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One-Dimensional Coordination Polymers Based upon Bridging Terephthalate Ions

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The design of supramolecular structures with interesting inclusion and magnetic properties has been extensively studied in recent years.[1] A rapidly developing area in this field is the synthesis of extended inorganic structures (i.e., coordination polymers) where the ability to control functionality (e.g., hydrogen bond donor/acceptor capabilities) along these networks is of much current interest.[2] Our interests, however, lie in the design of cavity-containing rectangular frameworks.[3] During studies aimed at constructing such two-dimensional (2D) networks using terephthalate ions, we have isolated two families of one-dimensional (1D) coordination polymers based upon this anion. Indeed, there are a limited number of examples of polymeric structures based upon transition metals and the terephthalate ion.[4] In this contribution we report the X-ray crystal structures of [M(terephthalate)-(4-picoline)$_2$(H$_2$O)$_2$]·2(4-picoline) (**1**) and [M(terephthalate)-(pyridine)$_2$(H$_2$O)$_2$]·2(pyridine)·2(H$_2$O) (**2**) (where M = Co(II) is **1a** and **2a**, Ni(II) is **1b** and **2b**) which assemble in the solid state to form 1D coordination polymers. Both **1** and **2** possess multiple hydrogen bond donors/acceptors along the polymeric backbone, which gives rise to interactions between the polymer and included guest species by way of intermolecular O−H···X (X = N, O) forces (guests: 2(4-picoline) **1**; 2(pyridine), 2(H$_2$O) **2**).

A THF solution (1 mL) of $CoCl_2 \cdot 6H_2O$ (10.5 mg, 0.05 mmol) was added to an aqueous solution (3 mL) of disodium terephthalate (12 mg, 0.05 mmol) with the addition of either 4-picoline **1a** or pyridine **2a**. Red crystals suitable for X-ray analysis formed upon cooling for both **1a** (yield: 58%, single product) and **2a** (yield: 65%, single product). An aqueous solution containing anhydrous $NiBr_2$ (11 mg, 0.05 mmol) was added to disodium terephthalate solution (12 mg, 0.05 mmol) with either 4-picoline **1b** (yield 68%, single product) or pyridine **2b** (yield 78%, single product). Blue crystals suitable for X-ray determination for the nickel case formed over about 12 h. In **2**, THF was not required to form the desired product. Thus, the THF is essential for crystallization of **1**. The formulations of **1** and **2** were confirmed by X-ray diffraction.[5]

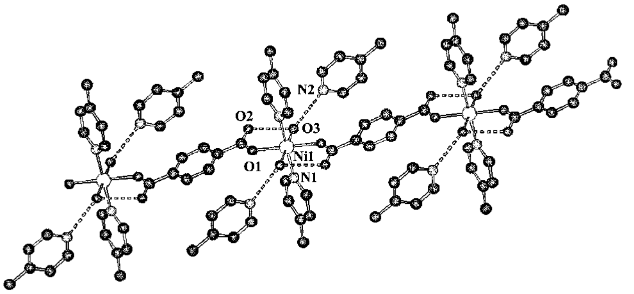

Figure 1. View of the 1D network depicting the coordination around the metal in **2a**. Noncovalent interactions in the form of O−H···O hydrogen bonding and edge-to-face $\pi-\pi$ stacking are demonstrated. We note that **1a** has the same numbering scheme. Selected interatomic distances (Å): for **2a**, Ni(1)−O(1) 2.061(2), Ni(1)−O(3) 2.084(2), Ni(1)−N(1) 2.103(3), O(2)−O(3) 2.686(4), O(3)−N(2) 2.829(4); for **1a**, Co(1)−O(1) 2.080(3), Co(1)−O(3) 2.120(3), Co(1)−N(1) 2.156(2), O(2)−O(3) 2.69, O(3)−N(2) 2.82.

