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Cite this: DOI: 10.1039/c0xx00000x

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**COMMUNICATION****Sterically controlled self-assembly of tetrahedral  $M_6L_4$  cages via cationic N-donor ligands†**Anssi Peuronen,<sup>a</sup> Samu Forsblom<sup>a</sup> and Manu Lahtinen<sup>a\*</sup>

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

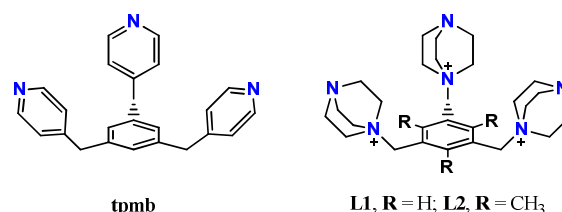
DOI: 10.1039/b000000x

**Tripodal cationic N-donor ligands exhibit sterically controlled self-assembly of tetrahedral  $M_6L_4$  coordination cages that promote selective anion encapsulation ( $PF_6^- > OTf^-$ ) in the solid state. The described method is a potential template for stepwise assembly of hetero-ligand coordination cages and polymers.**

Building and designing of hollow coordination cages, assembled from organic ligands and metal cations, has quickly become one of the hot topics in current chemistry.<sup>1</sup> Coordination cages have an increasing number of potential applications that include their use as microenvironments for chemical reactions<sup>2</sup> and molecular containers for storage and transport purposes but also for isolation of unstable<sup>3</sup> and non-crystalline species.<sup>4</sup> In building of various coordination cages perhaps the most utilized ligand species are bowl-shaped tripodal ligands, composed from either pnicogenic (amine or phosphine) or aromatic cores using coordinating groups based mainly on imidazole or pyridyl moiety. Such ligands are especially keen to form cages with  $M_6L_8$  composition if accompanied with metal cations that adopt square planar coordination geometry.<sup>5</sup> To alter the cage composition, participating metal centres can be capped with auxiliary ligands or replaced with metals that favour tetrahedral or octahedral coordination geometries. Employment of such strategies together with tripodal ligands enables self-assembly of several different cage topologies, including  $M_3L_2$ <sup>6</sup> and  $M_6L_4$ <sup>7</sup> species. To further expand the synthetic approaches for cage self-assembly and post-manipulation we report here a novel method of capturing an  $M_6L_4$  self-assembly intermediate from a process that would generally yield an  $M_6L_8$  species. This is done by steric crowding of the N-donor group of the tripodal ligand which effectively hinders the binding of several ligands to one metal cation. The described strategy allows labile auxiliary ligands to be coordinated to the metal nodes and thus presents a potential new route for carrying out post-synthetic structural manipulations. Furthermore, the cationic ligands used in this investigation promote selective anion binding inside the self-assembled cages.

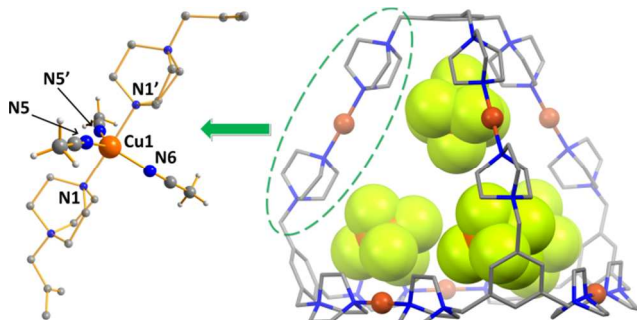
For the described task two cationic ligands, **L1** and **L2**, were synthesized. These consist of benzyl and mesityl cores, respectively, to which three 1,4-diazabicyclo[2.2.2]octane (DABCO) N-donor groups are connected by methylene bridges (Scheme 1). The geometry of **L1** and **L2** closely resembles that of 1,3,5-tris(4-pyridylmethyl)benzene (**tpmb**), a well establish

neutral ligand species for assembling  $M_6L_8$  cages.<sup>5a,8</sup> On the other hand, the two cationic ligands (**L2** in particular) are considerably less flexible compared to **tpmb**.<sup>9</sup> The steric properties of the two cationic ligands and **tpmb** are a key factor describing their different behaviour as building blocks for coordination cages. The bulky size and cationic charge of the DABCO moiety in **L1** and **L2** limits the number of distinct ligands coordinated to a single metal<sup>10</sup> and weakens the metal-ligand bond, respectively.<sup>11</sup> However, previous studies regarding mono-alkylated DABCOs show that they are applicable N-donors toward variety of electron deficient species.<sup>12</sup>



