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COMMUNICATION

## Room Temperature Spin Crossover Ionic Liquids

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**Two new paramagnetic ionic liquids (ILs) comprising a mononuclear iron(III) or manganese(III) complex cation, charge balanced by a dicyanamide anion are reported which show a range of spin states. Both are liquids at room temperature and the Fe(III) based IL exhibits a spin crossover close to 300 K. The spin crossover profile is independent of the solvation, and is both air and moisture stable.**

The molecular switching phenomenon of SCO has great potential in data storage and molecular switching and sensing.<sup>1</sup> However there is a need to have a processable, malleable material whose properties are less dependent on crystalline morphology. Recently there has been an interest in the investigation of the effects of crystalline defects in solid SCO materials.<sup>2</sup> The "breathing" of SCO molecules can propagate across a whole domain resulting in a macroscopic change in the lattice. Apart from breaking or damaging the sample, the presence of microscopic defects may strongly influence the way the SCO propagates at the macroscopic level.

One method to overcome crystalline defects could be the use of ionic liquid (IL) design strategies. Most of the work in SCO in the past 80 years has been carried out in the solid state but with increasing interest in development of processable spin switchable materials, there is a move towards investigation of the phenomenon in soft matter.<sup>3-10</sup> ILs are salts with melting temperatures below 373 K and room temperature liquids (RTILs) offering a promising vehicle to add flexibility to develop the range of SCO applications *e.g.* thermochromic inks or spin switchable reaction media. The main design criterion for an IL of a bulky asymmetric cation charge balanced by a bulky anion, offers much scope for combinations of cation and anion which in turn allows for a great variety of tunable interactions and applications. The negligible vapour pressure, wide temperature liquid range, high thermal stability, high ionic conductivity, wide

electrochemical window, and ability to solvate compounds of widely varying polarity have seen their increased use in organic synthesis,<sup>11, 12</sup> magnetism,<sup>13</sup> physical and analytical chemistry,<sup>14-16</sup> and, most prevalently, catalysis.<sup>17-20</sup>

In 2013 Okuhata *et al.* published the first and so far only example of a SCO IL,<sup>21</sup> utilising a terdentate equatorial N<sub>2</sub>O<sub>2</sub><sup>2-</sup> donor set around iron(III) with exogenous axial n-butylimidazole ligands. However the complex gradually decomposes by desorption of the axial ligands and hence is not suitable for further processing. Here we present a route to synthesising stable SCO complexes with RTIL characteristics. This is achieved by the covalent addition of bulky asymmetric cations to two different types of hexadentate Schiff base ligands, R-Sal<sub>2</sub>trien which facilitates SCO in Fe(III),<sup>22-27</sup> and R-Sal<sub>2</sub>323, known to promote SCO in Mn(III),<sup>28-34</sup> Fig. 1

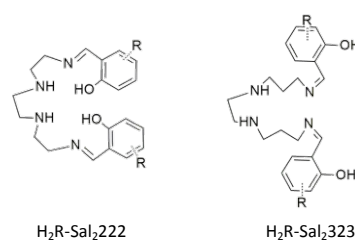
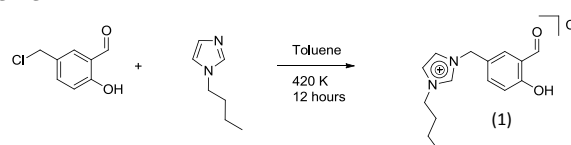


Fig. 1: Schiff base ligands known to promote SCO in Fe(III), (H<sub>2</sub>R-Sal<sub>2</sub>222) and Mn(III), (H<sub>2</sub>R-Sal<sub>2</sub>323).

The parent ligands were modified by appending N-butylimidazolium groups to the salicylaldehyde ligand precursor. This was achieved by reaction of N-butyl imidazole with 5-(methylchloro)salicylaldehyde,<sup>35</sup> to yield compound (1), Scheme 1.



Scheme 1: Synthesis of substituted salicylaldehyde, (1).

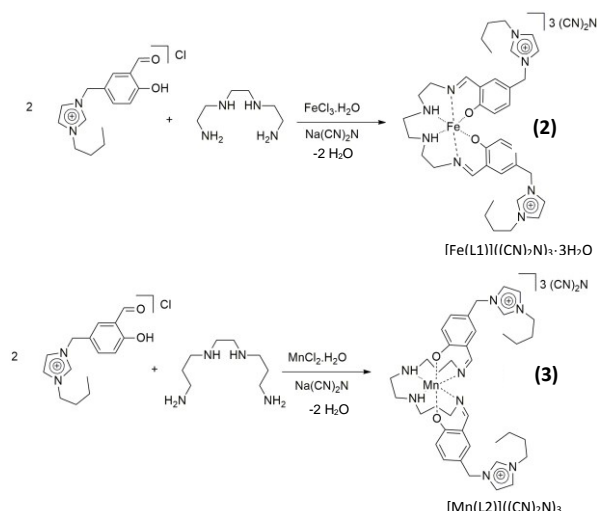
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The *N*-butylimidazolium functionalised salicylaldehyde, (**1**), was then reacted with triethylenetetramine (222) or *N,N'*-bis(3-aminopropyl)ethylenediamine (323), to form the Schiff base and the appropriate metal chloride was added directly to the solution. Anion metathesis was effected by addition of sodium dicyanamide to form complexes [Fe(L1)]((CN)<sub>2</sub>N)<sub>3</sub>•3H<sub>2</sub>O (**2**) and [Mn(L2)]((CN)<sub>2</sub>N)<sub>3</sub>, (**3**) as clean viscous liquids in good yield. As both (**2**) and (**3**) are liquids at room temperature it was not possible to obtain the glass transition temperatures on our current experimental setup but these will be reported separately as our low temperature studies develop.



