

# *cis*-Tach based pentadecadentate ligands as building blocks in the synthesis of Fe<sup>III</sup> and Pd<sup>II</sup> coordination clusters†

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A dodecanuclear Fe<sup>III</sup> complex, consisting of two {Fe<sub>6</sub>} units coupled across a single hydroxy-bridge and a cage-like Pd<sup>II</sup> trimer were synthesised using the highly branched, pentadecadentate chelating ligand *cis,cis*-1,3,5-cyclohexanetriamine-N,N,N',N',N'',N''-hexaacetic acid (H<sub>6</sub>hact).

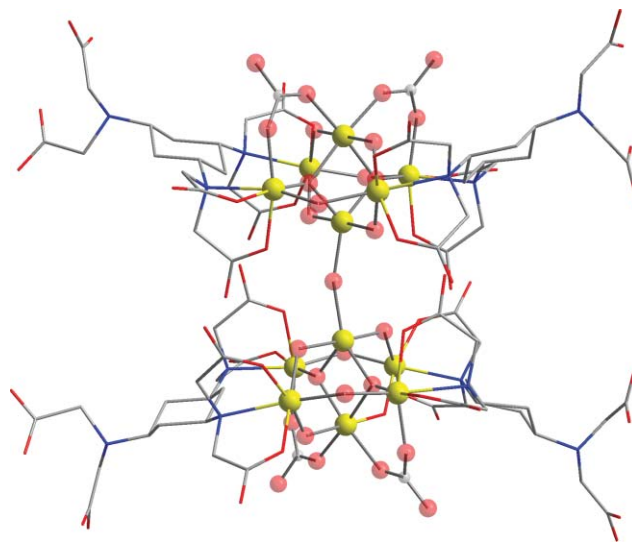
## Introduction

The self-assembly of polynuclear metal clusters is an area of interest as in principle it allows the creation of molecules with 'programmable' function *e.g.* as biological mimics<sup>1</sup> and catalysts,<sup>2</sup> and physical properties, *e.g.* non-linear optics (NLO)<sup>3</sup> and magnetism.<sup>4</sup> In particular, the use of highly branched ligand systems with many chelating arms has the potential to facilitate the formation of cluster-based building blocks<sup>5</sup> that can be used to form capsules,<sup>6</sup> and to organise these capsules into arrays. This requires many potential chelating groups to both form a polynuclear cluster, and then allow extended interactions between clusters within the array. Also, highly branched ligands have applications in medicine for chelation therapy,<sup>7</sup> and as sensors.<sup>8</sup>

Recently we have reported a number of transition metal clusters, based upon the aliphatic triamine ligand *cis,trans*-1,3,5-triaminocyclohexane (*trans*-tach).<sup>9</sup> *trans*-Tach possesses two non-interacting binding sites due to the rigidity of the cyclohexane backbone; the *bis*-chelating "head" and the monodentate "tail" group. In an extension to this methodology we reasoned that the design of new ligands based upon the *cis-cis* backbone<sup>10</sup> has the potential to offer several types of chelating sites, which could be interesting for the assembly of clusters that are also decorated on the outside with additional binding groups. Thus, the *cis* isomer was used as a starting point and the three amino groups derivatised to form *cis,cis*-1,3,5-cyclohexanetriamine-N,N,N',N',N'',N''-hexaacetic acid (hact).<sup>11</sup> Such carboxylate-based ligand systems can be used in the generation of Pd<sup>II</sup> complexes<sup>12</sup> and are especially suitable building blocks in the synthesis of high-nuclearity Fe<sup>III</sup> complexes as demonstrated by the {Fe<sub>10</sub>} of Taft and Lippard,<sup>13</sup> the {Fe<sub>19</sub>} of Powell *et al.*,<sup>14</sup> and the series of clusters from {Fe<sub>2</sub>} to {Fe<sub>5</sub>} of Boskovic *et al.*<sup>15</sup>

