

CHEMISTRY AN ASIAN JOURNAL

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Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Asian J. 10.1002/asia.202000156

Link to VoR: https://doi.org/10.1002/asia.202000156

A Journal of

ACES Asian Chemical Editorial Society A sister journal of Angewandte Chemie and Chemistry – A European Journal



Effect of Ligand Field Strength on Spin Crossover Behaviour in 5-X-SalEen (X = Me, Br and OMe) Based Fe(III) Complexes

Bijoy Dey, Arpan Mondal, and Sanjit Konar*^[a]

Dedicated to Prof. Amitava Das on his 60th Birthday

Abstract: The reaction of Fe(NCS)₃ prepared in situ in MeOH with 5-X-SalEen ligands (5-X-SalEen = condensation product of 5-substituted salicylaldehyde and N-ethylethylenediamine) provided three Fe(III) complexes, [Fe(5-X-SalEen)₂]NCS; X = Me (1), X = Br (2), X = OMe (3). All the complexes reveal similar structural features but very much different magnetic profile. Complex 1 shows a gradual spin crossover while complex 2 and 3 show a sharp spin transition. T_{1/2} for complex 2 is 237 K while for complex 3 it is much higher with a value of 361 K. The spin transition temperature is shifted towards higher temperature with increasing electron donation ability of the ligand substituents. This experimental observation has been rationalized with DFT calculations. UV-Vis and cyclic voltammetry studies support the fact that electron density on the ligand increase from Me to Br to OMe substituents. To understand the change in spin states temperature-dependent EPR spectra have been recorded. The spin state equilibrium in the liquid state has been probed with Evans NMR spectroscopic method and thermodynamic parameters have been evaluated for all complexes.

Introduction

Switching between two magnetic states by using some external stimuli has been a great scientific interest because these magnetic materials have the potential to be used in magnetic switches and memory device applications.¹ Transition metals with d⁴-d⁷ electronic configurations give access to this magnetic bistability which is called spin crossover (SCO).² Light, temperature and pressure are used as external stimuli to attain different magnetic states.³⁻⁴ SCO behaviour is highly dependent on counter anion⁵ and solvent molecules⁶ present in the crystal lattice as these affect the solid-state crystal packing⁷ and a lot of work has been done to explore these effects for both Fe(II) and Fe(III) complexes.8 Ligand field strength also plays a major role in determining the nature of spin transition⁹ but only a very few works have been reported on ligand field strength and its effect on SCO.¹⁰ Also, some theoretical studies have been done on Fe(II) and Fe(III) complexes and the theoretical results have been compared with the solid-state magnetic properties.¹¹ Harding and co-workers have done a detailed analysis on the effect of halogen substitution on spin transition temperature for a series of Fe(III) gunolylsalicylaldimine (q-sal) complexes¹² where the magnetic profile changed with different halogen substitutions on the ligand. Later, Murray and coworkers have done an extensive theoretical and experimental analysis on Fe(II) and Fe(III) complexes of halogen substituted qunolylsalicylaldimine (q-sal) ligands¹³ where they have shown that with changing π donor ability of the substituent the transition temperature changes. q-sal based Fe(III) complexes also have been explored with theoretical methods by Sirirak et. al. where they have explored the appropriate functionals and basis sets to accurately model spin crossover behaviour.14

SalEen based Fe(III) complexes are well known to show spin crossover behaviour and many complexes have been reported¹⁵ but no complete theoretical investigations have been performed in a group of molecules to understand how actually different ligand substitutions in this ligand family are affecting the spin

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transition temperature except in one paper by Kepp et al. where only one SalEen based Fe(III) complex has been analyzed theoretically.^{11a} With these aspects in mind, we have synthesized three 5-X-SalEen based Fe(III) complexes where the substituents are X = Me(1), Br(2) and OMe (3) (Scheme 1). Counter anion is the same for all the complexes so the effect of the counter anion can be ignored here. All the complexes are solvent free so the effect of solvent is also absent here. The substituents are chosen such that from complexes 1 to 3 there is an increase in electron density of the phenyl ring chelating to the metal center. This is because the electron donating ability of the substituents increases from Me to Br to OMe. Methyl group is only weak electron donating in nature due to the hyperconjugation effect, bromine is a weak π donor^{16a} and methoxy group is a good π donor.^{16b} To understand the role of differential electron donating substituents on spin crossover behaviour, solid-state magnetic properties have been compared with theoretical results obtained from DFT methodology.

Solid-state magnetic study reveals that complex 1 shows a gradual spin conversion whereas complexes 2 and 3 show sharp spin transitions. The spin transition temperature, $T_{1/2}$ is found to shift to higher temperature on moving from Me to Br to OMe substituted complexes. $T_{1/2}$ for complex 2 is 237 K and for complex **3** it is even higher ($T_{1/2} = 361$ K). UV-Vis spectroscopic and cyclic voltammetric analysis helps to assess the extent of electron donating ability of the different substituents. Liquid state magnetic susceptibility has been probed with Evans method which gives temperature dependence of magnetic susceptibility directly without any solid state packing effect. This allows for direct comparison with ligand field strength and spin crossover temperature.

DFT calculations have been performed to understand the details of the spin state energetics of these complexes. Small HS-LS gaps are found from the energy calculations and the different electron donating ability of the ligand substituents are found to influence the d-orbital energies of Fe(III) center leading to the difference in observed SCO characteristics. A variable temperature EPR data reveals the spin state conversion with temperature.

