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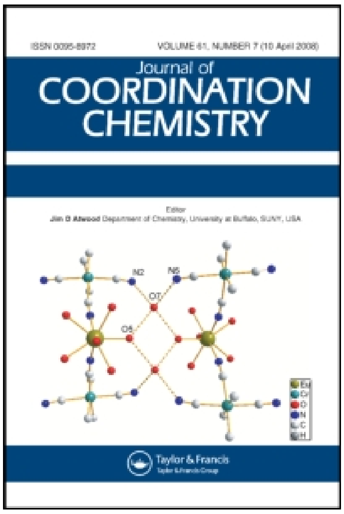

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CRYSTAL STRUCTURES OF $Cd(H_2O)_2Cu(CN)_3\cdot 2H_2O$, $K[Cd(H_2O)_2Cu_2(CN)_5]\cdot 2H_2O$ AND $K_2[Cd(H_2O)Cu_4(CN)_8]\cdot 1.5H_2O$. STRUCTURES OF MULTI-DIMENSIONAL FRAMEWORKS FORMED WITH CADMIUM(II), COPPER(I) AND BRIDGING CYANO GROUPS

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CRYSTAL STRUCTURES OF $Cd(H_2O)_2Cu(CN)_3 \cdot 2H_2O$, $K[Cd(H_2O)_2Cu_2(CN)_5] \cdot 2H_2O$ AND $K_2[Cd(H_2O)Cu_4(CN)_8] \cdot 1.5H_2O$. STRUCTURES OF MULTI-DIMENSIONAL FRAMEWORKS FORMED WITH CADMIUM(II), COPPER(I) AND BRIDGING CYANO GROUPS

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In an attempt to form new multi-dimensional structures of cyano complexes including cadmium(II) and copper(I), four new complexes were obtained successively from an aqueous solution at intervals of from a few days to a few months. The complex **1** obtained first was unstable in the atmosphere. The crystal structures of the other complexes (**2–4**) obtained from second to fourth were determined by single crystal X-ray structure determinations. Their crystal data are as follows: **2** $Cd(H_2O)_2Cu(CN)_3 \cdot 2H_2O$, monoclinic, $C2/m$, $a = 14.038(1)$, $b = 9.944(1)$, $c = 7.738(1)$Å, $\beta = 116.019(7)°$, $Z = 4$; **3** $K[Cd(H_2O)_2Cu_2(CN)_5] \cdot 2H_2O$, triclinic, $P\bar{1}$, $a = 17.429(9)$, $b = 16.519(7)$, $c = 10.085(5)$Å, $\alpha = 128.60(3)$, $\beta = 137.44(2)$, $\gamma = 45.82(2)°$, $Z = 4$; **4** $K_2[Cd(H_2O)Cu_4(CN)_8] \cdot 1.5H_2O$, monoclinic, $C2/c$, $a = 19.387(2)$, $b = 16.056(3)$, $c = 12.663(2)$Å, $\beta = 110.419(9)°$, $Z = 4$. The main structural feature found in the complexes is that the whole framework consists of two networks, a Cd-Cu(I)-CN complex network that has an infinite network formed with bridging cyano groups between the metal atoms and a network formed with hydrogen bonding among water molecules. The second network is connected to Cd in the Cd-Cu(I)-CN complex network *via* a water ligand coordinated to Cd. In **2** a planar network of $[CdCu(CN)_3]$ complexes are stacked along the *c* axis and the second network links the stacked complexes. **3** has a stacked structure of $[Cd(H_2O)_2Cu(CN)_5]^{2-}$ in a bi-layered structure. The second network of **3**, which includes K^+ ions with an electrostatic interaction, spreads over the crystal, penetrating vacant spaces of the metal complex network. **4** has a double lattice structure with a pair of enantiomeric three-dimensional $[Cd(H_2O)Cu_4(CN)_8]^{2-}$ complexes inter-penetrating each other. There are three structural factors for forming these framwork structures: (1) a non-planar coordination structure for Cd(II) that extends the planar structure of the Cu(I)-CN complex to a three-dimensional structure for the Cd-Cu(I)-CN complex; (2) a trigonal planar coordination structure for Cu(I) that generates vacant space in the metal complex network and makes possible hydrogen bonds to form the second network; (3) structural distortions of bridging cyano groups and a coordination structure of Cu(I) that cause variations of the metal complex network structure.

KEYWORDS: cyano complex, cadmium(II), copper(I), hydrogen bonding, supra-molecule

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INTRODUCTION

Recently it has been shown that cadmium cyano complexes have the possibility of forming various multi-dimensional framework structures with cyano groups bridging between cadmium atoms.[1] Moreover, addition of other ligands to the Cd-CN system gives structural variations to the framework structures.[2] Apart from the Cd-CN system, D. T. Cromer and other researchers have been investigating crystal structures of various copper cyano complexes for many years and have been clarifying multi-dimensional structural features of the Cu(I)-CN system constructed with bridging cyano groups.[3,4] It is possible that combination of Cd, Cu and cyano groups has the possibility to form new framework structures. The first evidence for this was $[H_{31}O_{14}][CdCu_2(CN)_7]$[5] which has a pyrite-like framework of $[CdCu(CN)_7]^{3-}$ with the positions of Cd(II) and Cu(I) corresonding to those of Fe and S in pyrite(FeS_2), respectively. Cd has an octahedral and Cu has a tetrahedral coordination structure, and all cyano groups bridge between Cd and Cu or two Cu atoms. In the vacant space of the pyrite-like framework, there are protonated water molecules which show the unusual structural feature of forming a 12-member ring structure around a cyano group bridging between two Cu atoms. This paper reports crystal structures of complexes that were prepared after the first paper, and structural factors for forming multi-dimensional framework structures in the Cd-Cu(I)-CN system.

EXPERIMENTAL

Preparation

Four new complexes were obtained successively at intervals of from a few days to a few months as crystals from an aqueous solution. Into 100 mL of water 2.06 g of $K_2[Cd(CN)_4]$ was dissolved, and then 1.26 g of CuCN was added to the solution with stirring and gentle warming. After the CuCN dissolved, the solution was filtered with filter paper and the filtrate was allowed to stand at room temperature. After a few days, the first complex (**1**) was obtained as colorless plates. During a few weeks after the appearance of **1**, the crystals of **1** changed to colorless crystals of the second complex $Cd(H_2O)_2Cu(CN)_3 \cdot 2H_2O$(**2**). After a few months **2** disappeared and the third complex $K[Cd(H_2O)_2Cu_2(CN)_5] \cdot 2H_2O$ (**3**) was obtained as colorless crystals. Moreover, after a few further months, pale yellow crystals of the fourth complex $K_2[Cd(H_2O)Cu_4(CN)_8] \cdot 1.5H_2O$ (**4**) appeared. Reproducibility in the appearance of **1** was not good. Sometimes, only **2** or a mixture of **1** and **2** appeared in the solution at first. **1** was too unstable to be handled in the atmosphere and detailed characterization has not been carried out. However, it was shown by infrared spectroscopy that **1** was a cyano complex and different from the other three complexes. During the conversion from one complex to another there were two kinds of crystals in the same mother solution. Under different conditions where 1.89 g of CuCN was used instead of 1.26 g of CuCN, **4** crystallized first, and after a few months crystals of $K[Cu_2(CN)_3] \cdot H_2O$ (**5**) appeared. **5** was the same complex that D. T. Cromer reported in 1962.[4] Chemical analysis; *Anal.* Calcd. for **2**: $Cd(H_2O)_2Cu(CN)_3 \cdot 2H_2O$ (%): C, 11.05; H, 2.47; N, 12.88; Cd, 34.47; Cu, 19.48.

Found: C, 10.9; H, 2.39; N, 12.8; Cd, 34.3; Cu, 19.5. *Anal.* Calcd. for **3**: $K[Cd(H_2O)_2Cu_2(CN)_5]\cdot 2H_2O$ (%): C, 12.43; H, 1.68; N, 14.56; Cd, 23.38; Cu, 26.43. Found: C, 12.3; H, 1.70; N, 14.4; Cd, 23.4; Cu, 26.2 *Anal.* Calcd. for **4**: $K_2[Cd(H_2O)Cu_4(CN)_8]\cdot 1.5H_2O$ (%): C, 13.76; H, 0.722; N 16.05; Cd, 16.10; Cu, 36.41. Found: C, 13.5; H, 0.81; N, 16.0; Cd, 16.1; Cu, 36.2.

