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2D and 3D Host Structures Built of $[Cd(py)_2\{Ag(CN)_2\}_{4/2}]_n$ Network and $[Cd\{Ag(CN)_2\}]_{6/2}]_n$ Latticework

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2D AND 3D HOST STRUCTURES BUILT OF $[Cd(py)_2\{Ag(CN)_2\}_{4/2}]_n$ NETWORK AND $[Cd\{Ag(CN)_2\}_{6/2}]_n$ LATTICEWORK

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Abstract The single crystal structures of $[Cd(py)_2\{Ag(CN)_2\}_2] \cdot C_6H_6$ and $[Cd\{Ag(CN)_2\}_3] \cdot G$ [G = K(15-crown-5)$_2$ • $2C_6H_6$ or Rb(15-crown-5)$_2$ • 2PhMe] determined in this work demonstrate the novel supramolecular features of not only the $Ag(CN)_2$-bridged host structures but also mode of the guest accommodation.

INTRODUCTION

We have been developing novel supramolecular structures by utilizing the Lewis basicity of the N-ends of linear $-NC-Ag-CN-$ as a rod to link two other coordination centers like Cd atoms. The secondary ligand such as unidentate NH_3,[1] 4-Mepy, [2] bridging 4,4'-bpy, [3] pyrazine(pyrz), [3] coordinating to the Cd is involved in our supramolecular structures to give the three-dimensional (3D) textile interwoven by the two-dimensional (2D) $[Cd(NH_3)_2\{Ag(CN)_2\}_2]$ networks,[1] the layer structure of the doubly interwoven networks of $[Cd(4\text{-Mepy})_2\{Ag(CN)_2\}_2]$ accommodating 4-Mepy molecules as the guests in the wavy networks,[2] the one-dimensional (1D) cationic chains of $[Cd(4\text{-Mepy})_4\{Ag_2(CN)_3\}]^+$ accommodating discrete $[Ag(CN)_2]^-$ anions in the interchain space,[2] the doubly interpenetrating 3D lattice of $[Cd(4,4'\text{-bpy})\{Ag(CN)_2\}_2]$,[3] and the triply interpenetrating 3D lattice of $[Cd(pyrz)\{Ag_2(CN)_3\}\{Ag(CN)_2\}]$.[3] As has been demonstrated by these structures, the linear $[Ag(CN)_2]^-$ and its dimeric condensate $[Ag_2(CN)_3]^-$ behave as versatile building blocks to give unprecedented polymeric coordination structures linked with

covalent coordination bonds.

This paper adds two types of the clathrate structures **1** and **2**. **1** has the 3D host structure interwoven by the 2D networks of $[Cd(py)_2\{Ag(CN)_2\}_2]$ accommodating C_6H_6 as the guest. The 3D host of **2** $[Cd\{Ag(CN)_2\}_3]^-$ does not involve any secondary ligands but accommodates $K(15C5)_2^+$ or $Rb(15C5)_2^+$ sandwich cation along with the neutral guest C_6H_6 or PhMe in the distorted Prussian blue-like 3D cage. The preparation and the single crystal structures of $[Cd(py)_2\{Ag(CN)_2\}_2] \cdot C_6H_6$ **1**, $[K(15C5)_2 \cdot 2C_6H_6][Cd\{Ag(CN)_2\}_3]$ **2a**, and $[Rb(15C5)_2 \cdot 2PhMe][Cd\{Ag(CN)_2\}_3]$ **2b** are reported in this paper.

