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A Zinc Carboxylate Network Containing Metal Sites with Low Coordination Numbers

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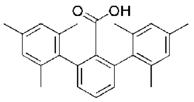
A bifunctional *m*-terphenyl, 2,6-diphenyl-1,4-dibenzoic acid (Ph_2BDC), was synthesized and used in the preparation of a 2-D metal–organic coordination polymer. The steric hindrance of the bulky bifunctional linker forces low coordination at the Lewis-acidic zinc center. A zinc carboxylate dimer was prepared as a model compound to examine the unusual tricoordinate geometry at the metal site.

The design of coordination polymers based on metal−organic frameworks is an area of intense research. Among the most extensively studied metal−organic frameworks are those based on carboxylate ligands. The pioneering research of Zaworotko and Moulton[1,2] and Yaghi and co-workers.[3] best illustrates the utility of this synthetic approach in the preparation of materials with predetermined structures and properties. The interest, in part, is driven by the desire to prepare functional 2-D clay-like or 3-D zeolite-like materials for applications including catalysis and gas sorption.[4] Among the challenges of this work is the lack of porous materials in which unusually low coordination numbers are *enforced* on a metal site, leading to enhanced acidity and molecular binding at the metal site in the framework solid.[5]

m-Terphenyls are perhaps the most reliable ligand class capable of enforcing low coordination numbers at metal sites. *m*-Terphenyls are molecules with at least two aryl substituents oriented meta to one another on a phenyl ring. The substituents twist out of the plane of the central ring, creating a hydrophobic bowl-shaped pocket. These ligands have been used to stabilize numerous unusual coordination geometries around metals within the *m*-terphenyl pocket.[6]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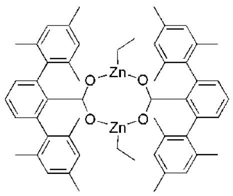
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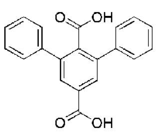
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The steric demands imposed on the metal sites by the *m*-terphenyl ligands are such that they *prevent aggregation* but still allow for *reactivity with small reagents* at vacant coordination sites on the metal. For example, *m*-terphenyl carboxylates have been used as metalloprotein mimics because of their ability to shield a coordinatively unsaturated metal inside a hydrophobic pocket.[7] In the case of metal−organic frameworks, the placement of the steric bulk directly adjacent to the carboxylate functionality on the *m*-terphenyl organic linker, rather than on a "blocker" ligand on the metal or farther from the functional group on the linker, should minimize interpenetration of the resulting networks.

Our interest in unusual bonding modes for main group elements and transition metals has led us to examine the preparation of such materials. In this report, we have (1)

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(1) (a) Bourne, S. A.; Lu, J.; Mondal, A.; Moulton, B.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2111−2113. (b) Abourahma, H.; McManus, G. J.; Moulton, B.; Walsh, R. D. B.; Zaworotko, M. J. *Macromol. Symp.* **2003**, *196*, 213−227.

(2) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629−1658.

(3) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705−714.

(4) (a) Biradha, K.; Dennis, D.; MacKinnon, V. A.; Krishnamohan Sharma, C. V.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 11894−11903. (b) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2003**, 2781−2804. (c) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1466−1496. (d) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334−2375. (e) Chae, H. K.; Siberio-Pérez, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.; Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523−527. (f) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469−472. (g) Rowsell, J. L. C.; Millward, A. R.; Park, K. S.; Yaghi, O. M. *J. Am. Chem. Soc.* **2004**, *126*, 5666−5667.

(5) Li, H.; Davis, C. E.; Groy, T. L.; Kelley, D. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 2186−2187.

(6) For reviews, see: (a) Twamley, B.; Haubrich, S. T.; Power, P. P. *Adv. Organomet. Chem.* **1999**, *44*, 1. (b) Clyburne, J. A. C.; McMullen, N. *Coord. Chem. Rev.* **2000**, *210*, 73−99.

