DOI: 10.1002/chem.200700431

# Self-Assembly and Anion-Exchange Properties of a Discrete Cage and 3D Coordination Networks Based on Cage Structures

Ying Wang,[a] Peng Cheng,*[a] You Song,[b] Dai-Zheng Liao,[a] and Shi-Ping Yan[a]

**Abstract:** By using tridentate ligand 4-(3-pyridinyl)-1,2,4-triazole (pytrz), cage-like complexes of $\{[Cu(\mu_2\text{-pytrz})_2](ClO_4)(SO_4)_{0.5}\cdot C_2H_5OH\cdot 0.25\,H_2O\}_6$ (**1**), $\{[Cu_3(\mu_3\text{-pytrz})_4(\mu_2\text{-Cl})_2(H_2O)_2](ClO_4)_2Cl_2\cdot 2\,H_2O\}_n$ (**2**), and $\{[Cu_3(\mu_3\text{-pytrz})_3(\mu_3\text{-O})(H_2O)_3](ClO_4)_{2.5}(BF_4)_{1.5}\cdot 5.25\,H_2O\}_n$ (**3**) have been synthesized with different copper(II) salts. Complex **1** represents the second example of a $M_6L_{12}$ metal–organic octahedron with an overall $T_h$ symmetry. Complex **2** is constructed from a $3^8$ cage-building unit (CBU) and each CBU connects six neighboring cages to give the first 3D metal–organic framework (MOF) based on octahedral $M_6L_{12}$. Complex **3** is built from $Cu_{24}(pytrz)_{12}$ CBUs with the trinuclear copper clusters serving as second building units (SBUs) and decorating each corner of the $M_{24}L_{12}$ polyhedron. The $Cu_{24}(pytrz)_{12}$ building unit is linked by extra ligands to give an extended 3D framework that has the formula $Cu_{24}(pytrz)_{24}$ and possesses a $CaB_6$ topology. The mixed anions $ClO_4^-$ and $BF_4^-$ in **3** are both included in the inner cavity of the cage and can be completely exchanged by $ClO_4^-$ through the open windows of the cage, as evidenced by the crystal structure of the 3D MOF $\{[Cu_3(\mu_3\text{-pytrz})_3(\mu_3\text{-O})(H_2O)_3](ClO_4)_4\cdot 4.5\,H_2O\}_n$ (**4**). Complex **4** can also be synthesized when employing **1** as a precursor in an extensive study of the anion-exchange reaction. This represents the first successful conversion of a discrete cage into a 3D coordination network based on a cage structure. Complex **2** remains invariable during anion-exchange reactions because uncoordinated $Cl^-$ ions are located in the comparatively small inner cavity.

**Keywords:** anion-exchange properties · anions · cage compounds · copper · self-assembly

## Introduction

Coordination cages that incorporate small molecules or anions with the appropriate size and geometry to match the central cavities have attracted much attention in the past few decades owing to their aesthetically appealing structures and their eminently promising properties which make them suitable for applications as storage,[1] recognition,[2] and delivery materials,[3] as well as catalysts for specific chemical transformations.[4] Moreover, they display rich host–guest behavior with a range of counter-ions or solvent molecules in their large central cavities.[5] The mechanisms of the assembly process that leads to their formation are of immense interest. Therefore, the assembly of high-symmetry polyhedral cage complexes built from labile metal centers and multidentate bridging ligands is becoming one of the most active areas of research in metallo-supramolecular chemistry.

A variety of organic bridging spacers involving carboxylate or alkoxide,[6] multidentate heterocycles,[7] phosphonate or phosphinate,[8] pyridazine,[9] pyrimidine,[10,11] tetrazine,[12] pyrazolate,[13] open-chain diazine (N–N),[14] and other spacers[15] have been employed in the design of coordination cages in which tetradentate ligands with two bidentate chelating termini are usually used.[16] When they react with labile six-coordinate metal centers without any help from other ligands, the isolated complex must have a M/L ratio of 2:3. Simple variation of the aromatic spacer used to connect the two coordinating arms results in quite dramatic changes in the structures of higher members of these complexes, such as tetrahedron $M_4L_6$, cube $M_8L_{12}$, truncated tetrahedron $M_{12}L_{18}$, and tetra-capped truncated tetrahedron $M_{16}L_{24}$.[17] In all cases, each metal ion is located at the meeting point of three edges so that each ion receives three bi-

---

[a] Dr. Y. Wang, Prof. Dr. P. Cheng, D.-Z. Liao, S.-P. Yan
Department of Chemistry, Nankai University, Tianjin 300071 (China)
Fax: (+86) 22-2350-2458
E-mail: pcheng@nankai.edu.cn

[b] Dr. Y. Song
Coordination Chemistry Institute
and the State Key Laboratory of Coordination Chemistry
Nanjing University, Nanjing 210093 (China)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

dentate-coordinating units and a bridging ligand spans each edge of a tetrahedral array of metal ions. In contrast, when employing a tris-bidentate ligand which caps one triangular face of a metal polyhedron and provides six donor atoms, 1:1 cage complexes will be generated in which the metal ions maintain the octahedral geometry, as exemplified by the $M_4L_4$ tetrahedron.[18] Despite the fact that the link between the stoichiometry of the complexes and the topologies of the cages is clear, the structure of the cage that will form with a given ligand cannot be predicted. We can at most narrow down the range of possible cage topologies. Support for this complication is manifested in the dinuclear cage $M_2L_4$,[19] trigonal bipyramidal $M_3L_2$[20] and $M_5L_6$,[21] macropentacyclic double-walled square $M_4L_8$,[22] truncated octahedral $M_6L_8$,[23] $4^3$ cube-like $M_{12}L_8$,[24] hexahedral $M_{15}L_6$ and $M_{18}L_6$,[25] fullerene-like $M_{21}L_{12}$,[26] and octahedral $M_{24}L_8$.[27]

Inspired by the aforementioned progress in the study of these novel self-assembled cages and capsules, in this contribution, we employ 4-(3-pyridinyl)-1,2,4-triazole (pytrz) in which one 1,2,4-triazole ring is directly linked to a pyridine core through the N4 atom. It is known that 1,2,4-triazole and its derivatives are very interesting ligands because they combine the coordination geometry of both pyrazoles and imidazoles in respect of the arrangement of their three heteroatoms. Up to now, a large number of mononuclear, polynuclear, and multi-dimensional coordination compounds with interesting magnetic properties and novel topologies have been prepared and characterized.[28] Herein, with the help of copper(II) ions and mixed anions $ClO_4^-$ and X (X = $SO_4^{2-}$, $Cl^-$, and $BF_4^-$), pytrz ligands have been connected to form cage-like complexes **1**–**3**. They have been characterized by single-crystal X-ray diffraction, mass spectrometry (MS), elemental analysis, FTIR spectroscopy, and TGA. Anion-exchange properties have also been investigated. Experimental results indicate that under the prevailing reaction condition of excess $ClO_4^-$ ions, **1** and **3** can be transformed into 3D coordination network **4** based on a $M_{24}L_{12}$ cage during an anion-exchange process.

$$\{[Cu(\mu_2\text{-pytrz})_2](ClO_4)(SO_4)_{0.5}\cdot C_2H_5OH\cdot 0.25\,H_2O\}_6 \quad \mathbf{1}$$

$$\{[Cu_3(\mu_3\text{-pytrz})_4(\mu_2\text{-Cl})_2(H_2O)_2](ClO_4)_2Cl_2\cdot 2\,H_2O\}_n \quad \mathbf{2}$$

$$\{[Cu_3(\mu_3\text{-pytrz})_3(\mu_3\text{-O})(H_2O)_3](ClO_4)_{2.5}(BF_4)_{1.5}\cdot 5.25\,H_2O\}_n \quad \mathbf{3}$$

$$\{[Cu_3(\mu_3\text{-pytrz})_3(\mu_3\text{-O})(H_2O)_3](ClO_4)_4\cdot 4.5\,H_2O\}_n \quad \mathbf{4}$$

## Results and Discussion

**Structural descriptions of a discrete cage and 3D coordination networks based on cage structures**: The structures of **1**–**4** were determined by single-crystal X-ray diffraction analysis (Table 1). Selected bond lengths and angles for **1**–**4** are listed in Table 2. The self-assembly of pytrz, $CuSO_4$, and $NaClO_4$ in the molar ratio of 1:1:10 in $H_2O/CH_3CH_2OH/CH_3CN$ gave well-shaped blue crystals of **1**. Single-crystal

Table 1. Crystallographic data and details of refinements for complexes **1**–**4**.