Results and Discussion

Structural analysis of complexes 1-3

All the complexes crystallize in the monoclinic space group with $P2_1/c$ and contain a cation and an anion in the asymmetric unit. In all cases, two tridentate ligands bind with Fe(III) center in a meridional fashion giving the N₄O₂ coordination environment around the metal center (Scheme 1). The unbound nature of NCS⁻ counter anion is further confirmed by strong v_{CEN} IR stretches between 2065-2030 cm⁻¹ (Table 1).¹⁷ The single crystal structures for complexes are collected at low temperatures at 140 K and high temperatures at 273 K, 296 K, and 350 K for complexes 1-3 respectively (Table 2). For all the complexes thiocyanate (NCS⁻) anion is present as a counter anion. At 140 K the Fe-N/O bond lengths for complexes 1-3 are on average 1.873 and 1.980 which are characteristic to low spin Fe(III) centers.¹⁸ At the higher temperature (273 K for complex **1**. 296 for complex 2 and 350 K for complex 3) the Fe-N/O bond lengths increase which indicates the occurrence of spin crossover (Table 3).



X = Me(1), Br(2), OMe(3)Scheme 1. Synthesis of [Fe(5-X-SalEen)₂]NCS.

There are clear IR stretches (1630-1619 cm⁻¹) that are assignable to the imine bond of the 5-X-SalEen ligand.¹² In each complex two strong hydrogen bonds are found between the cationic amine hydrogens and the nitrogen atom of the NCS⁻ anion. These hydrogen bonding interactions are tabulated in Tables S1-S6.

Table 1. Physical and IR spectroscopic data for [Fe(5-X-SalEen)2]NCS.

			IR ^a (cm ⁻¹)	
Compound	Color	Yield (%)	VCEN	V _{C=N}
1	Black	76	2063	1619
2	Black	68	2030	1628
3	Black	70	2030	1629
^a As KBr discs				

Supramolecular assembly of complexes

Supramolecular packing of all the complexes is almost similar so the structure of complex 1 has been explained in detail and the structural differences with the other two complexes are discussed. The asymmetric unit of complex 1 contains a cationic unit and an anion which are bound together by strong hydrogen bonding interactions (N1-H1...N5, $d_{D-A} = 2.941(5)$ Å and N3-H3····N5, d_{D-A} = 2.943(5) Å) (Figure 1a). Strong interactions between two cations consist of four C-H---O interactions among the imine hydrogen (C5-H5) and ethylene hydrogen (C4-H4B) with metal-bound phenolate oxygen (O1 and O2) atoms and one Sp²-C-H···N interaction between aromatic hydrogen (C11-H11) and imine nitrogen (N4) (Figure 1b). These interactions extend itself along crystallographic c-axis forming a 1D zigzag cationic chain having Fe...Fe separation distance of 7.316(3) Å (Figure 2a). Now the 1D cationic chains are also interconnected via a pair of C-H···π interactions along crystallographic a-axis having a Fe---Fe separation distance of 10.076(5) Å. The aromatic C-H···π distance between C21-H21···centroid (C6-C11) is 3.158(7) Å (Figure 2b).



Figure 1. (a) Asymmetric unit of complex 1 and (b) C-H---O, C-H---N interactions between cations.

Due to the presence of NCS⁻ anion, C-H...S interactions are found with the C-H group of the cations. These C-H...S interactions connect the 1D chains along *b*-axis (Figure S1) with a Fe...Fe separation distance of 9.188(3) Å.



Figure 2. (a) 1D cationic chain along the crystallographic c-axis and (b) Interactions among the cations along crystallographic a-axis.

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Crystallographic and structure re	finement for comple	xes 1-3 at various te	mperatures			
Compound	1	1	2	2	3	3
Temperature / K	140 K	273 K	140 K	296 K	140 K	350 K
Formula	$C_{25}H_{34}FeN_5O_2S$	$C_{25}H_{34}FeN_5O_2S$	$C_{23}H_{28}Br_2FeN_5O_2S$	$C_{23}H_{28}Br_2FeN_5O_2S$	$C_{25}H_{34}FeN_5O_4S$	$C_{25}H_{34}FeN_5O_4S$
MW [g mol ⁻¹]	524.48	524.48	654.43	654.43	556.48	556.48
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	P21/c	P21/c	P21/c	P21/c	P21/c	P21/c
a [Å]	10.076(5)	10.3478(6)	9.9463(4)	10.061(15)	9.993(4)	10.3667(16)
b [Å]	25.545(13)	25.6861(15)	28.5695(10)	29.06(4)	24.9764(12)	25.768(5)
c [Å]	10.512(5)	10.6783(7)	10.4937(4)	10.742(15)	11.5079(6)	11.339(2)
α [°]	90	90	90	90	90	90
β [°]	110.92(3)	109.922(3)	111.694(2)	112.241(19)	113.752(2)	113.244(7)
γ [°]	90	90	90	90	90	90
cell V [ų]	2527(2)	2668.4(3)	2770.69(19)	2907(7)	2629(2)	2783.3(8)
Z	4	4	4	4	4	4
reflections collected	16697	48296	23859	11692	38106	41216
independent reflections, R _{int}	6257/ 0.0889	5430/0.130	4717, 0.0360	4806, 0.0888	5395, 0.0736	4763, 0.1227
restrains/parameters	0/319	0/319	0/328	0/304	0/329	0/329
goodness-of-fit	1.042	1.049	1.038	1.061	1.040	1.054
final R indices $[I > 2\sigma(I)]$: R ₁ ,	0.0623, 0.1929	0.0710, 0.1494	0.0467, 0.1477	0.1073, 0.3508	0.0401, 0.0856	0.0740, 0.1719
wR ₂						
CCDC no.	1938221	1966916	1966933	1966934	1966940	1966941

Table 2. Crystallographic data for complexes 1-3.

 $R_1 = \Sigma |F_0| - |F_c| / \Sigma |F_0|$ and $wR_2 = |\Sigma w(|F_0|^2 - |F_c|^2)| / \Sigma |w(F_0)^2|^{1/2}$.

