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Rolling Up the Sheet: Constructing Metal–Organic Lamellae and Nanotubes from a $[\{Mn_3(propanediolato)_2\}(dicyanamide)_2]_n$ Honeycomb Skeleton

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Supporting Information

ABSTRACT: Target synthesis of metal–organic nanotubes (MONTs) through a classic "rolling-up" mechanism remains a big challenge for coordination chemists. In this work, we report three 2D lamellar compounds and one (4,0) zigzag MONT based on a common honeycomb coordination skeleton. Our synthetic strategy toward sheet/tube superstructure transformation is to asymmetrically modify the inter-layer interactions by gradually increasing the size of the amine templates. Eventually, to relieve the surface tension of individual layers and to enhance surface areas and optimize host–guest interactions to accommodate bigger guests, spontaneous rolling up to form a tubular structure was achieved.

The discovery of carbon nanotubes (CNTs), especially single-walled carbon nanotubes (SWNTs), in conjunction with their outstanding physical and chemical properties,[1] has stimulated extensive investigation into nanotubes of other compositions, such as metal oxides, metal chalcogenides, and organic compounds.[2] In general, the formation of these tubular structures can be regarded as the rolling-up conversion of their corresponding layered materials. For example, asbestos can form cylindrical or tubular structures at high temperature, and a rolling-up process is proposed to explain this.[3] The rationale is that a hybrid layered compound, in which the unit cell of one layer differs from that of the second layer, is likely to bend upon heating because of the anisotropic thermal strain on either side of the individual layers. Similar curling processes have also been observed in layered perovskites through the "foliation and rolling" mechanism: partial exchange of the K^+ and H^+ inter-layer counterions by bulkier tetra(*n*-butyl)ammonium (TBA^+) molecules enhances the inter-layer spacing and eventually causes the foliation of multilayer structures; such an unstable unilamellar phase spontaneously rolls up and forms a tubular structure.[4] Weak inter-layer contacts and strong intra-layer coupling are usually suggested to be necessary for constructing the corresponding single-walled nanotubes. Such a curling-up process is much more challenging to achieve for strongly coupled sheet compounds because the strong inter-layer interaction prohibits the peeling off of a sheet.[5]

Recently, there has been considerable interest in the assembly of metal–organic nanotubes (MONTs), stimulated by the well-defined crystal structures of the bulk material and potential applications in gas storage, catalysis, and molecular magnetism.[6] Although the "rolling-up" concept has been proposed for the formation of MONTs,[6h,k] this has so far not been experimentally observed either through rolling-up a lamellar bulk compound into a MONT or by unzipping a given MONT into its corresponding sheet structure. Indeed, sheet-to-tube conversion for coordination compounds is extremely difficult to achieve through a single-crystal-to-single-crystal transformation using lamellar compounds as precursors, because this procedure requires the deconstruction and reconstruction of a very large number of chemical bonds. It remains a big challenge for coordination chemists to synthesize coordination sheets and tubes based on a common coordination skeleton.

Inspired by the formation mechanisms of asbestos, perovskite, and related tubular structures, we thus hypothesize that, for a bilayered coordination compound with an ABAB structure and weak inter-layer interactions, the corresponding tubular structure could be achieved by introducing anisotropic chemical stresses between the layers. Herein, we report a series of coordination networks based on $[Mn_3(propandiolato)_2]$ building blocks and dicyanamide (dca) linkers, which exhibit identical (6,3) honeycomb connectivity. As the size of the amine templates is gradually increased, the inter-layer distance also increases, and the inter-layer contacts become more and more anisotropic for individual layers. Eventually, in order to relieve the different surface tension on the top and bottom surfaces of an individual layer, spontaneous rolling up and formation of a tubular structure could be achieved. To the best of our knowledge, this is the first time that a classic rolling-up strategy is accomplished in the synthesis of MONTs and also the first observation of a guest-induced sheet/tube supra-

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molecular isomerism in metal–organic framework (MOF) chemistry.[7]