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| formula | $C_{96}H_{111}N_{48}O_{43.5}Cu_6Cl_6S_3$ | $C_{28}H_{32}N_{16}O_{12}Cu_3Cl_6$ | $C_{21}H_{31.5}N_{12}O_{17.76}Cu_3Cl_{2.49}F_6B_{1.5}$ | $C_{21}H_{19.26}N_{12}O_{24.5}Cu_3Cl_4$ |
| $M_r$ [g mol$^{-1}$] | 3323.40 | 1188.02 | 1145.55 | 1164.16 |
| $T$ [K] | 294(2) | 294(2) | 293(2) | 294(2) |
| crystal system | cubic | hexagonal | cubic | cubic |
| space group | $Pa\bar{3}$ | $R\bar{3}$ | $I\bar{4}3m$ | $I\bar{4}3m$ |
| $a$ [Å] | 23.248(2) | 24.777(5) | 21.146(2) | 21.1318(13) |
| $b$ [Å] | 23.248(2) | 24.777(5) | 21.146(2) | 21.1318(13) |
| $c$ [Å] | 23.248(2) | 26.489(9) | 21.146(2) | 21.1318(13) |
| $\alpha$ [°] | 90 | 90 | 90 | 90 |
| $\beta$ [°] | 90 | 90 | 90 | 90 |
| $\gamma$ [°] | 90 | 120 | 90 | 90 |
| $V$ [Å$^3$] | 12565.2(19) | 14083(6) | 9455.5(17) | 9436.5(10) |
| $Z$ | 4 | 9 | 8 | 8 |
| $\rho_{calcd}$ [Mg m$^{-3}$] | 1.757 | 1.261 | 1.609 | 1.639 |
| $\mu$ [mm$^{-1}$] | 1.282 | 1.320 | 1.576 | 1.656 |
| $F(000)$ | 6780 | 5373 | 4596 | 4642 |
| $2\theta_{max}$ [°] | 50.02 | 55.60 | 50.06 | 52.76 |
| Flack parameter | | | 0.06(4) | 0.01(5) |
| limiting indices | $-27 \leq h \leq 25$<br>$-20 \leq k \leq 27$<br>$-27 \leq l \leq 23$ | $-32 \leq h \leq 32$<br>$-32 \leq k \leq 19$<br>$-34 \leq l \leq 33$ | $-23 \leq h \leq 25$<br>$-24 \leq k \leq 25$<br>$-25 \leq l \leq 19$ | $-26 \leq h \leq 26$<br>$-26 \leq k \leq 17$<br>$-22 \leq l \leq 26$ |
| $R_{int}$ | 0.1904 | 0.1632 | 0.0576 | 0.0670 |
| observed reflections | 1735 | 2997 | 1367 | 1478 |
| reflections collected/unique | 59748/3653 | 31541/7378 | 26045/1580 | 27001/1819 |
| data/restraints/parameters | 3653/49/340 | 7378/86/357 | 1580/49/148 | 1819/58/156 |
| GOF on $F^2$ | 1.025 | 1.024 | 1.175 | 1.131 |
| $R_1/wR_2$ [$I > 2\sigma(I)$] | 0.0783/0.1987 | 0.0709/0.1813 | 0.0674/0.1829 | 0.0669/0.1933 |
| $R_1/wR_2$ (all data) | 0.1630/0.2822 | 0.1606/0.1965 | 0.0773/0.1968 | 0.0876/0.2221 |
| largest diff. peak/hole [e Å$^{-3}$] | 0.566/−0.494 | 0.835/−0.562 | 0.643/−1.146 | 0.953/−1.560 |

Table 2. Selected bond lengths [Å] and angles [°] for **1**–**4**.[a]

| | | | | | |
|---|---|---|---|---|---|
| complex **1** | | | | | |
| Cu(1)-N(4)#1 | 1.996(5) | Cu(1)-N(5) | 1.999(5) | Cu(1)-N(8)#2 | 2.011(5) |
| Cu(1)-N(1) | 2.024(5) | Cu(1)-O(1) | 2.400(5) | N(4)#1-Cu(1)-N(1) | 88.1(2) |
| N(4)#1-Cu(1)-N(5) | 175.7(2) | N(4)#1-Cu(1)-N(8)#2 | 91.2(2) | N(5)-Cu(1)-N(8)#2 | 90.0(2) |
| N(5)-Cu(1)-N(1) | 90.6(2) | N(8)#2-Cu(1)-N(1) | 179.3(2) | N(4)#1-Cu(1)-O(1) | 93.83(19) |
| N(5)-Cu(1)-O(1) | 90.2(2) | N(8)#2-Cu(1)-O(1) | 93.4(2) | N(1)-Cu(1)-O(1) | 86.6(2) |
| complex **2** | | | | | |
| Cu(1)-N(5)#1 | 2.017(5) | Cu(1)-N(4) | 2.023(5) | Cu(1)-N(8) | 2.051(5) |
| Cu(1)-N(2)#2 | 2.059(5) | Cu(1)-Cl(1) | 2.5868(18) | Cu(2)-N(1)#2 | 2.014(5) |
| Cu(2)-N(6)#4 | 2.025(5) | Cu(2)-Cl(1) | 2.6069(18) | N(4)-Cu(1)-N(8) | 88.8(2) |
| N(5)#1-Cu(1)-N(4) | 173.8(2) | N(5)#1-Cu(1)-N(8) | 89.3(2) | N(8)-Cu(1)-Cl(1) | 94.01(16) |
| N(5)#1-Cu(1)-N(2)#2 | 86.4(2) | N(4)-Cu(1)-Cl(1) | 95.17(16) | N(1)#2-Cu(2)-Cl(1) | 87.84(16) |
| N(4)-Cu(1)-N(2)#2 | 95.1(2) | N(8)-Cu(1)-N(2)#2 | 174.6(2) | N(5)#1-Cu(1)-Cl(1) | 90.81(15) |
| N(1)#2-Cu(2)-N(6)#1 | 88.8(2) | N(6)#4-Cu(2)-N(6)#1 | 180.0(4) | N(1)#2-Cu(2)-N(1)#3 | 180.000(1) |
| N(1)#3-Cu(2)-Cl(1) | 92.16(16) | N(1)#2-Cu(2)-N(6)#4 | 91.2(2) | N(2)#2-Cu(1)-Cl(1) | 89.42(15) |
| N(6)#4-Cu(2)-Cl(1) | 90.69(15) | N(6)#1-Cu(2)-Cl(1) | 89.31(15) | Cl(1)-Cu(2)-Cl(1)#5 | 180.00(7) |
| complex **3** | | | | | |
| Cu(1)-N(3) | 1.993(6) | Cu(1)-O(1) | 2.002(2) | Cu(1)-N(1) | 2.005(8) |
| O(1)-Cu(1)-N(1) | 179.4(4) | Cu(1)-O(2) | 2.362(12) | N(3)-Cu(1)-O(2) | 91.83(18) |
| O(1)-Cu(1)-O(2) | 82.1(4) | N(3)#1-Cu(1)-O(2) | 91.83(18) | N(3)-Cu(1)-N(1) | 89.98(17) |
| N(3)#1-Cu(1)-N(3) | 176.3(4) | N(1)-Cu(1)-O(2) | 97.3(4) | N(3)-Cu(1)-O(1) | 90.04(17) |
| complex **4** | | | | | |
| Cu(1)-N(3)#1 | 1.998(6) | Cu(1)-O(1) | 2.010(2) | N(3)#1-Cu(1)-N(3)#2 | 172.4(4) |
| Cu(1)-N(1) | 2.026(7) | Cu(1)-O(2) | 2.294(10) | N(3)#1-Cu(1)-N(1) | 90.21(18) |
| N(3)#1-Cu(1)-O(1) | 89.70(18) | O(1)-Cu(1)-N(1) | 178.7(4) | N(3)#1-Cu(1)-O(2) | 93.8(2) |
| N(3)#2-Cu(1)-O(2) | 93.8(2) | O(1)-Cu(1)-O(2) | 84.0(4) | N(1)-Cu(1)-O(2) | 97.3(4) |

