Inorg. Chem. **1996,** *35,* 1849−1856

A Dicyanoargentate(I) Rod Behaving as a Discrete Anion, a Monodentate Shaft or Shank, and an Ambidentate Shaft in the Crystal Structures of Imidazole-Blade Ligated Cadmium(II) Dicyanoargentate(I) Complexes: *trans*-Bis[dicyanoargentato(I)]tetrakis(imidazole)cadmium(II), [Dicyanoargentato(I)]pentakis(imidazole)cadmium(II) Dicyanoargentate(I), *catena*-Poly[tetrakis(*N*-methylimidazole)cadmium(II)-*trans*-*μ*-dicyanoargentato(I)] Dicyanoargentate(I), and *catena*-Poly[tetrakis(2-methylimidazole)cadmium(II)-*trans*-*μ*-dicyanoargentato(I)] Dicyanoargentate(I) Hydrate

Takayoshi Soma and Toschitake Iwamoto*

Department of Chemistry, College of Arts and Sciences, The University of Tokyo,
Komaba, Meguro, Tokyo 153, Japan

Received May 19, 1995[⊗]

The crystal structures of four [dicyanoargentato(I)]cadmium(II) complexes with the mixed ligation of imidazole (imH: $C_3H_4N_2$) or *N*-methyl- or 2-methylimidazole (*N*-Meim or 2-MeimH: $C_3H_6N_2$) on the cadmium(II), $[Cd(imH)_4\{Ag(CN)_2\}_2]$ (**1a**), $[Cd(imH)_5\{Ag(CN)_2\}][Ag(CN)_2]$ (**1b**), $[Cd(N\text{-Meim})_4\{Ag(CN)_2\}][Ag(CN)_2]$ (**2**), and $[Cd(2\text{-MeimH})_4\{Ag(CN)_2\}][Ag(CN)_2]\cdot H_2O$ (**3**), have been determined by single-crystal X-ray diffraction methods. Complex **1a** crystallizes in the orthorhombic *Pbmn* space group with $a = 22.206(2)$ Å, $b = 10.306(1)$ Å, $c = 10.318(1)$ Å, $Z = 4$. **1b**: monoclinic $P2_1/n$, $a = 9.028(4)$ Å, $b = 13.988(6)$ Å, $c = 22.079(4)$ Å, $\beta = 101.02(2)°$, $Z = 4$. **2**: monoclinic $C2/m$, $a = 11.1292(8)$ Å, $b = 11.435(3)$ Å, $c = 11.266(1)$ Å, $\beta = 94.252(8)°$, $Z = 2$. **3**: orthorhombic *Pnnm*, $a = 11.212(2)$ Å, $b = 11.156(5)$ Å, $c = 23.646(5)$ Å, $Z = 4$. Complex **1a** has the shape of a four-blade propeller consisting of $[Cd(imH)_4]^{2+}$ with the shaft being the monodentate $[-NCAgCN]^-$ anions. **1b** comprises the discrete $[Ag(CN)_2]^-$ and the umbrella-shaped $[Cd(imH)_5NCAgCN]^+$ in which the monodentate $[Ag(CN)_2]^-$ behaves as the shank; hydrogen-bond networks among the umbrellas build up a three-dimensional lattice. In **2** and **3** the four-blade propellers of $[Cd(N\text{-Meim})_4]^{2+}$ and $[Cd(2\text{-MeimH})_4]^{2+}$ are successively linked at every Cd by the ambidentate −NCAgCN− rods to form an infinite chain, respectively; the discrete $[Ag(CN)_2]^-$ anions and the H_2O in **3** are accommodated in the interchain space. The varieties in coordination behavior of $[Ag(CN)_2]^-$ can be interpreted in terms of the hydrogen-bond formation between a pyrrole H of the imidazole ligand and an unbridged N-end of $[Ag(CN)_2]^-$.

