Gradual spin crossover behaviour in a linear trinuclear FeII complex†

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The synthesis, structures and magnetic properties of a new trinuclear spin crossover complex, [FeII₃(npt)₆(EtOH)₄(H₂O)₂]₂(ptol)₂.4EtOH (1), and of its CoII(2 and 3) and NiII(4) analogues, are reported here. The complexes were synthesized by reacting a 1,2,4-triazole-based ligand, 4-(4'-nitrophenyl)-1,2,4-triazole (npt), with the p-tolylsulfonate (ptol) metal salts in methanol or ethanol. Structural analyses revealed that all complexes are isomorphous and consist of a linear trinuclear core where metal centres are bridged by triazole groups. For I, dc susceptibility measurements exhibit gradual spin transition with $T_{1/2} = 148$ K which corresponds to HS $\rightarrow$ LS crossover for the triazole bridged central FeII ion. This spin transition was confirmed by Single-Crystal X-Ray Diffraction data of I at 100 K and 181 K, where the low temperature measurement revealed a decrease in volume for the central FeII ion, which is in agreement with a HS $\rightarrow$ LS transition.

Introduction

With the development of crystal engineering and coordination chemistry, continuous efforts are made to design and study new materials displaying bistability with potential application in the field of nanoelectronics.1 Bistability at the molecular level was observed only for a few specific categories of compounds, one of them being Spin Crossover (SCO) complexes.2,3 Since the discovery of the first SCO complex, the magnetic and optical properties of molecules presenting such a behaviour have been extensively studied. Gültlich and co-workers demonstrated that SCO occurs mainly for $3d^7$–$3d^8$ transition metal ions coordinated to strong field ligands.4 Such transition can be triggered by variation in temperature or pressure and even by light irradiation.4 For an octahedral FeII complex, the spin transition occurs between the $t_{2g}^3e_g^1$ and the $t_{2g}^6e_g^2$ electronic configurations for the low spin (LS, $S = 0$) and high spin (HS, $S = 2$) states, respectively. Polynuclear iron-based SCO complexes, which undergo multistep SCO, were synthesized using either Schiff-base or triazole-based ligands.5 In the latter case, it was demonstrated that six 1,2,4-triazole derivatives coordinated to octahedral FeII ions could form a 1-D coordination polymer.1,6 In fact, alkylated 1,2,4-triazole ligands were extensively used to synthesize 1-D polymeric complexes with various first-row transition metals such as FeII, CoII, NiII or CuII.7 However, the synthesis of SCO coordination polymers using 1,2,4-triazole derivatives remains elusive due to the difficulty of designing substituted ligands with the right ligand-field strength. In addition only a few of these complexes’ SCO behaviour were analysed by magnetic measurements as well as Single-Crystal X-Ray Diffraction (XRD).8 Hence, structural information about these compounds in either of the low spin (LS) or high spin (HS) states is poorly available. It is clear that the ligand design has a direct influence on the structure of the complex as well as in its magnetic properties. It was reported in recent years that reacting 4-aryl- or 4-(N-heteroaryl)-1,2,4-triazole derivative ligands with $3d^7$–$3d^8$ transition metal precursor salts lead to analogous trinuclear compounds.9 We believed that fine tuning of this type of ligand, using the appropriate functionalized aryl groups on the 1,2,4-triazole-based ligand, could result in not only a similar SCO behaviour but also in a favoured supramolecular organization of the molecules as previously reported in our work.10

With this in mind, we functionalized the 1,2,4-triazole ligand with a p-nitrophenyl group, which resulted in the ligand 4-(4'-nitrophenyl)-1,2,4-triazole (npt), used to synthesize new designed triazole-based FeII, CoII and NiII discrete linear trinuclear compounds. Herein, we report the syntheses, structural studies, thermogravimetric analyses and magnetic properties of four novel trinuclear complexes based on the npt ligand: $[\text{Fe}^{III}(\text{npt})_6(\text{EtOH})_4(\text{H}_2\text{O})_2]_2(\text{ptol})_2.4\text{EtOH}$ (1, ptol = p-tolylsulfonate), and its CoII (2 and 3) and NiII (4) analogues.

