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A High-Symmetry Coordination Cage from 38- or 62-Component Self-Assembly

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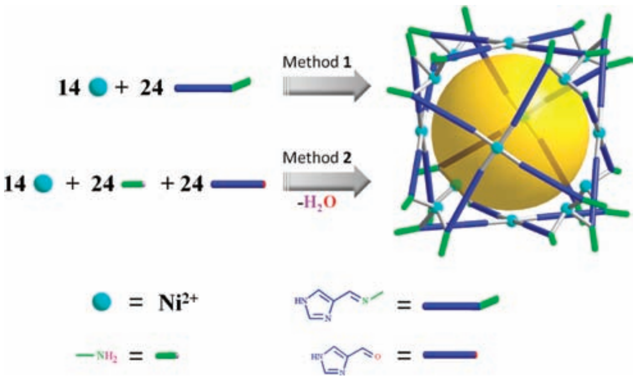
Ⓢ *Supporting Information*

ABSTRACT: Artificial molecular architecture from a large number of subcomponents (>50) via self-assembly remains a formidable challenge for chemists. Reaction of 38 components [14 Ni^{2+} and 24 *N*-methyl-1-(4-imidazolyl)methanimine] under solvothermal conditions reproducibly leads to the formation of a high-symmetry coordination cage. This polyhedral cage can also be obtained in high yield by self-assembly of 62 commercially available subcomponents (24 methylamine, 24 4-formylimidazole, and 14 Ni^{2+}) under mild conditions involving synchronized formation of both dynamic covalent bonds and coordination bonds. Guest molecules (e.g., water, methylamine, and methanol) are randomly imprisoned in the cage.

Natural systems are capable of fabricating supramolecular ensembles with complexity and diversity via a spontaneous self-assembly protocol. For example, elegant spherical virus structures (e.g., picornaviruses,[1,2] bluetongue virus,[3] and herpes virus[4]) are constructed by assembly of more than 60 subunits. To mimic natural self-assembly behavior, it is important to develop the principles whereby molecular recognitions and intermolecular interactions can be rationally used for self-assembled formation of multicomponent entities with complexity in a reproducible manner. Although remarkable successes have been made in the field of supramolecular chemistry, there are only limited examples of artificial architectures in the literature assembled from more than 50 subcomponents.[5,6] For the conventional formation of a supramolecular system, weak interactions and coordinative bonds between the subcomponents are usually involved. In recent years, a technique called *subcomponent self-assembly*,[7] involving the simultaneous formation of dynamic covalent bonds (e.g., imine or boron-based bonds) and coordination bonds, was introduced for the construction of various sophisticated supramolecules, including helicates,[8] macrocycles,[9] cages,[10] and Borromean rings,[11] which are emergent to supramolecular chemistry.

Coordination cages,[12−15] especially with highly symmetric polyhedra, have received growing attention for their structural beauty, advanced functions, and applications in storage,[16] recognition,[17] and catalysis.[18,19] In the present work, the polyhedral coordination cage **1** with *O* symmetry and formulated as $[Ni_{14}L_{24}]\cdot 4NO_3\cdot x$guest [HL = *N*-methyl-1-(4-imidazolyl)methanimine] was obtained by the solvothermal reaction (120 °C) of 24 **L** and 14 Ni^{2+} (method 1 in Scheme 1) or the one-pot assembly of 62 subcomponents, including 24 methylamine, 24 4-formylimidazole, and 14 Ni^{2+} (method 2) under an ambient atmosphere at 60 °C.

Scheme 1. Self-Assembly of 1 by Two Methods



The choice of the imidazole-type ligand **L** as the building unit was based on the following considerations: (i) imidazole is significantly smaller in size than pyridyl or dicarboxylate bridging ligands, consequently reducing the coordination uncertainty; (ii) the imidazole group and the imine group combined in **L** can chelate one metal ion to form a triangular ligand with C_3 symmetry, which may be a good building unit for the assembly of a highly symmetric system; (iii) imidazolate ligands are adaptive building units, as demonstrated by zeolitic imidazolate framework (ZIF) materials.[20,21]

Ligand **L** was conveniently synthesized by the condensation of methylamine and 4-formylimidazole in methanol [see the Supporting Information (SI) for details]. X-ray diffraction (XRD)-quality crystals of **1** were obtained by heating a mixture of **L** and $Ni(NO_3)_2\cdot 6H_2O$ in 4:1 (v/v) *N*,*N*-dimethylformamide (DMF)/ethanol at 120 °C in sealed Pyrex glass tubes or capped vials (method 1; for details, see the SI).