So, packing of complex **1** consist of a 1D zigzag assembly of cations which are interconnected by C-H··· π interactions along crystallographic *a*-axis and along crystallographic *b*-axis they are connected by C-H···S interactions (Figure 3a).

Bromine substituent in complex **2** helps in forming C-H···Br interactions. Similar as complex **1**, the 1D zigzag cationic chain is formed in complex **2** due to the presence of C-H···· π , C-H···Br and C-H···O interactions among the cations (Figure 3b) having a Fe···Fe separation distance of 7.958(9) Å (Figure 3c). Two types of C-H··· π interactions are present, one is aliphatic C-H··· π (C13-H13B···centroid (C6-C11), 3.677(2) Å) and another is aromatic C-H··· π (C11-H11···centroid (C17-C22), 3.658(18) Å). The 1D cationic chains are interconnected along crystallographic *a*-axis with two different interactions simultaneously, first is C-H··· π (C20-H20···centroid (C6-C11), 3.338(2) Å) and other is C-H··· π (C8-H8···Br2, 2.977(5) Å; C14-H14A···Br2, 3.086(5) Å) interactions (Figure 3d). Effect of this is reflected in the interchain distance of Fe···Fe along crystallographic *a*-axis which is 10.076(5) Å for complex **1** whereas it is 9.946(4) Å in complex **2**. Along crystallographic *b*-axis the C-H...S interactions connect the 1D chains (Figure S2) and due to more strong C-H...S interactions, the Fe...Fe separation along crystallographic *b*-axis is less in complex **2** (7.959(9) Å) than in complex **1** (9.1395(4) Å) which indicates that complex **2** have more compact supramolecular packing than complex **1**. So, complex **2** is expected to have more cooperative spin transition behaviour than complex **1**. This fact is also reflected in the solid-state magnetic property where complex **2** shows a sharp transition whereas complex **1** shows a gradual spin conversion.

Complex **3** also forms a cationic chain along the crystallographic c-axis including two C-H… π (C2-H2B…centroid (C18-C23), 3.622(16) Å and C16-H16B…centroid (C6-C11) 3.291(12) Å) interactions and two C-H…O interaction (C8-H8…O3, 3.219(12) Å and C17-H17…O2, 2.83(18) Å) with an interchain Fe…Fe separation distance of 7.683(6) Å (Figure 4).



Figure 3. (a) packing diagram of complex 1, (b) interaction between cations in complex 2, (c) 1D cationic chain for complex 2 and (d) interchain connections along crystallographic a-axis.

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Figure 4. Connections of the 1D chains along crystallographic *a*-axis for complex 3.

These previously mentioned interactions lead to the formation of a 1D zigzag cationic chain along the crystallographic c-axis (Figure S3). The molecules in one 1D chain interact with another via C-H···π (C9-H9···centroid (C18-C23), 2.941(10) Å) and C2-H2A···O3 (2.872(14) Å) interactions (Figure 5) and these interactions propagate in crystallographic a-axis. Another way the 1D chains interact with one another is through C-H...N, C-H...S interaction along with the hydrogen bonding with the cation and anion. This cation-anion interaction extends along the crystallographic b-axis which connects the 1D chains together so two anions hold altogether eight cations having four from each side of the 1D chain (Figure S4). So the intrachain Fe---Fe separation is 7.683(3) Å whereas the interchain Fe---Fe separation is 8.666(3) Å. When the temperature is increased to 350 K, some changes in the bond distance and bond angle parameters are observed which is indicative of spin state change of the Fe(III) center.



Figure 5. interchain interactions along a-axis in complex 3.

Table 3. Bond lengths (Å) and distortion parameters for complexes 1-3.

The main packing pattern is the same but some interactions became more weak, such as the C-H··· π and C-H···O interactions fall weak. The intrachain Fe···Fe distance at higher temperature decreases to 7.588(14) Å but the interchain Fe···Fe distance increased to 9.750(2) Å. The change in the Fe···Fe distance is well understood as the unit cell expands with the spin crossover thus the distances also change.

Hirshfeld surface analysis

Hirshfeld surface for the cation of complexes **1-3** is mapped with d_{norm} function¹⁹ which shows several red spots. Two strongest red spots are due to hydrogen bonding interactions (Figure 6a) and the weak red spots are due to C-H···O, C-H···S interactions (Figure 6b). H···H interaction is the major one here contributing to 64.1 % of all interactions. Then C-H··· π interactions are also present which has been shown by shape index plot (Figure S5), this constitutes 21.8 % of total interactions. The interaction between the cation and anion result in forming C-H···N and C-H···S interactions having 4.8 % and 4.7 % contributions respectively.



Figure 6. Intramolecular C-H···N interactions (hydrogen bonding) (a) and C-H··· π interactions (b) through Hirsfeld surface mapping by d_{norm} function.

For complex **2** there is substantial C-H…Br interaction (20.5 %) along with Br… π interaction (1.2 %) (Figure 7). d_{norm} mapped Hirshfeld surface for C-H…Br interactions is shown in Figure S6. These interactions indicate strong connectivity among the metal centers as C-H…Br interaction is stronger than C-H…H interaction. Similar hydrogen bonding and C-H… π interactions are present for complex **3** which is shown in Figure S7 by strong and weak red spots respectively. Due to the presence of the methoxy group (-OMe), there are C-H…O interactions (10.1 %). This interaction also helps in better communication among the metal centers. Analysis of the different types of interactions is shown in the fingerprint plots for complexes **1-3** (Figure S8).

