

Variations of Multi-Dimensional Supramolecular Structures Built of the Two-Dimensional $[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2]_n$ Network: Three-Dimensional Textile Structures of *catena*-Poly[*trans*-bis(pyridine)cadmium(II)-di- μ -{dicyanoargentato(I)-*N,N'*}]·G (G = Benzene or Pyrrole) and Two-Dimensional Layer Structure of *catena*-Poly[*trans*-bis(pyridine)cadmium(II)-di- μ -{dicyanoargentato(I)-*N,N'*}]

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Abstract. The three title supramolecular structures of $[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2] \cdot \text{C}_6\text{H}_6$ **1a**, $[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2] \cdot \text{C}_4\text{H}_5\text{N}$ **1b** and $[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2]$ **1c** (py = pyridine) have been determined by single crystal X-ray diffraction. **1a**: tetragonal $I4_122$, $a = 12.7816(8)$, $c = 13.062(1)$ Å, $U = 2133.9(3)$ Å³, $Z = 4$, $R = 0.030$ for 958 reflections; **1b**: orthorhombic, $I2_12_12_1$, $a = 12.861(2)$, $b = 12.438(3)$, $c = 13.105(2)$ Å, $U = 2096.3(5)$ Å³, $Z = 4$, $R = 0.045$ for 1272 reflections; **1c**: $C2/m$, $a = 8.665(2)$, $b = 14.139(1)$, $c = 7.549(1)$ Å, $\beta = 93.15(2)^\circ$, $U = 923.3(3)$ Å³, $Z = 2$, $R = 0.043$ for 977 reflections. All the structures involve a two-dimensional (2D) network of $[\text{Cd}(\text{---NCAgCN---Cd}_{1/4})_4]_n$ with a rhombus mesh from which network a pair of unidentate py ligands protrude at the trans positions of Cd. In clathrates **1a** and **1b** the 3D textile hosts interwoven by the layers of the 2D networks accommodate a benzene and pyrrole molecule at every centre of the mesh, respectively. **1c** has a simple layer structure stacked by the 2D networks the mesh of which is penetrated by the py ligands from the upper and lower layers.

Key words. Crystal structures, clathrate, dicyanoargentate, cadmium, benzene, pyrrole.

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1. Introduction

The varieties of $\text{Ag}(\text{CN})_2$ -linked multi-dimensional supramolecular structures obtained by us are the three-dimensional (3D) textile structure interwoven by two sets of two-dimensional (2D) network stacking in $[\text{Cd}(\text{NH}_3)_2\{\text{Ag}(\text{CN})_2\}_2]$ [1], the doubly interwoven 2D networks of $[\text{Cd}(4\text{-Mepy})_2\{\text{Ag}(\text{CN})_2\}_2]\cdot 4\text{-Mepy}$ (4-Mepy = 4-methylpyridine) accommodating 4-Mepy as the guest in the mesh of the wavy network [2], the Prussian blue-like 3D host structures in $[\text{K}(15\text{C}5)_2\cdot 2\text{C}_6\text{H}_6][\text{Cd}\{\text{Ag}(\text{CN})_2\}_3]$ and $[\text{Rb}(15\text{C}5)_2\cdot 2\text{PhMe}][\text{Cd}\{\text{Ag}(\text{CN})_2\}_3]$ (15C5 = 15-crown-5) [3]. In these structures dicyanoargentate(I) behaves as a rod ligand bridging Cd atoms, to which a pair of secondary ligands, NH_3 or 4-Mepy, coordinate at *trans* positions except for the last group whose host is built only by the bridges of the primary CN ligand between Cd atoms. Since the size of py (pyridine) is intermediate between NH_3 and 4-Mepy, we examined the formation of multi-dimensional structures with py ligands at the Cd^{2+} linked by $[\text{Ag}(\text{CN})_2]^-$ rods. $[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2]\cdot \text{G}$ (G = C_6H_6 **1a**; $\text{C}_4\text{H}_5\text{N}$ **1b**) clathrates and a complex $[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2]$ **1c** were obtained. Their single crystal structures revealed the role of the secondary ligand py and the flexibility of the $\text{Ag}(\text{CN})_2$ -linked multi-dimensional network. In this paper their structures are described in detail in comparison with the previously reported compounds $[\text{Cd}(\text{NH}_3)_2\{\text{Ag}(\text{CN})_2\}_2]$ **2** [1] and $[\text{Cd}(4\text{-Mepy})_2\{\text{Ag}(\text{CN})_2\}_2]\cdot 4\text{-Mepy}$ **3** [2]; as for **1a** a brief description of the structure has been reported [3].

2. Experimental

2.1. PREPARATION

2.1.1. catena-Poly[trans-bis(pyridine)cadmium(II)-di- μ -{dicyanoargentato(I)-N,N'}]-benzene(1/1), $[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2]\cdot \text{C}_6\text{H}_6$ **1a**

To an aqueous solution containing 5 mmol of CdCl_2 , 10 mmol of $\text{K}[\text{Ag}(\text{CN})_2]$ and 3 mL of py, appropriate amounts of 2-aminoethanol (mea) and citric acid were added to obtain 200 mL of a clear aqueous solution at pH 9.5. The solution was covered with a benzene layer and allowed to stand in a refrigerator at 5 °C for several weeks. Colourless block crystals were obtained. *Anal. Found*: C, 35.77; H, 2.45; N, 12.58%. *Calcd.* for $\text{C}_{20}\text{H}_{16}\text{Ag}_2\text{CdN}_6$: C, 35.93; H, 2.41; N, 12.57%.

