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# Supramolecular Structures in Solid State AgCN–$Cd(CN)_2$–(4–Picoline) Complexes. An Interwoven Double Network of $[Cd\{Ag(CN)_2\}_2]_n$ in[*trans*–Cd(4–Mepy)$_2$$\{Ag(CN)_2\}_2$]·(4–Mepy) and a Linear Chain of[–Cd–NC–Ag(CN)Ag–CN–]$_n$ in [Cd(4–Mepy)$_4$$\{Ag_2(CN)_3\}$][$Ag(CN)_2$]

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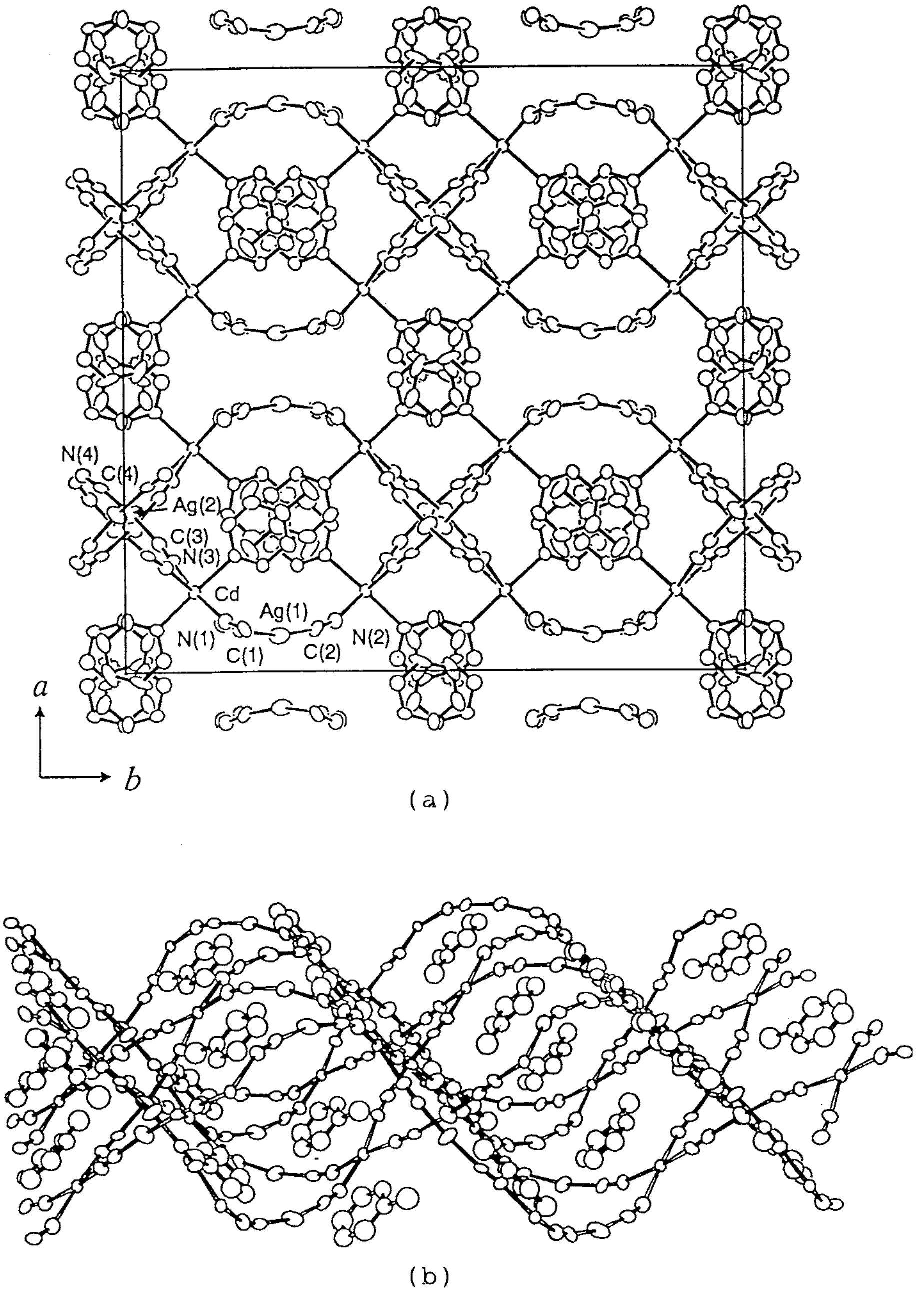
The title complexes in the compositions 2Ag(CN)·$Cd(CN)_2$·3(4–Mepy) and 3Ag(CN)·$Cd(CN)_2$·4(4–Mepy) crystallize from the same mother solution with the supramolecular structures remarkably different from each other. The former is a clathrate accommodating a guest 4–Mepy in the interwoven double network host. The latter host is comprised of –Cd(4–Mepy)$_4$–NC–Ag(CN)Ag–CN– linear chains among which discrete $[Ag(CN)_2]^-$ anions are incorporated.