Bond Lengths	[Fe(5-Me-Sa	alEen)2]NCS	[Fe(5-Br-Sa	alEen)2]NCS	[Fe(5-ON	/le-SalEen)2]NCS
-	140 K	273 K	140 K	296 K	140 K	350 K
Fe1-O1 (Å)	1.886(3)	1.917(3)	1.880(3)	1.885(9)	1.872(15)	1.880(4)
Fe1-O2 (Å)	1.886(2)	1.917(3)	1.885(3)	1.873(9)	1.875(15)	1.885(4)
Fe1-O _{Phenolate} (Avg)	1.886	1.917	1.883	1.879	1.874	1.883
Fe1-N1 (amine) (Å)	2.096(3)	2.203(3)	2.041(4)	2.083(10)	2.051(17)	2.134(4)
Fe1-N3 (amine) (Å)	2.104(3)	2.203(4)	2.036(3)	2.067(10)	2.037(18)	2.114(5)
Fe1-N _{amine} (Avg)	2.1	2.203	2.039	2.075	2.044	2.124
Fe1-N2 (imine) (Å)	1.984(3)	2.083(4)	1.939(3)	1.961(10)	1.935(17)	2.012(4)
Fe1-N4 (imine) (Å)	1.981(3)	2.081(4)	1.926(3)	1.941(10)	1.928(17)	2.005(5)
Fe1-N _{imine} (Avg)	1.983	2.082	1.933	1.951	1.932	2.009
Fe-L (Å) ^a	1.989	2.067	1.968	1.968	1.949	2.005
ξ ^b	0.593	0.602	0.349	0.426	0.378	0.490
Σ (°) ^c	48.26	63.27	44.9	44.3	42.47	45.72

 ${}^{a}\text{Fe-L} = (1/6) \sum d_{\text{Fe-L},} {}^{b}\xi = \sum |d_{\text{Fe-L}} - d_{\text{Fe-L}i}|, {}^{c}\sum = \sum |90-\phi_i|$





Figure 7. Percentage contributions of Interactions for complex 1 (a), complex 2 (b) and complex 3 (c).

Form the Hirshfeld analysis it is very clear that cooperative nature in complex 2 and 3 is much higher than complex 1 as in complex 2 C-H...Br and in complex 3 C-H...O interactions are more with respect to complex 1.

Magnetic Property Studies

Direct current magnetic susceptibility measurements

The phase purity of the complexes was checked by powder XRD (Figure S9) before magnetic measurements. In order to probe the magnetic properties, direct current (dc) magnetic susceptibility measurements were performed on polycrystalline samples under an applied field of 1000 Oe in the temperature range 2-380 K. The $\chi_M T$ value for complexes **1**, **2** and **3** are ca. 0.5 cm³ mol⁻¹ K at 2 K which is consistent for a low spin Fe(III) complex in all cases ($\chi_M T = 0.375$ cm³ mol⁻¹ K for a low spin Fe(III) complex) (Figure 8).

Complex 1 shows an incomplete and gradual spin crossover. The $\chi_M T$ value is almost constant up to 50 K and after that, it increases gradually and almost saturates after 350 K reaching a value of 3.07 cm³ mol⁻¹ K which is below the expected value for a Fe(III) high spin complex (4.037 cm³ mol⁻¹ K). This type of incomplete spin transition is may be observed because of the the structural constraints which prohibit the expansion of the system in solid-state. Complex 2 shows an almost full conversion to the high spin state and an abrupt spin transition having a $\chi_M T$ value of 4.0 cm³ mol⁻¹ K at 380 K, a little lower than the expected value of 4.375 cm³ mol⁻¹ K which may suggest that the HS fraction is underestimated. The shift in transition temperature for complex 2 as compared to complex 1 may be attributed due to the electron donating ability (π donor) of the Br group as compared to the methyl group. This statement is further supported by the DFT calculations. Complex 3 shows more shift in transition temperature and attains a constant value of 0.5 cm³ mol⁻¹ K up to 200 K after which it starts increasing and finally reaches a value of 3.2 cm³ mol⁻¹ K. The very good π donor ability of the OMe group is seen in the magnetic plot where the transition temperature is shifted far beyond the room temperature. The spin transition is incomplete and the conversion to the high spin is up to 65 % only. This higher transition temperature is expected due to a higher π donation of the methoxy group which leads to more separation in the energy gap between low spin and high spin states. The magnetic data have been fitted with the regular solution model (equation 1) to extract



Figure 8. Plots of $\chi_M T$ versus T for complexes 1 (Green), 2 (Brown) and-3 (Blue) at H = 1000 Oe. The red line indicates the fitting of the experimental data.

various thermodynamic parameters such as ΔS and ΔH which is given in Table 4. The thermodynamic parameters obtained from the fitting is quite in good agreement with the literature reported values for Fe(III) systems.²⁰

Table 4. Thermodynamic parameters from the fitting of magnetic susceptibility

 data using the ideal solution model (equation 1).

Complexes	ΔH	ΔS	g∟s	gнs	T _{1/2}
	(kJ mol⁻¹)	(J mol ⁻¹ K ⁻¹)			(K)
Complex 2	20	84	1.944	2.239	237
Complex 3	24	69	2.153	2.239	361

Solution Studies

Magnetic susceptibility measurement through the Evans method

The solution phase magnetic susceptibility measurement was performed by Evans NMR spectroscopic method.²¹ Chloroform– D solutions of complexes **1-3** (5 X 10⁻³ mol L⁻¹) have been used for this purpose. A double-walled coaxial NMR tube has been used in this experiment where the paramagnetic solution is in the outside tube and the pure solvent is in the inner tube. The solvent experiences two different types of the chemical environment due to the presence of paramagnetic samples in the outer tube and pure solvent in the inner tube. This difference (Δv in Hz) in the solvent signal is proportional to bulk magnetic mass susceptibility.²²

$$\chi = \frac{3\Delta\nu}{4\pi\nu m} + \chi_0 + \frac{\chi_0 (d_0 - d_s)}{m}$$
(2)

Where χ is the mass paramagnetic susceptibility, v is the operating radio frequency (500 MHz), m is the concentration of the paramagnetic sample in outer tube, χ_0 is the gram susceptibility (-59.30 X 10⁻⁶ cm³ mol⁻¹) of pure CDCl₃, d₀ and d_s

is the density of pure solvent and the paramagnetic solution respectively.²³ For strongly paramagnetic solutions the last terms can be neglected so the equation becomes

$$\chi = \frac{3\Delta\nu}{4\pi\nu m} + \chi_0 \tag{3}$$

The molar mass paramagnetic susceptibility then calculated considering the diamagnetic contribution taking from Pascal's table.²⁴ The temperature range of 228-318 K has been selected for spectroscopic measurement to avoid freezing or evaporation of the solvent.



