

## Controlled Spacing of Metal Atoms via Ligand Hydrogen Bonds

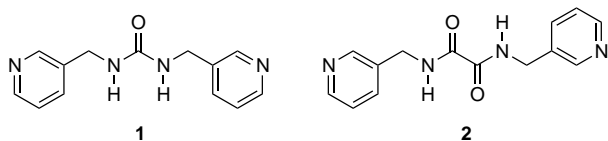
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The binary or host–guest approach is a powerful strategy for supramolecular synthesis<sup>1,2</sup> and crystal design. In the binary approach, the functionalities required for supramolecular structure and function are distributed over two molecules. We illustrated this convergent strategy by the design and preparation of a series of binary cocrystals in which a urea or oxalamide host determines the structure and spaces a diacetylene guest at the distance required for a topochemical polymerization, the desired function (Chart 1). The host–guest interaction is based upon the strong pyridine–hydroxyl hydrogen bond. Pyridyl-substituted ureas,<sup>4</sup> such as **1**, self-assemble into one-dimensional  $\alpha$ -networks<sup>3,4</sup> with a repeat distance of about 4.6 Å, while pyridyl-substituted oxalamides,<sup>5</sup> such as **2**, self-assemble at the slightly longer distance of 5.1 Å. In the diacetylene binary crystals, these intermolecular distances, characteristic of the host, are imposed upon the diacetylene guests.

These pyridyl-derivatized ureas and oxalamides designed as hosts for dicarboxylic acids and diols can also be used as ligand hosts for the controlled spacing of metal atoms in a designed crystal (Chart 2). We now wish to report the results of our initial studies in which we explored the cocrystallization of molecules<sup>6</sup> **1** and **2** with silver salts.<sup>7–9</sup>



The addition of 2 equiv of ligand **1** to a solution of  $\text{AgBF}_4$  gave the corresponding 2:1 coordination polymer  $[\text{Ag}(\text{L}1)_2]\text{BF}_4$ , **3**. The structure<sup>10</sup> consists of a one-dimensional  $\alpha$ -network of pyridine-substituted ureas with a repeat distance of 4.625(1) Å, corresponding to the  $c$  axis of a tetragonal unit cell (Figure 1). The pyridine nitrogen atoms are each coordinated to a  $\text{Ag}^+$

(1) Kane, J. J.; Liao, R. F.; Lauher, J. W.; Fowler, F. W. *J. Am. Chem. Soc.* **1995**, *117*, 12003–12004.

(2) Coe, S.; Kane, J. J.; Nguyen, T. L.; Toledo, L. M.; Winger, E.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 86–93.

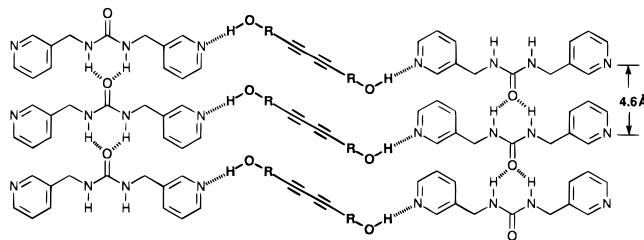
(3) Supramolecular assemblies can be divided into four groups depending upon the degree of translation symmetry. Discrete assemblies lack translation symmetry and are characterized by their point group symmetry. An  $\alpha$ -network has one degree of translational symmetry and is characterized by its rod group symmetry. A  $\beta$ -network has two degrees of translational symmetry and is characterized by its layer group symmetry. A  $\gamma$ -network has three degrees of translational symmetry and is characterized by its space group symmetry. See: Lauher, J. W.; Chang, Y. L.; Fowler, F. W. *Mol. Cryst. Liq. Cryst.* **1992**, *211*, 99–109.

(4) Zhao, X.; Chang, Y.-L.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 6627–6634. Chang, Y. L.; West, M. A.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5591–6000.

(5) We have prepared a variety of oxamide-based cocrystals analogous to the urea cocrystals described in ref 1.