Scheme 2: Synthesis of complexes (**2**) and (**3**).

The hydrated complex (**2**), [Fe(L1)]((CN)<sub>2</sub>N)<sub>3</sub>•3H<sub>2</sub>O, and its dehydrated analogue (**2'**) [Fe(L1)]((CN)<sub>2</sub>N)<sub>3</sub> both exhibit a gradual and incomplete SCO between 10-380 K, shown for four cycles of heating and cooling at 5 K min<sup>-1</sup> for (**2'**) in Figure 2. The initial scan on [Fe(L1)]((CN)<sub>2</sub>N)<sub>3</sub>•3H<sub>2</sub>O, (**2**), resulted in loss of water and a change in molar mass but no difference in the magnetic profile, (see Figure S1 in the ESI) or physical state, *i.e.* the liquid character is retained and the spin switching is impervious to solvation in contrast to what is normally observed in solid state SCO.<sup>36-38</sup>

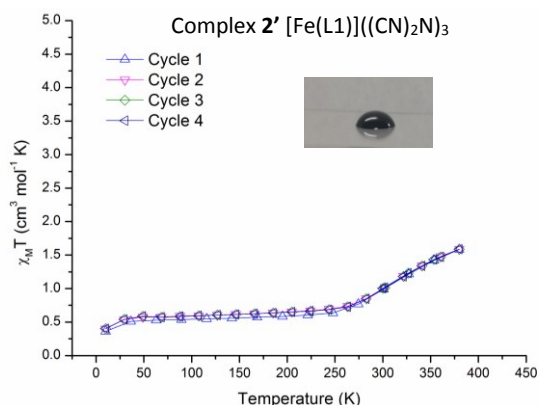


Fig. 2:  $\chi_M T$  vs T plot for **2'**. Inset: one drop of **2** at RT.

The moment of *circa* 0.5 cm<sup>3</sup> mol<sup>-1</sup> K between 10-250 K, is as expected for  $S = \frac{1}{2}$ , *i.e.* low spin Fe(III).<sup>22</sup> Above 250 K the moment starts to rise indicating onset of a switch to  $S = 5/2$  ( $\chi_M T = 4.38$  cm<sup>3</sup> mol<sup>-1</sup> K) reaching a value of  $\chi_M T = 1.58$  cm<sup>3</sup> mol<sup>-1</sup> K (36% HS) at the maximum recorded temperature. The liquid did not display an obvious colour change over this temperature range but electronic absorption spectra collected in methanol solution between 278-323 K showed a hypochromic shift on warming, Fig. S3.

Complex (**3**), [Mn(L2)]((CN)<sub>2</sub>N)<sub>3</sub>, is also a RTIL, however no spin crossover is observable between 300-10 K, Fig. 3. The  $\chi_M T$  value between 100-300 K is close to 3 cm<sup>3</sup> mol<sup>-1</sup> K, *i.e.* high spin Mn(III),  $S = 2$ .<sup>29, 32</sup> The slight decrease in the  $\chi_M T$  value at low temperatures is attributed to zero-field splitting.

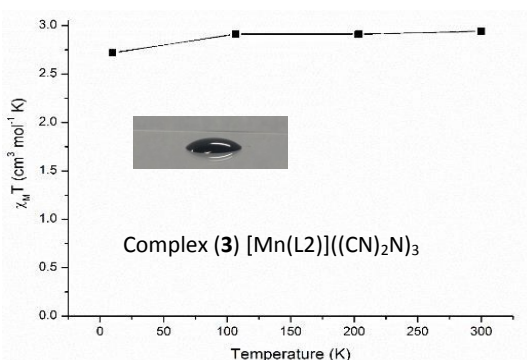


Fig. 3:  $\chi_M T$  vs T plot for [Mn(L2)]((CN)<sub>2</sub>N)<sub>3</sub>, (**3**). Inset: one drop of (**3**) at RT.

