Anion Influence on Spin State in Two Novel Fe(III) Compounds: [Fe(5F-sal$_2$333)]X

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Abstract: Structural and magnetic data on two iron (III) complexes with a hexadentate Schiff base chelating ligand and Cl$^{-}$ or BPh$_4^-$ counterions are reported. In the solid state, the Cl$^{-}$ complex [Fe(5F-sal$_2$333)]Cl, 1, is high spin between 5–300 K while the BPh$_4^-$ analogue [Fe(5F-sal$_2$333)]BPh$_4$, 2, is low spin between 5–250 K, with onset of a gradual and incomplete spin crossover on warming to room temperature. Structural investigation reveals different orientations of the hydrogen atoms on the secondary amine donors in the two salts of the [Fe(5F-sal$_2$333)]$^+$ cation: high spin complex [Fe(5F-sal$_2$333)]Cl, 1, crystallizes with non-meso orientations while the spin crossover complex [Fe(5F-sal$_2$333)]BPh$_4$, 2, crystallizes with a combination of meso and non-meso orientations disordered over one crystallographic site. Variable temperature electronic absorption spectroscopy of methanolic solutions of 1 and 2 suggests that both are capable of spin state switching in the solution.

Keywords: Fe(III) coordination complexes; hexadentate ligand; Schiff base; spin crossover; UV-Vis spectroscopy; SQUID; EPR spectroscopy

1. Introduction

Spin crossover complexes (SCO) constitute an interesting class of materials exhibiting interconversion between different electronic states by varying temperature or pressure or by light. Many potential applications have been suggested for their use, including their utilization in data storage, sensors, and display technologies. Fe(II) SCO complexes are more studied in the literature in comparison to Fe(III), and spin crossover is observed only very rarely in Mn(III). We have studied the effect of ligand flexibility on spin state choices in both Fe(III) and Mn(III) using some of the families of hexadentate Schiff base ligands of the type shown in Figure 1 [1–6].

Such chelates are formed by a condensation reaction of linear tetra-amines and substituted salicylaldehydes, and our studies to date have focused mostly on complexes from the “222”, “323”, and “232” series, where the numbers indicate the number of methylene groups connecting adjacent nitrogen atoms. Here, we show the results of our studies into the effect of the longer chain ligand formed from the “333” polyamine on spin state choices in the resultant Fe(III) complexes. The results of our studies into spin state choices with various metal–ligand combinations, including those reported here, are summarized in Table 1.
mon in the red by binding to the type of N

2019 Crystals nanowires [21]. We have also observed SCO in Fe(III) complexes from the R-Sal

Langmuir-Blodgett film formation with amphiphilic complexes [6,29], and preparation of templated
due to the ease of derivatization which has led to the synthesis of ionic liquids [27], liquid crystals [28],

R-Sal in Table 1 as LS.

SCO in Mn(III) [3] and several crystal engineering studies on such complexes followed [1,2,9,11,13].

four ligand types. However in 2006, our group discovered that the R-Sal

lightscope which has led to the synthesis of ionic liquids [27], liquid crystals [28],

In Figure 1, (a) Depiction of hexadentate ligands with different chain lengths and (b) resulting coordination
genometry around a trivalent 3-D metal ion.

Table 1. Donor orientations and spin states for Fe(III) and Mn(III) complexes with selected hexadentate
Schiff base ligands. (LS = low spin; HS = high spin; SCO = spin crossover).

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>R-Sal2-222</th>
<th>R-Sal2-232</th>
<th>R-Sal2-323</th>
<th>R-Sal2-333</th>
</tr>
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<tbody>
<tr>
<td>O</td>
<td>cis</td>
<td>cis</td>
<td>trans</td>
<td>trans</td>
</tr>
<tr>
<td>Namine</td>
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<td>cis</td>
</tr>
<tr>
<td>Nilmine</td>
<td>trans</td>
<td>trans</td>
<td>cis</td>
<td>cis</td>
</tr>
</tbody>
</table>

* G.G. Morgan unpublished results.

