Single-Crystal Metal-Organic Microtubes Self-Assembled from designed *D_3* symmetrical nano clusters with a capped triple-helix pentanuclear M_5O_6 core

Sisi Feng, Miaoli Zhu*, Liping Lu* and Maolin Guo
Correspondence e-mail: miaoli@sxu.edu.cn, luliping@sxu.edu.cn)

S.1 Synthesis of 1,2-di(1H-benzoimidazol-2-yl)ethane-1,2-diol

5 mL glycol was added to a mixture of tartaric acid (0.4994 g, 3.33 mmol) and o-phenylenediamine dihydrochloride (1.2059 g, 6.66 mmol). The mixture was irradiated for 4 minutes intermittently with WP700 LG microwave oven (output power 350W). When it is cooled to room temperature, 10 ml distilled water was added in and neutralized with an aqueous solution of NH_3, then the free 1,2-di(1H-benzoimidazol-2-yl)ethane-1,2-diol was obtained. The yellowish solid product was collected by filtration, recrystallized twice from 2:1 $EtOH:H_2O$. A white solid was collected and washed with Et_2O and dried *in vacuo* (60% yield). ^{1}H NMR (DMSO-d_6): δ=5.99 (d, 2H; alcohol-H); 7.50 (s, 4H benzimidazole-H); 7.13 (q, 4H, benzimidazole-H); 12.34 (s, 2H, benzimidazole-H); 5.33 (d, 2H; methine -H). IR (KBr pellet) υ/cm^{-1}: 3438m, 3182br, 1622w, 1456s, 1142s, 1311w, 1275s, 1111w, 1076m, 846w, 741s.

S.2 Synthesis of complexes *3* and *4*

Complex ***3***: The synthesis was performed under hydrothermal conditions as complex ***2***. A mixture of ZnO, $NiCl_2 \cdot 6H_2O$, 1,2-di(1H-benzoimidazol-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 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 under RT. Yellow crystals were collected in 30% yield. Elemental Analysis for $C_{96}H_{74}Cl_4N_{24}Ni_2O_{10}Zn_3$: calc. C 52.91; H 3.42; N 15.43; Found: C 52.53; H 3.45; N 15.28. ICP: Ni 5.39; Zn 9.00; Found: Ni 5.74; Zn 8.96. IR (KBr) υ/cm^{-1}: 1611s, 1542m, 1455m, 1399m, 1340s, 1284m, 1066w, 996m, 874w, 743s.

Complex ***4*****:** This was made using the same procedures as those in making complex ***3*** but only one metal salt ($NiCl_2 \cdot 6H_2O$) was used. Red brown crystals were collected in 15% yield. Elemental Analysis: for $C_{96}H_{74}Cl_4N_{24}Ni_5O_{10}$: calc. C 53.40; H 3.45; N 15.57. Found: C 52.92; H 3.50; N 15.42; ICP: Ni 13.59. Found: Ni 13.40. IR (KBr) υ/cm^{-1}: 1612s, 1543m, 1454m, 1399m, 1339s, 1284m, 1067w, 997m, 876w,746s.

S.3 Characterization of the tubular structures of complex *2*

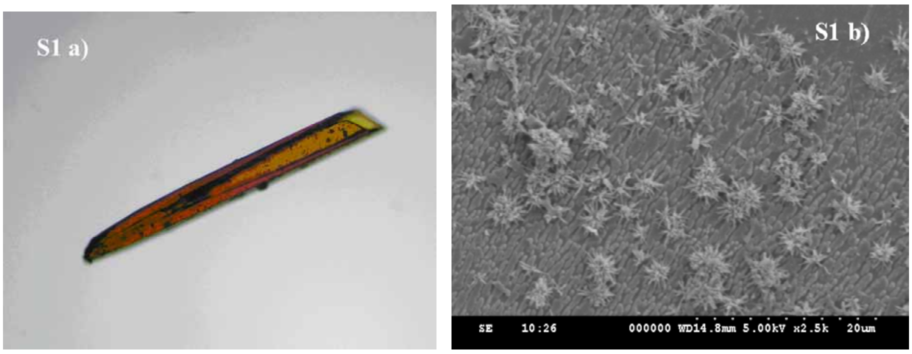

Figure S1 a) Light microscope image of a tube formed by complex ***2***, showing the tetragonal subuliform hollow. b) High-magnification SEM image of the adsorbed matters on the surface of the tube.

