

## Supporting information for the manuscript

### Assembly of High-Spin [Fe<sub>3</sub>] Clusters by Ligand-Based Multielectron Reduction

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### General consideration

Unless otherwise noted, all manipulations were carried out under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen level were always kept at less than 0.1 ppm. Glassware was dried overnight at 150°C prior to use. Unless otherwise noted, reagents were acquired from commercial sources and used without further purification. The solvents were purchased from Sigma Aldrich or Cortecnet (deuterated solvents) in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone (THF, THF- $d_8$ ), Na sand/benzophenone (*n*-hexane) or dried with molecular sieves 3 Å (py, py- $d_5$ ). The syntheses were performed using glass coated stirring bars. The ligand H<sub>2</sub>salophen (*N,N'*-phenylene-bis-(salicylideneimine)) and its sodium salt Na<sub>2</sub>salophen were prepared according to published procedures.<sup>1</sup> The complex [Fe(salophen)(THF)] was prepared using a modified literature procedure.<sup>2</sup> <sup>1</sup>H and <sup>13</sup>C NMR experiments were carried out using NMR tubes adapted with J. Young valves. The NMR spectra were recorded on a 400 MHz Bruker spectrometer. <sup>1</sup>H chemical shifts are reported in ppm and were measured relative to residual solvent peaks, which were assigned relative to an external TMS standard set at 0.00 ppm. Elemental analyses were performed under nitrogen with a ThermoScientific Flash 2000 Organic Elemental analyzer. The UV-Vis-NIR spectra were performed with a PerkinElmer Lambda 750 spectrometer. The IR spectra were performed with PerkinElmer Frontier spectrometer. The magnetic measurements were performed using a QuantumDesign MPMS-5T superconducting quantum interference device (SQUID) magnetometer in a temperature range between 5 and 300 K. The microcrystalline samples were enclosed in a quartz tube and flame sealed under vacuum. The samples were restrained with eicosane to prevent torquing

during the measurement. Magnetic measurements were reproduced on three different batches.

Magnetic measurements were carried out on 5.7, 4.8 and 2.1 mg of **1-THF** and 5.0, 6.0 and 5.0 mg of **1-py**.

The magnetic moment of **1-THF** and **1-py** was also measured in THF and pyridine solutions respectively using Evans method.<sup>3</sup>

## Synthesis

**[Fe(salophen)(THF)]**. A solution of Na<sub>2</sub>salophen (1.87 g, 3.9 mmol, 1 eq) in THF (25 mL) was added at room temperature to a suspension of FeCl<sub>2</sub> (500 mg, 3.9 mmol, 1 eq) in THF (25 mL). The mixture was stirred at room temperature for 7 days affording a dark suspension. The mixture was filtered to remove NaCl and the solvent volume was reduced under vacuum to approximately 10 mL. Storage of the resulting concentrated solution at -40 °C afforded dark green crystals of [Fe(salophen)(THF)] (1.40 g, 80 % yield).

The magnetic data measured in solution and in the solid state are comparable to those reported in the literature<sup>4</sup> ( $\chi_M T = 3.7$  emu K/mol in solid state and  $\chi_M T = 3.5$  emu K/mol in THF solution at 300 K).

<sup>1</sup>H NMR spectrum of the crystals in py-d<sub>5</sub> (400 MHz, py-d<sub>5</sub>, 298 K):  $\delta = 60.72$  (s, 1H), 44.11 (s, 1H), 14.77 (s, 1H), 10.63 (s, 2H), -7.51 (s, 1H), -17.04 (s, 1H). Elemental analysis calcd. for [Fe(salophen)/THF] (444.2 g mol<sup>-1</sup>): C, 59.86; H, 4.27; N, 6.18. Found: C, 59.66; H, 4.59; N, 5.80.

**[Na<sub>6</sub>Fe<sub>3</sub>(tris-cyclo-salophen)(py)<sub>9</sub>], 1-py and [Na<sub>6</sub>Fe<sub>3</sub>(tris-cyclo-salophen)(THF)<sub>7</sub>]<sub>2</sub>, 1-THF**. Sodium metal (20.8 mg, 0.904 mmol, 2 eq) was added to a solution of [Fe(salophen)(THF)] (200 mg, 0.452 mmol, 1 eq) in THF (4 mL) at room temperature. The reaction was stirred overnight at room temperature affording a brown solution and an orange precipitate. The precipitate was separated from the solution by centrifugation and the resultant solid was washed three times with THF (2 mL). Dissolution of the orange precipitate in pyridine afforded a dark brown solution. Diffusion of n-hexane into the pyridine solution afforded the complex [Na<sub>6</sub>Fe<sub>3</sub>(tris-cyclo-salophen)(py)<sub>9</sub>], **1-py** (188 mg, 72 % yield). Crystals suitable for X-ray

diffraction were obtained by slow diffusion of *n*-hexane into a pyridine solution of **1-py**.

The  $^1\text{H}$  NMR spectrum of **1-py** in py-d5 did not show any resonance attributable to the complex when recorded either at  $-40\text{ }^\circ\text{C}$  or at room temperature.

A magnetic moment  $\mu = 10.8\ \mu_{\text{B}}$  ( $\chi_{\text{M}}T = 14.6\text{ emu K mol}^{-1}$ ) was measured for **1-py** in pyridine solution at 298 K using the Evans method.<sup>3</sup>

Elemental analysis calcd. for  $[\text{Na}_6\text{Fe}_3(\text{tris-cyclo-salophen})(\text{py})_7]$  ( $1801.5\text{ g mol}^{-1}$ ): C, 63.34; H, 4.31; N, 10.11. Found: C, 63.02; H, 4.55; N, 10.23.

SQUID magnetometry was performed in samples containing different amounts of pyridine (7-10) due to different exposure times of the isolated solid to vacuum. No significant differences were observed among the measurements.

