A metal–organic framework containing discrete single-walled nanotubes based on curved trinuclear $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(triazolate)_2]^+$ building blocks†

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A metal–organic nanotubular architecture was built from parallel-aligned single-walled nanotubes which interlink by means of μ_3-bridged counterions, representing the first example of coordination nanotubes presumably generated from two-dimensional (2D) sheets.

As one type of metal–organic frameworks (MOFs), nanotubular frameworks remain largely unexplored as compared to other MOFs, which behave like related inorganic topological nets,[1] such as zeolitic binary metal imidazolates.[2] On the other hand, carbon nanotubes (CNTs) and other inorganic nanotubes containing other elements such as boron nitride (BN) have received much attention due to their uniform internal diameters, and accordingly produce well-defined applications in photoelectronics, molecular devices and sensors *etc*.[3] The common ground in these inorganic tubular compounds is that the main element behaves in a similar hybrid mode to another isomer possessing a planar layered structure. The former could be viewed as the product from rolling up the latter, therefore it is also a useful strategy for generating single-walled coordination nanotubular frameworks.

To date, the strategies or routes utilized to assemble coordination nanotubular architectures or discrete nanotubes are very limited with just a few reported examples, which could be summarized as: (i) winding helical chains into hollow chiral nanotubes which is the most common and successful strategy though in most cases the hollow parts are filled with counterions;[4] (ii) assembling specifically designed multidentate ligands and metal ions into nanotubular structures, and sometimes a templating effect being introduced;[5] (iii) occasional formation of nanotubes, for example, through interweaving of two independent, undulating networks.[6] In principle, it is a feasible strategy to utilize variable and versatile 2D planar structures to generate 1D nanotubes like CNTs. However, to the best of our knowledge, there is no example documented for assembling of coordination nanotubular frameworks making use of this strategy.

1,2,4-Triazolate (Htz), as a multifunctional ligand, combining the coordination modes of both imidazolate and pyrazolate, exhibits a strong bridged bonding ability for transition metal ions. A variety of MOFs assembled by binary univalent d^{10} metal ions and substituted tz anions were reported which fully displayed the coordination diversity and rigidity of this ligand.[7] However, for divalent metal ions and unsubstituted tz anions, few structures have been documented.[8] Recently, a porous coordination polymer constructed from trinuclear triangular second building units (SBUs) $[Cu_3(\mu_3\text{-}O)(\mu_3\text{-}tz)_3]$ was reported by three groups[9] at almost the same time, in which a 3D MOF was built from this six-connected SBU. We speculate that introduction of another bridged ligand would increase the possibility of forming a 2D layer structure through decreasing the connection number of the SBU, and therefore reducing the spatial hindrance between SBUs. Fortunately, on addition of the ancillary ligand cyanuric acid (H_3CA) into the original $CuCl_2$–Htz reaction system, a surprising new crystal phase appeared with a peculiar single-walled nanotubular structural character, which implies that the strategy for constructing 2D layer networks could also be used to generate 1D nanotubular structures when the SBUs exhibit appropriate flexibility.

We report herein a novel coordination nanotubular crystalline material, $\{[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu_3\text{-}tz)_2]_3(\mu_3\text{-}Cl)_2(\mu_3\text{-}H_2\text{-}CA)\}\cdot 8.5H_2O$, (**1**) where the discrete nanotubes contained correspond to supposed 2D planar sheets, and this relationship has not previously been documented for coordination nanotubular frameworks. Single crystals of **1** were obtained in good yield by solvothermal reaction of $CuCl_2$ and Htz (3 : 2 molar ratio) in the presence of H_3CA.‡ The product is stable in air and insoluble in water and common organic solvents and was formulated on the basis of microanalysis, and thermogravimetric analysis (TGA). The phase pure was testified by X-ray powder diffraction determination.

