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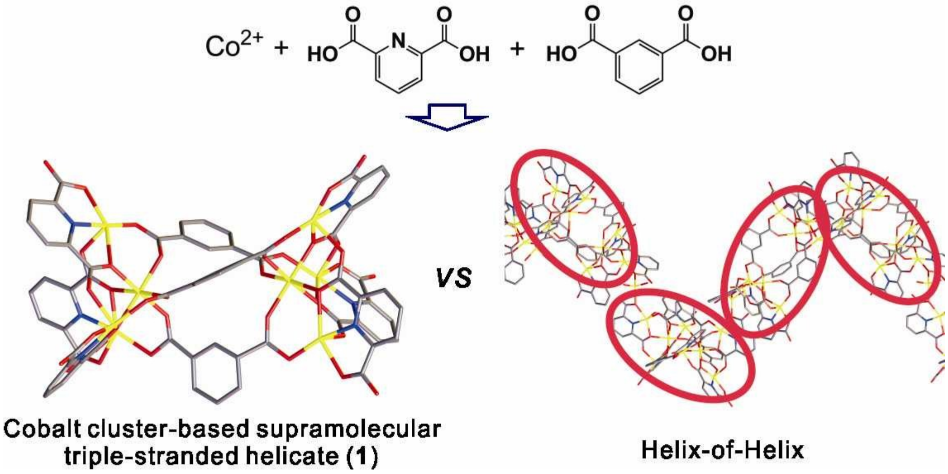
Graphical Abstract

Cobalt cluster-based supramolecular triple-stranded helicate (**1**) and helix-of-helix coordination structure (**2**) were successfully synthesized and fully characterized.



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COMMUNICATION

Synthesis of Cobalt Cluster-based Supramolecular Triple-Stranded Helicates

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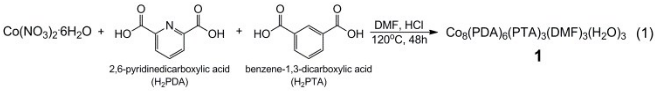
A cobalt cluster-based triple-stranded helicate, $Co_8(PDA)_6(PTA)_3(DMF)_3(H_2O)_3$ (1) (PDA = 2,6-pyridinedicarboxylate, PTA = benzene-1,3-dicarboxylate, DMF = dimethylformamide) was successfully synthesized and fully characterized. Complex 1 can be used as a supramolecular building block in constructing a higher-order helix-of-helix struture, $[Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4–0.51(Co(OH_n)_2)]$ (n = 1 or 2) (2).

Over the past decades, the use of supramolecular building blocks in constructing novel higher-order platforms, which have a high degree of symmetry and connectivity as well as intricate directional and structural information, has been extensively investigated. [1-4] These attributes are rarely attained in those constructed using the conventional molecular building block approach. The fabricated structures may enable the maximization of the number of unique functional sites in specific geometrical arrangements through rational supramolecular ligand design and appropriate self-assembly considerations. For example, metal-organic polyhedra and supramolecular building layers were rationally assembled to build metal-organic frameworks.[2] Supramolecular cyclic oligosaccharides (cyclodextrins) gave rise to three-dimensional polymeric structures, consisting of crystalline architectures and with properties inherent to natural products.[3,4] Although these examples are innovative, more advanced synthetic strategies are required to construct more variable supramolecular building block-based secondary polymeric organelles, which have multiple functional sites and unique structural properties. To construct metallosupramolecular building block-based polymeric conformations with higher-order structures, noncovalently bridging and chelating ligands capable of retaining the desired structural properties and extending the network can be employed.[5]

Supramolecular transition metal clusters, which can be assembled into outstanding secondary structures, are potential candidates for providing distinctive properties.[6-8] Varying the metal coordination geometry and the orientation of interaction sites in ligands can provide a controllable design strategy for the proposed metallosupramolecular clusters. The secondary assembly of primary clusters, which may be prepared by the self-assembly of metal ions and organic ligands, is an excellent strategy for fabricating higher-order networks. Herein, we report a novel cobalt cluster-based supramolecule, $Co_8(PDA)_6(PTA)_3(DMF)_3(H_2O)_3$ (**1**) (PDA = 2,6-pyridinedicarboxylate, PTA= benzene-1,3-dicarboxylate, DMF = dimethylformamide). The self-assembled coordination compound, which contains two different chelating ligands (PDA and PTA) and eight cobalt ions, exhibits a fascinating triple-stranded helicate as its primary structure. In addition, the one-dimensional helix-of-helix structure, $[Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4–0.51(Co(OH_n)_2)]$ (n = 1 or 2) (**2**), which comprises **1** as the basic building block with cobalt(II) ions serving as linkers, was successfully synthesized. In **2**, the tetrahedral cobalt ions connect the complex **1** moieties, thereby yielding a crystals with a secondary helix-of-helix structural motif.