Introduction

Dicyanoargentate(I), $[Ag(CN)_2]^-$, is a versatile rod-shaped ligand that can bridge coordination centers such as Cd^{2+} ligated with a secondary ligand L to build up multidimensional coordination polymers. As we have reported previously,[1] Cd^{2+}, $[Ag(CN)_2]^-$, and monodentate 4-methylpyridine (4-Mepy) are self-assembled from an aqueous solution to build up a one-dimensional (1D) chain complex $[Cd(4\text{-Mepy})_4\{Ag_2(CN)_3\}][Ag(CN)_2]$ (**I**) and an interwoven two-dimensional (2D) network host clathrate $[Cd(4\text{-Mepy})_2\{Ag(CN)_2\}_2]\cdot 4\text{-Mepy}$ (**II**). When L is an ambidentate bridging ligand such as 4,4′-bipyridine (4,4′-bpy) and pyrazine (pyrz), three-dimensional (3D) complexes $[Cd(4,4'\text{-bpy})_2\{Ag(CN)_2\}_2]$ (**III**) with doubly interpenetrating and $[Cd(pyrz)\{Ag_2(CN)_3\}\{Ag(CN)_2\}]$ (**IV**) with triply interpenetrating lattice structures are obtained.[2] On the other hand, the less bulky monodentate NH_3 in $[Cd(NH_3)_2\{Ag(CN)_2\}_2]$ (**V**) gives a 3D warp-and-woof interwoven structure of two sets of 2D networks.[3] The simple rod of −NCAgCN− connecting two Cd atoms is observed in **II**−**V**, the rod of the dimeric condensate −NCAg(CN)AgCN− in **I** and **IV**, and the coordination-free discrete anion in **I**. The monodentate behavior of $[Ag(CN)_2]^-$ has been reported for $[Cr(en)_2\{Ag(CN)_2\}]ClO_4$[4] and $[SnCl\{Ag(CN)_2\}Ph_3][N(PPh_3)_2]$,[5] and the simple rod 1D connection and discrete anion have been reported for $[Zn(en)_2\{Ag(CN)_2\}_2][Ag(CN)_2]$[6] and $[Cu(o\text{-phen})_2\{Ag(CN)_2\}_2][Ag(CN)_2]$.[7] As for the multiply interpenetrating lattice of the dicyanoaurate(I) rod with another coordination center, Abrahams *et al.* reported a 3-fold one in $K[Co\{Au(CN)_2\}_3]$[8] and a 6-fold one in $[Co\{Au(CN)_2\}_2]$[9] with no particular comments on their topologies; an isostructural Rb−Cd−Ag analog of the former, $Rb[Cd\{Ag(CN)_2\}_3]$, was also reported.[10]

In the course of our systematic study of what kinds of self-assembled structures are possible for $Cd^{2+}-[Ag(CN)_2]^--L$ systems upon selecting the secondary ligand L, we obtained

---

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.

(1) Soma, T.; Iwamoto, T. *Chem. Lett.* **1994**, 821.

(2) Soma, T.; Yuge, H.; Iwamoto, T. *Angew. Chem.* **1994**, *106*, 1746; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1765.

(3) Soma, T.; Iwamoto, T. *Chem. Lett.* **1995**, 271.

(4) Sakaguchi, U.; Tomioka, K.; Yoneda, H. *Inorg. Chim. Acta* **1985**, *101*, 23.

(5) Carcelli, M.; Ferrari, C.; Pelizza, C.; Pelizza, G.; Predieri, G.; Solinas, C. *J. Chem. Soc., Dalton Trans.* **1992**, 2127.

(6) Kappenstein, C.; Ouli, A.; Guerin, M.; Cernak, J.; Chomic, J. *Inorg. Chim. Acta* **1988**, *147*, 189.

(7) Cernak, J.; Gerard, F.; Chomic, J. *Acta Crystallogr.* **1993**, *C49*, 1294.

(8) Abrahams, S. C.; Zynotz, L. E.; Bernstein, J. L. *J. Chem. Phys.* **1982**, *76*, 5458.

(9) Abrahams, S. C.; Bernstein, J. L.; Liminga, R.; Eisenmann, E. T. *J. Chem. Phys.* **1980**, *73*, 4585.

(10) Hoskins, B. F.; Robson, R.; Scarlett, N. V. Y. *J. Chem. Soc., Chem. Commun.* **1994**, 2025.

0020-1669/96/1335-1849$12.00/0

Table 1. Crystallographic and Experimental Dara for **1a**−**3**[a]

	1a	**1b**	**2**	**3**
formula	$C_{16}H_{16}N_{12}Ag_2Cd$	$C_{19}H_{20}N_{14}Ag_2Cd$	$C_{20}H_{24}N_{12}Ag_2Cd$	$C_{20}H_{26}N_{12}Ag_2CdO$
fw	704.53	772.61	760.65	778.65
crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	*Pbmn* (No. 53)	$P2_1/n$ (No. 14)	*C*2/*m* (No. 12)	*Pnnm* (No. 58)
a, Å	22.206(1)	9.028(4)	11.1292(8)	11.212(2)
b, Å	10.306(1)	13.988(6)	11.435(3)	11.156(5)
c, Å	10.318(1)	22.079(4)	11.266(1)	23.646(5)
β, deg	90	101.02(2)	94.252(8)	90
V, Å^3	2360.1(5)	2737(2)	1429.8(4)	2964(1)
Z	4	4	2	4
ϱ_m, g cm^{-3} [b]	1.98(1)	1.86(1)	1.77(1)	1.73(1)
ϱ_x, g cm^{-3}	1.98	1.88	1.77	1.74
μ(Mo Kα), cm^{-1}	25.47	22.06	21.09	20.39
R, R_w[c]	0.054, 0.064	0.059, 0.074	0.039, 0.046	0.059, 0.058
GOF[c]	1.50	1.68	1.21	1.70

[a] Conditions in common: Rigaku AFC-5S diffractometer, graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å), 296 K, SHELX76, weighting scheme $w^{-1} = \sigma^2(F_o) + g(F_o)^2$. [b] Flotation method in bromoform−mesitylene mixture. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]$, GOF $= [\Sigma(|F_o| - |F_c|)^2/(N_r - N_p)]^{1/2}$.

