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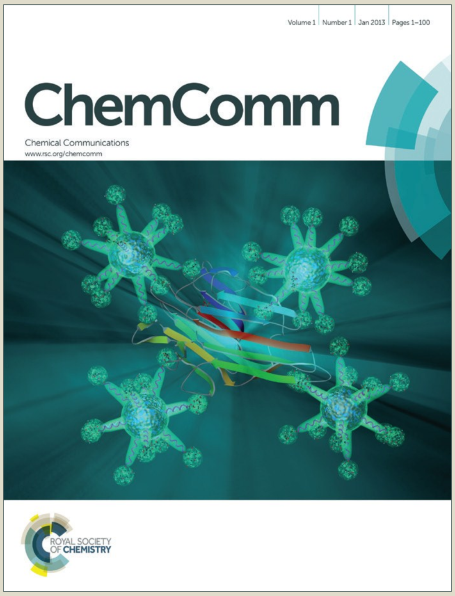

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Ligand effects in a Heteroleptic bis-Tridentate Iron (III) Spin Crossover Complex showing a Very High $T_{1/2}$ Value‡

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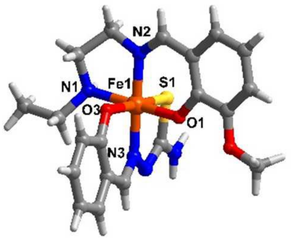
We describe the first example of a bis-tridentate heteroleptic iron(III) spin crossover (SCO) complex, [Fe(3-OMe-SalEen)(thsa)]. Compared to the parent homoleptic compounds, the spin crossover features in the heteroleptic species are enhanced with a gradual-abrupt spin transition at 344 K. Clear correlations between π-π interactions and the $T_{1/2}$ value have been revealed.

Mixed ligand iron(III) d^5 spin crossover compounds have long been known in coordination environments of types $[Fe(tetradentate)(imidazole)_2]^+$,[1] with donor sets of N_4O_2. Bis-tridentate Fe(III) homoleptic species $[FeL_2]^+$, also with donor sets N_4O_2, continue to attract attention and display features such as multi-step spin transitions[2, 3] and light induced excited spin state trapping (LIESST).[4] Many of these features emanate from the nature of the intermolecular interactions within the crystal packing.[5,6] Heteroleptic bis-tridentate species, $[Fe^{III}(L)(L^{'})]$, have not been reported to date and provide the opportunity to explore intramolecular and intermolecular effects from each ligand. Here we describe the first such example, [Fe(3-OMe-SalEen)(thsa)], **1**, where 3-OMe-HSalEen = (E)-2-(((2-(ethylamino)ethyl)imino)methyl)-6-methoxyphenol and H_2thsa = thiosemicarbazone-salicylaldimine (see ligands in Fig. 1). The structural, magnetic, Mőssbauer and DSC properties are discussed and comparisons to homoleptic analogues made, where appropriate.

Complex **1** was reproducibly made by a multi-layering method. Li_2thsa was the bottom aqueous layer, $FeCl_3$ in n-BuOH the middle, with 3-OMe-HSalEen and Et_3N in MeOH on top. Black crystals were formed in good yield. A single crystal structure was performed at 100 K and results revealed that an asymmetric unit of [Fe(3-OMe-SalEen)(thsa)], **1** contains a molecule of neutral Fe(III) complex (Figure 1). The metal centre coordinates in a meridional fashion to N_3O_2S donors derived from a 3-MeO-SalEen$^-$, L1, and a thsa^{2-}, ligand L2. This is the first mixed 3-MeOSalEen and thsa ligand combination in Fe(III) SCO complexes. According to the Fe-L bond lengths (Fe-O ≈ 1.89, Fe-N ≈ 1.91-2.06 and Fe-S ≈ 2.26 Å) and octahedral distortion parameters (Σ = 44° and Θ = 80°), the low-spin (LS) state is suggested for the Fe(III) centre at 100 K. This is well in accord with the magnetic and Mössbauer results.