2.1.2. catena-Poly[trans-bis(pyridine)cadmium(II)-di- μ -{dicyanoargentato(I)-N,N'}]-pyrrole(1/1), $[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2]\cdot \text{C}_4\text{H}_5\text{N}$ **1b**

By using pyrrole instead of benzene in 2.1.1., colourless block crystals were obtained. *Anal. Found*: C, 32.86; H, 2.34; N, 14.81%. *Calcd.* for $\text{C}_{18}\text{H}_{15}\text{Ag}_2\text{CdN}_6$: C, 32.88; H, 2.30; N, 14.91%.

2.1.3. catena-Poly[trans-bis(pyridine)cadmium(II)-di- μ -{dicyanoargentato(I)- N,N' }], $[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2]_n$ **1c**

To an aqueous solution containing 5 mmol of CdCl_2 , 10 mmol of $\text{K}[\text{Ag}(\text{CN})_2]$ and 3 mL of py, appropriate amounts of mea and citric acid were added to obtain 200 mL of a clear aqueous solution at a pH of 9.5, which solution was allowed to stand in a refrigerator at 5 °C for a few days. Colourless prismatic crystals were obtained. *Anal. Found*: C, 28.24; H, 1.78; N, 14.39%. *Calcd.* for $\text{C}_{13}\text{H}_{10}\text{Ag}_2\text{CdN}_6$: C, 28.48; H, 1.71; N, 14.23%.

2.2. X-RAY CRYSTALLOGRAPHY

Table I summarises the crystallographic and experimental data for compounds **1a–c**. The intensity data were collected at room temperature on a Rigaku AFC-5R diffractometer for **1a** and on a Rigaku AFC-5S for **1b** and **1c**, using graphite-monochromated MoK_α radiation ($\lambda = 0.71069 \text{ \AA}$) by the 2θ - ω scan technique. The unit cell dimensions were refined using 25 reflections in the 2θ range of $48.05^\circ < 2\theta < 49.75^\circ$ for **1a**, $30.38^\circ < 2\theta < 39.15^\circ$ for **1b** and $23.87^\circ < 2\theta < 29.77^\circ$ for **1c**. Three standard reflections were monitored after ever 150 reflections; no significant decay was observed for each crystal. Empirical absorption corrections via ψ scans of three reflections were made for L_p -corrected intensity data for **1b** and **1c** using the programme ADC80 in UNICSIH [4]. An extinction correction was applied for **1a** using the equation $F_{\text{corr}} = F_c[1 - \{x(F_c)^2/\sin \theta\}]$; x was refined to $5.6(3) \times 10^{-8}$.

The structures were solved by the heavy-atom method. Cd and Ag were located by the direct method using SHELXS 86 [5]; the remaining non-H atoms were found from successive Fourier and Fourier-difference syntheses. These atoms were refined anisotropically by full-matrix least-squares procedures. In the final F_c calculation all H atoms fixed at calculated positions with the isotropic thermal parameters of 6.0 \AA^2 were included. Absolute configurations were determined for **1a** and **1b** based on Flack absolute structure parameters x using SHELXL 93 [6]. Neutral atomic scattering factors including those for real and imaginary anomalous dispersion corrections for Cd and Ag were taken from Ref. 7; those for O, N and C from SHELX 76 [8].

The refined atomic parameters are listed in Table II; the selected bond distances and angles in Table III. The structures are illustrated in Figures 1 to 4 for **1a**, **1b**, **1c** and **2**, respectively.

Table I. Crystallographic and experimental data for **1a–1c**.

	1a	1b	1c
Formula	C ₂₀ H ₁₆ Ag ₂ CdN ₆	C ₁₈ H ₁₅ Ag ₂ CdN ₇	C ₁₄ H ₁₀ Ag ₂ CdN ₆
Formula mass	668.53	657.51	590.42
Crystal system	tetragonal	orthorhombic	monoclinic
Space group	<i>I</i> 4 ₁ 22	<i>I</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> 2/ <i>m</i>
<i>a</i> /Å	12.7816(8)	12.861(2)	8.665(2)
<i>b</i> /Å	≅ <i>a</i>	12.438(3)	14.139(1)
<i>c</i> /Å	13.062(1)	13.105(2)	13.062(1)
β /°	90	90	93.15(2)
<i>U</i> /Å ³	2133.9(3)	2096.3(5)	923.3(3)
<i>Z</i>	4	4	2
<i>F</i> (000)	1280	1256	556
<i>D</i> _m /g cm ^{-3b}	2.08(1)	2.08(1)	2.12(1)
<i>D</i> _x /g cm ⁻³	2.08	2.08	2.12
μ (MoK α)/cm ⁻¹	28.04	28.54	32.26
2 θ range/°	5 < 2 θ < 65	5 < 2 θ < 60	4 < 2 θ < 60
<i>h</i> , <i>k</i> , <i>l</i> range	0 ≤ <i>h</i> ≤ 19 0 ≤ <i>k</i> ≤ 13 0 ≤ <i>l</i> ≤ 19	0 ≤ <i>h</i> ≤ 18 0 ≤ <i>k</i> ≤ 17 0 ≤ <i>l</i> ≤ 18	0 ≤ <i>h</i> ≤ 12 0 ≤ <i>k</i> ≤ 19 -10 ≤ <i>l</i> ≤ 10
Scan width/°	1.31 + 0.30 tan θ	1.63 + 0.30 tan θ	1.58 + 0.30 tan θ
Refins. measured	2328	1803	1526
Unique refins.	1074	1585	1237
Refins. used: <i>N</i> _r	958[> 4 σ (<i>F</i> ₀)]	1272[> 4 σ (<i>F</i> ₀)]	977[> 3 σ (<i>F</i> ₀)]
Parameters: <i>N</i> _p	79	128	59
<i>g</i> ^c	1.5 × 10 ⁻⁴	2.0 × 10 ⁻⁴	1.0 × 10 ⁻⁴
<i>R</i> ^c , <i>wR</i> ^c	0.029, 0.036	0.044, 0.046	0.042, 0.040
GOF	1.5455	1.4452	1.3895
Maximum Δ /σ	0.02	0.01	0.00
$\Delta\rho$ /e Å ⁻³	+0.78, -0.96	+1.16, -1.10	+0.67, -1.15

