An $M_{18}L_{24}$ stellated cuboctahedron through post-stellation of an $M_{12}L_{24}$ core

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Platonic and Archimedean polyhedra, well-known to mathematicians, have been recently constructed by chemists at a molecular scale by defining the vertices and the edges with metal ions (M) and organic ligands (L), respectively. Here, we report the first synthesis of a concave-surface ‘stellated polyhedron’, constructed by extending the faces of its precursor polyhedron until they intersect, forming additional nodes. Our approach involves the formation of an $M_{12}L_{24}$ cuboctahedron core, the linkers of which each bear a pendant ligand site that is subsequently able to bind an additional metal centre to form the stellated $M_{18}L_{24}$ cuboctahedron. During this post-stellation process, the square faces of the $M_{12}L_{24}$ core are closed by coordination of the pendant moieties to the additional metal centres, but they are re-opened on removing these metals ions from the vertices. This behaviour is reminiscent of the analogous metal-triggered gate opening–closing switches found in spherical virus capsids.

stellated polyhedra are a unique family of polyhedra with concave surfaces, constructed by extending the faces of a polyhedron until they intersect (Fig. 1). Although the molecular self-assembly of polyhedral architectures is a topic of current interest, their stellated derivatives—in which the stellated frameworks are clearly defined by metal vertices—have never been synthesized. In the literature, an $M_6L_8$ ‘stellated octahedron’ has been described by Hardie and colleagues, in which the stellated vertices are defined by the pronounced pyramidal shape of the ligand. Topologically similar $M_6L_8$ complexes have been described using terms such as ‘cubes’, ‘balls’ or ‘spheres’. Hardie and colleagues have also reported a unique $M_4L_4$ cube whose hexameric aggregate is closely related to the stellated truncated hexahedron. Here, we report the self-assembly of a stellated cuboctahedron in which all the vertices are clearly defined by metal centres, through the post-stellation of a polyhedral precursor by metal coordination.

On complexation of tris(4-pyridyl) ligands (comprising a benzene core bearing two A and one B coordination sites) (1) with Pd(II) ions, coordination sites A (1,3-positions of the benzene core) predominantly participate in self-assembly to form an $M_12L_{24}$ cuboctahedral core with an M:L ratio of 1:2, leaving sites B uncomplexed. On further addition of Pd(II), the dangling pyridyls at sites B coordinate to these additional metal centres, converting the cuboctahedron into an $M_{18}L_{24}$ stellated cuboctahedron. These structures were subsequently characterized by X-ray crystallography, nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry (MS). The large square windows (Fig. 1) of the $M_{12}L_{24}$ cuboctahedron are closed by the stellation, but can be re-opened by removal of the metal ions from the vertices, thereby providing a reversible gate opening–closing function for a large cuboctahedral cage. This post-stellation approach also provides an easy and efficient method for functionalizing and stabilizing the original polyhedral core framework.

Results and discussion

Ligand 1 was synthesized from 3,5-dibromobenzyl alcohol in two steps: Mitsunobu displacement with 4-hydroxypyridine at the benzylic position, followed by Suzuki coupling with 4-pyridylborate at the 3,5-positions (Supplementary Scheme S1). In ligand 1, the coordination ability of the pyridyl groups at coordination sites A and B is comparable. It was therefore anticipated that, upon addition of metal ions, the random complexation of these two sites would generate numerous oligomeric products, which in turn would be kinetically trapped, resulting in a gel or a precipitate. However, when a 2:1 mixture of 1 and Pd(BF$_4$)$_2$ was heated in dimethyl sulfoxide-d$_6$ (DMSO-d$_6$) at 80 °C for 12 h, selective complexation was observed (by $^1$H-NMR) at site A only. Only site A pyridyl protons were significantly shifted downfield.
characteristic of metal coordination, and no distinct chemical shift change was observed for the site B pyridyl protons (Fig. 2a,b). The number of signals derived from ligand 1 remained unchanged, indicating a product with a highly symmetrical structure. Diffusion-ordered NMR spectroscopy (DOSY) showed the formation of a single product with a single band at diffusion coefficient $D = 3.80 \times 10^{-11} \text{m}^2 \text{s}^{-1}$ (log $D = -10.42$); this value is comparable to that of previously reported $M_{12}L_{24}$ complexes with the same shell framework.$^{12}$ These observations strongly support the formation of $M_{12}L_{24}$ cuboctahedron 2, in which 48 site A pyridyl groups are selectively used for self-assembly. Finally, the formation of 2 in solution was proven by cold-spray ionization time-of-flight mass spectrometry (CSI-TOF-MS)$^{27}$, which revealed a series of prominent peaks for $[\text{Pd}_{12}(\text{BF}_4)_2]^{2-}$ (see Supplementary Information).

