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Coordination Polymers of La(III) as Bunched Infinite Nanotubes and Their Conversion into an Open-Framework Structure

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Pyridine-2,6-dicarboxylic acid (pdcH_2) reacts with $LaCl_3{\cdot}7H_2O$ under hydrothermal conditions followed by evaporation at room temperature to give a metal–organic framework structure of the empirical formula, $[La(pdc)(H_2O)_4]{\cdot}Cl$ (**1**), in the form of infinitely long bunched nanotubes. The chloride ions and water molecules occupy the tubular as well as the inter-tubular spaces. When $La(NO_3)_3{\cdot}7H_2O$ is used in place of $LaCl_3{\cdot}6H_2O$, a similar structure is formed with the empirical formula, $[La(pdc)(H_2O)_4]{\cdot}NO_3$ (**2**), where water molecules and the nitrate anions occupy the voids as in the case of **1**. When an aqueous solution of $AgNO_3$ is added to an aqueous solution of **1**, the Cl^- ions are replaced completely by NO_3^- ions to form **2**; thus, the tubular structure is conserved. However, when $AgBF_4$ is used in place of $AgNO_3$, the tubular structure breaks down, and a new 3-D MOF structure, $[La(pdc)(pdcH)(H_2O)_2]{\cdot}4H_2O$ (**3**), is formed where the cavities are occupied by hexameric and dimeric water clusters. Structure **3** is also formed as the sole product when $La(OAc)_3{\cdot}xH_2O$ is treated with pyridine-2,6-dicarboxylic acid following the method adopted for **1** and **2**. Formation of the tubular structure depends on the molar ratio of the ligand and the metal. When higher than 1 equiv of the metal is taken, a linear coordination polymer, $[La_2(pdc)_3(H_2O)_6]{\cdot}2H_2O$ (**4**), is formed. This study provides the first nanotubular structure of a pure lanthanide metal.

Introduction

Synthesis of metal−organic framework (MOF) structures by the modular approach utilizes the coordination tendencies of the metal ions toward multi-dentate organic ligands. For transition metal ions, the directional properties of the *d* orbitals can dictate the mode of coordination. In contrast, the valence orbitals in lanthanides are buried inside; hence, these metal ions do not show a preference for a particular coordination geometry. The nature of the coordination modes should, therefore, be controllable by metal−ligand and inter-ligand steric interactions and also by the counteranion. Recent years have seen[1−6] an upsurge in the synthesis of lanthanide MOFs due to their potential applications as magnetic[7] and luminescent[8] materials, in selective gas absorption,[9] and so on.

Framework structures with open pores of different shapes and sizes are potentially useful in areas[10] such as molecular sieves, molecular devices, gas absorption, and catalysis, among others. Synthesis of such materials from metal ions and bridging organic ligands is often plagued by lattice interpenetration[11] or framework breakdown[12] upon the removal of guest molecules and low thermal stability of the host framework, etc. Therefore, current research efforts have

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been focused on the synthesis of robust open framework structures with high porosity and thermal stability.

The MOFs consisting of nanoscale metal rings occupy an important place in supramolecular chemistry.[13] These metal ring complexes can be tailored to act as secondary building units (SBU) that arrange themselves through supramolecular bonding to form nanotubular structures. Such open nanotubular frameworks are important in providing clues for understanding the mechanism of the assembly process leading to their formation and the host−guest chemistry associated with their large uniform internal diameter.

Considerable progress has been made in the synthesis of organic nanotubular architectures from cyclic peptides,14 cyclodextrins,[15] lipids,[16] and other related organic compounds.[17] The discovery of carbon nanotubes[18] has spurt research activities in inorganic nanotubular structures[19] containing elements other than carbon and different metal ions. However, only a few nanotubular coordination polymers are available in the literature. A nanotubular complex of Ag(I) with a flexible tripodal ligand, bearing pyridine moieties at the periphery, was reported[20] earlier. Since then, a nanotubular structure[21] of dodecanuclear Cd(II) was synthesized, where the metal rings joined via pyridine-4-carboxylate spacers. A large tubular open framework structure of germanate could be achieved[22] with the flexible tripodal ligand, tris(2-aminoethyl)amine, in a DMF/water mixture. Recently, solvothermal synthesis of tubular MOFs has been reported[23] with 3-amino-1,2,4-triazole or 3-amino-1,2,4-triazole-5-carboxylic acid and a number of Zn(II) salts. While only one 3d−4f heterometallic nanotubular molecular architecture was reported[24] recently, no other lanthanide tubular structure is available.

