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Polyhedral Metal-Imidazolate Cages: Control of Self-Assembly and Cage to Cage Transformation

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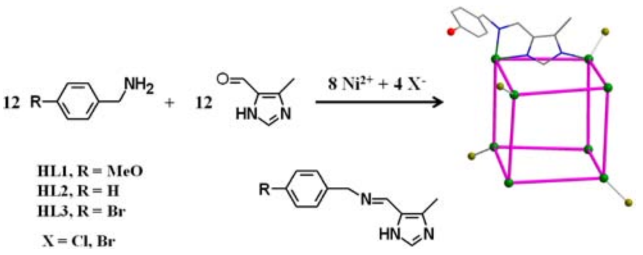
Supporting Information

ABSTRACT: A series of neutral cubic nickel(II)-imidazolate $Ni_8L_{12}X_4$ cages were prepared by rational choices of substituents and anions with solvothermal subcomponent self-assembly technology. Both substituents and halide anions play a critical role in the formation and stabilization of cubic cages. Changing one of the factors in the reaction will switch the final structure to a $Ni_{14}L_{24}$ rhombic dodecahedral cage. The cubic cage can transform to a large rhombic dodecahedral cage in the presence of methylamine at room temperature accompanied by a color change from purple to light yellow.

Coordination cages have received great attention for their fascinating chemistry during self-assembly and promising functions[1] (e.g., recognition,[2] catalysis[3]). Coordination bonds involving a highly directional feature from d-orbitals of transition metals give rise to the rational design of coordination cages by using geometric design principles.[4] Many coordination cages with high symmetry (tetrahedron,[2c,5] cube,[6] octahedron,[7] rhombic dodecahedron,[8] and dodecahedron,[9] etc.) have been successfully made with this strategy. However, arising from relatively weaker and more flexible coordination bonds compared to covalent bonds, some subtle factors (e.g., ligand bend angle,[10] template,[11] and solvents[12]) may disturb the self-assembly balance and lead to unpredictable architectures. For examples, Fujita and co-workers demonstrated that the formation of the giant $M_{24}L_{48}$ rhombicuboctahedron or $M_{12}L_{24}$ cuboctahedron depends on the slight change in ligand bend angles (L = dipyridylthiophene or dipyridylfuran).[10] Nitschke and co-workers found recently that anion templates can switch their coordination cage products, in which a $Co_{10}L_{15}$ pentagonal prism was induced by perchlorate and a Co_4L_6 tetrahedron by trifluoromethanesulfonate (L = 6-formyl-6′-tolyliminomethyl-3,3′-bipyridine).[11] In most cases, resulting products are scarcely obtainable as anticipated. Therefore, the control of self-assembly of coordination cages with desired and definite structures is still a challenge.

In our previous study,[13] a rhombic dodecahedral nickel(II)-imidazolate cage ($Ni_{14}L_{24}$, HL = *N*-methyl-1-(4-imidazolyl)-methanimine) was successfully constructed by multicomponent self-assembly of 38 or 62 components. In this case, we describe the control of assembly for a series of neutral cubic nickel(II)-imidazolate cages formulated as $Ni_8L_{12}X_4$ **1**, L = *N*-((5-methyl-1*H*-imidazol-4-yl)methylene)(4-methoxyphenyl)methanamine (HL1), X = Br; **2a** and **2b**, L = *N*-((5-methyl-1*H*-imidazol-4-yl)methylene)(phenyl)methanamine (HL2), X = Cl and Br; and **3**, L = *N*-((5-methyl-1*H*-imidazol-4-yl)methylene)(4-bromophenyl)methanamine (HL3), X = Br; Scheme 1 by the variation of substituents and anions. The structures of this multicomponent system are sensitive to both substituents and anions. A change of a substituent of imidazole ligand or anion switches the final structure observed across the ensemble of building blocks between cubic $Ni_8L_{12}X_4$ and dodecahedral $Ni_{14}L_{24}$ cages. Cubic cage **1** can transform to a rhombic dodecahedral cage **4** in the presence of methylamine molecules. The transformation is irreversible and accompanies an obvious color change.