The structures of **1b** and **2b** are shown in Figures 1 and 2, respectively. In both **1** and **2**, the metal atoms exist in distorted octahedral coordination environments in which two trans water molecules, two trans pyridine-based ligands, and two trans terephthalate ions have assembled around each metal center. As a result, 1D coordination polymers have formed. In **1** the polymer backbone propagates along the crystallographic *c*-axis; however, this is not the case for **2**. The metal−metal distances across each

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(1) (a) Fujita, M.; Kwon. Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (b) Lu, J.; Paliwala, T.; Lim S. C.; Yu, C.; Niu, T.; Jacobsen, A. J. *Inorg. Chem.* **1997**, *36*, 923. (c) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. *Supramolecular Architecture*; American Chemical Society: Washington, DC, 1992; Chapter 19. (d) Subramanian, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2127. (e) Losier, P.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2779. (f) Fujita, M.; Yazaki, J.; Ogura, K. *Tetrahedron Lett.* **1991**, *40*, 5589.

(2) (a) Li, H.; Davis, C. E.; Groy, T. L.; Kelley, D. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 2186. (b) Bakalbassis, E.; Tsipis, C. *Inorg. Chim. Acta* **1991**, *186*, 113. (c) Bakalbassis, E.; Bozopoulos, A. P.; Mrozinski, J.; Rentzeperis, P. J.; Tsipis, C. *Inorg. Chem.* **1988**, *27*, 529. (d) Bakalbassis, E.; Bergerat, P.; Kahn, O.; Jeannin, S.; Dromzee, Y.; Guillot, M. *Inorg. Chem.* **1992**, *31*, 625.

(3) (a) MacGillivray, L. R.; Groeneman, R. H.; Atwood, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 2676. (b) Tong, M.-L.; Chen, X.-M.; Yu, X.-L.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1998**, 5.

(4) (a) Cano, J.; De Munno, G.; Sanz, J.; Ruiz, R.; Lloret, F.; Faus, J.; Julve, M. *J. Chem. Soc., Dalton Trans.* **1994**, 3465. (b) Sobota, P.; Utko, J.; Lis, T. *J. Organomet. Chem.* **1990**, *393*, 349. (c) Deng, Z.-L.; Shi, J.; Jiang, Z.-H., Liao, D.-Z.; Yan, S.-P.; Wang, G.-L.; Wang, H.-G.; Wang, R.-J. *Polyhedron* **1992**, *11*, 885. (d) Dusek, M.; Petricek, Kamenicek, J.; Sindelar, Z. *Acta Crystallogr.* **1992**, *C48*, 1579. (e) Cano, J.; De Munno, G.; Sanz, J. L.; Ruiz, R.; Faus, J.; Lloret, F.; Julve, M.; Caneschi, A. *J. Chem. Soc., Dalton Trans.* **1997**, 1915. (f) Burrows, A. D.; Mingos, D. M.; Lawrence, S. E.; White, A. J. P.; Williams, D. *J. Chem. Soc., Dalton Trans.* **1997**, 1295. (g) Bakalbassis, E. G.; Tsipis, C. A.; Bozopoulos, A. P.; Dreissig, W.; Hartl, H.; Mrozinski, J. *Inorg. Chim. Acta* **1991**, *186*, 113. (h) Bakalbassis, E. G.; Bergeret, P.; Kahn, O.; Jeanin, S.; Jeanin, Y. Dromzee, Y.; Guillot, M. *Inorg. Chem.* **1992**, *31*, 75. (i) Bakalbassis, E. G.; Bozopoulos, A. P.; Mrozinski, J.; Rentzeper, P. J.; Tsipis, C. A. *Inorg. Chem.* **1988**, *27*, 529. (j) Cueto, S.; Gramlich, V.; Petter, W.; Rys, P. *Acta Crystallogr.* **1991**, *C47*, 75.