We have used pyridine-2,6-dicarboxylic acid (pdcH$_2$) as a rigid tecton, for synthesizing **1** and **2**. Earlier, we had shown[25] that when a lanthanide salt is allowed to react with pdcH$_2$ hydrothermally, infinite single helical chains with large widths and pitches are formed where each helix is further bonded on either side via carboxylate bridging producing 3-D metal−organic framework structures. Compounds **1** and **2** are formed when a large amount of water is used in the hydrothermal reaction showing that the reaction condition can lead to very different products even if the stoichiometry of the reactants remains the same. Both the tubular and the intertubular spaces in the structures are occupied by either Cl$^-$ or NO$_3^-$ anions. The tubular framework is quite robust as the Cl$^-$ ions in **1** can be completely replaced by NO$_3^-$ keeping the framework intact, although with other anions such as BF$_4^-$, the structure breaks down.

Experimental Procedures

Materials. Pyridine-2,6-dicarboxylic acid, AgNO$_3$, AgBF$_4$, La(NO$_3$)$_3$·6H$_2$O, LaCl$_3$·7H$_2$O, and La(OAc)$_3$·xH$_2$O were acquired from Aldrich and used as received.

Physical Measurements. Spectroscopic data were collected as follows: IR (KBr disk, 400−4000 cm^{-1}) Perkin-Elmer model 1320; X-ray powder pattern (Cu Kα radiation at a scan rate of 3°/min, 293 K) Siefert ISODEBYEFLEX-2002 X-ray generator; thermogravimetric analysis (heating rate of 10 °C/min) Perkin-Elmer Pyris 6. Microanalyses for the compounds were obtained from CDRI, Lucknow.

X-ray Structural Studies. Single-crystal X-ray data on **1**−**3** were collected at 100 K, on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The data integration and reduction were processed with SAINT[26] software. An empirical absorption correction was applied to the collected reflections with SADABS[27] using XPREP.[28] The structure was solved by the direct method using SHELXTL[29] and was refined on F^2 by the full-matrix least-squares technique using the SHELXL-97[30] program package. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in successive difference Fourier maps, and they were treated as riding atoms using SHELXL default parameters.

Single-crystal X-ray data on **4** was collected at room temperature on an Enraf-Nonius CAD4 Mach2 X-ray diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The cell parameters were determined by least-squares refinement of the diffractometer setting angles from 25 centered reflections that were in the range of $15° \leq 2\theta \leq 20°$. Three standard reflections were measured every hour to monitor the instrument and crystal stability. Because of the poor quality of the crystals of **4**, no appreciable diffraction was observed beyond 45° in 2θ; therefore, data collection was limited to 45°. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The

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Table 1. Crystal Data and Structure Refinement for **1**−**4**

	1	**2**	**3**	**4**
empirical formula	$C_7H_{11}ClLaNO_8$	$C_7H_{11}LaN_2O_{11}$	$C_{14}H_{19}LaN_2O_{14}$	$C_{21}H_{25}La_2N_3O_{20}$
formula weight	411.53	438.09	578.22	917.26
temperature (K)	100	100	100	293
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
crystal system	cubic	cubic	monoclinic	triclinic
space group	$Pa\bar{3}$	$Pa\bar{3}$	$P2_1/c$	$P\bar{1}$
a, Å	19.9818(6)	20.3661(5)	14.036(2)	10.456(3)
b, Å	19.9818(6)	20.3661(5)	11.229(3)	11.859(2)
c, Å	19.9818(6)	20.3661(5)	12.999(2)	13.731(3)
α (deg)	90	90	90	93.939(4)
β (deg)	90	90	101.983(5)	110.801(5)
γ (deg)	90	90	90	111.043(3)
V, $Å^3$	7978.2(4)	8447.4(4)	2004.1(14)	1447.4(11)
Z	24	25	4	2
ρ_{calc}, mg/m^3	2.056	2.067	1.916	2.105
μ, mm^{-1}	3.443	3.092	2.209	3.008
F(000)	4752	5088	1144	892
reflns collected	10703	52214	12514	4043
independent reflns	3182	3493	4753	3794
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
GOF	1.304	1.189	1.074	1.060
final *R* indices	R1 = 0.0933	R1 = 0.0462	R1 = 0.0284	R1 = 0.0353
$[I > 2\sigma(I)]$	wR2 = 0.2352	wR2 = 0.1295	wR2 = 0.0684	wR2 = 0.0911
R indices	R1 = 0.0976	R1 = 0.0482	R1 = 0.0303	R1 = 0.0491
all data	wR2 = 0.2373	wR2 = 0.1304	wR2 = 0.0694	wR2 = 0.0967