Experimental section

General

The iron precursor salt, $[\text{Fe}(\text{H}_2\text{O})_6][\text{ptol}]_2$, was prepared by heating two equivalents of p-tolylsulfonic acid with one
equivalent of iron powder in water. The $p$–tolylsulfonate salts of Co$^{11}$ and Ni$^{11}$ were prepared by reacting the metal hydroxide salts with $p$-tolylsulfonic acid in water. The salts were recrystallized from the mother solution at $2--8^\circ C$ over two days after filtration to remove the excess of metal hydroxide. Formylhydrazine was synthesized as reported previously by reacting ethylformate and hydrazine hydrate in methanol.$^{11}$ All other reagents were bought from Thermo Fisher Scientific and were used without further purification.

4(4'-nitrophenyl)-1,2,4-triazole (npt)

The ligand was prepared according to a modified known synthetic strategy$^{12}$ by first mixing formylhydrazine (0.90 g, 15 mmol), triethylorthoformate (3.7 mL, 25 mmol) and ethanol (40 mL) in a Synthware Glass High-Pressure Vessel. The solution was stirred at $180^\circ C$ for 30 min. The latter was cooled down to $60^\circ C$ in a warm water bath and 4-nitroaniline (2.1 g, 15 mmol) was slowly added to the solution followed by four drops of sulfuric acid as a catalyst. The mixture was heated again at $180^\circ C$ for 30 min resulting in a dark red solution. While the solution was cooled, a dark yellow precipitate appeared. The powder was filtered out, washed with ethanol (3 x 5 mL) and ether (3 x 5 mL) and dried in vacuo for 1 h. Yield = 1.18 g, 42%. $^1$H NMR (Acetone-d6, 400 MHz): 9.04 (s, 2H), 8.46 (d, 2H), 8.07 (d, 2H).

IR (npt, KBr, cm$^{-1}$): 3324 (br), 3175 (m), 3045 (m), 2935 (m), 2859 (m), 1621 (s), 1596 (s), 1428 (s), 1305 (s), 1195 (s), 1080 (m), 991 (s), 848 (s), 751 (s), 680 (s).

$[\text{MII}_{x}(\text{npt})_{y}(\text{EtOH})_{z}](\text{H}_{2}\text{O})_{a}(\text{ptol})_{b} \cdot 4\text{EtOH (1, 2)}$

The complexes were synthesized by adding 5 mL of an ethanolic solution of $[\text{M(H}_2\text{O)}_{6}]_{x}(\text{ptol})_{y} (0.125 \text{ mmol, M = Fe (1), Co (2)})$ to a solution of npt (0.047 g, 0.25 mmol) in methanol (25 mL). The solutions were stirred for 10 min at room temperature which led to a coloured solution. Crystallization of the complexes was performed over a period of six hours to provide light green or light brown plates for 1 and 2, respectively, suitable for Single-Crystal XRD. Yield = 43% (1, 0.046 g) and 37% (2, 0.040 g), based on the metal salts.

IR (1, KBr, cm$^{-1}$): 3379 (br), 3097 (w), 1657 (s), 1618 (s), 1600 (s), 1526 (m), 1494 (s), 1441 (s), 1344 (s), 1258 (s), 1218 (s), 1173 (s), 1122 (s), 1051 (s), 1033 (s), 1010 (s), 854 (s), 815 (s), 750 (s), 682 (s).

IR (2, KBr, cm$^{-1}$): 3293 (br), 3097 (w), 2970 (s), 1617 (s), 1600 (s), 1531 (m), 1495 (s), 1442 (s), 1343 (s), 1256 (s), 1216 (s), 1164 (s), 1121 (s), 1061 (s), 1033 (s), 1008 (s), 952 (s), 850 (s), 815 (s), 749 (s), 678 (s).

$[\text{MII}_{x}(\text{npt})_{y}(\text{MeOH})_{z}(\text{H}_2\text{O})_{a}](\text{ptol})_{b} \cdot x\text{MeOH} \cdot y\text{H}_2\text{O (3, 4)}$

Compounds 3 and 4 were synthesized by adding a solution of $[\text{M(H}_2\text{O)}_{6}]_{x}(\text{ptol})_{y} (0.125 \text{ mmol, M = Co (3), Ni (4)})$ in methanol (5 mL) to a solution of npt (0.047 g, 0.25 mmol) in methanol (15 mL). The solutions were stirred at room temperature for 3 min. Crystallization of the complexes was performed over 24 h to provide light brown or purple plate-like crystals for 3 ($x = 4, y = 0$) and 4 ($x = 2, y = 1$), respectively. Yield = 13% (3, 0.014 g) and 50% (4, 0.053 g), based on the metal salts.