(5) Crystal data for **1a**: crystal size 0.30 × 0.25 × 0.30 mm, triclinic $P\bar{1}$, $a = 8.2675(6)$ Å, $b = 9.1598(7)$ Å, $c = 11.4274(9)$ Å, $\alpha = 82.612(1)°$, $\beta = 88.950(1)°$, $\gamma = 65.081(1)°$, $V = 777.08(5)$ Å^3, Mo Kα radiation ($\lambda = 0.710\ 70$ Å) for $Z = 1$. Least-squares based on 3239 reflections with $I_{net} > 2\sigma(I_{net})$ (out of 4665 unique reflections) gave a final value of $R = 0.045$. Crystal data for **2a**: crystal size 0.25 × 0.30 × 0.25 mm, monoclinic $P2_1/n$, $a = 12.4812(7)$ Å, $b = 15.3521(9)$ Å, $c = 23.235(1)$ Å, $\beta = 90.918(1)°$, $V = 4451.5(4)$ Å^3, Mo Kα radiation ($\lambda = 0.710\ 70$ Å) for $Z = 8$. Least-squares based on 8011 reflections with $I_{net} > 2\sigma(I_{net})$ (out of 8666 unique reflections) gave a final value of $R = 0.051$. Crystal data for **1b**: crystal size 0.20 × 0.30 × 0.30 mm, triclinic $P\bar{1}$, $a = 8.2727(7)$ Å, $b = 9.1320(8)$ Å, $c = 11.386(1)$ Å, $\alpha = 82.604(2)°$, $\beta = 89.406(1)°$, $\gamma = 65.152(1)°$, $V = 773.21(2)$ Å^3, Mo Kα radiation ($\lambda = 0.710\ 70$ Å) for $Z = 1$. Least-squares based on 1999 reflections with $I_{net} > 2\sigma(I_{net})$ (out of 3261 unique reflections) gave a final value of $R = 0.041$. Crystal data for **2b**: crystal size 0.25 × 0.30 × 0.30 mm, monoclinic $P2_1/n$, $a = 12.466(1)$ Å, $b = 15.323(1)$ Å, $c = 23.033(2)$ Å, $\beta = 90.892(2)°$, $V = 4399.2(6)$ Å^3, Mo Kα radiation ($\lambda = 0.710\ 70$ Å) for $Z = 8$. Least-squares based on 6053 reflections with $I_{net} > 2\sigma(I_{net})$ (out of 17 214 unique reflections) gave a final value of $R = 0.071$. Intensity data were collected with the use of the Siemens SMART system at 173 K.

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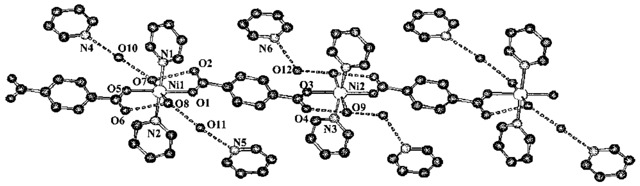

Figure 2. View of the 1D network depicting the coordination around the metal in **2b**. Noncovalent interactions in the form of O−H···O hydrogen bonding and edge-to-face $\pi-\pi$ stacking are demonstrated. We note that **1b** has the same numbering scheme. Selected interatomic distances (Å): for **2b**, Ni(1)−O(1) 2.054(4), Ni(1)−O(5) 2.055(4), Ni(1)−O(7) 2.054(5), Ni(1)−O(8) 2.080(6), Ni(1)−N(1) 2.108(5), Ni(1)−N(2) 2.109(4), Ni(2)−O(3) 2.067(4), Ni(2)−O(9) 2.049(5), Ni(2)−N(3) 2.095(5), O(2)−O(7) 2.639(7), O(6)−O(8) 2.654(8), O(7)−O(10) 2.662(8), O(8)−O(11) 2.658(8), O(4)−O(9) 2.634(7), O(9)−O(12) 2.706(8), O(10)−N(4) 2.794(9), O(11)−N(5) 2.809(8), O(12)−N(6) 2.936(10); for **1b**, Co(1)−O(1) 2.088(2), Co(1)−O(5) 2.082(2), Co(1)−O(7) 2.082(2), Co(1)−O(8) 2.086(2), Co(1)−N(1) 2.163(2), Co(1)−N(2) 2.162(2), Co(2)−O(3) 2.095(2), Co(2)−O(9) 2.077(2), Co(2)−N(3) 2.095(5), O(2)−O(7) 2.656(3), O(6)−O(8) 2.660(3), O(7)−O(10) 2.652(3), O(8)−O(11) 2.666(3), O(9)−O(12) 2.680(3), O(10)−N(4) 2.791(4), O(11)−N(5) 2.803(3), O(12)−N(6) 2.887(5).