The orange precipitate obtained from the reduction of  $[\text{Fe}(\text{salophen})(\text{THF})]$  in THF could also be solubilized in THF but this required stirring the solid for 4 weeks at room temperature and led to a dark red solution. Slow diffusion of *n*-hexane into the resulting solution afforded the complex  $[\text{Na}_6\text{Fe}_3(\text{tris-cyclo-salophen})(\text{THF})_7]_2$ , **1-THF** as dark brown microcrystalline solid (205 mg, 84% yield). The  $^1\text{H}$  NMR spectrum of **1-THF** in THF-d8 did not show any resonance attributable to the complex when recorded either at  $-40\text{ }^\circ\text{C}$  or at room temperature.

Crystals suitable for X-ray diffraction were obtained by slow diffusion of *n*-hexane into a THF solution **1-THF**. Elemental analysis calcd. for  $[\text{Na}_{12}\text{Fe}_6(\text{tris-cyclo-salophen})_2(\text{THF})_{14}]$  ( $3506.4\text{ g mol}^{-1}$ ): C, 60.29; H, 5.63; N, 4.79. Found: C, 60.64; H, 5.28; N, 4.86.

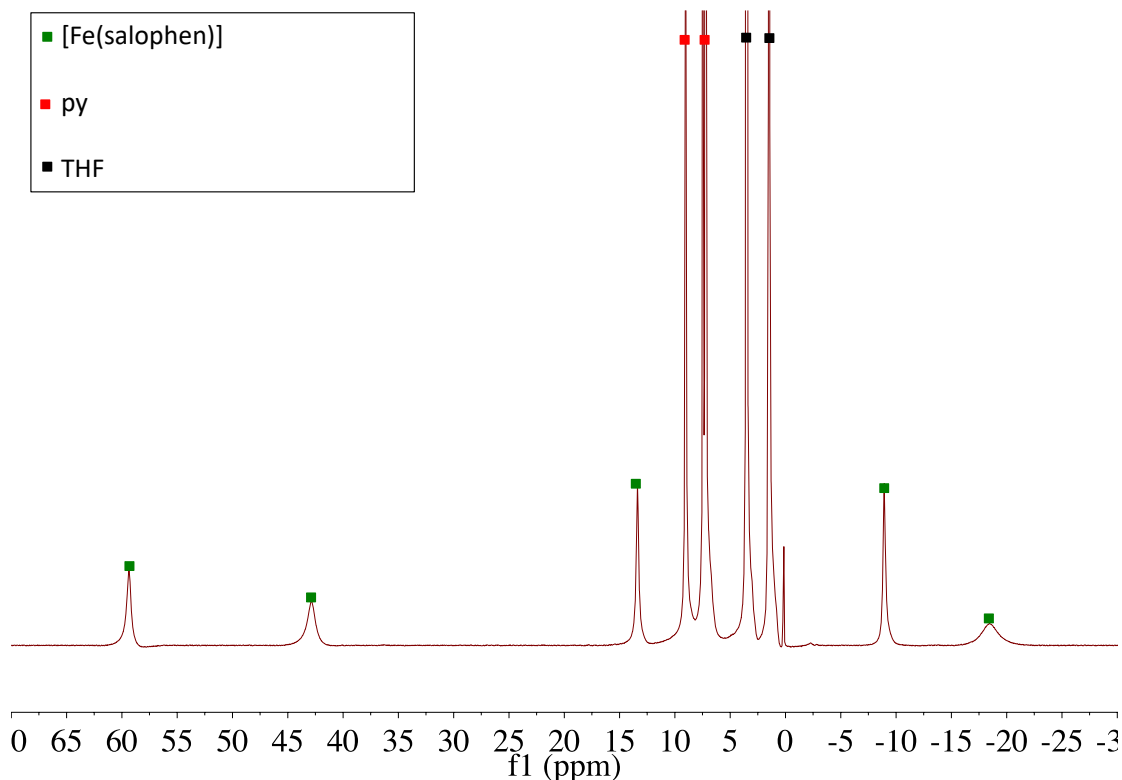
A magnetic moment  $\mu = 11.2$  ( $\chi_{\text{M}}T = 15.7\text{ emu K mol}^{-1}$ ) was measured for **1-THF** at 298 K in THF solution by Evans method.<sup>3</sup>

The amount of coordinated THF is dependent on the drying time. The amount of THF present in the solid, detected by elemental analysis, does not affect the magnetometry measurements, suggesting that the trinuclear structure is retained independently on the amount of coordinated THF.

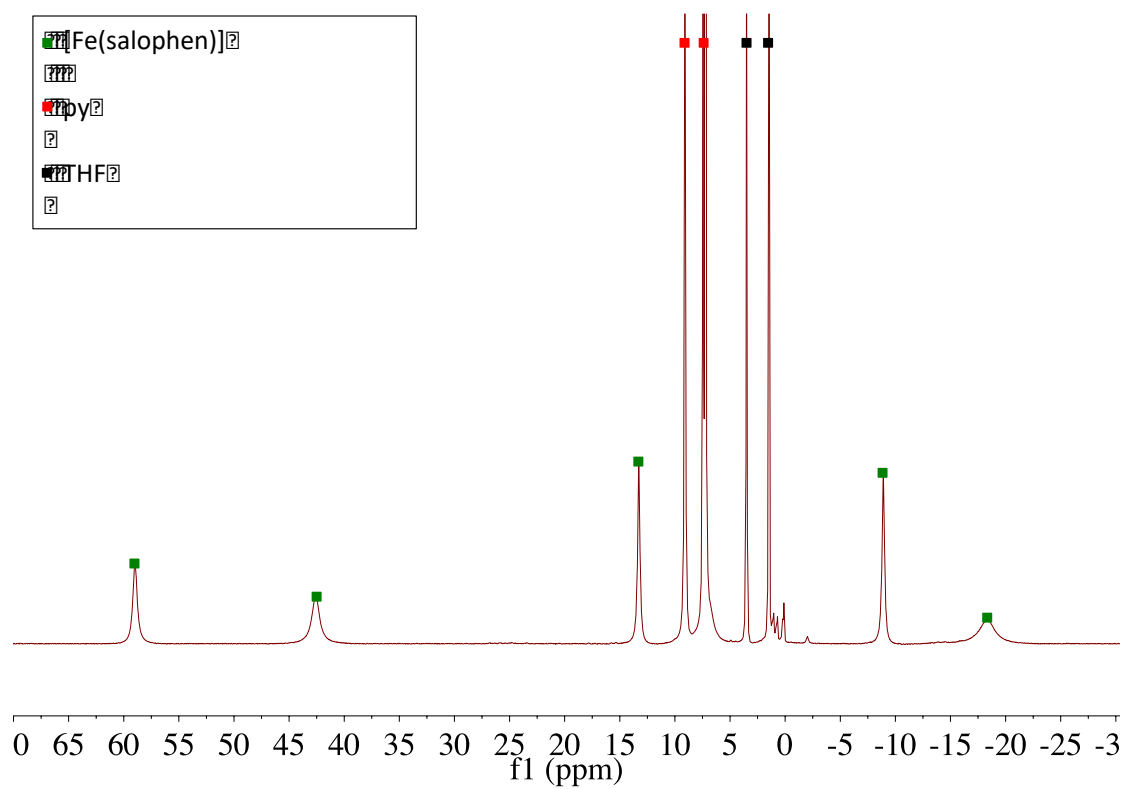
**Reaction of 1-py with  $^{13}\text{CO}_2$ .** The complex **1-py** (10 mg, 0.0028 mmol, 1 eq) was dissolved in py-d5 (0.4 mL) in an NMR tube equipped with a J Young valve under an argon atmosphere. The solution was degassed by three cycles of freeze-pump-thawing.