structures were solved by the direct method using SIR-92[31] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97 program package. The non-hydrogen atoms were refined anisotropically. The H atom positions or thermal parameters were not refined but were included in the structure factor calculations. The crystal data for the four structures are given in Table 1.

Synthesis. [La(pdc)(H_2O)$_4$]·Cl, 1. Standard hydrothermal conditions did not afford compound **1**. A different approach was adopted for its synthesis. In a typical experiment, 1 mmol of $LaCl_3·7H_2O$ and 2 mmol of pyridine-2,6-dicarboxylic acid ($pdcH_2$) and a few drops of triethylamine were taken in 10 mL of water in a Teflon-lined autoclave. The autoclave was heated under autogenous pressure to 180 °C for 3 days and then left to cool to room temperature. The colorless liquid from the autoclave was filtered and allowed to evaporate at room temperature, whereupon colorless prismatic crystals of **1** could be isolated in ~45% yield. Anal. Calcd. $C_7H_{11}N_1O_8ClLa$: C, 20.43; H, 2.69; N, 3.40%. Found: C, 21.01; H, 2.52; N, 3.56%.

[La(pdc)(H_2O)$_4$]·NO_3, 2. When $La(NO_3)_3·6H_2O$ was taken in place of the chloride salt keeping the hydrothermal reaction condition same as in **1**, compound **2** could be isolated in ~50% yield as colorless prismatic crystals. Anal. Calcd. $C_7H_{11}N_2O_{11}La$: C, 19.19; H, 2.53; N, 6.39%. Found: C, 19.81; H, 2.61; N, 6.52%.

[La(pdc)(pdcH)(H_2O)$_2$].4H_2O, 3. When ~1 mmol of $La(OAc)_3·xH_2O$ and 2 mmol of pyridine-2,6-dicarboxylic acid ($pdcH_2$) were taken keeping the hydrothermal reaction condition the same as in the case of **1** or **2**, compound **3** could be isolated as rectangular parallelopipeds in ~55% yield. Anal. Calcd. $C_{14}H_{19}N_2O_{14}La$: C, 29.08; H, 3.31; N, 4.84%. Found: C, 28.89; H, 3.53, N, 4.91%.

[La_2(pdc)$_3$(H_2O)$_6$]·2H_2O, 4. When 1 mmol of $LaCl_3·7H_2O$ and 1 mmol of pyridine-2,6-dicarboxylic acid ($pdcH_2$) and a few drops of triethylamine in 5 mL of water were heated under autogenous pressure to 180 °C for 3 days and allowed to cool to room temperature, colorless crystals of **4** could be isolated in ~35% yield. No crystalline product could be isolated on evaporation of the filtrate. Anal. Calcd. $C_{21}H_{25}N_3O_{20}La_2$: C, 27.49; H, 2.74; N, 4.58%. Found: C, 27.16; H, 2.81, N, 4.34%.

Results and Discussion

All four compounds are stable in air, and high yields of the products indicate that these compounds are thermodynamically stable under the prevailing reaction conditions. They are moderately soluble in water but insoluble in common organic solvents. Each shows strong infrared absorption bands between 1350 and 1550 cm^{-1} that are diagnostic[25] of coordinated carboxylates.