X-ray Diffraction Structure Determination

X-ray diffraction data for the single crystals of **2**, **3** and **4** were measured on a Rigaku AFC5 automated four-circle diffractometer using graphite monochromated MoKα radiation at room temperature. An absorption correction[6] was applied to all the diffraction data. All crystal structures of the complexes were solved by direct methods using the SHELX-86 program,[7] and refinement of the parameters was carried out by successive differential Fourier synthesis and full matrix least-squares calculation procedures by use of the SHELX-76 program.[8] All atoms found in the Fourier synthesis were refined anisotropically. No hydrogen atoms were included in the refinement. The assignment of atomic species in bridging cyano groups will be discussed later. In the cases of **2** and **3** an empirical extinction correction[8] was applied. All the calculations were carried out on a HITACHI M-680H computer. Details of crystal data, data collection, structure analyses and final reliability factors are listed in Table 1. Final coordinates, and selected lengths and angles are listed in Tables 2 and 3, respectively.

^{113}Cd NMR

^{113}Cd NMR measurements were carried out on a Chemagnetics CMX-300 nmr spectrometer with 66.61 MHz and 300 MHz Larmor frequencies for ^{113}Cd and ^{1}H, respectively. The ^{113}Cd CP/MAS NMR spectrum of **2** was measured under the conditions: 5 μs ^{1}H 90° pulse width, 5 ms contact time, 10 s recycle time, 100 kHz spectrum width, 1 k data length and 3800 Hz and 5000 Hz sample spinning rates. The ^{113}Cd NMR spectrum of **4** was measured by the single resonance method because the signal intensity obtained from CP experiment was weak. The measuring conditions were as follows: 6.5 μs ^{113}Cd 90° pulse width, 20 s recycle time and 4000 Hz and 5200 Hz sample spinning rates. NMR measurement for **3** was not carried out because insufficient pure sample was obtained. $Cd(NO_3)_2\cdot 4H_2O$ was used as an external reference for the chemical shifts.

RESULTS

^{113}Cd-NMR

Sometimes, it is difficult to distinguish two atomic species having similar atomic numbers by the X-ray diffraction method. The assignment of C and N in the bridging cyano group is difficult. High resolution solid state NMR gives useful information about this problem in the case of cadmium cyano complexes.[9] The chemical shift value of Cd reflects the coordination structure of Cd and makes it possible to determine the atomic species coordinated to Cd.

Table 1 Summary of crystal data, data collection and structure analysis for 2, 3 and 4.

Compound	**2** $Cd(H_2O)_2Cu(CN)_3 \cdot 2H_2O$	**3** $K[Cd(H_2O)_2Cu_2(CN)_5] \cdot 2H_2O$	**4** $K_2[Cd(H_2O)Cu_4(CN)_8] \cdot 1.5H_2O$
M	326.07	480.75	697.97
F(000)	624	920	2648
Crystal System	monoclinic	triclinic	monoclinic
Space group	C2/m	$P\bar{1}$	C2/c
a/Å	14.038(1)	17.429(9)	19.387(2)
b/Å	9.944(1)	16.519(7)	16.056(3)
c/Å	7.738(1)	10.085(5)	12.663(2)
α/°	90	128.60(3)	90
β/°	116.019(T)	137.44(2)	110.419(9)
γ/°	90	45.82(2)	90
U/Å^3	970.7(2)	1371(1)	3694(1)
Z	4	4	8
Dm/gcm^{-3}	2.20(1)	2.34(1)	2.51(1)
Dx/gcm^{-3}	2.231	2.335	2.510
μ/cm^{-1}	44.3	50.4	62.9
temperature/K	298	298	298
instrument		Rigaku AFC5	
radiation		MoKα 0.71069Å	
monochromater		graphite	
scan mode		2θ-ω	
scan range		$4° \leq 2\theta \leq 60°$	
scan speed/° min^{-1}	8	8	8
scan width	$1.418 + 0.3\tan\theta$	$1.103 + 0.3\tan\theta$	$0.892 + \tan\theta$
ref. measured	1538	8832	5722
ref. used(N_{ref})	$1376(\geq 3\sigma(F_o))$	$5833(\geq 3\sigma(F_o))$	$4039(\geq 3\sigma(Fo))$
parameter(N_{par})	65	326	234
correction	absorption extinction	absorption extinction	absorption
refinement		SHELX-76 (full matrix least squares)	
weight scheme[a]	g = 0.002185	g = 0.001587	g = 0.00135
R[b]	0.028	0.042	0.048
wR[c]	0.049	0.058	0.065
GOF[d]	0.9292	0.9855	1.175

[a] $w = \{\sigma(F_o)^2 + gF_o^2\}^{-1}$; [b] $R = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$; [c] $wR = \{\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2\}^{1/2}$; [d] $GOF = \{\Sigma w(|F_o| - |F_c|)^2/(N_{ref} - N_{par})\}^{1/2}$

A single peak at 190 ppm was observed for **2** and at 254 ppm for **4**. These findings suggest that the bridging cyano groups between Cd and Cu in **2** and **4** are coordinating to Cd with N and to Cu with C. There is no orientational disorder of the bridging cyano groups as often seen in cadmium cyano complexes.[9] In the X-ray structure determination, the above assignment was applied to the bridging cyano groups between Cd and Cu in all the complexes. However, each atom of the bridging cyano groups between two Cu atoms in **4** was treated as a hybrid atom composed of C and N, and the populations of C and N were refined in the least-squares calculations. In the case of **3**, the atoms were treated as a hybrid atom of 50% C and 50% N. The hybrid atoms are represented with X in this report. No structural abnormality was found in the final results of the structure determination based on the above assignments.

Table 2 Final coordinates and isotropic temperature factors for 2, 3, and 4.

$Cd(H_2O)_2Cu(CN)_3 \cdot 2H_2O$ (2).	x/a	y/b	z/c	B_{eq}/Å^2
Cd	0.14528(2)	0.0	0.20308(4)	1.98(1)
Cu	0.02992(4)	0.5	0.2161(1)	2.61(2)
O(1)	0.0480(3)	0.0	-0.1398(5)	2.5(1)
O(2)	0.1959(2)	0.0	0.5400(5)	3.0(1)
O(3)	0.0970(3)	0.1933(3)	0.6624(5)	4.1(1)
N(1)	0.3076(4)	0.0	0.2073(9)	3.8(2)
N(2)	0.1260(2)	0.2206(3)	0.2180(5)	2.98(9)
C(1)	0.3900(4)	0.0	0.210(1)	3.3(2)
C(2)	0.0949(2)	0.3266(3)	0.2230(5)	2.58(9)

