

Structural and functional versatility from bis-tridentate chelation in coordination cages Felix J. Rizzuto[†], Wen-Yuan Wu[‡], T. K. Ronson[†] and Jonathan R. Nitschke[†]

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On both the micro- and macroscopic scales, shape and function are implicitly intertwined. Improving structural diversity is consequently paramount to the development of molecules with targeted, designed functionality. Coordination cages, whose most fundamental feature is the presence of an internal void, allow for the infiltration, entrapment and storing of small molecules.^{1,2} The interactions between a host (cage) and its guest (molecule) rely on size, shape and electronic complementarity.³ Thus, small geometric changes can lead to large property differences, and the careful manipulation of ligand symmetry and coordination geometry can be used to synthesise bespoke structures capable of binding specific molecular units.

Coordination cages synthesised by *subcomponent self-assembly* involve the templated condensation of imines around metal centres.⁴ The discrete, polynuclear species that result are thus far exclusively composed of tris-bidentate corners (Figure 1a). We envisioned that the subcomponent self-assembly regime could be extended to incorporate tridentate units (Figure 1b), yielding large, rigid architectures that persist in solution. Three topologically distinct face-panelled architectures (with three-, four- and six-fold symmetric ligands) have resulted, each of which express guest-binding properties unique to their novel shape and cavity.



Figure 1. The subcomponent self-assembly of (a) tris-bidentate and (b) bis-tridentate coordinated complexes.

Threefold symmetric ligands

The subcomponent self-assembly of 2-formylphenanthroline with threefold symmetric amine A around Zn^{II} ions affords octahedron 1 with M_6L_4 stoichiometry (Figure 2). Adjacent to each occupied face is an unoccupied aperture that we can exploit for host-guest interactions. When titrated with tetraphenylborate (TPB), new resonances are observed in the ¹H NMR spectrum of **1** (Figure 3), consistent with binding in fast exchange on the NMR timescale.





Figure 4: Synthesis and characterisation of cuboctahedron 2: self-assembly of

Fourfold symmetric ligands

Cuboctahedra panelled with porphyrin faces are capable of selectively binding simple and asymmetric fullerenes. No binding was observed for planar aromatics or fullerenes greater than C_{70} .

ESI-MS confirms that two, and only two, fullerenes bind within the central cavity (Figure 5). Desymmetrisation of the proton environments in **B** was evidenced by paramagnetic ¹H NMR studies, consistent with localisation of the fullerenes at opposite corners of the





Figure 2: Ligand A and 2-formylphenanthroline condense with Zn^{II} ions to form octahedron 1, capable of binding TPB in fast exchange.

The encapsulation of TPB within **1** is only possible by extending into the windows of the architecture; the phenyl rings of TPB insert themselves between the phenyl rings of ligand A, forming π -stacked pockets.



Figure 5: Successful and unsuccessful guests for cuboctahedron 2 (left); ESI-MS evidence for charge distributions consistent with two fullerenes binding in each case (middle); and socially sorted host-guest complexes resulting from a mixture of fullerenes with 2 (right).

Sixfold symmetric ligands

The reaction of hexatopic amine C with 2-formylphenanthroline and Co^{II} ions leads to the formation of truncated tetrahedron 3 (Figure 6), a unique shape to supramolecular chemistry. The interior cavity of 3 far exceeds that of 2, touting the structure as a potential host for small proteins and carbon nanotube fragments.



Figure 3: Titration of TPB into octahedron 1. TPB shifts shown in green.

Figure 6: The subcomponent self-assembly of ligand C, 2-formylphenanthroline and Co^{II} ions forms truncated tetrahedron **3** with $M_{12}L_4$ stoichiometry.

Conclusions & future work

References

Larger structures can house larger guests. Exploiting the bis-tridentate chelation of the phenanthroline-imine motif, we can form unique structures with enclosed cavities capable of binding tetrahedral anions and multiple spherical aromatics. Future work will involve extending this method to non-planar, less symmetric ligands, towards the realisation of supramolecular structures with asymmetric cavities for targeted drug encapsulation.

1. Chem. Rev. 2011, 111, 6810-6918. 2. Acc. Chem. Res. 2005, 38, 371-380. 3. Science 1974, 183, 803-809. 4. Chem. Commun. 2013, 49, 2476-2490.

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