IR (3, KBr, cm$^{-1}$): 3248 (br), 3097 (w), 1618 (s), 1601 (s), 1550 (s), 1526 (m), 1496 (s), 1343 (s), 1257 (s), 1216 (s), 1167 (s), 1121 (s), 1062 (s), 1033 (s), 1008 (s), 984 (s), 852 (s), 815 (s), 750 (s), 710 (s), 681 (s), 666 (s).

IR (4, KBr, cm$^{-1}$): 3249 (br), 3098 (w), 1617 (s), 1601 (s), 1551 (s), 1524 (m), 1496 (s), 1343 (s), 1258 (s), 1229 (s), 1168 (s), 1120 (s), 1069 (s), 1032 (s), 1009 (s), 985 (s), 852 (s), 815 (s), 750 (s), 710 (s), 679 (s), 653 (s).

Physical measurements

Infrared analyses were obtained by using a Nicolet Nexus 550 FT-IR spectrometer in the 4000 – 650 cm$^{-1}$ range. The spectra were recorded in the solid state by preparing KBr pellets.

NMR analyses were conducted on a Bruker Avance 400 spectrometer equipped with an automatic sample holder and a 5 mm auto-tuning broadband probe with Z gradient.

Thermogravimetric analyses (TGA) were recorded using an SDT 2960 Simultaneous DSC-TGA instrument at a heating rate of 10 °C min$^{-1}$ between 25 and 300 °C, under a constant flow of nitrogen (100 mL min$^{-1}$).

X-ray Crystallographic data collection results for compounds 1–4 represent the best data sets obtained in several trials for each sample. We still obtained acceptable good R factors for each crystal (inferior to 8%). Crystals of all four complexes were grown from the mother liquors. Single plate-like crystals suitable for Single-Crystal XRD were mounted on glass fibre. Unit cell measurements and intensity data collections for 2, 3 and 4 were performed on a Bruker-AXS SMART 1 k CCD diffractometer using graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073 \AA$). For 1, the data were measured on a Bruker Kryoflex diffractometer at 100 and 181 K. For all four compounds, the data reduction included a correction for Lorentz and polarization effects with an applied multi-scan absorption correction (SADABS). The reflection data were consistent with triclinic systems; $P1$. The crystal structures were solved and refined using the SHELXTL program suite.$^{13}$ For compounds 1 and 4, disorder of some solvent molecules was observed (EtOH for 1; MeOH and H$_2$O for 4). Refinement of the disorder was undertaken however the quality of the best data obtained did not allow us to model the disorder. However, the disorder of some solvent molecule does not have any implication on the core structure of the complexes. Direct methods yielded all non-hydrogen atoms. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms. In all cases, all of the solvent molecules and one of the coordinated methanol or ethanol molecules were disordered. All non-hydrogen atoms were refined with anisotropic thermal parameters. Crystallographic data for the structure reported in this article can be obtained from Cambridge Crystallographic Centre as supplementary publication no. CCDC 815193 (1 at 100 K), 815194 (1 at 181 K), 815195 (2), 815196 (3), 815197 (4).

The magnetic susceptibility measurements were obtained through the usage of a Quantum Design SQUID magnetometer MPMS-XL that works between 1.8 and 400 K for dc applied fields ranging from –7 to 7 T. dc analyses were performed on polycrystalline samples of 13.8, 16.0, 16.8 and 16.9 mg for 1, 2, 3 and 4, respectively, wrapped in a polyethylene membrane. Diamagnetic corrections were applied for the sample holder and
the core diamagnetism from the sample (estimated with Pascal constants).

Results and discussion

Syntheses

The synthesis of the ligand was carried out according to a previously reported procedure with slight modifications (Scheme 1). The ligand npt was synthesized in a two-step procedure, using a Synthware Glass High-Pressure Vessel, by the acid-catalyzed reaction between 4-nitroaniline and diformylhydrazine, prepared in situ by mixing formylhydrazine and triethylthiophosphorin. Once the reaction finished, cooling the mixture to room temperature allowed the ligand to precipitate out of the solution as a dark yellow powder, which did not require any further purification.