In both Fe(III) and Mn(III) complexes, three possible spin arrangements are possible in
mononuclear complexes. These comprise the fully spin paired or low spin (LS) arrangement, the fully
unpaired or high spin (HS) combination, and a mixture of paired and unpaired, typically termed the
intermediate spin (IS) choice. In Fe(III) complexes, these descriptions (LS, IS, and HS) are regularly
and accurately used. However, due to the prevalence of the S = 2 HS state in Mn(III), any other spin
state was historically considered an oddity and the use of “LS” to describe the S = 1 state became
common usage. In Table 1, “LS” is therefore used to describe the S = 1 state as is common in the
literature. The true low spin S = 0 state has not yet been observed in any manganese (III) complex.
Table 1 summarizes the results of our investigations on spin state choices for Fe(III) and Mn(III) in
a range of coordination geometries engineered by binding to the type of N4(O2)− chelating ligands
depicted in Figure 1. The first point to note is that the S = 2 state is dominant for Mn(III) across the
four ligand types. However in 2006, our group discovered that the R-Sal2-323 ligand family promoted
SCO in Mn(III) [3] and several crystal engineering studies on such complexes followed [1,2,9,11,13].

Although most of these SCO transitions occur below room temperature, some Mn(III) complexes of the
R-Sal2-323 ligand family also persist in the S = 1 state up to room temperature, and these are defined
in Table 1 as LS.

In contrast to manganese, iron (III) shows a range of observed spin states with the four ligand types
highlighted in Table 1. It has long been known that the R-Sal2-222 ligand family promotes SCO in iron(III)
in addition to stabilizing both HS and LS complexes across a temperature range [15–24]. The Fe(III)
R-Sal2-222 complexes have, in recent years, been extensively developed as new switchable materials
due to the ease of derivatization which has led to the synthesis of ionic liquids [27], liquid crystals [28],
Langmuir-Blodgett film formation with amphiphilic complexes [6,29], and preparation of templated
nanowires [21]. We have also observed SCO in Fe(III) complexes from the R-Sal2-232 ligand type [4],
but the majority of this class of compound remains HS from room temperature down to 5 K. In contrast, the R-Sal$_2$323 ligand type has been shown by Reedijk [26] to promote the LS state in iron (III).

Less is known, however, about the iron (III) spin state preferences that would be conferred by coordination to the R-Sal$_2$333 ligand type. An early work by Ito and co-workers [25] reported the solid-state and methanolic solution-state properties of the nitrate salts of the iron (III) complexes with R-Sal$_2$323 and R-Sal$_2$333 ligands, where R was hydrogen [25]. In the solid state, the iron (III) complex with H-Sal$_2$323 was LS over the measured range, while that with H-Sal$_2$323 was HS. Ito also used the Evans’ NMR technique and variable temperature electronic absorption spectroscopy to monitor the spin state of both complexes in methanol solution. The LS complex with H-Sal$_2$323 showed no change in solution, i.e., remained LS with only weak thermochromism in methanol. The HS complex with H-Sal$_2$333, however, demonstrated a strong temperature dependence as shown by both NMR and UV-Vis absorption and a clear isosbestic point is apparent in the electronic absorption spectra recorded between 268–322 K.

At the outset of this work, the nitrate salt of the Fe(III) complex with H-Sal$_2$333 reported by Ito in 1983 was the only ferric complex with this ligand type in the literature. Given that SCO for this complex was detected in solution, the R-Sal$_2$333 ligand type was deemed to constitute a good basis for further investigations into the choice of Fe(III) spin state when coordinated to this ligand type. Here, we report two new Fe(III) complexes with 5-Fluoro-Sal$_2$333 in two crystalline lattices [Fe(5F-sal$_2$333)]Cl, 1, and [Fe(5F-sal$_3$333)]BPh$_4$, 2. Both compounds were examined by single crystal diffraction, and an important and new result to emerge from this study was the variation in orientation of the hydrogen atoms on the two secondary amine nitrogen atoms in the 9-carbon length ligand backbone between non-meso (Type A) and a disordered combination of meso and non-meso co-crystallized on the same site (Type B).