Scheme 1. Illustration of the Self-Assembly of Cubic Ni(II)-Imidazolate Cages



Subcomponent self-assembly technology is convenient and feasible in the assembly of molecular architectures and infinite polymeric compounds.[4c,13,14] Multicomponent reactions of 5-methyl-4-formylimidazole, NiX_2 (X = Cl, Br; or replacing with $Ni(NO_3)_2 \cdot 6H_2O$ and NaCl or NaBr), with different amines (4-methoxybenzylamine, benzylamine, and 4-bromobenzylamine) under solvothermal conditions yielded good-quality, purple single crystals of **1**, **2a**, **2b**, and **3**, respectively (Scheme 1; see Supporting Information for experimental details).

Products **1**, **2a**, **2b**, and **3** were characterized by single-crystal X-ray diffraction analyses. They all feature an 8-nucleus cubic structure (Figure 1) and crystallize in $P\bar{1}$ (**1**), $I\bar{4}3m$ (**2a**), $I\bar{4}3m$ (**2b**), and $C2/c$ (**3**) space groups, respectively. As an example, the structure of **1** will be described in detail. Due to the lower lattice symmetry of **1** ($P\bar{1}$), the asymmetric unit contains a complete cubic cage, in which there are 8 Ni(II), 12 L1, and 4 Br. The crystal structure study provides a direct observation for the successful in situ formation of ligand L1. Four Ni(II) ions adopt an octahedral coordination geometry, and each Ni(II) is

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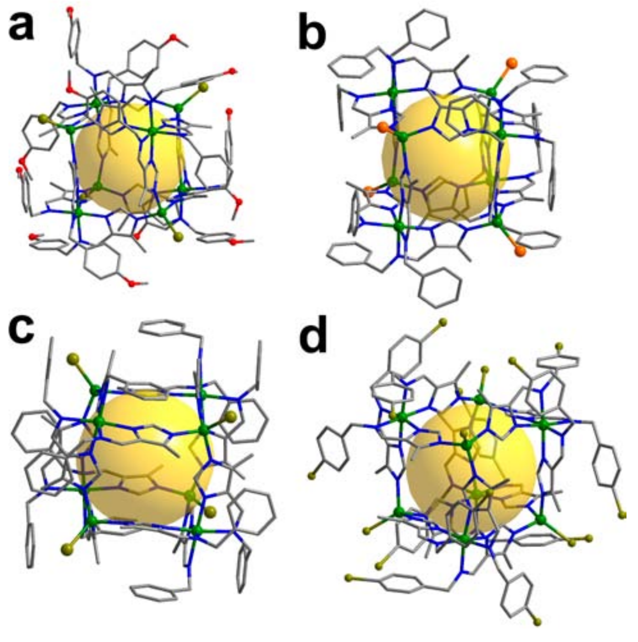

Figure 1. Cubic nickel(II)-imidazolate cages of **1** (a), **2a** (b), **2b** (c), and **3** (d), with the big yellow ball representing the cavities in the cages. Color codes: Ni, green; Br, brown; Cl, orange; O, red; C, gray; N, blue; H atoms are omitted for clarity.

chelated by three L1, with Ni−N bond lengths ranging from 2.034(8) to 2.167(10) Å. Other four Ni(II) ions adopt a tetrahedral geometry, and each one is coordinated by three nitrogen atoms and one bromine anion with Ni−N bond lengths from 1.958(9) to 1.999(10) Å. These distances are longer than those Ni−N bonds between square-planar Ni(II) and imidazolate (1.871 Å) in the rhombic dodecahedral cage.[13] Ni(II) and L1 are bound together through coordination bonds to form a cubic cage (Figure 1a) when both octahedral and tetrahedral Ni(II) centers act as vertices and L1 acts as edges. The edge lengths are around 6.1 Å (Ni···Ni distance), similar to the reported cubic metal-imidazolate cages, in which symmetrical imidazole derivatives as ligands were employed.[6b,15] The volume of cage **1** is about 227.0 Å^3, obviously smaller than that in the rhombic dodecahedral metal-imidazole cage (about 1000 Å^3).[13] The cubic cage is chiral due to the asymmetric chelating ligand L1 in the arrangement around octahedral Ni(II). However, both Λ and Δ enantiomers were presented in the crystal lattices; therefore, cage **1** crystallizes in a nonchiral space group. Similar cases occurred in the complexes of **2a**, **2b**, and **3**.