Compound **1**, $(Me_3NH)[Mn^{II}_2Mn^{III}(L)_2(dca)_2Br_2(CH_3OH)_4]$, was isolated by the reaction of $MnBr_2$, H_2L, and Na(dca) in a mixture of methanol and ethyl acetate, in the presence of trimethylamine (Me_3N). The asymmetric unit of the crystal structure of **1** is shown in Figure 1a. Both H_2L ligands have been doubly deprotonated, with the alkoxy oxygens bridging between Mn^{III} and Mn^{II} centers to form an almost linear trinuclear $Mn^{II}_2Mn^{III}$ unit. Similar bridging has been previously observed in related Mn-1,3-diol systems.[8] It should be noted that the two tolylsulfamide groups are to the same side of the $Mn_3(\mu_2\text{-}O)_4$ mean plane; their N–H groups both form hydrogen-bonds to the same bromide ligand, Br(2). The $\{Mn^{II}_2Mn^{III}(L)_2Br_2(CH_3OH)_4\}$ is thus not centrosymmetric, but instead has an idealized mirror plane defined by the Mn, Br, and methanol O atoms. Each dca ligand bridges two Mn^{II} ions from different $Mn^{II}_2Mn^{III}$ units via its two terminal nitrogen atoms, such that each unit is connected to four others via Mn^{II}-dca-Mn^{II} linkages, forming a 2D layered architecture (Figure 1b). Each of the four methanol O–H groups forms a hydrogen-bond to Br(1) or Br(2); the O–H···Br and N–H···Br hydrogen-bonds are thus all between atoms in the same asymmetric unit. One of the sulfamide oxygens also accepts a hydrogen-bond from the N–H group of the slightly disordered Me_3NH^+ cation (Figure 1a).

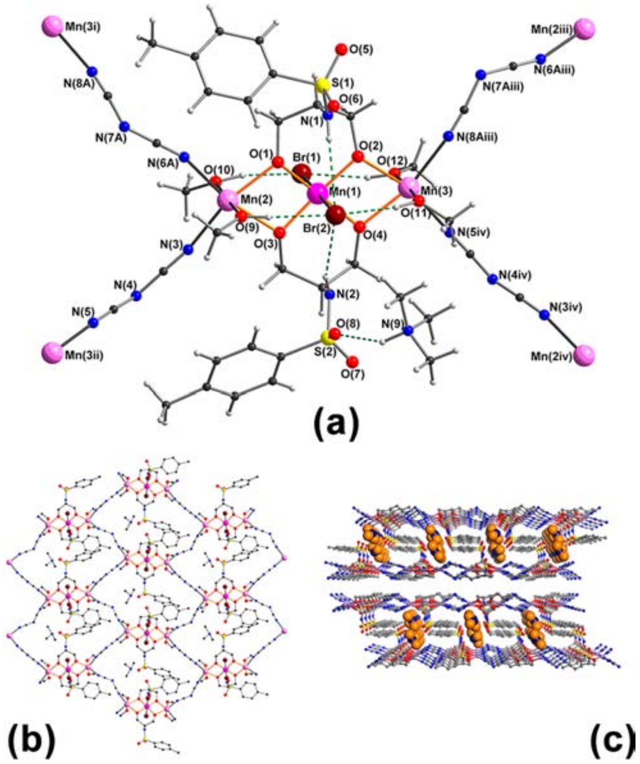

Figure 1. (a) The $(Me_3NH)[Mn^{II}_2Mn^{III}(L)_2(dca)_2Br_2(CH_3OH)_4]$ unit (**1**), highlighting the intra-trimer and host–guest H-bonds (dashed lines). (b) The honeycomb sheet of **1**. (c) ABAB stacking of the sheets, highlighting the amine counterions (C, dark gray; Mn^{II}, pink; Mn^{III}, purple; O, red; S, yellow; Br, brown; N, blue; H, light gray).