[a] Symmetry transformations used to generate equivalent atoms. For **1**: #1: $-y+{}^{1}\!/_{2}$, $-z$, $x-{}^{1}\!/_{2}$; #2: $-z+{}^{1}\!/_{2}$, $x-{}^{1}\!/_{2}$, $y$. For **2**: #1: $-y+1$, $x-y+1$, $z$; #2: $x-y+{}^{2}\!/_{3}$, $x+{}^{1}\!/_{3}$, $-z+{}^{1}\!/_{3}$; #3: $-x+y-{}^{2}\!/_{3}$, $-x+{}^{2}\!/_{3}$, $z-{}^{1}\!/_{3}$; #4: $y-1$, $-x+y$, $-z$; #5: $-x$, $-y+1$, $-z$. For **3**: #1: $z$, $y$, $x$. For **4**: #1: $-x+{}^{3}\!/_{2}$, $-z+{}^{3}\!/_{2}$, $y+{}^{1}\!/_{2}$; #2: $z-{}^{1}\!/_{2}$, $x-{}^{1}\!/_{2}$, $y+{}^{1}\!/_{2}$.

X-ray analysis revealed that each cationic octahedron of **1** is positioned around the crystallographic center of symmetry. The crystal structure consists of six $Cu^{II}$ ions occupying six vertices of the octahedron and 12 pytrz ligands forming the octahedron edges (Figure 1). Each $Cu^{II}$ center is coordinated to four nitrogen atoms from four pytrz ligands resulting in a tetra-connected $CuN_4$. The discrete cage, $Cu_6(pytrz)_{12}$, represents the second example of a $M_6L_{12}$ metal–organic octahedron with an overall $T_h$ symmetry.[29] Interesting structural features of **1** are its internal cavity and triangular windows. The radius of the largest ball that can occupy the pore without contacting the surface of the framework is 5.00 Å and the volume of the cavity is about 0.5 nm$^3$. Six $ClO_4^-$ and two $SO_4^{2-}$ anions point towards the eight triangular windows of the octahedron (Figure 2) and the last sulfate counter-anion is situated outside the cavity of the $M_6L_{12}$ cage (see the Supporting Information). Six $CH_3CH_2OH$ molecules, which are statistically disordered around the symmetric center, are situated in the cavity of the $M_6L_{12}$ cage. Oxygen atoms from water and $CH_3CH_2OH$ molecules weakly coordinate to $Cu^{II}$ ions at separations of 2.40 and 2.58 Å, respectively (see the Supporting Information).

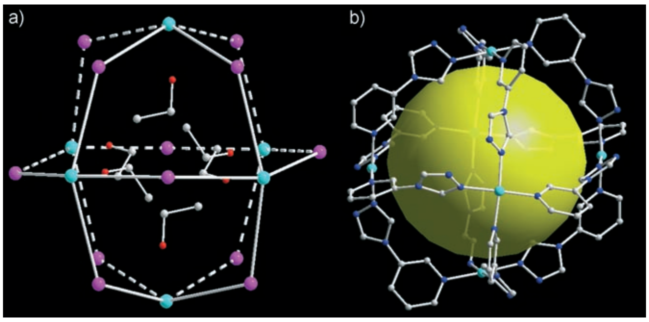


Figure 1. a) Schematic representation of discrete cage **1** with $CH_3CH_2OH$ molecules encapsulated in the cavity and b) view of the metal–organic octahedron $M_6L_{12}$ without guests. Cu: cyan; pytrz: purple; C: gray; N: blue; O: red; yellow ball: the largest sphere that can occupy the pore without contacting the surface of the framework.

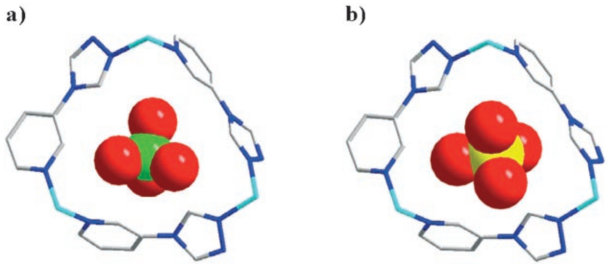


Figure 2. View of the triangular window showing a) $SO_4^{2-}$ and b) $ClO_4^-$ ions pointing towards the cavity of the discrete cage **1**. S: yellow; O: red; N: blue; C: gray; Cu: cyan; Cl: green.

When the same synthetic procedure was employed with $CuCl_2$ instead of $CuSO_4$, complex **2** was isolated in which linear trinuclear copper(II) clusters (Figure 3a) act as secondary building units (SBU). The arrangement of six terminal $Cu^{II}$ ions of different trinuclear clusters generates a $Cu_6$-

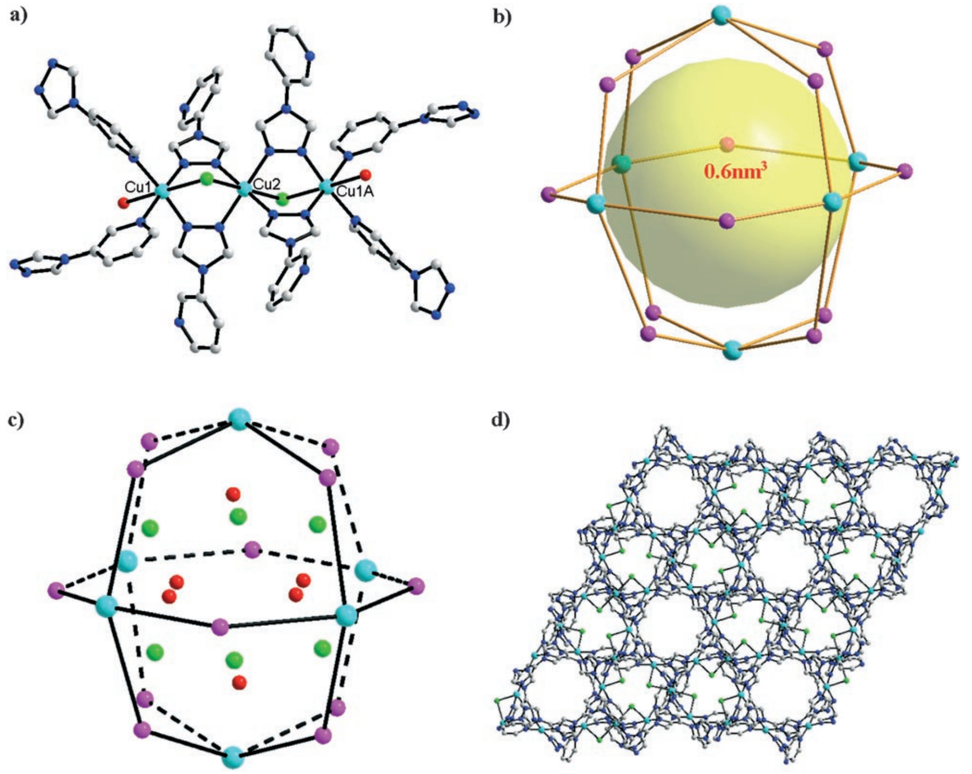


Figure 3. Structure of **2** showing a) the linear trinuclear copper(II) SBU, b) the inner cavity volume of the $3^8$ cage, c) $Cl^-$ ions and water molecules located in the $M_6L_{12}$ CBU, and d) the 3D network viewed along the *c* axis. Cu: cyan; N: blue; C: gray; Cl: green; O: red; pytrz: purple; black line: coordinated bond; yellow ball: the largest sphere that can occupy the pore without contacting the surface of the framework.