S.4 Tubular architectures of complexes 3 and 4.

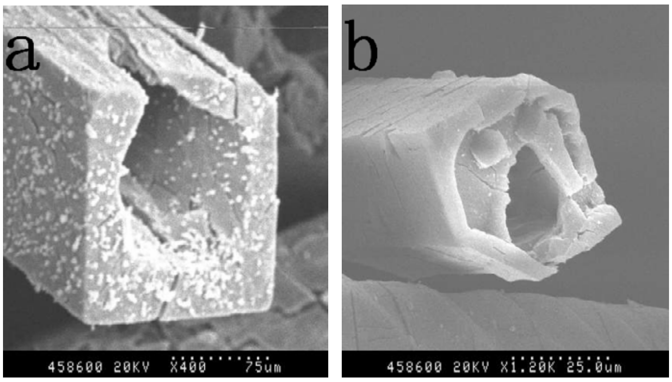

Figure S2 The tubular structures of complex ***3.*** The SEM images show tetragonal a) and pseudohexagonal b) prisms, respectively

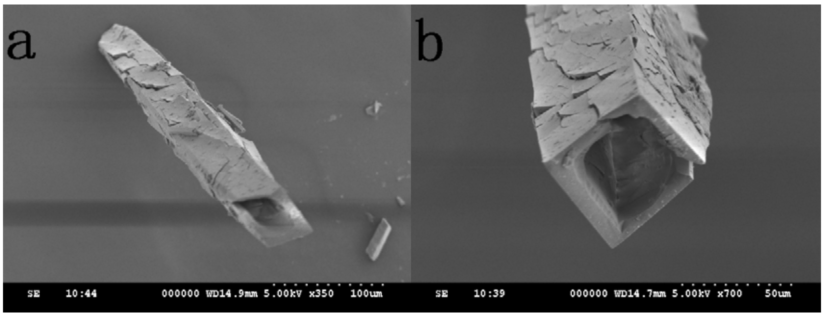

Figure S3 Tubular images of complex ***4***, demonstrating the crisp character (SEM images).

S.5 Crystal structures of complexes *3* and *4*

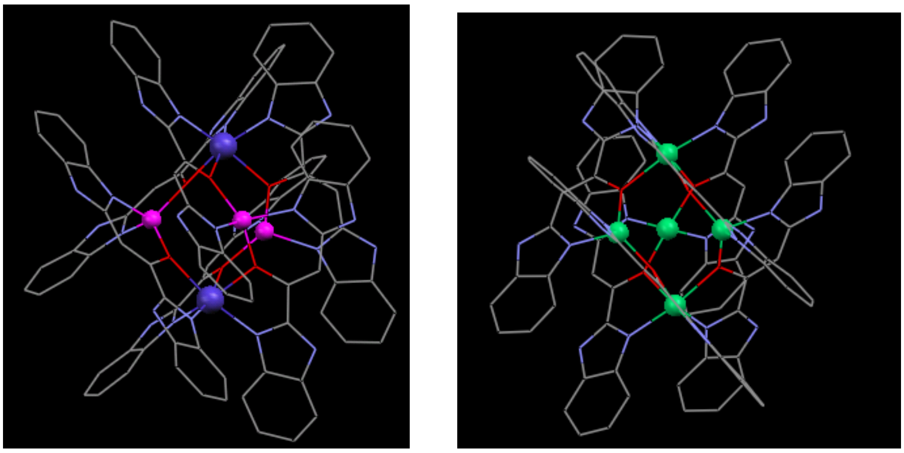

Figure S4 View of the cation of the molecular structure in ***3*** (left) and ***4*** (right) with hydrogen atoms omitted for clarity. The blue (left) and green (right) spheres represent Ni atoms, and amaranth spheres are Zn atoms. The wireframe represents the ligand with carbon atoms shown in gray, oxygen atoms in red and nitrogen atoms in blue.