IR spectra of **1**, **2a**, **2b**, and **3** show a strong absorption range around 1607−1616 cm^{-1} (Figure S1), which confirm the formation of dynamic imine bonds from the condensation reactions between 5-methyl-4-formylimidazole and corresponding amines. Cage **1** dissolves well in common solvents (e.g., $CHCl_3$, CH_2Cl_2, and THF), while cages **2a**, **2b**, and **3** show poor solubility. We try to characterize cage **1** with ESI-MS; however, no obvious peak belonging to the cage was observed except for some background peaks (Figure S4). The failure in the ESI-MS study is probably due to the neutral property of the cage, making it hardly ionized.

Our previously reported rhombic dodecahedral nickel(II)-imidazolate cage ($Ni_{14}L_{24}$, HL = *N*-methyl-1-(4-imidazolyl)-methanimine) was assembled by the reaction of methylamine and 4-formylimidazole with $Ni(NO_3)_2·6H_2O$.[13] It appears that the resulting product of dodecahedral or cubic cages was significantly influenced by the substituted groups of 4-formylimidazole and amine and the metal salt. To test the influence of the derivatives and the salt for the self-assembly of the cages, experiments were carried out (Scheme S1). The following reactions yielded dodecahedral cages (**5**−**13**): (i) formylimidazole and benzylamine (or 4-methoxybenzylamine) with $NiBr_2$; (ii) 5-methyl-4-formylimidazole and methylamine (or ethylamine) with $NiBr_2$; (iii) formylimidazole (or 5-methyl-4-formylimidazole) and benzylamine (or 4-methoxybenzylamine) with $Ni(NO_3)_2·6H_2O$. These experiments clearly showed that the reactants of 5-methyl-4-formylimidazole, benzylamine (or 4-methoxybenzylamine), and NiX_2 (X = Cl, Br) are essential in the formation of a cubic cage. A replacement of any of the three reactants with their derivatives will result in a dodecahedral cage. Interestingly, cubic cage **3** can also be obtained by reacting $Ni(NO_3)_2·6H_2O$ with 5-methyl-4-formylimidazole and 4-bromobenzylamine. It is reasonable that Br^- anions were generated in situ from the break of C−Br bonds of the 4-bromobenzyl group (partial 4-bromobenzylamine molecules were broken), probably catalyzed by Ni(II) ions. This phenomenon indicates that halide anions may drive the formation of a cubic Ni(II)-imidazolate cage in the assembly process. To further examine anion affect on self-assembly, we also employed ClO_4^- and PF_6^- as anions. ESI-MS of the resulting greenish yellow and clear solution found that no obvious peak belonging to the rhombic dodecahedral or cubic cage nickel(II)-imidazolate cage was observed (Figure S5). The preliminary results indicated that ClO_4^- and PF_6^- anions could disturb the self-assembly. Attempts to separate and characterize the resulting products failed.

From the structural data, a cubic cage (**1**, **2a**, **2b**, or **3**) contains both octahedral and tetrahedral Ni(II) in the structure, while a rhombic dodecahedral cage requires the existence of both octahedral and square-planar Ni(II) centers. Ni(II) can exhibit a great variety of coordination environments, including the majority showing octahedral and square-planar geometries and fewer examples showing trigonal bipyamidal, square pyramidal, and tetrahedral stereochemistry. Such stereopreference of Ni(II) indicates that a rhombic dodecahedral cage is probably formed more easily, in accord with our experimental findings. Halide anions can bind to Ni(II) and yield tetrahedral NiX_4^{2-} due to their special ligand field, thus inducing tetrahedral Ni(II) and stabilizing it. Undoubtedly, halide anions in **1**, **2a**, **2b**, and **3** play this important role, and the crystal structures have provided a direct evidence. To further test the role of halide ions in stabilizing the cubic cage, attempts were made to precipitate halide ions by adding Ag^+. Cage **1** was chosen for the test due to its good solubility in organic solvents. We found that cage **1** was stable in $CHCl_3$ but collapsed quickly upon the addition of $AgPF_6$. As a result, a binuclear silver complex $Ag_2(HL1)_2·2PF_6$ (**14**) was obtained (Figure S6). This result further demonstrated that the cubic nickel(II)-imidazolate cage was not stable in the absence of halides.