polymer backbone are 11.4 and 11.5 Å for **1** and **2**, respectively, whereas the closest metal−metal distances between neighboring strands are 8.2 and 8.6 Å.

In a similiar way to [M(isonicotinate)(4,4′-bipyridine)$(H_2O)_2$] (M = Co, Cd),[30] the coordinated water molecules form a single hydrogen bond to the carboxylate of the terephthalates, resulting in a slight twist of the carboxylate group with respect to the aromatic ring. The second hydroxyl group of each water then forms a hydrogen bond to an included guest: in **1**, an additional 4-picoline, and in **2**, an additional water. Notably, the latter also participates in an O−H···N hydrogen bond to an included pyridine. Evidence for other noncovalent forces between the polymer and the included guests are depicted in Figures 1 and 2, where the lattice pyridines in both structures are observed to engage in edge-to-face $\pi-\pi$ interactions with the terephthalates with distances ranging between 5.05 and 5.12 Å.[6]

In **2**, it must be noted that the water molecule found in the lattice forms a second hydrogen bond to an adjacent polymeric chain via a carboxylate oxygen of a terephthalate ion. This interaction, as shown in Figure 3, gives rise to a 2D hydrogen-bonded network in which the water molecule participates in a six-membered hydrogen-bonded ring[7] involving two coordinated water molecules, two lattice water molecules, and two carboxylate oxygen atoms.

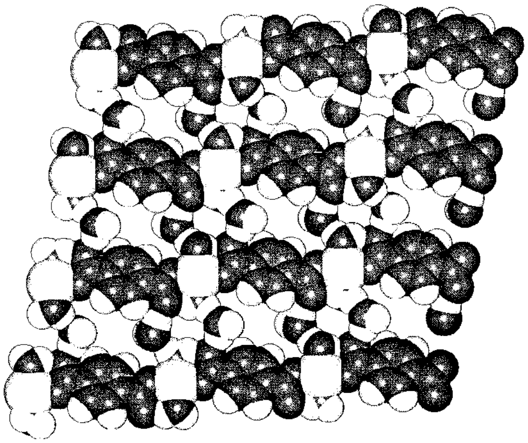

Figure 3. Space-filling view of the cyclic hydrogen-bonding network in **2**; the lattice water is required to form this given structural motif. The coordinated and lattice pyridines are omitted for clarity.

The results reported herein present two new families of coordination polymers based upon the terephthalate anion. By using simple pyridine-based ligands, 1D networks which effectively serve as multiple hydrogen bond donors have been isolated and their inclusion properties with appropriate hydrogen bond acceptors demonstrated. Indeed, we are currently in the process of attempting to construct rectangular frameworks based upon this coordination motif in which (1) the coordinated pyridines are replaced by exo-bidentate bridging ligands and (2) bifunctional hydrogen bond acceptors are used to align the strands via noncovalent forces. These results will be reported in due course.

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Supporting Information Available: Crystallographic reports and tables of atomic positional and thermal parameters, bond lengths, and bond angles for **1** and **2** (32 pages). Ordering information is given on any current masthead page.

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(6) Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768. This distance was determined by taking the centroid of the aromatic ring of the terephthalate with the aromatic ring of either 4-picoline or pyridine.

(7) The number of atoms within the ring is defined by the number of oxygen atoms.