Crystal Structure of $[Cd\{NH<(C_2H_4)_2>NC_2H_4NH_2\}_2\{Ag(CN)_2\}]_n\bullet n[Ag(CN)_2]$: A Cationic Three-Dimensional Framework Built of Hetero-Bridged Octahedral Cd^{2+} and Tetrahedral Ag^+ Accommodating Anionic Guest $[Ag(CN)_2]^-$

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In the title complex the *N*-(2-aminoethyl)piperazine and cyanide respectively bridge between octahedral Cd^{2+} and tetrahedral Ag^+ to form a positively-charged three-dimensional host framework accommodating $[Ag(CN)_2]^-$ anion as the guest.

Our recent X-ray diffraction studies have revealed that a variety of polymeric structures such as one-dimensional (1D) chains,[1,2] two-dimensional (2D) networks,[2-5] are given by the linkage between ambidentate dicyanoargentate(I) $[Ag(CN)_2]^-$ and Cd(II) coordinated with monodentate L ligands such as NH_3,[4] imidazoles,[1] py,[5] aminopyridine,[2] picoline,[3] etc.,[6] as has been demonstrated in the crystal structures of $[CdL_2\{Ag(CN)_2\}_2]$ complexes self-assembled from relevant aqueous solutions. In this study a tri-donating *N*-(2-aminoethyl)piperazine (aepipz) was examined as L which may behave as a chelating ligand at one side of the molecule and as a monodentate one at another side, viz., eventually as a bridging ligand. The complex obtained $[Cd(aepipz)_2\{Ag(CN)_2\}]_n\cdot n[Ag(CN)_2]$ **1** was found to be composed of a positively-charged three-dimensional (3D) host structure, topologically similar to the Hofmann-Td-type host,[7] accommodating an anion $[Ag(CN)_2]^-$ as the guest.

Colourless single crystals of **1** suitable for the X-ray analysis[8] were grown from an aqueous solution containing $CdCl_2$, $K[Ag(CN)_2]$ and aepipz in a 1:2:>10 molar ratio, the pH being adjusted to 8 with citric acid and 2-aminoethanol. Anal. Found: C, 27.71; H, 4.27; N, 20.29%. Calcd for $C_{16}H_{30}Ag_2CdN_{10}$: C 27.83; H 4.38; N 20.28%.

Figure 1 shows the solved structure. The Cd atom located on the inversion centre in the adopted space group *C*2/*c* is successively linked by the ambidentate $[Ag(CN)_2]^-$ at axial position of every octahedron to give an infinite 1D -{Cd-NCAgCN-}$_n$ linkage extending along the [101] direction. A pair of aepipz ligands chelate equatorially to the Cd by the aminoethyl-N(11) and the substituted piperazine-N(14) with the Cd−N(11) and Cd−N(14) distances of 2.330(4) and 2.505(3) Å. The non-substituted piperazine-N(17) coordinates to the Ag(1) atom on the adjacent 1D -{Cd-NCAgCN-}$_n$ linkage with the Ag(1)−N(17) distance of 2.555(4) Å. The Ag(1) on the twofold axis accomplishes the distorted tetrahedral coordination with N(1) of CN and N(17) of aepipz so that the -NCAgCN- span is bent at Ag(1) by 139.2(2)° to give the zigzag bending to the 1D linkage. The $[Ag(CN)_2]^-$-linked zigzag chain structure observed in $[Cu(2,2'\text{-bpy})_2\{Ag(CN)_2\}]_n\cdot n[Ag(CN)_2]\cdot nH_2O$ (2,2'-bpy = 2,2'-bipyridine)[9] is different in the way of bending from the present structure; the two linear $[Ag(CN)_2]^-$ coordinate to the octahedral Cu^{2+} at the *cis* positions. The piperazine ring of aepipz links between the octahedral Cd and tetrahedral Ag with the distance of 6.6929(2) Å, being longer than the CN span length between the Cd and Ag of 5.6135(2) Å.

