A Three-Dimensional Warp-and-Woof Structure Interwoven by a Couple of Two-Dimensional Network Layers in the Crystal Structure of [*trans*-$Cd(NH_3)_2\{Ag(CN)_2\}_2]_n$

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Two sets of the two-dimensional $[Cd\text{-}(NC\text{-}Ag\text{-}CN\text{-}Cd_{1/4})_4]_n$ network layers arrayed vertically to each other interpenetrate through every mesh without any direct chemical bonds to build up the three-dimensionally interwoven supramolecular structure of the title complex.

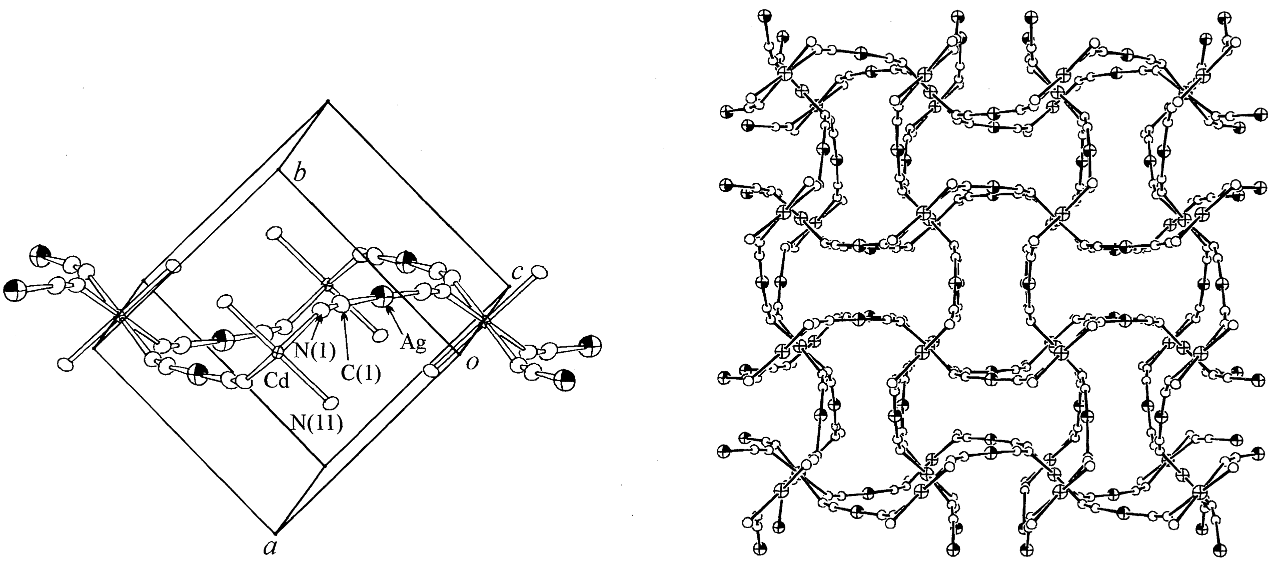
Our previous works[1,2] have exemplified the versatility of the -NC-Ag-CN- span between Cd atoms in building up the supramolecular structure such as a doubly interwoven two-dimensional (2D) network layer in $[Cd(4\text{-Mepy})_2\{Ag(CN)_2\}_2] \cdot (4\text{-Mepy})$,[1] a doubly interpenetrating three-dimensional (3D) framework in $[Cd(4,4'\text{-bpy})\{Ag(CN)_2)\}_2]$,[2] a triply interpenetrating 3D one in $[Cd(pyrz)\{Ag(CN)_2\}\{Ag_2(CN)_3\}]$[2] (4-Mepy = 4-methylpyridine; 4,4'-bpy = 4,4'-bipyridine; pyrz = pyrazine). This communication reports another 3D supramolecular structure observed for the complex with the rather simple composition $[Cd(NH_3)_2\{Ag(CN)_2\}_2]$ involving less bulky unidentate ligand NH_3 than the previous 4-Mepy;[1] two sets of the 2D network layers interpenetrate to each other layer to build up the 3D interwoven structure.

Colorless prismatic single crystals of $[Cd(NH_3)_2\{Ag(CN)_2\}_2]$, **1**, were obtained from an aqueous solution containing $CdCl_2$ and $K[Ag(CN)_2]$ in a 1:2 molar ratio, the pH being adjusted to 10 with aqueous NH_3 and citric acid. Anal. Found: C, 10.11; H, 1.28; N, 17.71%. Calcd for $C_4H_6Ag_2CdN_6$: C, 10.30; H, 1.30; N, 18.02%.[3]

The X-ray structure[4] of **1** is shown in Fig. 1. Although the crystal structure is constructed of two sets of the 2D network layers interpenetrating to each other, the structural element is the 2D network of $[Cd\text{-}(NC\text{-}Ag\text{-}CN\text{-}Cd_{1/4})_4]_n$ with a distorted rhombus mesh of the -NC-Ag-CN- span on the edge between the crystallographically equivalent Cd atoms on the corners, each of the Cd atoms being ligated by a couple of the NH_3 from both sides of the network respectively to accomplish the octahedral six coordination. No unusual bond distances and angles have been observed for the coordination structures about the Cd and Ag atoms. The Cd···Cd distance is *ca.* 10.52 Å through the span, and *ca.* 8.81 and 11.50 Å for the shorter and longer diagonals of the mesh. The network has a wavy structure due to the bent at N(1) with the Cd-N(1)-C(1) angle of 154.8(8)°; the -NC-Ag-CN- linkage is slightly bent with the angles of 175.5(2)° for $C(1)\text{-}Ag\text{-}C(1)^*$ and 174.4(9)° for Ag-C(1)-N(1). The wavy structure is approximated to having the wavelength of 11.50 Å and amplitude of 1.3 Å viewed along the *c* axis; the degree of bending is less than that of the doubly interwoven layer observed for $[Cd(4\text{-Mepy})_2\{Ag(CN)_2\}_2] \cdot (4\text{-Mepy})$, **2** , approximated to a stationary wave with the 26.95 Å wavelength and 4.95 Å amplitude. There are two sets of the 2D networks, one extending along the [110] and the other along the $[1\bar{1}0]$ plane, correlated to each other with the 4_2 screw along the *c* axis, *i.e.*, the two sets are crystallographically equivalent to each other.