Supramolecular structures in solid state are prospective materials to exhibit expected and/or unpredicted physico–chemical properties. Those systems formed between multi–dimensional cyanometal complex as the host and discrete organic molecules as the guest is advantageous to designing novel supramolecular structures because of the varieties in the coordination number of metals as the building blocks *e.g.,* from 2 for linear $[Ag(CN)_2]^-$ to 6 for octahedral $[Fe(CN)_6]^{4-}$, or more than 6 for late transition metals, rare earths, *etc.* One of the strategies we have applied to develop novel multi–dimensional cyanometal complex structures starting from the Hofmann–type $Cd(NH_3)_2Ni(CN)_4$ structure1) is to replace the ammine ligand by other unidentate ligands. Recently we have been examining to replace the square planar Ni(–CN–)$_4$ linking moieties by linear linkages of –NC–Ag–CN– to expand the mesh size of the network. By combining the two strategies using 4–picoline (4–Mepy) as the unidentate ligand and using Ag(–CN–)$_2$ as the linkage builder, we have obtained a novel clathrate [Cd(4–Mepy)$_2$$\{Ag(CN)_2\}_2$]·(4–Mepy) **1** and a complex [Cd(4–Mepy)$_4$$\{Ag_2(CN)_3\}$] [$Ag(CN)_2$] **2** from the same solution.

From an aqueous solution containing $CdCl_2$, K[$Ag(CN)_2$] and 4–Mepy in a 1:2:>10 molar ratio, the pH of the solution being adjusted to 10 with 2–aminoethanol and citric acid, colorless plate–like crystals of **1** were grown at first within a few hours; a few days later prismatic crystals of **2** were mixed with those of **1**. In the meantime, some portions of **1** crystals re–dissolved into the mother solution; the yield of **1** was decreasing and that of **2** increasing upon the relative increase of the 4–Mepy concentration in the mother solution. Discrimination between **1** and **2** is feasible by their appearance. Anal. **1**. Found: C, 36.31; H, 3.00; N, 13.15%, Calcd for $C_{22}H_{21}N_7Ag_2Cd$: C, 37.10; H, 3.01; N, 13.43%. **2**. Found: C, 37.01; H, 3.00; N, 13.50%. Calcd for $C_{29}H_{28}N_9Ag_3Cd$: C, 37.13; H, 2.97; N, 13.78%. Clathrate **1** liberates the guest 4-Mepy molecule gradually under ambient atmosphere. These crystals were subjected to the single crystal X-ray experiments.[2)]



(a)

(b)

Fig. 1. (a) The host structure of $[Cd(4\text{-}Mepy)_2\{Ag(CN)_2\}_2]\cdot(4\text{-}Mepy)$ **1** viewed along the *c* axis; the atomic notations are -N(4)-C(4)-Ag(2)-C(3)-N(3)-Cd-N(1)-C(1)-Ag(1)-C(2)-N(2)- in the linkage involving the Cd atom at 0.13180(4), 0.11205(3), 0.12011(8). (b) A view of the interwoven networks and the guests intercalated in the meshes; each 4-Mepy ligated to Cd has been omitted for the sake of clarity; one of the disordered orientations is shown for the guest 4-Mepy.