## Results and discussion

Herein we report the synthesis and characterisation of a dodecanuclear Fe<sup>III</sup> hact complex (**1**, Fig. 1) and a cage-like Pd<sup>II</sup> hact trinuclear complex (**2**, see Fig. 5 later). **1** comprises two identical [Fe<sub>6</sub>(H<sub>2</sub>hact)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub>O<sub>2</sub>]<sup>4+</sup> units linked through an hydroxo-bridge which are further linked by potassium and lithium cations in a hydrogen-bonded network containing disordered water molecules to give an overall composition of K<sub>6</sub>Li<sub>3</sub>[Fe<sub>12</sub>(H<sub>2</sub>hact)<sub>4</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>13</sub>O<sub>4</sub>]<sub>2</sub>·45H<sub>2</sub>O (**1**).



**Fig. 1** The {Fe<sub>12</sub>} cluster **1**, Fe centres in yellow; oxygen, red; nitrogen, blue; carbon, grey. Hydrogen atoms, solvent molecules and counterions are excluded for clarity.

Orange crystals of compound **1**‡ can be isolated from an aqueous solution of hact, which has been adjusted to pH 8 *via*

‡ Crystal data for **1**: (C<sub>76</sub>H<sub>195</sub>Fe<sub>12</sub>K<sub>6</sub>Li<sub>3</sub>N<sub>12</sub>O<sub>122</sub>), *M* = 4155.06 g mol<sup>-1</sup>, monoclinic, space group *C2/c*, *a* = 23.7886(10) Å, *b* = 33.5635(14) Å, *c* = 20.5333(10) Å, β = 92.438(3)°, *V* = 16379.5(13) Å<sup>3</sup>, *Z* = 4, μ(Mo-Kα) = 1.304 mm<sup>-1</sup>, 57192 reflections measured, 9556 unique (*R*<sub>int</sub> = 0.0835) that were used in all calculations. Final *R*<sub>1</sub> = 0.0756 and *wR*<sub>2</sub> = 0.2481 (all data). Crystal data for **2**: (C<sub>36</sub>H<sub>82</sub>N<sub>6</sub>Na<sub>6</sub>O<sub>44</sub>Pd<sub>3</sub>), *M* = 1760.22 g mol<sup>-1</sup>, triclinic, space group *P-1*, *a* = 11.0988(2) Å, *b* = 12.1253(2) Å, *c* = 25.4032(5) Å, α = 76.923(1)°, β = 84.969(1)°, γ = 81.665(1)°, *V* = 3289.49(10) Å<sup>3</sup>, *Z* = 2, μ(Mo-Kα) = 0.954 mm<sup>-1</sup>, 42117 reflections measured, 11929 unique (*R*<sub>int</sub> = 0.0489) that were used in all calculations. Final *R*<sub>1</sub> = 0.0617 and *wR*<sub>2</sub> =

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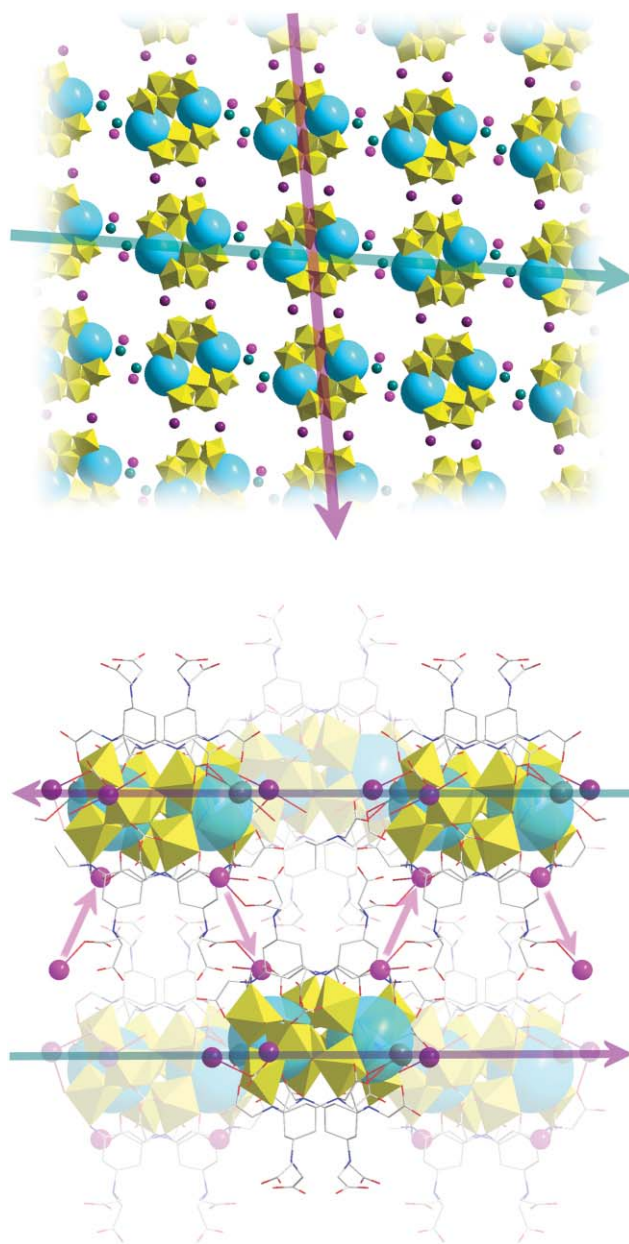
† CCDC reference numbers CCDC 700668 and 700669 for **1** and **2**, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b815200d

