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Interwoven 2-D Coordination Network Prepared from the Molecular Host Tris(isonicotinoyl)cyclotriguaiacylene and Silver(I) Cobalt(III) Bis(dicarbollide)

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A new 3-fold symmetric molecular host, tris(isonicotinoyl)cyclotriguaiacylene, has been synthesized from cyclotriguaiacylene and isonicotinoyl chloride hydrochloride in 70% yield. Its crystal structure shows dimerization of the host molecules into a capsule-like arrangement. When reacted with $Ag[Co(C_2B_9H_{11})_2]$, the host forms a 1-D $[ML_2]_n$ coordination polymer, which assembles into a 2-D interwoven network through a similar dimerization of the host moieties around acetonitrile guests. Thus, the network structure represents an elegant example whereby the solid state structure of the building blocks is echoed in the resulting supramolecular assembly. The 2-D sheets are further stabilized by $\pi\cdots\pi$ stacking interactions between pyridyl donors of alternate 1-D coordination polymers.

Host−guest or inclusion chemistry, where the two, or more, molecules form a noncovalently bound complex, continues to receive wide attention in the chemical sciences.[1] Correspondingly, the synthesis of coordination polymers or metal−organic frameworks has seen a dramatic increase in study over the past decade.[2] Central to this study is the challenge of incorporating the conformation and spatial organization of the donor atoms in a ligand precursor (the encoded information) into the resulting coordination polymer. The unification of these two diverse fields of supramolecular science by employing molecular hosts as building blocks for the construction of coordination polymers has received more limited attention[3] and is the focus of our current research. The incorporation of molecular hosts introduces a number of aspects not necessarily achievable with conventional ligands, such as multiple inclusion behaviors, unusual ligand topologies, and employment of host−guest interactions as supramolecular synthons.

The molecular host, cyclotriveratrylene (CTV, **1**), is a rigid bowl-shaped molecule that, while being a poor host to small organic molecules, has been shown to bind large molecules such as *o*-carborane, fullerenes,[4] and organometallic complexes[5] within its molecular cavity. Two- and three-dimensional crystal-engineered materials have been prepared using the dimethoxy functionality of CTV as either a hydrogen bond donor[6] or as a ligand for alkali metals.[4,7] However, despite being able to construct 2-D and 3-D networks of CTV incorporating specific host−guest interactions, the resulting materials are not of a sufficiently predictable nor robust nature to be suitable for many of the proposed applications of coordination networks.[2] Thus, herein, as part of a study of ligand functionalized derivatives of CTV,[8] we describe the synthesis of a threefold symmetric trisubstituted derivative, tris(isonicotinoyl)cyclotriguaiacylene (**3**), where, by incorporating nitrogen-containing heterocyclic donor groups, we have simultaneously extended the molecular cavity and improved the transition metal binding properties of the parent compound. There are a small number of previous examples of attaching pyridyl or bipyridyl functionality to the CTV framework.[9] In this Communication, we report that, on reaction of the new derivative **3** with silver cobalt(III) bis(dicarbollide), a 1-D $[ML_2]_n$ coordination

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(1) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*: John Wiley & Sons: Ltd: Chichester, 2000.

(2) For reviews, see: (a) Janiak, C. *Dalton Trans.* **2003**, 2781. (b) James, S. L. *Chem. Soc. Rev.* **2003**, *32*, 276. (c) Robson, R. *Dalton Trans.* **2000**, 3735. (d) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Schröder, M.; Withersby, M. A. *Coord. Chem. Rev.* **1999**, *183*, 117.