Figure 9. $\chi_M T$ vs T plot for complexes 1-3 in the liquid state by Evans method. Complex 1 (Brown), complex 2 (Green) and complex 3 (Blue). Red lines indicate the fitted line.

¹H NMR data has been collected for all the complexes in a double walled NMR tube and after doing all the corrections the data have been plotted (Figure 9). The lower temperature values are close to the solid state measurement data (0.5 cm³ mol⁻¹ K) but at the higher temperature, the value is much less as compared to the solid state data. This anomaly can be easily explained if we consider the fact that in solid state cooperativity acts so the spin transition more often can become abrupt due to high cooperativity but in the liquid state, this effect is absent as the SCO active units are far apart from each other in solution and there is less communication among themselves. So, the transition in the liquid state is more gradual than the solid state where it is more abrupt and thus the $\chi_{M}T$ value for the liquid sample at higher temperature is below the value of the solid sample. T_{1/2} and other thermodynamic parameters (ΔH and ΔS) have been calculated by the fitting of $\chi_M T vs T$ data obtained by Evans method using equation 1. The trend in $T_{1/2}$ indicates the increase in ligand field strength from complex 1 to 3 (Table 5).

Table	5.	Thermody	vnamic	parameters	form	Evans	plo
1 0010	۰.	monitod	ynanno	paramotoro	101111	Lvano	pio

Complexes	ΔН	ΔS	T _{1/2} (K)
	(kJ mol⁻¹)	(J mol ⁻¹ K ⁻¹)	
Complex 1	18.97	71.34	267
Complex 2	18.77	67.53	278
Complex 3	17.47	59.12	295.5

UV-Vis spectroscopic studies

UV-Vis spectra for complexes **1-3** were recorded in methanol solution at room temperature with 50 X 10^{-6} mol L⁻¹ concentration. All the complexes show an intra-ligand charge

transfer and π to π^* transition below 400 nm with varying ϵ value of 9000-30000 L⁻¹ cm⁻¹ (Figure 10). For all the complexes two additional bands have been observed which is assigned to the ligand to metal charge transfer (LMCT) bands. Spectroscopic studies for Fe(saltrien)₂ complex²⁵ has shown that the band at higher energy corresponds to the high spin species (450 nm < λ_{max} < 650 nm) and the lower energy transition (650 nm < λ_{max} < 800 nm) is due to low spin species. The absorption maxima for all the three complexes changes which clearly indicate the effect of substituents. Ongoing from Me to Br to OMe substitution electron density on the ligand increases as can be understood from the shift of $\pi - \pi^*$ transition to lower energy (λ_{max} (1) = 340 nm, λ_{max} (2) = 360 nm, λ_{max} (3) = 395 nm). Also, a similar effect is observed on LMCT bands for the HS species. For complex 1 and **2**, the λ_{max} for LMCT band is almost the same (λ_{max} (**1**) = 552 nm, λ_{max} (2) = 550 nm and λ_{max} (3) = 594 nm) but for complex 3 it shifts to higher wavelength (lower energy) due to good π donating ability of methoxy group (-OMe). The absorption band for low spin species is almost similar for all the complexes.



Figure 10. UV-Vis spectroscopic data for complexes 1 (Black), 2 (Red) and 3 (Blue).

Cyclic voltammetric studies

The cyclic voltammogram of all the complexes is given in Figure 11 which shows a quasi-reversible reduction peak around -0.85 V and a quasi-reversible oxidation peak around 0.75 V. $E_{1/2}$ value for the redox process of Fe centers are -0.802, -0.809 and -0.813 V for complexes **1**, **2** and **3** respectively.





The ΔE_p values for complexes 1-3 are 0.088, 0.105 and 0.079 V respectively. The redox process around 0.75 V is because of the ligand.^{8p,} To prove redox active property of the ligands, the ligands were isolated and they have been studied separately with similar conditions and found that indeed there is redox activity due to the ligand in solutions (Figure S10). The free ligands show redox behaviour as expected. The shift of the cathodic potential (reduction potential of Fe(III)/Fe(II) couple) shifts to more negative value ongoing from Me to Br to OMe substituents as the electron density on the chelating phenyl ring increases the reduction process becomes less favourable. So, the fact that ligand substitution increases the electron density on the metal center is confirmed by this observation (Table 6).

Table 6.	Electrochemical	data of	complexes	1-3.