^a The cell constants were refined with $\lambda = 0.71069$ Å.

^b The density was measured by flotation in a bromoform–mesitylene mixture.

^c $R = \sum ||F_0| - |F_c|| / \sum |F_0|$, $wR = [\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2]^{1/2}$, GOF = $\sum w(|F_0| - |F_c|)^2 / (N_r - N_p)]^{1/2}$, $w^{-1} = \sigma^2(F_0) + gF_0^2$.

3. Results and Discussion

3.1. STRUCTURE DESCRIPTION

3.1.1. [Cd(py)₂{Ag(CN)₂}]₂·C₆H₆ **1a** and [Cd(py)₂{Ag(CN)₂}]₂·C₄H₅N **1b**

The non-centrosymmetric space groups *I*4₁22 and *I*2₁2₁2₁ were determined for **1a** and **1b** respectively. Other space groups *I*222, *Imm*2 and *Immm*, possible for **1b** according to the systematic absences, were rejected because application of

Table II. Atomic parameters for $[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2]\cdot\text{C}_6\text{H}_6$ **1a**, $[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2]\cdot\text{C}_4\text{H}_5\text{N}$ **1b** and $[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2]$ **1c**.

Atom	x/a	y/b	z/c	$B_{\text{eq}}/\text{\AA}^2$ ^a
$[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2]\cdot\text{C}_6\text{H}_6$ 1a				
Cd	0.0	0.5	0.25	2.301(8)
Ag	0.25855(4)	0.74145(4)	0.0	3.125(9)
N	0.1019(4)	0.5851(4)	0.1204(3)	2.92(9)
C	0.1574(4)	0.6355(4)	0.0716(4)	2.7(1)
N(11)	0.1267(3)	0.3733(3)	0.25	2.53(7)
C(12)	0.2291(4)	0.4005(5)	0.2525(5)	3.2(1)
C(13)	0.3077(5)	0.3252(7)	0.2517(6)	4.7(1)
C(14)	0.2796(6)	0.2204(6)	0.25	5.7(2)
C(21)	0.0	0.5	-0.1446(7)	4.5(2)
C(22) ^b	0.086(1)	0.530(2)	-0.196(2)	5.1(4)
C(23) ^b	0.090(2)	0.530(2)	-0.306(2)	5.7(5)
$[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2]\cdot\text{C}_4\text{H}_5\text{N}$ 1b				
Cd	0.5	0.25	0.37772(7)	2.15(1)
Ag	0.23792(6)	0.48183(5)	0.1234(1)	3.66(1)
C(1)	0.3396(7)	0.3791(7)	0.1993(6)	3.0(2)
N(1)	0.3980(5)	0.3333(6)	0.2502(6)	3.1(1)
C(2)	0.1336(6)	0.5872(7)	0.0556(6)	3.0(2)
N(2)	0.0868(6)	0.6460(6)	0.0094(6)	3.6(1)
N(11)	0.3760(5)	0.1168(4)	0.3794(5)	2.6(1)
C(12)	0.2747(6)	0.1379(7)	0.3795(7)	3.6(2)
C(13)	0.2002(8)	0.057(1)	0.3752(9)	4.9(2)
C(14)	0.234(1)	-0.051(1)	0.373(1)	6.5(3)
C(15)	0.341(1)	-0.0722(8)	0.375(1)	5.1(2)
C(16)	0.4077(7)	0.0130(6)	0.3759(7)	3.6(2)
N(21)	0.0	0.25	0.256(1)	5.8(3)
C(22)	0.033(1)	0.331(1)	0.196(1)	8.5(4)
C(23)	0.024(1)	0.302(1)	0.0876(9)	7.5(4)
$[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2]$ 1c				
Cd	0.0	0.5	0.0	2.22(2)
Ag	0.25	0.75	0.5	4.50(2)
N	0.0918(6)	0.6194(4)	0.1987(7)	3.9(1)
C	0.1463(8)	0.6654(5)	0.3059(8)	3.7(1)
N(11)	0.2357(8)	0.5	-0.1334(9)	3.0(1)
C(12)	0.3059(8)	0.4174(5)	-0.165(1)	4.4(2)
C(13)	0.4555(8)	0.4151(6)	-0.231(1)	5.0(2)
C(14)	0.528(1)	0.5	-0.266(1)	4.3(2)

^a $B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i a_j^* a_i^* a_j$.