(3) For examples, see: (a) Jaunky, W.; Hosseini, M. W.; Planeix, J. M.; De Cain, A.; Kyritsakas, N.; Fischer, J. *Chem. Commun.* **1999**, 2313. (b) Beer, P. D.; Drew, M. G. B.; Gale, P. A.; Ogden, M. I.; Powell, H. R. *CrystEngComm* **2000**, 30. (c) Fox, O. D.; Drew, M. G. B.; Wilkinson, E. J. S.; Beer, P. D. *Chem. Commun.* **2000**, 391. (d) Ikeda, A.; Udzu, H.; Zhang, Z.; Shinkai, S.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2001**, *123*, 3872. (e) Webb, H. R.; Hardie, M. J.; Raston, C. L. *Chem. Eur. J.* **2001**, *7*, 3616. (f) Dalgarno, S. J.; Raston, C. L. *Chem. Commun.* **2002**, 2216. (g) Dalgarno, S. J.; Hardie, M. J.; Raston, C. L. *Cryst. Growth Des.* **2004**, *2*, 227.

(4) Hardie, M. J.; Raston, C. L. *Chem. Commun.* **1999**, 1153.

(5) Holman, K. T.; Steed, J. W.; Atwood, J. L. *Angew. Chem., Int. Ed.* **1997**, *36*, 1736.

(6) Recent review: Hardie, M. J. *Struct. Bonding* **2004**, *111*, 139.

(7) Hardie, M. J.; Raston, C. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 3835.

(8) Hardie, M. J.; Mills, R. M.; Sumby C. J. *Org. Biomol. Chem*., published online Sep. 17, http://dx.doi.org/10.1039/B407165D.

(9) (a) Zhong, Z.; Ikeda, A.; Shinkai, S.; Sakamoto, S.; Yamaguchi, K. *Org. Lett.* **2001**, *3*, 1085. (b) Wytko, J. A.; Boudon, C.; Weiss, J.; Gross, M. *Inorg. Chem.* **1996**, *35*, 4469. (c) Cram, D. J.; Weiss, J.; Helgeson, R. C.; Knobler, C. B.; Dorigo, A. E.; Houk, K. N. *Chem. Commun.* **1988**, 407.

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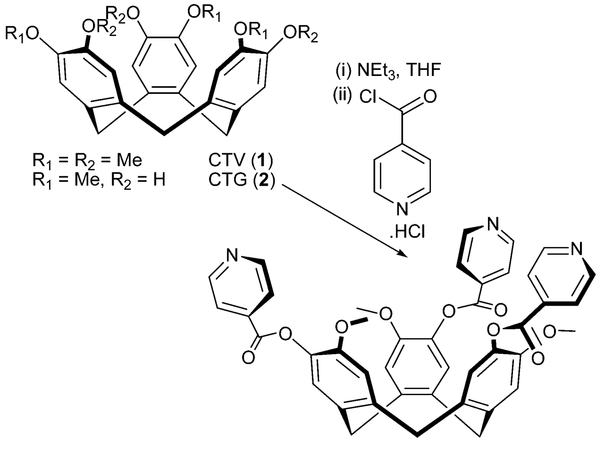
Scheme 1. Synthetic Route to Compound **3**



(**3**)

polymer was formed that, in the crystal structure, packs to form an interwoven 2-D sheet. This infinite 2-D sheet is held together by dimeric host−guest interactions between coordinated molecules of the ligand, which echo the packing observed in the crystal structure of **3**, and $\pi\cdots\pi$ stacking between pendant (not involved in coordination) pyridyl groups of alternate $[ML_2]_n$ polymer chains. While there have been a handful of CTV-based metal complexes reported,[9a,b,10] this is the first example of a transition metal coordination polymer utilizing such ligands.

Ligand **3** was prepared by reaction of the trihydroxy derivative of CTV, cyclotriguaiacylene (CTG, **2**),[11] with isonicotinoyl chloride hydrochloride (Scheme 1). Compound **3** was isolated as a racemic mixture in 70% yield and characterized by a combination of NMR spectroscopy, mass spectrometry, and elemental analysis. Small colorless crystals of **3**, suitable for X-ray crystallography,[12] were obtained by vapor diffusion of hexane into a dichloromethane solution of **3**. Compound **3** crystallizes in the trigonal space group $R\bar{3}c$ with one-third of a molecule of **3** in the asymmetric unit. The compound has the anticipated bowl-shaped conformation with the isonicotinoyl groups orthogonal to the central CTG core. These pyridyl donors are ideally placed to coordinate to three transition metal centers in subsequent complexes, and **3** displays an enlarged molecular cavity.