Our experiments also showed that 5-methyl and benzyl derivative groups of imidazole ligands are also critical in the assembly of cubic cages. In the crystal structures of **1**, **2a**, **2b**, and **3**, tetrahedral Ni(II) and halide ions are surrounded closely by three 5-methyl and three benzyl or its derivative groups through six directions, as shown in Figure 2. The C−H···X (X = Cl, Br) distances are very short, which range from 3.2 to 3.6 Å (Figure 2). Transforming a tetrahedral Ni(II) to a square-

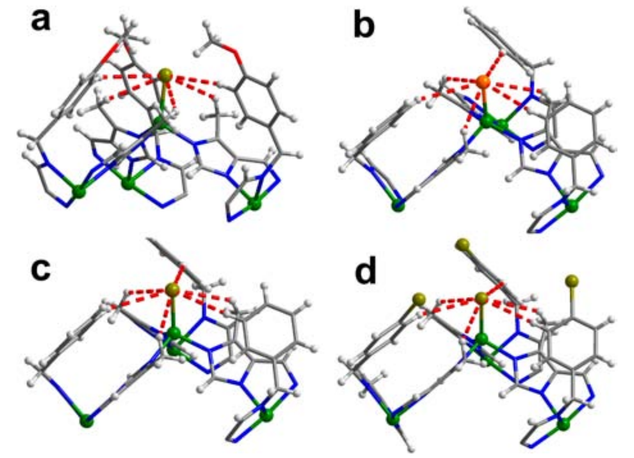

Figure 2. Surrounding environment of tetrahedral Ni(II) and X ions (X = Cl, Br) of **1** (a), **2a** (b), **2b** (c), and **3** (d); red dotted lines highlight the short distances of C−H···X. Color codes: Ni, green; Br, brown; Cl, orange; O, red; C, gray; N, blue; H, white.

planar or an octahedral Ni(II) must first overcome the steric hindrance of these substituents, before the ligand substitution of replacing the halide ions that would change the ligand field. Therefore, both substituents are important in stabilizing the tetrahedral Ni(II) geometry. Without these substituents, the 8-nucleus cubic cages cannot be obtained successfully. Similar phenomena are observed in the reported $[Ni(PR_3)_2X_2]$ (X = Cl, Br, I) complexes. The tetrahedral forms are favored by PR_3 = PPh_3 and the square-planar forms by R = alkylphoshphines.[16]

Supramolecular coordination complexes originating in their weaker coordination and intermolecular interactions can be organized to hierarchical soft materials[17] and transform within two or multiple states after inducing outer stimuli, including light,[18] templates,[11,19] heating,[20] solvent,[12,21] and crystallization.[22] The transformations between different coordination cages have been reported recently.[11,22,23] However, the transformation involving the change in stereoelectronic preference of metal ions and color remains elusive. The in situ imine exchange reactions have been reported.[14a,23b] The benzylamine in **1**, **2a**, **2b**, and **3** can probably be replaced by alkylamine (e.g., methylamine) due to their difference in electronic and steric properties. Once benzylamine is replaced by methylamine, the tetrahedral Ni(II) should probably be unstable and change to a square-planar species, which may lead the transformation from a cubic cage to a rhombic dodecahedral one (Figure 3a).

The addition of methylamine (in methanol) into cage **1** in THF at room temperature resulted in a change in solution color from purple to colorless quickly (Figure 3). As shown in Figure 3b (vial 2), the reaction rate is even quicker than the diffusion velocity of **1**. The obvious color change indicates that the reaction occurred. ESI-MS and UV−visible spectroscopy (Figures S18 and S19) studies showed that, although the solution color of **1** turned colorless immediately, **1** did not directly transform to a rhombic dodecahedral cage in a short time. There should be some intermediate states existing during the transformation process. Trials to separate the intermediates failed. The colorless solution gradually turned light yellow after remaining steady for 3 days at room temperature. ESI-MS and UV−visible spectra of the resulting solutions presented the feature peaks of a product formulated as $\{[Ni_{14}L4_{24}]\cdot x\text{guest}\}^{4+}$ and $\{[Ni_{14}L4_{24}]\cdot Br\cdot x\text{guest}\}^{3+}$ (**4**, HL4 = (*N*-((5-methyl-1*H*-

