

Single-crystal metal–organic microtubes self-assembled from designed D_3 symmetrical nanoclusters with a capped triple-helix pentanuclear M_5O_6 core†

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Received (in Cambridge, UK) 1st August 2007, Accepted 31st August 2007

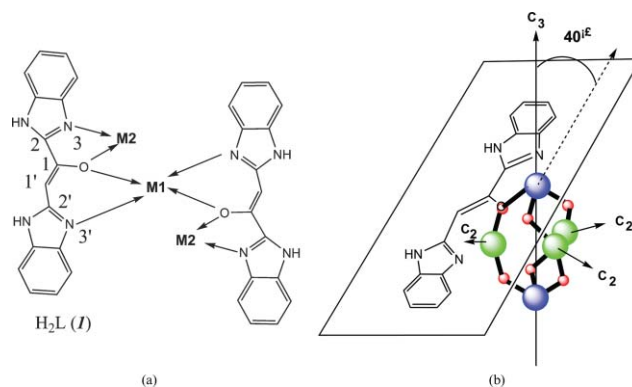
First published as an Advance Article on the web 10th September 2007

DOI: 10.1039/b711695k

Single-crystal metal–organic microtubular architectures have been fabricated from designed D_3 symmetrical nano clusters with a capped triple-helix pentanuclear M_5O_6 core under hydrothermal conditions.

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima,¹ synthetic tubular architectures are of great interest because of their exceptional properties and wide range of potential applications in material science, chemistry and biology.² In fact, significant progress has been made in the realms of organic or inorganic architectures.³ Nevertheless, tubular metal–organic complexes are very rare. Up to now, only one tubular metal–organic architecture, based on a hexanuclear $Zn_6F_6(\text{AmTAZ})_6$ metallacycle repeating unit (AmTAZ = 3-amino-1,2,4-triazole) has been described.⁴ Indeed, supramolecular architectures of metal–organic complexes have considerable advantages and properties as well as potential applications in the areas of ion exchange, gas absorption, single-molecule magnets and so on.⁵ So, could supramolecular architectures also be fabricated to tubular or nanotubular structures, like organic or inorganic compounds, and thereby improve their functional properties? If so, the tubular architectures of metal–organic complexes would greatly increase the variety in the fabrication of functional materials. In this communication, we describe the *in situ* synthesis of crystal microtubes consisting of rationally designed D_3 symmetrical nanoclusters with a capped triple-helix pentanuclear M_5O_6 core under hydrothermal conditions.

Inspired by the building principles for mixed-metal helicates (or mesocates) proposed by Raymond and co-workers,⁶ we have designed a planar tridentate ligand $\{(Z)-1,2\text{-di}(1H\text{-benzimidazol-2-yl})\text{ethanol}, H_3L\}$ (**1**) which contains a three-fold interaction site and an orthogonal two-fold (or mirror plane) interaction site while the M_5O_6 core is formed. The coordination of six ligands of **1** with five metals ($M_2M_1_3$) can generate a C_3 axis and three C_2 axes (Scheme 1) when their hydroxyl O and benzimidazole N3 coordinate to M2 (pseudo-octahedral coordination) at polar positions, while



Scheme 1 Coordination models of M and ligand **1**: (a) with M1 tetrahedral and M2 octahedral configurations, (b) the orientation of the two types of interaction sites and the approach angles, blue spheres represent pseudo-octahedral metal centers, green spheres are tetrahedral metal centers and red spheres are bridging atoms.

the hydroxyl O and the other benzimidazole N3' are coordinated to M1 (tetrahedral coordination) at the equatorial positions. The pentanuclear cluster thus possesses a D_3 point group symmetry.

The tubular architecture was obtained as following: a mixture of CuO, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 1,2-di(1*H*-benzimidazol-2-yl)ethane-1,2-diol and distilled water in a molar ratio of 1 : 1 : 2 : 1000 was mixed in a 25 ml stainless-steel reactor with a Teflon liner and heated from room temperature (RT) to 448 K in 0.5 h. The temperature was kept constant at 448 K for 92 h, then cooled down naturally to RT. Brown tubular crystals were collected in 30% yield.‡

The images of the tubular crystals of the complex showed hollow tetragonal or groove-like prisms and cones with opened and closed termini (Fig. 1). The length of the tubes varies from 250 to 750 μm and their diameters are in the range of 30–70 μm . The wall thickness (*ca.* 15 μm on average) varied greatly (Fig. 1(b)).