$^{13}\text{CO}_2$  (6 eq) was added to the frozen solution. The reaction mixture rapidly changed colour from dark brown to dark green upon thawing and a dark precipitate formed. The  $^1\text{H}$  NMR spectrum was recorded after one night at 298 K, this showed only the resonances assigned to  $[\text{Fe}(\text{salophen})(\text{THF})]$ . Volatiles were removed under vacuum and basic  $\text{D}_2\text{O}$  (pD = 13.4) was added to the residue. The  $^{13}\text{C}$  NMR spectrum in  $\text{D}_2\text{O}$  showed the presence of a signal at 168 ppm assigned to  $\text{CO}_3^{2-}$ . A reproducible yield in carbonate of 98(5)% (calculated with respect to the reaction of **1-py** with 6  $\text{CO}_2$  molecules) was measured by quantitative  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy using a labelled  $\text{CH}_3^{13}\text{COONa}$  solution as an internal standard. No dependence of the yield in carbonate from the concentration of **1-py** was found.

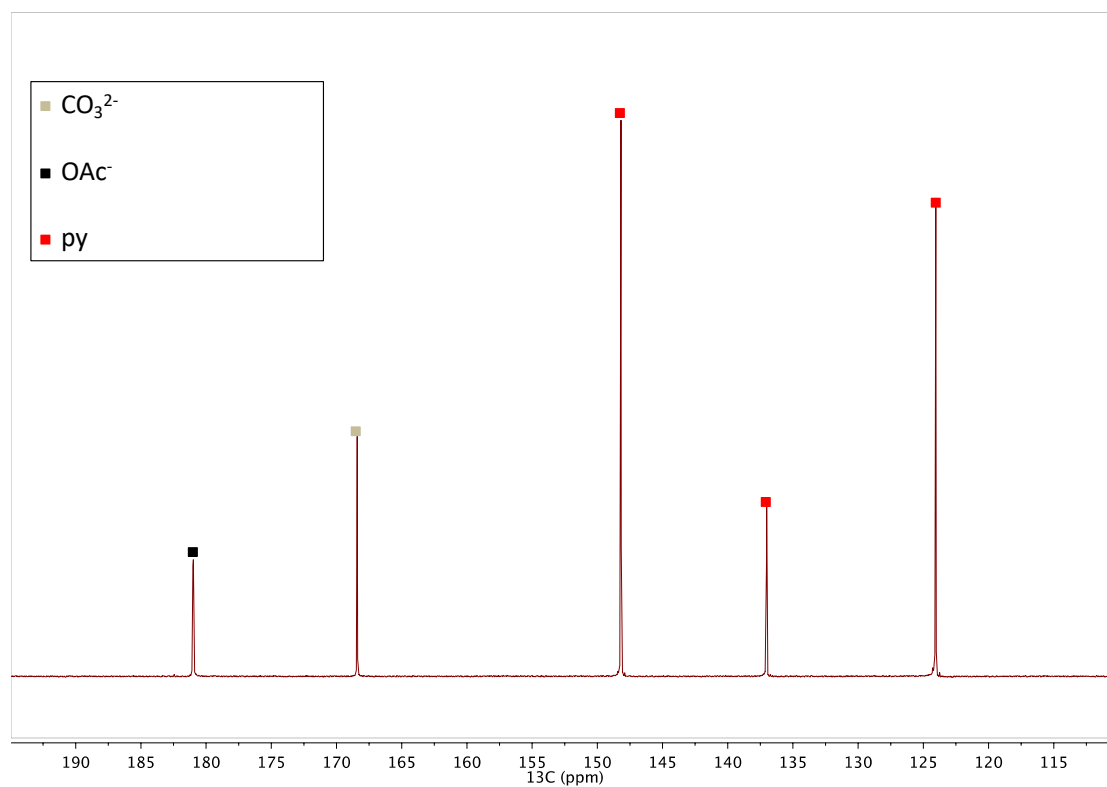
### NMR spectra



**Figure S1**  $^1\text{H}$  NMR spectrum of  $[\text{Fe}(\text{salophen})]$  (py-d<sub>5</sub>, 400 MHz, 298 K).

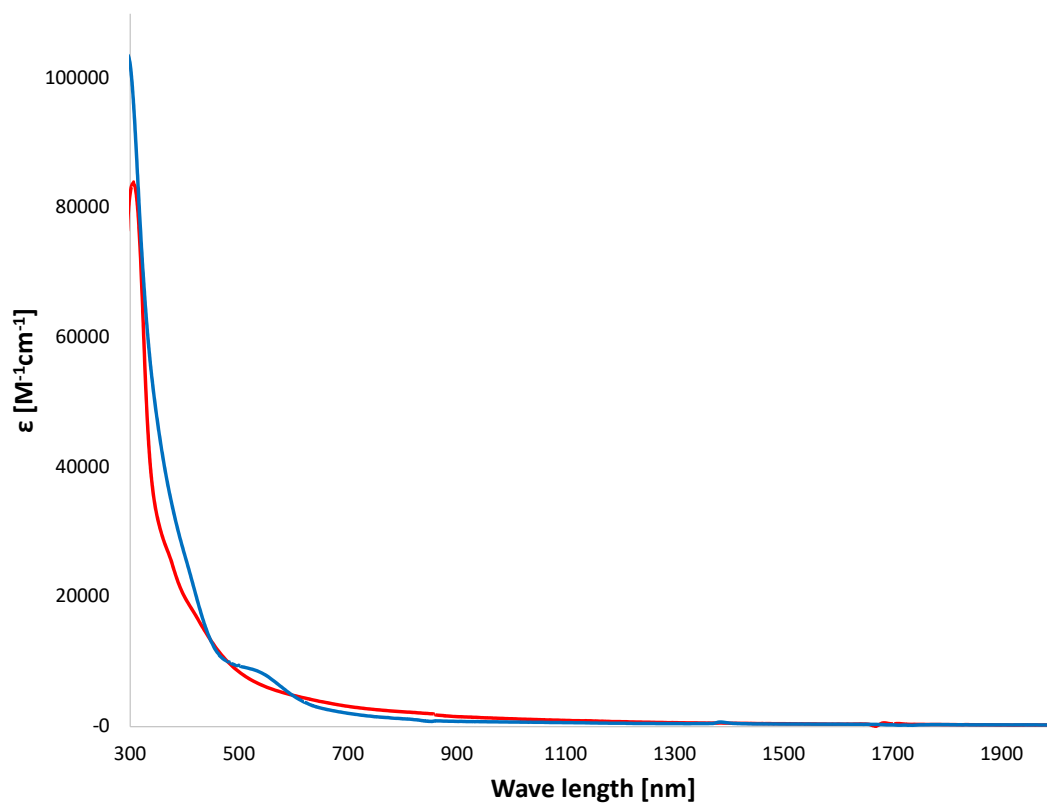


**Figure S2**  $^1\text{H}$  NMR spectrum of the reaction mixture of **1-py** and  $^{13}\text{CO}_2$  after one night (py-d5, 400 MHz, 298 K).

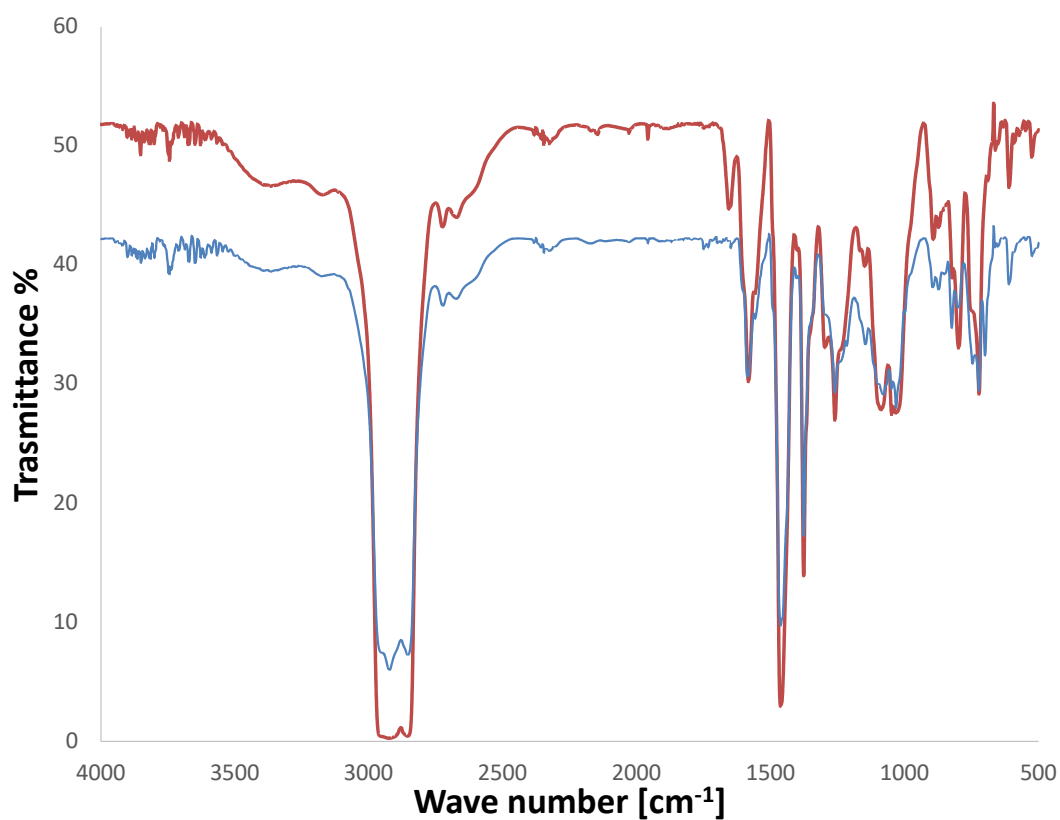


**Figure S3**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the reaction mixture of **1-py** and  $^{13}\text{CO}_2$  ( $\text{D}_2\text{O}$ , 400 MHz, 298 K).

## UV-Vis-NIR and IR spectra



**Figure S4** UV-Vis-NIR spectrum of a 0.14 mM solution of **1-THF** in THF (blue) and 0.28 mM solution of **1-py** in py (red).