The solved structures are shown in Fig. 1 and 2 for **1** and **2**, respectively. Clathrate **1** has the layered host comprised of the interwoven double networks. The *trans*-$Cd(4\text{-}Mepy)_2$ moieties are spanned with four each of –NC–Ag–CN– edges to form the mesh of a distorted rhombus. One network with the knots of the Cd atoms is interlaced through the meshes with the –NC–Ag–CN– threads of the other network. The projection of the coupled networks along the *c* axis has a shape of a stationary wave with the approximate node and antinode of Ag(2) and Ag(1) and with the wavelength of *b* = 26.945(10) Å and the amplitude of *ca.* 4.95 Å. In the Cd–2.36(1)–N(4)–1.15(2)–C(4)–2.10(1)–Ag(2)–2.09(2)–C(3)–1.14(2)–N(3)–2.40(1)–Cd–2.40(1)–N(1)–1.11(2)–C(1)–2.08(2)–Ag(1)–2.08(1)–C(2)–1.11(2)–N(2)–2.40(1)–Cd span, the respective bond distances being given in Å, the gradual bending is due to the angles of 159(1), 168(2), 166.2(7), 170(2) and 163(1)° at N(1), C(1), Ag(1), C(2) and N(2), respectively; the sequence of Cd–N(4)–C(4)–Ag(2)–C(3)–N(3)–Cd is almost on a straight line. The coordination structure about the octahedral Cd and linear Ag are not unusual. The layers of the coupled networks interwoven at the nodal region extend along the *bc* plane and are stacked along the *a* axis so as to provide channels of the intra- and interlayer cavities for the 4–Mepy ligands coordinating to the Cd atoms. The 4–Mepy ligands in both cavities are arranged respectively with the distance of *ca.* 3.5 Å of van der Waals contacts between the aromatic planes almost in parallel. The guest 4–Mepy molecule is trapped in the mesh with its aromatic plane parallel to the slope of the wavy network; its molecular orientation is disordered independent of the symmetry elements of the *Ibca* space group. A feature to be noted is the short interlayer distance of 3.081(3) Å between the Ag(1) atoms at the antinodes of neighboring stationary waves, which distance is greater than the interatomic separation in cubic close–packed silver metal (2.89 Å).

As shown in Fig. **2**, the Cd in complex **2** is ligated with four 4–Mepy's equatorially to form a propeller-like structure, and linked to two other Cd atoms along the axial direction by the dimeric condensates of