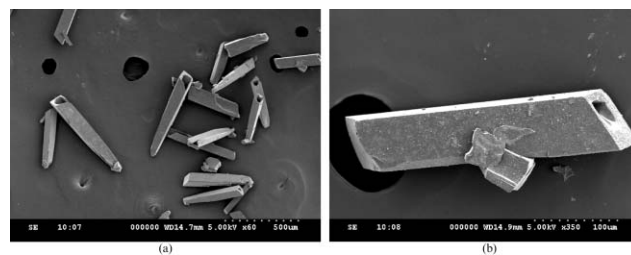


Fig. 1 Characterizations of the tubular structures of complex **2**. (a) Lower magnification SEM image, (b) higher magnification SEM image of a tube, showing a tubular tetragonal prism with a closed and an open end.

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† Electronic supplementary information (ESI) available: Experimental details, SEM and microscope images, IR spectra, elemental analysis results, crystal data. See DOI: 10.1039/b711695k

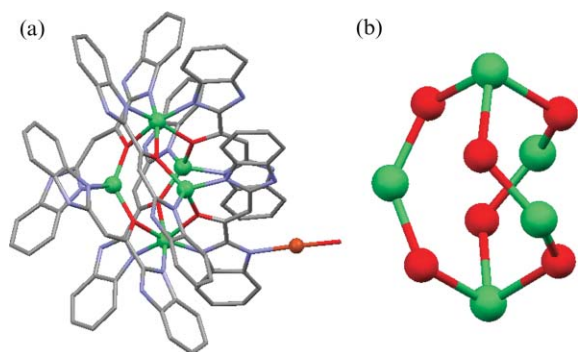


Fig. 2 (a) The structure of the pentanuclear cationic cluster of **2**, with hydrogen atoms, solvent molecules and ions omitted. The green spheres represent Ni atoms, and the orange sphere is Cu. The wireframe represents the ligand with carbon atoms shown in gray, oxygen atoms in red and nitrogen atoms in blue. (b) The triple-helix M_5O_6 core.

Closer inspection revealed that there were ‘weedlike’ structures adsorbed on the surface of the tubular crystals (see ESI†).

Single-crystal X-ray diffraction§ and elemental analysis‡ demonstrate that the tubular crystal is composed of a tetravalent cluster with a pentanuclear M_5O_6 core (Fig. 2), four chloride anions and three and a half solvent water molecules. The cation cluster is constructed by six planar ligands of **1** around the M_5O_6 core, while a linear monovalent copper⁷ coordinated by a water is attached to one benzimidazole N(N10) with a Cu–N bond of 2.137(9) Å. The diameter of about 1.78 nm indicates that complex **2** is a nanocluster. If not considering the linear monovalent copper coordinated by a water, the cluster has a D_3 symmetry. Theoretically, there should be three Ni and three Cu or two Ni and four Cu or five Ni and one Cu or six Cu atoms in the cluster, however, ICP analysis reveals that the cluster has 4.57 nickel atoms and 1.43 copper atoms. Therefore, ignoring the attached monovalent copper atom, the ratio of Ni/Cu should be $(5 - x)/x$ in the M_5O_6 core, $x = 0.43$. Hence, 0.43 copper atoms are likely disordered over the Ni positions in the crystal structure.⁸ In the cluster (Fig. 2), three pairs of almost parallel ligands are arranged around a pentanuclear, trigonal bipyramidal $Ni_{5-x}Cu_xO_6$ core with interbedded distances in range 3.3–3.4 Å, demonstrating strong π – π interactions between the planar aromatic ligands. Within the $Ni_{5-x}Cu_xO_6$ core, each apical metal atom lies on a C_3 axis with distorted octahedral coordination and the three other metal atoms occupy the equatorial positions with distorted tetrahedral structures. Each apical metal atom is linked to three equatorial metal atoms by three oxygen bridges. While each equatorial metal atom is linked to the two apical metal atoms by two oxygen bridges, thus forming an M–O–M–O–M triple-helix. The distance between two apical metals is 5.518(2) Å, and those between three equatorial metals are 3.660(2)–3.856(3) Å, while the separations between apical and equatorial metals fall in the range of 3.485(2)–3.569(2) Å. The M–O–M angles are from 118.2(4) to 121.4(4)°. Although there is a triple-helix cavity of about 4.4 Å in diameter, which may be available for occupation by small ions, no guest was found.

The packing diagram of the pentanuclear complex **2** is shown in Fig. 3. It is evident there are many hydrogen bonds between the non-coordinated N atoms, Cl anions and water molecules. These interactions between neighbouring clusters construct the pentanuclear complex into a three-dimensional architecture.

