Coordination Nanotubes

Columnar Supramolecular Architecture Self-Assembled from S_4-Symmetric Coordination Nanotubes Encapsulating Neutral Guest Molecules**

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Synthetic tubular architectures are of broad interest in the fields of materials science, nanotechnology, molecular sieves, ion sensors, and fluidic transport systems. Inorganic nanotubes consisting of pure carbon,[1] boron nitride,[2] metal dichalcogenides,[3] and other layered materials[4] have been the focus of many research efforts and, similarly, many advances have been reported in the realm of organic nanotubular ensembles.[5] For example, open-ended hollow nanotubes have been created from cyclic peptides,[6] lipids,[7] oligocyclodextrins,[8] and related organic systems,[9] and have been investigated for their potential applications. Inorganic/organic coordination nanotubes, on the other hand, remain largely unexplored in spite of the fast moving developments in the area of self-assembled inorganic/organic molecular and polymeric architectures.[10]

Recently, the columnar channels in a number of tubular coordination networks were created by the connection of macrocyclic molecules.[11] To date, and to the best of our knowledge, discrete coordination nanotubes have only been reported by Fujita and co-workers.[12] These tubular structures, templated by rod-shaped guest molecules, were obtained by the reaction between oligo(3,5-pyridine)s and ethylenediamine-protected Pd^{II} ions. We report herein a similar discrete coordination nanotube formed from Hg^{II} ions and a semirigid ditopic ligand.

In recent studies we demonstrated control over product formation—either coordination polymers or metallamacrocycles—by utilizing semirigid di- or tritopic benzimidazolyl-based ligands. The choice of ligand structure and morphology provided us with selective control over the product type, and was accomplished by the designed adjustment of the location and spatial extent of the tethered benzimidazolyl rings by using a variety of different cores or spacers.[13] Herein we describe the synthesis and characterization of a novel coordination architecture—a neutral tetranuclear nanotube $[Hg_4Cl_8(bbimms)_4]$ (**1**)—assembled from $HgCl_2$ and the semi-

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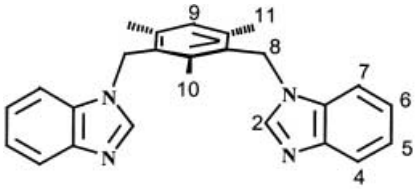
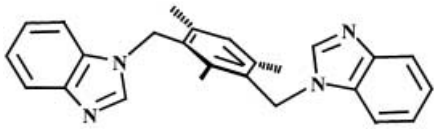
rigid ditopic ligand 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (bbimms).

The semi-rigid bbimms ligand is capable of adopting either the *syn* or the *anti* conformation depending on the orientation of the two benzimidazolyl arms. These two



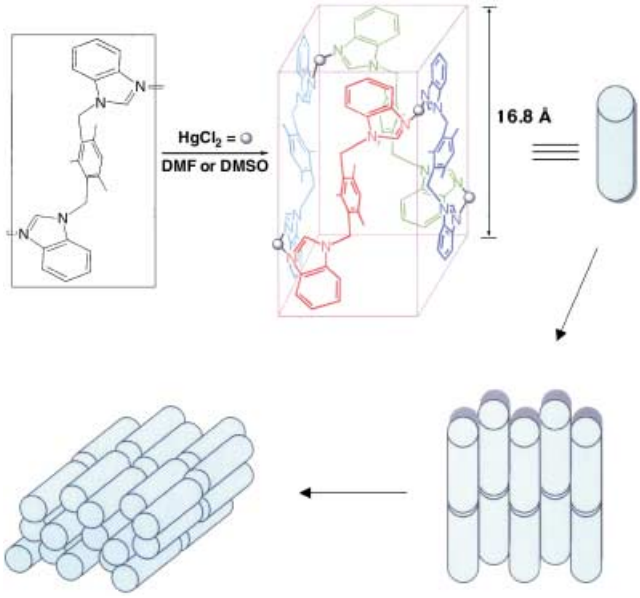
syn conformation



anti conformation

conformations lead to the formation of complexes with completely different structural topologies that are further shaped by the coordination preference of the metal ion used. When metal ions with inherent C_2 (linear) or C_4 (square-planar) symmetry, such as Ag^{I} or Pd^{II}, were used without blocking ligands, the bbimms ligand was found to take on the *syn* conformation and generate dinuclear metallacycles with a rectangular or tetragonal prismatic shape.[14] On the other hand, when metal cations that favor bent coordination environments, such as Hg^{II}, were treated with bbimms, it was observed that the ligand inevitably bridges the ions in an *anti* conformation to form discrete tubular tetramers by self-cyclization, as in **1** (Scheme 1).