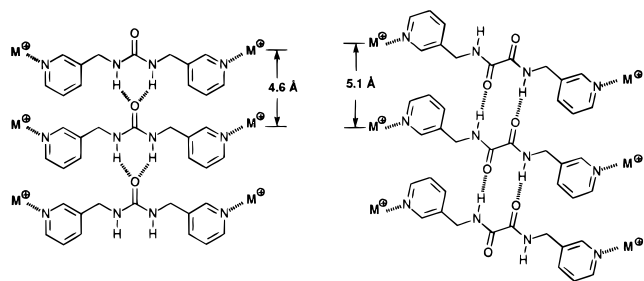
(6) Compounds **1** and **2** were synthesized by the direct stoichiometric reaction of diphenyl carbonate or diethyl oxalate with 3-aminomethylpyridine. The silver derivatives were prepared by cocrystallizing 2 mol of the ligand with 1 mol of silver salt from water or methanol/water solutions. Details are given in the Supporting Information.

**Chart 1.** An Illustration of a Two-Dimensional  $\beta$ -Network Formed from the Bipyridyl Urea, **1**, and a Diacetylene Dicarboxylic Acid or Diol<sup>a</sup>



<sup>a</sup> The intermolecular spacing is determined by the urea–hydrogen bonds.

**Chart 2.** Proposed One-Dimensional  $\alpha$ -Networks Formed by the Bipyridyl Urea, **1**, and the Bipyridyl Oxalamide, **2**, Each Bridging a Pair of Metal Ions<sup>a</sup>



<sup>a</sup> The expected characteristic spacings shown are determined by the dimensions of the hydrogen bond functionalities.

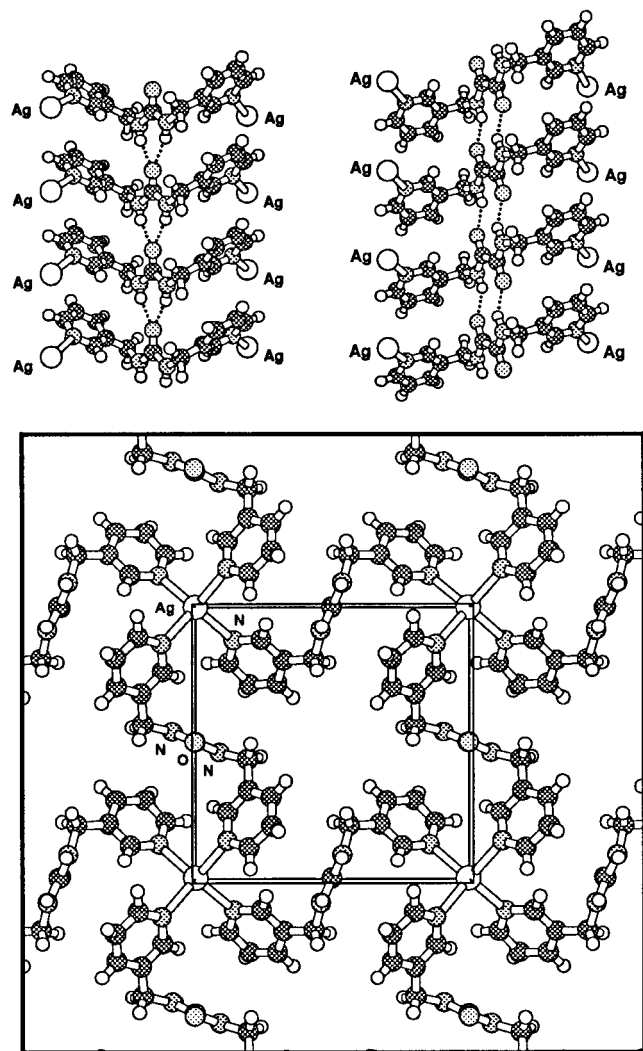
ion, yielding a four-coordinate tetrahedral  $\text{Ag}^+$  cation with the closest  $\text{Ag}^+ - \text{Ag}^+$  spacing equal to the 4.625(1) Å cell constant. The resulting structure, Figure 1, consists of two-dimensional layers held together by metal–ligand bonds. These layers are aligned by the ligand–ligand hydrogen bonds. The  $\text{BF}_4^-$  counteranions sit in the aligned channels between the urea ligands.