In the crystal structure, **3** forms a face-to-face dimeric capsule-like assembly (Figure 1) which is stabilized by very weak $\pi\cdots\pi$ stacking interactions between the pyridine rings at slightly longer distances than usually seen for interactions between nitrogen-containing ligands (centroid separation 4.21(1) Å).[13] More significantly, although not well defined, residual electron density within the molecular cavity of the capsule-like assembly suggests the dimers are stabilized by host−guest interactions. Unfortunately, this diffuse residual electron density within the cavity could not be sensibly modeled in the final structure. Furthermore, the dimeric capsule may be the favored packing arrangement as the self-hosting behavior observed for other CTV derivatives is sterically unfavorable due to the orientation of the carbonyl groups and pyridine rings.

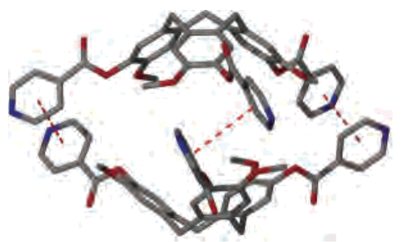


Figure 1. Dimeric capsule formed by association of two molecules of **3**, with weak face-to-face $\pi\cdots\pi$ stacking interactions between the pyridine rings indicated. For clarity, hydrogen atoms are not shown.

Ligand **3** was reacted with various silver salts, which offer flexible coordination geometries including linear and tetrahedral, and could be anticipated to form 3-connected hexagonal networks or 3,4-connected networks. We were unable to obtain crystals using common counteranions such as NO_3^-, BF_4^-, or PF_6^-, and hence we employed the cobalt(III) bis(dicarbollide) anion, $[Co(C_2B_9H_{11})_2]^-$, a stable, weakly coordinating anion, that readily crystallizes with CTV and its derivatives.[6,7] Combining warm acetonitrile solutions of **3** and $Ag[Co(C_2B_9H_{11})_2]$ gave a bright yellow solution, that, following slow evaporation, yielded crystalline yellow plates. These had the composition, determined by X-ray crystallography, of $[Ag(\mathbf{3})_2][Co(C_2B_9H_{11})_2]\cdot 9(CH_3CN)$ (**4**).[14] Compound **4** crystallizes in the triclinic space group $P\bar{1}$ with one silver atom, two molecules of **3**, one $[Co(C_2B_9H_{11})_2]^-$ anion, and nine CH_3CN solvent molecules in the asymmetric unit. The two molecules of **3** have distinct conformations, with one having all carbonyl groups directed into the host cavity, while the other shows two carbonyl groups likewise pointing in, but with the third directed outward. The silver atom has a tetrahedral geometry (Ag−N bond lengths between 2.233(7) and 2.448(7) Å) and is bound by four different (two sets of symmetry-related) ligand molecules. Each molecule of **3** acts as a bidentate bridge of two symmetry-related silver atoms to form a 1-D $[ML_2]_n$ coordination polymer (Figure 2), which propagates along the *c*-axis of the unit cell. The two molecules of **3** that bridge between adjacent symmetry-related silver atoms have op-

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(10) (a) Bohle, D. S.; Stasko, D. J. *Chem. Commun.* **1998**, 567. (b) Bohle, D. S.; Stasko, D. J. *Inorg. Chem.* **2000**, *39*, 5768. (c) Matouzenko, G.; Vériot, G.; Dutasta, J.-P.; Collet, A.; Jordanov, J.; Varret, F.; Perrin, M.; Lecocq, S. *New J. Chem.* **1995**, *19*, 881. (d) Vériot, G.; Dutasta, J.-P.; Matouzenko, G.; Collet, A. *Tetrahedron* **1995**, *51*, 389.