Under carefully controlled conditions the straightforward reaction is nearly quantitative. Combining bbimms with $HgCl_2$ in a MeOH/MeCN (1:1 v/v) solution leads to the rapid precipitation of a solid crystalline product whose structure has not been fully characterized.[15] However, this poorly crystalline intermediate has a structure different from that of **1**, as evident from the analysis of powder X-ray diffraction data (see Supporting Information). The addition of DMF or DMSO while heating results in the rapid dissolution of this precipitate, and the subsequent formation of colorless octahedral-shaped crystals suitable for single-crystal X-ray analysis occurs upon letting the solution sit for several days at ambient conditions. The uniform appearance (see Supporting Information) of all the crystals suggested the presence of one single phase, an assumption that was validated by powder X-ray diffraction measurements. The observed diffraction pattern closely matches the intensities and exactly matches the peak positions of the pattern



Scheme 1.

simulated using the single-crystal structure data (see Supporting Information).

The tubular structure of **1** was unambiguously established by single-crystal X-ray diffraction analysis, which also determined that **1**·2 DMF and **1**·2 DMSO are isostructural and differ only in the nature of guest molecules (DMF or DMSO). In both cases, systematic absences in the intensity data were consistent with the space group $I4_1/a$. The $[Hg_4Cl_8(bbimms)_4]$ cage is situated about a $\bar{4}$ site (0,1/4,1/8), and consequently has crystallographically imposed S_4 point symmetry. The asymmetric unit contains one $HgCl_2$ unit, one bbimms ligand, and half of one encapsulated DMF or DMSO molecule of crystallization that is disordered over a twofold rotational axis. Thus, as shown in Figure 1, a neutral tubular structure $[Hg_4Cl_8(bbimms)_4]$ is generated by self-cyclization of four $[HgCl_2(bbimms)]$ subunits whose orientation alternates successively up and down. This molecular tube consists of an approximately rectangular-prismatic shape with four S_4-symmetrically arranged Hg^{II} ions occupying the four edges while four bbimms ligands occupy the four faces of the rectangular prism. The bbimms ligand has to take on the *anti* conformation to achieve this structural topology. In fact the two benzimidazolyl rings of the ligand are nearly coplanar (dihedral angle 16.8°) and perpendicular to the bridging mesityl group (dihedral angles 95.6 and 79.0°, respectively), and exist in the expected *anti* conformation. The Hg^{II} ions are in the common distorted tetrahedral geometry[16] with a Cl-Hg-Cl angle of 115.97(3)° and an N-Hg-N angle of 101.96(10)°, which is necessary for completing this rectangular tube structure.

The overall dimensions of the molecular tube can be estimated from the length of the ligand and the separation between the parallel benzimidazolyl rings, and yields an approximate interior cavity of $4.6 \times 8.6 \times 16.8$ Å after consideration of the van der Waals radii (C 1.71, H 1.16, N 1.52 Å).