the addition of dilute  $\text{K}_2\text{CO}_3$  prior to the addition of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{LiCl}$ . The solution is then returned to pH 8.5 with  $\text{K}_2\text{CO}_3$  and crystallised by the slow diffusion of ethanol over a period of one month.

The individual  $\{\text{Fe}_6\}$  subunits are of known topology<sup>16</sup> and at the core of each, six  $\text{Fe}^{\text{III}}$  centres describe the vertices of a highly distorted octahedron and are linked to one another through  $\mu_2$ - and  $\mu_3$ -oxo and hydroxo bridges with each of the metal centres also showing slightly distorted octahedral geometry. Each hexanuclear sub-unit comprises six hydroxo and two oxo bridges as determined by bond valence sum calculations, where the oxo ligands are the two  $\mu_3$  groups linking three  $\text{Fe}^{\text{III}}$  centres into a “butterfly” configuration. The two hexanuclear sub-units are linked together through a  $\mu_2$ -bridging hydroxo ligand with Fe–O bond lengths of 2.004(2) Å. The outer coordination sites of the sub-units are taken up by bridging carbonate anions and  $\text{H}_2\text{hact}$  ligands, each binding the  $\text{Fe}^{\text{III}}$  centres in the cluster through two of the three binding groups. Again, the expected binding motif is observed in which each binding domain of the ligand is coordinated to one  $\text{Fe}^{\text{III}}$  cation through the tertiary amine nitrogen atom and one oxygen atom of each carboxymethyl group. The interactions with  $\text{H}_2\text{hact}$  allow Fe–O bonds between 2.02(1) and 2.08(1) Å while the Fe–N interactions vary from 2.28(1) to 2.32(1) Å. The cluster is capped by four  $\text{H}_2\text{hact}$  ligands, each with an overall charge of 4- due to the deprotonation of five carboxylate groups and protonation of the pendant amine group. The only carboxylate moiety not to have been deprotonated is attached to this amine and has C–O bond lengths of 1.208(14) Å and 1.276(14) Å.

In the crystal structure of **1**, each cluster unit is associated with eight different potassium positions (filled by six cations) which bridge between cluster units. Three disordered lithium cations further decorate the cluster and furthermore, the exclusion of lithium chloride from the reaction mixture prevents any crystallisation of **1** while the analogous reaction with sodium in place of potassium and lithium cations gives rise to an  $\{\text{Fe}_6\}$  cage structure which is described elsewhere.<sup>11b</sup>