Treatment of 2 eq. of $Co(NO_3)_2·6H_2O$, 1 eq. of 2,6-pyridinedicarboxylic acid (H_2PDA), and 1 eq. of benzene-1,3-dicarboxylic acid (H_2PTA) with HCl in DMF for 48 h at 120 °C led to the formation of $Co_8(PDA)_6(PTA)_3(DMF)_3(H_2O)_3$ (**1**), which was isolated as a purple crystalline product (48.7 % yield) (Eq. 1).



The structure of **1** in the solid state was determined by single-crystal X-ray diffraction (Figure 1 and S1, and Table S1-S3). The structure was solved and refined as the space group of P3(1)21. One of the PDA ligands was found to be disordered and thus was modeled in two different orientations. The solid state structure reveals that the two tetranuclear cobalt clusters, each bound by three PDA ligands, are interconnected via three PTA ligands. One of the carboxylate groups in the tridentate PDAs chelating to cobalt forms a μ-carboxylato bridge with the central cobalt atom. The three terminal Co(II) ions have an octahedral coordination

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Electronic Supplementary Information (ESI) available: detailed experimental methods and supporting data. See DOI: 10.1039/x0xx00000x geometry, which includes one nitrogen and two oxygens from the chelating PDA, one oxygen from the neighboring PDA, one oxygen from PTA, and one oxygen from either H_2O or DMF. The solid state structure of **1** also shows the coordination of H_2O and DMF molecules. However, the number of coordinating H_2O and DMF molecules is not the same in every synthesis, which leads to some discrepancies in the elemental analyses (Supporting Information). The central cobalt ion has an octahedral coordination geometry, with three oxygen atoms connected to the three bridging carboxylate groups of PDA and three to those of PTA. Due to the coordination of ligands, the central cobalts (Co1) could have +3 oxidation state. However, as the calculation of bond valence sums were conducted on using bond distances in the crystal structural data (Table S6),[9,10] the analysis suggests that the complex **1** only contain Co(II). The tetranuclear cobalt clusters are diagonally linked through three PTA ligands forming a novel metallosupramolecular cluster with helical geometry containing eight cobalt atoms, six PDAs, and three PTAs.

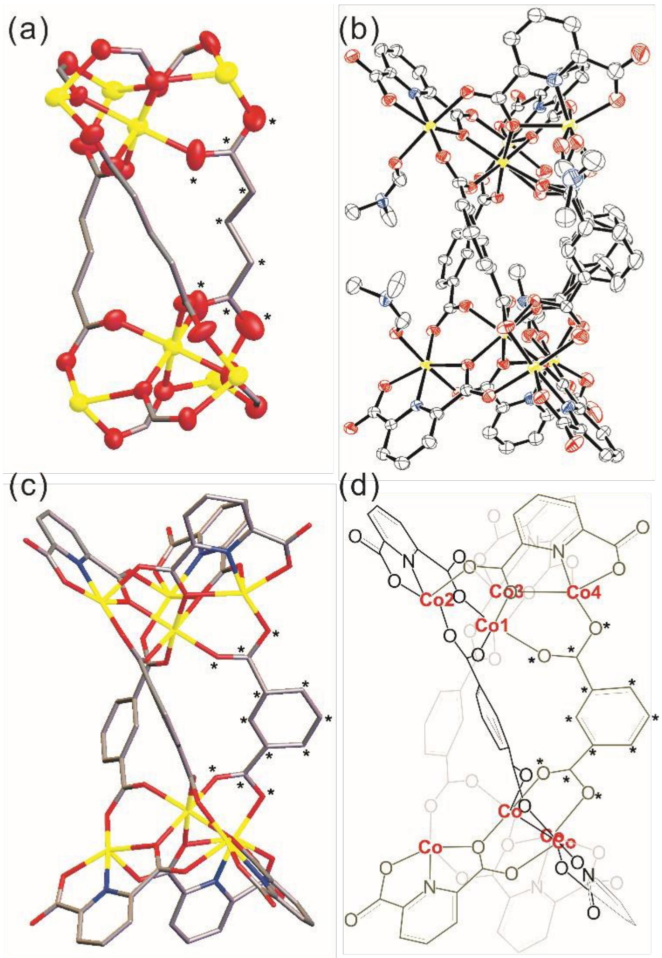

Fig. 1 Crystal structure of $Co_8(PDA)_6(PTA)_3(DMF)_3(H_2O)_3$ (**1**). (a) A ball-and-stick diagram of two tetranuclear cobalt clusters with the diagonal linkage through three PTA ligands shown schematically (yellow balls show cobalts and red ones show oxygens); (b) ORTEP drawing of **1** with 30% probability thermal ellipsoids; (c) a stick diagram of **1** (DMF and water molecules are omitted for clarity) and (d) a drawing of its molecular structure. (Disordered atoms were marked by asterisks (*))