$(pytrz)_{12}$ cage. The radius of the largest ball that can occupy the pore without contacting the surface of the $Cu_6(pytrz)_{12}$ cage is 5.25 Å and the volume of the cavity is about 0.6 nm$^3$ (Figure 3b). If pytrz is considered as a linker, the $Cu_6(pytrz)_{12}$ cage can be represented as a $3^8$ cage building unit (CBU) which traps six water molecules and six $Cl^-$ anions (Figure 3c). Each face of the octahedron can be regarded as a regular triangle in which $Cu^{II}$ ions occupy three vertices and a pytrz ligand forms each side of the triangle with a length of 8.21 Å. The diameter of the inscribed circle of such a regular triangle is 4.74 Å. Each CBU is connected by six neighboring cages through the central $Cu^{II}$ ions leading to a unique 3D MOF (Figure 3d). The Cu2 atom is coordinated to two chloride anions and four nitrogen atoms from four triazole rings. Single-crystal X-ray diffraction analysis indicated that Cu2 is located at the symmetric center of the linear trinuclear copper cluster and adopts a slightly distorted octahedral geometry. The oxygen atoms from water molecules weakly coordinate to $Cu^{II}$ ions with an interaction distance of 2.61 Å. As is depicted in Figure 4, the 3D network of **2** displays the same 1D channels along the *a* or *b* direction along which the $ClO_4^-$ anions exist. Calculations from the X-ray structure parameters determined by PLATON[30] show that the volume of the void space occupied by the solvent and anions in the cavity of the cage is approximately 4134.5 Å$^3$. When the guest molecules are removed, the free volume increases up to 8268.8 Å$^3$, which amounts to 58.7 % void space per unit volume (14083.0 Å$^3$). To the best of our knowledge, **2** represents the first example of a 3D MOF based on a $M_6L_{12}$ CBU.

Note that the building block in **1** and **2** is the $Cu_6(pytrz)_{12}$ cage. Owing to their large size, the anions $ClO_4^-$ and $SO_4^{2-}$ cannot be hosted in the small cavity of the $3^8$ cage, whereas the relatively small $Cl^-$ ions act as both terminal and bridging groups to link $3^8$ CBUs to form the 3D MOF of **2**. An anomalous feature is the apparent absence of a second counter-anion of $ClO_4^-$ to be included within the cage itself owing to insufficient space. To further explore the influence of mixed anions on the resultant network, the reaction of $Cu(BF_4)_2$ instead of $CuSO_4$ with pytrz and $NaClO_4$ by a method similar to that used for the synthesis of **1** yielded blue block crystals of **3**. The remarkable change in the framework has been best realized by the slight differences in the $Cu^{II}$ salt.

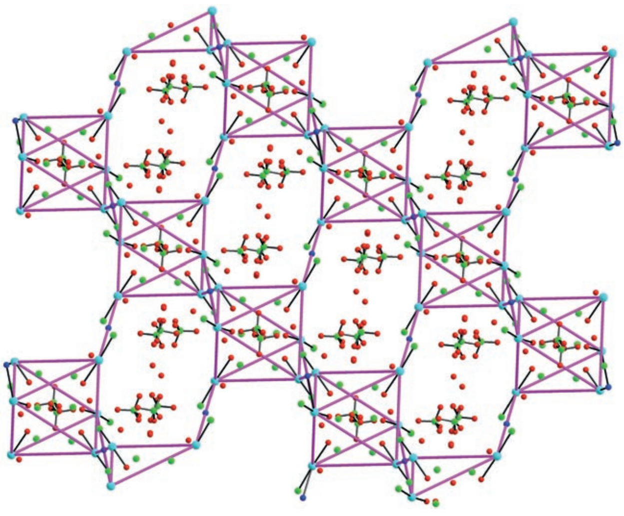


Figure 4. Uncoordinated $ClO_4^-$ ions of **2** exist in 1D channels along the *a* or *b* direction. Cu: cyan; Cl: green; O: red; N: blue; purple line: Cu–Cu connection; black line: coordinated bond.

Structural analysis of **3** shows that a $\mu_3$-oxo-centered triangular trinuclear core $Cu_3(\mu_3\text{-}O)(pytrz)_6$ with three-fold sym-

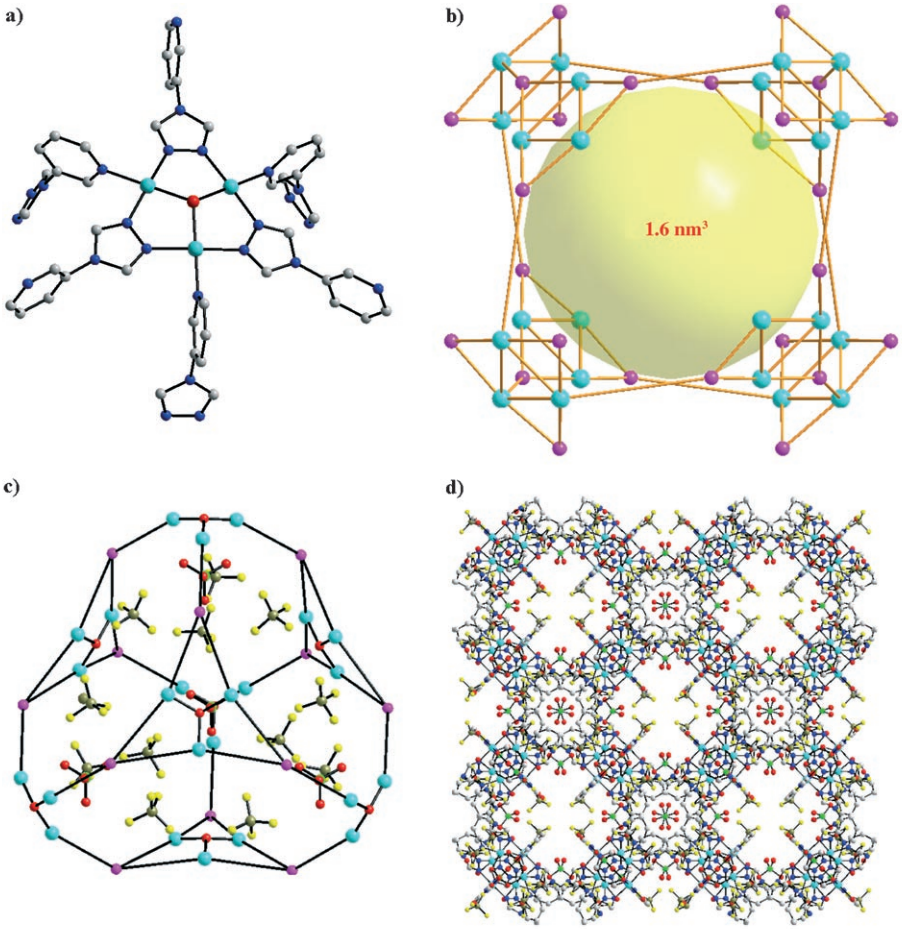


Figure 5. Structure of **3** showing a) the triangular trinuclear copper(II) SBU, b) the inner cavity volume in the CBU, c) guest molecules encapsulated in the $M_{24}L_{12}$ cage, and d) the 3D network viewed along the *a* axis. Cu: cyan; pytrz: purple; C: gray; N: blue; O: red; Cl: green; F: yellow; B: brown; yellow ball: the largest sphere that can occupy the pore without contacting the surface of the framework.