EXPERIMENTAL

Preparation

$[Cd(py)_2\{Ag(CN)_2\}_2] \cdot C_6H_6$ **1** — To an aqueous solution containing 1.14 g (5 mmol) of $CdCl_2 \cdot 2.5H_2O$, 1.99 g (10 mmol) of $K[Ag(CN)_2]$ and *ca.* 3 ml of py, appropriate amounts of 2-aminoethanol and citric acid were added to adjust the pH to 9.5 in a final volume of 200 cm^3. The solution was covered with C_6H_6 and allowed to stand at 5 ℃; colorless block crystals of **1** were obtained in a few weeks. Found: C, 35.77; H, 2.45; N, 12.58 %; calculated for $C_{20}H_{16}Ag_2CdN_6$: C, 35.93; H, 2.41; N, 12.57 %.

$[K(15C5)_2 \cdot 2C_6H_6][Cd\{Ag(CN)_2\}_3]$ **2** — To an aqueous solution containing 1.14 g (5 mmol) of $CdCl_2 \cdot 2.5H_2O$, 1.99 g (10 mmol) of $K[Ag(CN)_2]$, the pH was adjusted to *ca.* 8.5 by adding appropriate amounts of KOH and citric acid in a final volume of 200 cm^3. The aqueous phase was covered with the organic layer of C_6H_6 containing *ca.* 50 mg (0.23 mmol) 15-crown-5 ether (15C5). Colorless prismatic crystals of **2a** were obtained after a few days leaving at 5 ℃. Since the product was too unstable to liberate the guest C_6H_6 immediately, the composition was determined from the value of density measured in bromoform-benzene mixture and the results of the X-ray structure refinement.

$[Rb(15C5)_2 \cdot 2PhMe][Cd\{Ag(CN)_2\}_3]$ **2b** — In an aqueous solution containing

1.14 g (5 mmol) of $CdCl_2 \cdot 2.5H_2O$ and 1.82 g (10 mmol) of $Na[Ag(CN)_2]$, 0.60 g (5 mmol) of RbCl was added and the pH was adjusted to *ca.* 8.5 using NaOH and citric acid. The aqueous phase was covered by a PhMe layer containing 15C5 as similar to the above. Colorless prismatic crystals of **2b** were also too unstable under ambient conditions similar to **2a**. The composition was determined on the basis of the density measurement in bromoform-toluene and the structure refinement.

X-ray crystallography

Table 1 summarizes the crystallographic and experimental data for **1**, **2a** and **2b**. Each of the single crystals was coated with epoxy resin. The intensity data were collected on a Rigaku AFC5R diffractometer at ambient temperature for **1** and **2a**, and on a Rigaku AFC5S at 243 K (Oxford cryosytems) for **2b**, using graphite-monochromated Mo-K α radiation (λ = 0.71070 Å) by 2θ-ω scan technique. Empirical absorption corrections were applied for Lp-corrected intensity data using the program ADC80 in UNICSIII.[4]

The structures were solved by the heavy-atom method after the Cd and Ag atoms had been found by the direct method using SHELXS 86.[5] All the remaining non-hydrogen atoms were located and refined anisotropically by the Fourier difference and full-matrix least-squares procedures[6] except for those of C_6H_6 and 15C5 in **2a** and PhMe and 15C5 in **2b**, those being refined isotropically. Neutral atomic scattering factors were taken from ref. 7 for Cd and Ag and from SHELX 76[6] for C, N, O.

RESULTS AND DISCUSSION

Structure of $[Cd(py)_2\{Ag(CN)_2\}_2] \cdot C_6H_6$ 1

Between the chiral space groups $I4_122$ or $I4_322$ suggested from the systematic absences, the former was applied for the structure refinement; absolute configuration has not yet been determined. As is illustrated in FIG. 1, the host has a 3D textile structure interwoven by the 2D networks of $[Cd(py)_2\{Ag(CN)_2\}_2]$,

