

Preparation, Clathration Ability, and Catalysis of a Two-Dimensional Square Network Material Composed of Cadmium(II) and 4,4'-Bipyridine

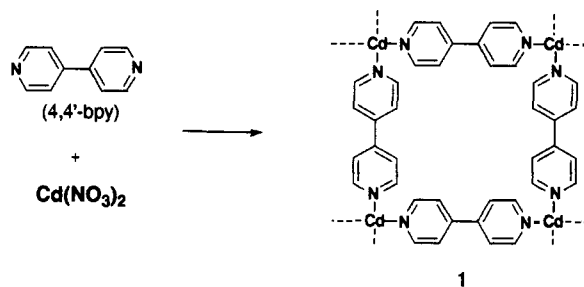
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Inorganic materials with inner cavities such as zeolites are known to bind many organic molecules in the cavity and often exhibit unique catalysis for organic reactions, in which high regioselectivity, stereoselectivity, and shape selectivity are observed.^{1,2} Construction of the inner cavities mainly surrounded by organic components is attractive since the shape, size, and function of the cavity become designable. This paper reports the formation and clathration ability of a two-dimensional square network material $\{[\text{Cd}(4,4'\text{-bpy})_2](\text{NO}_3)_2\}_\infty$ (**1**) (bpy = bipyridine).³⁻⁵ Having inner cavities surrounded by 4,4'-bpy units, this material easily clathrates some aromatic guests with high shape specificity. Heterogeneous catalysis of **1** for cyanosilylation of aldehydes is also disclosed here. Although Robson et al. reported closely related materials, $[\text{M}(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2]\text{X}$ (M

= Zn, Cd, Cu; X = PF₆, SiF₆)^{6a} and $[\text{Cd}(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2]\text{PF}_6 \cdot 2(4,4'\text{-bpy}) \cdot 4\text{H}_2\text{O}$,^{6b,c} their clathrate formation and catalysis have been not explored.



(Counter ions are omitted for clarity.)

When $\text{Cd}(\text{NO}_3)_2$ was treated with 4,4'-bpy (1–2 molar equiv) in H_2O –EtOH at ambient temperature, colorless crystals easily grew within a day.⁷ Elemental analysis⁸ and X-ray crystallography⁹ supported the formation of the square network material **1**. The network structure of **1** was confirmed by preparing a clathrate with *o*-dibromobenzene (**2**). Thus the crystallization of **1** in the presence of **2** gave a clathrate complex, $\{[\text{Cd}(\text{bpy})_2](\text{NO}_3)_2 \cdot (\text{C}_6\text{H}_4\text{Br}_2)_2\}_\infty$ (**3**),^{10,11} whose crystal structure was analyzed by an X-ray diffraction study (Figures 1–3).

The crystal structure is characterized by the following features.

- (1) The clathrate complex **3** consists of two-dimensional networks; each network is made up of layers stacked on each other, as in graphite, with an interplane separation of 6.30 Å (Figure 3).
- (2) A layer consists of an edge-sharing, perfectly planar square with a Cd(II) ion and 4,4'-bpy at each corner and side, respectively, though each square is distorted to some extent ($\angle \text{N8}–\text{Cd1}–\text{N2}' = 86.3^\circ$; $\angle \text{N15}–\text{Cd1}'–\text{N2}'' = 93.7^\circ$) (Figure 2).
- (3) Two molecules of *o*-dibromobenzene are clathrated in each square cavity.
- (4) While pyridine rings A and A' linking Cd1 and Cd1' are twisted by 139.2° , pyridine rings B and B' are in the same plane ($\angle \text{C4}'\text{C5}'\text{C5}''\text{C4}'' = 0.00^\circ$).¹³ This difference is most likely attributed to host–guest interactions; i.e., the guest molecule (C) stacks B and B' with a face-to-face distance of 3.56–3.98 Å.^{14–16}
- (5) The cadmium atom has distorted octahedral geometry with

(7) A typical procedure: an aqueous solution (8 mL) of cadmium(II) nitrate (1.0 mmol) and an ethanol solution (2 mL) of 4,4'-bpy (2.0 mmol) were combined. The initially formed fine precipitate (a very small amount) was filtered, and the clear filtrate was allowed to stand overnight at ambient temperature to give colorless crystals. The crystals were collected (ca. 50% yield) and subjected to elemental analysis⁸ and X-ray crystallography.⁹

(8) Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{CdN}_4\text{O}_6 \cdot \text{H}_2\text{O} \cdot [\text{Cd}(\text{bpy})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$: C, 42.38; H, 3.20; N, 14.83. Found: C, 42.22; H, 3.14; N, 14.69.