Single crystal structural analysis§ revealed that **1** crystallizes in the hexagonal centrosymmetric space group $P6_3/m$ (no. 176), which consists of parallel-arranged 1D single-walled nanotubes through cooperative μ_3-Cl and μ_3-H_2CA (H_3CA = cyanuric acid) coordinately linked. The 1D nanotube could be rationally regarded as a wrapped planar broad belt constructed by trinuclear triangular SBUs, $[Cu_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu_3\text{-}tz)_2]$, as shown in Fig. 1, including two crystallographically independent copper atoms, where Cu2, μ_3-O and μ_2-OH are located on a mirror plane. This SBU is different from the reported trinuclear $[Cu_3(\mu_3\text{-}O)(\mu_3\text{-}tz)_3]$ SBUs in ref. 9 which possess C_3 symmetry and nearly coplanar character and are further linked each other to give a 3D MOF. The difference is mainly due to

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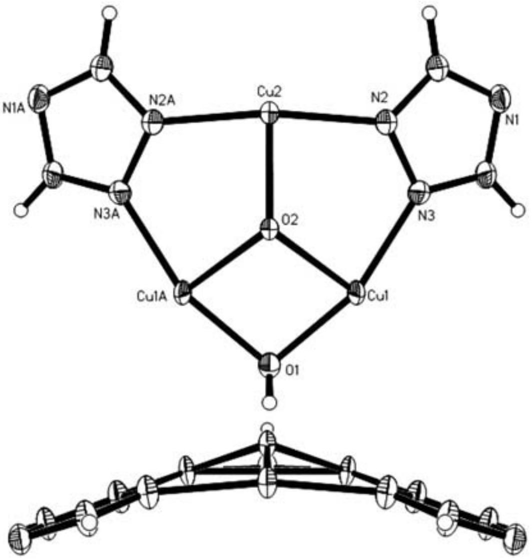

Fig. 1 Upper: ORTEP plot (50% probability ellipsoids) of the trinuclear triangular SBU in **1**; lower: side view of the SBU. Selected bond length (Å) and bond angles (°): Cu1–O1 1.953(2); Cu1–O2 1.974(2); Cu1–N3 2.021(3); Cu2–O2 1.944(3); Cu2–N2 1.977(3); Cu1–O2–Cu2 120.0(1); Cu1–O2–Cu1A 96.8(1); Cu1–O1–Cu1A 98.2(1); N2–Cu2–N2A 165.9(2); N3–Cu1–O1 161.0(1), symmetry code: (A) *x*, *y*, 1/2 − *z*.

the μ_2-OH in our case replacing one of the μ_3-tz units in their example, consequently exhibiting different bond lengths between the Cu and μ_3-O atoms (1.974(2) and 1.944(3) Å in **1**, 1.9561(5) Å in ref. 9) and Cu···Cu distance (2.952 and 3.393 Å in **1**, 3.388 Å in ref. 9). In contrast to the planar conformation of the trinuclear SBU in ref. 9, a slightly curved plane was observed for the Cu_3 SBU in **1** (Fig. 1, lower, the O2 atom having a small deviation (*ca.* 0.549 Å) from the plane consisting of three copper atoms). This is believed to be a key factor for the formation of a nanotube rather than a 2D layer sheet.[10]

Trinuclear SBUs are linked by each other through two tz-nitrogen atoms and two Cu atoms (Cu1 and Cu1A), which could be viewed as four-connected triangle nodes. If the SBUs were completely planar, the extension of nodes should give a 2D (4,4) network (Fig. 2, top). However, in this case, they just propagate infinitely in one direction parallel to the *c* axis, and in another six limited interlaced rows of SBUs are found, thus the final 1D nanotube is produced while the original broad belt is wrapped like a cylinder (Fig. 2, bottom). This open-ended, hollow tube possesses windows comprised of hexanuclear crown-like metallamacrocycles $[Cu_6(tz)_6]$ (Fig. S1†) with a crystallographically imposed three-fold rotoinversion axis in the center of the tube. This single-walled nanotube has an exterior diameter of *ca.* 12.6 Å calculated through three C_3 symmetry related O2 atoms, and the smallest aperture diameter of the tube is *ca.* 5.5 Å calculated on the slightly concave tz moieties as well as taking into account the van der Waals radii.

