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Correlation between Supramolecular Connectivity and Magnetic Behaviour of [Fe^{III}(5-X-qsal)₂]⁺-Based Salts Prone to Exhibit SCO Transition

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Abstract: We present an extensive study to determine the relationship between structural features of spin crossover (SCO) systems based on N-(8-quinolyl)salicylaldimine (qsal) ligand derivatives and their magnetic properties. Thirteen new compounds with general formula $[Fe^{III}(5-X-qsal)_2]^+$ (X = H, F, Cl, Br and I) coupled to Cl⁻, ClO₄⁻, SCN⁻, PF₆⁻, BF₄⁻ and BPh₄⁻ anions were prepared and magnetically characterized. The structure/properties correlations observed in these compounds were compared to those of salts with the same $[Fe^{III}(qsal-X)_2]^+$ cations previously reported in the literature. These cations favour the LS configuration in compounds with the weakest connectivity. As connectivity increases most of them present HS states at room temperature and structures may be described as arrangements of parallel layers of interacting cation dimers. All the compounds based on these cations undergoing complete SCO transitions within the 4–300 K temperature range have high intralayer connectivity. If, however, the interlayer connectivity becomes very strong they remain blocked in the HS or in the LS state. The SCO transition may be affected by the slightest change of solvent molecules content, disorder or even crystallinity of the sample and it remain difficult to predict which kind of ligand substituent should be selected to obtain compounds with the desired connectivity.

Keywords: spin crossover; Fe (III); magnetic properties; Schiff base ligands; supramolecular chemistry

1. Introduction

Spin crossover (SCO) is the ability that some complexes have to switch reversibly between two possible spin configurations, a low-spin (LS) and a high-spin (HS) state. This phenomenon can be observed in octahedral complexes with d^4 - d^7 electronic configuration [1]. It can be triggered by variation in temperature, pressure or by light irradiation and can be monitored by a wide variety of techniques [1-3]. SCO can be incomplete, complete, gradual or abrupt, hysteretic, in one-step or in multiple steps. These various behaviours are connected to the way the structural changes induced by the SCO transition are propagated through the entire solid structure, i.e., the cooperativity between the SCO centres. This cooperativity can be understood as the sum of the contributions of a series of parameters correlated with supramolecular interactions between the molecules that constitute each system, cations, anions and solvating molecules. To obtain compounds with different levels of cooperativity it is necessary to synthesize them considering several supramolecular contacts such as hydrogen [4,5] and halogen bonding [6,7], and π - π stacking [8,9]. However, it has proven difficult to understand how a specific combination of these interactions can result in structures that have a desired SCO behaviour. Often in the literature structures that have SCO behaviour are described but no information is given regarding the specific type of supramolecular structure and the interactions that correlate with the observed SCO



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). behaviour. This kind of studies are however important since they provide useful design clues in the search for stable, hysteretic SCO complexes at room temperature.

In this work we present an extensive study to determine the relationship between structural features or patterns common in SCO systems based on N-(8-quinolyl)salicylaldimine (qsal, Figure 1) ligand derivatives and the resulting magnetic properties. We have prepared a series of Fe^{III} SCO complexes with general formula $[Fe(5-X-qsal)_2]^+$ (X = H, F, Cl, Br and I) coupled to Cl⁻, ClO₄⁻, SCN⁻, PF₆⁻, BF₄⁻ and BPh₄⁻ anions in Table S1. The resulting compounds were magnetically characterized, and their structure analysed in order to detect structural similarities between those with similar magnetic behaviour. The structure/properties correlations observed in this work were also compared to those of salts with the same cations [Fe^{III}(5-X-qsal)₂]⁺ previously reported in the literature. Hereafter the reference to the compounds will have one of the following numerical prefixes depending on X, 1 (X = H), 2 (X = F), 3 (X = Cl), 4 (X = Br), 5 (X = I), 6 (X = OCH₃) and 7 (X = 5-tBu). Complexes coupled with transition metal anions such as dithiolates like $[Ni(dmit)_2]$ -(dmit = 4,5-dithiolato-1,3-dithiole-2-thione) were excluded from this study due to their disparity of supramolecular arrangements arising from the ease with which they create segregated layers of highly connected anions. These materials are expected to follow different supramolecular arrangements than the compounds addressed in this work.



Figure 1. Qsal ligand.

2. Results and Discussion

2.1. Magnetic Characterisation

Figures 2–4 show the temperature dependence of $\chi_P T$, product of the paramagnetic susceptibility, χ , by temperature for all the compounds synthesized. All compounds shown in Figure 2 are in the LS state up to approximately 200 K with low temperature $\chi_P T$ values (considering 20 K for all compounds) ranging from 0.40–0.46 emu K mol⁻¹. The magnetic behaviour of compound **3.PF₆.MeCN** is typical of a SCO compound with a sharp transition and transition temperature $T_{1/2} \sim 256$ K, calculated as the maximum of the first derivative $\partial \chi T / \partial T$. At 315 K **3.PF₆.MeCN** has a $\chi_P T$ value of 3.72 emu K mol⁻¹ which can be attributed to an incomplete spin transition. A far as the remaining compounds are concerned, gradual transitions to the HS state start to occur approximately at 250 K. At 320 K the values of $\chi_P T$ for **3.Cl.MeCN.H₂O**, **3.ClO₄**, **3.BF₄** and **3.BPh₄** are 1.53 emu K mol⁻¹, 0.60 emu mol K⁻¹, 0.93 emu K mol⁻¹ and 1.96 emu K mol⁻¹, respectively. Magnetic susceptibility measurements were also obtained on cooling but no evidence of hysteresis was found for these compounds.

Compounds in Figure 3 exhibit three distinct magnetic behaviours. **4.SCN.0.5H₂O** has a magnetic behaviour consistent with a HS species with an average value of $\chi_P T \sim 4.14$ emu mol K⁻¹ in the 50–320 K range and $\chi_P T = 4.23$ emu mol K⁻¹ at 320 K. **4.PF₆.H₂O** reveals a spin transition with $T_{1/2} \approx 203$ K. At low temperature $\chi_P T = 0.30$ emu K mol⁻¹, the usual value for a LS state in these compounds [1]. At 317 K $\chi_P T = 3.90$ emu K mol⁻¹ indicating an almost complete spin transition. Compounds **4.ClO₄**, **4.BF₄.0.5H₂O**, **4.Cl.MeCN.H₂O** and **4.BPh₄** have similar magnetic behaviour with $\chi_P T$ values at low temperatures (20 K) of 0.45 emu mol K⁻¹, 0.57 emu mol K⁻¹, 0.53 emu mol K⁻¹ and 0.70 emu mol K⁻¹, respectively, consistent with LS Fe^{III} species. The values of $\chi_P T$ remain stable until around 200 K where a gradual transition starts to appear. The values at high temperature are 0.96 emu K mol⁻¹, 1.73 emu K mol⁻¹ and 1.74 emu K mol⁻¹ for compounds **4.ClO₄**,

4.BF₄**.0.5H**₂**O**, **4.Cl.MeCN.H**₂**O** and **4.BPh**₄, respectively. These values are indicative of incomplete transitions. No hysteresis was found.



Figure 2. Temperature dependence of the $\chi_P T$ product in a field of 1 T.



Figure 3. Temperature dependence of the $\chi_P T$ product in a field of 1 T.



Figure 4. Temperature dependence of the $\chi_P T$ product in a field of 0.05 T.

The magnetic behaviour of the compound **5.Cl.MeOH.2.5H₂O** (Figure 4) is consistent with HS behaviour with an average $\chi_P T \sim 3.96$ emu K mol⁻¹ slightly increasing with temperature up to $\chi_P T = 4.01$ emu K mol⁻¹ at 300 K. In the case of **5.PF₆.1.5H₂O** it is consistent with SCO transition with $T_{1/2} \approx 270$ K. At low temperatures (20 K) $\chi_P T = 0.47$ emu K mol⁻¹, a typical value for a LS Fe^{III} compound [1]. At 314 K $\chi_P T = 4.31$ emu K mol⁻¹ is indicative of a HS state. The χT curves obtained on cooling and warming overlap with no evidence of hysteresis.

2.2. Structural Characterization

In the $[Fe(X-qsal)_2]^+$ cations two X-qsal⁻ ligands are coordinated to the central Fe(III) atom in a nearly perpendicular manner, yielding distorted octahedral FeN₄O₂ coordination environments.

