sup> paralleled by the Def2SVP all-electron split-valence BS, including polarization functions.<sup>60</sup>

Whatever the combination of BSs and functional, HS and LS configurations show different structural features, in particular as far as the metal ion is involved, so that a comparison between theoretically optimized and structural metric parameters allows for the attribution of the correct spin state. A validation of the computational setup chosen for this work was therefore carried out by comparing the structural bond distances and angles determined for the complex  $[Fe(qsal-F)_2]^+$  (4<sup>+</sup>), isolated in 4(NCS)<sup>17</sup>, featuring a LS at 100 K and a HS Fe<sup>III</sup> center at 270 K, with the

corresponding optimized metric parameters. An examination of the bond distances involving the central metal ion shows that on passing from LS to HS the Fe–N distances are sensibly modified [average values 1.960(2) and 1.983(2) Å at 100 and 270 K, <sup>[14]</sup> respectively], while the Fe-O bond lengths remain almost unaltered [average values 1.875(2) and 1.866(2) Å at 100 and 270 K,<sup>[14]</sup> respectively]. DFT optimized distances are in very good agreement with the structural ones and display the trend found experimentally on passing from LS to HS configurations [LS: Fe-N, 1.973; Fe–O 1.857; HS: Fe–N, 2.173; Fe–O, 1.898 Å]. Notably, the uncorrected total electronic energies of the LS and HS configurations calculated for  $4^+$  in the gas phase differ by only 2.80 kcal mol<sup>-1</sup>, while the enthalpy contribution  $\Delta H_{\rm SCO}$  to the spin-crossover (SCO) amounts to 3.84 kcal mol<sup>-1</sup>, in agreement with the temperature-controlled SCO behavior observed experimentally.<sup>[14]</sup> The structures of the neutral protonated compounds Hqsal-5,7- $X_2$  (1–3) and the corresponding O-deprotonated  $(qsal-5,7-X_2)^{-}$  anions were optimized at the same level of theory. A comparison of the metric parameters calculated for 3 with the corresponding ones determined by single crystal X-ray diffraction (see above) clearly shows an excellent agreement. In particular, it is worth noting that the C–I distances are optimized at values extremely close to the experimental ones (optimized C–I distance = 2.109 Å). Also the formation of the intramolecular O12-H12...N2 bond is reproduced correctly with an optimized O...N distance only slightly overestimated [calculated 2.598 Å; structural value 2.652(4) Å]. In agreement with the crystal structure analysis, the aminoquinoline moiety is twisted with respect to the plane of phenyl ring ( $\tau = 44.63^{\circ}$ ). On passing from **3** to the corresponding deprotonated form qsal-5,7-I<sub>2</sub>, the metric parameters remain almost unvaried, with a small decrease in the  $\tau$  dihedral angle [ $\tau$  =  $39.98^{\circ}$  for  $(qsal-5,7-I_2)^{-1}$  and the loss of planarity of the 2-hydroxyphenylmethanimine moiety. In the deprotonated form, Kohn-Sham (KS) frontier molecular orbitals can be envisaged with large

contributions from the lone pairs of electrons located on the two nitrogen and the oxygen atoms (KS-HOMO-6, HOMO-3, and HOMO-1 for  $(qsal-5,7-I_2)^-$ ; Figure 7].



Figure 7. Isosurface drawings of KS-HOMO-6 (MO 83), KS-HOMO-3 (MO 86), and KS-HOMO-1 (MO 88) with large contributions from the LPs on the N and O donor atoms in (qsal- $5,7-I_2$ )<sup>-</sup>. Cutoff value = 0.05 |e|.

MO 86

MO 83

These atoms feature remarkable negative natural<sup>61,62</sup> charges Q ( $Q_{N1} = -0.463$ ,  $Q_{N2} = -0.504$ , and  $Q_{012} = -0.645$  |e|) and are therefore all available to interact with the iron(III) ions. On passing from qsal-5,7-I<sub>2</sub>)<sup>-</sup> to the corresponding brominated and chlorinated anions, the natural charges are basically unvaried [(qsal-5,7-Cl<sub>2</sub>)<sup>-</sup>:  $Q_{N1} = -0.465$ ,  $Q_{N2} = -0.499$ , and  $Q_{012} = -0.650$  |e|; (qsal-5,7-Br<sub>2</sub>)<sup>-</sup>:  $Q_{N1} = -0.464$ ,  $Q_{N2} = -0.500$ , and  $Q_{012} = -0.647$  |e|), thus indicating similar donor abilities of the three donor atoms. On varying the nature of the halogen substituents, KS-HOMO-1, KS-HOMO-3, and KS-HOMO-6 keep the same composition in terms of their constituent atomic orbitals, their eigenvalues becoming progressively slightly more stable on passing from