In the extended structure of **1,** relevant to spin crossover and cooperativity, there are two sets of π-π interactions between each ligand (L1-L1 and L2-L2) that hold Fe molecules in a chain oriented along the *c* axis (Figure 2). The π-π interaction between L1-L1 is also observed in related, abrupt SCO complexes; $[Fe(3\text{-}OMe\text{-}SalEen)_2](Anion)$ where Anion = PF_6[7] and ClO_4[8]. However, in $[Fe(3\text{-}OMe\text{-}salEen)_2][Ni(dmit)_2]\cdot CH_3OH$[9], which shows gradual SCO over a range of 200 K, it is absent. This π-π interaction is therefore believed to be responsible for the gradual/abrupt spin transition taking place in this family.

3-OMe-HSalEen, L1



H_2thsa, L2

[Fe(3-OMe-SalEen)(thsa)], **1**

Figure 1 Molecular structure of L1 and L2 and an asymmetric unit of **1**

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†Electronic Supplementary Information (ESI) available: Tables S1 to S2 structural data; Table S3 Mőssbauer data; Figs S1 to S5, structures, Mőssbauer spectra, DSC and PXRD plots]. CCDC number 1420398. See DOI: 10.1039/x0xx00000x

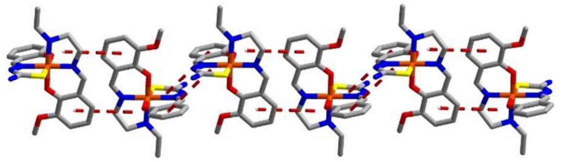

Figure 2 Representation of π-π interactions between thsa-thsa and 3-MeOSalen/3-MeOSalen component in **1**

3-MeOSalEen, **L1** thsa, **L2** qsal

Figure 3 Representation of L1 and L2 ligands coordinating to Fe(III) centres in **1** and the qsal ligand in [Fe(qsal)(thsa)][10]

According to the comparison of this π-π interaction shown in Table **1**, it is clear that the stronger this π-π interaction is, the higher $T_{1/2}$ becomes in the abrupt SCO complexes. Although π-π interactions have been often mentioned as a factor leading to abrupt SCO,[5,11] this is the first time that the correlation has been clearly identified.

Although composed of two different ligands, observation of two sets of π-π interactions in **1** is distinct as none of other [Fe(3-OMe-SalEen)$_2$](Anion) complexes display this intermolecular interaction in their structures. We suggest that it is a result of anions and solvents that prevent the Fe(III) molecules to form two sets of π-π interaction to adjacent molecules. Compared to the homoleptic species (Table 2), we rationally designed, here, neutral species that have no counter-anions. Consequently, ligand effects have been specifically elucidated.

Consistently, these sets of π-π interactions were not observed in our ongoing work involving a heteroleptic molecule of mixed qsal/thsa ligands, [Fe(qsal)(thsa)], (where qsal = quinolylsalicylaldimine) which shows a [LS-HS]→[HS-HS] transition.[10] It is interesting that the ligands L1 and L2 appear to balance the chain in symmetrical packing and create a straight-chain. This is believed to be due to an identical core component of the two ligands (see Figure 3) that allow the structure to pack in a high degree of order and consequently give rise to abrupt SCO.

The adjacent chains further interact mainly through the N-H···N interactions involving the amine groups on thsa ligands together with π-π interactions between L1-L1, as shown in Figure S1. This is similar to a chain observed in the mixed qsal/thsa complexes[10] and is a characteristic of mixed L/thsa systems. For higher dimension packing, there are C-H···π interactions concerning the L1 ligand that link Fe(III) molecules in a *pseudo*-three dimensional structure as shown in Figure S2. This lends further support for L1 promoting SCO taking place in **1**. Hence, we conclude that L1 and L2 provide a good mixed ligand system in Fe(III) SCO compounds for the following reasons; 1) L1 and L2 contain the same core ligand/fragment giving rise to highly symmetrical packing that promotes SCO, 2) A combination of L1 and L2 provides a neutral Fe(III) complex, without need for an anion, which can prevent the important π-π interaction occurring, 3) L1 and L2 contain substituent groups in the opposite directions (OMe from L1 and NH$_2$ from L2) giving rise to a variety of potential interactions to form in multiple directions compared to the more conventional homoleptic analogues. These facts result in high cooperativity in **1** thus yielding a gradual/abrupt spin transition with hysteresis, as now discussed.