^b Italicised atoms are in disorder with 50% probability at the coordinates.

Table III. Interatomic distances (Å) and angles (°) for **1a**, **1b** and **1c**.

[Cd(py)₂{Ag(CN)₂]₂·C₆H₆ 1a					
Cd—N	2.397(4)	Cd—N(11)	2.290(6)	Ag—C	2.093(5)
C—N	1.150(8)	N(11)—C(12)	1.354(7)	C(12)—C(13)	1.39(1)
C(13)—C(14)	1.39(1)	C(21)—C(22)	1.34(2)	C(22)—C(23)	1.44(3)
C(23)—C(21)* ¹	1.36(2)	Ag...Ag* ⁴	3.273(0)		
N—Cd—N(11)	86.4(2)	N—Cd—N* ²	172.8(2)	N—Cd—N* ³	90.3(2)
C—Ag—C* ⁴	177.5(2)	Cd—N—C	168.6(4)	Ag—C—N	171.8(5)
Cd—N(11)—C(12)	120.1(4)	C(12)—N(11)—C(12)* ²	120.0(5)		
N(11)—C(12)—C(13)	121.4(6)	C(12)—C(13)—C(14)	118.7(6)		
C(13)—C(14)—C(13)* ²	120.0(7)	C(22)—C(21)—C(23)	104(1)		
C(21)—C(22)—C(23)	123(2)	C(21)* ¹ —C(23)—C(22)	116(2)		
Symmetry operations: * ¹ : -y + 0.5, -x + 0.5, -z + 0.5; * ² : 1 - y, x + 0.5, z + 0.25*; * ³ : -y + 0.5, -x + 0.5, -z + 0.5; * ⁴ : -y + 1, -x + 1, -z.					
[Cd(py)₂{Ag(CN)₂]₂·C₄H₅ N 1b					
Cd—N(1)	2.363(7)	Cd—N(11)	2.300(6)	Cd—N(2)* ¹	2.429(8)
Ag—C(1)	2.081(9)	Ag—C(2)	2.076(8)	Ag...Ag* ³	3.249(3)
Ag...Ag* ⁴	3.349(2)	C(1)—N(1)	1.16(1)	C(2)—N(2)	1.12(1)
N(11)—C(12)	1.33(1)	N(11)—C(16)	1.354(9)	C(12)—C(13)	1.39(1)
C(13)—C(14)	1.40(2)	C(14)—C(15)	1.40(2)	C(15)—C(16)	1.37(1)
N(21)—C(22)	1.36(1)	C(22)—C(23)	1.47(2)	C(23)—C(23)* ²	1.42(2)
N(1)—Cd—N(11)	86.4(2)	C(1)—Ag—C(2)	176.8(3)	Ag—C(1)—N(1)	171.0(7)
Cd—N(1)—C(1)	170.2(7)	Ag—C(2)—N(2)	171.0(8)	Cd—N(11)—C(12)	122.5(5)
N(1)—Cd—N(2)* ¹	90.8(3)	N(2)* ¹ —Cd—N(11)	93.4(3)		
Cd—N(11)—C(16)	118.6(5)	C(12)—N(11)—C(16)	118.9(7)		
N(11)—C(12)—C(13)	121.9(8)	C(12)—C(13)—C(14)	119(1)		
C(13)—C(14)—C(15)	119(1)	C(14)—C(15)—C(16)	118(1)		
N(11)—C(16)—C(15)	123.4(9)	C(22)—N(21)—C(22)* ²	109(1)		
N(21)—C(22)—C(23)	110(1)	C(22)—C(23)—C(23)* ²	105(1)		
Symmetry operations: * ¹ : 0.5 - x, 1 - y, 0.5 + z; * ² : -x, 0.5 - y, z; * ³ : 0.5 - x, y, -z; * ⁴ : x, 1 - y, 0.5 - z.					
[Cd(py)₂{Ag(CN)₂]₂ 1c.					
Cd—N	2.369(5)	Cd—N(11)	2.326(7)	Ag—C	2.059(6)
C—N	1.120(8)	N(11)—C(12)	1.345(8)	C(12)—C(13)	1.41(1)
C(13)—C(14)	1.387(9)				
N—Cd—N* ¹	91.1(2)	N—Cd—N(II)	90.1(2)	Cd—N—C	169.6(5)
Ag—C—N	178.9(6)	Cd—N(11)—C(12)	119.6(4)	C(12)—N(11)—C(12)*	120.6(7)
N(11)—C(12)—C(13)	121.0(7)	C(12)—C(13)—C(14)	118.8(8)		
C(13)—C(14)—C(13)*	119.8(8)				
Symmetry operations: * : x, 1 - y, z.					

$I2_12_12_1$ led to the most reasonable crystal structure; the absolute configurations were determined for both based on the Flack absolute structure parameters x (cf. 2.2).