$K[Cd(H_2O)_2Cu_2(CN)_5] \cdot 2H_2O$ (3).	x/a	y/b	z/c	B_{eq}/Å^2
Cd(1)	-0.07192(3)	0.75551(3)	0.17242(6)	2.10(2)
Cd(2)	0.44894(3)	0.75140(3)	0.18124(6)	2.00(2)
Cu(1)	-0.11235(7)	0.49887(6)	0.2472(1)	3.11(4)
Cu(2)	0.36039(7)	0.51994(6)	0.2202(1)	3.44(4)
Cu(3)	0.04570(8)	0.08913(6)	0.1931(1)	3.46(4)
Cu(4)	0.54319(8)	0.11769(6)	0.2324(1)	3.39(4)
K(1)	0.7224(1)	0.8872(1)	0.7091(2)	4.06(9)
K(2)	0.2063(2)	0.6115(1)	0.6801(3)	4.32(9)
O(1)	-0.0859(4)	0.8966(4)	0.1348(7)	3.1(3)
O(2)	-0.1492(4)	0.6853(4)	-0.1749(6)	3.1(3)
O(3)	0.3705(4)	0.6781(4)	-0.1721(6)	3.0(3)
O(4)	0.4327(4)	0.8911(4)	0.1327(7)	3.4(3)
O(5)	0.1746(6)	0.8503(4)	0.3364(8)	4.5(4)
O(6)	0.2100(4)	0.8729(4)	0.6766(7)	3.5(3)
O(7)	0.6844(5)	0.8495(5)	0.3508(9)	4.7(4)
O(8)	0.2833(4)	0.4328(4)	0.3953(8)	4.2(3)
N(1)	-0.0533(6)	0.6241(5)	0.2211(9)	3.7(3)
N(2)	0.1254(5)	0.64978(4)	0.2284(8)	3.3(3)
N(3)	0.4317(5)	0.6238(4)	0.1752(9)	3.4(3)
N(4)	0.6502(5)	0.6409(4)	0.2588(9)	3.3(3)
N(5)	-0.2700(5)	0.8894(4)	0.1056(8)	3.1(3)
N(6)	0.2414(4)	0.8769(4)	0.0821(8)	3.1(3)
N(7)	0.0089(5)	0.8452(5)	0.5173(7)	3.2(3)
N(8)	0.5074(5)	0.8588(5)	0.5077(8)	3.5(4)
C(1)	-0.0682(6)	0.5752(5)	0.2391(9)	2.9(3)
C(2)	0.2128(6)	0.6053(5)	0.230(1)	3.1(3)
C(3)	0.4089(6)	0.5836(5)	0.1964(9)	2.9(3)
C(4)	0.7405(5)	0.5913(5)	0.263(1)	2.9(3)
C(5)	-0.3445(5)	0.9749(5)	0.1429(9)	2.7(3)
C(6)	0.1620(5)	0.9516(5)	0.1107(9)	2.6(3)
C(7)	-0.0158(5)	0.8762(5)	0.6241(8)	2.4(3)
C(8)	0.4902(5)	0.8690(5)	0.6081(9)	2.8(3)
X(1)[a]	-0.0336(5)	0.3343(5)	0.222(1)	3.5(3)
X(2)[a]	-0.0035(6)	0.2411(5)	0.196(1)	3.4(3)
X(3)[a]	0.4503(6)	0.3585(5)	0.229(1)	4.0(3)
X(4)[a]	0.4853(6)	0.2668(5)	0.221(1)	4.1(4)

$K_2[Cd(H_2O)Cu_4(CN)_8] \cdot 1.5H_2O$ (4).	x/a	y/b	z/c	B_{eq}/Å^2
Cd	0.22167(2)	0.27231(3)	0.24947(3)	2.00(2)
Cu(1)	0.47645(4)	0.18631(6)	0.54147(6)	3.21(3)
Cu(2)	0.28848(5)	0.43959(6)	-0.05881(7)	3.34(3)
Cu(3)	-0.00414(5)	0.12849(6)	-0.05175(7)	3.48(4)

Table 2 — (Continued)

Cu(4)	0.16425(5)	0.47820(5)	0.52495(6)	3.01(3)
K(1)	0.12302(9)	0.0180(1)	0.2788(1)	3.71(6)
KO(1)[b]	0.4390(2)	0.0146(3)	0.2761(2)	5.6(1)
KO(2)[b]	0.4047(3)	0.1961(3)	0.1715(5)	9.0(3)
O(1)	0.1813(3)	0.1806(3)	0.3872(4)	3.5(2)
O(2)	0.0	0.1101(5)	0.25	5.5(4)
N(1)	0.3346(3)	0.2419(4)	0.3607(5)	3.1(2)
N(2)	0.2618(4)	0.3373(4)	0.1241(5)	3.8(2)
N(3)	0.1294(3)	0.2075(3)	0.1274(4)	2.6(2)
N(4)	0.1916(3)	0.3704(3)	0.3455(5)	2.9(2)
X(51)[c]	0.0438(3)	0.6070(4)	0.5095(5)	2.9(2)
X(52)[d]	0.0866(3)	0.5588(4)	0.5070(5)	2.8(2)
X(61)[e]	0.2409(3)	0.4380(4)	0.7786(5)	2.8(2)
X(62)[f]	0.2143(3)	0.4520(4)	0.6838(5)	2.7(2)
X(71)[g]	0.4194(3)	0.5606(4)	0.9694(5)	2.7(2)
X(72)[h]	0.3729(3)	0.5176(4)	0.9717(5)	2.9(2)
X(8)[a]	0.4942(3)	0.1896(4)	0.7021(5)	2.8(2)
X(9)[a]	0.4983(4)	0.6268(4)	0.7943(5)	3.1(2)
C(1)	0.3903(3)	0.2267(4)	0.4281(5)	2.7(2)
C(2)	0.2693(4)	0.3769(4)	0.0552(5)	2.9(2)
C(3)	0.0775(3)	0.1815(4)	0.0611(5)	2.3(2)
C(4)	0.1831(3)	0.4134(4)	0.4117(5)	2.5(2)

[a] a hybrid atom that consists of 50% N atom and 50% C atom; [b] a hybrid atom that consists of 50% K atom and 50% O atom; [c] a hybrid atom that consists of 66(6)% N atom and 34(6)% C atom; [d] a hybrid atom that consists of 34(6)% N atom and 66(6)% C atom; [e] a hybrid atom that consists of 51(6)% N atom and 49(6)% C atom; [f] a hybrid atom that consists of 49(6)% N atom and 51(6)% C atom; [g] a hybrid atom that consists of 13(6)% N atom and 87(6)% C atom; [h] a hybrid atom that consists of 87(6)% N atom and 13(6)% C atom. $B_{eq} = \frac{8\pi^2}{3} \Sigma_i \Sigma_j U_{ij} a^*_i a^*_j a_i a_j$.

Crystal Structural of $Cd(H_2O)_2Cu(CN)_3 \cdot 2H_2O$ *(2)*

The basic crystal structure of **2** is a layered structure of $[CdCu(CN)_3]$ planar complexes which are stacked along the *c* axis. The planar complex $[CdCu(CN)_3]$ has a network structure formed with cyano groups bridging between Cu(I) and Cd. The coordination structure of Cu has a trigonal planar configuration with three bridging cyano groups. Cd has an octahedral coordination structure and its meridional positions are occupied by the three bridging cyano groups. This bridging scheme makes a planar network structure with a distorted hexagonal mesh as shown in Fig. 1(A). Fig. 1(B) shows the stacked structure of the planar complexes.

Through the vacant space of the hexagonal mesh of the $[CdCu(CN)_3]$ complex, another network structure is running along the *c* axis as shown in Fig. 1(B). This second network is formed with hydrogen bonds among water molecules and coordination bonds between a water molecule and Cd in the planar metal complex. The second network links the stacked planar complexes along the *c* axis, so that a three-dimensional framework spreading over the crystal is built up with connection of the two networks.

In the second network there are two structures for linkage between the stacked planar complexes. One is a double bridge structure formed with two bridging water ligands. The other meridional positions of Cd, which correspond to the remaining equatorial position and the axial positions, are occupied by three oxygen atoms, O(1), $O(1)^{*5}$, O(2), of water molecules (Fig. 1(B)). The water molecule including O(1) makes a bridge between Cd and Cd^{*5}, which are included in the planar

Table 3 Selected interatomic distances and angles for 2, 3 and 4.