(11) (a) Canceill, J.; Collet, A.; Gottarelli, G. *J. Am. Chem. Soc.* **1984**, *106*, 5997. (b) Scott, J. L.; MacFarlane, D. R.; Raston, C. L.; Teoh, C. M. *Green Chem.* **2000**, *2*, 123. (c) Brotin, T.; Devic, T.; Lesage, A.; Emsley, L.; Collet, A. *Chem. Eur. J.* **2001**, *7*, 1561.

(12) Crystal data for **3**: $C_{42}H_{33}N_3O_9$, fw = 723.71, trigonal, $R\bar{3}/c$, a = 16.479(2) Å, c = 53.626(11) Å, V = 12612(4) Å^3, Z = 12, ρ = 1.143 Mg cm^{-3}, μ = 0.081 mm^{-1}, $F(000)$ = 4536, colorless block 0.36 × 0.30 × 0.24 mm^3, $2\theta_{max}$ = 43.78°, Mo Kα (λ = 0.7107 Å), T = 150(1) K, 17994 reflections, 1683 unique, R_{int} = 0.0837, (98.6% completeness), 164 parameters, GOF = 1.131, $wR2$ = 0.2491 for all data, R_1 = 0.0854 for 1409 data with $I > 2\sigma(I)$.

(13) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885. Additional details for π-stacking given in SI.

(14) Crystal data for **4**: $C_{106}H_{115}AgB_{18}CoN_{15}O_{18}$, fw = 2248.51, triclinic, $P\bar{1}$, a = 12.254(3) Å, b = 15.449(3) Å, c = 33.084(7) Å, α = 92.35(3)°, β = 92.62(3)°, γ = 112.93(3)°, V = 5750(2) Å^3, Z = 2, ρ = 1.299 Mg cm^{-3}, μ = 0.385 mm^{-1}, $F(000)$ = 2328, yellow plate 0.36 × 0.17 × 0.08 mm^3, $2\theta_{max}$ = 43.96°, Mo Kα (λ = 0.7107 Å), T = 150(1) K, 49470 reflections, 13584 unique (96.5% completeness), R_{int} = 0.1087, 1416 parameters, GOF = 1.134, $wR2$ = 0.2128 for all data, R_1 = 0.0856 for 10153 data with $I > 2\sigma(I)$.

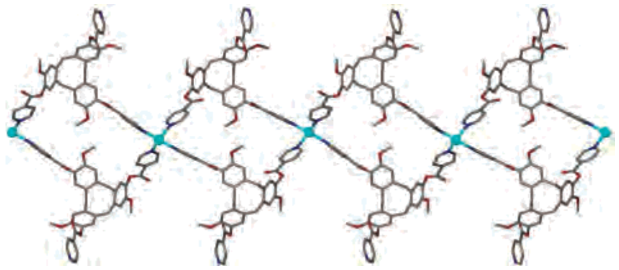

Figure 2. 1-D coordination polymer of complex **4**. Hydrogen atoms, anions, and solvate molecules are omitted for clarity.