Selective complexation at site A to form cuboctahedron 2 is explained by the kinetic trap of the stable $M_{12}L_{24}$ core in the self-assembly process. We have previously shown that, once self-assemblyed from bis(4-pyridyl) bent ligands and Pd(II) ions, the $M_{12}L_{24}$ framework gains remarkable kinetic stability with a half-life of $\sim 20$ days for ligand exchange.$^{28}$ A range of metal–ligand oligomers are initially formed, but because the highly symmetric $M_{12}L_{24}$ cuboctahedral framework (2) is the only stable structure, it is the one that eventually assembles during equilibration.

After counter-anion exchange with PF$_6^-$, the structure of 2 (PF$_6^-$ salt) was unambiguously determined by X-ray crystallography. Slow vapour diffusion of ethyl acetate into a DMSO solution of 2 (PF$_6^-$ salt) resulted in single crystals suitable for X-ray analysis. Structure refinement revealed the $M_{12}L_{24}$ cuboctahedral skeleton with dangling uncoordinated pyridyl arms at site B (Fig. 3). The dangling arms are disordered but aligned towards the centre of the square windows of the cuboctahedron, presumably to optimize crystal packing.

It was expected that the dangling pyridyl arms (site B) at the convex of 2 could further accommodate six metal ions on the square windows of the cuboctahedron to give an $M_{18}L_{24}$ stellated cuboctahedron 3 (Fig. 4a). Accordingly, Pd(BF$_4$)$_2$ was added portionwise to a solution of 2, and the complexation was monitored by $^1$H NMR spectroscopy (Fig. 4b). The proton signals of the pyridyl groups in site B were gradually shifted downfield (indicated by blue and red dashed lines in Fig. 4b), while those of site A on the $M_{12}L_{24}$ core remained unchanged. DOSY also demonstrated the formation of a new discrete product with a similar diffusion coefficient (Supplementary Fig. S17). Unlike complexation at site A, free and complexed pyridyl groups at sites B are averaged on the NMR timescale, indicating weaker coordination at site B than at site A. We assumed that each Pd(II) ion is cooperatively coordinated by the four site B pyridyl groups at every square window. A Job plot confirmed this hypothesis—the clear 1:1 complexation of one Pd(II) ion per square window (1/6 partial structure of 2) was revealed from the plot of $\Delta \delta$ versus $\chi$ (where $\chi = [\text{Pd(II)}] / ([\text{Pd(II)}] + 1/6$)., and $\Delta \delta$ indicates the change in chemical shift in $^1$H-NMR) (Fig. 4c). Nonlinear curve fitting revealed cooperative 1:4 complexation at every Pd(II) centre with an apparent associate constant $K_a$ (between the Pd(II) ion and the square window) of $1.79 \times 10^3$ M$^{-1}$ (Fig. 4d).

Owing to the weaker coordination ability of the site B pyridyls at the vertices, CSI-TOF mass measurements failed to detect the expected $M_{18}L_{24}$ species directly. Nonetheless, prominent peaks corresponding to $[\text{Pd}_{12+n}(\text{BF}_4)_2]^{2-}$ (where $n = 0–3$, $m = 14–8$) were observed, probably generated by the loss of some of the Pd(II) ions from 3 under CSI-MS conditions, taking into account the weaker Pd(II)–pyridine coordination at site B (Supplementary Figs S22 and S23).

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**Figure 2** | Synthesis and structural analyses of cuboctahedron 2. a. Cartoon illustration of the self-assembly of 2. b. $^1$H NMR spectra (500 MHz, 300 K, DMSO-$d_6$) of ligand 1 and complex 2, with blue and red dashed lines indicating the change of chemical shift on pyridyl sites A (α, β) and B (α’, β’). c. CSI-TOF mass spectrum of complex 2 (BF$_4^-$ salt). Inset: expanded spectrum of the 9+ peaks (top, simulated; bottom, observed).