The temperature dependence of $\chi_M T$ for [Fe(3-OMe-SalEen)(thsa)], **1** was examined between 250 - 400 K (Figure 4) with different scan rate *i.e.* 2, 5 and 10 K/min. Below 250 K, X_MT remains independent of temperature at LS values. Gradual-abrupt spin crossover is present with $T_{1/2}\uparrow$ = 344 K and $T_{1/2}\downarrow$ = 342 K, suggestive but not definitive of hysteresis. Interestingly, the magnetic profile is stable and repeatable over multiple cycles, and it is independent of scan rate, which is akin to recent data for mononuclear Fe(II) SCO complexes also showing small hysteresis but with more abrupt transitions.[12] To the best of our knowledge, this is the first Fe(III) complex with mixed tridentate ligands that shows relatively abrupt SCO at or above room temperature. This can be considered as the very first compound of this class that improves magnetic properties and shows a complete spin transition at higher temperature compared to the parental homoleptic compounds (Table 2).[1-8] Attempts to measure the photomagnetic LIESST effect in **1** under irradiation wavelengths of 405 nm, 510 nm, 640nm, 830 nm and 980 nm showed no light induced effects, probably because of the high $T_{1/2}$ temperature. In comparison, [Fe(qsal)$_2$]$^+$ salts have smaller $T_{1/2}$ values and display weak LIESST (~8%) thought due to π-π intermolecular effects (*vide infra*).[4] More efficient LIESST has recently been reported for another bis-tridentate Fe(III) complex showing a two-step transition and symmetry breaking.[2]

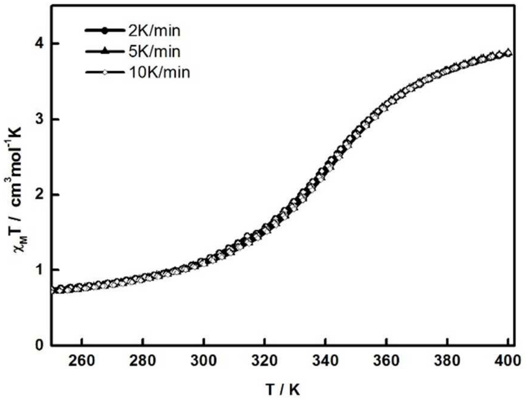

Figure 4 Thermal variation of $\chi_M T$ versus T plot for **1** between 200 and 400 K using the scan rates shown.

Table 1 Comparison of π-π interaction between 3-OMe-SalEen moieties in Fe(III) complexes (plane-plane distances)

Compound	SCO, $T_{1/2}$ heat	Distance/Å	Temperature/K	Ref
[Fe(3-OMe-SalEen)(thsa)]	Abrupt SCO, 344 K	3.028	100	This work
$[Fe(3\text{-}MeO\text{-}SalEen)_2]PF_6$	Abrupt SCO, 165.5 K	3.678	120	7
		3.690	200	
		3.643	300	
$[Fe(3\text{-}MeO\text{-}SalEen)_2]ClO_4$	Abrupt SCO, 196 K	3.436	90	8
		3.719	298	
$[Fe(3\text{-}OMe\text{-}salEen)_2]$- $[Ni(dmit)_2]\cdot CH_3OH^{a)}$	Gradual SCO, 345 K (MeOH Solvate), 275 K (desolvated form)	-	-	9

Table 2 SCO properties and transition temperatures of parent homoleptic compounds

Compound	SCO	$T_{1/2}$ heat/K	$T_{1/2}$ cool/K	Ref
$pyridineH[Fe(thsa)_2]\cdot H_2O$	Incomplete			13
$Na[Fe(thsa)_2]\cdot 3H_2O$	Incomplete			14
$Li[Fe(thsa)_2]\cdot 2H_2O$	LS			14
$NH_4[Fe(thsa)_2]$	LS			15
$Cs[Fe(thsa)_2]$	HS			16
$[Fe(Hthsa)(thsa)]\cdot H_2O$	Abrupt and two-steps	274	262, 232	17
$[Fe(3\text{-}MeO\text{-}SalEen)_2]PF_6$	Abrupt	165.5	162.5	7
$[Fe(3\text{-}OMe\text{-}SalEen)_2]ClO_4$	Abrupt	196		8
$[Fe(3\text{-}OMe\text{-}SalEen)_2]$- $[Ni(dmit)_2]\cdot CH_3OH^{a)}$	Gradual	345 (only 1st cycle)	275	9