As shown in Figures 1 and 2, each of the 3D host structures of **1a** and **1b** is constructed of the flat 2D networks of $[\text{Cd}(\text{---NCAgCN---Cd}_{1/4})_4]_n$ stacked along the $[110]$ and $[2\bar{2}0]$ directions respectively. The network has a rhombus mesh of a *ca.* 11.15 Å edge length cornered by Cd to which a pair of py ligands coordinate at the *trans* positions. There are no direct chemical bonds between the 2D networks but each of the meshes in the network extending along one direction is interpenetrated by a pair of the networks extending along the other direction. Thus, the whole crystal structure is seen as a 3D textile interwoven by two sets of the 2D networks as warp and woof running orthogonally to each other.

In **1a** the two sets of the networks with an interlayer distance of 9.04 Å are correlated to each other with the 4_1 screw axis to generate channels extending along the c axis at $x = 1/4, y = 1/4$, and $x = 3/4, y = 3/4$; these channels are occupied by the py ligands stacked along the c axis with a plane-to-plane distance of 3.27 Å. A py ring from one set of the network is sandwiched by two py rings from the other set. Another kind of cavity is generated at the centre of the mesh of one set into which the two networks of the other set penetrate to give the interlayer space. The guest benzene molecule trapped here, e.g. at 0, 0, 1/2, takes a statistical disorder of molecular orientation about the twofold axis along the $[1\bar{1}0]$ direction with the site occupancy of 0.5 for C(22) and C(23). The aromatic plane of the benzene molecule is inclined against the average mesh plane by *ca.* 27°.

The 3D textile host of **1b** is topologically the same as that of **1a**. The 2D networks stacking along the $[110]$ and $[\bar{1}10]$ directions correlate to each other with the twofold axes along the a or b axes, the angle formed by the two layers deviating by 1.9° from the right angle, though the section of the channel viewed along the c axis is approximated to a square with an edge length of 8.95 Å. The atom of the guest pyrrole on the twofold axis along the c axis was assignable to N(21) because of the smallest isotropic thermal parameter among the three crystallographically independent atoms in the ring that had been assumed to be C at the earlier stages of the refinement procedure. The inclination of the ring plane from the average mesh plane is *ca.* 23° comparable to that observed in **1a**.

3.1.2. $[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2] \mathbf{1c}$

The centrosymmetric $C2/m$ space group was applied. As shown in Figure 3, complex **1c** has a layer structure of the almost flat 2D $[\text{Cd}(\text{---NCAgCN---Cd}_{1/4})_4]_n$ network extending along (102), these networks being stacked with a shift of *ca.* 12.59 Å along the $[102]$ direction to give the interlayer distance of 3.84 Å along the $[0\bar{2}0]$ direction. The structure of the network itself is similar to those in **1a** and **1b** with the ---NCAgCN--- span length of 11.05 Å and the diagonal lengths of 14.14 and 22.09 Å respectively. As for the *trans*- $\text{Cd}(\text{py})_2$ moiety, Cd, and N(11)