Scheme 1

Cage formation of **L1** was studied by reacting its  $PF_6^-$  salt with copper(II) trifluoromethanesulfonate ( $Cu(OTf)_2$ ) in acetonitrile (MeCN) at ambient conditions to give a bright green solution. Slow evaporation of the solvent yielded prismatic pale green crystals (see pictures of crystals in Fig. S1†) of **1** which were studied with X-ray diffraction. The formation of  $M_6L_8$  species, suggested by the ligand geometry, was not observed. Instead, the self-assembly process is halted halfway and the described reaction yields a cage with  $M_6L_4$  composition, more specifically  $[Cu_6(L1)_4(MeCN)_{18}(PF_6)_4](PF_6)_{20} \cdot (MeCN)_{32}$  (henceforth abbreviated to  $Cu_6(L1)_4$ ). The asymmetric unit of **1** is composed of two Cu-atoms, one half of the **L1** ligand, three distinct  $PF_6^-$  anions and six MeCN molecules, four of which are coordinated to the two Cu(II)-centres. Each of the Cu(II) centres acts as a linear link between two distinct ligands generating a cage with +24 charge which exhibits slightly distorted  $[d(Cu \cdots Cu) = 10.61\text{--}10.93 \text{ \AA}]$  tetrahedral symmetry (Fig. 1). The described  $M_6L_4$  composition is exceptional for a tetrahedral cage since each of metal cations are required to occupy the edges of the tetrahedron (*cf.* octahedral  $M_6L_4$  architecture with cornering Pd(II) cations<sup>13</sup>) and thus need to adopt linear coordination between the tripodal ligands. This has been previously achieved by using a metal cation capable of octahedral coordination together with an

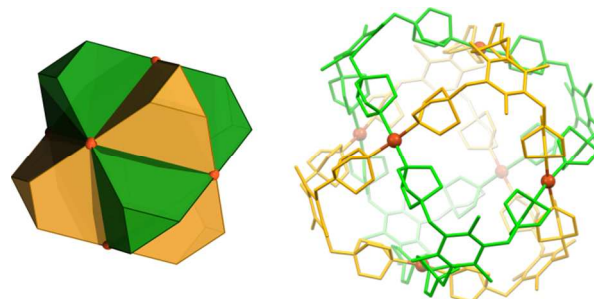


**Fig. 1.** Right: structure of cage  $\text{Cu}_6(\text{L1})_4$  found in **1** with the four encapsulated anions  $\text{PF}_6^-$  anions shown. Left: detailed structure of one of the six metal coordination centres (disordered MeCN molecules and certain hydrogen atoms are omitted for clarity). Distances (Å): Cu1-N1 = 2.079(3), Cu1-N5 = 2.027(5), Cu1-N6 = 2.055(10); angles (°): N1-Cu1-N1' = 178.7(2), N5-Cu1-N1 = 90.73(16), N6-Cu1-N1 = 91.0(3), N5-Cu1-N5' = 132.6(3). Symmetry code (') = 1/2-x, y, 3/2-z.

equatorial capping ligand.<sup>7</sup> In  $\text{Cu}_6(\text{L1})_4$ , however, no auxiliary ligands on the Cu(II) cations are required to create the tetrahedral cage as steric hindrance between the DABCO groups of adjacent ligands inhibits any further coordination of **L1** to the Cu(II) cation. Instead, the equatorial coordination sites of each Cu(II) centre are occupied by three MeCN molecules, two of which lie outside (exohedral) and one inside (endohedral) the cage, resulting in a distorted trigonal bipyramidal coordination geometry. Since MeCN ligand is very labile, the Cu(II) nodes are expected to be susceptible to post-synthetic modifications particularly at the exohedral equatorial sites.

Interestingly, the solid state structure of **1** also features encapsulation of four  $\text{PF}_6^-$  anions inside the central cavity of  $\text{Cu}_6(\text{L1})_4$  cage which are exclusively selected from the reaction mixture of both  $\text{PF}_6^-$  and OTf in 1:1 ratio. The endohedral  $\text{PF}_6^-$  are each located between the three DABCO groups of one **L1** ligand [ $d(\text{P1}\cdots\text{C}_6\text{-centroid})=4.763(2)$  Å] at the corner of the  $\text{Cu}_6(\text{L1})_4$  tetrahedron (Fig. 1). Thus, the anion binding seems to be driven by an electrostatic interaction between the  $\text{PF}_6^-$  anion and the triangular pocket of the cationic ligand. The remaining space inside the cage is taken by the six disordered Cu-coordinated MeCN molecules which exhibit close contacts to the endohedral anions (Fig. S6†). As a result, they are likely to have a stabilizing role in the  $\text{PF}_6^-$  encapsulation.