(7) (a) Chavez, F. A.; Que, L., Jr.; Tolman, W. B. *J. Chem. Soc., Chem. Commun.* **2001**, 111−112. (b) Lee, D.; Hung, P.-L.; Spingler, B.; Lippard, S. J. *Inorg. Chem.* **2002**, *41*, 521−531.

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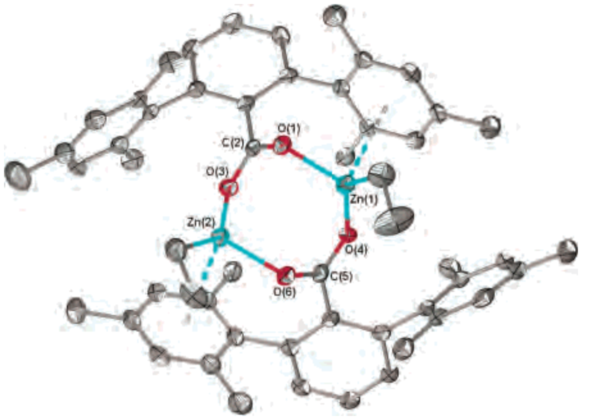

Figure 1. Solid-state structure of **2** showing 50% probability displacement ellipsoids. Hydrogen atoms were removed for clarity.

prepared a sterically congested model compound to examine the coordination geometry of a zinc *m*-terphenyl carboxylate, (2) prepared a bifunctional *m*-terphenyl carboxylate ligand,[8] and (3) incorporated this bifunctional ligand into a network solid and determined the structure of the network with coordinated ethanol at the Lewis acidic metal sites.

The reaction of 2,6-bis-(2,4,6-trimethylphenyl)benzoic acid, **1**,[9] with diethylzinc in CH_2Cl_2 results in the formation of the dimeric complex **2**. The ^1H NMR spectrum shows a triplet and a quartet at 1.27 and 0.08 ppm, respectively, due to the ethyl group attached to zinc. The IR spectrum shows strong ν C═O absorptions at 1586 and 1551 cm^{-1}, significantly different from the corresponding absorptions in the free acid **1** (1733 and 1704 cm^{-1}).

The structure of **2** was confirmed by single-crystal X-ray diffraction.[10] The carboxylate groups bridge two tricoordinate zinc atoms, forming a puckered eight-membered $Zn_2O_4C_2$ ring. The metal centers, which are separated by 3.5769(6) Å, exhibit trigonal planar geometry and no metal−metal bonding.[11] There is a *possible* η^6 interaction with a flanking aryl of the *m*-terphenyl ($\mathrm{Zn}\cdots$centroid = 3.083, 3.154 Å) as shown in Figure 1. Both the low coordination number at the metal and the heterocyclic core are rare.[12] The presence of a still-reactive ethyl group and the unusual coordination geometry of the zinc center, combined with the proven versatility of carboxylates, indicated that *m*-terphenyls would be ideal ligands to enforce low coordination numbers in a coordination polymer based on a metal organic framework.

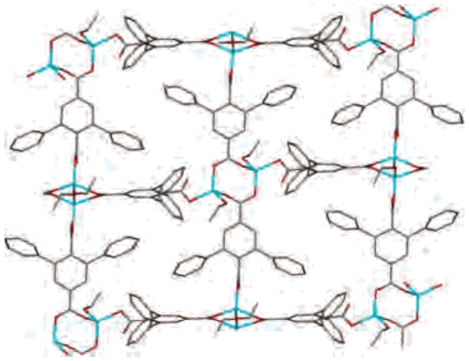

Figure 2. Packing diagram of **4** showing a 2 × 2 segment of the network. For clarity, hydrogen atoms and free solvent have been removed.