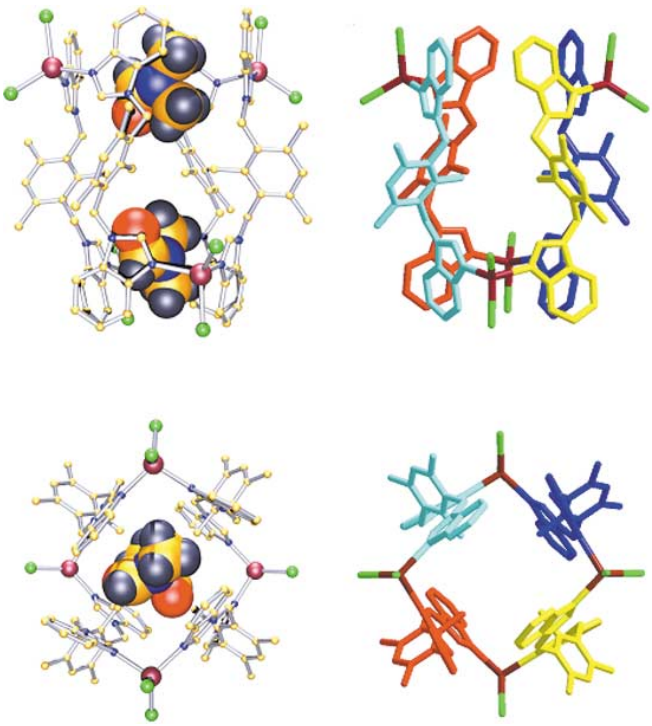


Figure 1. Representation of the $[Hg_4Cl_8(bbimms)_4]$ nanotube with (left) or without (right) guest molecules, which are shown in a space-filling mode.

Consequently, the diameter of a molecule that can enter the cavity is on the order of 4 Å. This cavity is further subdivided into two rectangular compartments (see Supporting Information) that are separated by four methyl groups (5.9 Å apart) pointing to the center of the tube, thus restricting the passage of large guest molecules through this bottleneck. One disordered guest molecule, either DMF or DMSO, is found in each compartment and leads to a stoichiometry of **1**·2 DMF or **1**·2 DMSO, respectively. Despite the disorder, identification of the guest molecules is readily accomplished by other characterization techniques. The IR spectra of **1**·2 DMF and **1**·2 DMSO display almost identical patterns of absorption peaks that can be assigned to the ligand. As expected, there is a strong $\tilde{\nu}_{C=O}$ vibration observed at 1670 cm^{-1} for **1**·2 DMF and a $\tilde{\nu}_{S=O}$ vibration at 1061 cm^{-1} observed for **1**·2 DMSO, which is indicative of DMF and DMSO molecules, respectively. Further information supporting the structure was obtained by ^{1}H NMR spectroscopy: while **1**·2 DMF exhibits two CH_3 signals at 2.88 and 2.76 ppm in its spectrum **1**·2 DMSO exhibits one CH_3 signal at 2.519 ppm. Thermogravimetric (TGA) analysis of **1**·2 DMF and **1**·2 DMSO suggests that the tubes are thermally stable up to 200 °C. The guest molecules are lost between 200–220 °C, and a massive weight loss in the 220–360 °C range is indicative of sample decomposition.

It is evident from the above discussion that the guest molecules, either DMSO or DMF, play an important role in the formation and stabilization of the tube structures. In addition to dissolving the intermediates formed in the MeOH/MeCN mixture, they appear to participate in what Fujita et al. termed "guest-induced assembly,"[17] which can be monitored by NMR spectroscopy.

The ^{1}H NMR spectra of **1** and **2** recorded in warm CD_3CN exhibit a single set of well-resolved proton signals (slightly broadened relative to those of the free ligands). All of the proton resonances are shifted downfield except for those of the H10 atoms belonging to the methyl groups pointing into the center of the tube, which are shifted upfield. These data support both the hypotheses that metal complexation occurs and that, based on the unusual upfield shift of H10, the tube structure is retained in the CD_3CN solution. Interestingly, the chemical shifts of DMSO or DMF remain unchanged relative to those of the free molecules, which indicates that the guest molecules are free to move. Any conclusion concerning the retention of the tube structure in solution based on ^{1}H NMR spectroscopy alone is, of course, rendered less certain by the known lability of the Hg–N bond. The experiment of choice to settle this issue, electrospray mass spectroscopy analysis, proved uninformative, and alternative investigations of the solution structure and dynamics by temperature-dependent NMR spectroscopy are precluded by the sparing solubility of **1** and **2** in common solvents. Nonetheless, the available data, plus the fact that these complexes form only in the presence of DMSO and DMF (numerous other solvents were tried unsuccessfully), favor the suggestion that these tube structures, once formed by guest-induced assembly, can survive in solution even after removal of the guest.