$Cd(H_2O)_2Cu(CN)_3 \cdot 2H_2O$ (2).			
Distances (d/Å).			
Cd - N(1)	2.265(7)	Cd - N(2)	2.219(3)
Cd - O(2)	2.382(4)	Cd - O(1)	2.393(3)
Cd - O(1)^{*5}	2.537(4)	Cu - C(1)	1.943(6)
Cu - C(2)	1.941(3)	N(1) - C(1)	1.148(9)
N(2) - C(2)	1.148(4)	O(1) ... O(1)^{*5}	3.009(6)
O(2) ... O(3)	2.770(5)	O(3) ... O(3)^{*6}	2.780(4)
O(3) ... O(3)^{*1}	3.844(4)	O(3) ... O(1)^{*5}	4.119(4)
O(2) ... O(1)^{*5}	3.868(6)	O(3) ... O(1)^{*8}	2.726(4)
O(3) ... Cd	4.347(4)	Cu ... Cu^{*9}	3.070(1)
Angles(δ/°).			
O(1) - Cd - N(1)	95.6(2)	O(1) - Cd - N(2)	92.0(1)
O(1) - Cd - O(1)^{*3}	75.2(1)	O(1) - Cd - O(2)	164.7(1)
O(1)^{*3} - Cd - O(2)	89.5(1)	N(1) - Cd - O(2)	99.7(2)
N(1) - Cd - N(2)	98.3(2)	N(2) - Cd - O(2)	85.9(1)
O(2) - Cd - O(1)^{*5}	89.5(1)	Cd - N(1) - C(1)	179.9(6)
Cd - N(2) - C(2)	165.0(3)	Cd - O(2) - O(3)	114.9(1)
Cd - O(1)^{*5} - O(3)^{*6}	113.8(1)	Cd - O(1)^{*5} - Cd^{*5}	104.8(2)
C(2) - Cu - C(2)^{*2}	125.4(1)	C(2) - Cu - C(1)^{*3}	117.3(2)
Cu - C(1)^{*3} - N(1)^{*3}	179.5(6)	Cu - C(2) - N(2)	174.9(3)
O(3) - O(2) - O(3)^{*1}	87.9(2)	O(2) - O(3) - O(3)^{*6}	97.5(1)
O(2) - O(3) - O(1)^{*8}	89.5(1)	O(3)^{*6} - O(3) - O(1)^{*8}	96.8(1)
O(3)^{*7} - O(1)^{*5} - O(3)^{*6}	89.7(2)		
Key to symmetry operations; ^{*1}: $x, -y, z$; ^{*2}: $x, 1-y, z$; ^{*3}: $-1/2+x, 1/2+y, z$; ^{*4}: $1/2+x, -1/2+y, z$; ^{*5}: $-x, -y, -z$; ^{*6}: $-x, y, 1-z$; ^{*7}: $-x, -y, 1-z$; ^{*8}: $x, y, 1+z$; ^{*9}: $-x, 1-y, -z$, ^{*10}: $x, 1+y, z$; ^{*11}: $1/2+x, 1/2+y, z$.			
$K[Cd(H_2O)_2Cu_2(CN)_5] \cdot 2H_2O$ (3).			
Distances (d/Å).			
Cd(1) - O(1)	2.410(9)	Cd(1) - O(2)	2.364(5)
Cd(1) - N(1)	2.27(1)	Cd(1) - N(2)	2.279(8)
Cd(1) - N(5)	2.248(6)	Cd(1) - N(7)	2.353(5)
Cd(2) - O(3)	2.404(5)	Cd(2) - O(4)	2.438(9)
Cd(2) - N(3)	2.29(1)	Cd(2) - N(4)	2.250(7)
Cd(2) - N(6)	2.278(5)	Cd(2) - N(8)	2.306(5)
Cu(1) - C(1)	1.94(1)	Cu(1) - C(4)^{*1}	1.95(1)
Cu(1) - X(1)	1.946(7)	Cu(2) - C(2)	1.94(1)
Cu(2) - C(3)	1.93(1)	Cu(2) - X(3)	1.959(8)
Cu(3) - C(6)^{*3}	1.915(7)	Cu(3) - C(7)^{*2}	1.92(1)
Cu(3) - X(2)	1.997(9)	Cu(4) - C(5)^{*4}	1.929(6)
Cu(4) - C(8)^{*5}	1.93(1)	Cu(4) - X(4)	1.95(1)
N(1) - C(1)	1.14(2)	N(2) - C(2)	1.13(1)
N(3) - C(3)	1.147(2)	N(4) - C(4)	1.137(1)
N(5) - C(5)	1.150(8)	N(6) - C(6)	1.133(9)
N(7) - C(7)	1.14(1)	N(8) - C(8)	1.14(2)
X(1) - X(2)	1.13(1)	X(3) - C(8)	1.14(1)
K(1) ... O(1)^{*6}	2.895(5)	K(1) ... O(2)^{*6}	2.848(7)
K(1) ... O(4)	2.920(5)	K(1) ... O(7)	2.85(1)
K(2) ... O(3)^{*8}	2.771(9)	K(2) ... O(8)	2.888(7)
O(1) ... O(5)	2.97(1)	O(1) ... O(6)^{*9}	2.887(6)
O(2) ... O(8)^{*3}	2.74(1)	O(3) ... O(6)	2.792(9)
O(4) ... O(6)	3.149(6)	O(4) ... O(7)	2.83(1)
O(5) ... O(6)	2.81(1)		
Angles(δ/°)			
O(1) - Cd(1) - O(2)	82.2(2)	O(1) - Cd(1) - N(2)	83.9(3)
O(1) - Cd(1) - N(5)	82.7(3)	O(1) - Cd(1) - N(7)	88.6(2)

Table 3 — (Continued)

N(1) - Cd(1) - N(7)	89.3(3)	N(1) - Cd(1) - O(2)	99.9(3)
N(1) - Cd(1) - N(5)	98.0(3)	N(1) - Cd(1) - N(2)	95.4(4)
O(2) - Cd(1) - N(5)	90.7(2)	N(5) - Cd(1) - N(7)	89.5(2)
N(7) - Cd(1) - N(2)	90.8(2)	N(2) - Cd(1) - O(2)	86.8(2)
O(3) - Cd(2) - O(4)	81.2(2)	O(3) - Cd(2) - N(3)	91.4(3)
O(3) - Cd(2) - N(6)	85.5(2)	O(3) - Cd(2) - N(4)	90.7(2)
N(8) - Cd(2) - O(4)	86.6(3)	N(8) - Cd(2) - N(4)	92.8(2)
N(8) - Cd(2) - N(3)	100.3(3)	N(8) - Cd(2) - N(6)	89.2(2)
N(6) - Cd(2) - N(3)	89.6(3)	O(4) - Cd(2) - N(6)	83.5(3)
N(4) - Cd(2) - O(4)	88.3(3)	N(3) - Cd(2) - N(4)	98.2(3)
C(1) - Cu(1) - C(4)^{*1}	118.4(5)	C(4)^{*1} - Cu(1) - X(1)	113.6(4)
X(1) - Cu(1) - C(1)	127.8(5)	C(2) - Cu(2) - C(3)	124.8(5)
C(3) - Cu(2) - X(3)	124.7(5)	X(3) - Cu(2) - C(2)	110.5(4)
C(7)^{*2} - Cu(3) - X(2)	105.8(4)	X(2) - Cu(3) - C(6)^{*3}	117.8(3)
C(6)^{*3} - Cu(3)-C(7)^{*2}	131.1(4)	C(8)^{*5} - Cu(4) - X(4)	113.8(5)
X(4) - Cu(4) - C(5)^{*4}	121.1(4)	C(5)^{*4} - Cu(4) - C(8)^{*5}	123.7(4)
Cd(1) - N(1) - C(1)	166(1)	Cd(1) - N(2) - C(2)	167.4(7)
Cd(1) - N(5) - C(5)	154.8(5)	Cd(1) - N(7) - C(7)	133.2(6)
Cd(2) - N(3) - C(3)	163.4(9)	Cd(2) - N(4) - C(4)	165.2(6)
Cd(2) - N(6) - C(6)	153.6(5)	Cd(2) - N(8) - C(8)	126.8(8)
Cu(1) - C(1) - N(1)	174(1)	Cu(1) - C(4)^{*1} - N(4)^{*1}	175.0(9)
Cu(1) - X(1) - X(2)	170.8(6)	Cu(2) - C(2) - N(2)	176.0(9)
Cu(2) - C(3) - N(3)	177(1)	Cu(2) - X(3) - X(4)	169.7(7)
Cu(3) - C(6)^{*3} - N(6)^{*3}	170.9(6)	Cu(3) - C(7)^{*2} - N(7)^{*2}	174(1)
Cu(3) - X(2) - X(1)	168.6(9)	Cu(4) - C(5)^{*4} - N(5)^{*4}	174.5(6)
Cu(4) - C(8)^{*5} - N(8)^{*5}	177(1)	Cu(4) - X(4) - X(3)	173(1)
O(1)^{*6} - K(1) - O(2)^{*6}	66.2(2)	O(1)^{*6} - K(1) - O(4)^{*7}	81.3(1)
O(1)^{*6} - K(1) - O(7)	140.2(2)	O(2)^{*6} - K(1) - O(7)	116.3(2)
O(7) - K(1) -O(4)^{*7}	121.2(2)	O(2)^{*6} - K(1) - O(4)^{*7}	119.2(2)
O(3)^{*8} - K(2) - O(8)	84.6(2)	O(5) - O(1) - O(6)^{*9}	108.4(3)
O(5) - O(1) - Cd(1)	109.1(2)	O(5) - O(1) - K(1)^{*12}	125.4(4)
Cd(1) - O(1) - K(1)^{*12}	99.7(2)	K(1)^{*12} - O(1) - O(6)^{*9}	103.4(1)
O(6)^{*9} - O(1) - Cd(1)	110.1(3)	O(8)^{*3} - O(2) - Cd(1)	115.8(4)
O(8)^{*3} - O(2) - K(1)^{*12}	117.0(2)	Cd(1) - O(2) - K(1)^{*12}	102.3(2)
K(2)^{*11} - O(3) - Cd(2)	102.5(3)	K(2)^{*11} - O(3) - O(6)^{*10}	104.0(2)
Cd(2) - O(3) - O(6)^{*10}	105.4(2)	O(7) - O(4) - K(1)	115.0(2)
O(7) - O(4) - Cd(2)	106.4(2)	O(7) - O(4) - O(6)^{*10}	136.0(4)
K(1) - O(4) - Cd(2)	102.5(3)	Cd(2) - O(4) - O(6)^{*10}	94.8(2)
O(6)^{*10} - O(4) - K(1)	96.7(2)	O(6) - O(5) - O(1)	83.9(4)
O(3)^{*8} - O(6) - O(4)^{*8}	63.7(2)	O(3)^{*8} - O(6) - O(5)	119.6(3)
O(3)^{*8} - O(6) - O(1)^{*9}	123.3(3)	O(4)^{*8} - O(6) - O(5)	131.0(4)
O(5) - O(6) - O(1)^{*9}	117.1(3)	O(1)^{*9} - O(6) - O(4)^{*8}	77.6(1)
K(1)^{*7} - O(7) - O(4)	89.7(4)	K(2)^{*5} - O(8) - O(2)^{*3}	102.1(4)