As is illustrated in Figure 1(b), the spans of the -CN- and the piperazine ring between the Cd and the Ag make an approximate square mesh cornered by the metal atoms and edged by the linking moieties. The meshes are arrayed to form a 1D meshed chain by sharing every octahedral Cd as the joint, the chains running along the [110] and $[1\bar{1}0]$ directions. Both sets of the meshed chains are connected to one another by sharing every tetrahedral Ag with a twisting angle of *ca.* 118.6° eventually to form a 3D framework structure. The skeletal topology that two sets of square-meshed chains arrayed almost orthogonally to each other are coupled with one another by substantially tetrahedral joints like PtS structure is similar to those observed for the Hofmann-Td-type[7] and analogous structures $[Cd(R)M(CN)_4]$ (M = Cd, R = $(NH_3)_2$,[10] py,[11] $(CH_3CN)_2$;[12] M = Hg, R = $(NH_3)_2$[13]), where the octahedral coordination centre Cd^{2+} axially ligated by R and tetrahedral M are linked alternately with CN to give an electrically neutral 3D framework. The skeletal lattice of **1** is considerably distorted from the original Hofmann-Td-type structure owing to the hetero-ligation by CN and aepipz different in the span length and the twisting angle at the Ag deviated from the right angle in a regular tetrahedron. Except for the py-ligated structure,[11] the electrically neutral Hofmann-Td-type and analogous frameworks accommodate neutral guest molecules. The positively charged framework of **1** accommodates the guest $[Ag(CN)_2]^-$ anion in the cavity produced between the interchain space.

As for our series of the multidimensional $[Ag(CN)_2]^-$-linking structures of $[CdL_2\{Ag(CN)_2\}_2]_n$,[1-5] the present host has two novel features. Firstly, the 3D framework involves not only the dicyanoargentate(I) span but also the additional neutral bridging ligand aepipz between the Cd and Ag so that one of the dicyanoargentate moieties goes out of the host framework; the hetero-bridged 3D host is positively-charged to accommodate the $[Ag(CN)_2]^-$ as the guest. Secondly, the 3D framework involves the tetrahedral Ag. A neutral hetero-bridging 3D structure has been obtained for $[Cd(4,4'\text{-bpy})_2\{Ag(CN)_2\}_2]$[14] in which the 4,4'-bpy (4,4'-bipyridine) bridges between the octahedral Cd and the trigonal Ag respectively on different 2D networks of $[Cd\{Ag(CN)_2\}_2]_n$ resulting in the formation of the doubly interpenetrating 3D framework structure. Negatively-charged 3D frameworks are seen in our $[K(15\text{-Crown-}5)_2]$-$[Cd\{Ag(CN)_2\}_3]\cdot 2C_6H_6$ clathrate,[5] and $Rb[Cd\{Ag(CN)_2\}_3]$ reported by another group.[15]

The guest $[Ag(CN)_2]^-$ is also bent at Ag(2) with the bending angle of 161.3(2)°. The distance of 3.057(1) Å between the Ag(1) in the host and the Ag(2) in the guest is slightly longer than the interatomic distance of 2.89 Å in the silver metal, as is often seen in other $[Ag(CN)_2]$-linked structures.[1-3,5,14] The N(2) atom of the guest anion is hydrogen-bonded to the N(11) of aepipz in the host with the distance of 3.037(7) Å.

