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A novel synthetic strategy for hexanuclear supramolecular architectures†

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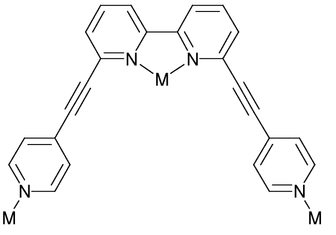
Hexanuclear cage complexes $[M_6L_6X](X)_5$ [M = Cu(I), Ag(I); L = 6,6′-bis(4-ethynylpyridine)2,2′-bipyridine; X = BF_4^-, SbF_6^-] have been prepared using a self-assembly approach; these architectures encapsulate anions in the solid-state and are fluxional in solution.

The self-assembly of molecular architectures using metal–ligand interactions is a highly topical area of current research which has yielded many fascinating structures[1–6] with intriguing properties which act as molecular containers.[2] Two popular approaches for the synthesis of these species have been developed. Firstly, work pioneered by Fujita[2] and Stang,[1a] uses a 'blocking ligand' to protect co-ordination sites at the metal centre thus controlling the positions available for binding of bridging ligands and enabling the construction of the desired architecture. The second strategy[3–5] does not employ blocking ligands but generally uses bridging, chelating ligands to control the metal geometry. We now report what may be considered a hybrid of these two strategies using a ligand, 6,6′-bis(4-ethynylpyridine)-2,2′-bipyridine (L), (Scheme 1), which acts as both a 'blocking' chelating ligand *via* the ligand's 2,2′-bipyridyl fragment, and as a bridge *via* two 4-pyridyl donors. We have previously developed related ligands, which we term multi-modal ligands, for the construction of polymeric co-ordination frameworks[6] and carboxylate-bridged clusters and polymers.[7]

The ligand (L) was prepared *via* a coupling reaction between 6,6′-dibromo-2,2′-bipyridine and 4-ethynylpyridine using a $PdCl_2(PPh_3)_2$ catalyst in triethylamine. Reaction of the ligand with $Cu(MeCN)_4BF_4$ **1** or AgX (X = BF_4^- **2**, SbF_6^- **3**) affords a red $[Cu^I]$ or colourless $[Ag^I]$ product upon evaporation of the solvent.

Single crystals of the complexes were grown by vapour diffusion of diethyl ether into DMF (**1**, **2**) or MeCN (**3**) solutions of the complexes. Structural determinations‡ for **1**–**3** by single crystal X-ray diffraction reveals a hexanuclear framework structure, $[M_6L_6X](X)_5$ (**1**, M = Cu, X = BF_4^-; **2**, M = Ag, X = BF_4^-; **3**, M = Ag, X = SbF_6^-) (Fig. 1). The metal centres adopt distorted tetrahedral environments with each metal centre co-ordinated by three different ligands, *via* a chelating 2,2′-bipy site and by two 4-pyridyl donors from two separate ligands. Thus, each ligand acts as both a *blocking* and a *bridging* ligand encouraging the formation of a discrete architecture.



Scheme 1 Schematic representation of the multi-modal ligand L showing the 2,2′-bipyridyl *blocking* and 4-pyridyl *bridging* sites.

In all three cases the dimensions of the hexanuclear cage, which can be simply represented as the volume of the octahedron formed by joining the six metal centres, are similar [1028 Å³ (**1**), 1012 Å³ (**2**), 1048 Å³ (**3**)]. A single anion, either BF_4^- (**1**, **2**) or SbF_6^- (**3**), is encapsulated within the cage. In the case of **3** one of the 4-pyridyl rings of the ligand is twisted by 82° with respect to the bipyridyl fragment and so the cage can breathe in order to accommodate the significantly larger SbF_6^- anion (Fig. 2). In **1**–**3** the hexanuclear units pack *via* π–π interactions between 2,2′-bipy fragments in adjacent cages generating large cavities which, in **1** and **2**, accommodate highly disordered non-encapsulated anions and guest solvent molecules.