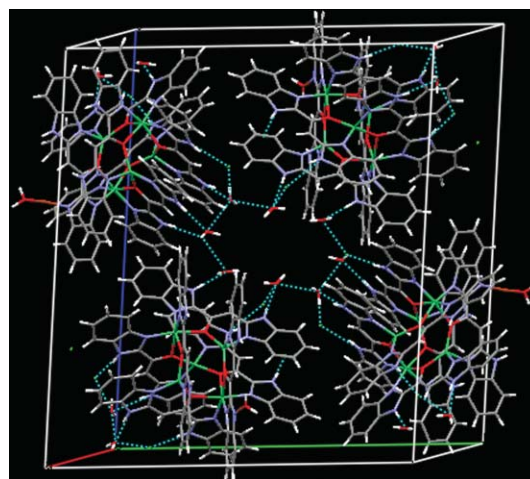


Fig. 3 The packing diagram of complex **2** in the crystal. Dashed lines represent the hydrogen bonds between the non-coordinated N atoms, Cl anions and water molecules. Ni or Cu atoms in the $Ni_{5-x}Cu_xO_6$ core ($x = 0.43$) are shown in green. The carbon atoms are shown in gray, oxygen atoms in red, nitrogen atoms in blue, hydrogen atoms in white, and the hydrogen bonds bonded green atoms are chloride.

In order to probe the factors which may affect the formation of the tubular crystals, we varied the length of heating time, temperature and the pH. Tubular crystals can be produced with temperatures varying from 423 to 448 K and heating time longer than 92 h with pH between 4 and 7. If heating time is less than 89 h, only crystals but no tubular structures were observed. Neither crystals nor tubular architectures were formed if pH is higher than 7 or below 4. These results indicate that pH is important for the formation of the tubular crystals, possibly because much lower or higher pH affects the dehydration of 1,2-di(1*H*-benzimidazol-2-yl)ethane-1,2-diol to form ligand **1**, then further influence the generation of the cluster, thus resulting in no either crystals or tubular architectures.

We also studied the effect of different anions on the formation of the tubular architecture. When $NiCl_2$ was substituted with $NiBr_2$ or $Ni(NO_3)_2$, fewer tubular architectures but more non-tubular crystals were formed. Using NiI_2 , only crystals but no tubular architectures were formed. If $NiCl_2$ was substituted by $NiCO_3$ or $NiSO_4$, neither tubular architecture nor any crystals were obtained. These results suggest that with an increase in anion radii, the ability of forming tubular architectures was decreased. The influence of anions on the formation of the tubular architectures is probably due to their difference in radius that may affect specific H-bonding schemes and subsequently affect the packing of the tubular architectures or even the formation of the clusters.

Another two tubular crystals consisting of pentanuclear clusters with $Ni_{5-y}Zn_yO_6$ (complex **3**, $y = 3$)‡ or Ni_5O_6 (complex **4**)‡ cores have also been fabricated similarly (see ESI†). Compared with the smooth tubular structure formed by complex **2**, their surfaces are much crisper and rougher (see ESI†). Both the pentanuclear clusters have almost the same X-ray structures§ as that of complex **2** except that they lack the tailed monovalent copper coordination and are completely D_3 symmetrical pentanuclear clusters. Indeed, the morphologies and symmetries of molecules are important for many self-assembled materials to form tubular architectures.⁹ These results suggest that the D_3 symmetrically intrinsic structures

of the nanoclusters are possibly related to the self-assembly of the tubular architectures under suitable conditions.

All the previous characterizations have confirmed that single-crystal metal–organic microtubular architectures have been successfully fabricated from designed D_3 symmetrical nanoclusters, so how do they form? Qian and co-workers reported tellurium nanotubes formed under hydrothermal conditions, giving us some enlightenment.¹⁰ The groove-like prisms and cones with one end closed (Fig. 1) indicates they possibly share similar mechanism of formation as the tellurium nanotubes. Namely, under our experimental conditions, the first step is possibly that the clusters form some nanoparticles, and then because ligand **1** is formed *in situ* and needs to react with metal ions to form the clusters, the speed of the formation of the clusters will be slow and can not provide enough clusters for the growth of the growing rodlike crystals, leading to undersaturation in the central part of the growing regions of crystal nanoparticles. The continuous feeding of clusters on the surface of nanoparticles can diffuse into two directions: circumferential diffusion and diffusion parallel to the tuber axis, resulting in formation of groove-like and tubular architectures. The details of the mechanism is still underway.