Hereafter cation–cation and cation–anion interactions will be referred to as DD and DA interactions, respectively. The extended aromatic systems of the X-qsal ligands give rise to quite strong $\pi\pi$ cation–cation, DD interactions, which play a dominant role in the crystal packing of these compounds. Strong DD pairwise $\pi\pi$ interaction due to the extensive overlap of ligands from neighbouring cations, often reinforced by hydrogen bonds, CH ... O, and type II halogen bonds, CX ... π , result in the appearance of two distinct basic structural motives, either dimers or chains of cations.

In the crystal structures of the salts with anions such as Cl⁻, SCN⁻, BF₄⁻ and ClO₄⁻, weaker interdimer $\pi\pi$ interactions between the cations give rise to 2D cationic layers, while in the salts of the B(Ph)₄⁻ anions, strong cation–anion, DA, interactions, mostly concerning $\pi\pi$ and CH ... π contacts, are responsible for the existence of chains of weakly interacting dimers isolated by the bulky B(Ph)₄⁻ anions.

In the PF_6^- salts weaker DD $\pi\pi$ interactions give rise to crystal structures based on layers of parallel chains of cations.

The studied compounds may thus be sorted in four sets with different supramolecular configurations: Dimer Chains, Type I and Type II Dimer Layers and Chain Layers.

2.2.1. Dimer Chains

In $3.BPh_4$ and $4.BPh_4$ the cations are associated as dimers through strong interactions between both cations in the dimer, resulting from the overlap of the 5-X-qsal ligands from each cation. This overlap is extended through the entire length of the ligands, the phenyl, Ph, rings of each 5-X-qsal ligand sitting on top of the quinoline, Qn, fragment of the neighbouring ligand. The $\pi\pi$ interactions are further assisted by two-fold CH ... O hydrogen bonds and type II C-X ... π halogen bonds. The crystal packings in **3.BPh**₄ and **4.BPh**₄ are similar and their crystal structures are based on an arrangement of parallel chains of cationic dimers aligned along a. Weaker intrachain DD interactions, type I halogen bond contacts C-X ... π , between the cations located in neighbouring dimers are observed. The cations display strong interactions with the phenyl rings of the BPh₄⁻ anions through $\pi\pi$ and C-H ... π contacts. The chains of cation dimers are isolated from each other by the BPh_4^- anions and no interchain DD contacts are observed. The more relevant parameters describing the intra and interdimer DD interactions of 3.BPh4 and 4.BPh4 are summarized in Table S2. Figure 5 shows a projection of the structure of **4.BPh₄** along the direction of the chains of cation dimers. The intrachain arrangements of the cations and the DD contacts in the crystal structure of **4.BPh**₄ are shown in Figure S1.

The BPh₄⁻ anions display strong interactions with the cations mostly through a large number of DA $\pi\pi$ and CH . . . π contacts, as illustrated in Figure S2, where the arrangement of the most relevant DA contacts around one anion with cations from three neighbouring cationic chains, is shown. Some of the DA interactions mediated by the BPh₄⁻ anions appear to give rise to relatively rigid DAD interchain arrangements such as those involving the cations in orange, connected by DA $\pi\pi$ contacts through a single Ph group of the anion. Despite the strong DD intradimer and DA interactions, the weak DD interdimer and the softness of the BPh₄⁻ anion is expected to lead to a quite flexible crystal lattice from the point of view of the structural rearrangements associated with the SCO processes.



Figure 5. Top view of the crystal structure of 4.BPh₄ along the chain direction parallel to the *a* axis. The cations of one of the chains are depicted in dark blue.

Both compounds with this Dimer Chains supramolecular configuration are in the LS state at low temperatures with incomplete transitions up to 320 K (Figures 2 and 3).

2.2.2. Dimer Layers

The crystal structures of the salts with the Cl⁻, SCN⁻, BF₄⁻ and ClO₄⁻ anions are also based on arrangements of dimers of cations; however, distinctively from those observed in the BPh₄⁻ based salts, these salts exhibit significant interdimer DD interactions, giving rise to crystal structures that are based on arrangements of parallel layers of dimers. The intradimer arrangements are similar to those described for **3.BPh**₄ and **4.BPh**₄, with an overlap of the 5-X-qsal ligands from each cation extended through the entire length of the ligands. In the Dimer Layers structures, two distinct types of layers were observed. In 3.Cl.MeCN.H₂O, 4.Cl.MeCN.H₂O, 3.BF₄, 4.BF₄.0.5H₂O, 3.ClO₄ and 4.ClO₄ salts, displaying "type I" layer arrangements, each of the two 5-X-qsal ligands dimers that is not involved in the intradimer contacts, shows sizable $\pi\pi$ interactions with the ligands from two neighbouring dimers, through Ph-Qn partial overlaps. In **5.Cl.MeOH.2.5H₂O** and 4.SCN.0.5H₂O, exhibiting "type II" layer arrangements, each of the four 5-X-qsal ligands displays quite strong $\pi\pi$ interactions to a ligand from a neighbouring dimer through the overlap of both rings from the Qn fragments of two ligands. These two interdimer arrangements are shown in Figure 6a,b for 3.Cl.MeCN.H₂O (type I) and 5.Cl.MeOH.2.5H₂O (type II), respectively. The crystal packing of both these salts based on both types of arrangements will be described below, in detail. The crystal packings of the other salts displaying these types of the Dimer Layers arrangements will be compared with those of **3.Cl.MeCN.H**₂**O** and 5Cl.MeOH.2.5H₂O. The main parameters describing the intradimer interactions (DD^d) as well as the interdimer intra (DD^L) and interlayer (DD^{iL}) DD interactions are summarized in Tables S3 and S4.



Figure 6. View of the interdimer intralayer arrangements of (a) **3.Cl.MeCN.H₂O** and (b) **5.Cl.MeOH.2.5H₂O**, exhibiting type I and type II Dimer Layers arrangements respectively. The cations depicted in orange show relatively strong $\pi\pi$ interactions to the cations from the central dimer.

2.2.3. Type I Dimer Layers

The crystal structure of **3.Cl.MeCN.H₂O** is based on an arrangement of layers of $[Fe(5-X-qsal)_2]^+$ dimers parallel to the *ac* plane. Figure S3 shows a view of the structure of **3.Cl.MeCN.H₂O** along *b*, where the atoms belonging to one of the cationic layers are depicted in dark blue. Figure S4 shows the arrangement of the cations, anions and H₂O molecules within the layers. One of the dimers is depicted in "ball and stick" mode and the four cations showing $\pi\pi$ interdimer interactions with the central pair are displayed in orange. In the case of the type I layer of cation dimers configuration the anions are located in the centre of vacancies within the dimer arrangements. The water molecules in **3.Cl.MeCN.H₂O**, **4.Cl.MeCN.H₂O**, and **4.BF₄.0.5H₂O**, displaying strong H bonds interactions with the anions (and also with the cations), are slightly displaced towards the edges of the layers, while the MeCN molecules in **3.Cl.MeCN.H₂O** and **4.Cl.MeCN.H₂O** are actually segregated to the edges of the layers.

Despite the similar intralayer arrangement of the $[Fe(5-X-qsal)_2]^+$ cations in the crystal structures of the **3.Cl.MeCN.H₂O**, **4.Cl.MeCN.H₂O**, **3.BF**₄, **4.BF**₄.**0.5H₂O**, **3.ClO**₄ and **4.ClO**₄ a few differences are observed in the crystal packing, mostly concerning the intradimer and interlayer interactions, which appear to be related with the presence of the MeCN and H₂O molecules in the crystal structure.

The crystal structure of the **3.BF**₄, **3.ClO**₄ and **4.ClO**₄ salts, includes two crystallographic distinct $[Fe(5-X-qsal)_2]^+$ cations, D_A and D_B , that are associated as $D_A D_A$ and $D_B D_B$ dimers. The intradimer interactions appear to be significantly weaker in one of these dimers, $D_B D_B$, due to a reduction of the overlaps and larger separations between the aromatic systems of the interacting 5-X-qsal ligands. The intradimer interactions for the $D_A D_A$ pair appear to be as strong or even stronger, considering the slight shortening of the ligand separation, than those in the **3.Cl.MeCN.H**₂**O**, **4.Cl.MeCN.H**₂**O** and **4.BF**₄.0.5H₂**O** salts.

In the case of salts displaying the Type I Dimer Layers configuration, minor variations were also observed in intralayer DD interactions, resulting from the overlap between the Qn and Ph-X fragments of the ligands. The variation in the separation of the two aromatic systems suggests that those interactions appear to be slightly stronger for **3.Cl.MeCN.H**₂**O**, **4.Cl.MeCN.H**₂**O** and **4.BF**₄.**0.5H**₂**O** than for the **3.BF**₄, **3.ClO**₄ and **4.ClO**₄ salts.