To recall the definition of meso and non-meso in stereochemistry, there is the special case where a molecule exhibits two stereo centres but is achiral, since one conformation shows an intramolecular C$_s$-symmetry which is then defined as the meso form. By using a hexadentate Schiff base ligand formed from condensation of a substituted salicylaldehyde and N,N’-bis(3-aminopropyl)-propylenediamine (333) and by forming the iron (III) complex, the binding amine nitrogen atoms, N2 and N3 (shown in turquoise in Figure 2), can have their attached hydrogen atoms either both pointing in the same direction leading to the meso form or in opposite directions, leading to the non-meso form. The results of our structural studies into the iron (III) complexes 1 and 2 reveal two structural types (Figure 2): (i) pure non-meso (Type A) and (ii) a disordered combination of meso and non-meso, which co-crystallize on the same Fe site (Type B).

![Figure 2](image-url)  
*Figure 2.* Hydrogen atoms at the amine nitrogen of the R-Sal$_2$333 backbone, forming the non-meso Type A form (Left) and meso form (Middle) of the ligand. Co-crystallization of both modes (Right) was observed in the tetraphenylborate complex 2 and this crystallization mode was termed Type B.
2. Materials and Methods

2.1. Materials and Instrumentation

All chemicals used were supplied as described: N,N’-Bis-(3-aminopropyl)-1,3-propandiamine (Sigma-Aldrich, 90%), 5-fluorosalicylaldehyde (Fluorochem, 98%), iron (III) chloride hexahydrate (Sigma-Aldrich, 97%), sodium tetraphenylborate (Sigma-Aldrich, ≥ 99.5%), acetonitrile (Fisher Scientific, 99.8%), and ethanol (Fisher Scientific, ≥ 99.5%). Elemental analysis was recorded on an Exeter Analytical CE-440 CHN analyzer, for Carbon, Hydrogen, and Nitrogen. Infrared spectra were recorded using a Bruker Alpha Platinum attenuated total reflection (ATR) spectrometer. Mass spectrometry was recorded using a Waters 2695 separations module electrospray spectrometer on acetonitrile solutions of 1 and 2.

2.2. Synthesis

The synthesis of compounds 1 and 2 is straightforward, and the complexes were recovered in varying yields. Solid 5-fluorosalicylaldehyde (1.0 mmol) was added to a solution of N,N’-bis(3-aminopropyl)-1,3-propandiamine (0.5 mmol) in 50:50 ethanol/acetonitrile (15 mL), causing a yellow color to form. After stirring for 15 min, solid iron (III) chloride hexahydrate (0.5 mmol) was added whereupon the solution turned dark black. For synthesis of complex 2, solid sodium tetraphenylborate (0.5 mmol) was then added. For both complexes 1 and 2, the dark solution was stirred at room temperature for 30 min, then gravity filtered and allowed to stand for slow evaporation for 3–4 days. Dark purple crystals were collected for both compounds 1 (ca. 15%) and 2 (ca. 20%) which were suitable for single crystal X-ray structural analysis.

Complex 1, [Fe(5F-sal$_2$333)]Cl: Elemental analysis calculated for C$_{23}$H$_{28}$N$_4$O$_2$F$_2$ClFe. Calculated: C 52.94, H 5.41, and N 10.74. Found: C 52.86, H 5.37, and N 10.72. Mass Spec: 486.33 ES$^+$. Complex 2, [Fe(5F-sal$_2$333)]BPh$_4$: Elemental analysis calculated for C$_{47}$H$_{48}$BN$_4$O$_2$F$_2$Fe. Calculated: C 67.33, H 5.77, and N 6.68. Found: C 67.10, H 5.75, and N 6.57. Mass Spec: 519.24 ES$^+$. 

2.3. Single-Crystal X-Ray Structure Determinations

X-ray crystallography was carried out on suitable single crystals using an Oxford Supernova diffractometer (Oxford Instruments, Oxford, United Kingdom). Datasets were measured using monochromatic Cu-Kα and Mo-Kα radiation for 1 and 2 respectively and corrected for absorption. The temperature was controlled with an Oxford Cryosystem instrument. A complete dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical absorption correction based on the shape of the crystal was performed [30]. All structures were solved by dual-space direct methods (SHELXT) [31] and refined by full matrix least-squares on F$^2$ for all data using SHELXL-2016 [31]. The hydrogen atoms attached to nitrogen were located in the difference Fourier map and allowed to refine freely. All other hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic displacement parameters were fixed to 1.2 times the equivalent one of the parent atom. Anisotropic displacement parameters were used for all non-hydrogen atoms. Crystallographic details for both compounds are summarized in Table A1 (Appendix A) and crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-1884365 (1, 100 K), CCDC-1884366 (2, 100 K), and CCDC-1884367 (2, 293 K).