If we consider Mn^{II} ions as nodes in the lamellar structure, then these can be regarded as being linked by two types of linkers: (a) the alkoxo bridges and the Mn^{III} within the unit, and (b) the dicyanamide bridges between the units. If we represent these by orange and blue lines, respectively, then it is clear that the layers have a topology consisting of fused six-membered rings (see Table of Content, TOC). The plane of the $\{Mn_3(\mu_2\text{-}OR)_4\}$ moiety within the Mn_3 unit is in fact rotated about its Mn_3 axis by 29.7° out of the plane of the 2D sheet. As a consequence, the two sulfamide groups are not equivalent within the structure; the one containing S(2) is rather embedded within the hybrid 2D layer, whereas that containing S(1) is oriented with its tolyl group lying above one surface of the layer, and closely parallel to it. Consequently, the layers are thus anisotropic, and the inter-layer contacts are of two types (Figure 1c). However, neither of these sets of inter-layer interactions involves hydrogen-bonding or $\pi-\pi$ interactions. The layers are therefore primarily held stacked together by weak dipolar interactions between C–H groups (aromatic, or aliphatic adjacent to O) and either the bromide ligands or sulfamide oxygens, in addition to simple van der Waals interactions. Given the lack of stronger supramolecular interactions (hydrogen-bonding or $\pi-\pi$ stacking) between adjacent layers, the slightly puckered lamellar structure appears to be the stable form for this complex.

The size of the amine templates was then systematically increased. Using *N,N*-dimethylethylamine ($EtMe_2N$) or *N,N*-diethylmethylamine (Et_2MeN), we obtained $(EtMe_2NH)[Mn^{II}_2Mn^{III}(L)_2(dca)_2Br_2(CH_3OH)_4]$ (**2**) and $(Et_2MeN)[Mn^{II}_2Mn^{III}(L^1)_2(dca)_2Br_2(CH_3OH)_4]$ (**3**), respectively, under the same reaction condition as for **1**. The asymmetric units and extended 2D networks of both compounds are closely isostructural, with slight (but systematic) differences in unit cell dimensions (see Supporting Information (SI)). If one considers the two distinct inter-layer separations and defines the plane of a sheet as the mean plane of the metal atoms contained, then the inter-sheet separations for **1** are 10.52 and 7.10 Å, with the larger value corresponding to adjacent sheets with $(Me_3NH)^+$ cations intercalated between them, and the lower value to pairs of sheets not separated by these cations. For **2** and **3**, the corresponding values are 10.95 and 6.90 Å, and 10.96 and 6.96 Å, respectively. Increasing the size of the cation from $(Me_3NH)^+$ to $(EtMe_2NH)^+$ has, as might be expected, increased the corresponding inter-layer separation. However, additing the second CH_2 group to the cation in **3** did not result in a further increase in this separation. In **3**, the larger cation is accommodated by a swing of the tolylsulfamide pendants on the surface of the layer (Figures S1–S3). Such a rotation enhances the surface area to accommodate the bigger guest, but also dramatically weakens the host–guest H-bonding strength between the amine cations and the sulfamide, with the NH···O distance changing from 2.84 to 3.15 Å for **2** and **3**, respectively. Increasing the size of the amine templates also results in a slipping of the adjacent sheets. This shearing of the structure results in an increase in both the unit cell length *a* and the monoclinic angle *β* (see SI).

Using Et_3N as the template, $(Et_3NH)[Mn^{II}_2Mn^{III}(L)_2(dca)_2Br_2(CH_3OH)_{3.25}(OH_2)_{0.75}]\cdot{}^3/_4MeOH\cdot{}^1/_4H_2O$ (**4**) was isolated under the same reaction conditions as **1**–**3**. It crystallizes in the tetragonal space group *P*4/*n* with $Z = 16$ (see SI). The asymmetric unit of **4** (Figure S4) contains two $(Et_3N)^+$ cations and two trinuclear complex units, which are both closely isostructural to those in **1**–**3**. Although the trinuclear $Mn^{II}_2Mn^{III}$ complex units in **4** are also linked via dicyanamide linkers, the two independent units have $Mn_3(\mu_2\text{-}OR)_4$ mean planes that are mutually perpendicular, so that, in contrast to **1**−**3**, these linkages results in 1D tubular structures (Figure 2). According to the classification of CNTs,[1] this topology can be viewed as equivalent to a (4,0) zigzag nanotube, resulting from "rolling up" the 2D network in **1**−**3**. All the sulfamide groups are now directed toward the outside of the tubes. Of the two $(Et_3NH)^+$ cations in the asymmetric unit, one hydrogen-bonds to the sulfamide oxygen, and one is disordered across an inversion center and hydrogen-bonds to Br; the remaining half cation is inside the tube, extensively disordered by the four-fold symmetry axis. The mean outer diameter of the tube is given by $a/\sqrt{2}$ = 20.4 Å. Using a space-filling model, the accessible inner diameter is variable along the tube: "pinching in" to 3.5 Å between the bromide ligands, but expanding to 6.5 Å between the dicyanamide linkers.