![Scheme 1](https://example.com/scheme1.png)

Scheme 1 Synthesis of the npt ligand.

The complexes were prepared by reacting the ligand npt with the $p$-tolylsulfonate metal salts in ethanol or methanol. The use of EtOH (1 and 2) and MeOH (3 and 4) were critical for the isolation of X-ray quality crystals. Recrystallizations of the complexes from the mother liquors were achieved between 6 and 24 h and resulted in plate-like crystals suitable for Single-Crystal XRD. For all four compounds, slight change in the reaction conditions, the ligand/metal ratio or the use of other solvents (MeOH for the reaction with FeII, EtOH for the reaction with NiIII, PrOH, DMF, acetonitrile or water, and even mixture of DMF and water, and three nitrogen atoms from bridging triazole groups) resulted in polycrystalline powders of the complexes unsuitable for Single-Crystal XRD analysis. The moderate and low yields in good quality crystals suitable for Single-Crystal XRD can be explained by the concomitant presence of poly-crystalline powders, even after reaction conditions optimization. Crystal packing reveals the presence of co-crystallizing solvents; therefore, to prevent any solvent loss samples were handled carefully and rapidly before measurements on freshly prepared batches.

Structural analyses

Structural analyses revealed that all four complexes consist of isomorphous triazole bridged linear trinuclear core molecules. The molecular structure of 1 is presented in Fig. 1 (and Supporting Information, Fig. S1†) while the structures of 2, 3 and 4 are presented in the Supporting Information as Figs S2, S3 and S4.† The crystallographic data for all four complexes are reported in Table 1. Selected bond distances and angles for all compounds are presented in Table 2, using the labelled description of the trinuclear core presented in Fig. 1c. Fully labelled molecular structure is displayed in Fig. S5.† The molecules crystallize in the triclinic space group $P1$. In all complexes, the octahedral MII ions are arranged in a linear fashion, where the metal centres are bridged by six triazoles from the ligand molecules. Therefore the central metal centre (M2) is coordinated to six nitrogen atoms from triazole groups (M4, M6) while the peripheral MII ions (M1, M1′) are coordinated by three oxygen atoms from two terminal solvent molecules and one molecule of water, and three nitrogen atoms from bridging triazole groups (MO3N3). For 1 and 2, the axial bonds (N10-M2 and N10′-M2) of the central ions are elongated leading to M2-N10 bond distances of 2.170(1) and 2.162(1) Å, respectively (black bonds in Fig. 1a and 1c). Whereas the peripheral ions are in a near ideal octahedral environment.

The +2 oxidation state of each metal centre was confirmed by charge consideration and bond-valence sum calculations (Table 3), using the M–O and M–N bond lengths reported in Table 2 (with the values obtained at 181 K for 1).

For 1, it can be seen in the packing diagram (Fig. 2) that the molecules are organized in a lamellar-like arrangement due to supramolecular interactions between the npt ligands and the $p$-tolylsulfonate counter anions. All six sulfonate moieties of the counter anions are located close to the metal centres, which cause these molecules to be interlocked between the aromatic phenyl

### Table 1 Crystallographic data of 1, 2, 3 and 4

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<th>Complex</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<td>100</td>
<td>202</td>
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<td>C$<em>{106}$H$</em>{130}$Fe$<em>3$N$</em>{24}$O$_{40}$S$_6$</td>
<td>C$<em>{106}$H$</em>{130}$Co$<em>3$N$</em>{24}$O$_{40}$S$_6$</td>
<td>C$<em>{98}$H$</em>{114}$Co$<em>3$N$</em>{24}$O$_{40}$S$_6$</td>
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<td>14.6775(7)</td>
<td>15.3049(16)</td>
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<td>15.0789(7)</td>
<td>15.2680(7)</td>
<td>14.7832(18)</td>
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<td>16.319(1)</td>
<td>16.480(5)</td>
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<td>110.825(4)</td>
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<td>3022.8(3)</td>
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<td>3294.6(66)</td>
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<td>$R_1 (I &gt; 2\sigma(I))^a$</td>
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<td>$wR_2 (I &gt; 2\sigma(I))^b$</td>
<td>0.0995</td>
<td>0.1011</td>
<td>0.1541</td>
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</table>

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$a R_1 = \Sigma[||F_o|| - |F_c||]/\Sigma|F_o||$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + hp]$; where $p = \max (F_o^2, 0) + 2F_c^2/3$. 

