

Self-Assembly of a Unique Extended-Tetrahedral 3,3',5,5'-Tetrakis(4-pyridyl)bimesityl Ligand into Discrete Supramolecular Cubes by Face-Directed Metal Coordination

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ABSTRACT: Twelve unique D_{2d} -symmetric extended-tetrahedral tetrapyridylbimesityl ligands **1** and six metal cations (Ni^{2+} and Cu^{2+}) assemble to generate *discrete* cubic architectures with an O_h symmetry, as revealed by X-ray crystallographic analyses. The internal cavity dimensions of the cubes are in excess of ca. 3000 Å³. The metal-organic cuboid discrete cages with such large internal cavity have been characterized by X-ray crystallography for the first time.

The concepts of molecular self-assembly offer the unique opportunity to assemble molecules in a predetermined manner.¹ In this regard, the strong and highly directional attributes associated with metal-coordination bonds, as compared to hydrogen bonds, can be conveniently exploited to construct a variety of metal-organic frameworks (MOFs) and to accomplish the syntheses of diverse supramolecular architectures.² A rational exploitation of the knowledge of coordination geometry of the metal and ligand structure to achieve spontaneous self-assembly in a way that emulates the natural events continues to be of great contemporary interest in supramolecular chemistry.³ In this context, a variety of cage-type molecular ensembles equivalent to Platonic and Archimedian solids have been synthesized.^{3,4} Insofar as the platonic “cube” is concerned, the possible ways by which it may be assembled by metal-coordination bonds are shown in Figure 1. The cubes A and B constructed via “edge-directed” protocols have open faces, while C and D derived from “face-directed” assembly have closed faces with open windows toward the corners. The synthesis of cubes that correspond to the topologies of A, B, and D has been accomplished through coordinate covalent bonding.^{5,6} We are aware of two instances of X-ray structural elucidations of cages with a perfect octahedral symmetry (O_h) constructed by a self-assembly of eight tritopic ligands and six tetratopic metal cations;⁷ these cage-complexes are more spheroidal in shape by virtue of the spatial disposition of the ligands. The M_6L_{12} cube of the type “C”, a fundamental unit of the NbO network,⁸ exhibited in Figure 1 constructed by a straightforward *face-directed* self-assembly of a ditopic ligand is unprecedented. Herein, we wish to document the realization of the cube “C” using a unique bimesityl-based tetrapyridyl ligand **1**.

Our motivation to synthesize the extended-tetrahedral ligand **1** and explore its utility in the metal-directed self-assembly of novel architectures was spurred by our recent studies on the self-assembly of sterically hindered carboxylic acids.⁹ The steric crowding between two mesityl rings of the bimesityl forces them to be orthogonal to each other, thereby causing the four tetrapyridyl rings to assume the geometry of an extended tetrahedron corresponding to the topology of a D_{2d} -symmetric allene. The tetrapyridyl ligand **1** was synthesized starting from the readily prepared bimesityl.¹⁰ A slow evaporation of the solution of a 1:1 molar equivalent of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and the tetrapyridyl ligand **1** in MeOH over a period of 7–10 days yielded dark blue crystals **2** in 60–65% yield (cf. Supporting Information). In a similar manner, pale green crystals **3** were obtained from a methanolic solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and

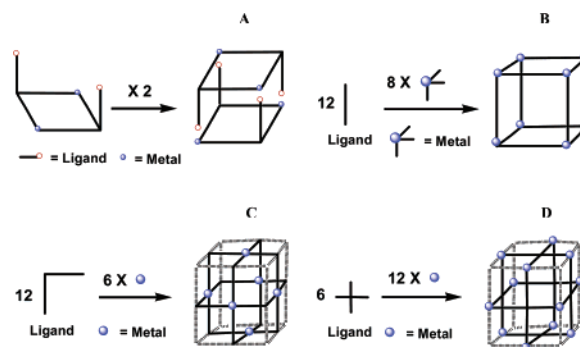


Figure 1. The ways in which the supramolecular cubes A–D may be assembled based on coordinate covalent bonds.