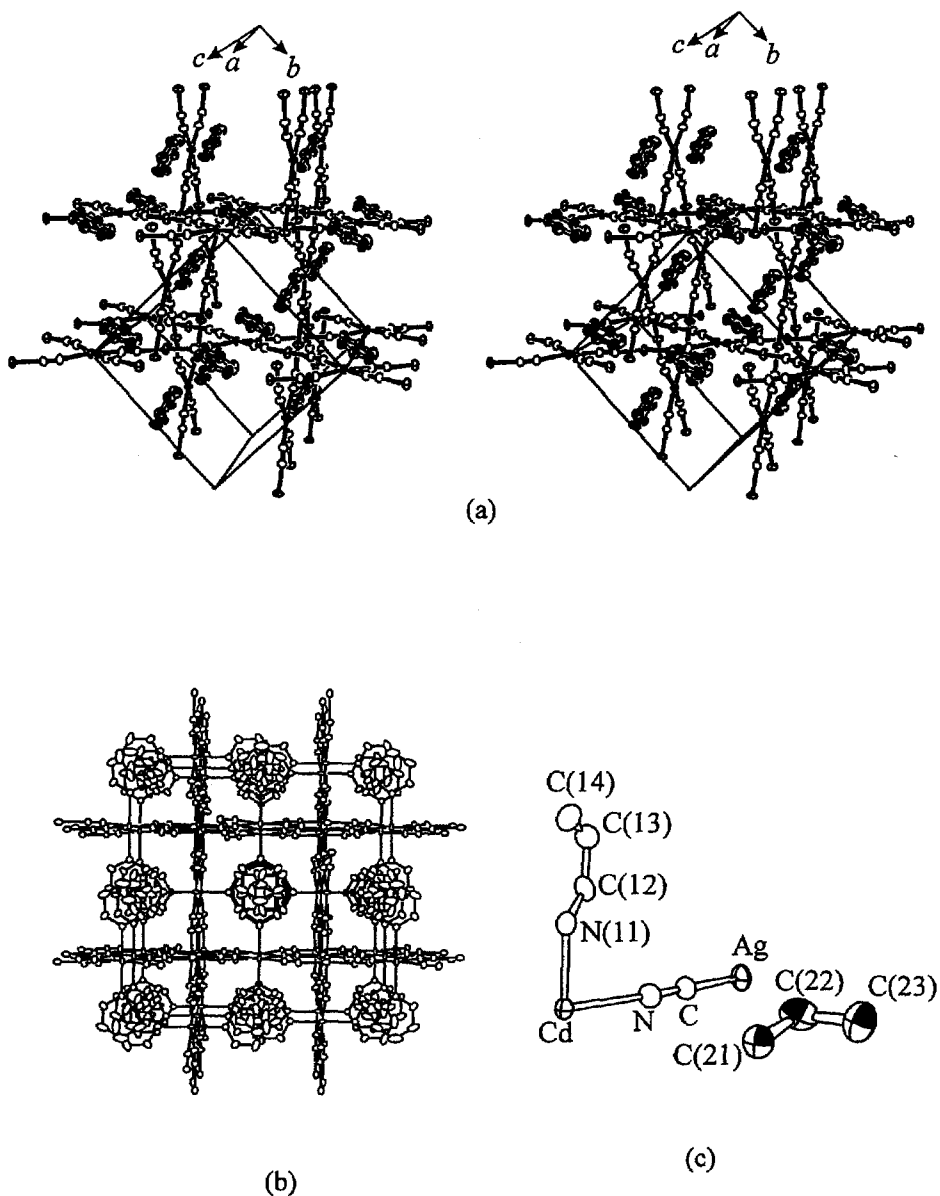


Figure 1. Structure of **1a**. (a) A stereoscopic view: py ligands have been omitted for the sake of clarity; one of the disordered orientations has been shown for each of the guest C_6H_6 whose C atoms are depicted with anisotropic sections as well as Cd atoms in the network; Ag atoms with anisotropic peripheries. (b) A view along the c axis showing py ligands stacking in the channel; C_6H_6 molecules have been omitted for the sake of clarity. (c) The asymmetric unit with atomic numbering scheme.

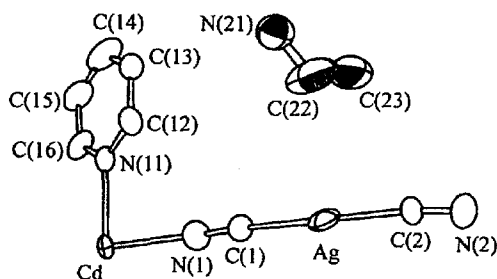
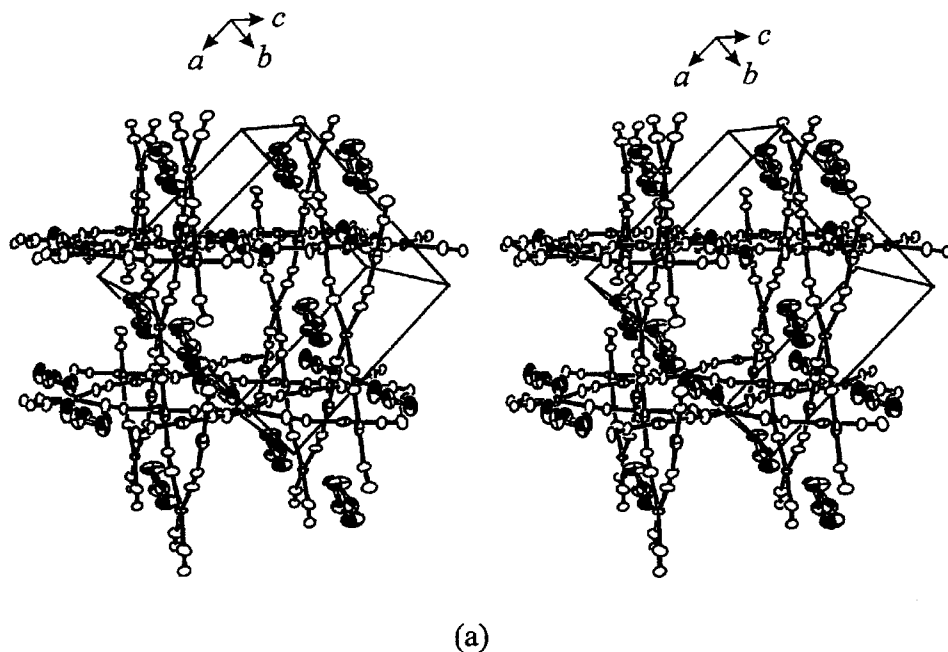
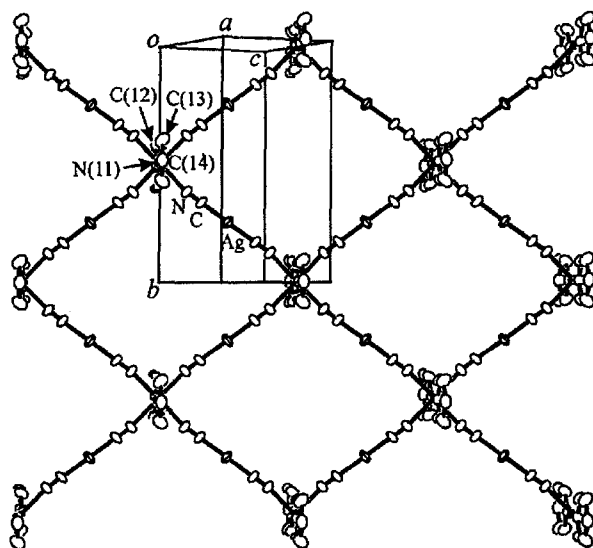
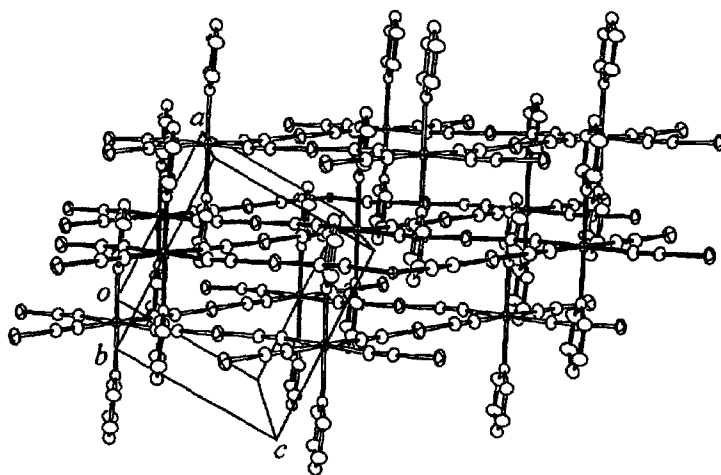