TABLE 1. Summary of the crystallographic and experimental data

	1	2	3
formula	$C_{20}H_{16}Ag_2CdN_6$	$C_{38}H_{52}Ag_3CdKN_6O_{10}$	$C_{40}H_{56}Ag_3CdN_6O_{10}Rb$
formula mass	668.53	1227.98	1302.40
cryst. system	tetragonal	orthorhombic	orthorhombic
space group	$I4_122$ (No. 93)	*Pnma* (No.62)	*Pnma* (No.62)
a/Å	12.7816(8)	16.267(4)	16.508(10)
b/Å	= *a*	21.849(4)	21.996(5)
c/Å	13.062(1)	14.223(5)	14.177(4)
U/Å^3	2133.9(3)	5055(2)	5041(3)
Z	4	4	4
μ, cm^{-1}	28.04	16.87	25.46
D_x, D_m, g cm^{-3}	2.08, 2.08(1)	1.61, 1.60(1)	1.72, 1.72(1)
scan range, deg	4−65	4−55	4−50
h, *k*, *l* range	0−19, 0−13	0−22, 0−30	0−19, 0−26
	0−19	0−19	0−16
reflns. measd (unique)	2328 (1074)	6545 (4960)	5143 (3629)
reflns. used, N_p	958 [$>4\sigma(F_o)$]	2749 [$>4\sigma(F_o)$]	1981 [$>4\sigma(F_o)$]
parameters, N_r	79	156	160
$g^{a)}$	3.0×10^{-4}	3.0×10^{-4}	1.0×10^{-4}
R, wR $^{a)}$	0.037, 0.047	0.077, 0.076	0.084, 0.072
goodness of fit$^{a)}$	1.64	1.82	1.76

a. $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$, $wR = [\Sigma w(| F_o | - | F_c |)^2 / \Sigma | F_o |^2]^{1/2}$, goodness of fit = $[\Sigma w(| F_o | - | F_c |)^2/(N_r - N_p)]^{1/2}$ where $w = [\sigma(F_o)^2 + g(F_o)^2]^{-1}$

which has a rhombus mesh of *trans*-Cd(py)$_2$ at every corner edged by −NC−Ag−CN− spans. There are two sets of the 2D networks arrayed orthogonally to each other without any direct connections; one set of a staking along the [110] and the other along the [1$\bar{1}$0] with the interlayer distance of 9.04 Å to provide a channel extending along the *c* axis. The channel is occupied by the py ligands protruding from the Cd atoms located on the origin and the equivalent positions of the $I4_122$ unit cell. The py protruding from one network is sandwiched by the py's from the other with the plane-to-plane distance of *ca.* 3.27 Å. The guest C_6H_6 is trapped around the center of the mesh of one network where is the interlayer space between the networks of the other set.

Structures of $[K(15C5)_2 \cdot 2C_6H_6][Cd\{Ag(CN)_2\}_3]$ **2a** and $[Rb(15C5)_2 \cdot 2PhMe][Cd\{Ag(CN)_2\}_3]$ **2b**

The centrosymmetric space group *Pnma* was finally chosen for both **2a** and **2b** after checking another non-centrosymmetric $Pn2_1a$ possible from the systematic absences. As is shown in FIG. 2, the anionic 3D host is built of the octahedral Cd at every corner and the $-NC-Ag-CN-$ span between the corners. The 3D framework has a 3D topology same to that of Prussian blue lattice[8] but distorted rhombohedrally. The cavity with the volume of *ca.* 1260 $Å^3$ is large enough to accommodate the bis-crown-ligated alkali cation and a couple of the aromatic guests. These two clathrates exemplify the supramolecular structures of the Prussian blue-like lattice speculated by Keggin and Miles[9] to accommodate an alkali cation inside a small cube, although the speculation has been denied by the single crystal work.[8] The present host structure of **2** with the expanded lattice dimensions is favorable to the accommodation of the bis-crown-clad alkali cation along with the neutral guests as packing materials.