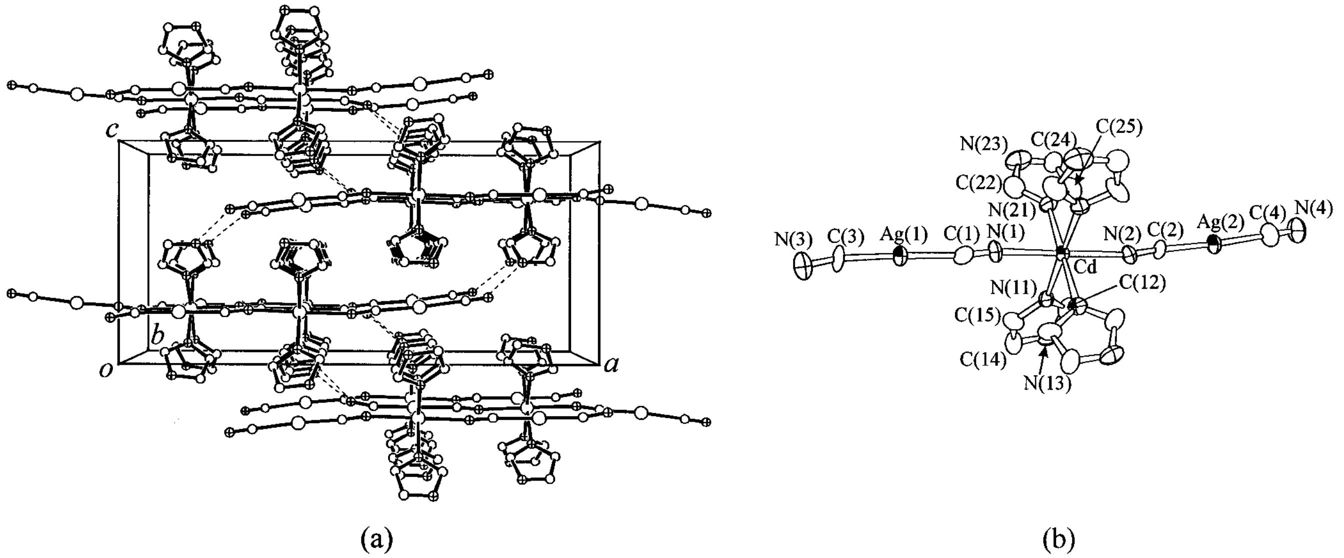

Figure 1. Structure of $[Cd(imH)_4\{Ag(CN)_2\}_2]$, **1a**: (a) view along the *b* axis (hydrogen bonds shown with broken lines); (b) the propeller-with-shaft molecular structure with atomic numbering. Anisotropic peripheries are shown for N atoms, and with sections for Ag and Cd atoms.

four complexes as well-developed single crystals from the systems involving imidazole (imH) and its two derivatives *N*-methylimidazole (*N*-Meim) and 2-methylimidazole (2-MeimH) as L. The five-membered heteroaromatic ring of imH is smaller than the six-membered pyridine ring, *N*-Meim and 2-MeimH are bulkier by a CH_3 group than imH, and hydrogen-bond formation is blocked for *N*-Meim by the replacement of a pyrrole H by a CH_3 group. Three of the four complexes obtained are tetraligated with the imidazole ligands, the other one being pentaligated. The coordination behavior of $[Ag(CN)_2]^-$ differs among the respective structures. It behaves as a monodentate ligand to give the molecular complex *trans*-$[Cd(imH)_4\{Ag(CN)_2\}_2]$ (**1a**); both the monodentate ligand and the discrete anion are found in the salt $[Cd(imH)_5\{Ag(CN)_2\}][Ag(CN)_2]$ (**1b**); the salts [*trans*-Cd(*N*-Meim)$_4\{Ag(CN)_2\}]_n[Ag(CN)_2]_n$ (**2**) and [*trans*-Cd(2-MeimH)$_4\{Ag(CN)_2\}]_n[Ag(CN)_2]_n\cdot n H_2O$ (**3**) comprise the 1D $-[CdL_4-NCAgCN-]_n$ chain and the discrete anion $[Ag(CN)_2]^-$, in **3** a water of crystallization being added.

Experimental Section

Preparation of Single Crystals. (a) *trans*-$[Cd(imH)_4\{Ag(CN)_2\}_2]$, 1a. To *ca.* 50 cm^3 of H_2O were added with stirring $K[Ag(CN)_2]$ (10 mmol, 1.99 g), $CdCl_2\cdot 2.5H_2O$ (5 mmol, 0.56 g), and imH (20 mmol, 1.36 g). The white precipitate once formed was dissolved by adding appropriate amounts of 2-aminoethanol and citric acid to adjust the pH to 9 to a final volume of *ca.* 100 cm^3, after which the solution was allowed to stand in a refrigerator at 5 °C. Colorless prismatic crystals were obtained. Anal. Found (calcd): C, 27.1 (27.3); H, 2.3 (2.3); N, 23.7 (23.9).