A summary of crystal data, intensity measurements, structure solution, and refinement for all the four compounds are collected in Table 1. The asymmetric unit of [La(pdc)(H_2O)$_4$]·Cl (**1**) consists of a [La(pdc)(H_2O)$_4$]$^+$ cation and three Cl^- anions. Each anion position is coincident with a 3-fold crystallographic symmetry. The structure is built from hexanuclear metal rings with a diameter of 11.81 Å. The six La(III) ions are arranged in a circular fashion through bridging carboxylates (Figure 1), where each La(III) ion

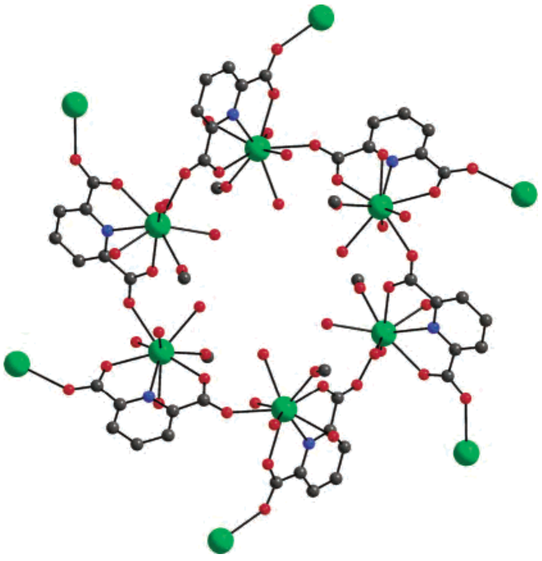

Figure 1. Perspective view of a carboxylate bridged metal ring showing six La(III) ions.

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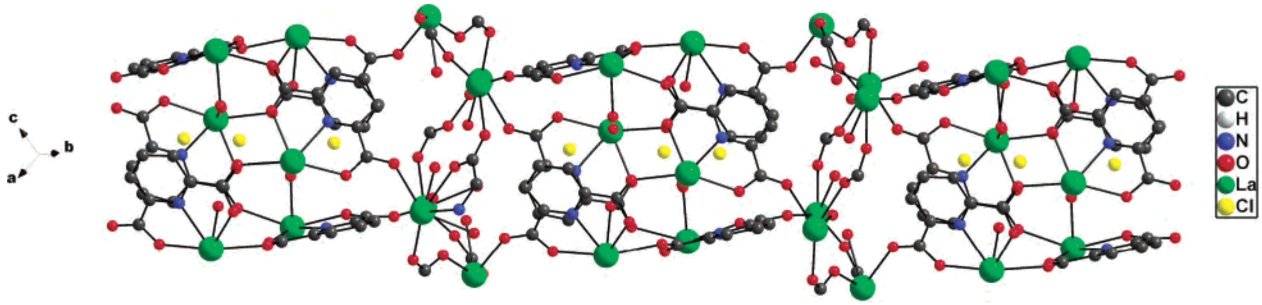

Figure 2. Side view of an infinite nanotubular structure of **1** showing Cl^- ions inside the tube as a solid circle.

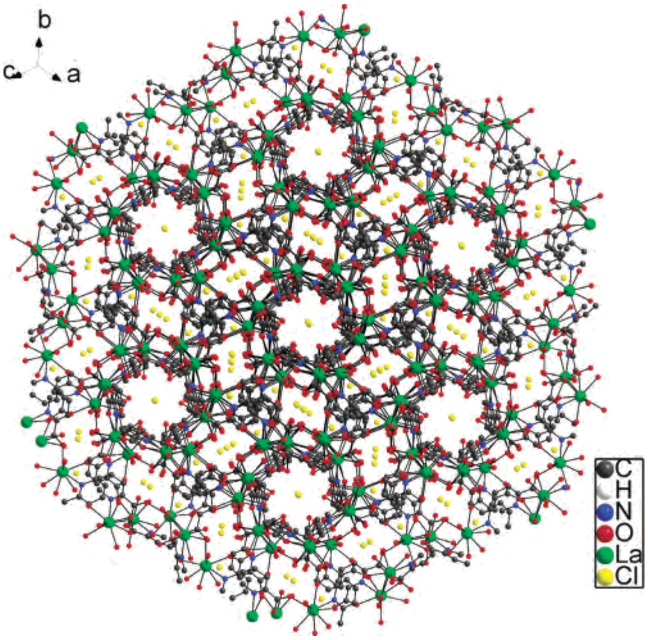

Figure 3. Perspective view of the structure of **1** showing each nanotube and its surroundings.