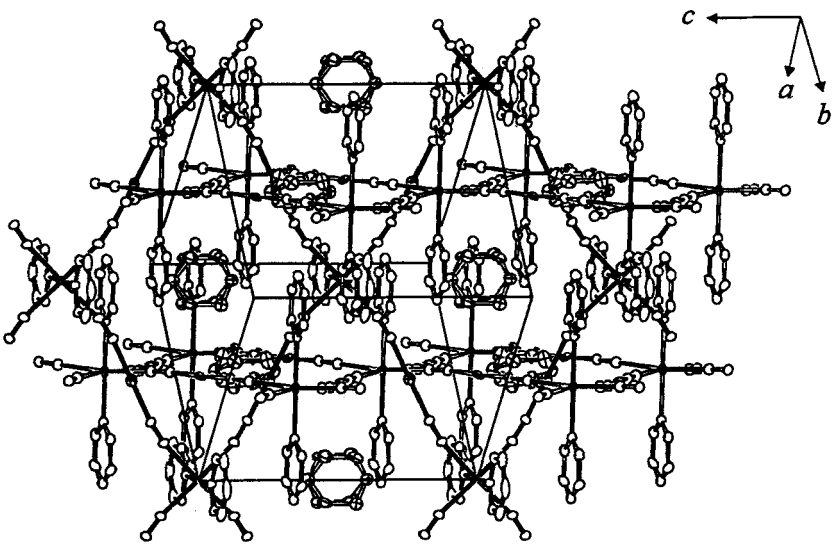

FIGURE 1. Unit cell structure of $[Cd(py)_2\{Ag(CN)_2\}_2] \cdot C_6H_6$ **1**. Thermal ellipsoids with 30 % probability have been shown for Cd and Ag with an anisotropic section; for C of C_6H_6 with a cross. One of the networks stacking along the [1$\bar{1}$0] has been drawn with solid bonds.

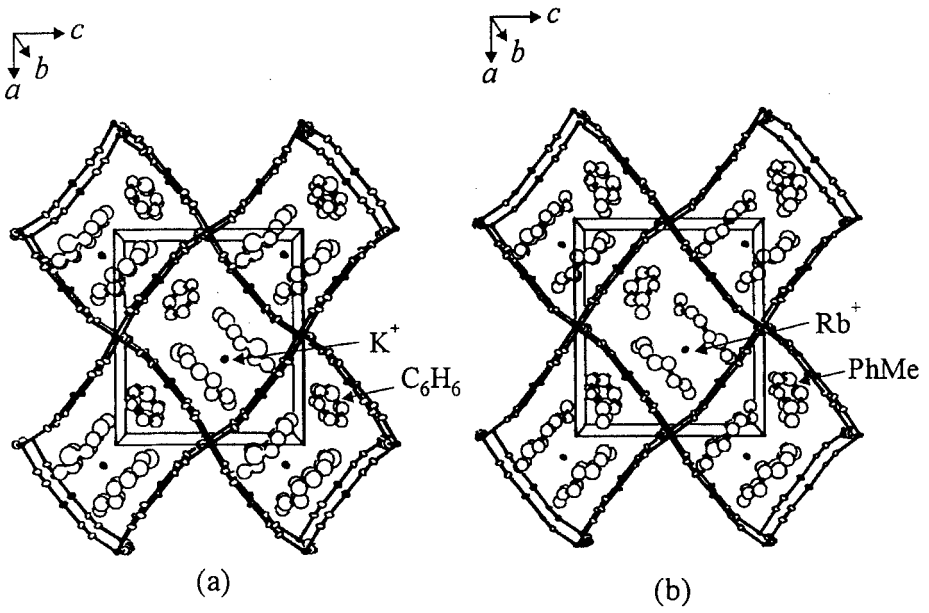

FIGURE 2. Perspective views of the 3D framework structures along the *b* axes of (*a*) $[K(15C5)_2 \cdot 2C_6H_6][Cd\{Ag(CN)_2\}_3]$ **2a** and (*b*) $[Rb(15C5)_2 \cdot 2PhMe][Cd\{Ag(CN)_2\}_3]$ **2b**.

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