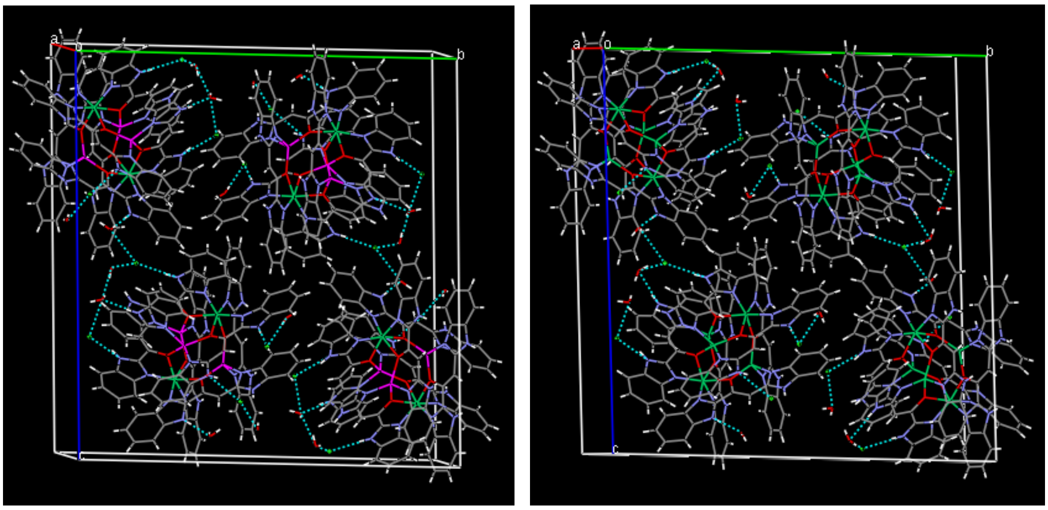

Figure S5 Packing diagram of complex in ***3*** (left) and ***4*** (right). The blue (left) and green (right) represents Ni atoms, and amaranth for Zn atoms. Carbon atoms are shown in gray, oxygen atoms in red, nitrogen atoms in blue and hydrogen atoms in white. The green dots are chloride anions

S.6 Crystal data for complexes 3 and 4

CCDC633739, 633741contain the supplementary crystallographic data for complexes 3 and 4. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

S.7 Comments on crystal structure refinements

The structural models of complexes 2, 3, and 4 are resolved following normal processes by programs SHELXTL[1] and PLATON[2]. H atoms attached to C and N atoms of all three complexes are placed in geometrically idealized positions, with Csp^2-H=0.93, and Nsp^3-H=0.86 A and refined with $U_{iso}(H)=1.2U_{eq}$(C or N). H atoms attached to O are located from difference Fourier maps and refined as riding in their as-found positions with $U_{iso}(H)=1.5U_{eq}(O)$.

In 2, the report of ICP analysis in complex 2 indicates that 6 metal ions (Ni and Cu) are divided into two parts, Ni 4.57 and Cu 1.43. How to assign the six metal sites to Ni or Cu in refinement? The coordination number of metal ion binding to N10 atom is 2 and this position should be Cu atom with 100% occupancy because its coordinated geometry is linear with character of monovalent copper(I). Residual 0.43 Cu atoms will be dispersed to 5 metal sites in M_5O_6 core. Ni1 site has the least U_{eq} value in all five Ni positions, so it is the most possible site for 0.43 disordered Cu atoms. The extent of disorder of Ni1 & Cu1 at this $Ni1_x/Cu1_{1-x}$ site is established by refinement of a free variable occupancy factor, x (final refined values x = 0.57), with SHELXL97 EXYZ and EADP instructions rigorously enforcing identical atomic coordinates and displacement parameters. Cu2 atom with a very large U_{eq} value [0.295(2)] and Uii values possibly results from its high disorder while it is attached to the M_5O_6 cluster.

Fourier maps also show that there are severe disorders for Cl ions and water molecules. Considering the accordance of the structural model with experimental results, we haven't further refined using less occupancy for these disordered atoms except O11 with 50% occupancy.

In 3, Fourier maps show that there are fewer densities for O10 and O11 sites, indicating 50% oxygen occupancies at both sites. All four Cl ions also have large U_{eq} values. This should be the results of disordered anions.

In 4, atoms C26 and C27 are refined anisotropically using 12 restraints (ISOR instruction) because of the unacceptable parameters of their ellipsoids. Ni1 atom is obviously disordered. The final occupancies of Ni1 atom from the refinement are Ni1A 0.93(1) and Ni1B 0.07(1), respectively. The small occupancy of Ni1B is not worth refining anisotropically and set free binding to atoms around it.

Cl1 atom is dealt with disorder. The final occupancies for Cl1 are Cl1A 0.46(1) and Cl1B 0.54(1). Fourier maps also show that there are fewer densities for other Cl sites which are refined using 50% occupancies.

References

1. Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.

2. Spek, A. L. (2003). J. Appl. Cryst. 36, 7-13.