In addition to the hydroxo bridge between subunits, two potassium cations stabilise the cluster (Fig. 2, light blue). Each of these is bound to two of the bridging hydroxo ligands in each subunit and two carboxymethyl oxygen atoms of an  $\text{Fe}^{\text{III}}$  coordinated  $\text{H}_2\text{hact}$  ligand with potassium-oxygen bond lengths varying between 2.89(1) and 3.15(1) Å. This leads to each of these potassium cations taking part in eight coordinative interactions. Further potassium positions are found in the crystal structure and these are involved in linking adjacent cluster units. Cluster units are linked in the crystallographic  $(+a, +c)$  direction both by potassium cations which bridge between  $\text{Fe}^{\text{III}}$  coordinated carboxymethyl arms of adjacent clusters and also by potassium cations which are coordinated by those carboxymethyl arms not coordinated to  $\text{Fe}^{\text{III}}$  in adjacent clusters. These interactions give rise to chain like arrangements of clusters which are cross linked in the crystallographic  $(+a, -c)$  direction by coordination of the  $\text{Fe}^{\text{III}}$  coordinated carboxymethyl arms of adjacent clusters to a fourth potassium cation. Further, the interactions mediated by



**Fig. 2** (top) The crystal packing of **1**, viewed along the crystallographic  $b$ -axis. The cluster subunits sandwich two potassium cations (shown in light blue-spacefilled) and the clusters are linked along the  $a/c$  plane into a 2D network *via* further potassium cations (shown in green to depict one *pseudo*-chain, and purple to illustrate the other); (bottom) The crystal packing of **1** viewed along the crystallographic  $a$ -axis illustrating the links between the 2D networks through potassium cations (pink). Hydrogen atoms, solvent molecules, lithium cations and highly disordered potassium cations are omitted for clarity.

coordination of potassium cations lead to close packing of the cluster units in the crystallographic  $a/c$  plane. These packed layers are separated from one another by a space of *ca.* 4.5 Å which contains disordered water molecules. One carboxymethyl arm from each  $\text{H}_2\text{hact}$  ligand which is not coordinated to  $\text{Fe}^{\text{III}}$  is also found in this space and is bound to a potassium and a lithium cation of the next layer of clusters.

0.1610 (all data). Data were measured at 150(2) K on a Nonius Kappa-CCD diffractometer equipped with a molybdenum source ( $\lambda = 0.7107$  Å). Structure solution with SHELXS97 and refinement with SHELXL97 using WinGX.<sup>18</sup>

The magnetic susceptibility for polycrystalline samples of complex **1** was collected in the temperature range 1.8–300 K in an applied magnetic field of 1 T. The data for **1** are displayed in Fig. 3 as  $\chi_M T$  vs.  $T$ . The  $\chi_M T$  value for the  $[\text{Fe}^{\text{III}}_{12}(\text{O})_4(\text{OH})_{13}(\text{CO}_3)_4(\text{H}_2\text{hact}^{4-})_4]^{9-}$  core of **1** is  $31.22 \text{ cm}^3 \text{ K mol}^{-1}$  at 300 K and is much smaller than the spin-only value of  $\chi_M T = 52.5 \text{ cm}^3 \text{ K mol}^{-1}$  expected for twelve uncoupled  $\text{Fe}^{\text{III}}$  ions with  $g = 2.00$ . On lowering the temperature,  $\chi_M T$  decreases monotonically with decreasing temperature until it reaches a value of  $3.10 \text{ cm}^3 \text{ K mol}^{-1}$  at 1.8 K. This temperature dependence of the magnetic behaviour clearly indicates an overall antiferromagnetic exchange interaction. The magnetic data obey the Curie-Weiss law [ $\chi_M = C/(T - \theta)$ ], affording  $C = 67.57 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  and  $\theta = -351 \text{ K}$  (above 240 K); confirming the presence of strong antiferromagnetic interactions between Fe centres.