(7) Bipyridyl ligands have been used by many groups for metal based supramolecular syntheses. Stang, P. J.; Persky, N. E.; Manna, J. *J. Am. Chem. Soc.* **1997**, *119*, 4777–4778 and references therein, 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. Losier, P.; Zaworotko, M. *J. Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2779–2782. Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151–1152. Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1995**, *117*, 4562–4569. Baxter, P. N. W.; Hanan, G. S.; Lehn, J.-M. *Chem. Commun.* **1996**, 2019–2020. Baxter, P. N. W.; Lehn, J.-M.; Fischer, J.; Youinou, M.-T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2284–2289.

(8) Hydrogen bonds between coordinated ligands have been studied by others. Schroder, G.; Lippert, B.; Sabat, M.; Lock, C. J. L.; Faggiani, R.; Son, B.; Sigel, H. *J. Chem. Soc., Dalton Trans.* **1995**, 3767–3775. Burrows, A. D.; Chan, C. W.; Chowdry, M. M.; McGrady, J. J.; Mingos, D. M. P. *Chem. Soc. Rev.* **1995**, 329–339. Munakata, M.; Wu, L. P.; Yamamoto, M.; Kuroda-Sowa, T.; Mackawa, M. *J. Am. Chem. Soc.* **1996**, *118*, 3117–3124.

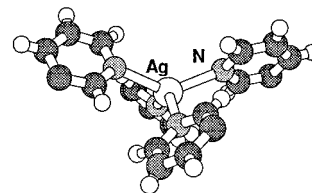
(9) DNA based methods for spacing small gold particles have been reported: Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. *Nature* **1996**, *382*, 607–609. Alivisatos, A. P.; Johnson, K. P.; Peng, X.; Wilson, T. E.; Loweth, C. J.; Bruchez, M. P., Jr.; Schultz, P. G. *Nature* **1996**, *382*, 609–611.

(10) X-ray data for **3**:  $\text{C}_{26}\text{H}_{28}\text{AgBFN}_8\text{O}_2$ ;  $M = 679.2$ ; tetragonal;  $a = 11.984(2)$  Å,  $c = 4.625(1)$  Å,  $V = 664.2$  Å<sup>3</sup>;  $Z = 1$ ;  $\rho_{\text{calc}} = 1.698$ ; space group  $P4$  (No. 81); 1236 observations ( $I > 3\sigma$ ); 124 variables;  $R = 0.032$ ,  $R_w = 0.039$ . **4** ( $X = \text{NO}_3^-$ ):  $\text{C}_{28}\text{H}_{28}\text{AgN}_9\text{O}_7$ ;  $M = 710.7$ ; tetragonal;  $a = 16.869(2)$  Å,  $c = 5.123(1)$  Å;  $V = 1457.9$  Å<sup>3</sup>;  $Z = 2$ ;  $\rho_{\text{calc}} = 1.683$ ; space group  $P4/n$  (No. 85); 923 observations ( $I > 3\sigma$ ); 114 variables;  $R = 0.032$ ,  $R_w = 0.041$ . **4** ( $X = \text{BF}_4^-$ ):  $\text{C}_{28}\text{H}_{28}\text{AgBF}_4\text{N}_9\text{O}_4$ ;  $M = 735.2$ ; tetragonal;  $a = 16.957(2)$  Å,  $c = 5.129(1)$  Å;  $V = 1475.1$  Å<sup>3</sup>;  $Z = 2$ ;  $\rho_{\text{calc}} = 1.655$ , space group  $P4/n$  (No. 85); 596 observations ( $I > 3\sigma$ ); 96 variables;  $R = 0.068$ ;  $R_w = 0.072$ . All data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with use of Mo radiation.