the ligand **1**. In both cases, the crystals were highly fragile and degraded immediately upon removal from the mother liquor, which suggests the inclusion of solvent molecules in the crystal lattice. The ¹H NMR spectroscopic and mass spectrometric characterization of the compounds **2** and **3** was compounded by the problems of insolubility and instability. For ¹H NMR spectroscopy, the compounds were virtually insoluble in almost all the solvents with the exception of DMSO. In the latter, however, the compounds decomposed as revealed by a color change as well as the signals that corresponded only to the free ligand **1** in ¹H NMR spectroscopy.¹¹ Both MALDI and ESI mass analyses of the Cu and Ni compounds **2** and **3** yielded M^+ ions corresponding to the free ligand **1**, suggesting thereby that the complexes are not sufficiently stable for ready characterization. From X-ray diffraction studies (vide infra) and elemental analyses (Supporting Information), the following compositions were formulated for compounds **2** and **3**: **2**: $\text{Cu}_6(\text{C}_{38}\text{H}_{34}\text{N}_4)_{12}(\text{CH}_3\text{COO})_{12} \cdot n\text{H}_2\text{O}$; **3**: $\text{Ni}_6(\text{C}_{38}\text{H}_{34}\text{N}_4)_{12}(\text{NO}_3)_{12} \cdot n\text{H}_2\text{O}$.

The single-crystal X-ray crystallographic analyses of both of the compounds **2** and **3** showed that they crystallize in the cubic space group, *viz.*, $Pn\bar{3}n$, with only a marginal difference in their cell parameters attesting to their isostructurality. While the crystals of compound **2** diffracted with reflections of moderate intensity up to $2\theta \leq 44^\circ$ (MoK α), those of **3** were found not to diffract at all beyond 37° . From innumerable experiments with a large collection of crystals grown independently, it was established that the poor intensity data was not due to bad quality crystals, but indeed due to the high symmetry and severe motions of the solvent molecules in the large cavities of the crystal lattice. The structure solution in both cases revealed the structures of the compounds to be supramolecular cubes with a perfect O_h symmetry. As can be seen from Figure

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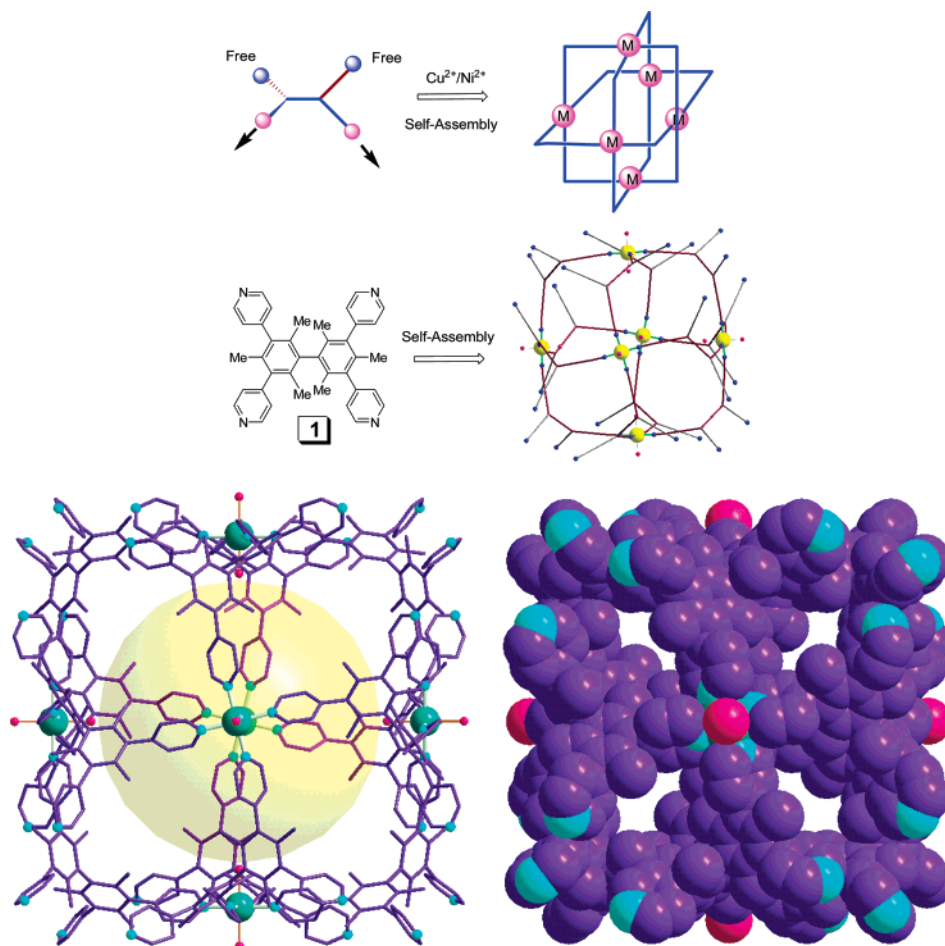