A recent experimental study on the structural fatigability of crystalline SCO complex by Guionneau *et al.*<sup>39</sup> showed that after numerous thermal SCO cycles (HS→LS→HS) the mosaicity of the crystal significantly increases. The mosaic model describes a crystal as an ordered domain in an array of slightly misaligned tiles. Even after one cycle the mosaicity increases and the increase continues after every cycle until at 20 cycles there is a plateau. This highlights the potential structural instability of crystalline SCO complexes for use in applications, although in this case the magnetic properties were not affected. However the complex used in this study only exhibits a gradual SCO which shows very low cooperativity. Structural fatigability, is expected to have greater consequences for hysteretic transitions that are dependent on solid state interactions to improve cooperativity. Here a route which overcomes structural fatigability has been employed whereby the spin active centres are present in liquid form rather than as components in a crystalline lattice. Work is ongoing to introduce design features which may promote more abrupt spin state switching in such media.

In conclusion, a novel route to the synthesis of robust and chemically stable magnetically switchable room temperature ionic liquids, is reported here. The addition of large cationic groups to the SCO promoting ligands was successfully used to confer liquid characteristics on the resulting complexes with room temperature spin state switching observed in one example. The potential tunability of this system is great as many known SCO families comprise ionic salts and we have shown here that through relatively facile transformations liquid character can be conferred with very little change to the

immediate coordination sphere of the metal ion. This method of depressing the melting point of solid complexes to become intrinsic liquids by ligand design has a wide array of applications from catalysis to materials chemistry.

## Notes and references

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‡ Synthesis of (**1**) - Under a nitrogen atmosphere, 5-chloromethyl-2-hydroxybenzaldehyde (4.824 g, 28.3 mmol) was added to 1-butylimidazole (4.46 mL, 33.9 mmol) in toluene (30 mL). The resulting yellow solution was stirred for 24 hours before washing with de-ionised water, drying with Na<sub>2</sub>SO<sub>4</sub>, and removing the solvent using rotary evaporation to yield a yellow viscous liquid in 83% yield. <sup>1</sup>H: δH(300 MHz; CDCl<sub>3</sub>) 0.9 (t, 3H), 1.3 (m, 2H), 1.8 (m, 2H), 4.2 (t, 2H), 5.7 (s, 2H), 6.9-7.5 (m, 3H), 10.0 (s, 1H).

Synthesis of (**2**) - Ligand (**1**), (1 mmol, 0.294 g) was dissolved in 25 mL/5 mL CH<sub>2</sub>Cl<sub>2</sub>/MeOH before triethylenetetramine (0.07 mL, 0.5 mmol) was added and stirred for 10 minutes at room temperature. The formation of the Schiff-base ligand was indicated by the yellow solution that formed. FeCl<sub>3</sub>·6H<sub>2</sub>O (0.135 g, 0.5 mmol) was added subsequently which led to formation of the complex as indicated by the colour change from yellow to brown/black. Anion exchange was performed using sodium dicyanamide (0.178 g, 2 mmol) and the solution was stirred for 30 minutes at room temperature. The resulting solution was filtered and placed into a round-bottom flask and the solvent was removed by rotary evaporation. The dark liquid that remained was extracted using CH<sub>2</sub>Cl<sub>2</sub> before being dried over sodium sulfate and filtered. Removal of the solvent afforded complex **2** as a dark brown/red coloured liquid. Yield = 70 %, Elemental Analysis: Calc. for [Fe(L1)]((CN)<sub>2</sub>N)<sub>3</sub>·3H<sub>2</sub>O, C<sub>42</sub>H<sub>50</sub>FeN<sub>17</sub>O<sub>2</sub>·3H<sub>2</sub>O, Theory: C, 55.02; H, 5.94; N, 25.97, Found: C, 54.99; H, 5.84; N, 25.83.

Synthesis of (**3**) - Ligand (**1**), (1 mmol, 0.294 g) was dissolved in 25 mL/5 mL CH<sub>2</sub>Cl<sub>2</sub>/MeOH before N,N'-bis(aminopropyl)ethanediamine (0.09 mL, 0.5 mmol) was added and stirred for 10 minutes at room temperature. The formation of the Schiff-base ligand was indicated by the yellow solution that formed. MnCl<sub>2</sub>·4H<sub>2</sub>O (0.099 g, 0.5 mmol) was added subsequently which led to formation of the complex as indicated by the colour change from yellow to brown. Anion exchange was performed using sodium dicyanamide (0.178 g, 2 mmol) and the solution was stirred for 30 minutes at room temperature. The resulting solution was filtered and placed into a round-bottom flask and the solvent was removed by rotary evaporation. The liquid that remained was extracted using CH<sub>2</sub>Cl<sub>2</sub> before being dried over sodium sulfate and filtered. Removal of the solvent afforded complex **3** as a dark brown coloured liquid. Yield = 64 %, Elemental Analysis: Calc. for [Mn(L2)]((CN)<sub>2</sub>N)<sub>3</sub>, C<sub>44</sub>H<sub>54</sub>MnN<sub>17</sub>O<sub>2</sub>, Theory: C, 54.88; H, 6.38; N, 24.73, Found: C, 54.57; H, 6.40; N, 24.68.

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