To assess the influence of the counter-anion a significantly larger anion, $[Co(C_2H_{11}B_9)_2]^-$, was used in the reaction of Ag^I salts with L. Reaction of $AgBF_4$ with L, in $MeCN/CH_2Cl_2$, in the presence of an equivalent of $Na[Co(C_2H_{11}B_9)_2]$ affords yellow single crystals which were structurally characterised.‡ The product $[Ag_6L_6(BF_4)][Co(C_2H_{11}B_9)_2]_5$ **4** was found to still contain a hexanuclear cage, which encapsulates a BF_4^- anion, with similar structural dimensions to those observed in **2**. All of

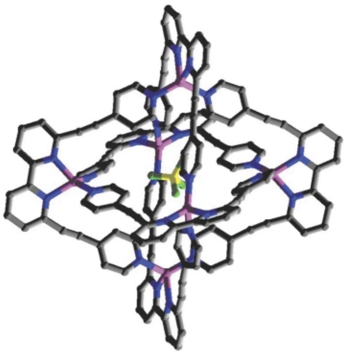


Fig. 1 View of the hexanuclear cage formed by $\{[Cu_6L_6(BF_4)](BF_4)_5\}$ illustrating the encapsulation of the BF_4^- anion in the solid state (copper–purple, nitrogen–blue, boron–yellow, fluorine–green, carbon–grey).

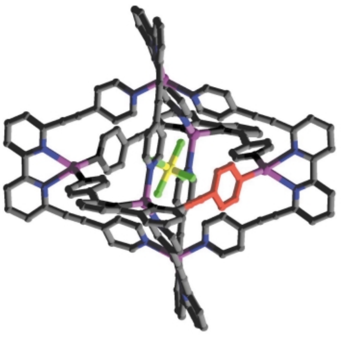


Fig. 2 View of the hexanuclear cage formed by $\{[Ag_6L_6(SbF_6)](SbF_6)_5\}$ illustrating the encapsulation of the SbF_6^- anion in the solid state. The (4-pyridyl)ethynyl arm which twists to accommodate the larger SbF_6^- anion is highlighted in red (silver–purple, nitrogen–blue, antimony–yellow, fluorine–green, carbon–grey).

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† Electronic supplementary information (ESI) available: synthesis and single crystal X-ray diffraction. See http://www.rsc.org/suppdata/cc/b3/b300605k/

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the $[Co(C_2H_{11}B_9)_2]^-$ anions were located external to the cage, filling channels within the structure. Thus, $Ag[Co(C_2H_{11}B_9)_2]$ was reacted with L in a 1 : 1 ratio in MeCN and single crystals of the product grown by solvent diffusion of water into a solution of the complex in MeCN. In this instance the product, $(AgL)_2[Co(C_2H_{11}B_9)_2]_2$ **5**, adopts a binuclear structure (Fig.3) in which each Ag^I cation adopts a distorted trigonal planar geometry and is coordinated by a chelating 2,2′-bipy site and a 4-pyridyl donor from another ligand. Thus, it can be seen that in the absence of a suitable anion the formation of the hexanuclear $(AgL)_6{}^{6+}$ cage is not favoured and a simpler binuclear structure is adopted.

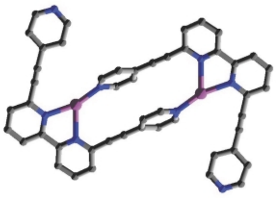

Fig. 3 View of the dinuclear cation formed by $(AgL)_2[Co(C_2H_{11}B_9)_2]_2$ **5** (silver–purple, nitrogen–blue, carbon–grey).

Solution phase studies of **1** and **2** by ^{19}F NMR spectroscopy show that the Cu^I complex (**1**) is more stable than the corresponding Ag^I complex. ^{19}F NMR spectra of **1** in MeCN solution shows two distinct environments, the proportions of which vary with temperature. Thus, we can observe one peak corresponding to untrapped $BF_4{}^-$ anions [δ −152.2 (298 K), −151.2 (230 K) ppm] and a second peak corresponding to an anion encapsulated within the hexanuclear cage [δ − 157.3 (298 K), 156.3 (230 K) ppm]. This ratio is 5 : 0.2 at 298 K whereas at 230 K it changes to 5 : 0.7, approaching the theoretical value of 5 : 1 observed in solid state (Fig. 4). The stability of the hexanuclear cage in **1** is further confirmed by electrospray mass spectrometry of MeCN solutions of the complex. Four multiply-charged ions are observed at low cone voltage in the mass spectrum of **1** (930, 676, 523 and 422 *m*/*z* which correspond to $[Cu_6L_6(BF_4)_n]^{(6-n)+}$ where $n = 3–0$, respectively). In contrast, neither ^{19}F NMR spectroscopy nor electrospray mass spectrometry studies of **2** in MeCN gives any indication of the hexanuclear complexes in solution and only smaller aggregates were observed. The comparative lack of stability of the Ag^I complex can be rationalised by the greater lability of the Ag–pyridine bond.