Figure 2. Self-Assembly of 3,3',5,5'-tetrakis(4-pyridyl)bimesityl ligand **1** into discrete cubes by metal coordination with $\text{Cu}(\text{OAc})_2$ and $\text{Ni}(\text{NO}_3)_2$. Hydrogen atoms have been omitted for clarity.

2, 12 ligands and 6 copper metal ions assemble to generate the cube of the type "C" in Figure 1; the six metal cations lie at the centers of six faces of the cube. The coordination geometry of the metal in both of the compounds **2** and **3** is octahedral, while the pyridine rings of four distinct tetraptopic ligands **1** are coordinatively bonded to the metal along the equatorial positions ($d_{\text{Cu-N}} = 2.024(10)$ and $d_{\text{Ni-N}} = 2.037(7)$ Å), two H_2O molecules coordinate axially ($d_{\text{Cu-O}} = 2.353(2)$, $2.630(2)$ Å and $d_{\text{Ni-O}} = 2.170(10)$, $2.398(10)$ Å). Overall, the formation of the cubes may be described as resulting from coordinate covalent bonding between two orthogonally disposed pyridyl rings of the tetraptopic ligand **1** and the metal cations effectively functioning as square-planar centers (Figure 2). Each of the ligands contributes two pyridyl rings toward coordination with the metal ion, while the other two remain uncoordinated. The latter are disposed toward the corners and serve to close up the edges of the cube (Figure 2). Insofar as the dimensions of the cube are concerned, the distance between any two adjacent face-centered metal atoms is ca. 14.75 Å, while that between two opposite face-centered ones is ca. 21.00 Å. Thus, one estimates the volume of the inner cavity for solvent and counterion occupation in excess of 3000 Å³, and this represents the cavity with the largest volume known for any of the metal-organic cuboid cages to date.¹³

Figure 3 shows the crystal packing of **2**. A careful analysis reveals that the lattice is constructed by a vertex-to-vertex alliance of the cubes sustained presumably by solvent-mediated interactions (cf. Supporting Information), which results in *intracube* as well as *intercube* void enclosures. Each cube is surrounded by eight symmetry-

