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Assembling the Cage-Based Metal–Organic Network from a Cubic Metalloligand

Ai-Ling Cheng, Na Liu, Jian-Yong Zhang, and En-Qing Gao*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, China

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A novel 3D assembly of molecular cobalt cubes, where the mixed-valence cubes are linked by macrocyclic nickel(II) complexes through coordination and hydrogen bonds, has been constructed by the metalloligand strategy.

The rational design and synthesis of metal−organic networks are of great interest because of their intriguing structural diversity and their potential applications as functional solid materials.[1] While most metal−organic networks have been synthesized directly from metal ions and organic ligands, the "complex as ligand" or "metalloligand" strategy, i.e., the use of metal complexes with "free" donor groups for further metal binding as synthetic precursors, has also been developed.[1c,2] This strategy has been proved to be very useful for the design and syntheses of materials with specific structures and functions, such as cyano- or oxalate-bridged heterometallic magnetic materials[3,4] and porous coordination polymers furnished with coordinatively unsaturated metal centers.[5] It is expected that polynuclear metal−organic cages that possess peripheral donor atoms can also serve as metalloligands, and this represents an approach to polymeric networks based on cages.

Imidazole-4,5-dicarboxylic acid (H_3IDC) is a multifunctional ligand that can be successively deprotonated to generate H_2IDC^-, $HIDC^{2-}$, and IDC^{3-} with versatile metal-binding and hydrogen-bonding capabilities, and it has recently been used to construct some fascinating metal−organic architectures, such as the molecular square,[6] cubes,[7] and 3D frameworks.[8] The cubic compounds have been shown to exhibit interesting magnetic properties, gas absorption, or catalytic activities.[7] It is worth noting that the molecular cube, $[Ni_8(IDC)_{12}]^{20-}$,[7b,c] has a high negative charge with a rich store of peripheral carboxylate O atoms, which are potential coordination donors and hydrogen-bond acceptors. Therefore, the cube may act as a metalloligand to interact with metal ions (and hydrogen-bond donor groups), and in this way, 1D, 2D, or 3D metal−organic networks based on cubes can be constructed. To achieve this, we choose the well-known square-planar nickel(II) tetraazamacrocyclic complexes, which are positively charged and have vacant axial sites on the metal centers, as the building blocks to link the cubes. Herein we present the first example of this approach, in which the mixed-valence $[Co_8(IDC)_{12}]^{14-}$ cubes are linked by $[Ni(cyclam)]^{2+}$ and $[Ni(cyclam)(H_2O)_2]^{2+}$ through coordination and hydrogen bonds, respectively, generating a novel 3D metal−organic network of formula $[Ni(cyclam)]_4[Ni(cyclam)(H_2O)_2]_2\{[Ni(cyclam)][Co_8(IDC)_{12}]\}\cdot 41H_2O$ (**1**; cyclam = 1,4,8,11-tetraazacyclotetradecane).

From the synthetic view, metalloligands had better be soluble with the structural integrity retained during the reaction. The previously reported cubic compounds, $M_{20}[Ni_8(IDC)_{12}]\cdot$solvent (M = Na, Li),[7b,c] which were synthesized directly from H_3IDC and Ni^{II}, are insoluble in common solvents and, hence, are not suitable for further reactions. We succeeded in obtaining a cobalt(II) cubic compound, $[Me_4N]_{20}[Co_8(IDC)_{12}]\cdot$solvent (**2**) (see the Supporting Information), which is soluble in water and, hence, can be used

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* To whom correspondence should be addressed. E-mail: eqgao@chem.ecnu.edu.cn.

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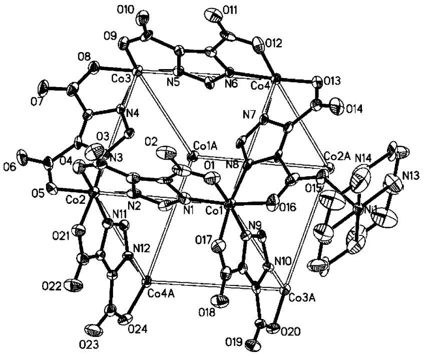

Figure 1. View of the cubic structure in **1**.

as the metalloligand to prepare compound **1** (see the Supporting Information).

According to single-crystal X-ray analyses,[9] the structure of complex **1** consists of the $[Co_8(IDC)_{12}]^{14-}$ cubic anions, $[Ni(cyclam)]^{2+}$, $[Ni(cyclam)(H_2O)_2]^{2+}$, and water molecules. In the crystallographically centrosymmetric $[Co_8(IDC)_{12}]^{14-}$ cubic unit, each vertical Co ion is octahedrally ligated by three N and three O atoms from three IDC^{3-} ligands, and each ligand chelates two individual Co ions to form two five-membered rings coplanar with the imidazole ring (Figure 1). The structure represents the first cobalt cube derived from IDC^{3-}. Different from the previously reported nickel(II) analogues,[7] the present cube is mixed-valence with six Co^{III} and two Co^{II} ions, as suggested by the metal-to-donor distances, the charge balance requirement, and the analytic data. Among the four Co atoms in the asymmetric unit, the Co−N/O bond lengths around Co1, Co2, and Co3 lie in the range of 1.88−1.99 Å, indicating the III+ oxidation state, while those around Co4 are in the range of 2.01−2.05 Å, indicating the II+ oxidation state. As a result of the mixed-valence nature, the geometric distortion of the present cube is more appreciable than that of the previous nickel(II) analogues, as evidenced by the wider ranges of the Co···Co···Co angles (86.0−94.2°) and the Co···Co distances (6.02−6.20 Å) along the edges. Particularly, the Co···Co4 distances are longer than others, supporting the II+ oxidation state for Co4.