2.4. Magnetic Measurements

The magnetic susceptibility measurements were obtained using a Quantum Design Magnetic Property Measurement System, the MPMS-XL SQUID Magnetometer (Quantum Design, San Diego, CA, USA) operating between 5 and 300 K. Direct current (DC) measurements were performed on a polycrystalline sample of 11.1 mg of complex 1 and of 11.9 mg of complex 2. Each sample was wrapped in a polyethylene membrane, and susceptibility data were collected at 0.1 T between 5–300 K.
in cooling and warming mode. The magnetization data was collected at 100 K in order to check for ferromagnetic impurities, which were found to be absent in the samples. Diamagnetic corrections were applied to correct for contribution from the sample holder, and the inherent diamagnetism of the sample was estimated with the use of Pascal’s constants.

2.5. UV-Vis and Electron Paramagnetic Resonance (EPR) Spectroscopy

UV-Vis solution spectra of [Fe(5F-sal$_2$333)]Cl, 1, and [Fe(5F-sal$_2$333)]BPh$_4$, 2, were recorded on an Agilent UV-Vis spectrometer fitted with an Oxford Instruments cryostat insert. Solid state variable temperature EPR spectra were recorded on a Magnettech X-band EPR spectrometer (Freiberg Instruments, Freiberg, Germany) (9.430 GHz) at variable temperatures. A modulation amplitude of 0.7 mT was used in conjunction with a microwave power of 0.1 mW and a gain of 10.

3. Results

3.1. Synthetic Route

Synthesis of [Fe(5F-sal$_2$333)]Cl, 1, and [Fe(5F-sal$_2$333)]BPh$_4$, 2, was achieved in a facile reaction by condensation of N,N’-bis(3-aminopropyl)-1,3-propanediamine (333) with two equivalents of 5-fluorosalicylaldehyde followed by addition of hydrated iron (III) chloride (complex 1) with further addition of sodium tetraphenylborate counterion in the case of complex 2, Scheme 1. The filtered reaction mixture on slow evaporation yielded complexes 1 and 2 as dark purple crystals.

Both complexes were characterized by mass spectrometry, elemental analysis, IR spectroscopy, single crystal diffraction, and SQUID magnetometry. Both showed a characteristic C=N stretch at 1611 cm$^{-1}$, confirming formation of the Schiff base and a resonance at 3051 cm$^{-1}$ in the case of 2 and confirming the anion methathesis to the tetraphenylborate counterion. Elemental analysis confirmed the purity of both crystalline samples.

3.2. Structural Analysis

For crystallographic details for complexes 1 and 2, see Table A1 (Appendix A). Complex 1 crystallized in orthorhombic and non-centrosymmetric space group Pccn where the asymmetric unit comprises half of one complex [FeL]$^+$ cation and half of one chloride counterion. The two halves of the complex cation are related by a C2 axis which passes through the central carbon of the middle propylene chain on the ligand backbone. The well-ordered non-meso arrangement of the amine on N2 is illustrated in Figure 3.

The chloride counterion within the crystal lattice exhibits short contacts to the hydrogen atoms of the amine nitrogen atoms of the ligand backbone, which leads to the formation of a 1D-chain, Figure 4. Bond length data at 100 K are in line with an S = 5/2 spin state assignment at this temperature as the three bond types, Fe-O$_{phenolate}$ (1.9426(9) Å), Fe-N$_{amine}$ (2.1398(11) Å), and Fe-N$_{amine}$ (2.1837(11) Å) are all typical for the HS state with these types of donor [21].
The order was modelled meso well-ordered BPh crystals 2019 different crystal, after analysis of the SQUID data which revealed the change in spin state between amine nitrogen positions co-crystallized on single site are clear, Figure 5.

The amine nitrogen atoms over two positions. Each component of the disorder was modelled separately within the crystal structure crystallize on a single site leading to ordered BPh unit at 100 K comprises one full occupancy disordered [FeL]+ on both amine nitrogen positions co on both amine nitrogen positions co separately within the crystal structure the amine nitrogen atoms over two positions. Each component of the dis the amine nitrogen atoms of the ligand backbone, which leads to the formation of a 1D chain, Figure 4.