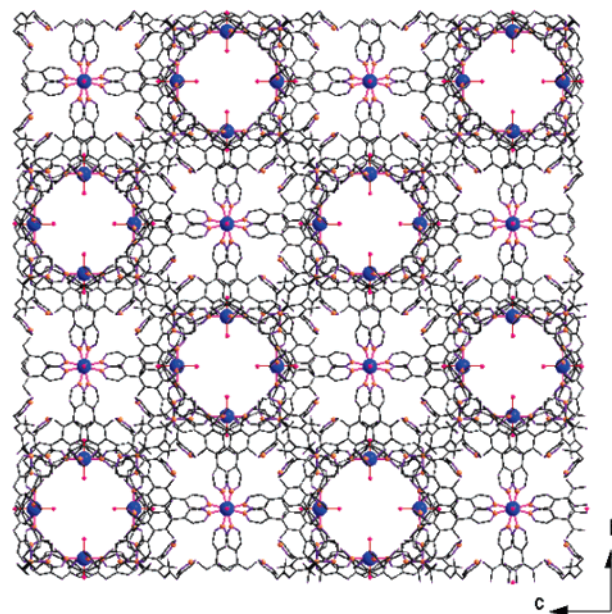


Figure 3. The packing of discrete cubes in the crystal lattice of the complex of tetrapyridylbimesityl ligand **1** with $\text{Cu}(\text{OAc})_2$. Notice that the vertex-to-vertex association of the cubes leads to intercube voids in the lattice. Hydrogen atoms and solvent molecules have been omitted for clarity.

related cubes at the vertices forming a three-dimensional (3D)-checkerboard network. The integrity of the crystal

lattice appears to be sustained by the solvent molecules occupying the void spaces in the crystal lattice. The counteranions, namely, OAc^- , could not be identified from difference electron density maps. Supposedly, these anions do not have an ordered structure, and the dynamic nature of their interaction with the atoms of the main skeleton prevents their detection by X-ray diffraction analyses. Further, the large voids, high symmetry, and dynamic motions precluded thorough identification of the solvent molecules in the crystal lattice (cf. experimental section and Supporting Information). Our best efforts with the data for the compound **2** led to the location of 344 water and 48 methanol solvent molecules in the unit cell, which is generated by 48 symmetry operations on the crystallographically unique 1/2 of the ligand **1** and 1/4 of the metal cation; of course, these solvent molecules include 24 axially coordinated water molecules and 24 acetate counteranions, which could not be modeled. In view of this, we restrain ourselves from discussing the otherwise unusual and interesting structures of water clusters located in the cages of the cubes as well outside of them (cf. Supporting Information). Although the SQUEEZE¹⁴ analysis at the end still suggested some solvent accessible volume, the difference Fourier revealed no meaningful electron density that could be reliably assigned to the solvent. Thus, the compound **2** is highly porous with an estimated solvent accessible volume of ca. 50%. Indeed, the thermogravimetric analyses for both **2** and **3** show that the solvent molecules escape from the lattice gradually upon heating (see Supporting Information).

A similar exercise for **3** as carried out for **2** was unsuccessful due to poor intensity data, as mentioned earlier. The limited number of reflections (596 with $F > 4\sigma(F)$, see Supporting Information) that yielded the structure with poor figures of merit and precluded a stepwise identification of solvent molecules. Therefore, the cationic framework was subjected to a PLATON/SQUEEZE procedure, which permitted an assessment of solvent accessible volume of 45% after accounting for counteranions. We wish to emphasize again that the unreasonable figures of merit as to the structure are due to the limitations imposed by the nature of the packing of the matter in the crystals, and not due to the quality of the crystals. Regardless of this, there cannot be any dispute as to the cationic structural framework. In this regard, we reiterate the view by Cotton and co-workers that "despite relatively poor figures of merit, crystal structures of molecules are conclusive as to their general shape of the molecule, and having such a structure is better than having to rely upon other indirect evidences".¹⁵