(9) In spite of many attempts, the crystal structure of **1** itself has not been fully solved. However, low-quality diffraction data showed that the alignment of Cd^{2+} and 4,4'-bpy in **1** consists of a layered array of infinite square networks and is essentially the same as that in **3** except that nitrate ions are accommodated in the microchannels. Water molecules seem disordered and could not be found. As a referee suggested, the presence of labile water molecules would help explain the catalysis of **1** discussed later.

(10) Crystal data of **3**: monoclinic, $C2/c$; $a = 21.828(4)$ Å, $b = 11.769(2)$ Å, $c = 13.878(2)$ Å, $\beta = 100.54(1)^\circ$; $V = 3505(1)$ Å³; $Z = 4$; $d_{\text{calc}} = 1.98$ g cm⁻³; $F(000) = 1976$; $\mu(\text{Cu K}\alpha) = 102.82$ cm⁻¹; $\lambda(\text{Cu K}\alpha) = 1.5418$ Å; 3286 reflections measured, 2582 observed ($F > 3.00(\sigma(F))$); number of parameters 258; $R = 0.074$; $R_w = 0.101$. Diffractionometer used: Mac Science MXC18.

(11) Anal. Calcd for $\text{C}_{32}\text{H}_{24}\text{Br}_4\text{CdN}_6\text{O}_6 \cdot [\text{Cd}(\text{bpy})_2](\text{NO}_3)_2 \cdot (\text{C}_6\text{H}_4\text{Br}_2)_2$: C, 37.66; H, 2.37; N, 8.23. Found: C, 37.69; H, 2.23; N, 8.15.

(12) TG and DSC analyses of **3** showed that dibromobenzene was desorbed endothermally at 149 °C. After about 50% weight loss at 140–220 °C, the resulting Cd–bpy skeleton was thermally stable before its decomposition at 434 °C. The clathrate $1 \cdot (\text{C}_6\text{H}_4\text{Br}_2)_2$ completely liberated the guest at 60 °C in methanol suspension as shown by both ¹H NMR and elemental analysis. Whether the material adsorbs and desorbs without destroying and recrystallizing the network is uncertain at present.

(13) The pyridine rings B and B' lean from the perpendicular by 50.1°.

(14) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.

(15) A short distance (3.2 Å) between Br22 and H9' attached to C9' of pyridine ring B' also implies electrostatic attraction between them.

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(3) Macrocyclic tetranuclear complexes, $[(\text{en})\text{M}(4,4'\text{-bpy})_4](\text{NO}_3)_8$ (en = ethylenediamine; M = Pd or Pt), having a square cavity: (a) Fujita, M.; Yazaki, J.; Ogura, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645–5647. (b) Fujita, M.; Yazaki, J.; Ogura, K. *Chem. Lett.* **1991**, 1031–1032. (c) Ability of these complexes for clathration of aromatic compounds in aqueous solution: Fujita, M.; Yazaki, J.; Ogura, K. *Tetrahedron Lett.* **1991**, *32*, 5589–5592.