**MO 88** 

(qsal-5,7-I<sub>2</sub>)<sup>-</sup> to (qsal-5,7-Cl<sub>2</sub>)<sup>-</sup> [eigenvalues *ε:* KΣ–HOMO-1: -2.082, -2.156, -2.230; HOMO-3: -3.504, -3.570, -3.605; HOMO-6: -4.760, -4.734, and -4.601 eV for (qsal-5,7-Cl<sub>2</sub>)<sup>-</sup>, (qsal-5,7-Br<sub>2</sub>)<sup>-</sup>, and (qsal-5,7-I<sub>2</sub>)<sup>-</sup>, respectively].

DFT calculations have been extended to the monomer cationic complexes [Fe(qsal-5,7-X<sub>2</sub>)<sub>2</sub>]<sup>+</sup> [X = Cl (1c<sup>+</sup>), Br (2c<sup>+</sup>), I (3c<sup>+</sup>)], identified in solution by mass spectrometry (see above). These complexes, although not isolated in the solid state, represent interesting model complexes of the potential spin crossover (SCO) behavior. In order to model the possible electron configurations, both the HS (S = 5/2, sixtuplet) and LS (S = 1/2, doublet) configurations<sup>63</sup> were modeled for the three Fe<sup>III</sup> complexes. The optimized structures of complexes  $1c^+-3c^+$  show the central ion in a distorted octahedral coordination achieved by the two N1 and N2 atoms and by the O atoms (Figure S8 for  $1c^+$  in the HS state). Notably, upon coordination the phenyl and the quinolyl rings assume tend to a more planar structure as compared to the free ligand in order to maximize the interaction to the metal ion (for example  $\tau = 15.73^\circ$  for  $1c^+$  in the HS state).

In Table 2, the Fe-N and Fe-O bond lengths optimized for  $1c^+$ ,  $2c^+$ , and  $3c^+$  both in the LS and HS states are listed, showing that the nature of the halogen affects only marginally the bond distances, which depend as expected on the spin state.

Table 2: Fe-N and Fe-O bond distances optimized for the model complexes  $1c^+-3c^+$  at DFT level in the gas phase in the LS and HS configurations.<sup>a</sup>

		$1c^+$	$2c^+$	$3c^+$
HS	Fe-N2	2.131	2.129	2.126
	Fe-N1	2.192	2.192	2.192

#### Crystal Growth & Design

	Fe-O1	1.906	1.908	1.911
LS	Fe-N2	1.949	1.947	1.944
	Fe-N1	1.994	1.994	1.994
	Fe-O1	1.856	1.858	1.860

<sup>a</sup> Labels of the (qsal-5,7- $X_2$ )<sup>-</sup> ligands as in Figure 2 (X = Cl, Br, and I, for  $1c^+$ ,  $2c^+$ , and  $3c^+$ , respectively).

An examination of the crystal structures of compounds **1a**, **2a** and **3a** clearly shows that Fe-O distances fall in the range 1.92-1.94 Å, Fe-N1 bond lengths are all around 2.18 Å, while Fe-N2 distances are slightly shorter (2.13 Å). Therefore, the structural parameters clearly point to a HS configuration of the complexes. Accordingly, the total electronic energies calculated for HS and LS complexes  $1c^+-3c^+$  in the gas phase testify for a larger stability of HS as compared to LS, with energy differences  $\Delta E_{\rm SCO}$  of 3.0, 3.2, and 3.5 kcal mol<sup>-1</sup> for 1c<sup>+</sup>, 2c<sup>+</sup>, and 3c<sup>+</sup>, respectively, which are only slightly larger than those calculated for  $4(NCS)^+$  at the same level of theory. A thermochemical analysis shows that by taking into account the Zero Point Energy (ZPE) corrections and the thermal corrections to enthalpy, the same trend is confirmed ( $\Delta H_{\rm SCO} = 4.07$ , 4.28, and 4.52 kcal mol<sup>-1</sup> for  $1c^+$ ,  $2c^+$ , and  $3c^+$ , respectively). The sum of electronic and thermal free energy calculated for HS and LS model complexes in the gas phase ( $\Delta G_{\text{SCO}} = 7.59, 7.91$ , and 7.90 kcal mol<sup>-1</sup> for  $1c^+$ ,  $2c^+$ , and  $3c^+$ , respectively) shows that the entropy term is essentially independent on the nature of the halogen ( $\Delta S_{\text{SCO}} = 1.18 \cdot 10^{-2}$ ,  $1.22 \cdot 10^{-2}$ , and  $1.13 \cdot 10^{-2}$  kcal mol<sup>-1</sup> for  $1c^+$ ,  $2c^+$ , and  $3c^+$ , respectively), so that  $T_{1/2}$  depends exclusively on the enthalpy term ( $|\Delta H_{LS}|$  $_{\rm HS}/\Delta S_{\rm LS-HS}| = 344, 351, \text{ and } 359 \text{ for } 1c^+, 2c^+, \text{ and } 3c^+, \text{ respectively}).$  The trend in the  $\Delta H_{\rm SCO}$ values was confirmed when solvation was implicitly considered at IEF-PCM SCRF level<sup>64</sup>  $(\Delta E_{\text{SCO}} = 2.49, 2.78 \text{ and } 3.11 \text{ kcal mol}^{-1}; \Delta H_{\text{SCO}} = 3.50, 3.73, \text{ and } 4.62 \text{ kcal mol}^{-1} \text{ for } \mathbf{1c}^+, \mathbf{2c}^+,$ and  $\mathbf{3c}^+$ , in CHCl<sub>3</sub>, respectively).