Besides the above-mentioned differences in the intradimer arrangements, the major variations in the crystal packing are related with the interlayer DD interactions. These interactions appear to be quite strong in $3.BF_4$, $3.ClO_4$ and $4.ClO_4$ salts, where either the D_A or the D_B [Fe(5-X-qsal)₂]⁺ cations are involved in strong interactions with cations located in

neighbouring layers. While both D_A and D_B show strong interactions with two cations D_A and D_B in a neighbouring layer (DD^{iL}_1 , D_AD_A ; DD^{iL}_2 , D_AD_B and DD^{iL}_3 , D_BD_B) through $\pi\pi$ contacts between the Ph fragments further reinforced by CX ... π interactions, D_B shows an additional interaction (DD^{iL}_4) to another D_B cation, through $\pi\pi$ contacts between the Qn fragments. These interlayer interactions appear to be significantly weaker for **4.BF4.0.5H2O** and even weaker for **3.CI.MeCN.H2O**, **4.CI.MeCN.H2O**. In **4.BF4.0.5H2O** one cation shows relatively strong $\pi\pi$ interactions with a cation located in a neighbouring layer, due to the overlap between the Qn fragments, further reinforced by two-fold CX ... H contacts DD^{iL}_1 and weaker CH ... π contacts to two other cations DD^{iL} . In **3.CI.MeCN.H2O**, **4CI.MeCN.H2O**, the [Fe(5-X-qsal)₂]⁺ cations only show relatively weak contacts to cations located in neighbouring layers, the stronger DD^{iL}_1 corresponding to twofold CX ... H interactions with one cation and the weaker DD^{iL}_2 to CX ... π interactions with two cations. The interlayer contacts are illustrated in Figure S5a–c for **3.CI.MeCN.H2O**, **4.BF4.0.5.H2O** and **3.CIO**₄. Further details of the contacts are summarized in Table S3.

In the crystal structures of **3.Cl.MeCN.H**₂**O**, **4.Cl.MeCN.H**₂**O** and **4.BF**₄.0.5H₂**O** displaying the Type I Dimer Layers configuration strong interactions are observed between the cations and the anions and the H₂O molecules. The overall lattice DD connectivity is reinforced by the DAD and D-H₂O-D arrangements with quite strong DA interactions, mostly due to CH ... X contacts, and D-H₂O interactions mainly involving OH ... O and CH ... O contacts.

The connectivity resulting from the contacts mediated by the anions and solvent molecules is illustrated in Figure S6 for **3.Cl.MeCN.H₂O**, where the cations interacting with one strongly coupled Cl⁻ ··· H₂O pair are shown. The Cl⁻ anion and H₂O molecule strongly interact with five cations, four of them located in layer A and only one in a distinct layer B. Although the interactions between the cations, the anions and the H₂O molecules are expected to contribute to the overall DD lattice interconnectivity its effect on the interlayer reinforcement is expected to be relatively modest. The MeCN molecules that are present in **3.Cl.MeCN.H₂O** and **4.Cl.MeCN.H₂O**, only present modest interactions to a single cation and are not expected to contribute significantly to the lattice connectivity. The arrangements and interactions in **4.Cl.MeCN.H₂O** are similar to those described for **3.Cl.MeCN.H₂O**. In **4.BF₄.0.5H₂O**, while the interactions between the cations and the H₂O molecules seem to be weaker than those observed in the Cl⁻ salts, the interactions with the BF₄⁻ anions are stronger. As described for **3.Cl.MeCN.H₂O** and **4.Cl.MeCN.H₂O** and **4.Cl.MeCN.H₂O** and **4.Cl.MeCN.H₂O**, and **4.Cl.MeCN.H₂O**, in the **4.BF₄.0.5H₂O**, **3.BF₄**, **3.ClO₄ and 4.ClO₄** salts, the DA interactions are expected to enhance the overall DD lattice interconnectivity.

The **3.Cl.MeCN.H**₂**O**, **4.Cl.MeCN.H**₂**O**, **3.BF**₄, **4.BF**₄.**0.5H**₂**O**, **3.ClO**₄ and **4.ClO**₄ salts displaying the Type I Dimer Layers configuration show a roughly similar magnetic behaviour as those based on arrangements of weakly coupled chains of cation dimers. They are in the LS state at low temperatures and appear to present incomplete SCO transitions up to 320 K (Figures 2–4). The slower progress of the SCO processes that is clearly noticed in particular for the **3.BF**₄, **3.ClO**₄ and **4.ClO**₄ salts can be related to the larger rigidity of the lattice of these salts resulting from the stronger interlayer DD interactions, thus requiring more energy in order to distort the crystal lattice.

2.2.4. Type II Dimer Layers

The crystal structure of **5.Cl.MeOH.2.5H**₂**O** and **4.SCN.0.5H**₂**O** is based on an arrangement of layers of cationic dimers parallel to *ac*. The Cl⁻ anions and the MeOH and H₂O solvent molecules are segregated to empty spaces located in between the cationic layers, as shown in the Figure S7. This figure portrays a view of the structure of **5.Cl.MeOH.2.5H**₂**O** along *c*, where the atoms belonging to one of the cationic layers are depicted in dark blue. Figure S8 shows the intralayer arrangement of the dimers of the [Fe(5-I-qsal)₂]⁺ cations, where the four cations showing $\pi\pi$ interdimer interactions with the central pair represented in orange. The key parameters describing the various DD interactions in **5.Cl.MeOH.2.5H**₂**O** and **4.SCN.0.5H**₂**O** are summarized in Table S4. Besides the strong intradimer DD^d and interdimer DD^L_1 interactions, each [Fe(5-I-qsal)₂]⁺ cation displays a fairly strong interaction to one cation located in a neighbouring layer, through a $\pi\pi$ contact resulting from the overlap between two Ph fragments of neighbouring ligands. This interaction DD^{iL} is further assisted by two-fold type I halogen contacts C-I ... O in **5.Cl.MeOH.2.5H₂O** or C-Br ... O in **4.SCN.0.5H₂O**. The arrangement of the various DD contacts relative to a central cation is illustrated in Figure S9. The cation bonded to the central one within the dimer is depicted in light grey. The cations displayed in orange are located in the same layer as the central cation. In the case of the dark orange cation the $\pi\pi$ interaction is expected to be slightly stronger than the DD^L₂ interaction with the light orange cation. Finally, the cation located in a neighbouring layer, displayed in violet in Figure S9, interacts with the central cation through the combination of $\pi\pi$ overlap between two Ph groups and two-fold C-I ... O interactions DD^{iL}.

The anions and solvent molecules are confined within hollow channels formed by the cationic sub-lattice, and establish very strong OH ... O, CH ... O and OH ... Cl hydrogen bond type contacts that propagate along the channels. The Cl⁻ anions as well as the MeOH and H₂O molecules are involved in various contacts with the cations: CH ... O, CH ... π , CH ... Cl hydrogen bonds. These contacts are expected to reinforce the connectivity between the cations located in neighbouring layers. However, considering that the stronger contacts involve the MeOH molecules, which have half occupancy, the reinforcement of the connectivity is expected to be relatively modest. Figure S10 illustrates a detail of the interlayer coupling mediated by strongly coupled aggregates containing two Cl⁻ anions, six H₂O molecules and one methanol molecule with two possible locations. For clarity the contacts mediated by the H_2O molecules were omitted in Figure S10. For each molecule those contacts involve only cations located in one of the layers. In $4.SCN.0.5H_2O$, the H_2O molecules display quite strong interactions with two cations located in the neighbouring layers, and the SCN⁻ anions display relatively strong interactions to cations in distinct layers, which anticipates a much more effective contribution of these interactions to the overall lattice connectivity than in 5.Cl.MeOH.2.5H₂O.

The strong DD interactions found in the salts displaying the Type II Dimer Layers arrangements are expected to lead to more rigid crystal packings than in type I. The lattice rigidity in **5.Cl.MeOH.2.5H₂O** and **4.SCN.0.5H₂O** is consistent with the fact that the cations remain trapped in the HS state (Figures 3 and 4) and fail to display SCO down to low temperatures.

Besides 5.Cl.MeOH.2.5H₂O and 4.SCN.0.5H₂O, another compound reported in Ref. [10], 6.Cl.2MeOH.0.5H₂O, displays a similar structure based on arrangements of interacting layers of dimers through extensive strong $\pi\pi$ interactions. 6.Cl.2MeOH.0.5H₂O shows interdimer intralayer interactions quite similar to those observed for 5.Cl.MeOH.2.5H₂O and 4.SCN.0.5H₂O, with extensive overlaps between the phenyl fragments of the ligands. The interlayer DD interactions in the crystal packing suggest that the structures are quite rigid. 6.Cl.2MeOH.0.5H₂O however, although HS at high temperatures, shows a sharp SCO process at 140 K with a 10 K hysteresis involving 50% of the cations [10].