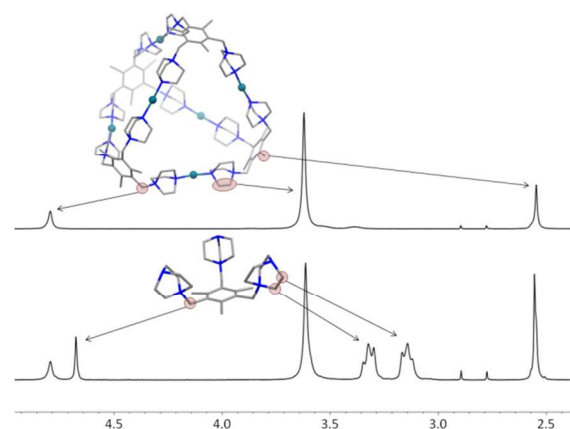
Next, a reaction similar to one described above was carried out using ligand **L2**. The pale green hexagon-shaped crystals of **2** (Fig. S1†) were obtained by slow evaporation of a dilute MeCN solution containing **L2** and  $\text{Cu}(\text{OTf})_2$ . Instead of the primitive tetragonal unit cell of **1**, crystals of **2** exhibit face centred cubic cell with twice the volume compared to **1**. The structure of **2** was successfully solved in space group  $Fm\bar{3}m$  where the asymmetric shows one third of the ligand, one Cu-atom, in addition to two anions and two acetonitrile molecules one of which is coordinated to the Cu(II). When the site specific symmetry operations are applied, a  $\text{Cu}_6(\text{L2})_8$  species is generated. However, after a thorough analysis of the composition of **2** and its structure we came to a conclusion that it is best described in terms of two  $\text{Cu}_6(\text{L2})_4$  tetrahedrons disordered in 0.5:0.5 ratio with overlaying Cu(II) nodes making the cage structurally equal to  $\text{Cu}_6(\text{L1})_4$  found in **1** (Fig. 2).<sup>14</sup> Similar to  $\text{Cu}_6(\text{L1})_4$  the endohedral environment of  $\text{Cu}_6(\text{L2})_4$  consist of six disordered MeCN



**Fig. 2.** Two illustrations, a truncated stellated octahedron (an Archimedean solid, left) and a simplified molecular model (right), of the two-fold disorder of the two tetrahedral  $\text{Cu}_6(\text{L2})_4$  units (shown in green and yellow) in structure of **2**.

molecules, each of which are coordinated to one of the six Cu(II) nodes. Furthermore, four  $\text{PF}_6^-$  anions are located in the cationic pockets of the ligands [ $d(\text{P1}\cdots\text{mesityl-centroid})=4.699(5)$  Å] as in  $\text{Cu}_6(\text{L1})_4$ .

The cage self-assembly was also studied by NMR spectroscopy in solution (details in ESI†). Small scale reactions were conducted using  $\text{Pd}(\text{BF}_4)_2$  with **L1** and **L2** in 6:4 metal-ligand ratios. <sup>1</sup>H NMR measurements show rapid and quantitative formation of highly symmetric species corresponding to  $\text{Pd}_6\text{L}_4$  demonstrating the stability of described cages also in solution (Fig. 3). The addition of another four equivalents of ligand affords no further complexation as the size of the DABCO groups sterically prevents the formation of  $\text{Pd}_6\text{L}_8$  species. These findings are consistent with the observations made on the basis of structures of **1** and **2**.

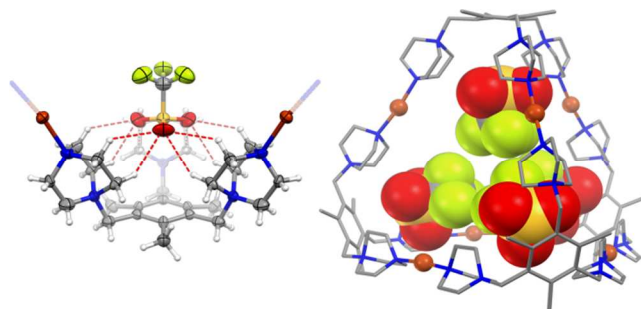


**Fig. 3.** Partial <sup>1</sup>H NMR spectrum showing the formation of  $\text{Pd}_6(\text{L2})_4$  cage in solution ( $\text{CD}_3\text{CN}$ ) upon mixing of  $\text{Pd}(\text{BF}_4)_2$  and **L2** in 6:4 ratio (top). Bottom: Addition of 4 more equivalents of **L2** does not result in further complexation.