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Fig. 1 (a) and (b) Molecular structure of 1 measured at 181 K. (c) and (d) Labelled core of the linear trinuclear complex corresponding to representations (a) and (b) respectively. Hydrogen atoms and counter ions are omitted for clarity. Colour code: Dark Yellow (metal, Fe for 1), Red (O), Blue (N), Grey (C).
intermolecular distances between the units, therefore it is possible to observe such transition using Single-Crystal XRD analysis in addition to magnetic measurements. Thus 1 was analysed by Single-Crystal XRD at 100 K and 181 K in order to confirm the occurrence of a spin transition. As described below, the observed structural changes correspond to HS-HS-HS (181 K) \(\rightarrow\) HS-LS-HS (100 K) transition.

The comparison of the coordination environment of the central Fe\textsuperscript{II} ion in 1, at 100 and 181 K (Fig. 3), displays the structural changes occurring during the spin transition. A shadow superposition, which details the differences between the structures at both temperatures is also available in the Supporting Information as Fig. S9.\(^\dagger\) For 1, at 100 K, the bond distances between the six ligands and the central ion are of 2.005(1), 2.004(1) and 2.017(1) \(\AA\) for Fe\textsubscript{2}-N\textsubscript{1}, Fe\textsubscript{2}-N\textsubscript{6} and Fe\textsubscript{2}-N\textsubscript{10}, respectively. These are significantly shorter than the bond distances measured at 181 K, which are of 2.145(1), 2.139(1) and 2.171(1) \(\AA\), respectively. These decrease in the coordination lengths is consistent with a Fe\textsuperscript{II} HS \(\rightarrow\) LS transition for which the coordination distances are shortened by approximately 0.15–0.20 \(\AA\).

Furthermore, the volume of the central ion decrease by approximately 20%, which is also consistent with the previously reported data for a HS \(\rightarrow\) LS transition (18–23\%).\(^\dagger\) Moreover, the unit cell volume of 1 decreases by 60.5(4) \(\AA\textsuperscript{3}\), which is lower than the average change usually accompanying a spin transition.

In fact, for the previously reported trinuclear linear compounds, the change in volume consisted of approximately 150 \(\AA\textsuperscript{3}\).\(^\dagger\) The bulkiness of the nitrophenyl ligands and the presence of bulky \(p\)-tolylsulfonate counter anions between the trinuclear units, which induces a rigidity to the supramolecular arrangement, may be the cause of this behaviour. As aforementioned, upon spin transition, the shortest Fe\textsuperscript{II}-Fe\textsuperscript{II} intermolecular distances at 100 K are also slightly shortened, leading to the distances of 11.53, 9.26 and 14.14 \(\AA\) along the \(a\), \(b\) and \(c\)-axis, respectively. This solid-state behaviour involves an intermolecular cooperativity between complexes which undergo SCO. The importance of this cooperativity has been estimated with regard to the magnetic measurements.

Thermogravimetric analyses

The TGA data for compounds 1–4 are presented in the Supporting Information as Fig. S10, S11, S12 and S13,\(^\dagger\) respectively. For 1, the data clearly indicates a four steps desolvation process. At room temperature, the positive derivative indicates a decrease of less than 1% of the total mass of the sample which may be caused by a loss of a small amount of solvent of crystallization. The exact percentage of this loss could not be calculated but the presence of a shoulder in the data at 41 \(^\circ\)C indicates that this loss consists a first desolvation step. Then, two steps are observed at 71 and 93 \(^\circ\)C for a total loss accounting for 5.9% of the mass of the sample, which corresponds approximately to the mass of four ethanol molecules (calc. 6.4%). This observation suggests the loss of the four ethanol molecules of crystallization present in the crystal structure of 1. The slight difference between the experimental and theoretical percentages is most likely due to the presence of the first desolvation step that is taking place at room temperature. At 150 \(^\circ\)C, a fourth desolvation step is observed.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ligand L1-L1</th>
<th>Ligand L2-L2</th>
<th>Ligand L3-L3</th>
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<tr>
<td>1</td>
<td>36.8</td>
<td>40.6</td>
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<td>2</td>
<td>34.9</td>
<td>41.8</td>
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<td>3</td>
<td>29.9</td>
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</tr>
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<td>4</td>
<td>37.3</td>
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Thermogravimetric analysis