Figure 2. Structure of **1b**. (a) A stereoscopic view: py ligands have been omitted for the sake of clarity; for $\text{C}_4\text{H}_5\text{N}$ C atoms are depicted with hatched anisotropic sections and N with solid section; Cd and Ag in the network with anisotropic peripheries. (b) The asymmetric unit with atomic numbering scheme.

and C(14) in the py ring are on the mirror plane along the b axis ($y = 1/2$) so that all of the py rings are arrayed along the $[102]$ direction. The mesh of each layer is penetrated by two py rings, one from the upper and the other from the lower layer, both rings partially overlapping each other with the interplane distance of 3.6 Å.



(a)



(b)

Figure 3. Structure of **1c**. (a) A view of the 2D network with atomic numbering scheme. (b) A perspective view: one of the networks including py ligands is shown with solid bonds.

A layer structure of the $\text{Ag}(\text{CN})_2$ -linked 2D networks with the protrusion of the secondary ligands is known for $[\text{Cd}(4,4'\text{-bpy})_2\{\text{Ag}(\text{CN})_2\}_2]$ [9] where two sets of stacked 2D networks of $[\text{Cd}\{\text{Ag}(\text{CN})_2\}_2]$ were supported by the 4,4'-bpy pillars to give a doubly interpenetrating 3D lattice structure. The 4,4'-bpy pillars penetrate into the meshes of the adjacent networks to link from Cd to Ag of the second next lower and upper networks giving an interlayer distance of *ca.* 6.42 Å between the networks, a value greater than that in **1c**.

3.2. DISCUSSION

The present 3D textile structures of **1a** and **1b** have a topology different from that of our precedent 3D textile in $[\text{Cd}(\text{NH}_3)_2\{\text{Ag}(\text{CN})_2\}_2]$ **2** [1], whose structure is shown in Figure 4a for the sake of comparison. Although the 2D network in **2** is puckered, the 3D textile is interwoven by two sets of the stacked networks running orthogonally, to the first approximation, similar to those in **1a** and **1b**. The difference is seen in the number of —NCAgCN— threads in one network passing through the mesh of another network, the number being 2 in **1** but 1 in **2**.

Another contrast is observed between the structures of **1c** ($L = \text{py}$) and **2** ($L = \text{NH}_3$) with similar compositions $[\text{Cd}L_2\{\text{Ag}(\text{CN})_2\}_2]$: the former has a layer structure. Including **1a** and **1b** textile structures, the $[\text{Cd}(\text{py})_2\{\text{Ag}(\text{CN})_2\}_2]$ network **1** is flat with the mesh of wider opening than that in the puckered $[\text{Cd}(\text{NH}_3)_2\{\text{Ag}(\text{CN})_2\}_2]$ network **2**. The structure with the wide opening appears to be stabilised by insertion of a pair of the py ligands in **1c** and a pair of —NCAgCN— spans and guest molecule in **1a** and **1b**. In other words, the ammine ligand in **2** is not bulky enough to keep a flat network structure like that in **1**. The puckered network is favourable to the stabilisation of crystal packing in **2** with the narrow mesh-opening interpenetrated by only one —NCAgCN— span. In this respect the layer structure of $[\text{Cd}(4\text{-Mepy})_2\{\text{Ag}(\text{CN})_2\}_2]\cdot 4\text{-Mepy}$ clathrate **3** [2] should be compared with **1** and **2**. The 2D network of $[\text{Cd}(4\text{-Mepy})_2\{\text{Ag}(\text{CN})_2\}_2]$ is far more smoothly puckered than **2** to form a doubly interpenetrating layer with a shape of a stationary wave, which can be described with a wavelength 26.95 Å and amplitude 4.95 Å (see Figure 4b). The puckering structure of **2** may also be approximated to a stationary wave of wavelength 11.50 Å and amplitude 1.3 Å for any pairs running in parallel. Introduction of a methyl group at the 4-position of py induces a drastic change in the clathrate structure of **2**, in which every mesh is not only interpenetrated by a span of —NCAgCN— but also accommodates the guest 4-Mepy molecule. The interlayer and intralayer cavities formed in the layer structure of **3** are occupied by the 4-Mepy ligands coordinating to Cd at *trans* positions. In the 3D textile structure of **2**, the channel cavity formed by one set of the stationary waves at the antinodal zone is occupied by the nodal parts of the other set and ammine ligands.