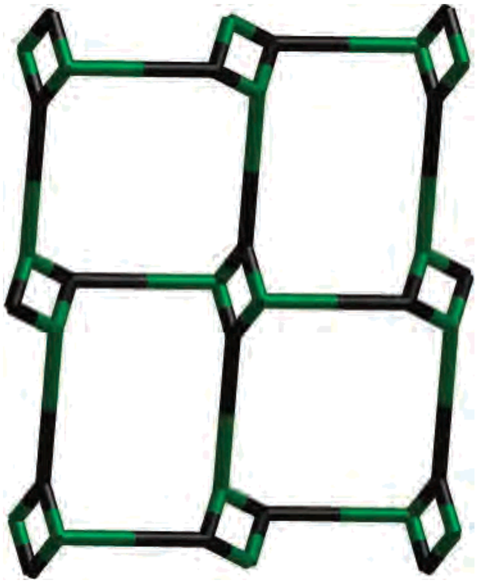

Figure 3. Schematic diagram (OLEX)[14] of **4** showing the network grid.

The bifunctional *m*-terphenyl carboxylate 2,6-diphenyl-1,4-dibenzoic acid (Ph_2BDC), **3**, was prepared by the oxidation of 4-methyl-2,6-diphenylbenzoic acid with $KMnO_4$ in water. The ^1H NMR spectrum of **3** shows a very broad signal at 13.1 ppm due to the hydrogen-bonded OH groups and two peaks at 167.1 and 170.2 ppm in the ^{13}C NMR spectrum that were assigned to the two carboxyl carbons. The IR spectrum shows a strong ν C═O absorption at 1692 cm^{-1}. X-ray crystallographic studies[10] show infinite linear hydrogen-bonded head-to-head and tail-to-tail chains. The ortho phenyl groups cause the carboxylate group in the pocket of the *m*-terphenyl to twist out of the plane of the central phenyl ring,[13] while that in the para position is coplanar to the central ring.

The reaction of the bifunctional ligand **3** with diethylzinc in either benzene or THF resulted in the formation of an

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(8) Bulky bifunctional *m*-terphenyl ligands have recently been used to prepare conjugated polymers. See, for example: Smith, R. C.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **2004**, *126*, 2268−2269.

(9) Hagadorn, J. R.; Que, L., Jr.; Tolman, W. B. *J. Am. Chem. Soc*. **1998**, *120*, 13531−13532.

(10) Crystallographic data for **2**−**4**. Full details are found in the Supporting Information. **2**: $C_{20}H_{14}O_4$, MW = 318.31, orthorhombic, space group *Pbcn* with $a = 13.5640(3)$ Å, $b = 13.5640(3)$ Å, $c = 17.0150(4)$ Å, $V = 3130.5(1)$ Å^3, $Z = 8$, $T = 173(2)$ K, $\mu = 0.094$ mm^{-1}, independent reflections = 2160, $R_{int} = 0.052$, R1 = 0.0683, wR2 = 0.1915. **3**: $C_{24}H_{24}O_6Zn$, MW = 473.80, triclinic, space group $P\bar{1}$ with $a = 11.1000(3)$ Å, $b = 13.6800(6)$ Å, $c = 15.7170(6)$ Å, $\alpha = 98.866(2)°$, $\beta = 90.857(2)°$, $\gamma = 95.610(2)°$, $V = 2345.69(15)$ Å^3, $Z = 4$, $T = 295(2)$ K, $\mu = 1.082$ mm^{-1}, independent reflections = 8256, $R_{int} = 0.051$, R1 = 0.0657, wR2 = 0.1806. **4**: $C_{54}H_{60}O_4Zn_2$, MW = 903.76, orthorhombic, space group *Pbca* with $a = 23.1334(4)$ Å, $b = 15.9039(2)$ Å, $c = 25.6396(4)$ Å, $V = 9433.1(2)$ Å^3, $Z = 8$, $T = 150(2)$ K, $\mu = 1.061$ mm^{-1}, independent reflections = 8322, $R_{int} = 0.108$, R1 = 0.0465, wR2 = 0.0.0949.

(11) Bimetallic building units commonly feature metal−metal bonds. See: Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759−771.

(12) Allen, F. H. *Acta Crystallogr. B: Struct. Sci*. **2002**, *58*, 380−388. Based on CSD version 5.25 (Nov 2003). Remarkably, out of 5448 zinc-containing structures in the Cambridge Structural Database, there were only 57 examples of tricoordinate alkylzinc, 121 examples of a $Zn_2O_4C_2$ heterocycle, and no combination of the two.