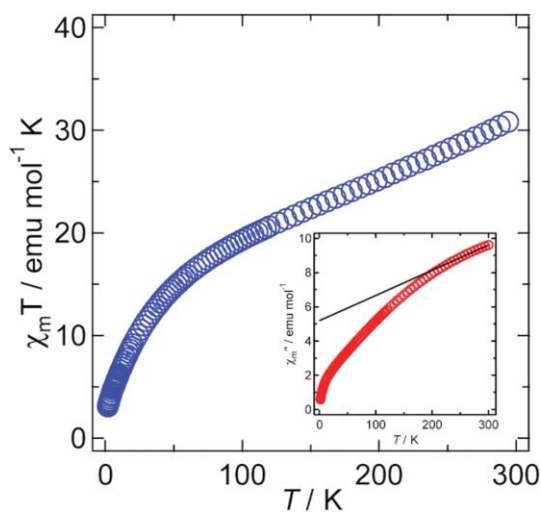


Fig. 3 (Main graph – blue circles)  $\chi_M T$  vs.  $T$  graph for **1**, (inset – red circles)  $\chi_M^{-1}$  vs.  $T$  plot for **1**, black line represents ideal Curie-Weiss behaviour.

The butterfly core of **1** has been previously reported as a system which exhibits antiferromagnetic interactions between metal centres.<sup>17</sup> We propose that each subunit has overall antiferromagnetic interactions, stabilised by the large  $\text{Fe}^{\text{III}}\text{--O--Fe}^{\text{III}}$  angles, as illustrated in Fig. 4.

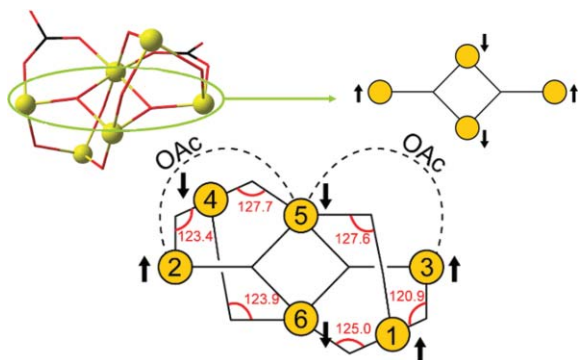


Fig. 4 Magnetic spin model for  $\{\text{Fe}_6\}$  subunit of **1**.

In stark contrast to the high-nuclearity  $\text{Fe}^{\text{III}}$  cluster (**1**), when a mixture of palladium (II) acetate and hact are heated to reflux in water for eight hours in the presence of sodium hydrogencarbon-

ate, a yellow solution is produced from which crystals containing the trinuclear  $\{\text{Pd}_3(\text{hact})_2\}$  cluster  $\text{Na}_6[\text{Pd}_3(\text{hact})_2] \cdot 20\text{H}_2\text{O}$  (**2**) are obtained by diffusion of acetone.

The structure of the anionic cage  $[\text{Pd}_3(\text{hact})_2]^{6-}$  (**2a**) (Fig. 5 (top)) has two hexa-deprotonated ligands arranged one above the other, linked by the metal centres. This arrangement is reminiscent of the previously described  $\{\text{Fe}_6(\text{hact})_2\}$  cluster, where the two ligands are linked by  $\{\text{Fe}_2\}$  dimers, and indeed the two clusters are very similar in size.<sup>11b</sup> As expected, the three binding domains of the hact ligand are non-interacting with each being bound to one square planar  $\text{Pd}^{\text{II}}$  centre with bite angles between  $83.3(2)^\circ$  and  $84.4(2)^\circ$ . Each binding domain complexes the metal through its tertiary amine nitrogen and one oxygen atom of one of the carboxymethyl arms with an average  $\text{Pd}\text{--N}$  distance of  $2.08(1) \text{ \AA}$  and an average  $\text{Pd}\text{--O}$  distance of  $2.00(1) \text{ \AA}$ . This leaves one carboxymethyl arm from each binding domain free to take part in further intermolecular interactions as well as the non-coordinated oxygen of the binding carboxymethyl group.