(b) $[Cd(imH)_5\{Ag(CN)_2\}][Ag(CN)_2]$, 1b. From an aqueous solution similar to that in (a) but containing 25 mmol (1.70 g) of imH, colorless plate-shaped crystals were obtained in 1 day. Anal. Found (calcd): C, 37.0 (37.1); H, 3.0 (3.0); N, 13.5 (13.8).

(c) [*trans*-Cd(*N*-Meim)$_4\{Ag(CN)_2\}]_n[Ag(CN)_2]_n$, 2. In *ca.* 50 cm^3 of H_2O were dissolved $K_2[Cd(CN)_4]$ (5 mmol, 1.47 g) and $AgNO_3$ (10 mmol, 1.70 g); the pH was adjusted to 10 by adding 2-aminoethanol and citric acid to a final volume of 100 cm^3. After addition and dissolution of *N*-Meim (125 mmol, *ca.* 10 cm^3), the solution was allowed to stand in the refrigerator to obtain colorless prismatic crystals. Anal. Found (calcd): C, 31.5 (31.5); H, 3.2 (3.2); N, 22.0 (22.1).

(d) [*trans*-Cd(2-Meim)$_4\{Ag(CN)_2\}]_n[Ag(CN)_2]_n\cdot nH_2O$, 3. In *ca.* 50 cm^3 of H_2O were dissolved $K[Ag(CN)_2]$ (10 mmol, 1.99 g) and $CdCl_2\cdot 2.5H_2O$ (5 mmol, 1.14 g), the pH being adjusted to 8 with 2-aminoethanol and citric acid to a final volume of 100 cm^3. After addition and dissolution of 2-MeimH (28 mmol, *ca.* 2.3 g), the solution was allowed to stand in the refrigerator; pale-yellow block crystals were obtained in a few days. Anal. Found (calcd): C, 30.9 (30.9); H, 3.4 (3.4); N, 21.7 (21.6).

X-ray Crystallography. Table 1 lists the crystallographic and experimental data for compounds **1a**−**3**. The intensity data were collected at room temperature on a Rigaku AFC5S four-circle diffrac-

Table 2. Positional Parameters and Equivalent Isotropic Thermal Parameters for Non-H Atoms in **1a**−**3**