In the crystal structure of **6.Cl.2MeOH.0.5H**₂**O** obtained at 100K there are two crystallographic distinct cations, one, A, shows a HS configuration and a second one, B, is LS. For both HS and LS cations in **6.Cl.2MeOH.0.5H**₂**O**, the intradimer and interdimer intralayer interactions are quite strong, comparable to those observed in the HS cations in the crystal structures of **5.Cl.MeOH.3H**₂**O** and **4.SCN.0.5H**₂**O**. In the case of the HS cations the interlayer DD interactions, DD^{iL}, are expected to be as strong as those observed for the HS cations of **5.Cl.MeOH.3H**₂**O** and **4.SCN.0.5H**₂**O**; however, the DD^{iL} interactions appear to be significantly weaker for LS cations, due to the much poorer overlap between the Ph fragments of both cations. The overlaps between the Ph fragments, corresponding to DD^{iL} interactions, are compared in Figure S11 for the HS cations of **5.Cl.MeOH.3H**₂**O**. Although the distinct arrangement of the cations suggests that in **6.Cl.2MeOH.0.5H₂O** the $\pi\pi$ interactions are somewhat weaker in the LS cation than in the HS cation, both in this compound and in **5.Cl.MeOH.2.5H₂O** and **4.SCN.0.5H₂O**, the complex variability in the interlayer DD interactions prevents a simple and straightforward interpretation of the fact that a partial transition occurs in the former compound.

2.2.5. Chain Layers

The crystal packings of **3.PF₆.MeCN**, **4.PF₆.H₂O** and **5.PF₆.1.5H₂O** are similar and consist of an arrangement of parallel chains of cations leading to a supramolecular configuration consistent with layers of cation chains. Within the chains the cations display very strong DD interactions resulting from the overlap of the 5-X-qsal fragments extending through the entire ligands. Short CH ... O contacts and even C-X ... π type II halogen bond contacts reinforce the strong $\pi\pi$ interactions. The more relevant parameters describing the intrachain, intra and interlayer DD contacts in the crystal structures of **3.PF₆.MeCN**, **4.PF₆.H₂O** and **5.PF₆.1.5H₂O** LS phases at 150 K are summarized in Table S5.

In 3.PF₆.MeCN and 4.PF₆.H₂O the cationic chains are parallel to *b*, while in 5.PF₆.1.5H₂O they are parallel to the *a* axis. The PF_6^- anions and the H₂O molecules or the MeCN molecules in 3.PF₆.MeCN, are located between the cationic chains, as illustrated in Figure 7 that shows a view of the crystal structure of 5.PF₆.1.5H₂O along the chain direction. Figure S12 illustrates the detail of the intrachain arrangement and the most relevant DD contacts in 5.PF₆.1.5H₂O.



Figure 7. Crystal structure of 5.PF₆.1.5H₂O along the *a* axis.

Besides the intrachain DD interactions, DD^{Ch}_1 and DD^{Ch}_2 , each cation shows a strong $\pi\pi$ interaction to another cation located in a neighbouring chain due to an overlap of the Qn fragments, reinforced by twofold CH ... π contacts. These strong interchain DD interactions, DD^L , give rise to strongly coupled layers of cations that are parallel to the *bc* plane in **3.PF_6.MeCN** and **4.PF_6.H_2O** or to the *ac* plane in **5.PF_6.1.5H_2O**.

Figure S13 illustrates the cation arrangement and interchain DD^L contacts of **5.PF₆.1.5H₂O**, where the cations that interact with those from the central chain are depicted in orange.

The combination of strong intra (DD^{Ch}_i) and interchain intralayer (DD^L) interactions in the **3.PF₆.MeCN**, **4.PF₆.H₂O** and **5.PF₆.1.5H₂O** salts is expected to lead to relatively rigid layers of cations, although less rigid in comparison with the Type II Dimer Layers due to differences in interlayer DD interactions. In the Chain Layers structure each of the [Fe(5-X-qsal)₂]⁺ cations show only weak interactions to three cations located in neighbouring layers. Figure S14 shows in the default colour scheme the cations that interact with a central one in **5.PF₆.1.5H₂O**. Those belonging to the same chain are depicted in light grey and the cation in orange corresponds to the one located in a neighbouring chain within the layer (contacts with these cations are omitted). The cation in violet and those in light blue are those that interact with the central cation and are located in the neighbouring layers. The stronger interlayer DD^{iL}₁ interactions concern the violet cation and consist of a two-fold CH ... I contact, along with a weaker CH ... π contact. The weaker, DD^{iL}₂, concerns halogen bond CI ... π contacts to two cations that are located in both neighbouring layers.

The PF_6^- anions show relatively strong interactions with several cations, mostly through CH ... F contacts. The MeCN molecules and the H₂O molecules display sizable interactions with the cations through either CH ... N or CH ... O contacts and also strong interactions with the anions through short OH ... F contacts in **4.PF₆.H₂O** and **5.PF₆.1.5H₂O** or slightly weaker CH ... F contacts in **3.PF₆.MeCN**. The indirect connectivity provided by the PF_6^- anions in the crystal structure of **5.PF₆.1.5H₂O** is illustrated in Figure S15, which portrays the five cations (D1-D5) that exhibit short contacts to one PF_6^- anion. Four of the cations are located in one layer, belonging to two neighbouring chains (D1and D2 in one chain and D3 and D4 in another) and a fifth, D5, is located in a distinct layer. The DA interactions are particularly strong to D1 and D2, slightly weaker to D3 and relatively weak to D4 and D5. The solvent molecules, H₂O in **4.PF₆.H₂O** and **5.PF₆.1.5H₂O** or MeCN in **3.PF₆.MeCN**, are found to display quite strong CH ... O or CH ... N interactions with two neighbouring cations, thus assisting the direct DD intrachain DD^{Ch}₁ interactions.

The reinforcement of the direct DD interactions (intrachain, DD^{Ch}_1 and DD^{Ch}_2 intralayer interchain, DD^L and interlayer, DD^{iL}_1) mediated by the PF₆ anions and H₂O molecules is illustrated in Figure S16. It is possible to observe that the indirect connectivity essentially reinforces the already strong intrachain and intralayer interactions, involving mostly cations that show already quite strong direct DD interactions between themselves, such as DD^{Ch}_1 , DD^{Ch}_2 and DD^L , while the reinforcement of the intralayer direct DD interactions is relatively modest in case of DD^{iL}_1 and non-existent for DD^{iL}_2 . In **3.PF₆.MeCN** and **4.PF₆.H₂O**, the indirect DAD connectivity is similar to that observed for **5.PF₆.1.5H₂O**, particularly concerning the interlayer connectivity. Unlike in **5.PF₆.1.5H₂O**, in these salts the interlayer DD^{iL}₂ interactions, corresponding to the interactions involving the blue cations in Figure S14, are also assisted by anion mediated interactions.

Furthermore, in **4.PF₆.H₂O**, the effect of the DA interactions is expected to be slightly enhanced, as in this salt there are two anions contributing to the reinforcement of DD^{iL_1} and the anions establish an additional DAD interaction to a second cation located in the neighbouring layer, reinforcing the overall interlayer connectivity. The indirect connectivity assistances to the direct DD intralayer, DD^L, and interlayer, DD^{iL}₁ and DD^{iL}₂, interactions regarding **3.PF₆.MeCN**, **4.PF₆.H₂O** and **5.PF₆.1.5H₂O** are compared in Figure S17.

A slight intrachain DD alternation is observed in the distances between the average planes of the interacting 5-X-qsal ligands (DD^{Ch}_1 and DD^{Ch}_2 , in Table S5). This seems to be mostly caused by the alternation of the interactions that are mediated either by the solvent molecules in DD^{Ch}_1 or by the PF_6^- anions in DD^{Ch}_2 . Since the connective path of the anions (C-H ... F-P-F ... H-C) is longer when compared to the solvent molecules (C-H ... N ... H-C or C-H ... O ... H-C), the DD contacts mediated by the anions (DD^{Ch}_2) lead to a larger separation in the intrachain. This effect appears to be slightly larger in

3.PF₆.MeCN that shows stronger DA interactions. The small differences observed on the intralayer DD contacts (DD^L, in Table S5), in particular for **3.PF₆.MeCN**, seems also to result from the stronger indirect connectivity provided by the PF_6^- anions and the solvent molecules in Figure S18.