These results strongly testify for a SCO nature of the complexes  $1c^+-3c^+$ , both in the solid state and in chloroform solution. Therefore, theoretical results suggest that while monomers could possibly show a SCO behavior, the formation of complexes with an even number of metal ions results in the strong anti ferromagnetic interactions, evidenced experimentally (see above), that prevent any SCO behavior in the solid state. In order to verify this hypothesis, the electronic structure of 1a was investigated at the same level of theory, in the open- and closed-shell singlet configurations (2S+1 = 1,  $1a^{sing}$ ), as independent HS Fe<sup>III</sup>-Fe<sup>III</sup> complex without coupling (2S+1 = 11,  $1a^{HS-HS}$ ), and eventually as antiferromagnetic singlet ( $1a^{afc}$ ). The latter configuration was obtained by using a broken symmetry approach<sup>65</sup> obtained from a guess of the ground state defined by molecular fragments, including one  $[Fe(qsal-5,7-X_2)]^{2+}$  ion with five unpaired  $\alpha$ -spin electrons (sextet), and another one with five  $\beta$ -spin electrons (sextet). The resulting wave function was optimized to avoid restricted/unrestricted spin instabilities and the geometry of the complex was finally re-optimized. In Table 3 some selected bond lengths are listed for the examined electronic configurations, along with the total electronic energies and spin densities (Figure S10) calculated for  $1a^{sing}$ ,  $1a^{HS-HS}$ , and  $1a^{afc}$ .

Table 3. Selected bond lengths calculated for 1a in the singlet configuration  $(1a^{sing})$ , with two independent HS Fe<sup>III</sup> ions without coupling  $(1a^{HS-HS})$ , and as antiferromagnetic singlet  $(1a^{afc})$ . For each configuration the total electronic energy  $E_{TOT}$  (Hartree) and the spin densities ( $|e|/au^3$ ) on the metal ions are also reported.

-	1a <sup>sing</sup>	1a <sup>HS-HS</sup>	1a <sup>afc</sup>	Struct.
2S+1	1	11	1	_
Fe-N2	1.946	2.196	2.196	2.139
Fe-N1	1.962	2.206	2.206	2.183
Fe-O1	1.900	1.948	1.948	1.920
Fe-O2/O2'	1.919/1.933	1.981/2.042	1.981/2.042	1.981/2.033
Fe-N1T	1.881	1.972	1.972	2.106
$E_{\mathrm{TOT}}$	-7177.6703036	-7177.7815725	-7177.7827629	_
Spin density on Fe <sup>III</sup>	0, 0	+4.30, +4.30	+4.29, -4.29 <sup>b</sup>	_

<sup>a</sup> Labels of the ligand donor atoms as in Fig. 2. <sup>b</sup> Figure S10.

A comparison of the optimized bond lengths and angles clearly shows that only the configurations of  $1a^{HS-HS}$  and  $1a^{afc}$  reproduce reliably the coordination pattern at the iron(III) centers. In addition, the closed-shell singlet displays, as expected, a RHF/UHF instability. The total electronic energies calculated for  $1a^{HS-HS}$  and  $1a^{afc}$  are consistent with the antiferromagnetic state being the ground state, in perfect agreement with the magnetic measurements discussed above. Notably, the spin densities of  $\pm 4.29$  |e|/au<sup>3</sup> (Figure S10) are in excellent agreement with 5 unpaired electrons on each Fe<sup>III</sup> center, since part of the spin density delocalizes onto the ligands.