atom	x	y	z	B_{eq}, Å$^{2\ a}$	atom	x	y	z	B_{eq}, Å$^{2\ a}$
[Cd(imH){Ag(CN)$_2$}$_2$], **1a**									
Cd	0.37537(4)	0	0.23688(7)	3.66(2)	N(11)	0.3742(6)	0.1584(7)	0.0788(6)	4.2(2)
Ag(1)	0.1232(1)	0	0.2371(1)	5.09(2)	C(12)	0.4195(8)	0.229(2)	0.038(2)	6.2(3)
Ag(2)	0.6266(1)	0	0.2610(1)	5.14(2)	N(13)	0.4006(7)	0.309(1)	−0.064(1)	6.5(3)
C(1)	0.221(1)	0	0.239(2)	5.3(4)	C(14)	0.3409(7)	0.292(2)	−0.079(2)	7.1(4)
N(1)	0.2688(9)	0	0.245(2)	6.2(4)	C(15)	0.3261(7)	0.190(2)	0.003(1)	6.6(4)
C(2)	0.0336(8)	0	0.230(2)	7.2(6)	N(21)	0.3772(5)	0.1586(8)	0.3955(7)	5.1(2)
N(2)	−0.0174(9)	0	0.213(2)	9.0(5)	C(22)	0.3303(8)	0.210(2)	0.451(1)	7.2(4)
C(3)	0.5356(7)	0	0.243(1)	4.8(4)	N(23)	0.3499(7)	0.308(1)	0.542(1)	8.2(4)
N(3)	0.4847(7)	0	0.231(1)	4.8(3)	C(24)	0.4082(8)	0.308(2)	0.536(2)	7.9(4)
C(4)	0.724(1)	0	0.289(2)	6.5(5)	C(25)	0.4250(8)	0.223(2)	0.447(2)	8.8(5)
N(4)	0.7700(9)	0	0.306(2)	10.5(6)					
[Cd(imH)$_5${Ag(CN)$_2$}][Ag(CN)$_2$], **1b**									
Cd	0.50701(8)	0.59762(5)	0.24638(3)	2.27(1)	N(23)	0.091(1)	0.6027(7)	0.0978(4)	4.1(2)
Ag(1)	0.3113(1)	0.35342(6)	0.41414(4)	3.83(2)	C(24)	0.031(1)	0.6549(9)	0.1393(7)	5.0(3)
Ag(2)	$^{3}/_{2}$	$^{1}/_{2}$	$^{1}/_{2}$	4.46(3)	C(25)	0.144(1)	0.6614(9)	0.1915(6)	4.8(3)
Ag(3)	0	1	$^{1}/_{2}$	4.63(3)	N(31)	0.451(1)	0.7262(6)	0.3085(4)	3.7(2)
C(1)	0.368(1)	0.4427(8)	0.3470(5)	3.3(2)	C(32)	0.420(1)	0.722(1)	0.3644(6)	5.5(3)
N(1)	0.403(1)	0.4952(7)	0.3133(4)	3.8(2)	N(33)	0.417(1)	0.814(1)	0.3848(6)	7.1(3)
C(2)	0.251(1)	0.2721(8)	0.4811(5)	4.3(3)	C(34)	0.448(2)	0.875(1)	0.344(1)	8.5(6)
N(2)	0.221(1)	0.2263(8)	0.5212(5)	5.3(3)	C(35)	0.465(2)	0.8217(9)	0.2928(8)	5.9(4)
C(3)	1.296(1)	0.566(1)	0.4969(5)	4.9(3)	N(41)	0.7438(9)	0.5800(6)	0.3097(3)	3.1(2)
N(3)	1.182(1)	0.600(1)	0.4947(5)	6.8(3)	C(42)	0.777(1)	0.5916(9)	0.3690(5)	4.0(2)
C(4)	0.210(1)	0.942(1)	0.4995(5)	4.4(3)	N(43)	0.926(1)	0.5742(7)	0.3930(5)	5.1(3)
N(4)	0.324(1)	0.9124(9)	0.4971(4)	5.3(3)	C(44)	0.992(1)	0.5501(9)	0.3440(7)	5.0(3)
N(11)	0.5463(9)	0.4605(6)	0.1896(4)	3.1(2)	C(45)	0.879(1)	0.5546(9)	0.2941(6)	4.5(3)
C(12)	0.638(1)	0.4470(9)	0.1488(4)	4.0(2)	N(51)	0.6221(9)	0.7005(6)	0.1835(4)	3.4(2)
N(13)	0.615(1)	0.3600(7)	0.1224(4)	4.0(2)	C(52)	0.576(1)	0.7176(9)	0.1227(5)	4.4(3)
C(14)	0.498(2)	0.3197(8)	0.1434(5)	4.4(3)	N(53)	0.654(1)	0.7934(7)	0.1086(5)	4.5(2)
C(15)	0.458(1)	0.3809(7)	0.1861(5)	3.4(2)	C(54)	0.752(1)	0.8253(8)	0.1589(7)	4.6(3)
N(21)	0.2720(9)	0.6162(6)	0.1806(4)	2.8(2)	C(55)	0.733(1)	0.7668(8)	0.2058(5)	3.7(2)
C(22)	0.235(1)	0.5810(8)	0.1233(5)	3.3(2)					
[Cd(*N*-Meim)$_4${Ag(CN)$_2$}]$_n$[Ag(CN)$_2$]$_n$, **2**									
Cd	0	0	0	2.684(9)	N(11)	−0.0060(3)	0.1473(3)	0.1410(3)	4.18(6)
Ag(1)	$^{1}/_{2}$	0	0	7.44(3)	C(12)	−0.0909(5)	0.1726(4)	0.2118(4)	4.98(9)
Ag(2)	0	0	$^{1}/_{2}$	6.22(2)	N(13)	−0.0612(5)	0.2688(3)	0.2781(4)	5.6(1)
C(1)	0.3162(5)	0	0.0141(7)	5.6(2)	C(14)	0.0445(6)	0.3083(6)	0.2468(6)	6.8(1)
N(1)	0.2151(4)	0	0.0176(5)	5.3(1)	C(15)	0.0799(6)	0.2325(5)	0.1629(6)	6.6(1)
C(2)	0.1818(8)	0	0.5501(6)	5.4(2)	C(16)	−0.1395(8)	0.3241(7)	0.3643(7)	9.5(2)
N(2)	0.2808(6)	0	0.5813(5)	5.7(1)					
[Cd(2-MeimH)$_4${Ag(CN)$_2$}]$_n$[Ag(CN)2]$_n$·*n*H$_2$O, **3**									
Cd	0	$^{1}/_{2}$	0.26318(6)	2.88(2)	N(13)	0.0227(9)	0.782(1)	0.3998(5)	4.2(3)
Ag(1)	$^{1}/_{2}$	$^{1}/_{2}$	0.26426(7)	4.98(3)	C(14)	−0.065(1)	0.830(1)	0.3654(6)	4.8(3)
Ag(2)	0.2797(2)	0.6723(2)	0	6.10(4)	C(15)	−0.080(1)	0.753(1)	0.3216(6)	4.0(3)
C(1)	0.3149(9)	0.509(1)	0.2652(6)	4.6(3)	C(16)	0.147(1)	0.593(1)	0.4024(7)	6.8(4)
N(1)	0.2136(8)	0.508(1)	0.2645(5)	4.8(2)	N(21)	−0.0020(9)	0.6454(8)	0.1909(4)	3.6(2)
C(2)	0.215(2)	0.847(2)	0	5.3(5)	C(22)	−0.063(1)	0.651(1)	0.1435(6)	4.6(3)
N(2)	0.189(2)	0.941(2)	0	6.9(5)	N(23)	−0.015(1)	0.743(1)	0.1099(5)	5.0(3)
C(3)	0.330(2)	0.496(2)	0	5.3(4)	C(24)	0.084(1)	0.791(1)	0.1394(6)	4.7(3)
N(3)	0.356(2)	0.395(2)	0	6.2(5)	C(25)	0.089(1)	0.730(1)	0.1886(6)	3.9(3)
N(11)	−0.0064(8)	0.6560(8)	0.3295(4)	3.4(2)	C(26)	−0.170(1)	0.580(2)	0.1262(7)	7.5(4)
C(12)	0.056(1)	0.673(1)	0.3772(6)	4.4(3)	O	0.097(2)	0.175(2)	0	11.0(5)