metry serves as the SBU (Figure 5a). Each triangular building block links six adjacent SBUs and an arrangement of eight SBUs generates a nano-sized $Cu_{24}(pytrz)_{12}$ CBU. The triangular trinuclear copper cluster decorates each corner of the CBU and the radius of the largest ball that can occupy the pore without contacting the surface of the framework is 7.30 Å. The volume of the cavity is about 1.6 nm$^3$ (Figure 5b). Four $ClO_4^-$ and 12 $BF_4^-$ ions are hosted in the cavity of the nano-sized $M_{24}L_{12}$ cage (Figure 5c) and the remaining uncoordinated $ClO_4^-$ ions exist among the cage-to-cage interstices. To date, a $M_{24}L_{12}$ cage has never been reported. The $M_{24}L_{12}$ CBUs are linked by extra ligands to give an extended 3D framework (Figure 5d) which has the formula $Cu_{24}(pytrz)_{24}$ and possesses a $CaB_6$ topology (see the Supporting Information). Each Cu$^{II}$ center in a square-planar geometry environment is four-coordinated to one $\mu_3$-$O^{2-}$ and three nitrogen atoms from three pytrz ligands. Oxygen atoms from water molecules and $ClO_4^-$ ions weakly coordinate to the Cu$^{II}$ ions with interaction distances of 2.36 and 2.49 Å, respectively. The dihedral angle formed between the pyridine and triazole rings is 90°, indicating an extremely strong spatial distortion effect. The potential free volume of the cationic MOF after removing the guest molecules is 5006.6 Å$^3$ per unit cell volume (9455.5 Å$^3$), which represents 52.9 % of void space in the unit cell.[30] Furthermore, it was observed that the triangular trinuclear $Cu_3(\mu_3$-$O)$ cores joined by pytrz ligands propagate in a zigzag conformation and eight such 1D chains are entwined around the surface of the $M_{24}L_{12}$ cage, as illustrated in Figure 6.

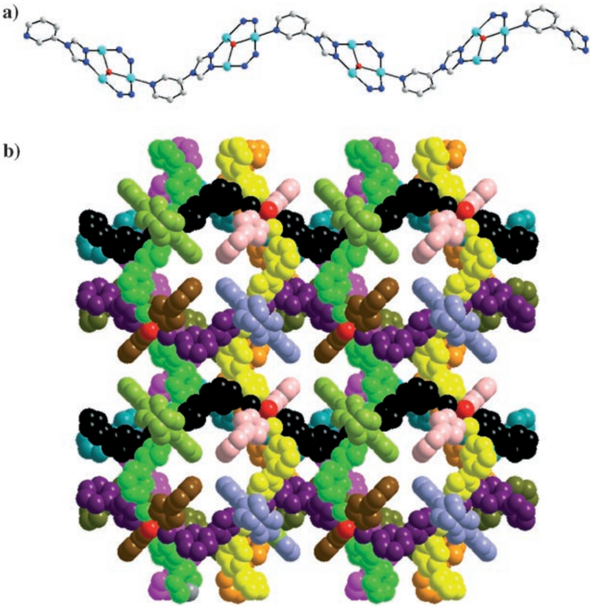
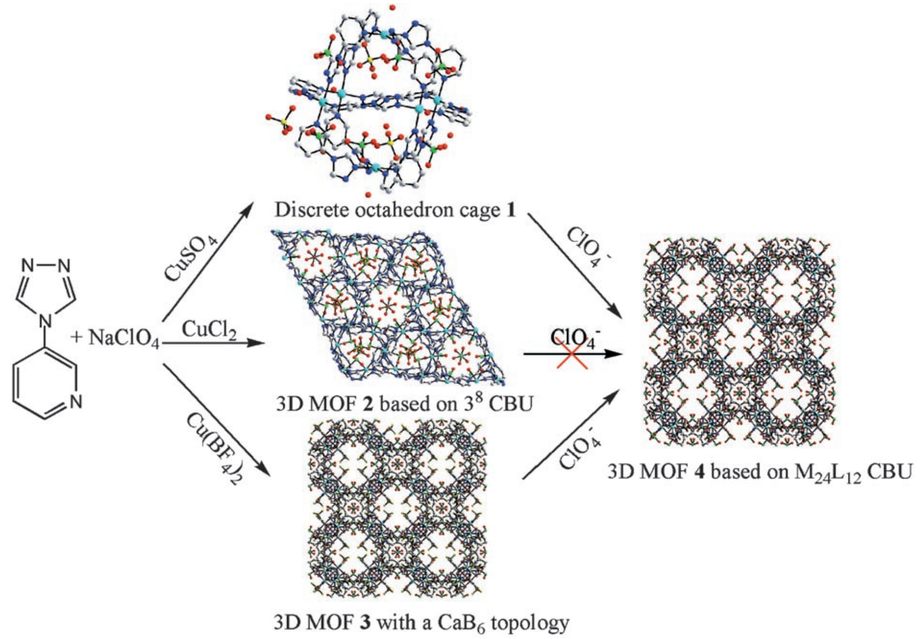


Figure 6. a) View of a 1D zigzag chain (Cu: cyan; O: red; N: blue; C: gray). b) Eight 1D chains entwined around the surface of the $M_{24}L_{12}$ cage in the 3D coordination network of **3** along the *a* axis.

Note that the trinuclear copper SBU in **3** as a six-connected node substitutes a single metal ion to decorate each corner of the $M_{24}L_{12}$ polyhedron, providing more tunable and larger cavities. Their optimal porosity and rigidity allows relatively large anions, such as $BF_4^-$ and $ClO_4^-$, to reside within the cavity. It is suggested that the overall structure of the network is strongly influenced by the geometry and the size of the anion, together with its ability to interact with the metal center.[31] The flexible dihedral angles between the pyridine and triazole rings also provide the curvature required for cage formation and dictate the direction of polymer extension. Such subtle factors are essential in determining the final structures of the assemblies.

**Anion-exchange properties and the transformation from discrete cage to 3D coordination network**: We explored the anion-exchange reactions of these cage-like architectures. After gently stirring **1** (0.5 mmol) in a 2:1 $H_2O/CH_3CN$ solution containing 5 mmol $NaClO_4$ for about 6 h the resultant mixture was evaporated at room temperature for two weeks. A remarkable reassembly process was observed and the original templated $3^8$ discrete octahedron cage was found to have been converted into 3D coordination network **4** based on the $M_{24}L_{12}$ CBU. Complex **4** could also be directly prepared when using **3** as a precursor in the aforementioned anion-exchange experiments (Scheme 1). During the preservation of the MOF topology and the anion-exchange process, $ClO_4^-$ ions occupy the same positions in the crystal lattice as the displaced $BF_4^-$ anions at similar distances and with similar geometries (see the Supporting Information). This means that the windows in **3** are large enough to facilitate movement of the $ClO_4^-$ ions in and out of the cage. In contrast, complex **2** remained unchanged when subjected to the anion-exchange process. Because some $Cl^-$ ions are coordinated to $Cu^{II}$ ions and others sit in the small inner cavity, it seems reasonable that it would be difficult to break up the framework and exchange $Cl^-$ for $ClO_4^-$. These findings could also be predicted on the basis that the anion-exchange process will occur when the structure of the resulting MOF is stable. Under the prevailing reaction conditions of excess $ClO_4^-$ ions, the $M_{24}L_{12}$ cage with a $CaB_6$ topology is the most thermodynamically stable structure. Overall, subtle changes in the anions used for crystallization have been seen to lead to significant changes not only in the overall coordination polymer architecture but also in maintaining the structural stability of the resultant framework.



Scheme 1. Synthesis of complexes **1**–**4**.

**Other structural characterizations**: The IR spectral peaks of complex **1** are located at 613 $cm^{-1}$ and in the range of 1022–1140 $cm^{-1}$ which arise from the coexistence of $SO_4^{2-}$ and $ClO_4^-$ ions. In complex **2**, infrared peaks appear at 957–1146 $cm^{-1}$ due to the occurrence of uncoordinated $ClO_4^-$ ions. In complex **3**, peaks emerge in the region of 1035–1146 $cm^{-1}$ confirming the presence of $ClO_4^-$ and $BF_4^-$ ions. Peaks indicative of the triazole rings were also present in the IR spectra of **1**–**3**.