The chloride counterion within the crystal lattice exhibit the relationship of the two halves of the complex. The chloride counterion within the crystal lattice exhibit the relationship of the two halves of the complex.

Bond length data at 100 K are in line with other LS complexes with comparable donors [21]. At 293 K [Fe(5F-sal333)]Cl, 1.

Complex 2, [Fe(5F-sal333)]BPh₄ crystallizes in triclinic space group P-1 where the asymmetric unit at 100 K comprises one full occupancy disordered [FeL]+ cation and one full occupancy well-ordered BPh₄− anion, Figure 5. Both the meso and non-meso orientations of the amine hydrogens co-crystallize on a single site leading to the disorder of most of the nine propylene carbons and one of the amine nitrogen atoms over two positions. Each component of the disorder was modelled separately within the crystal structure, and the meso and non-meso orientations of the hydrogen atoms on both amine nitrogen positions co-crystallized on single site are clear, Figure 5.

Structural data for complex 2 was collected initially at 100 K and some months later at 293 K on a different crystal, after analysis of the SQUID data which revealed the change in spin state between the two temperatures. Bond length data, Table 2, indicate a LS state at 100 K with markedly shorter bond lengths for the three bond types, Fe-Ophenolate (ca. 1.86 Å), Fe-Nimine (ca. 1.95 Å), and Fe-Namine (with disorder component ca. 2–2.10 Å) than those for HS complex 1 at the same temperature. The bond lengths for 1 at 100 K are in line with other LS complexes with comparable donors [21]. At 293 K SQUID data for 2 indicate a small HS fraction, and this is reflected in the small increase in bond...
lengths compared with those at 100 K: Fe-Ophenolate (ca. 1.87 Å), Fe-Nimine (ca. 1.97 Å), and Fe-Namine (with disorder component ca. 2–2.15 Å), suggesting that the majority of sites remain LS. The absence of hydrogen bond donors or acceptors on the BPh₄⁻ counterions and the large distance between the complex cations means no hydrogen bond network emerges to tether the complexes together as was the case with the fully HS analogue, complex 1. The absence of hydrogen bonding in complex 2 may contribute to the different spin state choices in the two complexes.

Figure 5. View of asymmetric unit of [Fe(5F-sal_333)]BPh₄, 2, showing (a) disorder of three propylene groups in ligand backbone due to co-crystallization of meso and non-meso forms; view of (b) the meso form and (c) the pure non-meso orientation.

<table>
<thead>
<tr>
<th></th>
<th>[Fe(5F-sal_333)]Cl</th>
<th>Fe-Donor</th>
<th>[Fe(5F-sal_333)]BPh₄</th>
<th>[Fe(5F-sal_333)]BPh₄</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>(1) 100 K</td>
<td>(2) 100 K</td>
<td>(2) 293 K</td>
<td></td>
</tr>
<tr>
<td>Fe-Ophenolate</td>
<td>1.9426(9)</td>
<td>Fe-O(2)</td>
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<td>1.8569(15)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe-O(1)</td>
<td>1.8721(15)</td>
<td>1.8801(16)</td>
</tr>
<tr>
<td>Fe-Nimine</td>
<td>2.1398(11)</td>
<td>Fe-N(1)</td>
<td>1.9480(15)</td>
<td>1.9667(18)</td>
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<td></td>
<td>Fe-N(3B)</td>
<td>2.134(4)</td>
<td>2.162(7)</td>
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</table>

3.3. Magnetic Characterization

Magnetic susceptibility of complexes 1 and 2 were recorded on an MPMS-XL magnetometer between 5–300 K in warming and cooling modes. The expected $\chi M$ values for $S = 5/2$ and $S = 1/2$ are 4.25 and 0.375 cm$^3$ K/mol respectively, and plots of $\chi M T$ versus $T$, Figure 6, indicate that complex 1 remains HS over the measured temperature range. Complex 2 persists in the predominantly LS state on warming from 5 K to around 250 K above which the $\chi M T$ value starts to rise, indicating some thermal population of the HS state.
and warming to 353 K.