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

tometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å) and the conventional $2\theta-\omega$ scan technique. The unit cell dimensions were refined using 25 reflections in the 2θ ranges 20.61−29.30° for **1a**, 38.91−39.83° for **1b**, 37.98−39.90° for **2**, and 35.92−39.97° for **3**. Three standard reflections were monitored after every 150 reflections; no significant decay was observed for any of the compounds. Empirical absorption corrections were applied for Lp-corrected intensity data using the program ADC80 in UNICSIII.[11] An extinction correction was carried out for **2** by applying the equation $F_{corr} = F_c[1 - \{x(F_c)^2/\sin\theta\}]$; x was refined to $2.03(7) \times 10^{-7}$.

The structures were solved by the heavy-atom method after the Cd and Ag atoms were found from direct methods using SHELXS 86.[12] The remaining non-H atoms were located and refined by Fourier difference and full-matrix least-squares procedures anisotropically. H atoms fixed at calculated positions with the isotropic thermal parameter $B_{iso} = 6.0$ Å^2 were included in F_c calculation. Neutral-atom scattering factors for Cd and Ag were taken from ref 13; those for o, N, C, and H, from SHELX 76.[14] All calculations were performed on a HITAC M-680H at the Institute for Molecular Science, Okazaki.

Results and Discussion

The refined atomic coordinates for compounds **1a**−**3** are listed in Table 2; Table 3 lists the bond distances and angles selected for the coordination structures about Ag and Cd, some interatomic distances for Ag···Ag in **1b**, and those of N···N

---

(11) Sakurai, T.; Kobayashi, K. *Rep. Inst. Phys. Chem. Res. (Riken, Jpn.)* **1979**, *55*, 69.

(12) Sheldrick, G. M. SHELXS-86 (Program for Crystal Structure Solution). University of Göttingen, 1986.

(13) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(14) Sheldrick, G. M. SHELX-76 (Program for Crystal Structure Determination). University of Cambridge, 1976.

suggesting hydrogen-bond formation. The structures are illustrated in Figures 1−4 for **1a**−**3**, respectively.

Table 3. Selected Interatomic Distances (Å) and Angles (deg)[a]

$[Cd(imH)_4\{Ag(CN)_2\}_2]$, **1a**

Distances

Cd−N(1)	2.38(2)	Ag(1)−C(3)	2.01(2)	C(3)−N(3)	1.15(3)
Cd−N(2)	2.42(2)	Ag(2)−C(2)	2.04(2)	C(4)−N(4)	1.06(3)
Cd−N(11)	2.320(6)	Ag(2)−C(4)	2.16(3)	N(3)···N(13^{i})	3.07(2)
Cd−N(21)	2.310(7)	C(1)−N(1)	1.09(3)	N(4)···N(23^{ii})	3.10(2)
Ag(1)−C(1)	2.13(3)	C(2)−N(2)	1.14(2)		

Angles

N(1)−Cd−N(2)	179.3(4)	Cd−N(2)−C(2)	170(2)
N(1)−Cd−N(11)	91.0(5)	Cd−N(11)−C(12)	127(1)
N(2)−Cd−N(11)	89.4(4)	Cd−N(11)−C(15)	126(1)
N(1)−Cd−N(21)	89.4(4)	Cd−N(21)−C(22)	126(1)
N(2)−Cd−N(21)	90.1(4)	Cd−N(21)−C(25)	129(1)
N(11)−Cd−N(21)	90.2(2)	Ag(1)−C(1)−N(1)	174(2)
C(1)−Ag(1)−C(3)	178.1(7)	Ag(1)−C(3)−N(3)	171(2)
C(2)−Ag(2)−C(4)	176.5(8)	Ag(2)−C(2)−N(2)	176(2)
Cd−N(1)−C(1)	172(2)	Ag(2)−C(4)−N(4)	180(2)