# Conclusions

A new series of the tridentate N-8-quinolyl-salicylaldimine ligands Hqsal-5,7-X<sub>2</sub> (X = Cl(1), Br(2), I(3)) and their corresponding complexes with Fe<sup>III</sup>, formulated as [Fe(qsal-5,7-X<sub>2</sub>)(NCS)(MeO)]<sub>2</sub>·solv. (X = Cl (1a), Br (2a), I (3a)), [Fe<sup>III</sup><sub>4</sub>(qsal-5,7-X<sub>2</sub>)<sub>4</sub>(NCS)<sub>2</sub>(MeO)<sub>2</sub>]·solv. (X = Br (2b), I (3b; solv = 4 CH<sub>2</sub>Cl<sub>2</sub>) have been synthesized and structurally characterized. 1a and 2a are isostructural dimers where each Fe<sup>III</sup> metal is bound by the N,N,O tridentate qsal-5,7-

 $X_2$  (X = Cl and Br) ligand, a SCN<sup>-</sup> anion and two bridging methanolate anions in a distorted octahedral environment. The SCN<sup>-</sup> anion exhibit a linear geometry since it is bound to the metal center through the nitrogen atom. Several Cl. Cl (3.39 Å) and Br. Br (3.51 Å) halogen intermolecular interactions with symmetry related halogen atoms, CH...S with the aromatic ring and the SCN<sup>-</sup> anion and  $\pi$ - $\pi$  stacks with adjacent bromo-quinoline rings occur between adjacent molecules. In **3a** iodine atoms interact through a linear  $I_{22} \cdots S_1 T$  geometry with  $S_1 T$  of the SCN<sup>-</sup> group via halogen bonding. 2b and 3b are centrosymmetric tetramers where each Fe<sup>III</sup> is bound by three nitrogen atoms and three oxygen atoms deriving from the tridentate qsal-5,7- $X_2$  (X = Br and I), a SCN- anion, a bridging methanolate and a bridging oxo moiety. Unexpectedly, the halosubstitution at the 5,7 position of the aminoquinoline moiety yield dimers and tetramers instead of the mononuclear complexes with a dramatic change of the magnetic properties of the reported complexes, on going from SCO magnetic behavior observed in the mononuclear complexes to strong antiferromagnetic interactions between Fe<sup>III</sup> centers (S = 5/2), mediated by the alkoxo bridges in dimers and tetramers herein reported. 66,67 DFT Calculations support the structural finding, showing that monomers could possibly show a SCO behavior, even though the formation of complexes with an even number of metal ions results in the strong anti ferromagnetic interactions. DFT clearly show as well that the antiferromagnetic coupling of the two HS Fe<sup>III</sup> centers in **1a** results in the lowest energy electron configuration of the complex.

In conclusion the search for halogen-bonded systems where halogen-bonds dominates the structure and influence the physical properties of a given material still represents a challenge in material science, even though the results reported in this work show that a proper choice of the halogen substitution on the ligand coordinated to the metal can provide chemists with a versatile strategy for the crystal-engineering design of new compounds with novel physical properties.

Further studies will involve the replacement of halogen atoms with different substituents in order to investigate their role, both at the electronic and supramolecular level, in determining the molecular packing pattern and the related physical properties.

#### **Experimental Section**

#### Materials.

All manipulations were performed in air with reagent grade solvents. All organic chemicals were purchased from TCI (Zentek) and were used without further purification, and inorganic chemicals were purchased from Sigma-Aldrich and used as received. FT-IR spectra were performed on KBr pellets and collected with a Bruker Equinox 55 spectrophotometer. Melting points were obtained on a Kofler hot stage microscope and are uncorrected. Elementary analyses were performed by –CHNS/O Perkin Elmer 2400 series II. The aminoquinoline derivative was separated by a chromatographic column (25mm x 180 mm) filled with DAVISIL silica gel (40-63 m), packed with Buchi C-670 cartridge.

**Synthesis of 5,7-dichloro-8-aminoquinoline.** A solution of sulfuryl chloride (60.0 mmol) in 12.5 mL of glacial acetic acid was added slowly with stirring to a solution of 8-aminoquinoline (4.38 g, 30.4 mmol) in 21 mL of glacial acetic acid cooled to 10°C by an ice bath. The mixture was then warmed gradually to room temperature and finally was heated for 25 min on the steam bath at 70-75°C. Then, the reaction mixture was quenched by a solution of 20 g of sodium acetate in 150 mL of water. The precipitated crude product was removed by filtration and dry in air. Yield: 4.98g (77 %) Melting point: 183-184°C. ESIMS(+): 213.00 m/z (M+H<sup>+</sup>) with the expected isotope distribution.