The EPR spectra of complex 1, recorded using a X-band EPR spectrometer, Figure 7. Complex 1 shows the characteristic broad S = 5/2 with g = 2 over the whole temperature range which fits well with the HS assignment from SQUID magnetometry. The EPR spectra of complex 2, [Fe(5F-sal2333)]BPh₄, are also in line with the SQUID data, showing a gradual thermal SCO in the solid state. A characteristic S = 1/2 signal at g = 2 with differentiation of the x, y, and z components is apparent at low temperatures for complex 2, which is diminished on warming to 353 K.

Figure 6. Plots of $\chi M T$ versus $T$ for complexes 1 (green) and 2 (blue) between 5–300 K in cooling and warming mode.

3.4. Solid State EPR Spectroscopy

Solid state variable temperature EPR spectra of complexes 1 and 2 were recorded on a Magnettech X-band EPR spectrometer, Figure 7. Complex 1 shows the characteristic broad S = 5/2 with g = 2 over the whole temperature range which fits well with the HS assignment from SQUID magnetometry. The EPR spectra of complex 2, [Fe(5F-sal2333)]BPh₄, are also in line with the SQUID data, showing a gradual thermal SCO in the solid state. A characteristic S = 1/2 signal at g = 2 with differentiation of the x, y, and z components is apparent at low temperatures for complex 2, which is diminished on warming to 353 K.

Figure 7. Variable temperature EPR spectra of complex 1 (left) and 2 (right) at variable temperature.

3.5. UV-Vis Solution Studies

It was also possible to collect solution state variable temperature electronic absorption for complexes 1 and 2 in methanol, Figure 8, using an Oxford Instruments cryostat insert for a benchtop UV-Vis spectrometer using a 1.0 × 10⁻⁴ mol/L methanolic solution of 1 and 1.46 × 10⁻⁴ mol/L methanolic solution of 2. The spectra suggest that thermal SCO could be achieved in both complexes in this medium despite the fixed HS moment observed between 5–300 K in the crystalline form of complex 1. The spectra of both complexes show two broad absorptions at around 380 and 620 nm; the latter of which were attributed to charge transfer absorptions rather than d-d transitions. The higher energy band is likely due to ligand only transitions. A strong similarity between the electronic spectra of 1 and 2 in solution is to be expected given that the cation is identical in each. It is also to be expected that the fixed meso/non-meso
differences arise in the solid state due to significant differences in packing between the two variously sized anions. In solution, it is most likely that the complex cation may be in a dynamic exchange between the two forms, and therefore, the spectra of 1 and 2 in methanol should be similar. The higher energy band at 380 nm grows on cooling for both compounds while that at 620 nm narrows on cooling, suggesting population of the LS state which has a narrower vibrational energy well.

![Figure 8. Variable temperature UV-Vis characterization of complex 1 (a) and 2 (b).](image)

4. Discussion

In this work, we have investigated the influence of geometry and counterion effects in determining the spin state choices in an iron (III) complex with the 5-Fluoro-sal$_2$333 ligand in a Cl$^-$ or BPh$_4^-$ lattice. In the solid state the [Fe(5F-sal$_2$333)]$^+$ complex adopts the S = 5/2 spin state in a chloride lattice and the S = 1/2 spin state in the tetraphenylborate lattice. The BPh$_4^-$ complex shows onset of a gradual spin crossover on warming from 5 K, but it is still mainly in the LS state by room temperature. An interesting result to emerge from the investigation was the observation that there were two possible orientations (meso and non-meso) for the hydrogen atoms on the amine nitrogen donors and that a magnetostructural correlation may be present. Complex 1, which adopted the pure non-meso form, showed a preference for the HS state while complex 2, which crystallized as a mixture of meso and non-meso, showed preference for the LS state with onset of a gradual SCO only above 250 K. In conclusion, we have established that R-sal$_2$333 ligands can promote SCO in Fe(III) both in the solid state and in solution. Moreover, we have shown that a new type of ligand distortion (meso/non-meso) exists that may affect the spin state choice and profile of the spin crossover thermal evolution. Future work will include detailed Mössbauer spectroscopy on existing samples reported here and preparation and characterization of further members of the series.