The crystal packing and in particular the direct DD contacts are very similar and the strong intrachain and interchain intralayer DD interactions are expected to lead to rigid layer of cations, which seem to be responsible for the easy propagation of the lattice distortions and the SCO processes.

2.2.6. [Fe(5-X-qsal)₂]⁺ Based Salts Reported in the Literature

Most of the salts based on [Fe(5-X-qsal)₂]⁺ cations and small anions reported so far have crystal structures displaying arrangements of parallel chains of cations, resulting from an extensive overlap of the 5-X-qsal ligands. In these salts, as in the case of **3.PF₆.MeCN**, **4.PF₆.H₂O** and **5.PF₆.1.5H₂O**, the cation chains are organized as strongly coupled layers, through relatively strong interchain DD interactions, mostly associated with close contacts between the Qn fragments of cations located in neighbouring chains, typically with relatively modest interlayer DD interactions.

A large number of these salts are essentially HS at room temperature 1.[Fe(CN)₅NO].MeOH [11,12], 1.I₃ [13], 1.SCN [14,15], 1.SeCN [15], 3.SCN.MeOH [16], 4.NO₃.2MeOH [17], 5.CF₃SO₃.nPrOH [18] 5.CF₃SO₃.EtOH [18], 5.CF₃SO₃.iPOH [18], 5.CF₃SO₃.MeOH [19], 5.N(SO₂CF₃)₂ [20], 6.Cl.MeCN.H₂O [10], 7.Cl.4MeOH.H₂O [21], 7.ClO₄.MeOH [21] and 7.NO₃ [21]. In a few cases both LS and HS states coexist at room temperature 1.[Fe(CN)₅NO].2MeCN [12], 2.PF₆ [22], 2.SCN.MeOH [16], 4.SCN.MeOH [16], 6.PF₆ [23] or the [Fe(5-X-qsal)₂]⁺ cations present essentially a LS configuration 1.I [24], 1.SCN.DCM [15], 1.SeCN.DCM [25], 2.ClO₄ [22], 2.BF₄ [22], 2.NO₃ [22], 2.SO₂CF₃ [22], 5.CF₃SO₃.Me₂CO [18], 5.CF₃SO₃.MeCN [18], 6.BF4.MeOH [23] and 6.SCN.DCM [23].

In spite of the crystal packing similarities of these salts, the progress of the SCO transitions is quite diverse, ranging from single step gradual SCO processes, typical of weak cooperativity, to relatively sharp SCO processes related to strong cooperativity, either in a single step or in multistep SCO processes (Table S6). In a few cases, the SCO processes were irreversible, possibly due to solvent loss or other severe structural modification as in 1.SCN.DCM [15], 1.SeCN.DCM [25], 5.CF₃SO₃.EtOH [18] and 6.SCN.DCM [23]. In 1.[Fe(CN)₅NO].MeOH and 1.[Fe(CN)₅NO].2MeCN [11], upon cooling, half of the [Fe(5-X-qsal)₂]⁺ cations remain blocked in the HS state and in 7.Cl.4MeOH.H2O, 7.ClO₄.MeOH and 7.NO₃ [21] all the cations remain blocked in the HS state and no SCO transition is observed.

As in **3.PF₆.MeCN**, **4.PF₆.H₂O** and **5.PF₆.1.5H₂O**, most salts, where the $[Fe(5-X-qsal)_2]^+$ cations are essentially in the HS configuration at room temperature, the observed SCO behaviours are consistent with strong cooperativity. The parameters characterizing the SCO behaviour of these salts are summarized in Table S6.

Apart from the six salts with gradual SCO processes or blocked HS cations (1.[Fe(CN)₅NO].2MeCN [12], 5.CF₃SO₃.nPrOH [18], 5.CF₃SO₃.iPOH [18], 7.Cl.4MeOH.H₂O, 7.ClO₄.MeOH and 7.NO₃ [21]) and those with irreversible SCO behaviours (5.CF₃SO₃.EtOH [18] and 6.SCN.DCM [23]), the salts based on essentially HS [Fe(5-X-qsal)₂]⁺ cations at 295K (1.I₃ [13], 1.SCN [14,15], 1.SeCN [15], 3.SCN.MeOH [16], 4.NO₃.2MeOH [17], 5.CF₃SO₃.MeOH [19], 5.N(SO₂CF₃)₂ [20] and 6.Cl·MeCN.H₂O [10]) display cooperative SCO processes (Table S6). These salts exhibit the Chain Layers type of supramolecular configuration with crystal packings roughly similar to that described for 3.PF₆.MeCN, 4.PF₆.H₂O and 5.PF₆.1.5H₂O, also with strong interchain DD interactions (Qn \cdots Qn) and relatively modest interlayer DD interactions (Ph-X \cdots Ph-X or Qn \ldots Ph).

Gradual processes are only observed for three salts, **1.**[Fe(CN)₅NO].2MeCN [11], **5.**CF₃SO₃.nPrOH [18] and **5.**CF₃SO₃.iPOH [18]. In **1.**[Fe(CN)₅NO].2MeCN [11], the crystal structure obtained at 100 K, consists of layers based on alternated chains of HS and LS cations, with an overall arrangement similar to that described for **5.**PF₆.**1.5**H₂O. The main

distinctive feature of the crystal packing of 1.[Fe(CN)₅NO].2MeCN concerns the much stronger interlayer DD, mostly D^{HS}-D^{HS} and D^{LS}-D^{LS} interactions. These interactions in LS cations are due to a combination of $\pi\pi$ and twofold CH ... π short contacts between the Ph fragments of the ligands, while in the case of the highly distorted HS cations involve a variety of $\pi\pi$ and CH ... π contacts between a Ph fragment of one cation and Ph and Qn fragments from two neighbouring cations. In $1.[Fe(CN)_5NO].2MeCN$ the strengthening of intra and interlayer DD coupling seems to induce both the blocking of HS configuration in one of the cation sites and the gradual nature of the SCO process in the second cation site. 5.CF₃SO₃.nPrOH and 5.CF₃SO₃.iPOH [18] exhibit crystal structures also quite similar to the one previously described for 5.PF₆.1.5H₂O. However, in those salts the interchain intralayer interactions between the two Qn fragments are expected to be considerably weaker due to a much poorer overlap between the aromatic systems of the interacting ligands, which is expected to lead to softer cationic layers and less cooperative SCO behaviours. The $[Fe(5-tBu-qsal)_2]^+$ cations were found to remain blocked in the HS state in 7.Cl.4MeOH.H₂O, 7.ClO₄.MeOH and 7.NO₃ [21]. These compounds display crystal structures similar to those observed in 3.PF₆.MeCN, 4.PF₆.H₂O and 5.PF₆.1.5H₂O, also based on arrangements of layers composed by strongly coupled parallel chains of cations. However, the bulky *t*-Bu groups located in the periphery of the layers leave them in close proximity to those located in neighbouring layers. The blocking of the HS state in these salts most probably results from the strong repulsive interactions between the *t*-Bu groups, which prevent the structural rearrangements associated with the SCO processes.

The slight reduction in the sharpness of the SCO process observed for 1.I₃ [13], 3.SCN.MeOH [16], 3.PF₆.MeCN and 4.PF₆.H₂O appears to correlate with two different factors. First, the lower rigidity in the cationic layer observed for 3.SCN.MeOH, where the distance between the interacting Qn fragments is considerably larger than for the other salts. Second, the stronger interlayer interactions, either due to the direct DD interactions in 3.SCN.MeOH and 3.PF₆.MeCN or to the DAD assisted connectivity that seems to be more effective in 1.I₃, 3.SCN.MeOH and 4.PF₆.H₂O.

It appears that the Chain Layers type of crystal packing consisting of an arrangement of relatively rigid 2D layers of HS [Fe(5-X-qsal)₂]⁺ cations is quite promising in order to obtain cooperative SCO behaviours. However, the increase of the strength of interlayer interactions seem to constitute an effective perturbation, which leads to the loss of cooperativity or eventually to prevent the SCO processes in the case those interactions are too strong as in the Type II Dimer Layers. This seems to suggest that although these relatively rigid 2D cationic layers favour the propagation of the distortion of the cations associated with the SCO process throughout the lattice, the extremely strong interlayer interactions bring in a resistance to the propagation of that distortion.

It should also be noted that no correlation is observed between the type of supramolecular structures or the magnetic behaviour and the octahedral distortions of the coordination sphere of the Fe³⁺ (Table S7).

3. Materials and Methods

3.1. Synthesis

Commercial solvents were used without further purification unless otherwise stated. The purity of the complexes and their solvation state were checked by determining the carbon, hydrogen, nitrogen and sulfur content at the C2TN Elemental Analysis Service.