**Figure 3** | Crystal structure of 2 (PF$_6^-$ salt) looking down through a triangular window (left) and a square window (right). Below each structure, palladium atoms (yellow balls) that define the cuboctahedral framework (shown in blue) have been extracted from the crystal structure. A disordered model was applied to the flexible pyridyl groups (pink) on the square windows. All the counterions (PF$_6^-$) present at the apical positions of each Pd(II) centre are omitted for clarity.
structure revealed the expected M18L24 stellated polyhedron with a separation of 3.64 nm between the most distant Pd(II) ions, suggesting potential applications in host–guest chemistry for giant guests on a biomolecular level, such as a small protein.

Cuboctahedral complex 2 has eight triangular and six square windows. The diameters of the inscribed circles of the triangular and square windows are 0.88 and 1.24 nm, respectively, indicating that the square windows are much larger portals for potentially incorporating a guest into the cuboctahedral cage. It is worth noting that the stellation can act as a gate closing process for the large square windows of 2. The re-opening of the windows was also examined by removal of the six Pd(II) ions from the vertices. We found that the addition of $N,N,N',N'$-TMEDA to a solution of 3 selectively sequestered the metals from the vertices to result in gate-opened complex 2 (Fig. 4b, bottom trace). DOSY measurements also confirmed that the M$_{12}$L$_{24}$ spherical framework was not damaged by the addition of the TMEDA (Supplementary Fig. S18). We therefore achieved reversible gate opening/closing (stellation/destellation) of the cuboctahedral structure.

**Conclusions**

We have established a post-stellation method for the self-assembly of an M$_{18}$L$_{24}$ stellated cuboctahedron by structural extension from an M$_{12}$L$_{24}$ cuboctahedron core. The method features the bottom-up construction of new, complicated, three-dimensional molecular polyhedra and, equally importantly, the manipulation and functionalization of known polyhedral molecular objects. We further

![Image](https://via.placeholder.com/150)
envisage that the reversible gate opening–closing process at the square windows will enable us to incorporate giant guests such as proteins and DNA through the opened gate and to subsequently incarcerate them in the stellated polyhedron by gate closing. We also note that such a controllable structural transformation by the crosslinking of component subunits resembles the metal-triggered gate opening–closing switches found in spherical virus capsids12–14.

Methods

X-ray structure determination. The diffraction data were collected at synchrotron facilities (Spring-8, beamline BL38B1 for 2; KEK, beamline NE3A for 4). Despite many attempts to optimize the measurement conditions based on synchrotron radiation, the crystals diffracted very weakly because of the large amount of disordered solvents and anions inside the huge void in the crystal. Most of the disordered molecules and residues could not be modelled, and the SQUEEZE procedure of PLATON33 was used in the refinement. Results for complex 2: cubic, Im3-α, a = 59.346(5) Å, V = 60,912(12) Å³, Z = 2, T = 300 K. Anisotropic least-squares refinement for the atoms on the polyhedral backbone and isotropic refinement for the other atoms on 2,437 independent merged reflections (Rint = 0.0675) converged at residual wR2 = 0.3715 for all data, residual R1 = 0.1944 for 2,374 observed data (I > 2σ(I)) and goodness of fit (GOF) = 1.822. Results for complex 4: cubic, I432, a = 53.34(6) Å, V = 151,709(3) Å³, Z = 4, T = 293 K. Anisotropic least-squares refinement for the atoms on the polyhedral backbone and isotropic refinement for the other atoms on 6,350 independent merged reflections (Rint = 0.0675) converged at residual wR2 = 0.2887 for all data, residual R1 = 0.0882 for 4,948 observed data (I > 2σ(I)) and goodness of fit (GOF) = 1.192.

The X-ray crystallographic coordinates for structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition nos CCDC 840807 (2) and CCDC 840814 (4). These data can be obtained free of charge (http://www.ccdc.cam.ac.uk/data_request/cif). Full experimental details and crystallographic analysis are given in the Supplementary Information.

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Author contributions

M.F. and Q.-F.S. conceived and designed the experiments and wrote the manuscript. Q.-F.S. requests for materials should be addressed to M.F.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper at www.nature.com/naturechemistry. Reprints and permission information is available online at http://www.nature.com/reprints. Correspondence and requests for materials should be addressed to M.F.