**Figure S5** IR spectrum of **1-THF** (blue) and **1-py** (red), crystals in nujol.



## X-ray crystallography structure determination details

### Experimental Part.

The diffraction data for both crystal structures were collected at low temperature using Cu (**1-THF**) or Mo (**1-py**)  $K_{\alpha}$  radiation on a Rigaku SuperNova dual system in combination with Atlas type CCD detector. The data reduction and correction were carried out by *CrysAlis<sup>Pro</sup>*.<sup>5</sup>

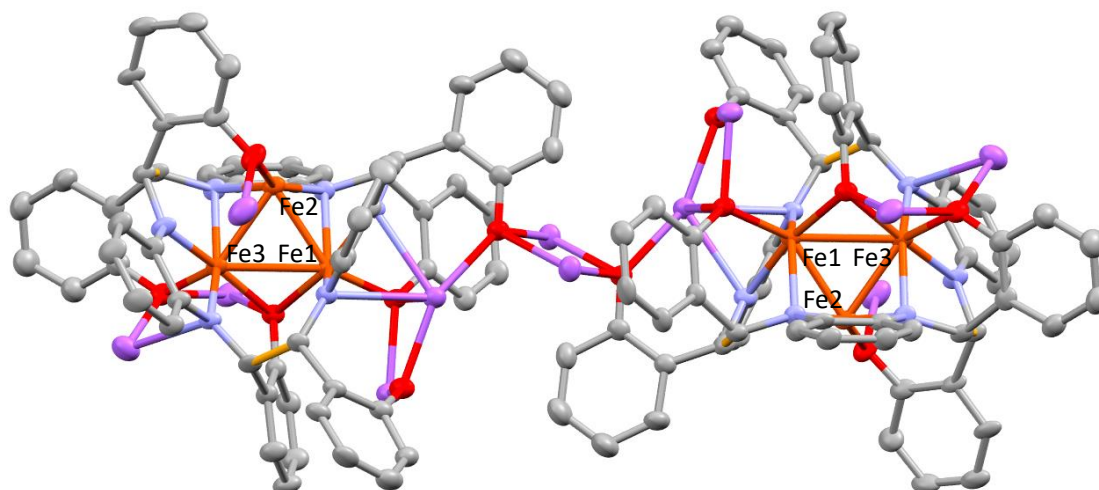
The solutions and refinements were performed by *SHELXT*<sup>6</sup> and *SHELXL*<sup>7</sup>, respectively. The crystal structures were refined using full-matrix least-squares based on  $F^2$  with all non-H atoms defined in anisotropic manner. Hydrogen atoms were placed in calculated positions by means of the “riding” model.

For compound **1-THF**, the major problems found during the refinement of the crystal structure dealt with disordered THF, bound to Na atoms. One of them was split and some restraints (DFIX, SADI, SIMU and RIGU cards) were applied to bond distances and to the adp's, in order to obtain acceptable values.

Due to the high degree of displayed disorder, the free solvent molecules (THF) were removed by applying the *SQUEEZE* algorithm of *PLATON*.<sup>8</sup>

The refinement of crystal structure **1-py** showed some problems concerning 2 pyridines (one bound to Na and one free). Two different orientations were found, their geometry were constrained to be regular (AFIX 66) and their adp's were similarly restrained (SIMU card).

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and correspond to the following codes: **1-THF** (1983316), and **1-Py** (1983317). These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.



**Figure S6.** Molecular crystal structure of **1-THF** (50% probability ellipsoids). The three C-C bonds formed by reduction of salophen<sup>2-</sup> are shown in yellow. Hydrogen atoms and the Na-bound THF molecules have been omitted for clarity.

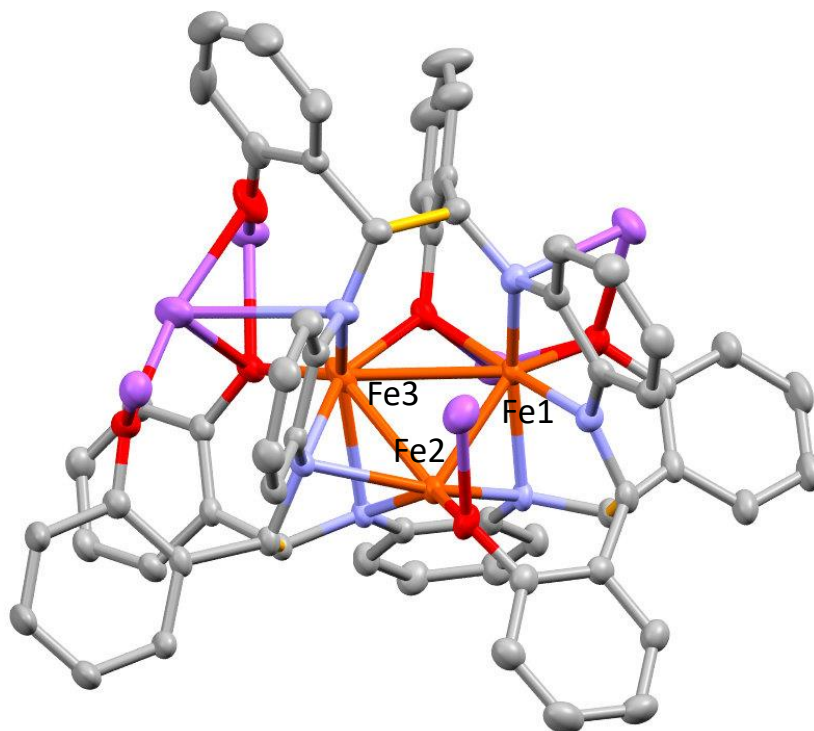
Complex **1-THF** crystallizes in the  $P2_1/c$  space group with half a molecule per asymmetric unit. The structure shows two identical moieties which are bridged via two sodium–aryloxide bonds. The two molecules are related by a crystallographic inversion center located between the bridging sodium cations. Each moiety consists of a triangular core of Fe(II) ions coordinated to the new dodecadentate macrocyclic *tris-cyclo-salophen* ligand, formed by the reductive coupling of the imino groups of three distinct salophen ligands resulting in three new C–C bonds. Twelve inner-sphere aryloxide-bound sodium cations balance the  $-12$  charge of the *tris-cyclo-salophen* ligand. Overall fourteen THF molecules complete the coordination sphere of the sodium cations. In each trinuclear moiety, two different coordination environments can be found for the Fe(II) ions. Fe(2) is tricoordinated in a distorted trigonal planar geometry by two bridging amide nitrogens and one aryloxide oxygen. The bond distances (Fe(2)-N(1) = 2.021(4) Å, Fe(2)-N(2) = 2.061(4) Å and Fe(2)-O(2) = 1.914(3) Å) are consistent with Fe(II) formulation.<sup>9</sup> The Fe(1) and Fe(3) ions are pentacoordinate in a distorted square pyramidal geometry ( $\tau_5 = 0.23$  and  $\tau_5 = 0.38$  respectively) by three amide nitrogen atoms and two aryloxide oxygen atoms. Fe(1) and Fe(3) exhibits two short Fe-N bonds (1.940(4) Å and 1.986(4) Å for Fe(3); 2.030(4) Å and 2.061(4) Å for Fe(1),) and one longer Fe-N bond (2.141(4) Å for Fe(3), 2.333(4) Å for Fe(1)), for amido groups bridging two Fe(II) ions. The Fe-Fe distances at 2.403(1) Å, 2.438(1) Å, and 2.703(1) Å are asymmetric but their value remain within range of bonding