The TGA data for compounds 1–4 are presented in the Supporting Information as Fig. S10, S11, S12 and S13,\(^\dagger\) respectively. For 1, the data clearly indicates a four steps desolvation process. At room temperature, the positive derivative indicates a decrease of less than 1% of the total mass of the sample which may be caused by a loss of a small amount of solvent of crystallization. The exact percentage of this loss could not be calculated but the presence of a shoulder in the data at 41 \(^\circ\)C indicates that this loss consists a first desolvation step. Then, two steps are observed at 71 and 93 \(^\circ\)C for a total loss accounting for 5.9% of the mass of the sample, which corresponds approximately to the mass of four ethanol molecules (calc. 6.4%). This observation suggests the loss of the four ethanol molecules of crystallization present in the crystal structure of 1. The slight difference between the experimental and theoretical percentages is most likely due to the presence of the first desolvation step that is taking place at room temperature. At 150 \(^\circ\)C, a fourth desolvation step is observed.
with a decrease of 3.1% in the sample’s total mass, corresponding to the loss of two ethanol molecules (calc. 3.2%). These observations suggest the loss of one of the coordinated ethanol molecules on each of the peripheral metal centres.

Complexes 2, 3 and 4 exhibit a similar behaviour over the same temperature range. However, the desolvation temperatures of solvent molecules from crystallization and from the two peripheral ions coordination spheres vary noticeably. Indeed, the temperatures of the desolvation steps are 49 and 169°C for 2, 55 and 170°C for 3. And in the case of 4, the data indicate a gradual loss of these solvent molecules over a wide range of temperatures.

Magnetic properties

The dc susceptibility measurements for all four complexes were performed between 1.8 K and 300 K under an applied dc field of 1000 Oe. The $\chi T$ vs. $T$ plot of 1 is presented in Fig. 4 while the data for 2, 3 and 4 are observed in Fig. 5. At room temperature, the $\chi T$ values are 10.12, 8.88, 8.57 and 3.04 cm$^3$ K mol$^{-1}$ for 1, 2, 3 and 4 respectively. For complexes 1, 2 and 3, the spin-only values, which are respectively 9.00 and 5.64 cm$^3$ K mol$^{-1}$ for three non-interacting HS Fe$^{II}$ (1) or Co$^{II}$ (2 and 3) ions (with $g = 2.00$), are not sufficient for a good prediction. Better approximations of the $\chi T$ values for three non-interacting HS Fe$^{II}$ (3d$^6$) or Co$^{II}$ (3d$^{8}$) ions are obtained considering the orbital contributions ($\mu_{eff} = (2S(S + 1) + L(L + 1))^{1/2}$): 11.26 cm$^3$ K mol$^{-1}$ for Fe$^{II}$ and 10.14 cm$^3$ K mol$^{-1}$ for Co$^{II}$. Moreover, the $\chi T$ values are in the range of the observed values for three non-interacting HS Fe$^{II}$ or Co$^{II}$ ions: between 9.75 and 12.18 cm$^3$ K mol$^{-1}$ for Fe$^{II}$, and between 6.93 and 10.14 cm$^3$ K mol$^{-1}$ for Co$^{II}$. For complex 4, the $\chi T$ is very close to the expected spin-only value of 3.00 cm$^3$ K mol$^{-1}$ for three non-interacting HS Ni$^{II}$ (3d$^8$) ions (with $g = 2.00$).

Upon cooling, compounds 2, 3 and 4 exhibit antiferromagnetic interactions between the central metal centre and the peripheral ions. At 5 K, slight variations in the $\chi T$ values are observed leading to the presence of shoulders in the curves at 2.16 and 1.98 cm$^3$ K mol$^{-1}$ for 2 and 3 respectively. These results suggest a spin ground state of $S = 3/2$ for both of the compounds. The fitting of the dc data was not achievable for cobalt complexes due to the presence of significant spin–orbit coupling.