shows 9-coordination binding of one pdc^{2-}, two bridging carboxylate O, and four water molecules (NO_8 donor set). Out of the four H_2O molecules, one is pointing to the center of the tube. These rings are connected through carboxylate groups that bridge the metal ions resulting in an infinite nanotubular framework (Figure 2). Each nanotube is surrounded by six other identical nanotubes showing a distance of 19.9 Å between the centers of any two tubes (Figure 3). The tubular as well as inter-tubular spaces are not empty but occupied by Cl^- anions. Each Cl^- anion inside the tube is held through hydrogen bonding with three metal-bound water molecules showing a Cl···O distance of 3.06 Å. The Cl^- ions in the inter-tubular spaces are involved in intricate hydrogen-bonding interactions with carboxylate and water, with Cl···O distances within 3.1 Å. The La(III)−O and La(III)−N distances in **1** are similar to those found in other complexes,[25] while all the distances and angles involving the ligand are within normal statistical errors. Coordination geometry around each metal ion is distorted from the D_3 symmetry due to ligand-imposed restrictions as well as the overall architecture.

The structure of $[La(pdc)(H_2O)_4]\cdot NO_3$ (**2**) is very similar to that of **1** with the exception that the NO_3^- anions occupy the spaces in place of Cl^-. The asymmetric unit consists of the $[La(pdc)(H_2O)_4]^+$ cation and three nitrate anions. The positions of the N atom of the nitrate anion inside the tube are coincident with crystallographic 3-fold inversion symmetry, and six O atoms are bonded to this N due to crystallographically imposed symmetry. The other two nitrate anions are disordered. The diameter of each nanotube is calculated to be 11.65 Å, while the approximate distance between the central tube and its neighbor is 19.9 Å, both of which are very similar as compared to **1**. This shows that the tubular structure is conserved in the two cases. All bond distances and bond angles in **2** including the coordination geometry of each metal are quite similar to those found in **1**. The NO_3^- ion inside the tube shows positional disorders for the O atoms and is hydrogen-bonded to six water molecules showing O···O distances of 2.714 and 2.816 Å. The NO_3 ions in the inter-tubular spaces are hydrogen bonded to the nearest water molecules.

To probe whether Cl^- ions in **1** can be replaced by other anions, keeping the overall tubular structure intact, it was treated with $AgNO_3$ or $AgBF_4$. On treatment of **1** with stoichiometric amount of $AgNO_3$ in water at room temperature, a white precipitate of AgCl forms readily. After removing AgCl formed in the reaction, the clear filtrate was allowed to evaporate at room temperature, which afforded a crystalline product in over 85% yield (with respect to the amount of **1** taken). The structure of this compound was found to be identical to that of **2**.

However, when **1** was treated with a stoichiometric amount of $AgBF_4$, the tubular structure broke down and the compound, $[La(pdc)(pdcH)(H_2O)_2]\cdot 4H_2O$ (**3**), was obtained in ~70% yield (calculated with respect to **1**), on evaporation of the filtrate at room temperature. Compound **3** can also be obtained when $La(OAc)_3\cdot xH_2O$ and $pdcH_2$ (1:2 molar ratio) are treated hydrothermally, using the same reaction conditions as used in the case of **1** and **2**. The breakdown of the tubular structure in the presence of the BF_4^- or OAc^- ion is due to the fact that hydrogen-bonding interactions with metal-bound water molecules are negligible with these ions. This particular type of hydrogen-bonding interaction is crucial for driving the reaction to the tubular structure. It is also observed that when 2 equiv of NaCl or $NaNO_3$ is added to the reaction mixture of $La(OAc)_3\cdot xH_2O$ and $pdcH_2$, only compound **3** can be isolated. It follows, therefore, that the tubular structure does not form if an anion such as OAc^- is present in addition to Cl^- or NO_3^-.