3.Cl.MeCN.H₂**O**—In dry conditions a methanolic solution (30 mL) of 5-chlorosalicylaldehyde (2.0 mmol, 313.13 mg) was added to a methanolic solution (70 mL) of 8-aminoquinoline (2.0 mmol, 288.35 mg). The resulting mixture was stirred for two hours at room temperature and changed its colour from pale yellow to yellow. Afterwards a methanolic solution (10 mL) of sodium methoxide (2.5 mmol, 135.05 mg) was added to the yellow mixture followed by a methanolic solution (20 mL) of iron (III) chloride anhydrous (1.0 mmol, 162.20 mg). The solution turned black and the volume was reduced to 50 mL. The resulting mixture was then placed at -20 °C overnight. A dark solid was recovered by filtration

(**3.Cl**) and washed with cold methanol (0.76 mmol, 497.60 mg). Elem anal. calcd: C, 58.70; H, 3.08; N, 8.55. Found: C, 58.53; H, 2.97; N, 8.51%. Yield: 76%. The material retrieved from the synthesis had an amorphous aspect and was successfully crystalized through slow evaporation of an acetonitrile solution resulting in **3.ClMeCN.H₂O**. Elem anal. calcd: C, 57.21; H, 3.53; N, 9.81. Found: C, 57.15; H, 3.61; N, 9.86%

3.ClO₄—To a methanolic solution (30 mL) of **3.Cl** (0.5 mmol, 327.37 mg) another methanolic solution (10 mL) of NaClO₄ (1.0 mmol, 122.44 mg) was added dropwise. The solution was kept at 60 °C with moderated stirring during the addition (60 min). After the addition was completed, the solution was left unstirred for another 60 min at 60 °C. The mixture was then slowly cooled to room temperature and placed at -20 °C for 12 h. Dark crystals of **3.ClO₄** were retrieved by filtration (0.35 mmol, 251.55 mg) and washed with cold diethyl ether. Yield: 70%. Elem anal. calcd: C, 53.46; H, 2.80; N, 7.80. Found: C, 53.57; H, 2.97; N, 7.72%

3.PF₆.MeCN—A methanolic solution (10 mL) of NaPF₆ (1.0 mmol, 167.95 mg) was slowly added to a hot (60 °C) methanolic solution of **3.Cl** (0.5 mmol, 327.37 mg) dropwise. The addition was performed over a period of 60 min. After the addition was completed, the solution was left unstirred for another 60 min at 60 °C. The mixture was then slowly cooled to room temperature and placed at -20 °C for 12 h. Dark powder (**3.PF₆**) was collected by filtration and washed with cold diethyl ether (0.405 mmol, 309.52 mg). Yield: 81%. Elem anal. calcd: C, 50.29; H, 2.63; N, 7.33. Found: C, 50.83; H, 2.94; N, 7.17%. The material retrieved from the synthesis had an amorphous aspect and was successfully crystalized through slow evaporation of an acetonitrile solution resulting in **3.PF₆.MeCN**. Elem anal. calcd: C, 50.71; H, 2.88; N, 8.70. Found: C, 50.75; H, 2.90; N, 8.68%.

3.BF₄—A methanolic solution (10 mL) of NaBF₄ (1.0 mmol, 109.79 mg) was slowly added to a hot (60 °C) methanolic solution of **3Cl** (0.5 mmol, 327.37 mg) dropwise. The addition was performed over a period of 60 min. After the addition was completed, the solution was left unstirred for another 60 min at 60 °C. The mixture was then slowly cooled to room temperature and placed at -20 °C for 12 h. Dark crystals (**3.BF**₄) were collected by filtration and washed with cold diethyl ether (0.395 mmol, 278.90 mg). Yield: 79%. Elem anal. calcd: C, 54.43; H, 2.86; N, 7.93. Found: C, 54.29; H, 3.01; N, 7.99%

3.BPh₄—A methanolic solution (10 mL) of NaBPh₄ (1.0 mmol, 342.22 mg) was slowly added to a hot (60 °C) methanolic solution of **3Cl** (0.5 mmol, 327.37 mg) dropwise. The addition was performed over a period of 60 min. After the addition was completed, the solution was left unstirred for another 60 min at 60 °C. The mixture was then slowly cooled to room temperature and placed at -20 °C for 12 h. Dark crystals (**3.BPh**₄) were collected by filtration and washed with cold diethyl ether (0.345 mmol, 323.78 mg). Yield: 69%. Elem anal. calcd: C, 71.67; H, 4.30; N, 5.97. Found: C, 71.51; H, 4.37; N, 6.03%

4.Cl.MeCN.H₂O—In dry conditions a methanolic solution (30 mL) of 5-bromosalicylaldehyde (2.0 mmol, 402.03 mg) was added to a methanolic solution (70 mL) of 8-aminoquinoline (2.0 mmol, 288.35 mg). The resulting mixture was stirred for two hours at room temperature and changed its colour from pale yellow to yellow. Afterwards a methanolic solution (10 mL) of sodium methoxide (2.5 mmol, 135.06 mg) was added to the yellow mixture followed by a methanolic solution (20 mL) of iron (III) chloride anhydrous (1.0 mmol, 162.20 mg). The solution turned black, and the volume was reduced to 50 mL. The resulting mixture was then placed at -20 °C overnight. A dark solid (**4Cl**) was recovered by filtration and washed with cold methanol (0.83 mmol, 617.22 mg). Yield: 83%. Elem anal. calcd: C, 51.68; H, 2.71; N, 7.53. Found: C, 51.25; H, 2.53; N, 7.67%. The material retrieved from the synthesis had an amorphous aspect and was successfully crystalized through slow evaporation of an acetonitrile solution resulting in **4.Cl.MeCN.H₂O**. Elem anal. calcd: C, 50.87; H, 3.14; N, 8.72. Found: C, 50.80; H, 3.02; N, 8.78%.

4.ClO₄—A methanolic solution (10 mL) of NaClO₄ (1.0 mmol, 122.44 mg) was slowly added to a hot (60 °C) methanolic solution of **4.Cl** (0.5 mmol, 371.82 mg) dropwise. The addition was performed over a period of 60 min. After the addition was completed, the solution was left unstirred for another 60 min at 60 °C. The mixture was then slowly

cooled to room temperature and placed at -20 °C for 12 h. Dark crystals (**4.ClO**₄) were collected by filtration and washed with cold diethyl ether (0.42 mmol, 339.20 mg). Yield: 84%. Elem anal. calcd: C, 47.59; H, 2.50; N, 6.94. Found: C, 47.62; H, 2.47; N, 7.00%.

4.SCN.0.5H₂O—A methanolic solution (10 mL) of KSCN (1.0 mmol, 97.18 mg) was slowly added to a hot (60 °C) methanolic solution of **4.Cl** (0.5 mmol, 371.82 mg) dropwise. The addition was performed over a period of 60 min. After the addition was completed, the solution was left unstirred for another 60 min at 60 °C. The mixture was then slowly cooled to room temperature and placed at -20 °C for 12 h. Dark powder (**4.SCN**) was collected by filtration and washed with cold diethyl ether (0.455 mmol, 348.65 mg). Yield: 91%. Elem anal. calcd: C, 51.73; H, 2.63; N, 9.14; S, 4.18. Found: C, 51.60; H, 2.42; N, 9.02; S, 4.72%. The material retrieved from the synthesis had an amorphous aspect and was successfully crystalized through slow evaporation of a methanol solution resulting in **4.SCN.0.5H₂O**. Elem anal. calcd: C, 51.12; H, 2.73; N, 9.03; S, 4.13. Found: C, 51.23; H, 2.92; N, 9.15; S, 4.02%.