To further investigate the anion encapsulation properties of reported  $\text{M}_6\text{L}_4$  species in solution, we measured the <sup>19</sup>F NMR spectrum of  $\text{Pd}_6(\text{L2})_4$  at multiple temperatures between 238 K and 300 K (Fig. S2†). The results show that both  $\text{PF}_6^-$  and  $\text{BF}_4^-$  exist only in one environment. The lack of peaks corresponding to either encapsulated  $\text{BF}_4^-$  or  $\text{PF}_6^-$  can be explained by rapid endo-exo exchange of anions through the four large openings on the triangular faces of the tetrahedral cage. Furthermore, the spacious interior of the  $\text{M}_6\text{L}_4$  assembly does not provide strong enough stabilization of the  $\text{PF}_6^-$  anions in solution in respect to the NMR timescale.<sup>15</sup> Instead, the anion encapsulation stems

from electrostatic attraction between the cationic ligand and  $\text{PF}_6^-$  and is supported by the endohedral MeCN molecules as observed in the solid state.

The flexibility of the interior of the  $\text{Cu}_6(\mathbf{L2})_4$  assembly was further demonstrated by an additional crystallization experiment where  $\text{PF}_6^-$  is excluded from the reaction mixture and replaced with a bulky bis(trifluoromethylsulfonyl)imide ( $\text{NTf}_2^-$ ) anion. The chartreuse coloured crystals of **3** were obtained by the procedure described above using  $\text{Cu}(\text{OTf})_2$  and  $\text{NTf}_2^-$  salt of **L2**. The subsequent single crystal X-ray analysis of **3** revealed a tetrahedral cage assembly analogous to **1** and **2**, but in which the endohedral surrounding consists of four OTf anions instead of  $\text{PF}_6^-$  (Fig. 4). OTf anions are encapsulated in the cationic pockets of the **L2** ligands (*cf.*  $\text{PF}_6^-$  in **1** and **2**) by facing the  $\text{SO}_3^-$  groups towards the cations. In addition, the endohedral Cu-coordinated MeCNs, observed in **1** and **2**, have been replaced by water molecules that better suit the endohedral space (Figs. S5 and S6 in ESI†). This gives **3** a total composition of  $[\text{Cu}_6(\mathbf{L2})_4(\text{MeCN})_{12}(\text{H}_2\text{O})_6(\text{OTf})_4](\text{OTf})_8(\text{NTf}_2)_{12} \cdot (\text{MeCN})$ .



**Fig. 4.**  $\text{Cu}_6(\mathbf{L2})_4$  cage assembly in structure **3** (right) showing the four encapsulated OTf anions. Left: a detailed view of the C-H...O interactions between one of the **L2** ligands of the cage and an OTf anion (ellipsoids are drawn at the 20 % probability level).

The described results show that OTf anion is readily encapsulated inside  $\text{Cu}_6(\mathbf{L2})_4$  in the absence of  $\text{PF}_6^-$  (**3**), but is excluded if  $\text{PF}_6^-$  is present in the reaction (**1** and **2**). The preference of  $\text{PF}_6^-$  over OTf, observed in **1** and **2**, most likely arises from stronger cation-anion interaction between  $\text{PF}_6^-$  and the cationic ligand in addition to better size-match of the four  $\text{PF}_6^-$  and the endohedral environment of the cationic  $\text{M}_6\text{L}_4$  cage.

In summary, we have established cationic tripodal N-donor ligands based on DABCO moiety, as useful tools in self-assembly of tetrahedral coordination cages exhibiting unusual tetrahedral  $\text{M}_6\text{L}_4$  composition. The cage self-assembly is controlled by the steric interactions between the DABCO N-donor groups hindering the generation of  $\text{M}_6\text{L}_8$  species. The described strategy is a promising route to controlled stepwise synthesis of hetero-ligand coordination cages and caged polymers. Moreover, the presented cages show selective anion encapsulation ( $\text{PF}_6^- > \text{OTf}^-$ ) towards fluorinated anions in the solid state which is based on the interaction between the cationic ligand and anion. Further investigation of cationic ligands, involving their modification and self-assembly with other *d*-block elements accompanied with guest-host studies, is currently ongoing in our laboratory.

Authors gratefully acknowledge the financial support of University of Jyväskylä and the Inorganic Materials Chemistry Graduate Program. The authors would also like to thank Ms. Elina Hautakangas for carrying out the elemental analyses.

## Notes and references

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- † Electronic Supplementary Information (ESI) available: Experimental section, computational analysis and additional figures. CCDC reference numbers: 978171, 978172 and 992712. See DOI: 10.1039/b000000x/
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