Key to symmetry operations;
^{*1}: $x-1, y, z$; ^{*2}: $-x, -y+1, -z+1$; ^{*3}: $-x, -y+1, -z$; ^{*4}: $x+1, y+1, z$; ^{*5}: $-x+1, -y+1, -z+1$; ^{*6}: $x+1, y, z+1$; ^{*7}: $-x, -y+2, -z+1$; ^{*8}: $x, y, z+1$; ^{*9}: $-x, -y+2, -z+1$; ^{*10}: $x, y, z-1$; ^{*11}: $-x+1, -y+1, -z$; ^{*12}: $-x, -y+2, -z$; ^{*13}: $x, y-1, z$; ^{*14}: $x+1, y, z$; ^{*15}: $x+1, y+1, z$; ^{*16}: $x, y+1, z$; ^{*17}: $-x, -y+2, -z$; ^{*18}: $x-1, y-1, z-1$; ^{*19}: $x-1$, y, $z-1$.

$K_2[Cd(H_2O)Cu_4(CN)_8]\cdot 1.5H_2O$ (4).
Distances (d/Å).

Cd - N(1)	2.206(5)	Cd - N(2)	2.253(8)
Cd - N(3)	2.178(5)	Cd - N(4)	2.190(6)
Cd - O(1)	2.603(6)	Cu(1) - C(1)	1.896(5)
Cu(1) - X(51)^{*1}	1.964(6)	Cu(1) - X(8)	1.942(6)
Cu(2) - C(2)	1.900(7)	Cu(2) - X(61)^{*3}	1.941(6)
Cu(2) - X(72)^{*3}	1.989(6)	Cu(3) - C(3)	1.921(5)

Table 3 — Continued

Cu(3) - X(71)*^{4}	1.932(7)	Cu(3) - X(9)*^{4}	1.967(7)
Cu(4) - C(4)	1.908(7)	Cu(4) - X(52)	1.938(7)
Cu(4) - X(62)	1.950(5)	N(1) - C(1)	1.145(7)
N(2) - C(2)	1.13(1)	N(3) - C(3)	1.141(7)
N(4) - C(4)	1.141(9)	X(51) - X(52)	1.142(9)
X(61) - X(62)	1.150(8)	X(71)*^{4} - X(72)*^{4}	1.145(9)
X(8) - X(8)*^{2}	1.154(8)	X(9)*^{4} - X(9)*^{5}	1.1454(9)
O(1) ... K(1)	2.983(5)	K(1) ... O(2)	2.720(5)
KO(1) ... KO(2)	3.173(6)	KO(1) ... KO(1)*^{7}	2.670(5)
KO(1) ... KO(2)*^{7}	4.088(6)	KO(2) ...KO(2)*^{7}	3.531(7)
Angles(σ/°).			
Cd - N(1) - C(1)	172.3(5)	Cd - N(2) - C(2)	166.9(7)
Cd - N(3) - C(3)	172.8(4)	Cd - N(4) - C(4)	167.8(6)
O(1) - Cd - N(1)	84.9(2)	O(1) - Cd - N(4)	80.4(2)
O(1) - Cd - N(2)	173.0(2)	O(1) - Cd - N(3)	80.8(2)
N(1) - Cd - N(2)	92.4(2)	N(1) - Cd - N(3)	137.2(2)
N(1) - Cd - N(4)	101.7(2)	N(2) - Cd - N(3)	96.9(2)
N(2) - Cd - N(4)	106.4(3)	N(3) - Cd - N(4)	115.2(2)
Cu(1) - C(1) - N(1)	171.7(5)	Cu(1) - X(51)*^{1} - X(52)*^{1}	170.3(6)
Cu(1) - X(8) - X(8)*^{2}	178.2(5)	X(8) - Cu(1) - C(1)	124.8(2)
C(1) - Cu(1) - X(51)*^{1}	122.6(3)	X(51)*^{1} - Cu(1) - X(8)	110.2(3)
Cu(2) - C(2) - N2(21)	175.8(7)	Cu(2) - X(61)*^{3} - X(62)*^{3}	167.9(5)
Cu(2) - X(72)*^{3} - X(71)*^{3}	167.8(5)	C(2) - Cu(2) - X(61)*^{3}	130.7(3)
X(61)*^{3} - Cu(2) - X(72)*^{3}	105.6(2)	X(72)*^{3} - Cu(2) - C(2)	123.5(3)
Cu(3) - C(3) - N(3)	174.3(5)	Cu(3) - X(71)*^{4} - X(72)*^{4}	173.5(7)
Cu(3) - X(9)*^{4} - X(9)*^{5}	178.1(6)	C(3) - Cu(3) - X(9)*^{4}	116.4(3)
X(9)*^{4} - Cu(3) - X(71)*^{4}	114.5(3)	X(71)*^{4} - Cu(3) - C(3)	128.3(3)
Cu(4) - C(4) - N(4)	175.4(6)	Cu(4) - X(52) - X(51)	172.2(6)
Cu(4) - X(62) - X(61)	176.7(5)	C(4) - Cu(4) - X(62)	120.1(3)
X(62) - Cu(4) - X(52)	110.6(2)	X(52) - Cu(4) - C(4)	128.4(3)
Cd - O(1) - K(1)	109.9(2)	O(1) - K(1) - O(2)	76.1(1)
K(1) - O(2) - K(1)*^{6}	114.2(3)	KO(2) - KO(1) - KO(1)*^{7}	88.4(1)

Key to symmetry operations;
*^{1}: $x+1/2, y-1/2, z$; *^{2}: $-x+1, y, -z+3/2$; *^{3}: $x, y, z-1$; *^{4}: $x-1/2, y-1/2, z-1$; *^{5}: $-x+1/2, y-1/2, -z+1/2$; *^{6}: $-x, y, -z+1/2$; *^{7}: $-x+1, y, -z+1/2$; *^{8}: $x, y, z+1$; *^{9}: $x+1/2, y+1/2, z$; *^{10}: $x+1/2, y+1/2, z+1$; *^{11}: $-x+1/2, y+1/2, -z+1/2$; *^{12}: $-x+1/2, y+1/2, -z+3/2$; *^{13}: $x-1/2, y+1/2, z$; *^{14}: $-x+3/2, y+1/2, -z+3/2$; *^{15}: $x+1/2, y-1/2, z+1$; *^{16}: $x+1, y, z+1$; *^{17}: $-x+1/2, y-1/2, -z+3/2$.