Synthesis of 2-[(5,7-Dichloroquinolin-8-ylimino)-methyl]-phenol (Hqsal-5,7-Cl<sub>2</sub>), 1. 5,7dichloro-8-aminoquinoline (3.34g, 15.7 mmol), salicylaldehyde (2.02g, 24.3 mmol) and glacial acetic acid (0.34 mL) were dissolved in 40 mL of dry ethanol . The reaction mixture was stirred at room temperature for 14 hours. The end of the reaction was verified by TLC (2:8 of diethylether: petroleum ether. When the reaction was completed, the mixture reaction was filtered, washed, dried in air. Yield: 3.74 (74.9 %). Melting point: 201°C with decomposition. Elem anal. Calcd for  $C_{16}H_{10}Cl_2N_2O$  (found), mass %: C, 60.59 (59.73); H, 3.18 (2.94); N, 8.33 (8.55). FTIR: vmax(KBr)/cm<sup>-1</sup> 3435 (vOH), 3057, 2921 (vCH), 1621 (vC=N). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>/DCl):  $\delta$  = 13.45 (s), 9.41 (s), 9.25 (dd), 8.89 (dd), 8.06 (s), 7.86 (m), 7.78 (dd), 7.74 (td), 7.61 (s), 7.37 (d), 7.28 (td). ESIMS(+): 317.1 m/z (M+H<sup>+</sup>), with expected isotope distribution.

**Synthesis of 5,7-dibromo-8-aminoquinoline**. N-Bromosuccinimide (2.44 g, 13.0 mmol ) was added slowly to a stirred solution of 8-aminoquinoline (1.0 g, 6.9 mmol) and (1.4g,) of NaClO<sub>4</sub>/SiO<sub>2</sub> 1:4 ratio in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The reaction mixture was stirred at room temperature for 5-10 min and the progress controlled by TLC (50:50 of diethyl-ether: petroleum ether). When the reaction was completed the mixture was filtered and the catalyst washed with CH<sub>2</sub>Cl<sub>2</sub> (2x10 mL). Then, the combined organic layer was washed with water, dried over anhydrous sodium sulfate and concentrated under reduced pressure using a rotary evaporator. Further purification was carried out by flash chromatography on silica gel (diethylether/ petroleum ether: 4/6). Yield: 1.39 (66.9 %). Melting point: 143 °C. ESIMS(+): 303.1 m/z (M+H<sup>+</sup>) with expected isotope distribution.

Synthesis of 2-[(5,7-Dibromoquinolin-8-ylimino)-methyl]-phenol (Hqsal-5,7-Br<sub>2</sub>), 2. 5,7dibromo-8-aminoquinoline (1.60g, 5.3 mmol), salicylaldehyde (1.00g, 8.1 mmol) and glacial

#### Crystal Growth & Design

acetic acid (0.1 mL) were dissolved in dry ethanol (40 mL). The reaction mixture was stirred at room temperature for 22 hours. The end of the reaction was verified by TLC (diethylether/ petroleum ether2:8). When the reaction was completed, the mixture reaction was filtered, washed, dried in air. Yield: 1.9g (89.0 %). Melting point: 180°C with decomposition . Elem anal. Calcd for C<sub>16</sub>H<sub>10</sub>Br<sub>2</sub>N<sub>2</sub>O (found), mass %: C, 47.33 (46.68); H, 2.48 (2.23); N, 6.90 (6.64). FTIR: vmax(KBr)/cm<sup>-1</sup> 3435 (vOH), 3049, 2962 (vCH), 1621 (vC=N). <sup>1</sup>H NMR (DMSOd<sub>6</sub>/DCl):  $\delta = 13.32$  (s), 9.30 (s), 9.19 (dd), 8.84 (dd), 8.41 (s), 7.84 (m), 7.76 (dd), 7.72 (td), 7.54 (s), 7.36 (d), 7.27 (td). ESIMS(+): 404.9 m/z (M+H<sup>+</sup>), with expected isotope distribution.

**Synthesis of 5,7-diiodo-8-aminoquinoline**. Potassium iodide (1.0 g, 6.0 mmol) was added slowly to a stirred solution of 8-aminoquinoline (0.43 g, 3.0 mmol), NaIO4 (1.28 g, 6.0 mmol), NaCl (0.69 g, 12.0 mmol) in 40 mL of acetic acid/water (9/1). The reaction mixture changes from orange to black, then it was stirred at room temperature for 3 hours. When the reaction was completed to the mixture was added 30 mL of water, extracted with  $CH_2Cl_2$  (3x20 mL). Then, the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure using a rotary evaporator. Further purification was carried out by flash chromatography on silica gel (diethylether/petroleum ether: 1/1 ). Yield: 0.66 g (44.0 %) Melting point: 144-145°C with decomposition. ESIMS(+): 397.1 m/z (M+H<sup>+</sup>).