In summary, we have, for the first time, synthesized crystal microtubes consisting of D_3 symmetrical nanoclusters with a capped triple-helix pentanuclear M_5O_6 core by facile and reliable hydrothermal treatments. Although the exact mechanism of the formation of these microtubes is still unclear, it does demonstrate that nanoclusters with desired symmetry can be rationally designed and these metal–organic clusters can be assembled into tubular architectures under appropriate conditions. Their D_3 symmetrical characteristics in the structures and the formation speed of the clusters possibly play an important role in the formation of the tubular architectures. Therefore, preparation of tubular architectures of various dimensions from some highly symmetrical metal–organic coordination complexes is thus promising and may facilitate the research and application of tubular structures in a much wider range.

This work is supported financially by the National Natural Science Foundation of China (grant No. 20471033), the Province Natural Science Foundation of Shanxi Province of China (grant No. 20051013) and the Overseas Returned Scholar Foundation of Shanxi Province of China in 2006.

Notes and references

† Elemental analysis (EA) and ICP for **2**: calc. for $C_96H_{74}Cl_4Cu_{1.43}N_{24}Ni_{4.57}O_{10.5}$: C 51.64; H 3.34; N 15.06; Ni 12.01; Cu 4.07. Found: C 51.32; H 3.35; N 14.82; Ni 12.04; Cu 4.08%. IR (KBr) ν/cm^{-1} : 1612s, 1541m, 1452m, 1398m, 1339s, 1285m, 1066m, 876w, 746s.

The synthesis of complex **3** was by the same procedure as for complex **2** with replacement of CuO by ZnO. Yellow tubular crystals were collected in 30% yield. EA and ICP: calc. for $C_96H_{74}Cl_4N_{24}Ni_2Zn_3O_{10}$: C 52.91; H 3.42; N 15.43; Ni 5.39; Zn 9.00. Found: C 52.53; H 3.45; N 15.28%. ICP: Ni 5.74; Zn 8.96%. IR (KBr) ν/cm^{-1} : 1611s, 1542m, 1455m, 1399m, 1340s, 1284m, 1066m, 874w, 743s.

The synthesis of complex **4** was by the same procedure as for complex **2** but without any CuO. Red brown tubular crystals were collected in 15% yield. EA and ICP: calc. for $C_96H_{74}Cl_4N_{24}Ni_5O_{10}$: C 53.40; H 3.45; N 15.57; Ni 13.59. Found: C 52.92; H 3.50; N 15.42. Ni 13.40%. IR (KBr) ν/cm^{-1} : 1612s, 1543m, 1454m, 1399m, 1339s, 1284m, 1067w, 997m, 876w, 746s.

‡ Crystal data for **2**: $[Ni^{II}_{5-x}Cu^{II}_x(OC_{16}H_{11}N_4)_5(OC_{16}H_{10}N_4)-Cu^I(H_2O)]Cl_4 \cdot 3.5H_2O$ ($x = 0.43$), monoclinic, space group $P2_1/c$, $a = 13.259(5)$, $b = 26.875(10)$, $c = 28.993(9)$ Å, $\beta = 105.48(1)^\circ$, $V = 9956(6)$ Å³,

$Z = 4$, $D_c = 1.488$ g cm⁻³, $T = 298(2)$ K, crystal size $0.40 \times 0.15 \times 0.10$ mm³, $R = 0.0783$, $R_w = 0.1851$, GOF = 0.670 with $I > 2.00\sigma(I)$. CCDC 633740.

Crystal data for **3**: $[Ni^{II}_{5-y}Zn^{II}_y(OC_{16}H_{11}N_4)_6]Cl_4 \cdot 5H_2O$ ($y = 3$), monoclinic, space group $P2_1/c$, $a = 13.0667(8)$, $b = 26.6002(17)$, $c = 29.0855(18)$ Å, $\beta = 104.976(3)^\circ$, $V = 9766.1(11)$ Å³, $Z = 4$, $D_c = 1.482$ g cm⁻³, $T = 298(2)$ K, crystal size $0.20 \times 0.19 \times 0.10$ mm³, $R = 0.0888$, $R_w = 0.2209$, GOF = 0.929 with $I > 2.00\sigma(I)$. CCDC 633739.

Crystal data for **4**: $[Ni^{II}_5(OC_{16}H_{11}N_4)_6]Cl_4 \cdot 4H_2O$, monoclinic, space group $P2_1/c$, $a = 13.1351(11)$, $b = 26.668(2)$, $c = 29.0984(19)$ Å, $\beta = 105.009(3)^\circ$, $V = 9845.1(13)$ Å³, $Z = 4$, $D_c = 1.457$ g cm⁻³, $T = 298(2)$ K, crystal size $0.20 \times 0.08 \times 0.08$ mm³, $R = 0.0518$, $R_w = 0.1996$, GOF = 1.042 with $I > 2.00\sigma(I)$. CCDC 633741.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b711695k

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