These observations suggest that structural control is delicate for the multi-dimensional structures involving —NCAgCN— spans between Cd atoms ligat-

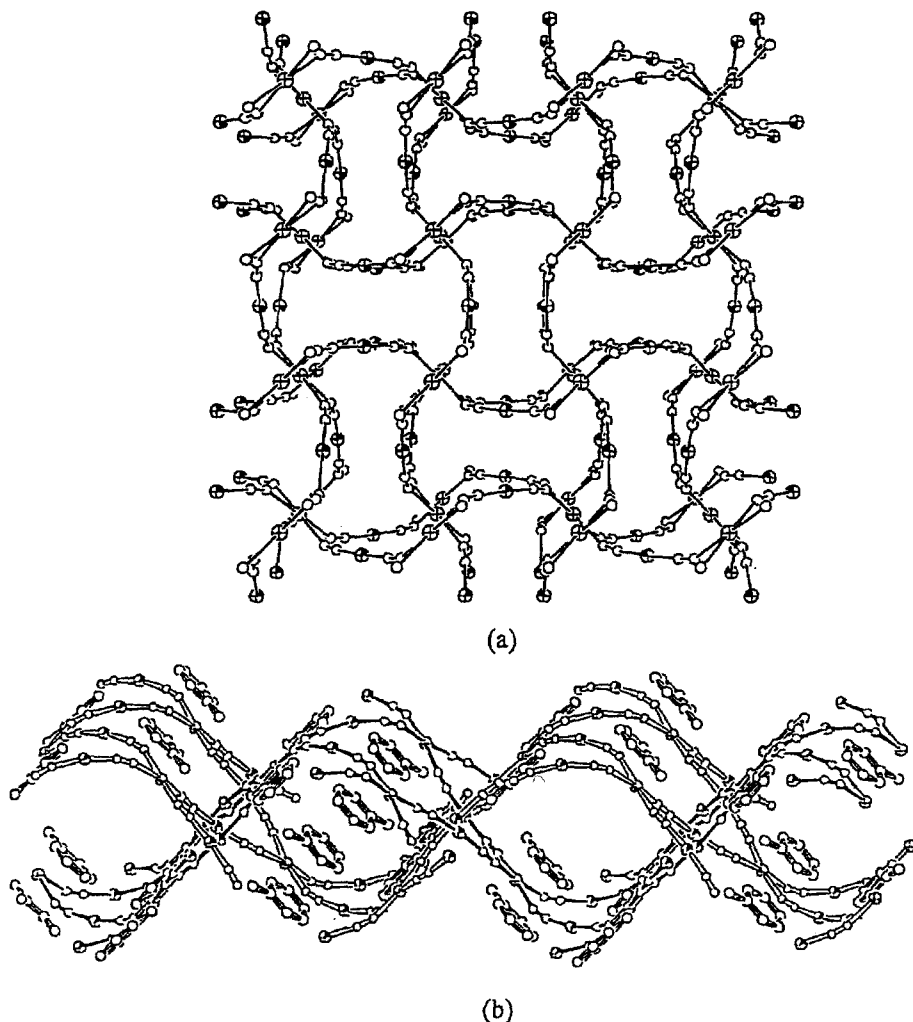


Figure 4. (a) 3D textile structure $[\text{Cd}(\text{NH}_3)_2\{\text{Ag}(\text{CN})_2\}_2]_2$: NH_3 ligands have been omitted for the sake of clarity; Cd with anisotropic peripheries and Ag with anisotropic sections. (b) One of the doubly inter-penetrating 'stationary wave' structures showing the 'floating' guests $[\text{Cd}(4\text{-Mepy})_4\{\text{Ag}(\text{CN})_2\}_2] \cdot 4\text{-Mepy}$ 3: one of the coupled networks is shown with solid bonds; 4-Mepy ligands at Cd with anisotropic peripheries have been omitted for the sake of clarity.

ed with a secondary ligand. The spanned structure is rather flexible. The selection of secondary ligand and guest gives possibilities of demonstrating a variety of unprecedented supramolecular structures. An attempt to use imidazole, 2-methylimidazole or *N*-methylimidazole which are bulkier than NH_3 but with the ring sizes smaller than py as the secondary ligand L gave 1D complexes of $[\text{CdL}_4\{\text{Ag}(\text{CN})_2\}]_n \cdot n[\text{Ag}(\text{CN})_2]$ in which four-bladed propellers of CdL_4 are

linked by the shaft of —NCAgCN— to form a linear array of $\text{—}[\text{CdL}_4\text{—NCAgCN—}]_\infty$ or a molecular complex of $[\text{CdL}_4\{\text{Ag}(\text{CN})_2\}_2]$ [10].

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