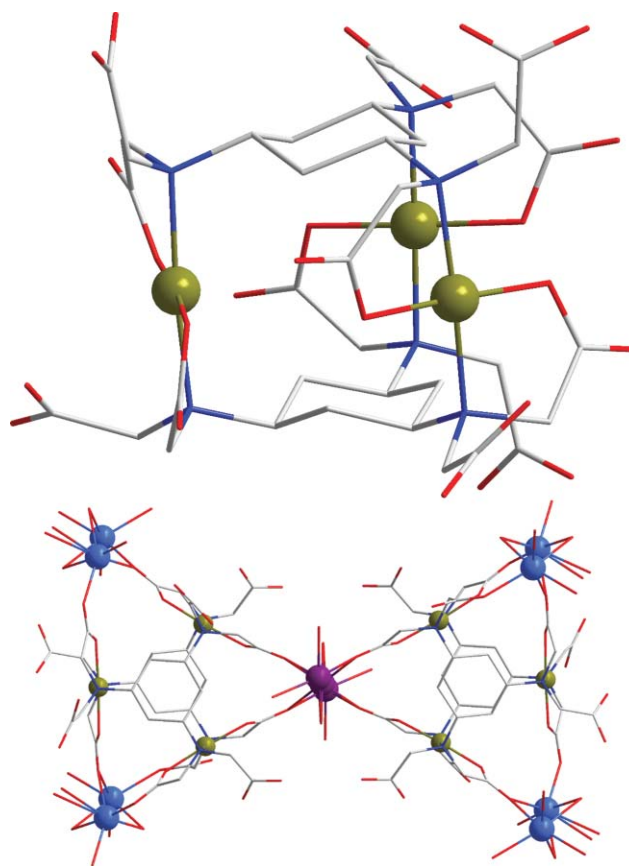


Fig. 5 (Top) the trinuclear  $\text{Pd}^{\text{II}}$  complex **2**, (bottom) trinuclear units linked together to form a pair. Units are linked through  $\text{Na}(3)$  and  $\text{Na}(4)$  (both shown in purple). The corners of the pair of trinuclear units are then further connected to  $\text{Na}(1)$  and  $\text{Na}(2)$  (shown in light blue). Palladium centres are shown as brown balls. All other elements are coloured as shown previously and solvent molecules are excluded for clarity.

Although the core of **2** has threefold symmetry, the variable positions of the noncoordinated arms of the ligand break the symmetry such that the overall structure of **2** has  $C_1$  symmetry.

The cluster units are found in pairs, linked by coordination to sodium cations which also bridge to neighbouring cluster pairs

(Fig. 5 (bottom)). The cluster units are oriented such that the plane of the three Pd<sup>II</sup> centres is roughly parallel to the crystallographic *a/c* plane and in each cluster pair, the triangular cluster units are arranged edge to edge, bridged by a column of three sodium cations running in the crystallographic *c*-axis. Of these, the central sodium cation, Na(3), is symmetrically coordinated to two oxygen atoms from each of the cluster units and two water molecules with Na-O bond lengths between 2.41(1) and 2.44(1) Å. These same six oxygen atoms are found to bridge between the central sodium cation and those found immediately above and below it, Na(4) (disordered over two positions). The coordination sphere of each of the two outer sodium cations is completed by three water molecules, through which the cluster is linked to the central sodium cations of the adjacent cluster in the crystallographic *c*-axis.

Sodium cations are also found at the four remaining edges of the triangular cluster units, which face away from the centre of the cluster pair. The structure is completed by a number of disordered sodium cations which ensure the cluster pairs align into slightly offset chains which run along the crystallographic *a*-axis (Fig. 6). The cluster pairs and their associated sodium cations may be described as rectangular units with the vertices of the triangular cluster units being found at the centres of the edges while the sodium cations are found at the corners. These are arranged in