complexes adjacent to each other. Each of the Cd atoms is coordinate not only by O(1) but also O(1)*^{5} which is equivalent to O(1) crystallographically. Therefore, the two planar complexes are bridged doubly by the two water ligands as seen in Fig. 1(B). The other linkage structure, formed with hydrogen bonding, is seen in the area between the planar complex including Cd and that including Cd*^{7}(Fig. 1(B)). The water molecule including O(2) is coordinated to Cd as a unidentate ligand. The O(2) atom is linked to O(1)*^{8} *via* O(3) by the hydrogen bond sequence of O(2)-O(3)-O(1)*^{8}. O(3) is the oxygen atom of a water molecule located between the two planar complexes. There are four O(3) atoms, the original O(3) and its equivalent three atoms O(3)*^{1}, O(3)*^{6} and O(3)*^{7}, in this area, so that there are four hydrogen bond sequences that are equivalent to O(2)-O(3)-O(1)*^{8}. This means that there are four hydrogen bonding sequences that link the two planar complexes, because O(2) and O(1)*^{8} are coordinated to Cd and Cd*^{7}, respectively. The four sequences are boundby the hydrogen bonds of O(3)-O(3)*^{6} and O(3)*^{1}-O(3)*^{7} to form a kind of

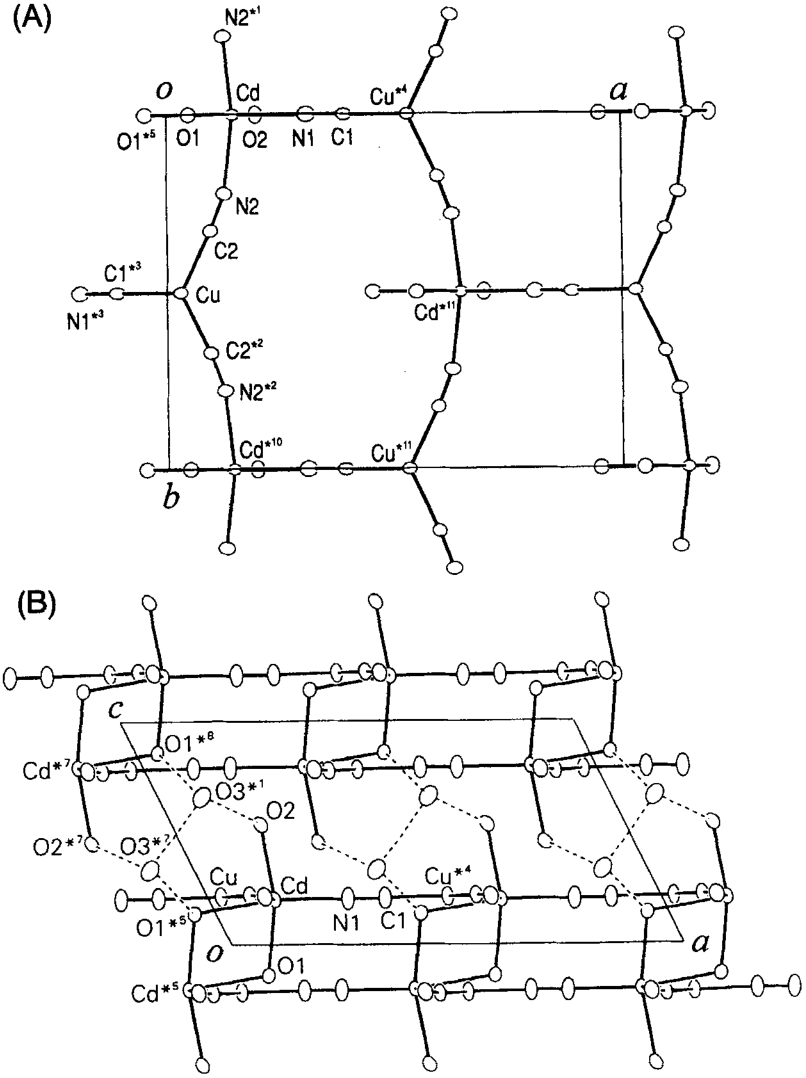

Figure 1 (A) Network structure with distorted hexagonal mesh of the [CdCu(CN)$_3$] planar complex in Cd(H$_2$O)$_2$Cu(CN)$_3\cdot$2]H$_2$O (**2**). (Projection along the *c* axis). (B) Crystal structure of **2**. (Projection along the *b* axis). Hydrogen bonds are indicated with dotted lines. Key to symmetry operations is listed in Table 3.

framework structure of hydrogen bonding in this local area (Fig. 1(B)). O(1)^{*8} is also the oxygen atom of the birdging water ligand of the first type linkage, so that a one-dimensional network that consists of coordination bonding and hydrogen bonding is built up along the *c* axis.

Crystal Structure of $K[Cd(H_2O)_2Cu_2(CN)_5]\cdot 2H_2O$ *(3)*

Complex **3** has a stacked structure of $[Cd(H_2O)_2Cu_2(CN)_5]^-$ complexes that have a bi-layered configuration. This bi-layered structure is formed with cyano groups bridging between two mono-layered $[Cd(H_2O)_2Cu_2(CN)_4]$ complexes. All the Cu(I) atoms in **3** have a distorted trigonal planar coordination structure with three cyano groups, and all the Cd(II) atoms have an octahedral coordination structure with two water molecules in *cis* positions and four cyano groups at the other positions. There are ten crystallographically independent cyano groups in the crystal. All the cyano groups make bridges between two metal atoms. Eight of them form the network structure of the $[Cd(H_2O)_2Cu_2(CN)_4]$ mono-layered complex. The network of the $[Cd(H_2O)_2Cu_2(CN)_4]$ complex has two kinds of mesh with similar shapes. The outlines of the mesh shapes are comprised of eight metal atoms: - Cd(1)-Cu(1)-Cu(3)-Cd(2)*^{13}-Cu(1)*^{4}-Cd(1)*^{4}-Cu(4)-Cu(2)-Cd(1)- and -Cd(2)-Cu(2)-Cu(4)-Cd(1)*^{1} -Cu(2)*^{4} -Cd(2)*^{4} -Cu(3)*^{14}-Cu(1)*^{14}-Cd(2) (Fig. 2(A)). Other two cyano groups, C(7)-N(7) and C(8)-N(8), make bridges between the two planar $[Cd(H_2O)_2 Cu_2(CN)_4]$ complexes to support the bi-layered structure of $[Cd(H_2O)_2Cu_2 (CN)_5]^-$ (Fig. 2(B)).

The two water molecules coordinated to Cd are unidentate ligands that do not take part in formation of the framework structure of the metal complex. However, they are part of another network formed with hydrogen bonding and electrostatic interactions among non-coordinating water molecules and K^+ ions in vacant spaces of the metal complex framework. The atomic distances between oxygen atoms in the second network are 2.792(9)Å – 3.149(6)Å, and those between an oxygen atom and a K^+ ion are 2.771(9)Å – 2.97(1)Å. In Fig. 2(A) and 2(B) the second network is indicated with dotted lines. Although the basic structure of the metal complex framework is a stacked structure of two dimensional complexes, the second network spreads over the crystal three-dimensionally, penetrating the metal complex framework as shown in Fig. 2(B).

Crystal Structure of $K_2\,[Cd(H_2O)Cu_4(CN)_8]\ 1.5H_2O$ *(4)*

Complex **4** has a double lattice structure, with pair of three-dimensional enantiomeric $[Cd(H_2O)Cu_4(CN)_8]^{2-}$ frameworks inter-penetrating each other (Fig. 3(A)). All Cu(I) atoms have a distorted trigonal planar coordination structure with three cyano groups and the Cd(II) has a five-coordinate structure with four cyano groups and a water molecule. All cyano groups make bridges between two Cu atoms or between Cu and Cd to form the three dimensional framework. The water molecule is a unidentate ligand, so that the molecule is not involved in forming the complicated framework structure. One approach to understanding the structure is to consider a spiral of-Cu(2)*^{5}-Cu(4)*^{17}-Cu(1)*^{2}-Cu(1)-Cd-Cu(4)-Cu(2)*^{8}-Cu*^{10}-Cu(3)*^{11}-Cd*^{11}-running along the *b* axis as indicated with round arrows in Fig. 3(B). All metal atoms in the spiral sequence are shared with adjacent spiral sequences. This framework has vacant sites in it as shown in Fig. 3(B). The vacant sites are reduced by the inter-penetrating structure of the enatiomeric pair (Fig. 3(A)).