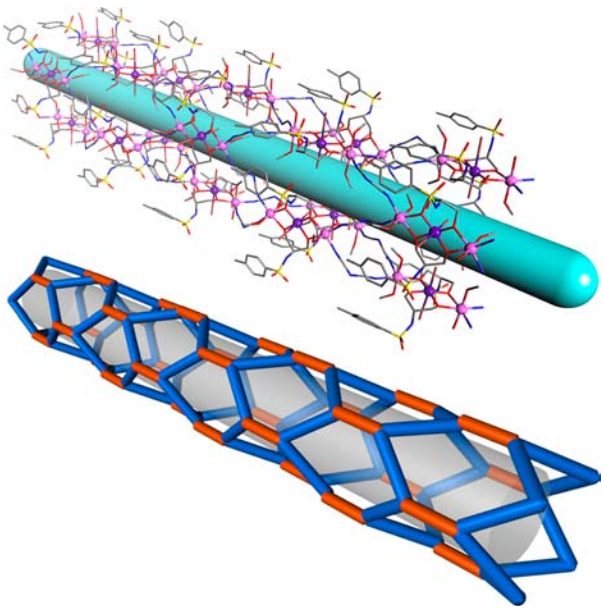

Figure 2. (Top) The 1D tubular structure resulting from linking the $Mn^{III}Mn^{II}_2$ units through dicyanamide bridges in **4**. (Bottom) The "(4,0) zigzag nanotube" topology resulting from linkage of the Mn^{II} nodes via dicyanamide (blue) and trinuclear complex (orange) linkers.

At this point, it must be asked why the relatively minor variations of the organic amine counterions have such dramatic effects on **3** and **4**. Throughout compounds **1**−**3**, varying the size of the amine countercations is counteracted by both increasing the inter-layer distance and subtle swinging of the tolylsulfamide pendants. If we sequentially increase the size of the amine templates, the hypothetical sheet aggregate would have to slip and further increase the inter-layer spacing to accommodate bigger guests. However, such an imaginary bilayer structure is thermodynamically unfavorable because of the increased inter-layer distance and the increased surface tension for the individual layers. As the result, the third CH_2 group added onto the template becomes the last straw that breaks the bilayer-stacking aggregates, and the honeycomb sheets are forced to roll up into tubes to enhance the surface areas and optimize host−guest interactions. The H-bonding strength between the amine cation and the sulfamide confirms this tendency, with the N−O distances 2.84, 2.84, 3.15, and 2.79 Å for **1**, **2**, **3**, and **4**, respectively. Theoretical calculations reveal the tendency toward increased surface areas from **1** to **4**, with the calculated values 190.6, 221.5, 261.5, and 373.2 Å^2 per unit cell for **1**, **2**, **3**, and **4**, respectively (see SI). It should be noted that there are multiple inter-tube supramolecular interactions in **4**, involving CH−O hydrogen-bonds and CH−π interactions (Figure S6). The cooperation of these weak interactions can then stabilize the "nanotube" structure, in preference to the less-puckered 2D structure found in **1**−**3**.

In conclusion, three 2D lamellar compounds and one (4,0) zigzag MONT from $[Mn^{II}_2Mn^{III}]$ building blocks and dca linkers are successfully prepared. For the first time, a classic rolling-up strategy is accomplished in the synthesis of MONTs, and the key factor is to asymmetrically verify the inter-layer interactions by increasing the size of the amine templates. Our results demonstrate that the spontaneous rolling-up process for bulk tubular compounds could be utilized in MOF chemistry, and we believe that our results could further the understanding of guest/template-induced supramolecular isomerism in dynamic supramolecular systems. In this system, it is quite plausible that armchair or chiral MONTs with tunable diameters could be obtained through further increasing the size of amine templates. This work is currently in progress in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional synthetic and structural details and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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