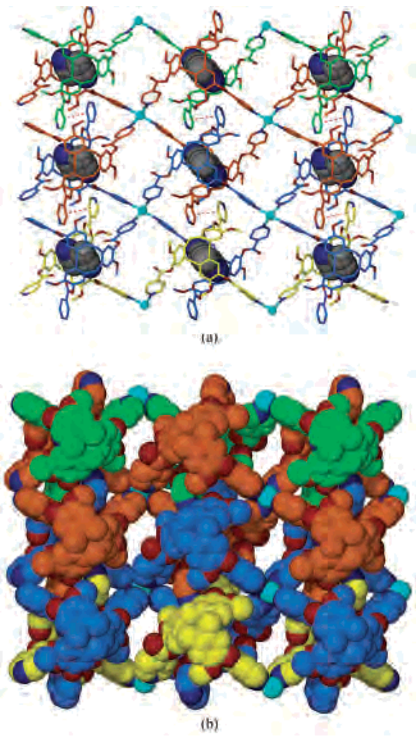

Figure 3. (a) Partial packing diagram from the crystal structure of **4**, showing how coordination chains are interwoven into a 2-D sheet structure by dimerization around guest acetonitrile molecules (space-filling atoms) and π···π stacking interactions between pendant pyridyl groups. (b) A space filling version of part a highlighting the interwoven nature of the 2-D network. Hydrogen atoms have been omitted. Carbon atoms of different $[ML_2]_n$ coordination polymers are shown in different colors.

posite bowl-up, bowl-down arrangements. Despite its tritopic nature, one of the pyridyl donors from each ligand does not coordinate to a Ag(I); hence, the ligand is hypodentate and does not form the anticipated 3-connected polymer.

The crystal packing reveals that the 1-D coordination polymers are interwoven through dimeric host−guest associations between the coordinated molecular host moieties of adjacent chains and π···π stacking interactions to give an extended 2-D network (Figure 3). Each molecule of **3** forms a head-to-head dimeric capsule-like assembly with a symmetry-equivalent molecule of **3** from an adjacent chain. Adjacent chains are interlinked due to the bowl-up, bowl-down arrangement of molecules of host molecules within the each coordination chain. Two symmetry-related acetonitrile solvent molecules lie within each capsule-like arrangement (Figure 3) with the methyl groups pointing toward the center of each hydrophobic cavity. This dimeric capsule-like packing motif is remarkably similar to that observed in the X-ray crystal structure of **3** itself; however, here it is devoid of weak stabilizing π···π stacking interactions as the pyridyl rings are orientated in a staggered rather than eclipsed arrangement. This structure is also noteworthy in that the host−guest synthon observed for a building block (**3**) of this network structure is retained in the final assembly. Within the 2-D coordination network, the dimeric host−guest associations are weaker as a consequence of the internalization of the majority of the carbonyl groups; in the structure of **3**, the carbonyl groups are all external to the cavity.

Additionally, pendant pyridyl groups from different coordination chains within the 2-D sheet further stabilize the crystal packing by forming exactly coplanar but long π···π stacking arrangements (centroid−centroid distances 4.16(1) and 4.12(1) Å).[13] These π···π stacking interactions form between 1-D $[ML_2]_n$ coordination polymers which are not directly associated through complementary host−guest associations. These pendant pyridyl groups from alternate 1-D $[ML_2]_n$ polymer chains are interlocked through the roughly square cavity formed by an $[M_2L_2]$ unit of a third interstitial coordination polymer. Hence, the overall 2-D assembly is interwoven through a combination of host−guest and π···π stacking interactions, rather than being simply interlocked.

The overall crystal packing of **4** shows additional acetonitrile solvent and $[Co(C_2B_9H_{11})_2]^-$ anions within channels created by packing of the interwoven 2-D sheets, with some hydrogen bonding interactions between these moieties (C−H···N distances 2.33−3.01 Å). Thus, we have both clathrate inclusion and specific host−guest interactions within this structure. While the anions do not appear to directly template formation of the interwoven network, their bulky nature encourages crystallization from solution.

In summary, when the new ligand and host molecule, **3**, was reacted with silver(I) cobalt(III) bis(dicarbollide), the formation of a 1-D $[ML_2]_n$ coordination polymer was observed. The association of these polymer chains, through host−guest synthons and π···π stacking interactions, leads to an infinite interwoven 2-D sheet topology in the solid state. This structure represents an elegant example whereby the solid state structure of one of the building blocks (**3**) is echoed in the resulting supramolecular assembly.

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Supporting Information Available: Preparative experimental details, CIF files, and additional crystallographic information for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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