**Synthesis of 2-[(5,7-Diiodoquinolin-8-ylimino)-methyl]-phenol (Hqsal-5,7-I<sub>2</sub>), 3**. 5,7diiodo-8-aminoquinoline (0.58 g, 1.5 mmol), salicylaldehyde (0.39 g, 1.6 mmol) and glacial acetic acid (0.1 mL) were dissolved in dry ethanol (20 mL). The reaction mixture was stirred at room temperature for 14 hours. The end of the reaction was verified by TLC (2/8 of diethylether/petroleum ether. When the reaction was completed, the mixture reaction was filtered, washed and dried in air. Yield: 0.35g (48.0 %). Melting point: 173-174°C with

decomposition. Elem anal. Calcd for  $C_{16}H_{10}I_2N_2O$  (found), mass %: C, 38.43 (39.12); H, 2.02 (2.31); N, 5.60 (5.32). FTIR: vmax(KBr)/cm<sup>-1</sup> 3441 (vOH), 3057, 2921 (vCH), 1612 (vC=N). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>/DCl):  $\delta$  = 13.19 (s), 9.23 (s), 9.17 (dd), 8.95 (s), 8.75 (dd), 7.86 (m), 7.81 (m), 7.62 (s), 7.44 (d), 7.34 (td). Mass spectrometry (MS): 501.1 m/z (M+H<sup>+</sup>).

Synthesis of [Fe(qsal-5,7-Cl<sub>2</sub>)(NCS)(MeO)]<sub>2</sub> (1a) Compound 1 (20.0 mg, 0.06 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5ml) with Et<sub>3</sub>N (8.36  $\mu$ L, 0.06 mmol) to give a yellow solution and was layered at the bottom of test tube. FeCl<sub>3</sub>·6H<sub>2</sub>O (8.10 mg, 0.03 mmol) in 1.5ml MeOH and NaSCN (2.68 mg, 0.03 mmol) in 1.5 mL MeOH were sonicated for 5 min to give dark purple solution and were carefully layered on top of the above layer. A blank solution of MeOH (1mL) was layered in between the above mentioned solutions. Dark red crystals were formed at the interface after 5 days. Yield = 54.5 %. Elem Anal. Calcd for C<sub>36</sub>H<sub>24</sub>Cl<sub>4</sub>Fe<sub>2</sub>N<sub>6</sub>O<sub>4</sub>S<sub>2</sub> (found), mass %: C, 46.88 (47.12); H, 2.62 (2.54); N, 9.11(8.87), Cl 15.38(15.22), O 6.94(6.95), S 6.95(6.56), Fe 12.11(12.01). FTIR: vmax(KBr)/cm<sup>-1</sup> 2920 (vAr-H), 2061 (vC=N), 1605 (vC=N). MS (ESI+): m/z 688 [Fe(qsal-Cl<sub>2</sub>)]<sup>+</sup>.

## Synthesis of [Fe(qsal-5,7-Br<sub>2</sub>)(NCS)(MeO)]<sub>2</sub> (2a), [Fe<sub>4</sub>(qsal-Br)<sub>4</sub>(NCS)<sub>2</sub>(MeO)<sub>2</sub>] (2b)

The synthetic procedure of **2a** was the same as **1a** but using **2** (25.0 mg, 0.06 mmol) instead of **1**. The use of a very slight excess of Et<sub>3</sub>N (10.03  $\mu$ L, 0.07mmol) yielded 2b. Yield=56.7 % (2a) and 48% (2b). Elem Anal. Calcd C<sub>36</sub>H<sub>24</sub>Br<sub>4</sub>Fe<sub>2</sub>N<sub>6</sub>O<sub>4</sub>S<sub>2</sub> 2a (found), mass %: C, 39.31 (39.12); H, 2.2 (2.31); N, 7.64 (7.32) Br, 29.05(28.62); O 5.82(5.78), S 5.83(5.56), Fe 10.15(10.91) Elem Anal. Calcd C<sub>68</sub>H<sub>42</sub>Br<sub>8</sub>Fe<sub>4</sub>N<sub>10</sub>O<sub>8</sub>S<sub>2</sub> 2b (found), mass %: C, 39.77 (39.12); H, 2.06 (1.99); N, 6.82 (6.32) Br, 31.12(30.52); O 6.23 (5.83), S 3.12 (3.42), Fe 10.88 (10.71). FTIR: vmax(KBr)/cm<sup>-1</sup> 2922 (vAr-H), 2049 (vC=N), 1603 (vC=N). MS (ESI+): m/z 866 [Fe(qsal-Br<sub>2</sub>)]<sup>+</sup>.