(4) Infinite frameworks consisting of transition metal and organic ligand: (a) Hoskins B. F.; Robson, R. *J. Am. Chem. Soc.* **1989**, *111*, 5962–5964. (b) Abrahams, B. F.; Hoskins, B. F.; Liu, J.; Robson, R. *J. Am. Chem. Soc.* **1991**, *113*, 3045–3051. (c) Abrahams, B. F.; Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1991**, *113*, 3606–3607. (d) Copp, S. B.; Subramanian, S.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 8719–8720. (e) Park, K.-M.; Iwamoto, T. *J. Chem. Soc., Chem. Commun.* **1992**, 72–74. (f) Park, K.-M.; Kuroda, R.; T., I. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 884–886. (g) Behrens, U.; Brimah, A. K.; Yünlü, K.; Fischer, R. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 82–83. (h) Munno, G. D.; Julve, M.; Nicolo', F.; Lloret, F.; Faus, J.; Ruiz, R.; Sinn, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 613–615. (i) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Grandjean, D.; Kahn, O. *Science* **1993**, *261*, 447–449. Also see refs 6a, c.

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(6) (a) They have interpenetrating structures possessing no inner cavity. For M = Zn, see the following. Gable, R. W.; Hoskins, B. F.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1677–1678. For M = Cu and Cd, see ref 6c. (b) The authors thank one of the referees for informing them that this complex consists of the same non-interpenetrating $[\text{Cd}(\text{bpy})_2]^{2+}$ square grid sheet,^{6c} but in that case two molecules of uncoordinated bipyridine were clathrated into each square cavity. (c) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. *Supramolecular Architecture*; Bein, T., Ed.; ACS Symposium Series 499; American Chemical Society: Washington, DC, 1992; Chapter 19.

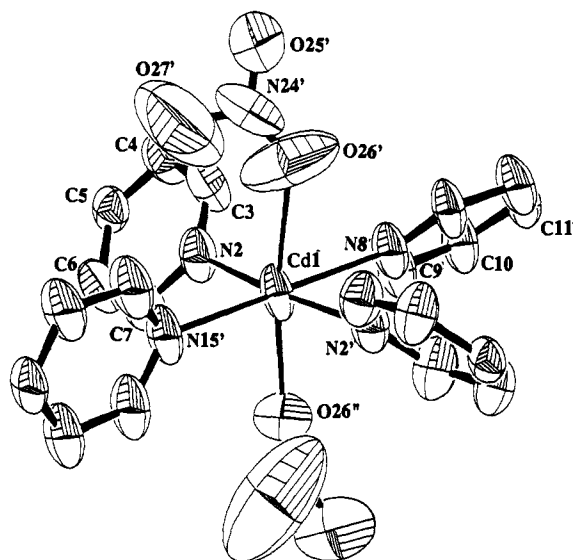


Figure 1. View around the Cd(II) ion of **3**, showing 50% probability ellipsoids. Important bond lengths (Å): Cd1–N2 = 2.372(7), Cd1–N8 = 2.36(1), Cd1–O26' = 2.489(7). Bond angles (deg): N2–Cd1–N8 86.3(2), N2'–Cd1–N2'' = 172.5(5), N8–Cd1–N15' = 180.000(4), N2–Cd1–O26' = 78.5(4), N8–Cd–O26' = 84.9(4), O26–Cd–O26' = 169.8(7).

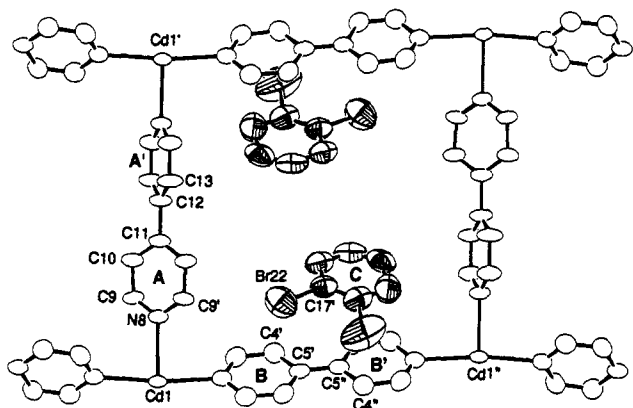


Figure 2. Top view of the square unit of the clathrate complex **3**, showing 50% probability ellipsoids. Nitrate ions are omitted for clarity. Cd...Cd separation: 11.77 Å for Cd1–Cd1'; 11.86 Å for Cd1–Cd1''.

four pyridyl groups at the equatorial positions and two nitrate ions at the apical positions (Figure 1).