**Figure 1.** At the top are views of the ligand  $\alpha$ -networks of the  $[\text{Ag}(\text{L1})_2]\text{BF}_4$ , **3**, and  $[\text{Ag}(\text{L2})_2]\text{NO}_3$ , **4**, structures. The intermolecular spacings are 4.625(1) Å for the urea and 5.123(2) Å for the oxalamide. This is in complete agreement with the design shown in Scheme 2. In each structure the  $\text{Ag}^+$  cations are bound to four of the bipyridyl ligands and have a flattened tetrahedral geometry. This brings four of the  $\alpha$ -networks together to form channels as shown at the bottom for structure **3**. The channel in **3** forms about an  $S_4$  axis; the similar channel of **4** forms about a  $C_4$  axis.

In a similar manner addition of 2 equiv of the oxalamide ligand **2** to  $\text{AgNO}_3$  or  $\text{AgBF}_4$  gave similar 2:1 coordination polymers,  $[\text{Ag}(\text{L2})_2]\text{X}$ , **4**. The  $c$  axes of the two isomorphous tetragonal unit cells are longer (5.123(2) Å,  $\text{X} = \text{NO}_3^-$ ; 5.130(2) Å,  $\text{X} = \text{BF}_4^-$ ) than the corresponding axis of the urea structure, which is consistent with the characteristic 5.1 Å intermolecular spacing<sup>10</sup> of other oxalamide structures. It is interesting to note that the network structure is the same for the two different anions.



The silver atoms of each structure have a flattened tetrahedral geometry, due to the restrained environment induced by the ligand-imposed repeat distances. The urea structure, **3**, the one with the shorter repeat distance, has the greater silver distortions with the top and bottom angles opened up to 135.0(2)° from the ideal tetrahedral angle, while the remaining four angles are compressed to 98.4(1)°. In the less compressed oxalamide structures, **4**, the silver tetrahedra show less distortion with angles of 130.7(1)° and 100.0(1)° for the  $\text{NO}_3^-$  salt and 127.4(1)° and 100.5(1)° for the  $\text{BF}_4^-$  salt.

It is also interesting to note that the molecular symmetries of the hosts and guests persist in these systems. In both the dicarboxylic acid and the  $\text{Ag}^+$  urea systems the urea molecules retain their 2-fold axes, while the analogous oxalamide molecules similarly retain their inversion centers. The  $\text{Ag}^+$  cations are tetrahedral with  $S_4$  point group symmetry. A combination of an  $S_4$  symmetry element with the  $C_2$  symmetry element of the urea molecule yields the acentric space group  $P\bar{4}$  for **3**. In contrast, the combination of an  $S_4$  symmetry element with the inversion center of the oxalamide **2** yields the centric space group  $P4/n$ . This persistence of molecular symmetry has been found in previously studied urea and oxalamide structures. Symmetrical urea derivatives commonly retain their 2-fold axes, while symmetrical oxalamides are commonly centrosymmetric.<sup>2,4</sup> Molecules **1** and **2** are thus not just chemically reliable hosts for a wide variety of guests, and they are also extraordinarily good molecules for crystal design as well. They reliably determine both crystallographic repeat distances and symmetry.

The significant point demonstrated by these three silver structures is that *the distances between the silver atoms have been determined by the spacing established by ligand hydrogen bonded  $\alpha$ -networks*. The control of the spacing and symmetry of a guest atom or molecule in a crystal is a problem of obvious significance. We demonstrated this earlier in our diacetylene work. This same control has now been extended to metal systems with use of the identical molecular hosts. Applications can be envisioned for crystals with controlled metal spacing and symmetry.<sup>11</sup>

**Acknowledgment.** This work is supported by the National Science Foundation under Grant No. CHE-9630042.

**Supporting Information Available:** Tables of crystallographic data as well as distances and angles, positional parameters, and  $U$  values for **3** and **4** and details of the experimental procedures (10 pages). See any current masthead page for ordering and Internet access instructions.

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(11) Magnetic, electronic, and optical properties of metal-containing solids all depend upon these parameters. Similarly, metal-containing solids with designed channels or cavities are of interest as catalysts.