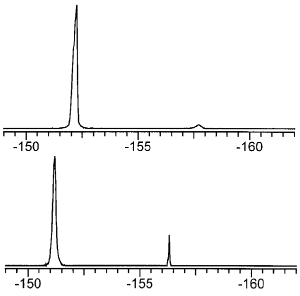

Fig. 4 ^{19}F NMR spectra of $\{[Cu_6L_6(BF_4)](BF_4)_5\}$ **1** in MeCN at 298 K (above) and 230 K (below). Untrapped $BF_4{}^-$ anions are observed downfield and trapped $BF_4{}^-$ anions, encompassed within the hexanuclear cage, are observed upfield.

There have been two recent reports of related hexanuclear Ag^I cages.[8,9] In both cases linear Ag^I cations are bridged by either hexadentate hexa(2-pyridyl)[3]radialene[8] or tridentate phosphine ligands[9] to generate the hexanuclear cage. A hexanuclear array in which the ligand acts as both blocking group and bridging ligand has been reported recently, but in this earlier example the product is cyclic rather than a cage architecture.[10]

In conclusion, we have demonstrated that L can be used to assemble discrete molecular architectures in which the ligand acts both to block metal coordination sites and to bridge metal centres. The complexes formed encapsulate guest anions in the solid-state, with expansion to accommodate the larger $SbF_6{}^-$ anion, but are less stable in solution, particularly in the case of the $(AgL)_6{}^{6+}$ cage. We are currently investigating the variety of anions that can be included in these, and related, cages and studying their influence upon the solution and solid-state behaviour of these products.

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Notes and references

‡ *Crystal data* (CCDC 201515–201519. See http://www.rsc.org/suppdata/cc/b3/b300605k/ for crystallographic files in CIF or other electronic format.

1: Rhombohedral, $R\bar{3}$, $a = b = 20.467(2)$ Å, $c = 40.139(6)$ Å, $U = 14561(3)$ Å^3, $Z = 18$, $T = 150(2)$ K, 7646 unique reflections [$R_{int} = 0.055$] [3221 with $I > 2\sigma(I)$]. Final $R_1 = 0.0761$, wR_2 (all data) = 0.242.

2: Rhombohedral, $R3$, $a = b = 20.803(3)$ Å, $c = 40.125(10)$ Å, $U = 15038(5)$ Å^3, $Z = 18$, $T = 150(2)$ K, 7605 unique reflections [$R_{int} = 0.065$] [2430 with $I > 2\sigma(I)$]. Final $R_1 = 0.0423$, wR_2 (all data) = 0.103.

3: Triclinic, $P1$, $a = 15.971(5)$Å, $b = 18.961(6)$ Å, $c = 19.029(6)$ Å, $\alpha = 113.311(4)°$, $\beta = 96.282(5)°$, $\gamma = 113.352(4)°$, $U = 4609.93$ Å^3; $Z = 1$, $T = 150(2)$ K, 16 125 unique reflections [$R_{int} = 0.109$] [7531 with $I > 2\sigma(I)$]. Final $R_1 = 0.0779$, wR_2 (all data) = 0.2485.

4: Triclinic, $P1$, $a = 15.7177(10)$ Å, $b = 20.1484(12)$ Å, $c = 20.3876(12)$ Å, $\alpha = 74.800(2)°$, $\beta = 70.7470(2)°$, $\gamma = 86.5800(2)°$, $U = 5879.6(6)$ Å^3; $Z = 1$, $T = 150(2)$ K, 22869 unique reflections [$R_{int} = 0.025$] [16377 with $I > 2\sigma(I)$]. Final $R_1 = 0.0944$, wR_2 (all data) = 0.297.

5: Monoclinic, $P2_1/c$, $a = .082(5)$ Å, $b = 38.364(3)$ Å, $c = 14.9966(11)$ Å, $\beta = 100.861(2)°$, $U = 4016.3(5)$ Å^3; $Z = 4$, $T = 120(2)$ K, 10 585 unique reflections [$R_{int} = 0.039$] [9236 with $I > 2\sigma(I)$]. Final $R_1 = 0.0465$, wR_2(all data) = 0.120.

For **1** and **2** severe disorder was encountered in the guest molecules and some of the unencapsulated anions. This disorder was treated using the SQUEEZE[11a] function as implemented in PLATON.[11b]

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