Complexes	E _{pc} /V	E _{pa} /V	E _{1/2} /V	ΔE _p /V		
Complex 1	-0.8462	-0.7578	-0.802	0.088		
Complex 2	-0.8617	-0.7566	-0.809	0.105		
Complex 3	-0.8519	-0.7733	-0.813	0.079		

 $E_{1/2} = \frac{1}{2}(E_{pa}+E_{pc}), \Delta E = E_{pa}-E_{pc} (V).$

EPR spectra analysis

EPR is a very powerful technique for characterizing different spin states of a spin crossover system as the number of EPR active unpaired electron changes with temperature. For a high spin Fe(III) system the Hamiltonian (4) have been used to describe the combined effect of axial ZFS (D), rhombic ZFS (E) and the Zeeman interaction on the ⁶A electronic term.²⁶

 $H^{sh} = \beta HgS + D(S_z^2 - 1/3S(S+1) + (E_x^2 - E_y^2))$ (4)In presence of spin orbit coupling, the degenerate spin states split into three Kramers doublets. The observed EPR spectrum depends on the ratio of D/E and the Zeeman quantum energy hv (v is the operating frequency of the EPR spectrometer).^{21b} In high-spin iron(III) complexes of cubic symmetry the resonance absorption occurs for D < hv (slight distortion) in the lowestenergy (ground-state) doublet and between separate doublets; the EPR spectrum can be described by an effective spin of 5/2 and the observed isotropic g factors are close to that of a free electron ($g_e = 2.0023$). For hv < D (E = 0), with strong distortion, the resonance absorption is possible only within a separate doublet and the EPR spectrum can be described by an effective spin of 1/2.27 Each doublet has its own observed values of the gtensor components. For a low-spin Fe(III) complex of cubic symmetry with tetragonal and orthorhombic distortions, the EPR spectrum is described by hamiltonian (5).28

$$H^{sh} = \beta (g_{xx}H_xS_x + g_{yy}H_yS_y + g_{zz}H_zS_z)$$

(5) Where $g_{ii} = g_i$ (i = x, y, z) is the diagonal components of the g tensor on its principal axes. EPR spectra were measured in the temperature range of 100-300 K with hv = 0.3 cm⁻¹ (X-band, 9.5 GHz) to characterize the changes in its EPR signals with the spin transition. Low spin ferric centers in pseudo octahedral ligand coordination ligand environment typically show axial or rhombic resonances near g = 2. Low spin EPR spectra for all the

and those g values are reported here.²⁹ For complex 1 the EPR spectra at lower temperatures show one isotropic spectrum having a giso value of 2.17 indicating isotropic nature of the low spin state (S = 1/2) (Figure 12a). But ongoing to higher temperatures the spectra is a mixture of high spin and low spin centers. At 150 K a broad peak is observed in the low field region with a g value of 5.38 which corresponds to high spin centers^{21c} and an isotropic signal at $g_{iso} = 2.2$. Upon increasing

complexes have been stimulated with simple spectrum software

the temperature to 250 K the low spin isotropic signal splits into two signals which are due to axial low spin centers having $g_x =$ $g_v = 2.118$ and $g_z = 1.958$.³⁰ Also the broad peak for high spin centers shift to more lower field having a g value of 4.30 at 250 K. At room temperature the axial nature of the EPR spectra of the low spin center decreases and at highest temperature (380 K) the axial peak vanishes and a nearly isotropic peak with $g_{iso} =$ 2.13 is obtained. At higher temperatures, the sharpness of the peaks is lost due to the thermal broadening of the peaks. The intensity of the signal near g = 2.17 decreases remarkably at higher temperatures due to the lowering of the low spin centers. EPR data for complexes 2 and 3 are very similar. At lower temperature in complex 2 (Figure 12b), a rhombic spectrum is observed with three g values, $g_x = 2.212$, $g_y = 2.092$ and $g_z =$ 2.058 with a gavg of 2.12 for the system. This signal corresponds to low spin Fe(III) systems with rhombic distortion.³¹ Upon increasing the temperature the intensity of the low spin signal decreases which indicates the lowering of low spin centers. At room temperature, the EPR spectra is an isotropic one with a g value of 2.14. Upon increasing the temperature along with the peak at 2.14, a new broad peak is observed around g value of 3.77 which corresponds to high spin Fe(III) centers with very small rhombicity.^{21a} This indicates that complex 2 undergoes spin transition above room temperature.

Similar features as complex 2 are obtained for complex 3, at a lower temperature (100 K) where three g values are observed with $g_x = 2.21$, $g_y = 2.09$ and $g_z = 2.058$ having a g_{avg} of 2.119 which corresponds to low spin (S = $\frac{1}{2}$) Fe(III) center with rhombic distortion (Figure12c). At room temperature, the anisotropic nature is diminished and an isotropic broad spectrum is observed with a giso value of 2.13. At the highest temperature (380 K) two new peaks are observed at $g_1 = 9.29$ and $g_2 = 3.78$ along with an isotropic peak at giso = 2, these signals correspond to Fe(III) high spin center with high rhombicity (E/D~0.33).8e It is important to note that separate observation of high spin and low spin signals in the same spectrum is an indication that the rate of spin state conversion is much slower than the frequency of EPR spectroscopy measurement (~10¹⁰ S⁻¹ in X-band).³²

Theoretical studies

B3LYP functional has been used for the density functional theory (DFT) calculations to rationalize the spin crossover behaviour for complexes 1-3. Although the DFT calculations didn't provide the correct ground state but the results gave some insights about the SCO behaviour. All the respective crystal structures have been optimized at their respective spin multiplicities such as high spin $(t_{2g}^{3}e_{g}^{2})$ (S = 5/2), intermediate spin $(t_{2g}^4 e_g^1)$ (S = 3/2) and low spin $(t_{2g}^5 e_g^0)$ (S = 1/2). All the geometry has been optimized in the gas phase. Table S7 in the supporting information represents the optimized structural parameters for complexes 1-3 at different spin states. The optimized structural parameters for a low spin (S = 1/2) and high spin (S = 5/2) match well with the low temperature and high temperature crystal data respectively. The optimized ground state structures have been shown in Figure S11.

For all the complexes 1-3 high spin state (S = 5/2) is the ground state (Figure 13) which is in contrast with our experimental observation.

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Figure 12. EPR spectrum of complex 1 (a), complex 2 (b) and complex 3 (c) at indicated temperatures.