(13) Braun, M. E.; Steffek, C. D.; Kim, J.; Rasmussen, P. G.; Yaghi, O. M. *J. Chem. Soc., Chem. Commun*. **2001**, 2532−2533.

amorphous insoluble white powder that was not further characterized. To obtain a crystalline network, Ph_2BDC (**3**) was combined with $Zn(NO_3)_2 \cdot 6H_2O$ in ethanol in the presence of triethylamine vapor. Over the course of days, colorless crystals formed. X-ray crystallographic analysis[10] showed the formation of 2-D network, **4** (Figure 2). The rectangular grid measures approximately 10.7 × 12.2 Å, with each edge defined by one doubly deprotonated molecule of Ph_2BDC. The para carboxylate of **3** bridges the zinc atoms to form an eight-membered heterocycle, similar to that seen **2**, at the corner of each repeat unit. This is shown schematically[14] in Figure 3. The C═O from the more sterically hindered carboxylate does not form a bond to the zinc atoms.

In contrast to the dimeric complex **2**, the zinc atoms in **4** are four-coordinate with an ethanol solvent molecule bound to each zinc atom, consistent with the anticipated Lewis acidity of low-coordinate zinc. For each zinc atom, there is also an additional equivalent of solvent *intercalated* in a clay-like manner into the space between the 2-D sheets (Figure 4) and held in place by hydrogen bonds to the zinc-coordinated solvent and the free carboxylate oxygen in the sterically hindered *m*-terphenyl pocket (Figure 5).

To probe the lability of the ethanol, TGA studies were performed on a crystalline sample of **4**. There was a two-step weight loss totaling 20% from 140 to 225 °C corresponding to two molecules of ethanol per zinc (19.4% calculated). No further loss occurred until the framework decomposed at ca. 350 °C. Attempts were made to insert new guest molecules into the framework and to characterize the desolvated network, but the results were inconclusive.

By merging the unusual coordination patterns of *m*-terphenyl carboxylates with the chemistry of metal−organic frameworks, we have developed a useful synthetic method for the preparation of stable 2-D networks containing low-coordinate Lewis acidic metal sites with the ability to intercalate guest molecules between the polymeric layers.

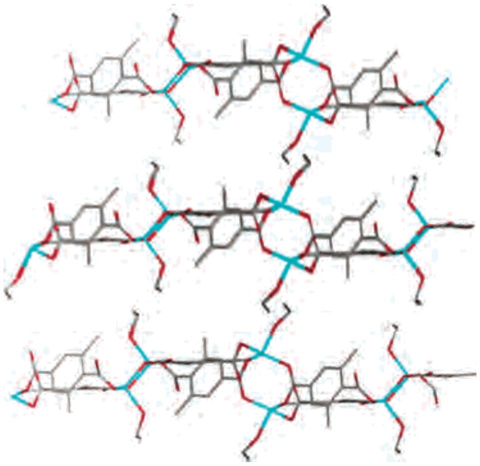

Figure 4. Intercalation of solvent molecules in **4**. For clarity, only the ipso C’s of the phenyl groups are shown.

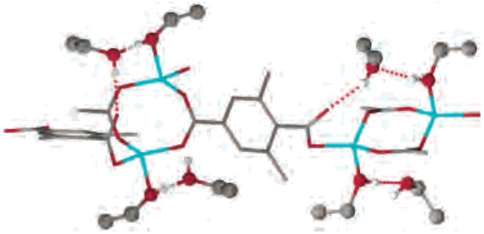

Figure 5. Hydrogen bonding of solvent molecules in **4**. For clarity, only the ipso C’s of the phenyl groups are shown.

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Supporting Information Available: Synthetic procedures, characterization data, and crystallographic data (CIF files) for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Dolomanov, O. V.; Blake, A. J.; Champness, N. R.; Schröder, M. *J. Appl. Crystallogr.* **2003**, *36*, 1283−1284.