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Conflicts of Interest: The authors declare no conflict of interest.
## Appendix A

### Table A1. Crystallographic details for complexes 1 and 2.

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<th>Compound</th>
<th>C\text{Fe}(5F-sal\text{ }^3\text{33})\text{Cl} \text{ (1)}</th>
<th>C\text{Fe}(5F-sal\text{ }^3\text{33})\text{BPh}_4 \text{ (2)}</th>
<th>C\text{Fe}(5F-sal\text{ }^3\text{33})\text{BPh}_4 \text{ (2)}</th>
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<td>P \text{\textendash}1</td>
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<td>10.7385(2)</td>
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<td>(b) (Å)</td>
<td>16.3083(2)</td>
<td>13.9687(3)</td>
<td>14.7851(2)</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>18.6359(2)</td>
<td>14.7851(2)</td>
<td>14.9232(2)</td>
</tr>
<tr>
<td>(\alpha) (°)</td>
<td>90</td>
<td>102.984(2)</td>
<td>103.0383(7)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>90</td>
<td>94.039(1)</td>
<td>94.2739(6)</td>
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<tr>
<td>(\gamma) (°)</td>
<td>90</td>
<td>109.415(2)</td>
<td>107.6673(7)</td>
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<tr>
<td>(V) (Å (^3))</td>
<td>2248.43(4)</td>
<td>2012.64(6)</td>
<td>2073.03(4)</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>(d_{\text{calc}}) (g cm (^{-3}))</td>
<td>1.541</td>
<td>1.329</td>
<td>1.291</td>
</tr>
<tr>
<td>(T) (K)</td>
<td>100(2)</td>
<td>100(2)</td>
<td>293(2)</td>
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<tr>
<td>(\mu) (mm (^{-1}))</td>
<td>6.871</td>
<td>0.429</td>
<td>0.416</td>
</tr>
<tr>
<td>(F(000))</td>
<td>1084</td>
<td>846</td>
<td>846</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>(h = \pm 9, k = \pm 20, l = \pm 23)</td>
<td>(h = \pm 13, k = \pm 17, l = \pm 8)</td>
<td>(h = \pm 13, k = \pm 17, l = \pm 18)</td>
</tr>
<tr>
<td>Reflections collected/unique</td>
<td>21831/2378</td>
<td>35866/8833</td>
<td>79115/7853</td>
</tr>
<tr>
<td>Completeness to (\Theta) (%)</td>
<td>99.7</td>
<td>99.5</td>
<td>99.7</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>2378/0/151</td>
<td>8833/0/578</td>
<td>7853/0/578</td>
</tr>
<tr>
<td>Goof on (F^2)</td>
<td>1.047</td>
<td>1.041</td>
<td>1.079</td>
</tr>
<tr>
<td>Final R indices (I &gt; 2(\sigma(I)))</td>
<td>(R_1 = 0.0274, \text{w}R_2 = 0.0760)</td>
<td>(R_1 = 0.0414, \text{w}R_2 = 0.0928)</td>
<td>(R_1 = 0.0396, \text{w}R_2 = 0.1068)</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>(R_1 = 0.0292, \text{w}R_2 = 0.0777)</td>
<td>(R_1 = 0.0479, \text{w}R_2 = 0.0963)</td>
<td>(R_1 = 0.0420, \text{w}R_2 = 0.1085)</td>
</tr>
<tr>
<td>Largest diff. peak/hole (e Å (^{-3}))</td>
<td>(0.255) and (\text{\textendash}0.457)</td>
<td>(0.332) and (\text{\textendash}0.723)</td>
<td>(0.292) and (\text{\textendash}0.584)</td>
</tr>
<tr>
<td>CCDC no.</td>
<td>1884365</td>
<td>1884366</td>
<td>1884367</td>
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### References


18. Sinn, E.; Sim, G.; Dose, E.V.; Tweedle, M.F.; Wilson, L.J. Iron(III) Chelates with Hexadentate Ligands from Triethylenetetramine and b-diketones or Salicylaldehyde. Spin State Dependent Crystal and Molecular Structures of [Fe(acac)₂trien]PF₆ (S = 5/2), [Fe(acacCl)₂trien]PF₆ (S = 5/2), [Fe(sal)₂trien]Cl·2H₂O (S = 1/2). *J. Am. Chem. Soc.* 1978, 100, 3375–3390. [CrossRef]


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