The coordination cage **1** crystallizes in the chiral space group *P*432. It features a 14-nucleus polyhedral structure (Figure 1) in

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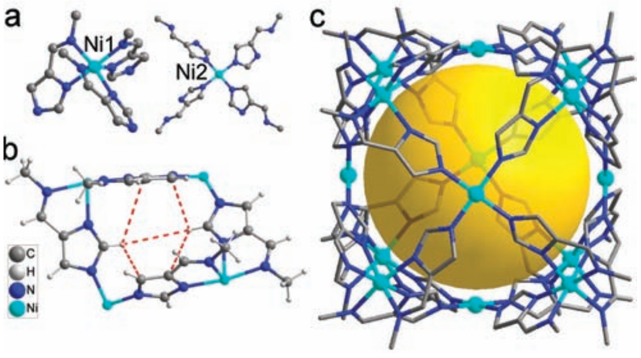

Figure 1. Single-crystal structure of **1**. (a) Arrangement of **L** ligands around Ni^{2+} ions (Ni1, octahedral; Ni2, square). (b) A rhombus window. Dotted red lines indicate the short H···H and C···H distances. (c) Polyhedral structure. The large yellow sphere indicates the large cavity. H atoms have been omitted for clarity in (a) and (c).

which the 14 Ni^{2+} ions are chelated and bridged by the 24 **L** ligands. There are two types of Ni^{2+} centers in the nonsymmetric unit (Figure 1a): Ni1 adopts an octahedral geometry chelated by three **L** (located on the threefold axis), and Ni2 adopts a square geometry bound by four **L** (located on the fourfold axis). It is notable that the square Ni2 is unsaturated and probably acts as an active site for further attack by other molecules, providing the possibility of postmodification of the polyhedron. The coordination bonds around Ni1, whose lengths range from 2.059 to 2.103 Å, are longer than the Ni2−N distances (1.871 Å). The polyhedral structure of **1** contains 14 vertices, 24 linkers, and 12 distorted rhombus windows (Figures 1c and 2a). Each rhombus window (Figure 1b) in **1** is small; the distance between the two central H atoms is 3.380 Å, and the distances of central the H atoms to the C atoms of the imidazole ring are 2.916 and 3.590 Å, respectively. The chelating arrangement of **L** restricts the rotation of the imidazole plane. The size of the rhombus window is fixed, thus preventing free passage of small guest molecules (e.g., water and methanol). As a whole, the polyhedron of **1** is on the nanometer scale. For example, the Ni−Ni distance between two opposite square Ni^{2+} centers is 11.339 Å, and the diagonal distance between two octahedral Ni^{2+} ions is 14.388 Å. Therefore, there exists a large cavity in **1** that can accommodate guest molecules. However, with the single-crystal XRD data it was difficult to model the disordered NO_3^- and other imprisoned guest molecules in **1** because of the highly symmetrical and porous nature of the coordination cage.

Supramolecular chirality usually arises from the typical asymmetric chelating ligand arrangements around the metal centers, which adopt a Λ or Δ absolute configuration. In the reported examples, cages containing eight or more chiral vertices are rare. Heterometallic $[Pd_6(AlL_3)_8](NO_3)_{12}$ [L = 1-(4-pyridyl)acetylacetonato] and cubic M_8L_6 [L = tetrakis(4-aminophenyl)porphyrin] cages having eight chiral vertices were reported by Wang[22] and Nitschke,[10] respectively. However, both Λ and Δ enantiomers were present in the crystal lattices of these two compounds, which crystallize in centrosymmetric space groups. The chiral *P*432 space group of **1** suggests that the pure Λ or Δ enantiomer should be separated in a single crystal. Unfortunately, the crystal data were not good enough (after many trials) for the absolute structure to be determined because of the bad Flack parameter.[23]

The topology of **1** can be defined by mapping the Ni atoms as triangular and square vertices and the **L** ligands as edges (Figure 2a). Such a polyhedron is described as a rhombic dodecahedron by Yaghi and O'Keeffe.[24,25] However, the four vertices constituting the "rhombus" are not located in the same plane. The dihedral angle between the two triangles that form the "rhombus" is 131.107° (Figure 2a and Figure S1 in the SI). The structure of **1** may be better regarded as a tetrahexahedron, in which the 12 "rhombuses" treated as 24 equilateral triangles (Figure 2b). It is worth noting that both the rhombic dodecahedron and the tetrahexahedron have O_h symmetry. Since the vertices are desymmetrized (asymmetric chelating arrangements of **L** around Ni^{2+} centers), **1** has *O* symmetry. This molecular symmetry is in agreement with the crystal symmetry of **1** (space group *P*432, containing C_4, C_3, and C_2 rotational axes).