The dotted lines in Fig. 3(A) show linkages formed with electrostatic interactions among water molecules and K^+ ions in **4**. The linkages are short and extend within a local area in the crystal. There are two kinds of linkages: a Cd-O(1)-K(1)-O(2)-

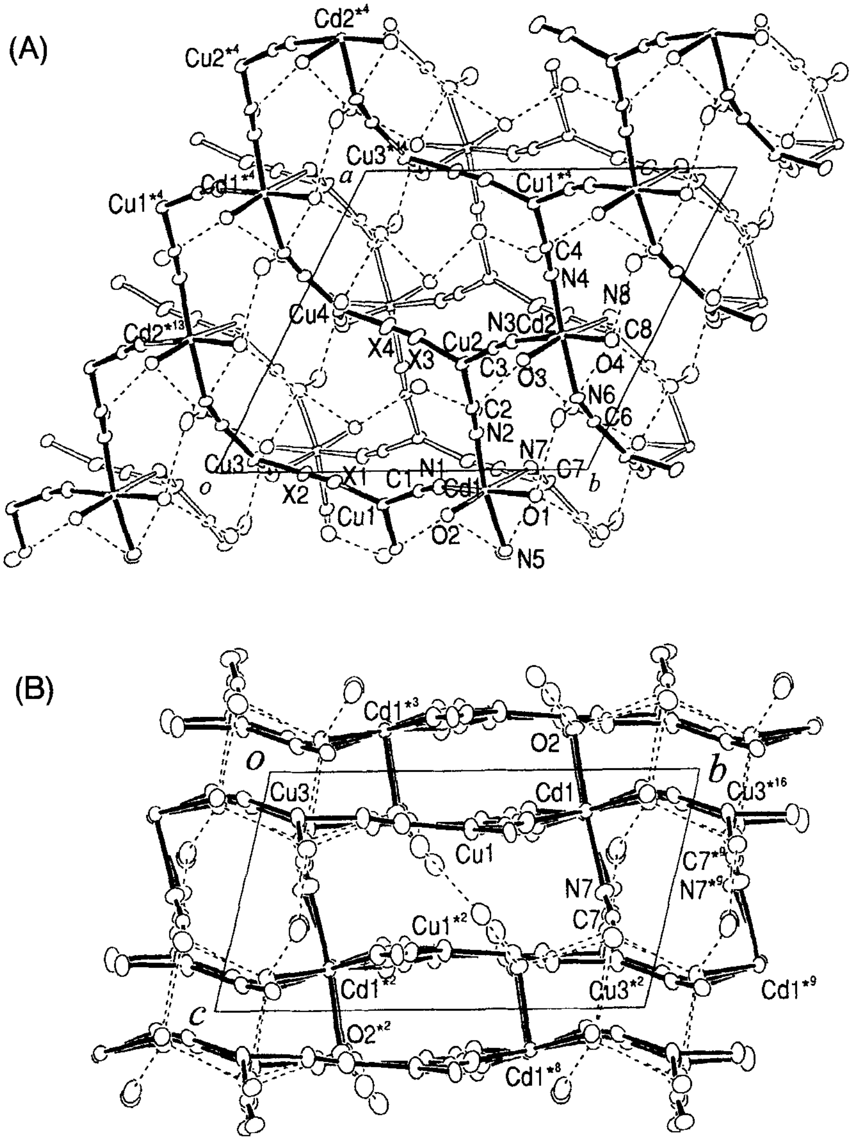

Figure 2 Crystal structure of K[$Cd(H_2O)_2Cu_2(CN)_5$]·$2H_2O$ (**3**). The network formed with hydrogen bonding and electrostatic interaction among water molecules and K + ions is indicated with dotted lines. (A) Projection along the *c* axis. Bonding sequence painted black indicated the network of the upper layer of the [$Cd(H_2O)_2Cu_2(CN)_5$]$^-$ bi-layered structure complex. (B) Projection along the *a* axis. Stacking structure of the [$Cd(H_2O)_2Cu_2(CN)_5$]$^-$ bi-layered complex is seen. The layer including Cd(1), Cu(1) and Cu(3) and that including Cd(1)^{*2}, Cu(1)^{*2}, and Cu(3)^{*2} are the two layers of the [$Cd(H_2O)_2Cu_2(CN)_5$]$^-$ bi-layered complex. The two layers are connected by bridging of -C(7)-N(7)- and -C(8)-N(8)-, which is not seen in the figure. Between the two layers and the other layers including Cd(1)^{*3} and Cd(1)^{*8} there is no connection by chemical bonding except by the network of hydrogen bonding. Key to symmetry operations is listed in Table 3.