$[Cd(imH)_5\{Ag(CN)_2\}][Ag(CN)_2]$, **1b**

Distances

Cd−N(1)	2.377(8)	Ag(1)−C(2)	2.02(1)	N(2)···N(13^{iii})	2.86(2)
Cd−N(11)	2.354(8)	Ag(2)−C(3)	2.05(1)	N(3)···N(43)	2.93(1)
Cd−N(21)	2.345(8)	Ag(3)−C(4)	2.07(1)	N(3^{iv})···N(53)	2.97(2)
Cd−N(31)	2.373(8)	C(1)−N(1)	1.13(1)	N(4)···N(33)	3.09(2)
Cd−N(41)	2.333(8)	C(2)−N(2)	1.16(1)	N(4^{v})···N(23)	2.96(1)
Cd−N(51)	2.373(8)	C(3)−N(3)	1.12(1)	Ag(1)···Ag(2^{vi})	3.077(1)
Ag(1)−C(1)	2.08(1)	C(4)−N(4)	1.12(1)		

Angles

N(1)−Cd−N(11)	87.6(3)	Cd−N(1)−C(1)	172.9(9)
N(1)−Cd−N(21)	91.9(3)	Cd−N(11)−C(12)	130.1(8)
N(11)−Cd−N(21)	88.3(3)	Cd−N(11)−C(15)	123.3(6)
N(1)−Cd−N(31)	86.8(3)	Cd−N(21)−C(22)	125.3(7)
N(11)−Cd−N(31)	174.2(3)	Cd−N(21)−C(25)	129.3(7)
N(21)−Cd−N(31)	90.4(3)	Cd−N(31)−C(32)	127.7(9)
N(1)−Cd−N(41)	89.4(3)	Cd−N(31)−C(35)	123.0(8)
N(11)−Cd−N(41)	91.1(3)	Cd−N(41)−C(42)	127.1(7)
N(21)−Cd−N(41)	178.5(3)	Cd−N(41)−C(45)	129.3(7)
N(31)−Cd−N(41)	90.3(3)	Cd−N(51)−C(52)	127.1(7)
N(1)−Cd−N(51)	177.1(3)	Cd−N(51)−C(55)	124.4(7)
N(11)−Cd−N(51)	93.2(3)	Ag(1)−C(1)−N(1)	176(1)
N(21)−Cd−N(51)	90.9(3)	Ag(1)−C(2)−N(2)	177(1)
N(31)−Cd−N(51)	92.5(3)	Ag(2)−C(3)−N(3)	178(1)
N(41)−Cd−N(51)	87.8(3)	Ag(3)−C(4)−N(4)	177(1)
C(1)−Ag(1)−C(2)	177.0(4)		

$[Cd(N\text{-}Meim)_4\{Ag(CN)_2\}]_n[Ag(CN)_2]$, **2**

Distances

Cd−N(1)	2.387(5)	Ag(1)−C(1)	2.063(6)	C(1)−N(1)	1.129(8)
Cd−N(11)	2.320(3)	Ag(2)−C(2)	2.060(8)	C(2)−N(2)	1.131(9)

Angles

N(1)−Cd−N(11)	91.3(1)	Cd−N(11)−C(15)	125.6(3)
Cd−N(1)−C(1)	173.2(6)	Ag(1)−C(1)−N(1)	177.6(7)
Cd−N(11)−C(12)	129.4(3)	Ag(2)−C(2)−N(2)	177.8(6)

$[Cd(2\text{-}MeimH)_4\{Ag(CN)_2\}]_n[Ag(CN)_2]_n \cdot nH_2O$, **3**

Distances

Cd−N(1)	2.406(8)	Ag(2)−C(2)	2.06(2)	C(3)−N(3)	1.17(3)
Cd−N(11)	2.341(8)	Ag(2)−C(3)	2.05(2)	N(2)···O^{vii}	2.81(3)
Cd−N(21)	2.350(8)	C(1)−N(1)	1.13(1)	N(3)···N(13^{viii})	3.01(2)
Ag(1)−C(1)	2.075(9)	C(2)−N(2)	1.10(3)	N(23)···O^{ix}	2.90(1)

Angles

N(1)−Cd−N(11)	89.7(3)	Cd−N(11)−C(15)	121.1(7)
N(1)−Cd−N(21)	89.7(3)	Cd−N(21)−C(22)	131.9(8)
N(11)−Cd−N(21)	88.6(3)	Cd−N(21)−C(25)	120.3(7)
C(2)−Ag(2)−C(3)	175.7(8)	Ag(2)−C(2)−N(2)	175(2)
Cd−N(1)−C(1)	179(1)	Ag(2)−C(3)−N(3)	178(2)
Cd−N(11)−C(12)	130.8(8)		

[a] Symmetry operations used to generate equivalent atoms: (i) $x + {}^{1}/_{2}, {}^{1}/_{2} - y, -z$; (ii) $x + {}^{1}/_{2}, y - {}^{1}/_{2}, 1 - z$; (iii) $x - {}^{1}/_{2}, {}^{1}/_{2} - y, z + {}^{1}/_{2}$; (iv) $x - {}^{1}/_{2}, -y + {}^{3}/_{2}, z - {}^{1}/_{2}$; (v) $-x - {}^{1}/_{2}, y - {}^{1}/_{2}, -z + {}^{1}/_{2}$; (vi) $x - 1, y, z$; (vii) $-x, -y, -z$; (viii) $x, y + 1, z$; (ix) ${}^{1}/_{2} - x, {}^{1}/_{2} + y, {}^{1}/_{2} - z$; (x) $1 - x, 1 - y, z$; (xi) $1 - x, -y, -z$; (xii) $-x, 1 - y, z$; (xiii) $1 - x, 1 - y, z$.