As has been exemplified,[6] dicyanoargentate shows a variety of

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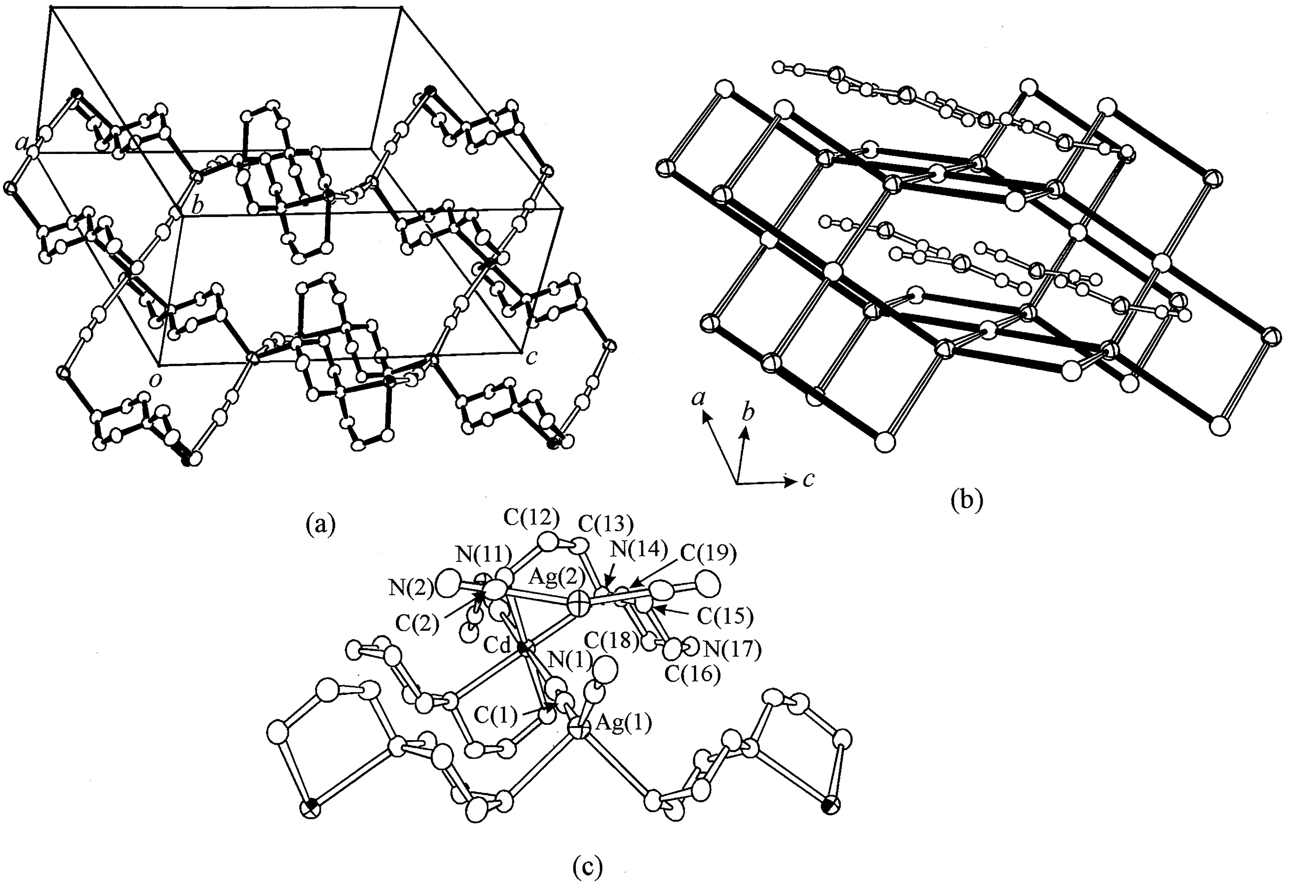

Figure 1. Structure of $[Cd(aepipz)_2\{Ag(CN)_2\}]_n \cdot n[Ag(CN)_2]$ **1**. (a) View of the framework; the guest $[Ag(CN)_2]$ has been omitted. (b) The framework drawn as ball-and-stick model and the guest anions; aepipz: solid stick; CN: lined stick; Ag: ball with a cross; Cd: large open ball; C and N: small open ball. (c) Partial structure of the framework with the atomic numbering scheme; anisotropic peripheries and sections are shown for Ag and Cd, respectively; selected interatomic distances (Å) and angles (°): Cd—N(1) 2.383(4); Cd—N(11) 2.330(4); Cd—N(14) 2.505(3); Ag(1)—C(1) 2.142(4); Ag(1)—N(17)^{*1} 2.555(4); Ag(1)···Ag(2) 3.057(1); N(1)—Cd—N(11) 88.0(1); N(1)—Cd—N(14) 76.7(1); C(1)—Ag(1)—C(1)^{*2}: 139.2(2); C(1)—Ag(1)—C(17)^{*1}: 105.8(1); C(17)^{*1}—Ag(1)—C(17)^{*3}: 91.0(1); C(2)—Ag(2)—C(2)^{*2}: 161.3(2).

coordination behaviour in our multidimensional structures: ambidentate bridging,[1-5] dimeric ambidentate bridging,[3] monodentate ligand,[1,2] and discrete anion[1,3] have been demonstrated. The Ag atoms in these structures take linear or trigonal coordinations. The present tetrahedral coordination accompanied with the chelate-monodentate bridging of aepipz suggests that the crystal engineering of cadmium dicyanoargentate gives more various multidimensional structures together with the use of a versatile secondary ligand such as aepipz.

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8 The crystal data are: $C_{16}H_{30}Ag_2CdN_{10}$, M = 690.63, monoclinic, $C2/c$, a = 15.5106(8), b = 8.697(1), c = 17.1236(9) Å, β = 103.449(4)°, U = 2246.4(3) Å^3, Z = 4, D_m = 2.04(1), D_x = 2.042 g cm^{-3}, 4531 reflections. 3186 used(> $3\sigma(F_o)$), 135 parameters to R = 0.033, R_w = 0.040, Rigaku AFC5S diffractometer, Mo-Kα radiation, 2θ-ω scan method in the range of 4° < 2θ < 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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