In the mass spectrum (MS) of **1**, the peaks observed in the positive MS are at *m/z* 386.03 and 599.94. Experimental results indicate that in DMF the discrete cage $M_6L_{12}$ decomposes into mononuclear motif $[Cu(pytrz)(Hpytrz)]^+$ and dinuclear motif $[Cu_2(DMF)(pytrz)_4(pytrz\text{-}H)_2]^{2+}$. The electrospray MS of **2** in DMF clearly demonstrates the formation of the $[Cu_2(pytrz)_2(Hpytrz)_2(H_2O)Cl]^+$ species by the location of a peak at *m/z* 825.19. The electrospray mass spectrometric measurements demonstrate that the trinuclear copper(II) cluster in **3** retains its integrity and that this coordination polymer decomposes into trinuclear SBUs in DMF. The peak observed in the positive MS appears at *m/z* 1227.31, corresponding to $[Cu_3(pytrz)_3(Hpytrz)_3(\mu_3\text{-}O)(H_2O)_3]^+$. All the peaks have an isotopic distribution in accord with the simulated spectra (see the Supporting Information).

The powder X-ray diffraction (PXRD) patterns measured for the crystal products of complexes **1**, **2**, and **4** are shown in Figure S10a in the Supporting Information. They are in good agreement with the PXRD patterns simulated from the corresponding single-crystal X-ray data (see Figure S10b in the Supporting Information), not only in respect of the positions of the peaks but also the sharpness of the lines. This confirms that the single-crystal structures are representative of the bulk of the corresponding samples.

The thermogravimetric profiles exhibit a 10.0% weight loss for **1** (theoretical 9.1%), a 6.9% weight loss for **2** (theoretical 6.0%), and a 13.8% weight loss for **3** (theoretical 13.0%) in the temperature range 25–200 °C. These results are consistent with the loss of solvent molecules. The three complexes do not completely decompose until 280 °C (see the Supporting Information). Above 280 °C, the frameworks collapse because the organic ligands have been removed. DTA data for **1–3** show a phase change upon dehydration, in accord with the TGA plots. These experimental results confirm that complexes **1–3** are of high stability compared with other cage-like complexes.

## Conclusion

In summary, we used tridentate ligand 4-(3-pyridinyl)-1,2,4-triazole (pytrz) to obtain different cage-like complexes. Complex **1** is a discrete $\mathrm{Cu_6(pytrz)_{12}}$ cage which represents the second example of a $\mathrm{M_6L_{12}}$ metal–organic octahedron with an overall $T_h$ symmetry. Complexes **2** and **3** are the first examples of 3D coordination networks based on $\mathrm{M_6L_{12}}$ and $\mathrm{M_{24}L_{12}}$ CBUs, respectively. An extensive study of the anion-exchange reactions of these complexes indicates that the mixed anions $\mathrm{ClO_4^-}$ and $\mathrm{BF_4^-}$ located in the cavity of **3** can be completely exchanged by $\mathrm{ClO_4^-}$, as evidenced by the crystal structure of **4**. Complex **4** can also be prepared by employing **1** as a precursor under the prevailing reaction conditions of excess $\mathrm{ClO_4^-}$ anions. The first successful conversion of a discrete cage into a 3D coordination network based on a cage structure has been reported herein. Mass spectral studies have demonstrated that **1** decomposes into mono- and dinuclear motifs in DMF and that **2** is broken down into dinuclear species, whereas the trinuclear copper(II) cluster in **3** retains its integrity in DMF.

## Experimental Section

**General remarks**: The triazole ligand was synthesized according to the literature method.[32] All other reagents were commercially available and used without further purification. The carbon, hydrogen, and nitrogen microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The FTIR spectra were recorded as KBr pellets in the range 4000–400 $\mathrm{cm^{-1}}$ with a Bio-Rad FTS 135 spectrometer. Thermal analyses, TGA and DTA (under an oxygenated atmosphere at a heating rate of 5 °C $\mathrm{min^{-1}}$) were carried out in a Labsys NETZSCH TG 209 Setaram apparatus. Electrospray ionization mass spectrometry (ESI-MS) spectra were obtained with a Sciex Qstar Pulsar spectrometer and an ESI source.

**Synthesis of $\{[\mathrm{Cu}(\mu_2\text{-pytrz})_2](\mathrm{ClO_4})(\mathrm{SO_4})_{0.5}\cdot\mathrm{C_2H_5OH}\cdot0.25\,\mathrm{H_2O}\}_6$ (1)**: A mixture of $\mathrm{CuSO_4\cdot5H_2O}$ (74.9 mg, 0.3 mmol), pytrz (43.8 mg, 0.3 mmol), and $\mathrm{NaClO_4\cdot H_2O}$ (421.4 mg, 3 mmol) was stirred for 5 h in $\mathrm{H_2O}$ (10 mL), $\mathrm{CH_3CH_2OH}$ (5 mL), and $\mathrm{CH_3CN}$ (5 mL). Upon slow evaporation of the filtrate at room temperature for two weeks, well-shaped blue crystals suitable for X-ray diffraction were obtained. Yield: 78 % based on the $\mathrm{Cu^{II}}$ salt. IR (KBr): $\tilde{\nu}=3520$, 3321, 1652, 1522, 1399, 1280, 1170, 1106, 1081, 1022, 886, 938, 813, 695, 615, 460 $\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $\mathrm{C_{96}H_{111}N_{48}O_{43.5}Cu_6Cl_6S_3}$: C 34.69, H 3.37, N 20.23; found: C 34.85, H 3.12, N 20.47.

**Synthesis of $\{[\mathrm{Cu_3}(\mu_3\text{-pytrz})_4(\mu_2\text{-Cl})_2(\mathrm{H_2O})_2](\mathrm{ClO_4})_2\mathrm{Cl_2}\cdot2\,\mathrm{H_2O}\}_n$ (2)**: A mixture of $\mathrm{CuCl_2\cdot2H_2O}$ (51.3 mg, 0.3 mmol), pytrz (43.8 mg, 0.3 mmol), and $\mathrm{NaClO_4\cdot H_2O}$ (421.4 mg, 3 mmol) was stirred for 5 h in $\mathrm{H_2O}$ (10 mL), $\mathrm{CH_3CH_2OH}$ (5 mL), and $\mathrm{CH_3CN}$ (5 mL). Upon slow evaporation of the filtrate at room temperature for 2 weeks, well-shaped dark-green crystals suitable for X-ray diffraction were obtained. Yield: 41 % based on the $\mathrm{Cu^{II}}$ salt. IR (KBr): $\tilde{\nu}=3442$, 3312, 1638, 1559, 1432, 1260, 1146, 1123, 1085, 957, 862, 809, 784, 761, 736, 722, 702, 677, 625, 564, 464, 429 $\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $\mathrm{C_{28}H_{32}Cl_6Cu_3N_{16}O_{12}}$: C 28.31, H 2.72, N, 18.86; found: C 28.59, H 2.57, N 18.66.

**Synthesis of $\{[\mathrm{Cu_3}(\mu_3\text{-pytrz})_3(\mu_3\text{-O})(\mathrm{H_2O})_3](\mathrm{ClO_4})_{2.5}(\mathrm{BF_4})_{1.5}\cdot5.25\,\mathrm{H_2O}\}_n$ (3)**: A mixture of $\mathrm{Cu(BF_4)_2\cdot6H_2O}$ (103.8 mg, 0.3 mmol), pytrz (43.8 mg, 0.3 mmol), and $\mathrm{NaClO_4\cdot H_2O}$ (421.4 mg, 3 mmol) was stirred for 5 h in $\mathrm{H_2O}$ (10 mL), $\mathrm{CH_3CH_2OH}$ (5 mL), and $\mathrm{CH_3CN}$ (5 mL). Upon slow evaporation of the filtrate at room temperature for two weeks, well-shaped blue block crystals suitable for X-ray diffraction were obtained. Yield: 65 % based on the $\mathrm{Cu^{II}}$ salt. IR (KBr): $\tilde{\nu}=3485$, 3351, 1641, 1562, 1520, 1481, 1252, 1146, 1083, 1035, 990, 884, 825, 778, 780, 697, 685, 532, 470 $\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $\mathrm{C_{21}H_{31.5}N_{12}O_{17.76}Cu_3Cl_{2.49}F_6B_{1.5}}$: C 22.02, H 2.77, N 14.68; found: C 21.85, H 2.95, N 14.39.