There are two crystallographically independent copper atoms in **1** exhibiting different coordination geometries, where Cu1 adopts a slightly distorted tetragonal pyramidal coordination environment (Fig. S2†) with four equatorial sites occupied by μ_3-O, μ_2-OH and two triazolate nitrogen atoms in the nanotubes and one apical site occupied by a μ_3-Cl anion, and Cu2 adopts a slightly distorted square planar geometry (Fig. S2†) with three equatorial sites occupied by μ_3-O and two triazolate nitrogen atoms in the nanotubes as well as another site occupied by a μ_3-CA nitrogen atom. This means that μ_3-Cl and μ_3-CA anions outside the nanotubes are in a 2 : 1 ratio and the Cl···Cl···CA··· packing mode along the *c* axis links the neighbouring three 1D nanotubes through Cu–Cl or Cu–N bonds to extend to be a 3D nanotubular framework (Fig. 3). In other words, each nanotube is surrounded by six nanotubes through six groups of μ_3-bridged linear Cl···Cl···CA··· packing aggregates. It should be noted that this 3D nanotubular architecture is composed of discrete 1D nanotubes which have no common vertices or edges. However, a majority of reported 3D coordination nanotubular frameworks exhibit edge-shared honeycomb networks.[11]

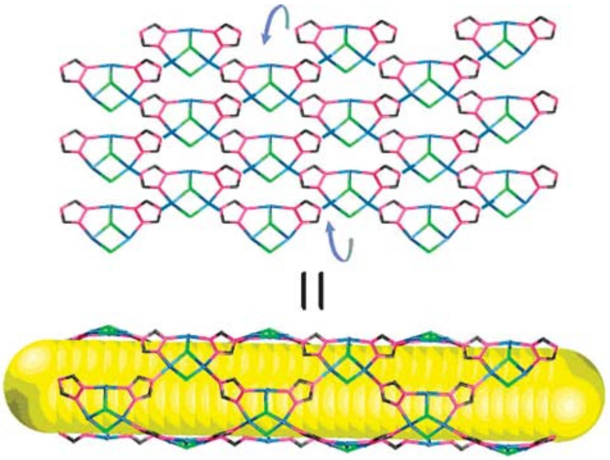

Fig. 2 Perspective view of 1D single-walled nanotube (bottom) in **1** which could be wrapped up from an imaginary planar sheet (top) based on four-connected trinuclear triangular SBUs (blue for Cu, green for O, aubergine for N, black for C).

The total solvent-accessible volume of this 3D framework in the unit cell is 326.0 Å^3, accounting for 17.2% of the total cell volume as calculated by PLATON.[12] TGA (as shown in Fig. S3†) revealed that *ca.* 5.6% weight loss occurred immediately upon heating and was completed before the

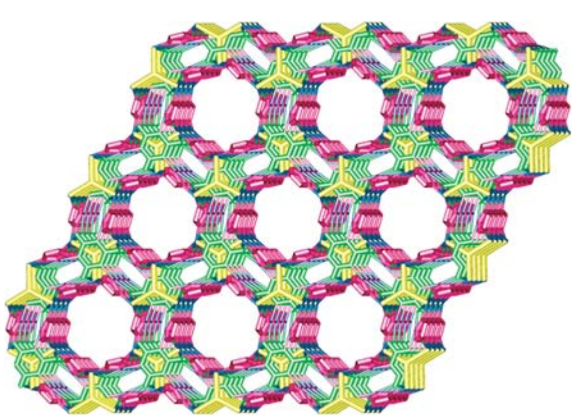

Fig. 3 The 3D nanotubular framework of **1** viewed along *c*-axis (aubergine for triazolate rings, cyan for Cu, yellow for Cl, green for O and CA rings, H atoms and guest water molecules omitted for clarity).