This mismatch may be due to the fact that all the calculations are performed on the gas phase while the experimental results are obtained in the solid-state. Interactions in the solid-state among the molecules have a great impact on spin crossover behaviour which is not accounted in the gas phase calculations. The high spin and low spin gap (ΔE_{HS-LS}) for complexes 1-3 are 8.45, 2.49 and 4.02 KJ mol⁻¹ respectively. These energy gap values lie in the range of reported values for showing spin crossover.³³⁻³⁴ Intermediate spin state (S = 3/2) for all the complexes are much higher in energy than the other two multiplets.

To understand and rationalize the spin transition behaviour splitting energies of the d-based orbitals have been studied (Figure 14). From the molecular orbital picture, it can be said that the d_z^2 orbital is along with the two imine nitrogen atoms from two ligands and the $d_x{}^2\mathchar`_y{}^2$ orbital lie in the plane perpendicular to the imine nitrogen where it gets N2O2 binding sites involving two amine nitrogen donor and two phenolate oxygen donor. Now, from complex 1 to 3, the interaction between metal and ligand increases, along the z-axis it is evidenced by the shortening of the Fe-N_{imine} average bond distances from complex 1 to 3 (Table 3). This results in an increase in the energy of the $d_{z^{2}}^{}$ orbital. Similarly due to the increased metal-ligand interaction average Fe-Namine and Fe-Ophenolate bond distances decreases in the equatorial plane which leads to an increase in the energy of the $d_x^2-v^2$ orbital from complex 1 to 3. The effect of π donation of the ligand is seen on the t_{2a} set of orbitals which is getting disturbed by the π donation of the substituents.



Figure 13. Energy diagram for different spin multiplicities for complexes 1-3.

d_{xz} and d_{yz} orbitals are also affected by the π bonding as these orbitals are in the proper orientation for π bonding with ligand porbitals. So, this is reflected by the loss in the degeneracy of the t_{2g} set of orbitals. As the π donor ability of the substituents increases from Me to Br to OMe. The metal ligand interaction increases and it destroys the degeneracy of the d_{xz} and d_{yz} orbitals (Figure 14). The increase in metal and ligand interaction along the xy plane is further supported by the decrease in average bond length of Fe-N_{imine} from complexes **1** to **3** (Table S7).

10.1002/asia.202000156

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Figure 15. Spin density plots for complex 1 (a), 2 (b) and 3 (c).

The spin density plots for complexes **1-3** have been shown in Figure 15. The electron density on the metal center decreases as we go from Me (1) to Br (2) to OMe (3) substituted complexes which indicates there may be increasing delocalization of metal electron density from complex **1** to **3**.

Conclusions

The effect of different electron donating ability of the ligand substituents on spin crossover behaviour for a family of 5-X-SalEen based Fe(III) complexes have been investigated in detail with theoretical and experimental methods. Solid-state magnetic studies show that transition temperature increases with increasing electron donation ability of the ligand substituents. This experimental observation is also compared with theoretical calculations using DFT methodology. Higher electron donation to the metal center has a direct effect on d-orbital energies which is the reason for different spin transition behaviour. So, increasing the electron density through the ligand substituents can be an effective strategy to tune spin crossover temperatures. Liquid state magnetic susceptibility also supports the observation. Hirshfeld analysis reveals that the presence of

different substituents also influences the nature of the spin crossover.

Experimental section

Materials and Methods

5-methyl-2-hydroxybenzaldehyde, 5-Bromo-2-hydroxybenzaldehyde, 5methoxy-2-hydroxybenzaldehyde, *N*-ethylethylenediamine, and metal salts, FeCl₂-4H₂O, KNCS were purchased from Merck. The ligands were prepared by Schiff-base condensation reaction between 5-Xsalicylaldehyde (X = Me, Br and OMe) and *N*-ethylethylenediamine *in situ* while performing metalation. The elemental analyses were carried out on Elemental Microvario Cube Elemental Analyser. FT-IR spectra (4000–400 cm⁻¹) were recorded on KBr pellets with a Perkin-Elmer Spectrum BX spectrometer. Thermogravimetric analysis was recorded on a PerkinElmer TGA 4000 instrument. Solid-state EPR spectra were recorded using a Bruker EMXplus instrument. Powder X-ray diffraction (PXRD) data were collected on a PANalytical EMPYREAN instrument using Cu-Kα radiation.





X-ray Crystallography

Intensity data were collected on a Brüker APEX-II CCD diffractometer using a graphite monochromated Mo-Ka radiation (a = 0.71073 Å) at various temperatures (140 K, 273 K, 296 K, and 340 K). Data collections were performed using ϕ and ω scan. Olex2^{35a} was used as the graphical interface and the structures were solved with the SheIXT^{35b} structure solution program using intrinsic phasing. The models were refined with SheIXL^{35c} with full matrix least-squares minimization on F^2 . All non-hydrogen atoms were refined anisotropically.

CCDC 1938221, 1966916, 1966933, 1966934, 1966940 and 1966941 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center *via* <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

Magnetic susceptibility measurements

Magnetic measurements were performed on polycrystalline samples using the SQUID VSM magnetometer (MPMS 3). The samples were ground properly before performing magnetic measurements. Susceptibility versus temperature sweep is done with an applied dc field of 1000 Oe. The temperature sweep is done with a scan rate of 5 K min⁻¹. The data were corrected for the diamagnetic contribution from the sample holder and for the ligand atoms using Pascal's table.²⁴

Hirshfeld surface analysis

Hirshfeld surface analysis is often adopted for exploring the intermolecular interactions in coordination complexes.³⁶ This surface indicates several regions where the interaction is strong and weak. Each point on the surface is defined as the distance from the surface to the inside atom (d_i) or outside atom (d_e).³⁷ The red regions indicate strong interaction as their distance is less than their sum of Van der Waals radii of the two atoms. Mathematical treatment of d_i and d_e with selected function (d_{norm}, curvedness, etc.) allows the representation of particular intermolecular interactions such as hydrogen bonding or $\pi \cdots \pi$ stacking, etc.³⁸ Additionally plotting the histogram (d_e and d_i) contacts give two dimensional fingerprint plots³⁹ which can be used as a graphical summary for the contacts with the HS.