a)dmit = 1,3-dithia-2-thione-4,5-dithiolato

^{57}Fe Mössbauer spectra of **1** were measured at 5.6 and 293 K. (Figure S3). At 5.6 K, the spectrum is dominated by the large quadrupole splitting, 2.98 mm s^{-1}, and isomer shift of 0.24 mm s^{-1} indicating the existence of pure LS Fe(III).[8, 17] On warming to 293 K, a doublet with small quadrupole splitting, 0.63 mm s^{-1}, and with larger isomer shift of 0.31 mm s^{-1} is also present suggesting a combination of 80% LS and 20% HS Fe(III). Overall, the Mössbauer spectra agree with the magnetic susceptibility studies and confirm the SCO is taking place above room temperature. Unfortunately, instrumental limitations do not allow us to get the measurement at higher temperature to confirm the fully HS state.

Differential scanning calorimetry (DSC) was collected on compound **1** in the range 253-443 K with 10 K/min scan rate. The DSC plot in Figure S4 shows two anomalies in the cooling and heating mode with maxima at $T_{1/2}$ = 330 and $T_{1/2}$ = 346 K, respectively. The values suggest a large hysteresis of about 16 K width, bigger than that suggested by magnetism. The entropy changes associated with the spin crossover in **1** (ΔS = 16.30 J K^{-1} mol^{-1}) is less than the values reported for other related Fe(III)-3MeO-SalEen compounds.[8,18] However, it is more than the value expected for a change in spin state only (9.13 J K^{-1} mol^{-1}.) The excess entropy is believed to be a result of the intramolecular vibrational changes.[19]

In conclusion, an Fe(III) complex with mixed 3-MeO-SalEen/thsa tridentate ligands, **1**, is reported and the magnetic study reveals a gradual/abrupt spin crossover at distinctively high temperature, 344 K, which significantly improves the magnetic profile of the parent homoleptic compounds. A clear connection between π-π interactions in the crystal and $T_{1/2}$ has been identified. Moreover, we have discovered a new strategy to enhance spin crossover properties in Fe(III) compounds *via* the combination of similar core ligand moieties within the two different ligands. It not only promotes strong cooperativity but also promotes a diversity of intermolecular interactions in the structures. Ongoing work involves changing ligand L1.[10]

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Notes and references

‡Compound **1** was reproducibly synthesized by mixing LiOH (17 mg, 0.4 mmol) and H_2thsa (39 mg, 0.2 mmol) in H_2O (3 ml) giving a yellow solution. In a separate flask, $FeCl_3$ (32 mg, 0.2 mmol) was dissolved in n-BuOH (3 ml) giving a yellow solution. The solution was layered on top of the Li_2thsa solution. At the top of the $FeCl_3$ solution, a mixture of 3-MeO-HSalEen (17 mg, 0.4 mmol) and NEt_3 (56 μl, 0.4 mmol) in MeOH was then layered and left for two weeks. The dark solution was filtered and evaporated in ambient conditions. The black block-shaped crystals were obtained after two days (50 mg, 53%). $\tilde{\upsilon}_{max}/cm^{-1}$ 3485 (υ_{NH2}), 3116 (υ_{Ar-H}), 2930 (υ_{O-CH3}), 1592 ($\upsilon_{C=N}$), 1312 (υ_{C-O}), 730 (υ_{CS}) cm^{-1}. (ESI): m/z = 470.1 [Fe(3-OMe-SalEen)(thsa)]. Calcd. for (found %) $C_{20}H_{24}FeN_5O_3S$: C, 51.07 (50.18); H, 5.14 (5.16); N, 14.89 % (14.57).

The powder of **1** can also be synthesized by mixing all the mentioned reactants and stirring for a few hrs. The PXRD pattern of the compound is shown in Figure S5.

§*Crystal data for* **1**: T = 100 K, triclinic, space group $P\bar{1}$, *a* = 8.3940(17) Å, *b* = 9.3500(19) Å, *c* = 13.675(3) Å, α = 82.26 (3)°, β = 73.44 (3)°, γ = 82.14 (3)°, V = 1013.9 (4) $Å^3$, *Z* = 2, μ = 0.880 mm^{-1}, 27497 reflections, 5929 unique, R_{int} = 0.0501, R_1 = 0.0401, $wR(F^2)$ = 0.1123 ($I > 2\sigma(I)$). CCDC number 1420398.

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