**Synthesis of $\{[\mathrm{Cu_3}(\mu_3\text{-pytrz})_3(\mu_3\text{-O})(\mathrm{H_2O})_3](\mathrm{ClO_4})_4\cdot4.5\,\mathrm{H_2O}\}_n$ (4)**: Method A: A mixture of **1** (1.662 g, 0.5 mmol) and $\mathrm{NaClO_4}$ (702.3 mg, 5 mmol) in $\mathrm{H_2O}$ (10 mL) and $\mathrm{CH_3CH_2OH}$ (5 mL) was stirred for about 6 h. The resultant mixture was evaporated at room temperature for two weeks and well-shaped blue block crystals suitable for X-ray diffraction were obtained. Yield: 35 %. Method B: A mixture of **3** (572.8 mg, 0.5 mmol) and $\mathrm{NaClO_4}$ (702.3 mg, 5 mmol) in $\mathrm{H_2O}$ (10 mL) and $\mathrm{CH_3CH_2OH}$ (5 mL) was stirred for about 6 h. The resultant mixture was evaporated at room temperature for two weeks and well-shaped blue block crystals suitable for X-ray diffraction were obtained. Yield: 52 %. IR (KBr): $\tilde{\nu}=3489$, 3345, 1638, 1559, 1517, 1485, 1256, 1143, 1086, 1032, 991, 885, 823, 775, 784, 695, 682, 535, 472 $\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $\mathrm{C_{21}H_{19.26}N_{12}O_{24.5}Cu_3Cl_4}$: C 21.67, H 1.67, N, 14.44; found: C 21.47, H 1.42, N 14.59.

**Crystallographic studies**: Single-crystal X-ray diffraction measurements of the complexes **1–4** were carried out with a Bruker Smart CCD diffractometer and an APEX II CCD area detector equipped with a graphite crystal monochromator situated in the incident beam for data collection at 293(2) and 294(2) K. The structures were solved by direct methods and refined by full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 programs.[33,34] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were placed in idealized positions and located in the difference Fourier map. The crystallographic data and selected bond lengths and angles for **1–4** are listed in Table 1 and Table 2, respectively.

CCDC-629126 (**1**), CCDC-610486 (**2**), CCDC-610485 (**3**), and CCDC-630658 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grants 20631030 and 20425103), the NSF of Tianjin (Grant 06YFJZJC009000), the State Key Project of Fundamental Research of MOST (Grant 2005CCA01200), and MOE of China (Grant 20060055039).

---

[1] a) T. Martin, U. Obst, J. Rebek, Jr., *Science* **1998**, *281*, 1842–1845; b) A. V. Davis, K. N. Raymond, *J. Am. Chem. Soc.* **2005**, *127*, 7912–7915; c) T. Kusukawa, M. Fujita, *J. Am. Chem. Soc.* **2002**, *124*, 13576–13582.

[2] a) T. Heinz, D. M. Rudkevich, J. Rebek, Jr., *Nature* **1998**, *394*, 764–766; b) S. Tashiro, M. Tominaga, M. Kawano, B. Therrien, J. M. C. A. Kerchoffs, F. W. B. van Leeuwen, A. L. Spek, H. Kooijman, M. Crego-Calama, D. N. Reinhoudt, *Angew. Chem.* **2003**, *115*, 5895–5900; *Angew. Chem. Int. Ed.* **2003**, *42*, 5717–5722.

[3] a) J. L. Turner, K. L. Wooley, *Nano Lett.* **2004**, *4*, 683–688; b) D. Pan, J. L. Turner, K. L. Wooley, *Chem. Commun.* **2003**, 2400–2401; c) K. K. Perkin, J. L. Turner, K. L. Wooley, S. Mann, *Nano Lett.* **2005**, *5*, 1457–1461.

[4] a) D. Fiedler, D. H. Leung, R. G. Bergman, K. N. Raymond, *Acc. Chem. Res.* **2005**, *38*, 349–358; b) M. Yoshizawa, Y. Takeyama, T.

Kusukawa, M. Fujita, *Angew. Chem.* **2002**, *114*, 1403–1405; *Angew. Chem. Int. Ed.* **2002**, *41*, 1347–1349.

[5] For recent reviews, see: a) N. Gimeno, R. Vilar, *Coord. Chem. Rev.* **2006**, *250*, 3161–3189; b) D. L. Caulder, K. N. Raymond, *Acc. Chem. Res.* **1999**, *32*, 975–982; c) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853–908; d) D. L. Caulder, K. N. Raymond, *J. Chem. Soc., Dalton Trans.* **1999**, 1185–1200; e) G. F. Swiegers, T. J. Malefetse, *Chem. Eur. J.* **2001**, *7*, 3636–3643; f) B. J. Holliday, C. A. Mirkin, *Angew. Chem.* **2001**, *113*, 2076–2097; *Angew. Chem. Int. Ed.* **2001**, *40*, 2022–2043.

[6] For selected examples, see: a) R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 1804–1816; b) C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, D. Gatteschi, *Phys. Rev. Lett.* **1997**, *78*, 4645–4648; c) Z. Sun, C. M. Grant, S. L. Castro, D. N. Hendrickson, G. Christou, *Chem. Commun.* **1998**, 721–722; d) A. L. Barra, A. Caneschi, A. Cornia, F. F. de Biani, D. Gatteschi, C. Sangregorio, R. Sessoli, L. Sorace, *J. Am. Chem. Soc.* **1999**, *121*, 5302–5303; e) Q. Fang, G. Zhu, M. Xue, J. Sun, Y. Wei, S. Qiu, R. Xu, *Angew. Chem.* **2005**, *117*, 3913–3916; *Angew. Chem. Int. Ed.* **2005**, *44*, 3845–3848.

[7] For selected examples, see: a) J. S. Fleming, K. L. V. Mann, C.-A. Carraz, E. Psillakis, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Angew. Chem.* **1998**, *110*, 1315–1318; *Angew. Chem. Int. Ed.* **1998**, *37*, 1279–1282; b) R. W. Saalfrank, N. Low, B. Demleitner, D. Stalke, M. Teichert, *Chem. Eur. J.* **1998**, *4*, 1305–1311; c) M. Ziegler, J. J. Miranda, U. N. Andersen, D. W. Johnson, J. A. Leary, K. N. Raymond, *Angew. Chem.* **2001**, *113*, 755–758; *Angew. Chem. Int. Ed.* **2001**, *40*, 733–736; d) Z. R. Bell, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Angew. Chem.* **2002**, *114*, 2625–2628; *Angew. Chem. Int. Ed.* **2002**, *41*, 2515–2518.

[8] For selected examples, see: a) M. G. Walawalker, H. W. Roesky, R. Murugavel, *Acc. Chem. Res.* **1999**, *32*, 117–126, and references therein; b) V. Chandrasekhar, S. Kingsley, *Angew. Chem.* **2000**, *112*, 2410–2412; *Angew. Chem. Int. Ed.* **2000**, *39*, 2320–2322; c) W. F. Ruettinger, G. C. Dismukes, *Inorg. Chem.* **2000**, *39*, 1021–1027; d) E. K. Brechin, R. A. Coxall, A. Parkin, S. Parsons, P. A. Tasker, R. E. P. Winpenny, *Angew. Chem.* **2001**, *113*, 2772–2775; *Angew. Chem. Int. Ed.* **2001**, *40*, 2700–2703; e) H.-C. Yao, J.-J. Wang, Y.-S. Ma, O. Waldmann, W.-X. Du, Y. Song, Y.-Z. Li, L.-M. Zheng, S. Decurtins, X.-Q. Xin, *Chem. Commun.* **2006**, 1745–1747.