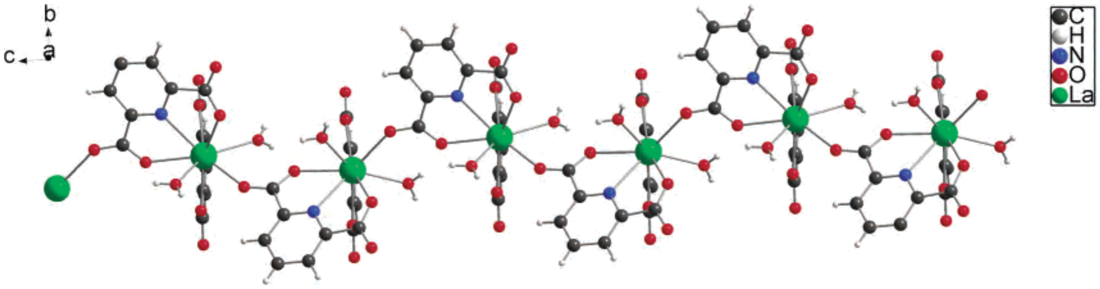

Figure 4. Linear coordination polymeric chain extending along the crystallographic *c* axis in **3**.

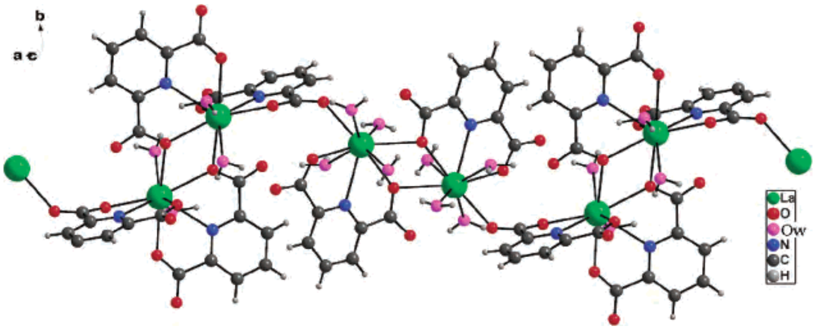

Figure 5. View of the polymeric chain built from dimeric units in **4**.

The structure of [La(pdc)(pdcH)$(H_2O)_2$]$\cdot 4H_2O$ (**3**) consists of linear chains of La(III) ions, where each metal shows 9-coordination binding two pdc^{2-} ligands, one bridging carboxylate O atom from a neighboring pdc^{2-}, and two water molecules (Ow1,Ow2). For charge neutralization, one of the ligands exists[32] as (pdcH)$^{-}$ although the hydrogen associated with the carboxylic acid could not be located in the difference map. The bridging carboxylate propagates the polymeric chain approximately along the crystallographic *c* axis (Figure 4). The structure of **3** is quite similar to that of the Pr(III) or Ce(III) coordination polymers of the same ligand reported by others[32a] as well as by us.[32b]

We have also found that formation of the tubular structure depends on the molar ratio of the ligand and the metal. When higher than 1 equiv of the metal is taken, a linear coordination polymer, $[La_2(pdc)_3(H_2O)_6]\cdot 2H_2O$ (**4**), can be isolated as the sole product. The structure of **4** consists of 1-D coordination polymeric chains of 9-coordinate La(III) ions. Each polymeric chain is built from dimeric units of La(III) connected through coordination bonding (Figure 5). There are two types of dimeric units present in the chain. For the first type, each La(III) ion is bonded to two pdc^{2-} and two water molecules. The two metal ions show double bridging of carboxylate thus attaining 9-coordination where the metal−metal distance is found to be 4.46 Å. In the second type, each metal ion binds one pdc^{2-}, one carboxylate from the other dimer, and four water molecules. The metal−metal distance in this case is found to be 4.57 Å. The coordination geometry around each metal ion has a slightly distorted D_3 symmetry. The vacant spaces between the two chains are not empty but contain water molecules that are hydrogen bonded to the carboxylate O atoms (Figure 6). Isolation of this compound suggests that a change in the hydrothermal conditions can lead to very different structures. This is because in La(III), the valence orbitals are buried inside, and there is significantly less metal−ligand interactions offering possibilities for a ligand to bind the metal ion in different ways.