interactions<sup>9-10</sup> and are similar to the Fe(II)-Fe(II) distances found in trinuclear complexes showing magnetic coupling arising from direct orbital overlap.<sup>9, 11</sup>

#### Experimental crystallographic section

**Table S1.** Crystallographic parameters for complex **1-THF** and **1-py**.

| Compound  | [Na <sub>12</sub> Fe <sub>6</sub> (tris-cyclo-salophen) <sub>2</sub> (THF) <sub>14</sub> ], <b>1-THF</b> | [Na <sub>6</sub> Fe <sub>3</sub> (tris-cyclo-salophen)(py) <sub>9</sub> ].2py, <b>1-py.2py</b>  |
|---|--|---|
| Formula   | C <sub>176</sub> H <sub>196</sub> Fe <sub>6</sub> N <sub>12</sub> Na <sub>12</sub> O <sub>26</sub>       | C <sub>115</sub> H <sub>97</sub> Fe <sub>3</sub> N <sub>17</sub> Na <sub>6</sub> O <sub>6</sub> |
| Crystal size [mm]                               | 0.572 x 0.217 x 0.164  | 0.339 x 0.269 x 0.089   |
| Wavelength [Å]                                  | 1.54184  | 0.71073   |
| Formula weight                                  | 3506.44  | 2118.58   |
| Space group                                     | <i>P</i> 2 <sub>1</sub> / <i>c</i>   | <i>P</i> 1  |
| Crystal system                                  | Monoclinic   | Triclinic   |
| Volume [Å <sup>3</sup> ]                        | 9865.5(5)  | 2536.26(12)   |
| a [Å]   | 13.4845(3)   | 13.3029(3)  |
| b [Å]   | 33.0195(12)  | 14.1443(3)  |
| c [Å]   | 22.9829(7)   | 15.9246(4)  |
| α [°]   | 90   | 112.076(2)  |
| β [°]   | 105.404(3)   | 111.146(2)  |
| γ [°]   | 90   | 92.244(2)   |
| Z   | 2  | 1   |
| Absorption coefficient [mm <sup>-1</sup> ]      | 4.209  | 0.516   |
| F (000)   | 3664   | 1098  |
| T [K]   | 140.00(10)   | 140.00(10)  |
| Reflections collected                           | 69497  | 55517   |
| Independent reflections [R(int)]                | 20221 [ <i>R</i> <sub>int</sub> = 0.0584]  | 33321 [ <i>R</i> <sub>int</sub> = 0.0360]   |
| Final R indices [I>2σ(I)]                       | <i>R</i> <sub>1</sub> = 0.0958, <i>wR</i> <sub>2</sub> = 0.2569  | <i>R</i> <sub>1</sub> = 0.0587, <i>wR</i> <sub>2</sub> = 0.1089                                 |
| Largest diff. peak and hole [eÅ <sup>-3</sup> ] | 2.379 and -0.752   | 1.136 and -1.067  |
| GOF   | 1.073  | 1.027   |



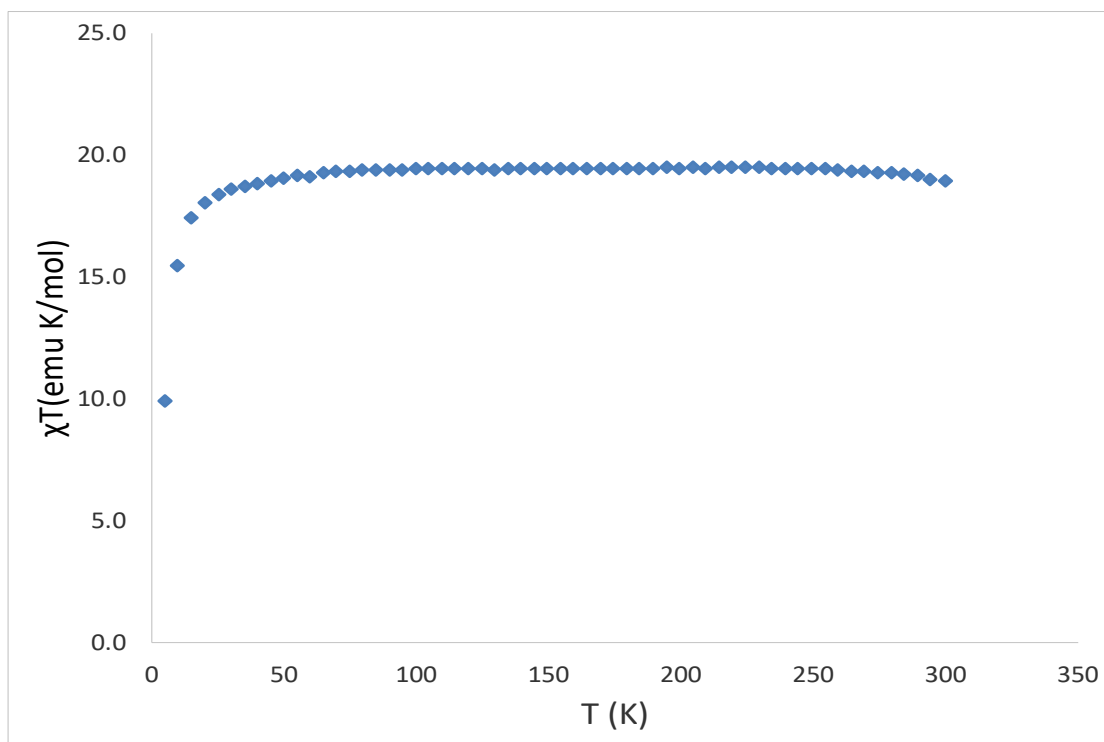
**Figure S7** Molecular crystal structure of **1-py** (50% probability ellipsoids). The three C-C bonds formed by reduction of salophen<sup>2-</sup> are shown in yellow. Hydrogen atoms, lattice pyridine molecules and the sodium-bound pyridine molecules have been omitted for clarity.