In addition to the intrinsic interest in this type of discrete molecular tube $[Hg_4Cl_8(bbimms)_4]$, there are other notable features resulting from its crystal packing mode. Figure 2 shows an extended view of the crystal packing in the [100] and [001] planes. It is fascinating to observe that all the tubes line-up to generate a pipeline structure that extends along the *c* direction. These pipes stack side-by-side in the [100] plane to form a layer, and the overlap of such layers in the *b* direction generates a three-dimensional columnar architecture. One potential driving force for the alignment of the tubes might be the weak Cl···H–C hydrogen-bonding interactions[18] (Cl1···H1 2.786 Å, Cl1···H1–C1 165.6°, Cl2···H6 2.735 Å, Cl2···H6-C6 152.6°) that exists between adjacent tubes. In fact, every tube is held in place by sixteen Cl···H–C hydrogen bonds that stabilize the resulting columnar architecture. The tubular stacking arrangement in $[Hg_4Cl_8(bbimms)_4]$ represents potential transport pathways for small molecules, which is of interest in the context of natural and artificial membrane structures.[5]

In summary, a neutral coordination nanotube was assembled from four $HgCl_2$ units and four ditopic bbimms ligands in a highly concerted fashion. Two directional binding sites on the Hg^{II} ion direct the assembly which is facilitated by the *anti* conformation adopted by the ligand. The molecular tube exhibits relatively high thermal stability and is capable of encapsulating guest molecules such as DMF or DMSO in its two rectangular compartments. Most exciting, however, is the fact that the tubes are aligned to resemble a pipeline and that these pipelines are arranged into a three-dimensional columnar architecture. To the best of our knowledge, such a columnar supramolecular architecture constructed from neu-

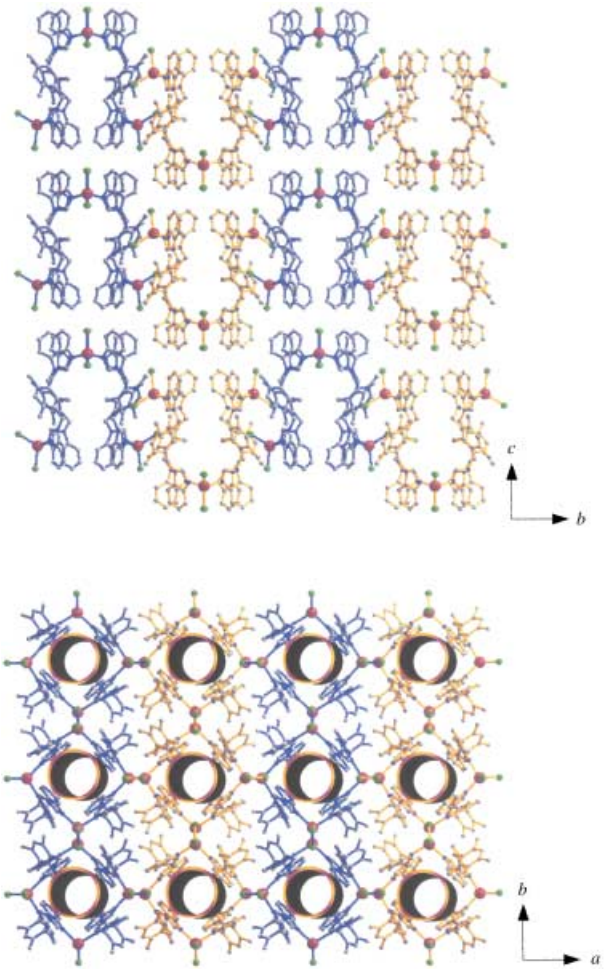


Figure 2. The extended alignment and "pipeline" formation of the molecular tubes in the [001] plane (top) and of the columnar architecture in the [100] plane with open cylinders in the cavities highlighting the "pipeline" nature of the architecture (bottom).

tral coordination tubes has not been reported before, and the synthetic strategy employed in its construction provides a means of expanding the general knowledge of tubular coordination networks[11] and cationic nanotubes.[12]

Experimental Section

General procedure for the preparation of **1**·2 DMF and **1**·2 DMSO: A solution of MeOH containing an equal molar amount of bbimms was added to a solution of $HgCl_2$ in MeCN and a colorless crystalline product appeared in a short time. DMF (or DMSO) was added on heating until the precipitate had dissolved completely and a clear solution was obtained again. The mixture was filtered and left to stand at room temperature for several days to yield colorless crystals having a pseudo-octahedral shape.