# Synthesis of [Fe(qsal-5,7-I<sub>2</sub>)(NCS)(MeO)]<sub>2</sub> (3a), [Fe<sub>4</sub>(qsal-5,7-I<sub>2</sub>)<sub>4</sub>(NCS)<sub>2</sub>(MeO)<sub>2</sub>] (3b)

The synthetic procedure of 3a was the same as 1a but using 3 (30 mg, 0.06 mmol) instead of 1. The use of a very slight excess of Et<sub>3</sub>N (10.03  $\mu$ L, 0.07 mmol) yielded 3b. Yield = 49.34% (3a) and 41% (3b). Elem Anal. Calcd C<sub>37</sub>H<sub>28</sub>Fe<sub>2</sub>I<sub>4</sub>N<sub>6</sub>O<sub>5</sub>S<sub>2</sub> 3a (found), mass %: C, 33.66 (33.75); H, 2.14 (2.39); N, 6.37 (6.22) I, 38.45(37.54); O 6.06 (7.1), S 4.86 (4.74), Fe 8.46(8.26) Elem Anal. Calcd C<sub>72</sub>H<sub>50</sub>Cl<sub>8</sub>Fe<sub>4</sub>I<sub>8</sub>N<sub>10</sub>O<sub>8</sub>S<sub>2</sub> 3b (found), mass %: C, 31.22 (30.24); H, 1.82 (1.85); N, 5.06 (4.77), Cl 10.24 (8.47) I, 36.66(34.54); O 4.62 (4.35), S 2.32 (2.18), Fe 8.07 (7.6). FTIR: vmax(KBr)/cm<sup>-1</sup> 2919 (vAr-H), 2054 (vC=N, 3a), 2046 (vC=N, 3b), 1601 (vC=N). MS (ESI+): m/z 1054 [Fe(qsal-I<sub>2</sub>)]<sup>+</sup>.

**X-ray Crystallography**. Single crystal data were collected with a Bruker APEX DUO diffractometer with a Quazar MX Multilayer Optics diffractometer (Mo K $\alpha$  radiation;  $\lambda$  = 0.71073 Å) at 100 K (1a, 2a, and 2b) and with a Bruker Smart APEXII at 200 K (3a and 3b). A summary of data collection and structure refinement for 1a-3a, 2b, and 3b are reported in Table 1. The structure was solved by direct methods (SHELXS-97) and refined on F2 with full-matrix least squares (SHELXL-97), using the Wingx software package. The non-H atoms were refined with anisotropic displacement parameters. The unit cell parameters were obtained using 60  $\omega$ -frames of 0.5° width and scanned from three different zone of reciprocal lattice. The intensity data were integrated from several series of exposures frames (0.3° width) covering the sphere of reciprocal space<sup>68</sup>. Absorption correction were applied using the program SADABS <sup>69</sup>. The structures were solved by the dual space algorithm implemented in the SHELXT code.<sup>70</sup> Fourier analysis and refinement were performed by the full-matrix least-squares methods based on F2 implemented in SHELXL-2014.<sup>71</sup> Graphical material was prepared with the Mercury 3.9<sup>72</sup>

program. CCDC 1812729-1812733 contain the supplementary crystallographic data for this paper.

**ESI-MS.** Mass spectra were recorded on a triple quadruple QqQ Varian 310-MS mass spectrometer using electrospray ionisation (ESI) technique. The mass spectra were recorded in positive ion mode in the m/z 50–1000 range. The sample solutions (10 mg/L) were prepared in CH<sub>3</sub>OH and infused directly into the ESI source using a Varian HPLC pump with a flow rate of 50  $\mu$ L/min. Needle, shield and detector were kept at 4500 V, 600 V and 1450 V respectively. Pressure of nebulizing and drying gas was 40 PSI, housing and drying gas temperature was 60 and 250 °C, respectively.

**Magnetic Measurements.** Magnetic measurements were carried out on polycrystalline powder samples. Each sample was secured inside a tight gel capsule, and transferred into the sample compartment of a Quantum Design MPMS-XL-7T SQUID magnetometer (Quantum Design, Inc, San Diego, CA, USA). Magnetic measurements were carried out under an applied field of 1000 Oe in the 2-300 K temperature range. Pascal's constants were used to estimate the diamagnetic corrections for compounds.