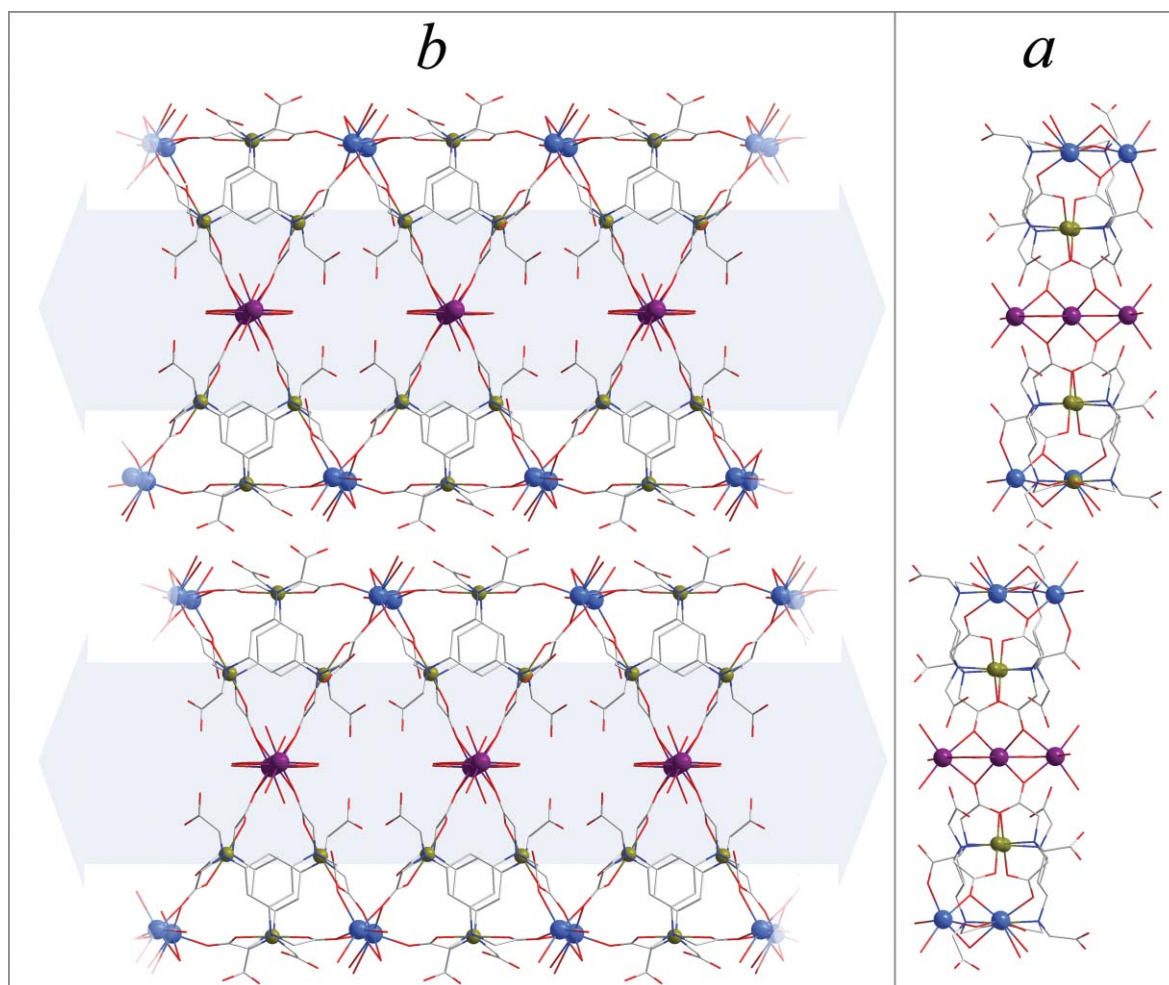
three dimensions such that they are linked together into chains running along the  $(+a,+b)$  vector within the crystal. These chains are further linked to one another in the crystallographic *b*-axis through the interactions mediated by the central column of sodium cations and also in the *c*-axis through the sodium cations at the corners of the rectangular units.

## Conclusions

We were able to obtain two new multinuclear clusters supported by the multidentate ligand *hact* through careful control of the reaction conditions. Compound **1** has been investigated for its magnetic properties and an explanation for the antiferromagnetic interactions suggested, whereas compound **2** illustrates the potential to form cage-type clusters based on *hact*, an avenue we hope to be able to exploit to form larger systems in future work.

## Experimental

All reagents were used as received from commercial sources, without further purification. The ligand H<sub>6</sub>*hact* was prepared as described in literature methods.<sup>11</sup>



**Fig. 6** (LHS) View along the crystallographic *b*-axis showing chains of paired trinuclear units. (RHS) view along the crystallographic *a*-axis showing the offset between chains.