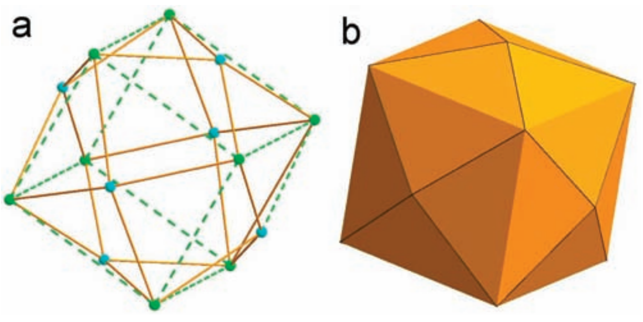

Figure 2. Simplified topology of (a) **1** (green and cyan spheres represent octahedral Ni1 and square Ni2, respectively) and (b) a tetrahexahedron.

We found that **1** can also be prepared using the technique of *subcomponent self-assembly*.[7] As shown in method 2 in Scheme 1, the microcrystalline product was obtained by the reaction of methylamine, 4-formylimidazole, and nickel(II) nitrate with a mole ratio of 4:2:1 in methanol at 60 °C followed by filtration (see the SI for synthetic details). In the reaction, an excess of methylamine was used because methylamine plays a dual role as an amine subcomponent and the deprotonation agent for imidazole in the self-assembly process. The IR spectrum of the product shows a strong absorption at 1625 cm^{-1}, and both the N−H and C═O vibration peaks are absent (Figure S2), indicating that dynamic imine groups and coordination bonds were formed synchronously in the resulting compound. A powder XRD (PXRD) study of the microcrystalline product revealed a pattern identical to both the simulated and observed patterns of single-crystalline **1** (Figure S3), suggesting that the microcrystalline product has the same phase as **1**. The cage can be assembled successfully with 62 subcomponents. To the best of our knowledge, this is the largest number of components among all of the literature examples obtained using subcomponent self-assembly, demonstrating the power of the technique in the self-assembly of complicated supramolecular systems.

To provide further confirmation of the successful assembly of the cage and the guest molecules trapped inside, the electrospray ionization−time of flight (ESI−TOF) mass spectrum of microcrystalline **1** in methanol was recorded (**1** is slightly soluble in polar organic solvents such as DMF, methanol, and ethanol). The prominent peaks for $[Ni_{14}\mathbf{L}_{24}](NO_3)_n\cdot x\mathrm{MeNH_2}\cdot y\mathrm{MeOH}]^{(4-n)+}$ (n = 0, 1; x = 0, 1; y = 0−6) are presented in Figure 3a, and the isotope distributions closely match the simulated patterns (Figure 3b,c and Figures S4 and S5), confirming the $Ni_{14}\mathbf{L}_{24}$ composition.

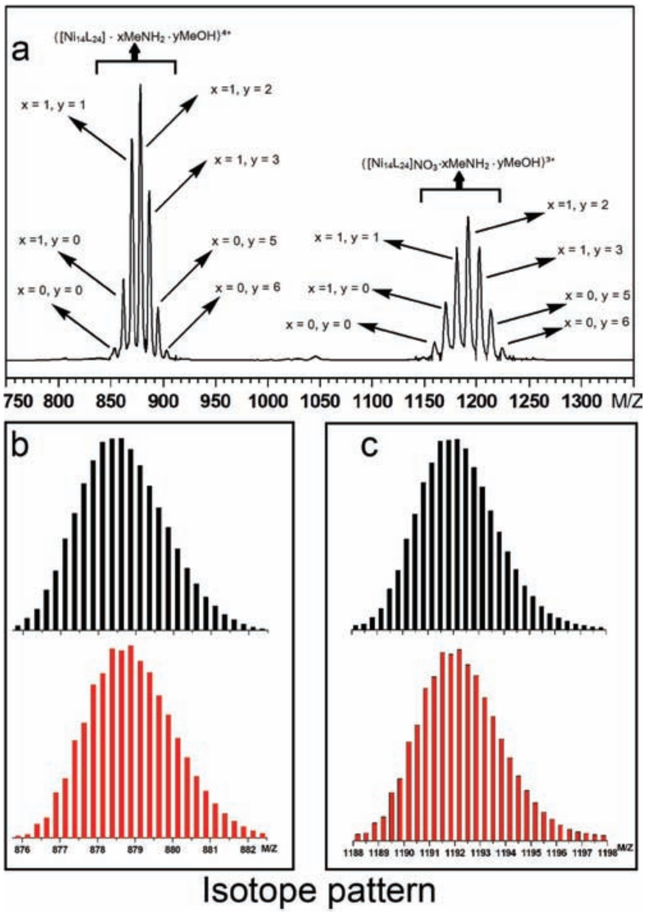

Figure 3. (a) ESI−TOF mass spectrum of microcrystalline **1**. (b, c) Expanded spectra for (b) $\{[Ni_{14}\mathbf{L}_{24}]\cdot MeNH_2\cdot 2MeOH\}^{4+}$ and (c) $\{[Ni_{14}\mathbf{L}_{24}]NO_3\cdot MeNH_2\cdot 2MeOH\}^{3+}$. The observed (black) and simulated (red) isotope patterns are shown.