Complex **1** is a distinctive example of a supramolecular cobalt cluster-based triple-stranded helical structure (helicate). There have been some synthetic examples of cobalt-based helical complexes.[11-14] In addition, transition metal-based triple-stranded helical compounds without cluster structures have been reported previously.[8, 15-19] Mainly oxygen- and nitrogen-donor ligands have been used to construct triple-stranded helicates, with the ligands coordinating to a single metal atom at the "hinge" sites. Recently, Severin and co-workers reported ruthenium cluster-based helicates prepared using bridging dihydroxypyridine ligands.[21-23] Complex **1** is an unique example of supramolecular transition-metal clusters, formed through the self-assembly of cobalt ions with two different organic ligands, H_2PDA and H_2PTA, which do not have any helical properties themselves.

It is worth pointing out that the tridentate PDA ligands are not symmetrically coordinated to the cobalt centers (Co1); one carboxylate of each PDA contains an unoccupied oxygen donor that is oriented to outwards. Therefore, this carboxylate oxygens on **1** may coordinate with other metal ions and generate secondary structures. The synthetic goal for this coordination mode was accomplished by using excess $Co(OAc)_2·4H_2O$ rather than $Co(NO_3)_2·6H_2O$ as the precursor. Treatment of $Co(OAc)·4H_2O$ (15 eq.) with, H_2PDA (6 eq.) and H_2PTA (3 eq.) in DMF/DMSO for 48 h at 120 °C led to the formation of a novel one-dimensional (1D) coordination structure, $[Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4–0.51(Co(OH_n)_2)]$ (**2**), which was isolated as a purple crystalline solid (44.5 % yield).[23] The solid state structure of **2**, which was determined by single-crystal X-ray diffraction, showed that this 1D structure is composed of **1** as a basic building block, with cobalt ions in tetrahedral geometry (Figure 2 and S2, Table S1, S4, and S5). Basically, the crystal structures of **1** and **2** are practically identical, except for the insertion of the $Co(OH_n)_2$ moiety in **2**. In particular, in the X-ray diffraction analysis, it is shown that Co5 has non-stoichiometric occupancy (0.51). The free carboxylates of **1** coordinate to these cobalt ions, which are also bound by two other oxygen atoms from OH_n ligands (Figure 2a). Although the hydrogen atoms on the OH_n ligands were not included in the refinement of calculated positions using group isotropic temperature factors, the lengths of the Co-O bonds are almost the same (Co5 – O22 = 1.99(2) (Å)) and are in the range of the Co-OH and Co-OH_2 bonds of cobalt complexes reported in the Cambridge Structural Database (CSD).[24] Further analyses to elucidate whether these L ligands are hydroxides or water molecules, were unsuccessful. Oxygen atoms from the tridentate PDA ligands in complex **1** form bonds with cobalt atoms, which are positioned at the "hinge" sites of the polymeric structure. Thermogravimetric analysis (TGA) of **2** under flowing N_2 gas shows multistep weight loss (Figure S4). The first weigh loss of 6.342% up to 168 °C corresponds to the loss of H_2O and DMF molecules that were coordinated within the structure. The next weigh loss of 64.06% up to 600 °C corresponds to the loss of PDA and PTA molecules ligated to the eight cobalt centers of the two tetranuclear cobalt clusters. In the powder X-ray diffraction pattern (PXRD) of **2**, the 100, 10-1, and 2-11 reflections appeared as sharp as the basal reflections, and there were no significant differences between the observed and expected patterns (Figure S10).