In the lattice, the cubic anions interact with the Ni^{II} macrocyclic complex cations through coordination and hydrogen bonds in three crystallographic directions. Along the *b* direction, each cube contributes two diagonal O atoms (O15 and the symmetry-related O) to interact with two centrosymmetric $[Ni(cyclam)]^{2+}$ cations (Ni1) via axial Ni−O bonds [2.147(4) Å], generating a 1D coordination chain with alternating cubes and macrocyclic complexes (Figure 2). In the *ac* plane, the cubes are linked by two sets of $[Ni(cyclam)(H_2O)_2]^{2+}$ macrocylic ions (Ni2 and Ni3) through hydrogen bonds, producing a 2D network (Figure 3). In the *a* direction, each Ni2 macrocylic cation links two neighboring cubes via four hydrogen bonds between the Ni2-bonded water molecules (O26) and the uncoordinated carboxylate O atoms [O26···O2($1-x$, $1-y$, $1-z$), 2.76 Å; O26···O11($x+1$, y, z), 2.96 Å]. In the *c* direction, the cubes and the Ni3 macrocylic cations are connected by hydrogen bonds involving the Ni3-bonded water molecules (O27) and the uncoordinated carboxylate O atoms [O27···O18($1-x$, $2-y$, $1-z$), 2.74 Å]. Taking into account the above coordination and hydrogen bonds, a 3D architecture with open interconnected channels along the *a*, *b*, and *c* directions is generated (Supporting Information Figure S1). *PLATON* calculations[10] show that the guest-accessible volume (2536.1 Å^3 per unit cell) comprises 50.1% of the crystal volume. Enclosed in the channels are the remaining macrocyclic $[Ni(cyclam)]^{2+}$ cations and water molecules, which form lots of hydrogen bonds.

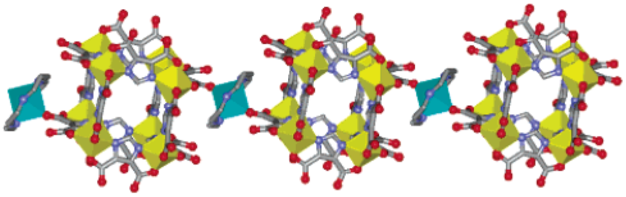

Figure 2. 1D coordination chain along the *b* direction in **1**.

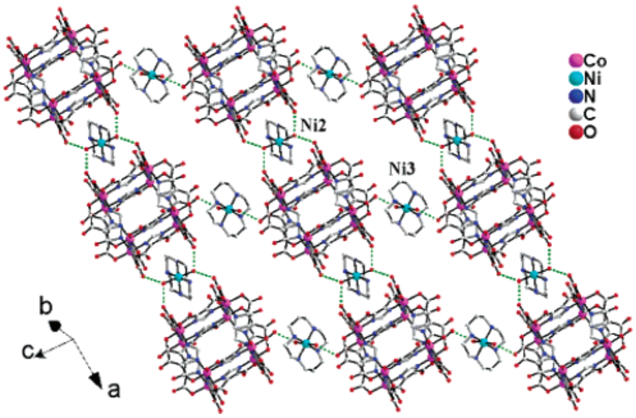

Figure 3. 2D hydrogen-bonded network parallel to the *ac* plane in **1**.

To summarize, we have succeeded in constructing a novel 3D network based on molecular cobalt cubes by using the [Ni(cyclam)] complexes as linkers between cubes, demonstrating the potential of creating new cage-based metal−organic networks by the metalloligand strategy. Furthermore, because of the intrinsic variable valence of cobalt, the $[Co_8]$ cubic compound **2** may exhibit interesting redox properties. Further studies, including the electrochemical behaviors of the cobalt cube and the construction of new networks of nickel/cobalt cubes using different linkers, are underway in our laboratory.

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Supporting Information Available: Experimental details and thermogravimetric analysis (PDF) and X-ray crystallographic information (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Crystal data for **1**: $C_{130}H_{270}N_{52}O_{93}Co_8Ni_7$, $M_r = 4932.39$, triclinic, $P\bar{1}$, $a = 18.057(4)$ Å, $b = 18.204(4)$, $c = 19.226(4)$, $\alpha = 112.441(3)°$, $\beta = 98.555(4)°$, $\gamma = 112.615(4)°$, $V = 5058(2)$ Å^3, $Z = 1$, μ(Mo Kα) $= 1.379$ mm^{-1}, $T = 293(2)$ K, R1 $= 0.0690$, wR2 $= 0.1467$ for observed reflections with $I > 2\sigma(I)$.

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