Carceplexes, which contain permanently entrapped guest molecules or ions, can be used as microscopic reaction chambers and for the stabilization of highly reactive species,[26] and they have traditionally been synthesized through covalent bonding.[27,28] In general, coordination cages have portals through which guest molecules or ions may enter and leave the interior freely. Few coordination cages have been found to act as carcerands to imprison small guest molecules or ions.[29,30] The multiple peaks (septets) in the spectrum (Figure 3a) reveal that **1** exhibits carceplex properties, with diverse numbers of methylamine and methanol guest molecules randomly incarcerated in the cavity. Because of the narrow rhombus windows (Figure 1b), once the cage is formed, the imprisoned methylamine and methanol cannot escape from the interior without bond rupture. Meanwhile, free organic molecules outside the cage are blocked from entry. A similar phenomenon was observed in a reported coordination cage of tetrakis(1-imidazolyl)borate, in which case small iodide anions were blocked from entering the cavity.[24] Similar to the reported covalent carceplexes,[27] cage **1** embraces different numbers of guest molecules during its molecular immobilization. In the mass spectrum of the reaction filtrate for the preparation of microcrystalline **1** (Figure S6), the peaks revealed that the cavity contained up to one methylamine, four H_2O, and nine methanol guest molecules. To study the incarcerating properties of **1** further, we also successfully synthesized **1** with deuterated methanol replacing the common methanol as the solvent. ESI−TOF mass spectrometry found that zero to five CD_3OD molecules were trapped in the cavities of **1** (Figures S7−S9). The synthesis of a covalent carceplex may take multiple steps, and the yield is relatively low. The current subcomponent self-assembly approach provides an efficient way to form enforced cavities (one step, high yield) for capturing molecular components of the medium, particularly unusual reaction intermediates.

For a multicomponent chemical ensemble, it would be reasonable to assume that the most energetically favored structure would result. Thermogravimetric analysis (TGA) showed that **1** is stable until it is heated to ~380 °C (Figure S10) under a nitrogen atmosphere. Interestingly, variable-temperature PXRD (VT-PXRD) measurements revealed that **1** remained in a crystalline form at ~450 °C (Figure S11). The inconsistent thermal stabilities obtained by TGA and VT-PXRD may be due to the different measuring environments (N_2 atmosphere for TGA and vacuum for VT-PXRD). The chemical stability was evaluated by immersing **1** into boiling water and toluene separately for 24 h. The PXRD patterns of the treated samples closely matched the simulated pattern for crystalline **1** (Figure S12), demonstrating that **1** is chemically stable under boiling water and toluene conditions.

In a preliminary study, ethylamine was employed to replace methylamine for a further assembly. Both the reaction of *N*-ethyl-1-(4-imidazolyl)methanimine (H**L′**) with nickel(II) salts and the reaction of ethylamine, 4-formylimidazole, and nickel(II) salts gave clear solutions. Attempts to obtain crystals suitable for XRD were not successful. ESI−TOF mass spectrometry of the reaction filtrate (Figure S13) indicated that a compound formulated as $[Ni_{14}\mathbf{L'}_{24}]\cdot 4NO_3\cdot x\text{guest}$ (guest = methanol and water) was successfully prepared. As shown in Figure S14, various sets of peaks with similar *m*/*z* ratios are present in the mass spectrum, indicating the carceplex property of the compound with diverse guest molecules in the cavity, which is similar to that of **1**.

In conclusion, a thermally and chemically stable, *O*-symmetric coordination cage with eight chiral vertices was successfully constructed by multicomponent self-assembly of 38 or 62 components. Guest molecules (e.g., water, methylamine, and methanol) were randomly imprisoned in the cage. The 62-component assembly involves synchronized formation of both dynamic covalent bonds and coordination bonds, demonstrating the vigorousness of the *subcomponent self-assembly* technique in complicated supramolecular self-assembly involving a large number of units. Further studies of the host−guest chemistry (imprisoning guest behavior) of the cage and its potential material applications (e.g., catalysis) will be carried out.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Syntheses and characterizations of HL and **1** and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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