**DFT Calculations.** Theoretical calculations were performed at the DFT<sup>[36]</sup> level with the Gaussian 09 commercial suite of programs<sup>73</sup> on the neutral compounds 1–3, the corresponding O-deprotonated compounds  $(qsal-5,7-X_2)^-$  (X = Cl, Br, I), the monomer iron(III) complex cations  $[Fe(qsal-5,7-X_2)_2]^+$  (1c<sup>+</sup>, 2c<sup>+</sup>, 3c<sup>+</sup> for X = Cl, Br, I) and the complex cation  $[Fe(qsal-F)_2]^+$  (4<sup>+</sup>).<sup>[14]</sup> The hybrid functional mPW1PW<sup>[54]</sup> was adopted along with all-electron Schäfer, Horn, and Ahlrichs split-valence plus polarization basis sets (BSs) for all atomic species in the Def2SVP Weigend formulation.<sup>[55]</sup> The molecular geometry optimizations were performed starting from structural data, when available. For all iron(III) complexes, the calculations were carried out both

in the High Spin (HS, S = 5/2) and the Low Spin (LS, S = 1/2) configurations. Tight SCF convergence criteria (SCF = tight keyword) and fine numerical integration grids [Integral(FineGrid) keyword] were used. The ZPE and enthalpy corrections at 298.15 K were calculated for  $1c^+-3c^+$  and added to the total electronic energy differences  $\Delta E_{SCO}$  to calculated the enthalpy differences  $\Delta H_{\rm SCO}$  between HS and LS. Entropy corrections to the energy differences between HS and LS ( $\Delta S_{SCO}$ ) were calculated from the sum of electronic and thermal enthalpies and free energies ( $\Delta G_{\rm SCO}$ ). It was presumed that the temperature difference from 298.15 K to the room temperature was negligible. The calculations were extended to 1a in the closed- and open-shell singlet configurations  $(1a^{sing}, 2S+1 = 1)$ , in the configuration featuring two uncoupled  $Fe^{III}$  HS ions (1a<sup>HS-HS</sup>, 2S+1 = 11) and in the antiferromagnetic complex (1a<sup>afc</sup>, 2S+1 = 1, with 5  $\alpha$ - and 5  $\beta$ -spin electrons on the two metal centers) following a brokensymmetry approach. Accordingly, for 1a<sup>afc</sup> six fragments were defined at the geometry optimized for  $1a^{\text{HS-HS}}$ : two  $[\text{Fe}^{\text{III}}(\text{gsal-5.7-X}_2)]^{2+}$  fragments (2S+1 = 6, charge 2+), two CH<sub>3</sub>O<sup>-</sup> anions (2S+1 = 1, charge -1), and two SCN<sup>-</sup> anions (2S+1 = 1, charge -1). Using the "guess=fragment" option, the wave functions of the fragments were combined to form a guess of the wave function of the whole complex. An MO calculation was then completed for the total complex, and the stability of the resulting wave function was verified (stable=opt). The complex was eventually re-optimized and the stability of the wave function verified again. The nature of the minima for all the optimized structures were verified by harmonic frequency calculations. Atomic charges were calculated in the framework of the Natural Bonding Orbital (NBO)<sup>[56,57]</sup> analysis at the optimized geometries at the same level of theory. In order to account for the influence of the solvent on the electron configurations of the compounds, calculations were also carried out in the presence of CHCl<sub>3</sub>, implicitly taken into account by means of the Polarizable Continuum Model

(PCM) approach (linear response; nonequilibrium solvation) in its Integral Equation Formalism variant (IEF-PCM), which describes the cavity of the solute within the reaction field (SCRF) through a set of overlapping spheres.<sup>[59]</sup> The optimized geometries were investigated by means of the program GaussView 5.0.9.<sup>74</sup> In order to investigate KS-MO isosurfaces, the Molden 5.7<sup>75</sup> program was used in a macOS compiled version (cutoff value = 0.05 |e|).<sup>76</sup>

# ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: ..... Additional figures and tables as mentioned in the text (PDF).

Accession Codes. CCDC 1816966, 1812729-1812733 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### NOTES

The authors declare no competing financial interest.

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#### Crystal Growth & Design

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#### Crystal Growth & Design

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# Structural Diversity on a New Series of Halogenated Quinolyl Salicylaldimides-Based Fe<sup>III</sup> Complexes Showing Solid-State Halogen-Bonding/Halogen…Halogen Interactions

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TOC GRAPHIC



# SYNOPSIS

Structural diversity has been observed in a new series of tridentate N-8-quinolyl-salicylaldimine, Hqsal-5,7-X<sub>2</sub> (X = Cl(1), Br(2), I(3)), -based Fe<sup>III</sup> complexes, showing halo-substitution at the 5,7 position of the Hqsal's aminoquinoline moiety. Antiferromagnetic dimers and tetramers are obtained in the solid state where Halogen…Halogen interactions (X=Cl, Br) and Halogen Bonding (X=I) dominate the molecular packing pattern. Theoretical calculations are in agreement with structural findings and magnetic properties.