4.PF₆.H₂O—A methanolic solution (10 mL) of NaPF₆ (1.0 mmol, 167.95 mg) was slowly added to a hot (60 °C) methanolic solution of **4.Cl** (0.5 mmol, 371.82 mg) dropwise. The addition was performed over a period of 60 min. After the addition was completed, the solution was left unstirred for another 60 min at 60 °C. The mixture was then slowly cooled to room temperature and placed at -20 °C for 12 h. Dark powder (**4.PF₆**) was collected by filtration and washed with cold diethyl ether (0.44 mmol, 375.38 mg). Yield: 88%. Elem anal. calcd: C, 45.05; H, 2.36; N, 6.57. Found: C, 45.21; H, 2.16; N, 6.68%. The material retrieved from the synthesis had an amorphous aspect and was successfully crystalized through slow evaporation of a methanol solution resulting in **4.PF₆.H₂O**. Elem anal. calcd: C, 44.12; H, 2.55; N, 6.43. Found: C, 44.05; H, 2.66; N, 6.57%

4.BF₄**.0.5H**₂**O**—A methanolic solution (10 mL) of NaBF₄ (1.0 mmol, 109.79 mg) was slowly added to a hot (60 °C) methanolic solution of **4.Cl** (0.5 mmol, 371.82 mg) dropwise. The addition was performed over a period of 60 min. After the addition was completed, the solution was left unstirred for another 60 min at 60 °C. The mixture was then slowly cooled to room temperature and placed at -20 °C for 12 h. Dark powder (**4.BF4**) was collected by filtration and washed with cold diethyl ether (0.465 mmol, 369.67 mg). Yield: 93%. Elem anal. calcd: C, 48.35; H, 2.54; N, 7.05. Found: C, 48.12; H, 2.40; N, 6.98%. The material retrieved from the synthesis had an amorphous aspect and was successfully crystalized through slow evaporation of a methanol solution resulting in **4.BF4.0.5H**₂**O**. Elem anal. calcd: C, 47.80; H, 2.63; N, 6.97. Found: C, 47.25; H, 2.50; N, 7.05%.

4.BPh₄—A methanolic solution (10 mL) of NaBPh₄ (1.0 mmol, 342.22 mg) was slowly added to a hot (60 °C) methanolic solution of **4.Cl** (0.5 mmol, 371.82 mg) dropwise. The addition was performed over a period of 60 min. After the addition was completed, the solution was left unstirred for another 60 min at 60 °C. The mixture was then slowly cooled to room temperature and placed at -20 °C for 12 h. Dark crystals (**4.BPh**₄) were collected by filtration and washed with cold diethyl ether (0.465 mmol, 369.67 mg). Yield: 80%. Elem anal. calcd: C, 67.47; H, 3.92; N, 5.45. Found: C, 65.21; H, 4.07; N, 5.39%.

5.Cl.MeOH.2.5H₂O—In dry conditions a methanolic solution (30 mL) of 5-iodosalicylaldehyde (2.0 mmol, 496.04 mg) was added to a methanolic solution (70 mL) of 8-aminoquinoline (2.0 mmol, 288.35 mg). The resulting mixture was stirred for two hours at room temperature and changed its colour from pale yellow to yellow. Afterwards a methanolic solution (10 mL) of sodium methoxide (2.5 mmol, 135.06 mg) was added to the yellow mixture followed by a methanolic solution (20 mL) of iron (III) chloride anhydrous (1.0 mmol, 162.20 mg). The solution turned black, and the volume was reduced to 50 mL. The resulting mixture was then placed at -20 °C overnight. Dark crystals (**5.Cl.MeOH.2.5H₂O**) were recovered by filtration and washed with cold methanol (0.82 mmol, 753.87 mg). Yield: 82%. Elem anal. calcd: C, 43.33; H, 3.20; N, 6.13. Found: C, 42.95; H, 3.16; N, 6.03%.

5.PF₆.1.5H₂O—A methanolic solution (10 mL) of NaPF₆ (1.0 mmol, 167.95 mg) was slowly added to a hot (60 °C) methanolic solution of **5.Cl.MeOH.2.5H₂O** (0.5 mmol, 461.86 mg) dropwise. The addition was performed over a period of 60 min. After the addi-

tion was completed, the solution was left unstirred for another 60 min at 60 °C. The mixture was then slowly cooled to room temperature and placed at -20 °C for 12 h. Dark crystals (5.PF₆.1.5H₂O) were collected by filtration and washed with cold methanol (0.33 mmol, 324.45 mg). Yield: 66%. Elem anal. calcd: C, 39.45; H, 2.38; N, 5.75. Found: C, 39.50; H, 2.28; N, 5.63%.

3.2. X-ray Crystallography

A summary of the crystal data, experimental details and refinement results are listed in Table S1. The X-ray diffraction, XRD, experiments were performed at 150 K with a Bruker AXS APEX CCD detector and a four-circle diffractometer using a graphite-monochromated Mo K α radiation source ($\lambda = 0.71073$ Å) in the ψ and ω scans mode. A semiempirical absorption correction was carried out using SADABS [26]. Data collection, cell refinement, and data reduction were done with the SMART and SAINT programs [27]. Structures were solved by direct methods using SIR97 [28] and refined by full-matrix least-squares methods using the program SHELXL97 [29] and a WINGX software package [30]. Nonhydrogen atoms were refined with anisotropic thermal parameters, whereas H atoms were placed in idealized positions and allowed to refine riding on the parent C atom. Molecular graphics were prepared using MERCURY [31]. Data are deposited at the Cambridge Crystallographic Data Centre with code numbers CCDC 124024, 2124025, 2124026, 2124027, 2124028, 2124030, 2124031, 2124032, 2124033, 2124034, 2124035 and 2124036.

3.3. Magnetic Characterization

Magnetic measurements on compounds were performed in a S700X SQUID magnetometer with a 7 T magnet (Cryogenic Ltd., London, UK) using polycrystalline samples inserted in gelatine capsules. The temperature dependences of the magnetic susceptibility in the temperature range 5 – 320 K, were measured in step mode under magnetic fields of 1 T for compounds 3 (X = Cl), and 4 (X = Br) and 0.05 T for compounds 5 (X = I), using the same rate on the heating/cooling cycles.

For each experimental point, the temperature of the sample was stabilized for at least 5 min. The paramagnetic susceptibility, $\chi_P T$, was deduced from the experimental magnetization data after correction of the diamagnetism of the sample holder and the diamagnetic susceptibility contribution of each compound, estimated from the tabulated Pascal constants. For the different set of compounds, the correspondent diamagnetic susceptibilities, χ_D , were the following:

3 (X = Cl): χ_D (**3.ClO**₄) = -545.0×10^{-6} emu/mol, χ_D (**3.BF**₄) = -466.6×10^{-6} emu/mol, χ_D (**3.PF**₆·**MeCN**) = -494.9×10^{-6} emu/mol, χ_D (**3.ClMeCNH**₂**O**) = -444.5×10^{-6} emu/mol, and χ_D (**3.BPh**₄) = -629.7×10^{-6} emu/mol; **4** (X = Br): χ_D (**4.ClO**₄) = -371.9×10^{-6} emu/mol, χ_D (**4.BF**₄·**H**₂**O**) = -500.6×10^{-6} emu/mol, χ_D (**4.ClMeCNH**₂**O**) = -428.9×10^{-6} emu/mol, χ_D (**4.ClMeCNH**₂**O**) = -428.9×10^{-6} emu/mol, χ_D (**4.BPh**₄) = -650.7×10^{-6} emu/mol, and χ_D (**4.SCN.05H**₂**O**) = -494.6×10^{-6} emu/mol; **5** (X = I): χ_D (**5.Cl.MeOH.2.5H**₂**O**) = -522.3×10^{-6} emu/mol.

4. Conclusions

In this work we have characterized the structure and magnetic properties of 13 compounds based on the $[Fe(5-X-qsal)_2]^+$ cation (X = Cl, Br and I). Four structural motives emerged: Dimer Chains, Dimer Layers (Type I and Type II) and Chain Layers. The compounds that share the same structural motive reveal similar magnetic behaviours from room temperature down to 4K.

A Dimer Chains type of structure characterized the compounds with the weakest connectivity. They are organized as isolated chains with no interchain cation–cation (DD) connectivity and a weak intrachain or interdimer connectivity. These compounds are LS up to around 250 K, where a broad spin transition starts to occur. The lack of connectivity between the cationic centres should be the source for the lack of cooperativity of the cations and the softness of the structural network.

The compounds characterized with the Type I Dimer Layers structure, based on arrangements of parallel layers of interacting cation dimers, are also LS at around 250 K but display some diversity in the magnetic behaviour. Some show no change of the $\chi_P T$ up to room temperature while others start to exhibit spin transition with various degrees of sharpness/broadening. These differences can be related to a degree of variability in the interlayer DD connectivity as the relatively weak intralayer connectivity of these compounds has few dissimilarities.

The Type II Dimer Layers compounds exhibit the highest degree of intra- and interlayer connectivity. The interlayer interactions are so strong that they intensify the rigidity of the structural network to a point where the transition from HS to LS states is blocked. In fact the compounds with this structure type remain in the HS state in the 295–4 K temperature range.

The Chain Layers structural motive shows significant intralayer interactions but weak interlayer interactions. These interactions allow for a relatively rigid layer of cations, which can induce easy propagation of the lattice distortions and more or less sharp SCO processes. The vast majority of the $[Fe(5-X-qsal)_2]^+$ based compounds reported in the literature show SCO transitions and their detailed structural analysis reveal that they are characterized as Chain Layers. The only Chain Layers compounds that remain blocked in the HS state at all temperatures are those based on the $[Fe(5-tBu-qsal)_2]^+$ cation. In these compounds the extreme steric hindrance provided by the bulky *tert*-butyl groups located in the periphery of the layers, may be the key factor for the HS trapping, as already theorized by the authors that first characterized these compounds.