1·2 DMF: ^{1}H NMR (300 MHz, CD_3CN): $\delta = 7.92$ (s, 1 H, -COH), 7.58 (s, 4 H, H2), 7.75 (ddd, 4 H, H4), 7.60 (ddd, 4 H, H7), 7.29–7.39 (m, 8 H, H5,6), 7.19 (s, 2 H, H9), 5.41 (s, 8 H, H8), 2.88 (s, 3 H, CH_3 (DMF)), 2.76 (s, 3 H, CH_3 (DMF)), 2.31 (s, 12 H, H11), 1.89 ppm (s, 6 H, H10). IR (KBr): $\tilde{\nu} = 3086$, 2970, 1670, 1609, 1504, 1462, 1396, 1327, 1296, 1234, 1196, 1092, 1015, 910, 752, 717, 575, 513 cm^{-1}.

1·2 DMSO: ^{1}H NMR (300 MHz, CD_3CN): $\delta = 7.57$ (s, 4 H, H2), 7.78 (ddd, 4 H, H4), 7.59 (ddd, 4 H, H7), 7.27–7.39 (m, 8 H, H5,6), 7.19 (s, 2 H, H9), 5.38 (s, 8 H, H8), 2.52 (s, 6 H, CH_3 (DMSO)) 2.34 (s, 12 H, H11), 1.90 ppm (s, 6 H, H10). IR (KBr): $\tilde{\nu} = 3086$, 2966, 1609, 1504, 1462, 1396, 1327, 1296, 1234, 1196, 1060, 1011, 910, 752, 718, 575, 513 cm^{-1}.

X-ray crystallographic analysis: X-Ray intensity data were measured at 150 K on a Bruker SMART APEX CCD diffractometer ($Mo_{K\alpha}$, graphite monochromator). Empirical absorption corrections were applied (SADABS). The structures were solved by Patterson methods followed by difference Fourier synthesis (SHELXS97) and refined anisotropically by full-matrix least-squares against F^2 using all data (SHELXTL).[19] Hydrogen atoms were included in calculated positions as riding atoms except where noted. Crystal data for **1**·2 DMF: Colorless octahedron, $M_r = 2754.08$, $0.40 \times 0.36 \times 0.32$ mm^3, tetragonal, space group $I4_1/a$, $a = 24.7294(8)$, $c = 17.3830(8)$ Å, $V = 10630.5(7)$ Å^3, $Z = 4$, $\mu = 6.02$ mm^{-1}, $\rho_{calcd} = 1.721$ g cm^{-3}. 41495 reflections measured; 5446 independent ($R_{int} = 0.0370$); 4794 with $I > 2\sigma I$. $R1$ (F, all data) = 0.0294, $wR2$ (F^2) = 0.0627, GOF = 1.067. Min./max. residual electron density, +1.08/−0.34 e Å^{-3}. The DMF guest is disordered over a twofold rotational axis. Crystal data for **1**·2 DMSO: Colorless octahedron, $M_r = 2764.14$, $0.26 \times 0.24 \times 0.18$ mm^3. tetragonal, space group $I4_1/a$, a = 24.7502(8), $c = 17.1254(7)$ Å, $V = 10490.5(6)$ Å^3, $Z = 4$, $\mu = 6.14$ mm^{-1}, $\rho_{calcd} = 1.750$ g cm^{-3}. 25295 reflections measured; 4635 independent ($R_{int} = 0.0549$); 3838 with $I > 2\sigma I$. R1 (F, all data) = 0.0374, $wR2$ (F^2) = 0.0969, GOF = 1.049. Min./max. residual electron density, +1.70/−1.14 e Å^{-3}. The DMSO guest is disordered over a twofold rotational axis. H atoms were not located or calculated. CCDC-196335–196336 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[15] Elemental analysis indicates a stoichiometric formula of [$HgCl_2$(bbimms)], calcd for $C_{25}H_{24}N_4HgCl_2$ (%): C 46.06, H 3.71, N 8.59; found: C 46.24, H 3.90, N 8.64. IR (KBr): $\tilde{\nu} = 3099$, 2929, 1610, 1500, 1460, 1389, 1363, 1290, 1186, 1011, 912, 744, 617 cm^{-1}.
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