The wavy network is stacked in parallel with the shift by a half wavelength along the extending direction so that the nearest and the farthest approach between adjacent networks are seen at the Ag atoms on the top and the bottom of the wave with the distances of *ca.* 3.2 and 8.3 Å. Hence the stacking of the wavy network gives a channel cavity along the *c* axis in one set, which cavity is filled with the NH_3 ligands from the Cd atoms and with the narrower parts of the two networks of the other set. Eventually both sets of the network layers interpenetrate to each other through every mesh to form a self-clathrate structure. The whole crystal structure is thus built up of one set of the 2D network layer as a warp and the other set as a woof to give a 3D textile. The crystallographic data, *i.e.*, the considerably large thermal parameter of Ag, B_{eq} = 5.45(2) Å^2, the residual electron density of *ca.* 2 eÅ^{-3} about the position of the Ag atom in the final Fourier-difference map, and the relatively large e.s.d. values for the *x* and *y* coordinates of C(1) and N(1) suggest the network has the slack in the -NC-Ag-CN- span to a certain extent; this tendency has been observed for the previously reported -NC-Ag-CN- span structures, too.[1,2] A topologically the same interpenetration of 2D networks has been reported for $[Zn(H_2O)_2(4,4'\text{-bpy})_2][SiF_6]$,[5] where the *trans*-$[Zn(H_2O)_2]^{2+}$ is linked to one another by the 4,4'-bpy spans to form a positively-charged host accommodating the anion as the guest.

As for the self-clathrate structure of multi-dimensional metal cyanides and cyanometallates, $Cd(CN)_2$ and $Zn(CN)_2$ have the anticuprite-type double framework structure, in which the H-cristobalite-like 3D lattices interpenetrate to each other without any direct chemical bonds.[6] When the structure of **1** is seen as a derivative from the Hofmann-type host of $[Cd(NH_3)_2Ni(CN)_4] \cdot 2G$[7] as well as that of **2**, the Cd-NC-Ag-CN-Cd span in **1** and **2**, almost twice longer than the Cd-NC-Ni span in the Hofmann-type 2D network, *ca.* 5.5 Å, is feasible to build up the interpenetrating structure owing to the expanded opening of the mesh. The difference in the way of interpenetration between **1** and **2** is induced from the bulkiness of the secondary ligand on the Cd atom. The bulkier 4-Mepy ligands in **2** are accommodated in the intra- and inter-layer spaces produced by the stacking of the doubly interwoven layer of $[Cd\text{-}(NC\text{-}Ag\text{-}CN\text{-}Cd_{1/4})_4]_n$ networks; in addition the guest 4-Mepy molecule is enclathrated in the mesh of the network. Although the wavy network structure in **1** is similar to that in **2**, the NH_3 in **1** is not bulky enough to fill up the intra- and inter-layer spaces like those in **2** to stabilize the crystal packing.



(a) (b)

Figure 1. (a) Perspective view of the puckered 2D network with a 24(4x6)-membered rhombus mesh along the *c* axis; crosses and sections of anisotropic thermal ellipsoids with 50% probability have been shown for Cd and Ag, respectively; the atomic notations of asymmetric unit are represented as -{N(11)-Cd}-N(1)-C(1)-Ag-, where the 4_2 screw passes through the Cd along the *c* axis and the twofold axis through the Ag along the *ab* plane. (b) the 3D warp-and-woof structure viewd along the *c* axis; each of the 2D netwoks arrayed both horizontally and vertically extends along the *c* axis; balls with corsses and sections for Cd and Ag, and without for C and N; N atoms of the NH_3 ligands, N(11) and its equivalents, have been omitted for the sake of clarity.

The present result suggests that the selection of the secondary ligand L is one of the important keys for the crystal engineering to build up variegated multi-dimensional and interpenetrating lattice structures of the Cd-L-$Ag(CN)_2$ systems.

References and Notes

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3 Crystals of the same composition and structure were also isolated from the aqueous solution containing $K_2[Cd(CN)_4]$, $AgNO_3$ and triazine in a molar ratio of 1:2:>0.8, the pH being adjusted to 10 with 2-aminoethanol and citric acid; the NH_3 appears to be generated from triazine.

4 The crystal data are: $C_4H_6Ag_2CdN_6$, M = 466.32, tetragonal, $P4_2/mbc$, a = 8.128(4), c = 17.611(4) Å, U = 1166.2(8) Å^3, Z = 4, D_m = 2.66(1), D_x = 2.66 g cm^{-3}, 2492 reflections, 658 (>4 σ (F_o)) used, 36 parameters to R = 0.057, R_w = 0.055, Rigaku AFC5S diffractometer, Mo-K$_\alpha$ radiation, 2 θ - ω scan method in the range of 4°< 2 θ < 65°, SHELX 76 refinement. The authors have deposited atomic coordinates at the Cambridge Crystallographic Data Centre. The coordinates can be obtained on the request from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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