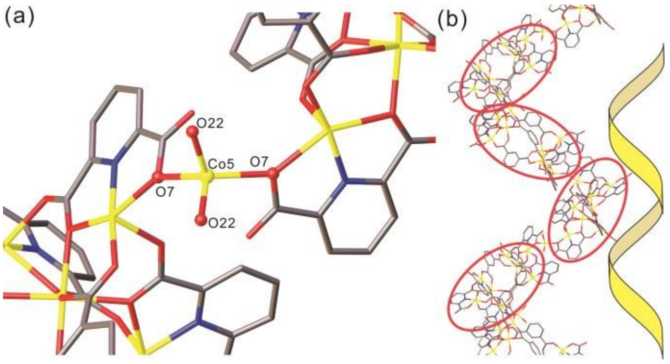

Fig. 2 (a) A ball-and-stick diagram of the tetrahedral cobalt(II) structure which connecting the two carboxylates of **1** in $[Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4–(Co(OH_n)_2)]$ (**2**); (b) crystal-structure (stick diagram) of **2** and depiction of its left-handed helical geometry. The red ovals depict the units of complex **1** that are positioned as building blocks.

Interestingly, in the solid state, complex **2** shows a left-handed S-helical structure with a pitch distance of 34.526 Å along the crystallographic c-axis (Figure 2b and 3a). In the crystalline networks, two S-helices intertwined to form a double-stranded helix with a half pitch distance of 17.246 Å (Figure 3b and c). Basically, the triple-stranded helicate **1**, which comprise the helical structure **2**, also have left-handed helical geometries. It is important that the primary structural information (helix) of a supramolecular building unit is successfully transferred, leading to the fabrication of the secondary left-handed helical 1D structure.

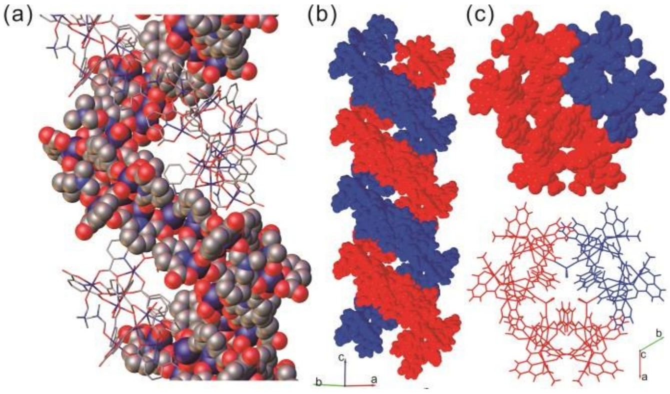

Fig. 3 Left-handed supramolecular helix along the crystallographic *c*-axis of **2**. (a) Space-filling and stick diagram of each single-stranded helix in the double helical structure; (b) side view of a double-stranded supramolecular helix in a space-filling model with the two single strands in red and blue, and (c) top view of the double-stranded supramolecular helix.

The higher-order structure often observed in biomolecules is critical to life. Examples include double stranded DNA, α-helices and β-sheets of proteins, and assembled protein structures such as ferritins.[25-29] Along with the great progress made in understanding these bio-structures over the past several decades, interest in designing and producing compact artificial structures with similar structural motifs has also grown rapidly. For example, fabrication of helical strands using organic or inorganic molecules (*i.e.* foldamers) can yield large structures with well-defined geometries.[30-34] Artificial mimics of the higher-order structure of biomolecules produced by the self-assembly of metal ions and simple organic ligands have opened a new area in supramolecular chemistry.[15-16,35-38] Fabrication of helical strands using helical supramolecular building blocks can yield functional polymeric structures with well-defined geometries.[39-41] The introduction of self-assembled helicates as building blocks in helical macromolecular structures may lead to new chiral and nonlinear properties.[15,42-43] Complex **2** is an unique example of the secondary helical structures composed of the supramolecular helicate building blocks (helix-of-helix), which could be an interesting mimic of the higher-order structure of biomolecules.

In conclusion, we have successfully synthesized a novel cobalt cluster-based supramolecule, $Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4$ (**1**) by the reaction of cobalt nitrate hexahydrate, H_2PDA, and H_2PTA. The tetranuclear cobalt clusters are diagonally linked through three PTA ligands to form a novel inorganic supramolecular triple-stranded helicate with left-handed helical geometry containing eight cobalt atoms, six PDAs, and three PTAs. An one-dimensional helix-of-helix structure, $[Co_8(PDA)_6(PTA)_3(DMF)_2(H_2O)_4–0.51(Co(OH_n)_2)]$ (n = 1 or 2) (**2**), which is composed of **1** as the basic building block, with cobalt(II) ions in tetrahedral geometry was also successfully synthesized and fully characterized. Due to the left-handed helical motif of complex **1**, coordination structure **2** also exhibits a left-handed S-helical geometry, with two S-helices intertwined to form a double-stranded helix.

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