The properties of the Hirshfeld surface for complexes **1-3** were generated using crystal explorer 17.5. The crystal structure was imported from cif files. Hirshfeld surface was generated using high resolution and mapped with the d_{norm} and shape indexed functions. 2D fingerprint plots were prepared using the same software.

Cyclic voltammetry measurements

The Cyclic voltammetry studies were done on complexes **1-3** with VersaStat 3 potentiostat. Dry acetonitrile solutions of the complexes (1 mmol) were used with Bu₄NBF₄ (100 mmol) as supporting electrolyte. Three electrode electrolytic cell has been used where the reference electrode is Ag/Ag⁺ and the working electrode is a platinum electrode and platinum wire behaving as the counter electrode.

EPR measurements

EPR spectra were recorded for all the complexes in Bruker EMXplus instrument. Powder samples have been taken for the measurement and for comparison of the temperature evolution of the EPR spectra all other parameters have been kept constant during measurement. X-band frequency has been used (9.5 GHz) for the measurements.

Computational details

X-ray structural coordinates have been used for the DFT⁴⁰ calculations using the Gaussian 09 suite.⁴¹ First, the nuclear coordinates of the x-ray structure have been optimized and then frequency calculations have been performed on these optimized geometries to extract the thermodynamic parameters. B3LYP functional is employed for all the calculations along with Ahlrichs polarized triple-z valence (TZVP)⁴² basis set for all the atoms. Frequency calculations have been performed with B3LYP/TZVP level of theory which has found to be superior in estimating thermodynamic parameters for spin-crossover complexes.

Synthesis of the ligands

5-X-salEen ligands where X = Me, Br, F, and OMe were synthesized according to the literature method.⁴³

Synthesis of the complexes

[Fe(L¹)₂]NCS 2-((E)-(2-**Svnthesis** of (1) [HL1 (ethylamino)ethylimino)methyl)-4-methylphenol] 2-hydroxy-5-Methylbenzaldehyde (296 mg, 1 mmol) was added to a solution of Nethylethylenediamine (88 mg, 1 mmol, 0.1 mL) in 10 mL methanol (solution A) and left for stirring for 30 minutes. In another solution FeCl_{2'4H2}O (120 mg, 0.5 mmol) and KNCS (97 mg, 1 mmol) taken in 10 mL methanol (solution B) and stirred for half an hour. After that solution A was added to solution B dropwise and stirred for another 30 minutes. After filtering the resulting mixture it was allowed for slow evaporation. Black crystals of complex 1 were separated from the filtrate after 3 days. Yield: 76% (based on Fe). Elemental analysis: calcd. (%) for C₂₅H₃₄FeN₅O₂S: C 57.25, N 13.35, H 6.53, S 6.11; found C 57.05, N 13.74, H 6.53, S 6.70. Selected IR data (KBr pellet; cm⁻¹): 3412 v(N-H, m), 2934 v(C-H_{arom}), 2063 v(CΞN), 1619 v(C=N), 1541 and 1470 v(C=C), 1166 v(C-O).

Following the similar synthetic methods, complexes **2-3** were synthesized using 2-hydroxy-5-Bromobenzaldehyde and 2-hydroxy-5-methoxybenzaldehyde respectively.

Synthesis of [Fe(L²)₂]NCS (2): Yield: 68% (based on Fe). Elemental analysis: calcd. (%) for C₂₃H₂₈Br₂FeN₅O₂S: C 42.23, N 10.70, H 4.31, S 4.9; found C 41.53, N 10.73, H 4.25, S 5.02. Selected IR data (KBr pellet; cm⁻¹): 3596 v(N-H, m), 2950 v(C-H_{arom}), 2030 v(C=N), 1628 v(C=N), 1540 and 1471 v(C=C), 1160 v(C-O).

Synthesis of [Fe(L³)₂]NCS (3): Yield: 70% (based on Fe). Elemental analysis: calcd. (%) for C₂₅H₃₄FeN₅O₄S: C 53.96, N 12.59, H 6.16, S 5.76; found C 53.74, N 12.71, H 6.180, S 5.46. Selected IR data (KBr pellet; cm⁻¹): 3339 v(N-H, m), 2955 v(C-H_{arom}), 2030 v(C=N), 1629 v(C=N), 1542 and 1470 v(C=C), 1160 v(C-O).

Acknowledgments

S.K. thanks SERB, Government of India (project no. SERB/CRG/2018/000072) and IISER Bhopal for generous financial and support. B.D. and A.M. thank IISER Bhopal for a Ph.D. fellowship.

Keywords: Spin crossover • 5-X-SalEen based ligand (X = Me, Br and OMe) • Theoretical investigation • Solid state magnetic property • Liquid state magnetic property.

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FULL PAPER

Entry for the Table of Contents FULL PAPER

A series of substituted 5-X-SalEen based complexes have been studied in detail by experimental and theoretical methods which gave the understanding of how the differential electron donation from a ligand can influence spin transition behaviour. Liquid state provided a magnetic susceptibility strong ground for claiming such trends. Other liquid state measurements such as UV-Vis and cyclic voltammetry also support the observation.



Spin Crossover

Bijoy Dey, Arpan Mondal, and Sanjit Konar*

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Effect of Ligand Field Strength on Spin Crossover Behaviour in 5-X-SalEen (X = Me, Br and OMe) Based Fe(III) Complexes