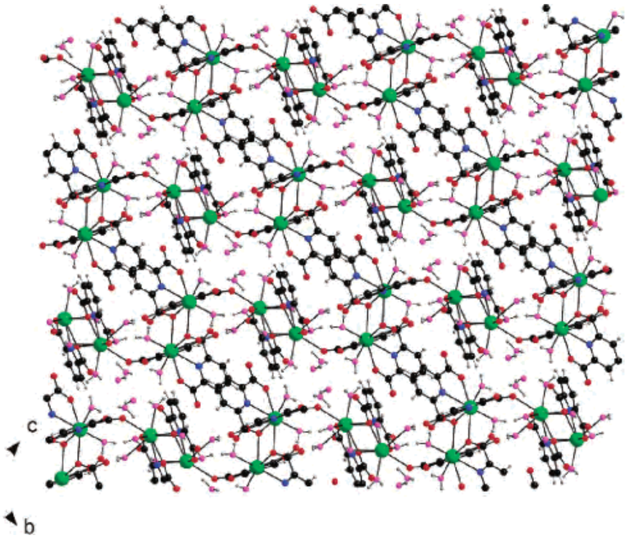

Figure 6. MOF structure of **4** viewed in the *bc* plane.

Structural studies have shown that the tubular structure in **1** and **2** results from multiple hydrogen-bonding interactions between the metal-bound water molecules and the anion. This association is quite strong as thermogravimetric analysis of **1** shows an onset of weight loss at 80 °C that continues up to ~150 °C, showing a ~15% weight loss corresponding to the removal of all the water molecules present in the lattice. Thereafter, no weight loss is observed till 450 °C, suggesting robustness of the material. The result of the thermogravimetric analysis for **2** is very similar. Drastic changes are

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[32] (a) Nobuo, O.; Hasuyo, K.; Ayumi, F. *Acta Crystallogr. E* **2002**, *E58*, m354. (b) Ghosh, S. K.; Bharadwaj, P. K. *Inorg. Chem.* **2003**, *42*, 8250.

observed in the X-ray powder diffraction patterns of either **1** or **2** taken before and after water removal. This is expected as the removal of water molecules would lead to a breakdown of the tubular structure. The 3-D structure of **3** is largely a consequence of hydrogen-bonding interactions between the water molecules and the MOF. The metal-bound water molecules are tightly held with the rest of the molecules of the water cluster. The thermal gravimetric analysis of **3** shows that weight loss occurs in stages beginning at 80 °C, and the loss of ∼19% corresponding to all of the water (calculated 18.68%) takes place above 170 °C. The complete decomposition of the compound is achieved above ∼500 °C. The association of water molecules with the MOF in **4** is found to be as strong as in the other cases. Thermogravimetric analysis of **4** shows that the loss of water molecules starts at ∼110 °C and completes only above 220 °C. The exclusion of water from the lattice leads to a breakdown of the 3-D structures of **3** and **4** as major changes are observed in the X-ray powder diffraction patterns taken before and after water exclusion.

The FT−IR spectrum of **3** shows a broad band centered around 3400 cm^{-1} attributable[25] to the O−H stretching frequency of the water cluster. This broad band vanishes on heating the compound under vacuum (0.1 mm) at 160 °C for 2 h. Deliberate exposure to water vapor for 3 days does not lead to reabsorption of water into the lattice as monitored by FT−IR spectroscopy. The FT−IR spectrum of compound **4** also exhibits a broad peak around 3400 cm^{-1} due to the O−H stretching frequency of the water cluster.

Conclusion

In conclusion, we describe here two nanotubular structures of La(III) with pyridine-2,6-dicarboxylic acid. The formation of the tubular structures depends on the reaction conditions as well as the counteranion. These structures are formed only in the presence of chloride or nitrate anions, which are involved in a strong hydrogen-bonding interactions with the metal-bound water molecules that drive the formation of the tubular structure. The chloride ions can be replaced completely by nitrate anions, keeping the overall structure intact. Other anions such as BF_4^- and OAc^- disrupt the tubular structure and form a zigzag 2-D framework. The 2-D frameworks are joined by a combination of hexameric and dimeric water clusters leading to the overall 3-D MOF. Interestingly, when an excess of Cl^- or NO_3^- anions is added as the Na salt to a solution of $La(OAc)_3$ and the ligand (i.e., filtrate from hydrothermal reaction), no tubular structure is formed. Presently, we are investigating formation of tubular structures with other metal−ligand ensembles.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **1**−**4** and IR, TGA, and X-ray powder diffraction patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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