## Synthesis of 1

The hydrochloride salt of hact ( $H_6\text{hact}\cdot 3\text{HCl}$ , 200.0 mg, 0.34 mmol) was dissolved in water (2 ml) and the pH was raised to 8.0 by the drop wise addition of a saturated aqueous potassium carbonate solution. A solution of iron (III) chloride hexahydrate (92 mg, 0.34 mmol) and lithium chloride (288 mg, 6.78 mmol) in water (8 ml) was added and the pH was further adjusted to 8.5 using saturated potassium carbonate solution. The reaction mixture was stirred for 5 min to give a strong yellow to orange coloured solution which was filtered through glass fibre paper. Diffraction quality red crystals of **1** were obtained by diffusion of ethanol into this solution over 3 to 4 weeks. Yield: 50.86 mg (0.0122 mmol, 43.2% based on  $\text{Fe}^{\text{III}}$ )  $\text{C}_{76}\text{H}_{195}\text{Fe}_{12}\text{K}_6\text{Li}_3\text{N}_{12}\text{O}_{122}$  (4155.9 g mol<sup>-1</sup>): found (*exp*): % C 20.29 (21.96), H 3.21 (4.75), N 3.92 (4.04); Relative Fe:K:Li content (FAAS) 12:6.37:1.25; IR (KBr),  $\nu/\text{cm}^{-1}$ : 3437(br), 2925(w), 1627(s), 1389(m), 1092(w), 926(w), 740(w), 651(w), 549(w). UV-VIS ( $\text{H}_2\text{O}$ ),  $\lambda_{\text{max}}/\text{nm}$  (Abs): 222 (1.50, shoulder), 287 (0.92, shoulder), 344 (0.55, shoulder). TGA analysis shows a mass reduction of 18% upon heating to 200 °C.

## Synthesis of 2

The hydrochloride salt of hact ( $H_6\text{hact}\cdot 3\text{HCl}$ , 50.0 mg, 0.085 mmol) was dissolved in water (2 ml) and the pH was raised to 6.0 by the drop wise addition of a saturated aqueous potassium carbonate solution. A solution of palladium (II) acetate (38.3 mg, 0.171 mmol) in a mixture of methanol and water (3 ml/3 ml) was added and the pH was further adjusted to 7.0 using saturated sodium hydrogencarbonate solution. The reaction mixture was heated at reflux for *ca.* 20 h, then filtered and concentrated to 2–3 ml under vacuum to give a strongly coloured yellow solution. Yellow crystals of **2** suitable for single crystal X-ray diffraction were obtained by slow diffusion of acetone into this solution over 10 to 14 days. Yield: 41.8 mg (0.024 mmol, 56%);  $\text{C}_{36}\text{H}_{82}\text{N}_6\text{Na}_6\text{O}_{44}\text{Pd}_3$  (1760.2 g mol<sup>-1</sup>): found (*exp*): % C 24.5 (24.6), H 5.1 (4.7), N 4.8 (4.8); FT-IR (KBr)  $\nu/\text{cm}^{-1}$ : 425(b), 2923(w), 1625(vs), 1392(s), 1328(m), 1311(m), 1164(w), 1052(w), 988(w), 884(m), 845(w), 727(w); UV-VIS ( $\text{H}_2\text{O}$ ),  $\lambda_{\text{max}}/\text{nm}$  (Abs): 215.0 (1.61), 247.0 (0.74, shoulder), 325.2 (0.06); <sup>1</sup>H-NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 2.48 (pd, 6H, J 11.1 Hz), 2.97 (pt, 6H, J 11.3 Hz), 3.16 (d, 6H, J 16.9 Hz), 3.65 (d, 6H, J 17.4 Hz), 3.68 (d, 6H, J 16.8 Hz), 3.96 (pq, 6H, J 12.0 z), 4.17 (d, 6H, J 17.4 Hz); <sup>13</sup>C-NMR (100 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 34.5 ( $\text{CH}_2$ ), 9.8 ( $\text{CH}_2$ ), 63.6 ( $\text{CH}_2$ ), 64.0 (CH), 172.9 (Cq), 183.2 (Cq).

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