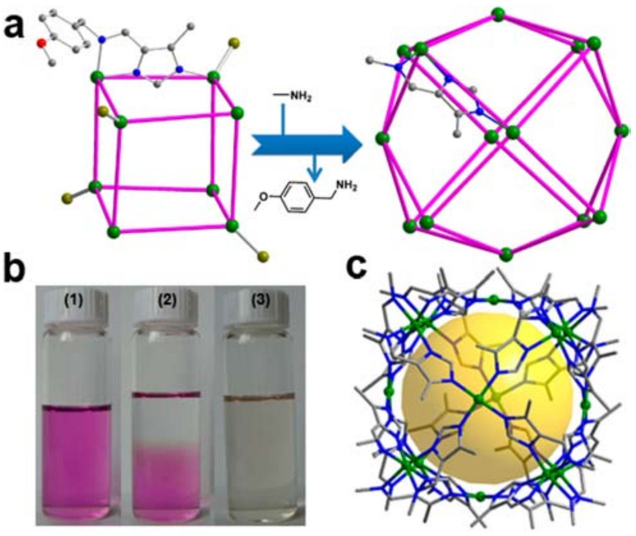

Figure 3. Transformation between cubic cage **1** and rhombic dodecahedral cage **4** (a); photo of the reaction phenomena of **1** before and after adding methylamine in THF solvent (b, vial 1 before, vial 2 adding immediately, and vial 3 after 3 days), and crystal structure of **4**. Color codes: Ni, green; O, red; C, gray; N, blue; H, omitted.

imidazol-4-yl)methylene)methanamine) (Figure S20) and a new UV−visible absorption at 450 nm (Figure S19).

Crystals of the reaction product of methylamine with **1** were obtained from solvothermal reactions. A reaction of the colorless mixture under solvothermal conditions (120 °C, 3 days) yielded polyhedral light yellow crystals. Single X-ray diffraction analysis reveals that the crystal crystallizes in the *P*4*nc* space group and features a 14-nucleus rhombic dodecahedral cage structure (**4**, Figure 3c), which is identical to our previously reported structure.[13] The asymmetric unit contains five crystallographically independent Ni(II) atoms (two Ni(II) lie on the four-fold axis, with 0.25 occupied site), six L4, and one Br^-, giving the formula of **4**: $[Ni_{14}L4_{24}]\cdot 4Br\cdot x\text{guest}$. The ESI-MS spectrum (Figure S21) of crystals is in accord with that (Figure S20) of the reaction solution of methylamine with **1** after remaining steady for 3 days at ambient temperature. Thus, both X-ray analysis and ESI-MS studies unambiguously document that the transformation from a cubic to a dodecahedral cage is successful. During the process, 4-methoxybenzylamine was replaced by methylamine, and the tetrahedral Ni(II) ions convert to square-planar ones.

To test the possibility of the reverse transformation from a dodecahedral cage to a cubic one, the addition of excess 4-methoxybenzylamine in **4** under solvothermal conditions (100 °C, DEF-ethanol solvent, 3 days) was carried out. Experiments found that cage **4** was stable and kept its state, indicating that the reverse transformation is not available, at least in the conditions employed. The failure of the transformation of a dodecahedral cage to a cubic cage is in accord with the Ni(II) preferring a square-planar geometry over a tetrahedral geometry and indicates that a dodecahedral cage is more stable.

Similar to our previously reported rhombic dodecahedral cages, **4** and others also act as carceplexes and imprison guest molecules (e.g., methanol, THF, and H_2O) in their cavities, as documented by the ESI-MS studies (see the Supporting Information). Notably, cage **4** obtained at room temperature contains more guest molecules in its cavity than that obtained under solvothermal conditions (Figures S20 and S21). This phenomenon indicates that the reaction condition is important for capturing guest molecules in such a coordination carceplex. Further studies are necessary to address the detailed mechanism and conditions for capturing and imprisoning guest molecules in the cage.

In summary, we successfully construct a series of cubic and rhombic dodecahedral Ni(II)-imidazolate cages under solvothermal conditions by subcomponent self-assembly. The factors influencing the assembly are well-examined. The self-assembly of the cubic or the rhombic dodecahedral cage is controlled by both substituents and anions. The cage to cage transformation involving the stereoelectronic preference of metal ions and color was discovered, which may provide a unique example to understand the supramolecular dynamic transformation process. The pervasive carceplex phenomena are observed in the Ni-imidazolate rhombic dodecahedral cages, which may be an excellent platform to study this unique property for coordination cages.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Syntheses and characterizations of Ni(II)-imidazolate cages, and crystallographic data (CCDC 958752-958760). 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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