Is the cage formation in both of the compounds templated by the counteranion? We have addressed this question by attempting the complex formation with different metal salts. For example, the complex formation under similar conditions as those employed for $\text{Cu}(\text{OAc})_2$ with $\text{Cu}(\text{NO}_3)_2$ led to a 3D coordination polymer and not the cage. Similarly, several attempts at the formation of the complex of **1** with NiCl_2 yielded only the crystals of the metal free ligand **1**. An amorphous complex was isolated each time with $\text{Ni}(\text{OAc})_2$ and its structure could not be characterized. Thus, the role of the counteranions in the cage formation appears indispensable. To establish the homogeneity of the complexes in terms of contamination with the possible linear polymeric material, we sought to compare the powder XRD pattern of the bulk isolated sample with that of the pattern simulated for the cage-complex based on a single crystal X-ray structure determination. Unfortunately, the fragile complex crystals in both instances, as mentioned earlier, fell out as amorphous powders on

removal from the mother liquor and exhibited no diffraction at all. Nonetheless, the cell parameters determined directly on a Bruker SMART diffractometer for several crystals picked randomly from various crystallization vials invariably corresponded to those of the crystals that yielded the cube structure. Thus, we have no evidence to suggest that the bulk complex sample is not homogeneously a cage complex.

In the context of the application of these architectures as porous MOFs, the voids extant in the cube as well as in the crystal lattice amount to significant porosity. The calculated solvent accessible void volume is ca. 50% in both Ni and Cu complexes and thus promise application as storage devices. Be that as it may, the construction of 3D cubic architectures via self-assembly of 12 unique ligands of orthogonal geometry and 6 metal cations with octahedral coordination yet effectively functioning as square-planar centers is conceptually remarkable and constitutes the first unequivocal X-ray characterization of a metal-organic cube of this particular type.

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Supporting Information Available: The details of X-ray structure determination and refinement, UV-vis absorption spectra of the Cu- and Ni-compounds, TGA scan and EPR spectrum of the Cu-cube, and crystallographic drawings of the Cu-compound with solvent molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) **Cu-cube 2**: Molecular formula $[\text{Cu}_6(\text{C}_{38}\text{H}_{34}\text{N}_4)_{12}(\text{CH}_3\text{COO})_{12}(\text{H}_2\text{O})_{12}] \cdot n(\text{H}_2\text{O})$. The air-dried samples of the compound isolated from three independent experiments consistently yielded the following microanalytical results within an error limit of ± 0.6 (%): C 54.93, H 7.26, N 6.14. These results, when subtracted for the contributions of the atoms of the cuboid skeleton and the counteranions, lead to the presence of 146 H_2O molecules per cube, so that the calculated composition is (%): C 54.93, H 7.30, N 6.41. The experimental elemental analyses underestimate the number of solvent molecules in the crystal lattice, as some molecules escape from the lattice as soon the crystals are removed from the mother liquor. Thus, the actual number of solvent water molecules in the crystal lattice is necessarily much larger than 146. The difficulty with formulating the exact number of guest molecules is inherent to porous metal-organic frameworks due to the volatile nature of the solvent molecules. This, indeed, is a general problem.¹⁶ Cubic, space group: $Pn\bar{3}n$ (no: 222); $a = 32.0660$ (3) Å, $V = 32971.18$ (53) Å³, $Z = 2$; $R_1 = 0.1472$; $wR_2 = 0.3940$ ($I > 2\sigma(I)$); Data/restraints/parameter = 2902/1/214. **Ni-cube 3**: Molecular formula $[\text{Ni}_6(\text{C}_{38}\text{H}_{34}\text{N}_4)_{12}(\text{NO}_3)_{12}(\text{H}_2\text{O})_{12}] \cdot n(\text{H}_2\text{O})$. As described for the Cu-compound, the microanalytical results for the complex isolated from two independent experiments were within an error of $\pm 0.6\%$ and the composition is C 52.31, H 5.76, N 9.62. A similar exercise as above leads to a calculated number of 144 water molecules, so that the calculated composition is C 52.31, H 6.93, N 8.03. Cubic, space group: $Pn\bar{3}n$ (no: 222); $a = 32.2839$ (10) Å; $V = 33647.91$ (18) Å³, $Z = 2$; After SQUEEZE $R_1 = 0.0622$; $wR_2 = 0.1191$ ($I > 2\sigma(I)$); Data/restraints/parameter = 2230/0/170. CCDC-243911-243912 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
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