**Table S2** Bond distances (Å) and angles (°) for **1-THF** and **1-py**.

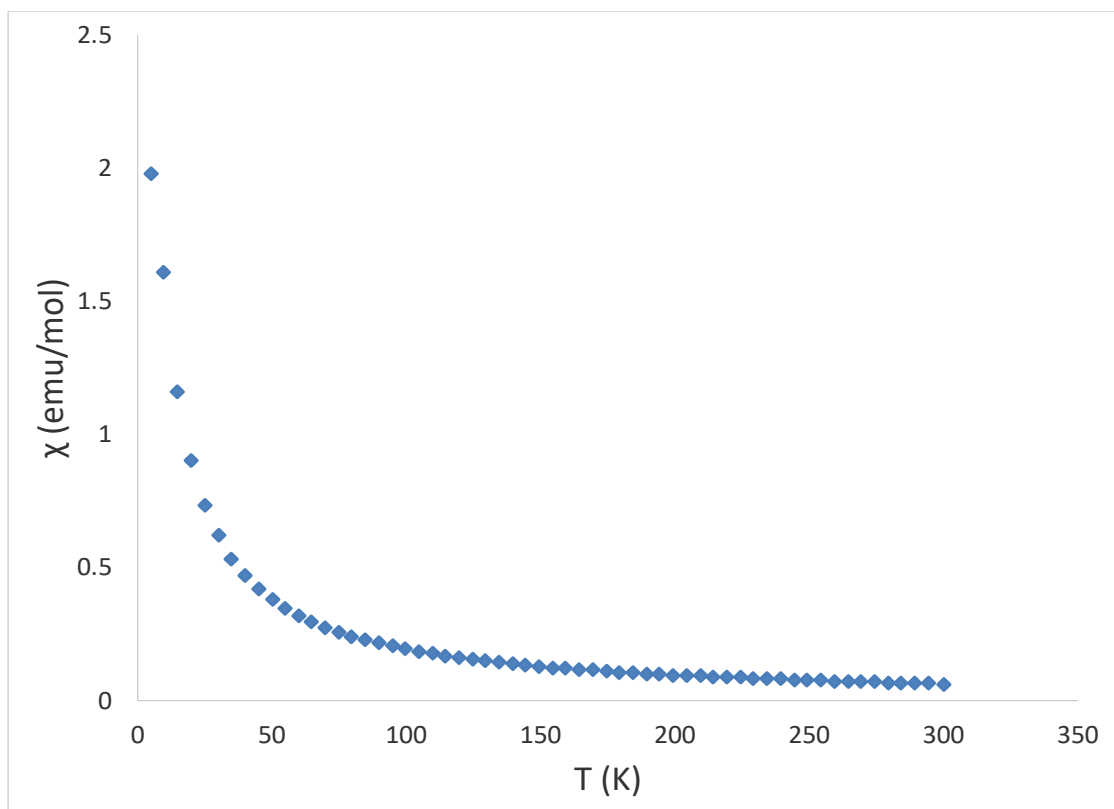
|                   | <b>1-THF</b> | <b>1-py</b> |
|-------------------|--------------|-------------|
| Fe(1)-Fe(2)       | 2.4032(10)   | 2.4405(7)   |
| Fe(2)-Fe(3)       | 2.4382(11)   | 2.5055(9)   |
| Fe(1)-Fe(3)       | 2.7031(11)   | 2.7942(7)   |
| Fe(1)-N(1)        | 2.333(4)     | 2.166(3)    |
| Fe(1)-N(3)        | 2.030(4)     | 1.983(3)    |
| Fe(1)-N(4)        | 2.061(4)     | 1.961(3)    |
| Fe(1)-O(1)        | 2.079(3)     | 2.131(3)    |
| Fe(1)-O(4)        | 2.098(3)     | 2.067(3)    |
| Fe(2)-N(1)        | 2.021(4)     | 2.085(3)    |
| Fe(2)-N(2)        | 2.061(4)     | 2.289(3)    |
| Fe(2)-N(5)        | -            | 1.998(3)    |
| Fe(2)-O(2)        | 1.914(3)     | 1.944(3)    |
| Fe(3)-N(2)        | 2.141(4)     | 2.060(3)    |
| Fe(3)-N(6)        | 1.986(4)     | 2.041(3)    |
| Fe(3)-O(3)        | 2.141(4)     | 2.027(3)    |
| Fe(3)-O(4)        | 2.035(3)     | 2.087(3)    |
| Fe(2)-Fe(1)-Fe(3) | 56.68(3)     | 56.71(2)    |
| Fe(1)-Fe(2)-Fe(3) | 67.88(3)     | 68.78(2)    |
| Fe(2)-Fe(3)-Fe(1) | 55.45(3)     | 54.51(2)    |

|               |          |          |
|---------------|----------|----------|
| C-C distances | 1.566(6) | 1.571(5) |
|               | 1.563(6) | 1.569(5) |
|               | 1.564(7) | 1.560(6) |