The main structural features determining the SCO behaviour of [Fe(5-X-qsal)₂]⁺ based salts were surveyed in the present study. Although it is still difficult to predict if a specific type of ligand substituent or counter ion leads to a desired supramolecular configuration, the categorization of these materials according to these supramolecular arrangements allows narrowing the pool of possible chemical combinations in order to achieve a desired arrangement. Further work is in progress, aiming to build such a library of compounds correlating supramolecular structure and magnetic behaviour, from which trends regarding the combination of ligands, counter ions and solvating molecules may emerge. The analysis of the data from this library will allow pre-selecting the best candidates for a desired magnetic behaviour, thus reducing laboratory time for the preparation and characterization of these materials, replacing the "bulk synthesis" approach by a more efficient "synthesis by design".

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/magnetochemistry8010001/s1, Figure S1: Intrachain arrangements of the cations and DD contacts in the crystal structure of 4.BPh₄, Figure S2: Top view of 4.BPh₄ showing the most relevant DA contacts arrangement around one anion with cations from three neighbouring cationic chains. The cations in orange show $\pi\pi$ contacts to the Ph groups of the anion, those in light green show strong CH ... π contacts to the anion and the ones depicted in light blue display weaker DA contacts, Figure S3: View of the crystal structure of **3.Cl.MeCN.H₂O** along *b*. The cations belonging to one of the cationic layers are depicted in dark blue, Figure S4: Arrangement of the cations, anions and H₂O molecules within one layer of **3.Cl.MeCN.H**₂**O**. The four cations in orange show $\pi\pi$ DD interactions with the central cationic dimer, Figure S5: View of the interlayer DD contacts and arrangements of the [Fe(5-X-qsal)₂]+ cations relative to a central cation (in the default colour scheme) for **3.Cl.MeCN.H₂O** (a), $4.BF_4.H_2O$ (b) and $3.ClO_4$ (c), Figure S6: Indirect (D ... X ... D) connectivity mediated by one strongly coupled Cl^{-...} H₂O pair in 3.Cl MeCN H₂O, Figure S7: View of the crystal structure of 5.Cl.MeOH.3H₂O along c. The cations belonging to one of the cationic layers are depicted in dark blue, Figure S8: Arrangement of the cations within one layer of 5.Cl.MeOH.3H₂O. The four cations in orange show strong $\pi\pi$ DD interactions with the central cationic dimer. The cations in darker orange correspond to cations with even stronger DD interactions, DD^{iL}_{1} , where the $\pi\pi$ interactions are reinforced by strong twofold CH \dots π interactions, Figure S9: View of the DD contacts and arrangements of the [Fe(5-I-qsal)₂]⁺ cations relative to a central cation (in the default colour scheme) for **5.Cl.MeOH.3H**₂**O**, Figure S10: Indirect D ... X ... D connectivity in **5.Cl.MeOH.3H**₂**O** mediated by strongly coupled aggregates containing two Cl⁻ anions, six H₂O molecules and one methanol

molecule with two possible locations. In one of those locations the MeOH atoms are depicted in light grey and its contacts are omitted, Figure S11: View of the overlaps between the Ph-X groups in the DD interlayer interactions, DD^{iL}, in 5Cl.MeOH.3H₂O (a), 4SCN.0.5H₂O (b), 6Cl.2MeOH.0.5H₂O HS (c) and 6Cl.2MeOH.0.5H₂O LS (d).. View of the overlaps between the Ph-X groups in the DD interlayer interactions, DD^{iL}, in 5Cl.MeOH.3H₂O (a), 4SCN.0.5H₂O (b), 6Cl.2MeOH.0.5H₂O HS (c) and 6Cl.2MeOH.0.5H₂O LS (d), Figure S12: Detail of the intrachain arrangement and the most relevant DD contacts in 5.PF₆.1.5H₂O, Figure S13: Arrangement of three cationic chains within one layer in 5PF₆.1.5H₂O. The cations in central chain are in the "ball and stick mode", while the cations of the other two are represented in the "stick mode". The cations in orange displays strong $\pi\pi$ interactions with cations from the central chain further reinforced by twofold CH \dots π interactions, Figure S14: View in the default colour scheme of the interlayer DD contacts and arrangements of the $[Fe(5-I-qsal)_2]^+$ cations relative to a central cation for 5.PF₆.1.5H₂O. Only the cations depicted in light blue and in violet belong to the neighbouring layers, those in light grey and orange are located in the same layer as the central cations (the contacts involving these cations are omitted for clarity), Figure S15: Indirect (D ... A ... D) connectivity mediated by one PF_6^- anion in 5.PF₆.1.5H₂O. The anion shows interactions to four cations (D1-D4) in one layer and to another cation (D5) located in a neighbouring layer, Figure S16: Indirect connectivity assistance to the direct DD intrachain, (a) DD^{Ch}_1 and (b) DD^{Ch}_2 , intralayer (c) DD^L and interlayer (d) DD^{L}_1 interactions in **5.PF_6.1.5H_2O**. DD^{Ch}_{1} is assisted by a pair of interactions mediated by the H₂O molecules and for DD^{Ch}_{2} , DD^{L} and DD^{iL} the DD interactions are assisted by a pair of DAD connections Figure S17: Intrachain indirect connectivity mediated by the solvent molecules and anions to the direct DD interactions (DD^{Ch}₁) and DD^{Ch}₂) in **3.PF₆.MeCN** (a and d), **4.PF₆.H₂O** (b and e) and **5.PF₆.1.5H₂O** (c and f), Figure S18: Indirect DAD connectivity assistance to the direct DD intralayer (DD^L) and interlayer (DD^{iL}_1 and DD^{iL}₂) interactions regarding **3.PF₆.MeCN** (a, d and g), **4.PF₆.H₂O** (b e and h) and **5.PF₆.1.5H₂O** (c, f and i), Table S1: Summary of the crystal data, experimental details and refinement results, Table S2: Key parameters describing the DD contacts in the crystal structures of 3.BPh₄ and 4.BPh₄, with the Dimer Chains supramolecular configuration, Table S3: Key parameters describing the DD contacts in the crystal structures of the salts with type I Dimer Layers supramolecular configuration, Table S4: Key parameters describing the DD contacts in the crystal structures of the salts with type II Dimer Layers supramolecular configuration, Table S5: Key parameters describing the DD contacts in the crystal structures of 3.PF₆.MeCN, 4.PF₆.H₂O and 5.PF₆.2H₂O, with the Chain Layers supramolecular configuration, Table S6: Summary of the parameters characterizing the SCO behaviour of the salts with the Chain Layers supramolecular configuration and with HS configurations at room temperature, Table S7 Summary of the parameters characterizing the octahedral distortion (Σ and θ).

Author Contributions: Conceptualization, B.J.C.V., L.C.J.P., V.d.G. and J.C.W.; methodology, B.J.C.V., L.C.J.P., V.d.G. and J.C.W.; validation, B.J.C.V., L.C.J.P., V.d.G., I.C.S., A.C.C. and J.C.W.; formal analysis, B.J.C.V., L.C.J.P., I.C.S., A.C.C. and J.C.W.; investigation, B.J.C.V., L.C.J.P., V.d.G. and J.C.W.; resources, B.J.C.V., L.C.J.P., V.d.G., I.C.S., A.C.C. and J.C.W.; writing—original draft preparation, B.J.C.V., L.C.J.P., V.d.G. and J.C.W.; writing—review and editing, B.J.C.V., L.C.J.P. and J.C.W.; supervision B.J.C.V., L.C.J.P., V.d.G. and J.C.W.; project administration, B.J.C.V. and J.C.W. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: CCDC-2124024, 2124025, 2124026, 2124027, 2124028, 2124029, 2124030, 2124031, 2124032, 2124033, 2124034, 2124035 and 2124036 contain the supplementary crystallographic data for $3.BF_4$, $3.ClO_4$, $3.PF_6.MeCN$, $3.Cl.MeCN.H_2O$, $4.Cl.MeCN.H_2O$, $4.ClO_4$, $4.BF_4.0.5H_2O$, $4.PF_6.H_2O$, $4.SCN.0.5H_2O$, $5.Cl.MeOH.2.5H_2O$, $5.PF_6.1.5H_2O$, $3.BPh_4$, and $4.BPh_4$, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (accessed on 26 November 2021).

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