For 1, the $\chi T$ product decreases slightly upon cooling before a pronounced gradual step between 200 – 100 K. The latter behaviour clearly indicates 1 undergoes a single gradual spin transition with $T_{1/2} = 148$ K. Below 50 K the $\chi T$ product decreases rapidly down to a value of 2.25 cm$^3$ K mol$^{-1}$ at 1.8 K. This rapid decrease at low temperature is attributed to either a presence of significant magnetic anisotropy or weak antiferromagnetic interactions between the peripheral ions. As denoted in the structural assessment, the symmetrical equivalence and the weak ligand-field surrounding the peripheral ions suggests that only the central ion, coordinated to six nitrogen from triazole ligands, undergoes SCO. At 100 K, the $\chi T$ product is 7.71 cm$^3$ K mol$^{-1}$, which is in good agreement with the expected values for two non-interacting Fe$^{II}$ HS ions linked by one Fe$^{II}$ LS ion with orbital contributions (7.51 cm$^3$ K mol$^{-1}$).

As previously reported in the literature, the gentle slope in the $\chi T$ vs. $T$ plot is usually associated with weak cooperative interactions between the molecules in the crystal lattice. From the close inspection of the structural analysis it is safe to conclude that the gradual transition is due to weak cooperative interaction between the ligands and large separation between the molecular units. The latter also reduces the possibility of long range magnetic ordering. The observed behaviour is consistent with previously reported compounds that were synthesized with bulky ligands promoting large separation of the units in the crystal lattice.

Fig. 4 The dc susceptibility of 1 from 1.8 to 300 K under an applied dc field of 1000 Oe.

Fig. 5 The dc susceptibility of 2, 3 and 4 from 1.8 to 300 K under an applied dc field of 1000 Oe.

For complex 4, the $\chi T$ product decreases with decreasing temperature indicating a dominant antiferromagnetic interaction between the spin carriers. Between 5 and 15 K the curve plateaus at 1.15 cm$^3$ K mol$^{-1}$ which suggests a spin ground state of $S = 1$. Above 15 K, the data was fitted to a Heisenberg model for...
a linear trinuclear HS Ni\textsuperscript{II} system (eqn (1) and Supporting Information, eqn S1†), resulting in the following fitting parameters:

\[ g = 2.116(2), \quad J_1 = -8.5(1) \text{ cm}^{-1}, \quad J_2 = 0 \text{ cm}^{-1} \]

The field dependence of the magnetization of 1 (Fig. 7), 2 (Fig. S14†), 3 (Fig. S15†) and 4 (Fig. 8) was measured at 3, 5 and 8 K between 0 and 7 T. For 1, 2 and 3, the plot slope is important below 1 T and then moderate until the maximum values of 6.18, 8 K between 0 and 7 T. For 4, the plot slope at 3 K is moderate until a plot slope at 7 T, which is consistent with a spin ground state of \( S = 1 \). Fitting of the \( M \) vs. \( H \) data yielded unsatisfactory results and this is presumably arising form the possible low lying excited states.

Conclusion

We designed a new family of linear trinuclear complexes based on the 4-(4'-nitrophenyl)-1,2,4-triazole ligand, and four complexes have been successfully synthesized and fully characterized. Structural analyses demonstrated that compounds 1, 2, 3 and 4 are isomorphous. The structural assessments also indicated that each trinuclear unit is composed of two types of metal centres: the central ion (M2) coordinated to six triazole functional groups, and the peripheral ions (M1, M1') coordinated to three triazole functional groups and three oxygenated molecules of solvent or water. In the case of 1, the coordination of the central Fe\textsuperscript{II} metal centre to six triazole functional groups in an octahedral environment is similar to the previously reported 1-D polymeric triazole chains. The structural analyses and the magnetic property measurements confirmed that the central Fe\textsuperscript{II} ion in 1 undergoes spin transition with a \( T_{1/2} \) of 148 K. The magnetic properties of the analogous complexes were also measured, and in the case of the Ni\textsuperscript{II} trinuclear compound 4, the magnetic data was in accordance with a trinuclear Heisenberg model, resulting in \( g = 2.116(2), \quad J_1 = -8.5 \text{ cm}^{-1}, \quad J_2 = 0 \text{ cm}^{-1} \). Thermogravimetric analyses of the trinuclear complexes demonstrated the lability of two of the peripheral solvent molecules and we believe that these solvent molecules could potentially be replaced by other ligands such as N-based ligands in order to induce the SCO of the peripheral ions. Such structural fine-tuning might lead to exciting multi-step crossover behaviour where in-depth structure-magnetism relationship can be investigated.

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Notes and references