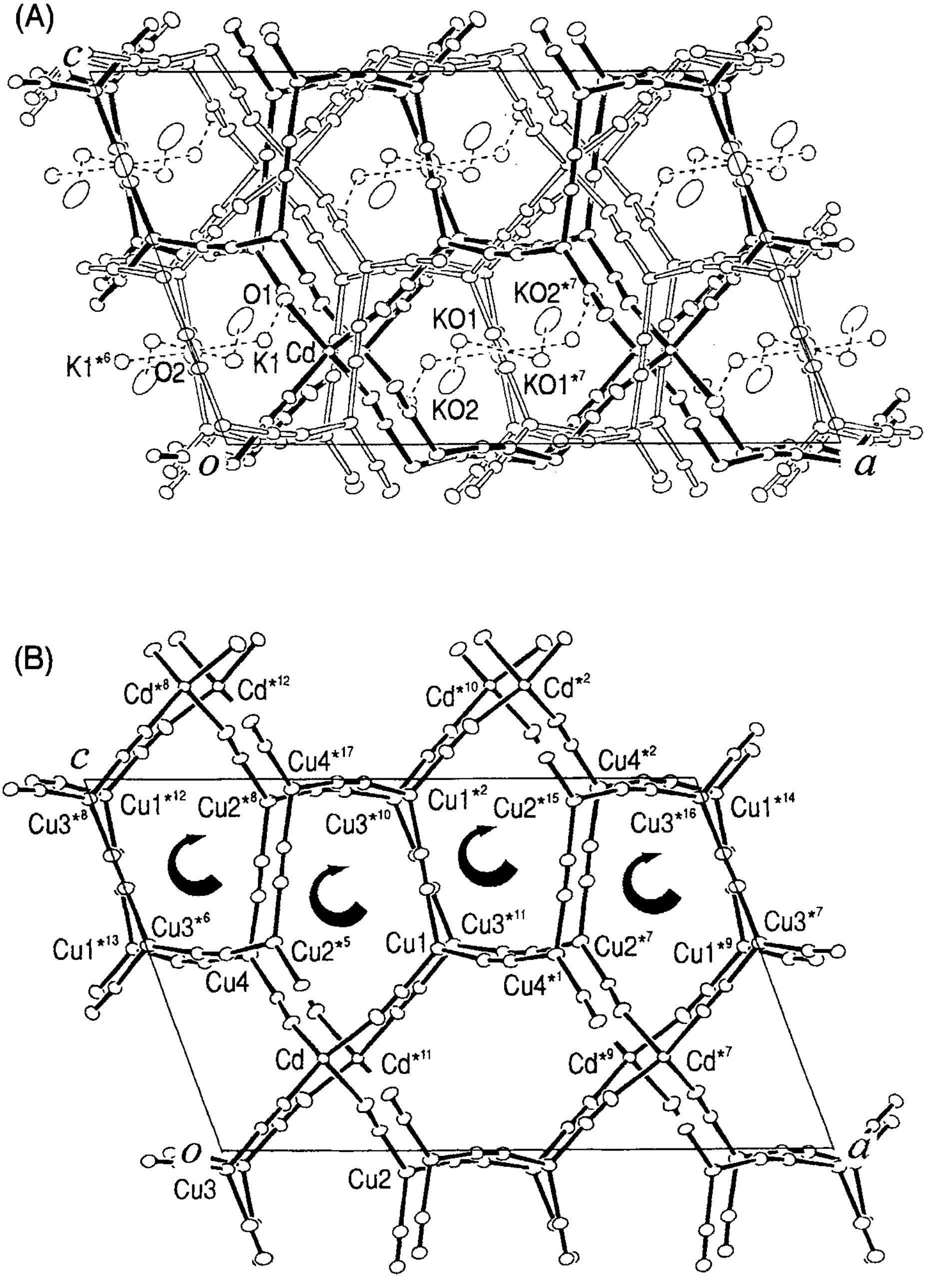

Figure 3 (A) Crystal structure of $K_2[Cd(H_2O)_2Cu_4(CN)_8]\cdot 1.5H_2O$ (4). Projection along the *b* axis. The linkages among water molecules and K^+ ions are indicated with dotted lines. One of the enantiomeric framework pair is painted black. (B) Structure of one of the enantiomeric framework pair. O(1) atom coordinated to Cd is omitted for clarity. Spiral sequence of $\text{-Cu(2)}^{*5}\text{-Cu(4)}^{*17}\text{-Cu(1)}^{*2}\text{-Cu(1)-Cd-Cu(4)-Cu(2)}^{*8}\text{-Cu(3)}^{*10}\text{-Cu(3)}^{*11}\text{-Cd}^{*11}\text{-}$ and its equivalent sequences are indicated with round arrows. Key to symmetry operations is listed in Table 3.

K(1)-O(1)-Cd linkage and a KO(2)-KO(1)-KO(1)-KO(2) linkage. In the former one, O(1) is the oxygen atom of the water ligand coordinating to Cd, and the two Cd atoms belong to one of the enatiomeric framework pairs. O(2) is the oxygen atom of a non-coordinating water molecule. In the latter one, a structural disorder was found. In the structure determination, the KO(2)-KO(1)-KO(1)-KO(2) linkage was treated as an averaged structure where 50% K-O-K-O and 50% O-K-O-K linkages exist at the same position. The least-squares calculation of other configurations gave abnormal thermal temperature factors to the atoms in the linkage. Neither coordination bonding nor hydrogen bonding connects this linkage to the metal complex framework.

DISCUSSION

The main function of the Cd(II) added into the Cu(I)-CN system is to provide the system with a structural base that develops a two-dimensional structure into a three-dimensional one. The coordination structure of Cu(I) found in the complexes obtained in this study was trigonal planar, which is a normal coordination structure for Cu(I) complexes. It is natural that the trigonal planar coordination forms a two-dimensional network structure. A typical example of such a planar network structure is seen in $K[Cu_2(CN)_3]\cdot H_2O$ (**5**), which was obtained at the final stage of the preparation. **5** contains only trigonal planar Cu(I) as a metal atom, so that the basic structure of **5** is a layered structure of $[Cu_2(CN)_3]^-$ planar complexes with hexagonal mesh.[3] Through the center of the hexagonal mesh runs the chain of water molecules and K^+ ions linked by electrostatic interactions. On the other hand, examples of the development of a planar structure into a three-dimensional structure are seen in the crystal structures of **2**, **3** and **4**. In **2** three meridional positions of the octahedral Cd are used for the coordination of the bridging cyano groups to form the $[CdCu(CN)_3]$ planar network. The other meridional positions of the Cd are coordinated by water molecules that are parts of the second network formed with hydrogen bonding, so that the whole framework of the crystal has a three-dimensional structure. The Cd in **2** is working as a joint that connects the two networks three-dimensionally. The octahedral Cd in **3** makes possible extension of the $[Cd(H_2O)_2Cu_2(CN)_4]$ mono-layered structure to the bi-layered structure. At the same time, the Cd gives a structural base for another network formed with water molecules and K^+ ions, so that the whole framework of **3** has the three-dimensional structure. In **4**, the Cd atom has a five-coordinate structure, with one site occupied by a unidentate water ligand. Therefore, the Cd functions as a *pseudo*-tetrahedral site in the Cd-Cu(I)-CN framework. This *pseudo* tetrahedral symmetry is an important structural factor for forming the enatiomeric spiral framework structural of **4** (Fig. 3(B)). These examples show that the Cd(II) in the Cu(I)-CN system forms three-dimensional framework structures in two ways. The one is as a structural base for extending the cyano complex from a planar structure to a three dimensional structure, as seen in **3** and **4**. The other is to work as a structural base for forming the second network of hydrogen bonding as seen in **2** and **3**.

The trigonal planar coordination structure of Cu(I) is also important for the frameworks formed by combination of two networks. Large amounts of vacant space in the metal complex network are indispensable for formation of the second network. This vacant space arises from the large mesh of the network based on the trigonal planar coordination of Cu(I). A network with hexagonal mesh is formed naturally on the basis of the trigonal planar configuration. Assuming a regular hexagonal mesh, a circle space with a radius of *ca.* 3Å is expected for the vacant space at the center of the mesh. This space is large enough for hydrogen bonding to penetrate into the mesh and extend its network as shown in the complexes. The networks of **2** and **5** have a distorted hexagonal mesh and that of **3** has more large mesh; the second networks spread over the crystal, penetrating the metal complex networks. Apart from the size of the mesh, the variations of the mesh shape may be important in the above example. Note that **4**, does not have a planar network structure but a spiral framework structure. This will be discussed later.

The third structural factor to be considered involves two structural distortions. One is observed in the briding cyano groups where the geometry of the bridging cyano groups is not linear. The angles of M-C-N and C-N-M′ were over the range of 126.8(8)°–179.9(6)°. The other is distortion of the trigonal planar coordination structure of Cu(I). The angle between C-Cu(I)-C in $[Cu(CN)_3]^{2-}$ was over the range of 105.6(2)°–131.1(4)°. These distortions give flexibility to the cyano complex network structure, and this structural flexibility makes it easy for the metal complex framework to generate structural variations. A remarkable distortion is seen in the bridging cyano groups that support the bi-layered structure of $[Cd(H_2O)_2Cu_2(CN)_5]^-$; the angles for Cd(1)-N(7)-C(7) and Cd(2)-N(8)-C(8) are 133.2(6)° and 126.8(8)°, respectively.

Examples of similar structural features and distortions are found in Hormann-type inclusion and related compounds.[10] A typical composition of the Hofmann-type related compound is $Cd(L)_2Ni(CN)_4 \cdot nG$, where L is a ligand such as NH_3, $(CH_3)_2NH$, *etc.*, and G is a guest molecule such as benzene, pyrrole, *etc.* The basic structure of $Cd(L)_2Ni(CN)_4 \cdot nG$ is a layered structure of planar $[Cd(L)_2Ni(CN)_4]$ complexes. The planar complex is built with cyano groups bridging between square planar Ni(II) atoms and octahedral Cd(II) atoms, so that the planar network has square mesh based on the square planar $[Ni(CN)_4]^{2-}$ structure. In the Hofmann-type related compounds, there is no network corresponding to the second network in the Cd-Cu(I)-CN system because there is no space for the formation of the second network at the center of the square mesh. The radius of the vacant space of the square mesh is estimated to be only only *ca.* 1Å. Distortions of the briding cyano groups and the square planar coordination structure are also observed in the Hofmann-type related compounds. However, the distortions generate not variations of mesh shape but transformation of the network structure from a flat surface to a wavy surface, because the square geometry is too rigid and close. Considering the above case, the trigonal planar coordination structure is more important for forming various framework structures than for structural distortions.

The ultimate conversion in the mother solution from the Cd-Cu(I)-CN complexes to $K[Cu_2(CN)_3] \cdot H_2O$ (**5**) indicates that the multi-dimensional framework including Cd(II) do not sufficiently stabilize the crystal structure, providing metastable crystal structures. It is possible that other variations of the frameworks of this system are possible; we continue to try to prepare and to collect structural data in order to clarify the structure chemistry of this system. Another attempt to prepare a framework to work as a host lattice for guest molecules has resulted in few new inclusion compounds with the Cd-Cu(I)-CN framework host.[11] Their details will be reported elsewhere.

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SUPPLEMENTARY MATERIAL

Lists of thermal factors, and observed and calculated structure factors can be obtained on request from the author.

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