High shape specificity in the clathration deserves attention. While *o*-dibromobenzene and *o*-dichlorobenzene were clathrated efficiently, their meta and para isomers were not included. The discrimination of the isomers in the clathration was applied to the separation of *o*-dibromobenzene from the isomeric mixtures.¹⁷ Thus treatment of a mixture of *o*- and *m*- (or *p*-)dibromobenzene (1:1) with Cd(NO₃)₂ and 4,4'-bpy in ethanol–water afforded only the clathrate **3** as crystals, from which **2** was recovered with >99% purity by acidic decomposition of the clathrate followed by extraction. Besides *o*-C₆H₄X₂ (X = Cl, Br), monohalobenzenes C₆H₅X (X = Br, Cl) were also complexed in the same host–guest ratio.¹⁸

(16) Host–guest interaction across the layers may exist since the hydrogens of pyridine ring B are close to the C ring of the next layer (edge-to-face distance between B and C (next layer): 3.5 Å). Edge-to-face interaction of aromatics: Burley, S. K.; Petsko, G. A. *Science* **1985**, *229*, 23–28.

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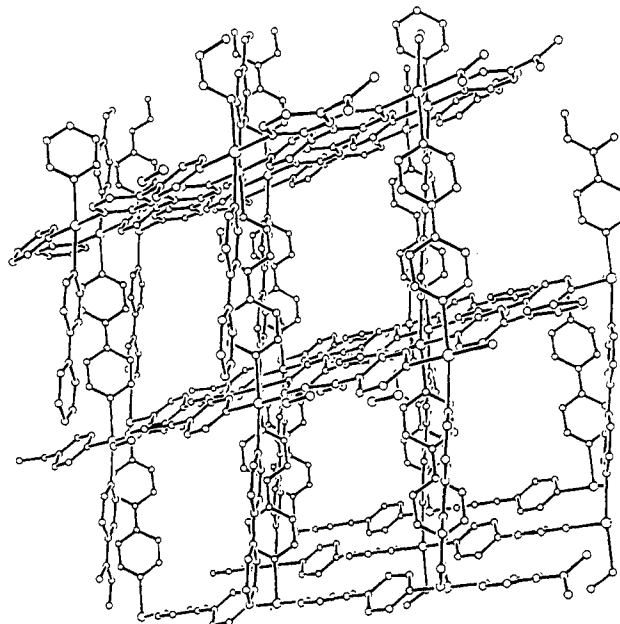


Figure 3. A view looking down the microchannel of **3**. Nitrate ions and *o*-dibromobenzene are omitted for clarity.

A unique character of the network material **1** is its catalysis for the cyanosilylation of aldehydes.¹⁹ Typically, treatment of benzaldehyde (0.5 mmol) and cyanotrimethylsilane (1.0 mmol) with a CH₂Cl₂ suspension (1.5 mL) of powdered **1** (0.1 mmol) (40 °C, 24 h) gave 2-(trimethylsilyloxy)phenylacetonitrile in 77% yield. The reaction is apparently promoted by heterogeneous **1** since no reaction took place with powdered Cd(NO₃)₂ or 4,4'-bpy alone or with the supernatant liquid of a CH₂Cl₂ suspension of **1**. Shape specificity similar to that in the clathration of dihalobenzenes was observed. While 2-tolualdehyde was cyanosilylated in moderate yield (40%), 3-tolualdehyde was poorly converted to the adduct (19%). Although α - and β -naphthaldehyde were good substrates to give the adducts in 62 and 84% yields, respectively, the more sterically demanding 9-anthraldehyde was hardly reacted. These shape specificities may be ascribed to the cavity size of the network material.

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Supplementary Material Available: X-ray diffraction data for **3** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(18) The following compounds were not included besides *m*- and *p*-C₆H₄X₂ (X = Br, Cl): toluene; *o*-, *m*-, and *p*-chlorotoluene; *o*-, *m*-, and *p*-dimethoxybenzene.

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