[9] M.-T. Youinou, N. Rahmouni, J. Fischer, J. A. Osborn, *Angew. Chem.* **1992**, *104*, 796–799; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 733–735.

[10] G. S. Hanan, D. Volkmer, S. S. Ulrich, J.-M. Lehn, G. Baum, D. Fenske, *Angew. Chem.* **1997**, *109*, 1929–1931; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1842–1844.

[11] D. M. Bassani, J.-M. Lehn, K. Fromm, D. Fenske, *Angew. Chem.* **1998**, *110*, 2534–2537; *Angew. Chem. Int. Ed.* **1998**, *37*, 2364–2367.

[12] C. S. Campos-Fernández, R. Clérac, K. R. Dunbar, *Angew. Chem.* **1999**, *111*, 3685–3688; *Angew. Chem. Int. Ed.* **1999**, *38*, 3477–3479.

[13] K. L. V. Mann, E. Psillakis, J. C. Jeffery, L. H. H. Rees, N. M. Harden, J. A. McCleverty, M. D. Ward, D. Gatteschi, F. Totti, F. E. Mabbs, E. J. L. McInnes, P. C. Riedi, G. M. Smith, *J. Chem. Soc. Dalton Trans.* **1999**, 339–348.

[14] P. J. Van Koningsbruggen, E. Müller, J. G. Haasnoot, J. Reedijk, *Inorg. Chim. Acta* **1993**, *208*, 37–42.

[15] For selected examples, see: a) S. Mann, G. Huttner, L. Zsolnai, K. Heinze, *Angew. Chem.* **1996**, *108*, 2983–2984; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2808–2809; b) R. Vilar, D. M. P. Mingos, A. J. P. White, D. J. Williams, *Angew. Chem.* **1998**, *110*, 1323–1326; *Angew. Chem. Int. Ed.* **1998**, *37*, 1258–1261; c) K. K. Klausmeyer, S. R. Wilson, T. B. Rauchfuss, *J. Am. Chem. Soc.* **1999**, *121*, 2705–2711.

[16] a) C. R. Rice, S. Wörl, J. C. Jeffery, R. L. Paul, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **2001**, 550–559; b) M. Albrecht, *Chem. Soc. Rev.* **1998**, *27*, 281–287; c) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005–2062.

[17] S. P. Argent, H. Adams, T. R. Johannessen, J. C. Jeffery, L. P. Harding, M. D. Ward, *J. Am. Chem. Soc.* **2006**, *128*, 72–73, and references therein.

[18] R. W. Saalfrank, H. Glaser, B. Demleitner, F. Hampel, M. M. Chowdhry, V. Schunemann, A. X. Trautwein, G. B. M. Vaughan, R. Yeh, A. V. Davis, K. N. Raymond, *Chem. Eur. J.* **2002**, *8*, 493–497.

[19] H. Amouri, L. Mimassi, M. N. Rager, B. E. Mann, C. G. Duhayon, L. Raehm, *Angew. Chem.* **2005**, *117*, 4619–4622; *Angew. Chem. Int. Ed.* **2005**, *44*, 4543–4546.

[20] H. B. Yang, K. Ghosh, A. M. Arif, P. J. Stang, *J. Org. Chem.* **2006**, *71*, 9464–9469.

[21] C. J. Matthews, L. K. Thompson, S. R. Parsons, Z. Xu, D. O. Miller, S. L. Heath, *Inorg. Chem.* **2001**, *40*, 4448–4454.

[22] D. K. Chand, M. Fujita, K. Biradha, S. Sakamoto, K. Yamaguchi, *Dalton Trans.* **2003**, 2750–2756.

[23] a) D. Moon, S. Kang, J. Park, K. Lee, R. P. John, H. Won, G. H. Seong, Y. S. Kim, G. H. Kim, H. Rhee, M. S. Lah, *J. Am. Chem. Soc.* **2006**, *128*, 3530–3531; b) D. K. Chand, K. Biradha, M. Fujita, S. Sakamoto, K. Yamaguchi, *Chem. Commun.* **2002**, 2486–2487.

[24] B. F. Abrahams, S. J. Egan, R. Robson, *J. Am. Chem. Soc.* **1999**, *121*, 3535–3536.

[25] a) K. Umemoto, H. Tsukui, T. Kusukawa, K. Biradha, M. Fujita, *Angew. Chem.* **2001**, *113*, 2690–2692; *Angew. Chem. Int. Ed.* **2001**, *40*, 2620–2622; b) N. Takeda, K. Umemoto, K. Yamaguchi, M. Fujita, *Nature* **1999**, *398*, 794–796; c) I. M. Müller, D. Möller, *Angew. Chem.* **2005**, *117*, 3029–3033; *Angew. Chem. Int. Ed.* **2005**, *44*, 2969–2973.

[26] W.-G. Lu, C.-Y. Su, T.-B. Lu, L. Jiang, J.-M. Chen, *J. Am. Chem. Soc.* **2006**, *128*, 34–35.

[27] I. M. Müller, S. Spillmann, H. Franck, R. Pietschnig, *Chem. Eur. J.* **2004**, *10*, 2207–2213.

[28] a) J. G. Haasnoot, *Coord. Chem. Rev.* **2000**, *200–202*, 131–185, and references therein; b) M. H. Klingele, S. Brooker, *Coord. Chem. Rev.* **2003**, *241*, 119–132; c) L. Yi, B. Ding, B. Zhao, P. Cheng, D.-Z. Liao, S.-P. Yan, Z.-H. Jiang, *Inorg. Chem.* **2004**, *43*, 33–43; d) B. Ding, L. Yi, Y. Wang, P. Cheng, D.-Z. Liao, S.-P. Yan, Z.-H. Jiang, *Dalton Trans.* **2006**, 665–675; e) Y.-Q. Huang, B. Ding, H.-B. Song, B. Zhao, P. Ren, P. Cheng, H.-G. Wang, D.-Z. Liao, S.-P. Yan, *Chem. Commun.* **2006**, 4906–4908; f) Y. Wang, L. Yi, X. Yang, B. Ding, P. Cheng, D.-Z. Liao, S.-P. Yan, *Inorg. Chem.* **2006**, *45*, 5822–5829; g) Y. Wang, B. Ding, P. Cheng, D.-Z. Liao, S.-P. Yan, *Inorg. Chem.* **2007**, *46*, 2002–2010; h) W. Ouellette, M. H. Yu, C. J. O'Connor, D. Hagrman, J. Zubieta, *Angew. Chem.* **2006**, *118*, 3577–3580; *Angew. Chem. Int. Ed.* **2006**, *45*, 3497–3500; i) B. Ding, L. Yi, P. Cheng, D.-Z. Liao, S.-P. Yan, *Inorg. Chem.* **2006**, *45*, 5799–5803.

[29] Y. L. Liu, V. Ch. Kravtsov, D. A. Beauchamp, J. F. Eubank, M. Eddaoudi, *J. Am. Chem. Soc.* **2005**, *127*, 7266–7277.

[30] PLATON, A Multipurpose Crystallographic Tool, A. L. Spek, Utrecht (The Netherlands), **2001**.

[31] S. R. Halper, L. Do, J. R. Stork, S. M. Cohen, *J. Am. Chem. Soc.* **2006**, *128*, 15255–15268.

[32] R. H. Wiley, A. J. Hart, *J. Org. Chem.* **1953**, *18*, 1368–1371.

[33] SHELXS 97, Program for the Solution of Crystal Structures, G. M. Sheldrick, University of Göttingen, Göttingen (Germany), **1997**.

[34] SHELXL 97, Program for the Refinement of Crystal Structures, G. M. Sheldrick, University of Göttingen, Göttingen (Germany), **1997**.

Received: March 20, 2007