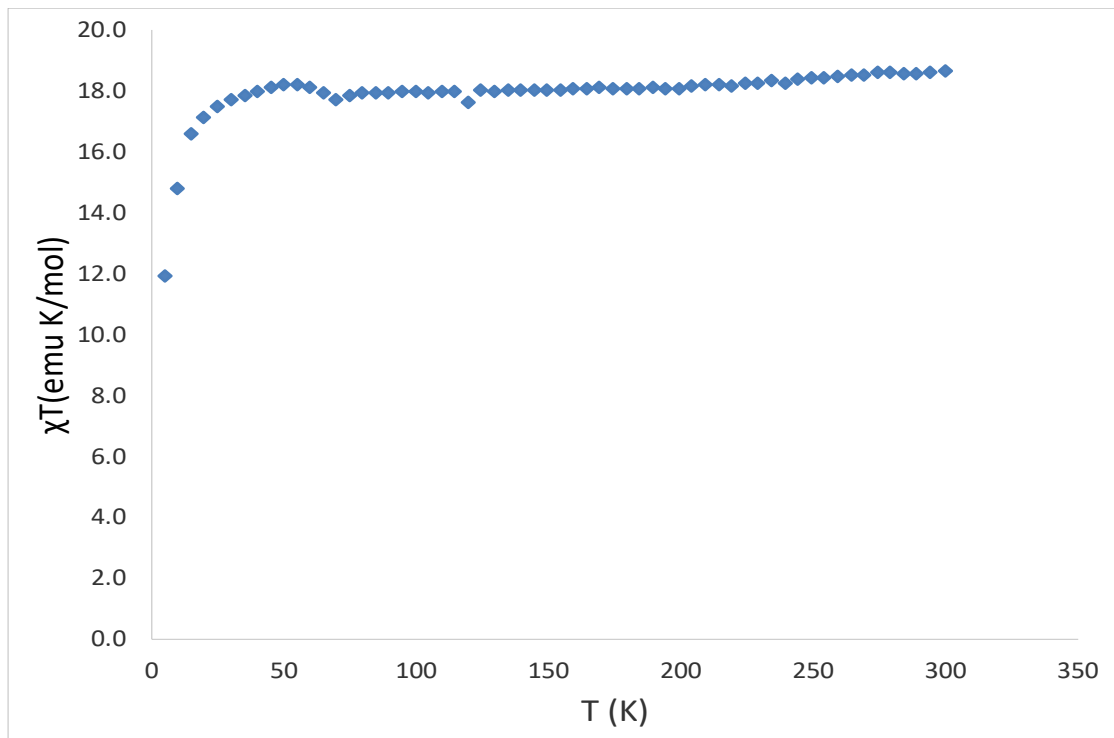
### Magnetic data



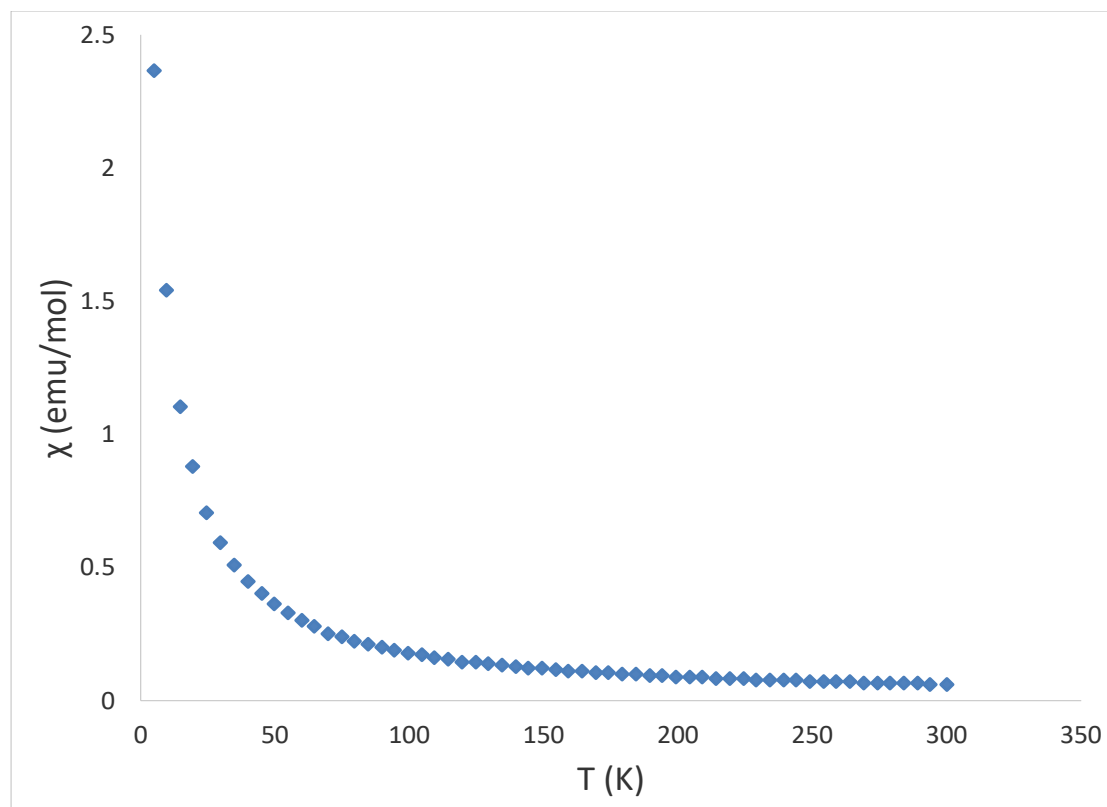
**Figure S8**  $\chi_M T$  vs.  $T$  graphic for  $[\text{Na}_{12}\text{Fe}_6(\text{tris-cyclo-salophen})_2(\text{THF})_{14}], \mathbf{1-THF}$ .



**Figure S9**  $\chi_M$  vs. T graphic for  $[\text{Na}_{12}\text{Fe}_6(\text{tris-cyclo-salophen})_2(\text{THF})_{14}]$ , **1-THF**.



**Figure S10**  $\chi_M T$  vs. T graphic for  $[\text{Na}_6\text{Fe}_3(\text{tris-cyclo-salophen})(\text{py})_9]$ .



**Figure S11**  $\chi_M$  vs. T graphic for  $[\text{Na}_6\text{Fe}_3(\text{tris-cyclo-salophen})(\text{py})_9]$ .

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