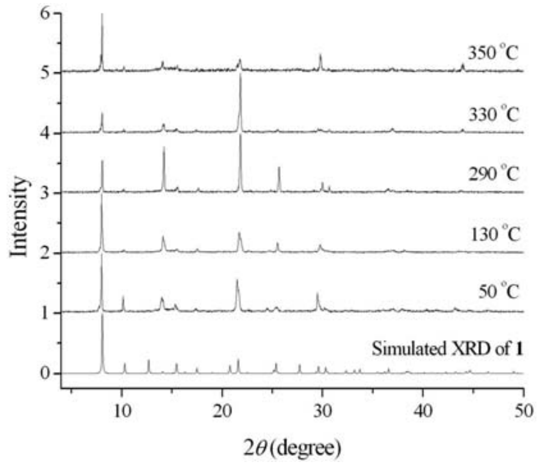

Fig. 4 X-Ray powder diffraction plots of **1**.

temperature reached 128 °C, and this weight loss is indicative of the loss of non-hydrogen bonded solvent molecules. Then a continuous, gradual weight loss was observed, which ceased at about 298 °C, and was followed by an abrupt weight loss indicative of framework decomposition. The total weight loss of guest molecules was about 9.1%, corresponding to the weight percent (10.7%) of lattice water molecules in a unit cell calculated from the formula of **1**, which is based on the elemental analysis results. Thermal stability of **1** was also checked by powder X-ray thermodiffraction analyses (Fig. 4). The results showed that they were stable up to 300 °C, in good agreement with the TGA result.

In conclusion, a neutral nanotubular framework was assembled from cupric chloride, 1,2,4-triazolate and cyanurate, wherein the interconnection of trinuclear SBUs, $[Cu_3(\mu_3\text{-}O)(\mu_3\text{-}tz)_2(\mu\text{-}OH)]$ resulted in parallel-aligned single-walled nanotubes which are further linked through μ_3-bridged chloride and cyanurate moieties to form a 3D metal–organic network. This kind of 1D nanotube could be shown to originate from a 2D planar network and this provided a novel unprecedented strategy for the construction of metal–organic tubular structures. Preliminary characterization demonstrates the thermal stability of the whole framework, and further adsorption properties as well as design and synthesis of other nanotubular structures are under investigation.

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Notes and references

‡ Synthesis of **1**: A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.22 g, 0.9 mmol), Htz (0.042 g, 0.6 mmol), NaCl (0.029 g, 0.5 mmol), H_3CA (0.065 g, 0.5 mmol), aqueous ammonia (25%, 3 mL) and EtOH–H_2O (v/v 1 : 1, 3 mL) was stirred for 15 min in air, then transferred and sealed in a 23 mL Teflon-lined reactor, which was heated in an oven to 160 °C for 70 h. The oven was cooled to room temperature at a rate of 5 °C h^{-1}. The resulting violet cylindrical crystals were filtered, washed, and dried in air (yield *ca.* 80% based on Cu). Elemental analysis calcd (%) for **1** $C_{15}H_{34}Cl_2Cu_9N_{21}O_{17.50}$: C 12.59, H 2.39, N 20.55; found: 12.71, H 2.53, N 20.34%.

§ Crystal data for **1**: hexagonal, space group $P6_3/m$ (no. 176), M_r = 1431.39, a = 12.5396(3) Å, b = 12.5396(3) Å, c = 13.9133(6) Å, V = 1894.65(10) $Å^3$, Z = 2, D_c = 2.509 g cm^{-3}, $F(000)$ = 1412, μ = 5.188 mm^{-1}, 13 763 reflections measured, 1170 unique (R_{int} = 0.0226), final R_1 = 0.0306, wR_2 = 0.0825, S = 1.038 for all data; Data collection of **1** was performed at 294 K with Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART Apex CCD diffractometer, using frames of 0.3° oscillation ($2\theta \leq 56°$), the structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL software suite, *ca.* 1.42 independent disordered lattice water oxygen atoms (17 water molecules per unit cell) are located inside the tubular channels and deduced from multiple diffuse electron density peaks.

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