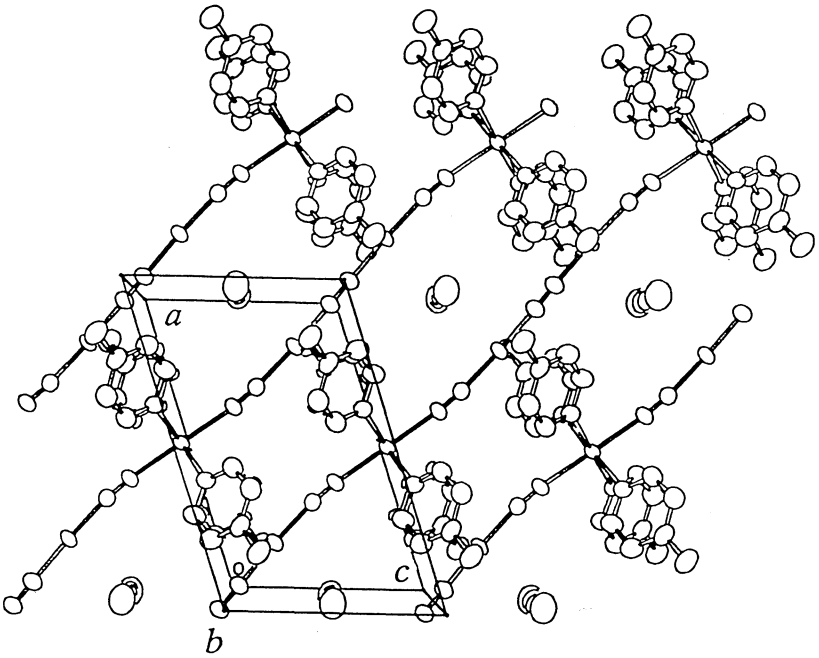


Fig. 2. Structure of $[Cd(4\text{-}Mepy)_4\{Ag_2(CN)_3\}][Ag(CN)_2]$ **2**: only a half of the unit cell contents is shown for the sake of clarity to illustrate the chains passing through the *C*–base–centered Cd atoms.

–NC–Ag(CN)Ag–CN– successively to form an infinite one-dimensional chain of a *ca.* 16.1 Å period running in parallel to the [102] of the crystal. As far as the authors' knowledge is concerned, this is the first example of the dimeric condensate of dicyanoargentate(I) in solid state. The interchain space is separated by the 4-Mepy ligands to give a cavity in which a discrete $[Ag(CN)_2]^-$ anion is accommodated. The bond angles in the chain are deviated by less than 6.4(8)° from 180°; the center of the condensate locates on the inversion center of the crystal so that the C and N of the central CN cannot be discriminated crystallographically. The 2.9879(9) Å distance between the Ag atoms in the chain, Ag(1), and in the discrete guest, Ag(2), is shorter than the comparable value in **1**.

An example of doubly interwoven network structure has already been known for $AgC(CN)_3$.3) The three-coordinate $Ag^+$, as well as the central C of $[C(CN)_3]^-$, is on the knot of the net with an Ag–NC–C spanned hexagonal mesh. The wavy structure is, however, smaller in scale with the wavelength of ca. 12.4 Å and the amplitude of *ca.* 1.75 Å due to the shorter span length of *ca.* 5 Å than *ca.* 10 Å of the present structure; no other chemical species are incorporated in the intra- and interlayer regions.

The presence of tricyanodiargentate(I) in liquid ammonia was suggested by Raman spectroscopy.4) At least in a transition state of the crystal growth for **2**, the dimeric anion may be formed in the aqueous solution. Another example of the condensate in (BEDT–TTF)$[Ag_4(CN)_5]$5) forms a two-dimensional network in place of the chain in **2**.

References

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2) The crystal data are: **1** $C_{22}H_{21}Ag_2CdN_7$, $M$ = 711.60, orthorhombic, *Ibca*, $a$ = 25.990(9), $b$ = 26.945(14), $c$ = 14.001(6) Å, $U$ = 9804(6) Å$^3$, $Z$ = 16, $D$m = 1.92(1), $D$x = 1.93 g cm$^{-3}$, 7719 reflections observed, 3054 ($>4\sigma(Fo)$) used, 259 parameters to $R$ = 0.066; **2** $C_{29}H_{28}Ag_3CdN_9$, $M$ = 938.62, monoclinic, *C2/m*, $a$ = 11.974(7), $b$ = 19.078(11), $c$ = 7.634(7) Å, $\beta$ = 108.55(5)°, $U$ = 1656(2) Å$^3$, $Z$ = 2, $D$m = 1.87(1), $D$x = 1.88 g cm$^{-3}$, 2748 reflections observed, 1800 ($>3\sigma(Fo)$) used, 106 parameters to $R$ = 0.050. In common for **1** and **2**: Rigaku AFC5R diffractometer, Mo–K$\alpha$ radiation, $2\theta$–$\omega$ scan in the range of $4° < 2\theta < 60°$, SHELX 76 refinement. The crystal of **1** coated with epoxy resin did never show any decay during the intensity measurement. The authors have deposited atomic coordinates for the structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, GB–Cambridge CB2 1EZ, UK.

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