Structure of *trans*-$[Cd(imH)_4\{Ag(CN)_2\}_2]$, 1a. The centrosymmetric space group *Pbmn* (No. 53) was finally adopted after checking for *Pb2n*, also possible from the observed systematic absences: the latter gave unreasonable thermal parameters for imH ring atoms. The nonstandard setting of crystal axes was applied for the sake of comparison among the present four structures. As for the discrimination between N and C atoms of the imH ring except for the N coordinating to the Cd, all the ring atoms were assumed to be C at earlier stages of the refinement; that giving the smallest isotropic thermal parameter was assigned to the remaining N with the reasonable chemical structure suggesting hydrogen bonds from the pyrrole N to the N-ends of the NC-Ag groups with distances shorter than 3.11 Å.

The crystal structure is constructed by the packing of the discrete complex molecule *trans*-bis[dicyanoargentato(I)]tetrakis(imidazole)cadmium(II), the molecular shape being approximated to a four-blade propeller of $Cd(imH)_4$ with a shaft of NCAgCN−Cd−NCAgCN. The shaft of *ca*. 17.5 Å length along the *a* axis lies on the mirror plane vertical to the *b* axis with an end-to-end N···N distance of *ca*. 4.7 Å to a neighboring shaft; the linear arrays of the shafts are arranged almost parallel to one another along the *b* axis separated by *b*/2 with a mutual shift by the Cd−NC−Ag distance of *ca*. 5.6 Å with respect to the hub Cd. The layer almost parallel to the *ab* plane is stacked along the *c* axis according to the symmetry requirements of the *Pbmn* space group. Both N-ends of the shaft are bent toward the nearest imH blade in the adjacent layers with the distances N(3)···N(13^{i}) = 3.07(2) and N(4)···N(23^{ii}) = 3.10(2) Å, respectively, suggesting hydrogen-bond formation.

The octahedral coordination sphere about the Cd is slightly elongated along the shaft; Cd−N(1) and Cd−N(2) are 2.38(2) and 2.42(2) Å and Cd−N(11) and Cd−N(21) are 2.316(6) and 2.310(7) Å, respectively. All the blades of the imH rings, with acceptable atomic distances in the ring, are almost parallel along the shaft; the dihedral angle between the two crystallographically independent imH blades is 89.7°. The monodentate behavior of $[Ag(CN)_2]^-$ in **1a**, as well as in **1b**, is rather rare: only two other cases have been reported, for $[Cr(en)_2\{Ag(CN)\}_2]ClO_4$[4] and $[SnCl\{Ag(CN)_2\}Ph_3][N(PPh_3)_2]$.[5]

Structure of $[Cd(imH)_5\{Ag(CN)_2\}][Ag(CN)_2]$, 1b. The space group $P2_1/n$ was determined uniquely from the systematic absences. One of the $[Ag(CN)_2]^-$ groups in the formula, similar to that in **1a**, is monodentate toward the octahedral Cd ligated with the five imH ligands, whereas the other behaves as a discrete anion in the crystal structure. As shown in Figure 2, the complex cation [dicyanoargentato(I)]pentakis(imidazole)cadmium(II) has a shape approximating to an umbrella skeleton with a top stick and ribs of imH's and a shank of monodentate −NCAgCN. The octahedral coordination about the Cd is normal with Cd−N distances of 2.354(8)−2.377(8) Å, in comparison with those in $[Cd(imH)_6](NO_3)_2$, 2.361(3) Å,[15] and $[Cd(imH)_6](OH)(NO_3)\cdot 4H_2O$, 2.364(3) Å.[16] As for the molecular planes of the five imH's, the top and two ribs are parallel to the shank, but the two other ribs are nearly perpendicular. A structure similar to that of the **1b** umbrella may be the $SnPh_3$ three-rib structure of $[SnCl\{Ag(CN)_2\}Ph_3]^-$ with the linear arrangement of Cl−Sn−NCAgCN.[5]

There are two crystallographically independent discrete $[Ag(CN)_2]^-$ anions in the unit cell; the Ag atoms are located at the inversion centers 0, 0, 0 and 0, 0, $^{1}/_{2}$, respectively. The molecular axes are almost parallel to the *ab* plane, so that the

---

(15) Mighell, A. D.; Santoro, A. *Acta Crystallogr*. **1971**, *B27*, 2089.
(16) Atti, B. M.; Jundberg, B. K. S.; Ingri, N. *J. Chem. Soc., Chem. Commun.* **1972**, 712.

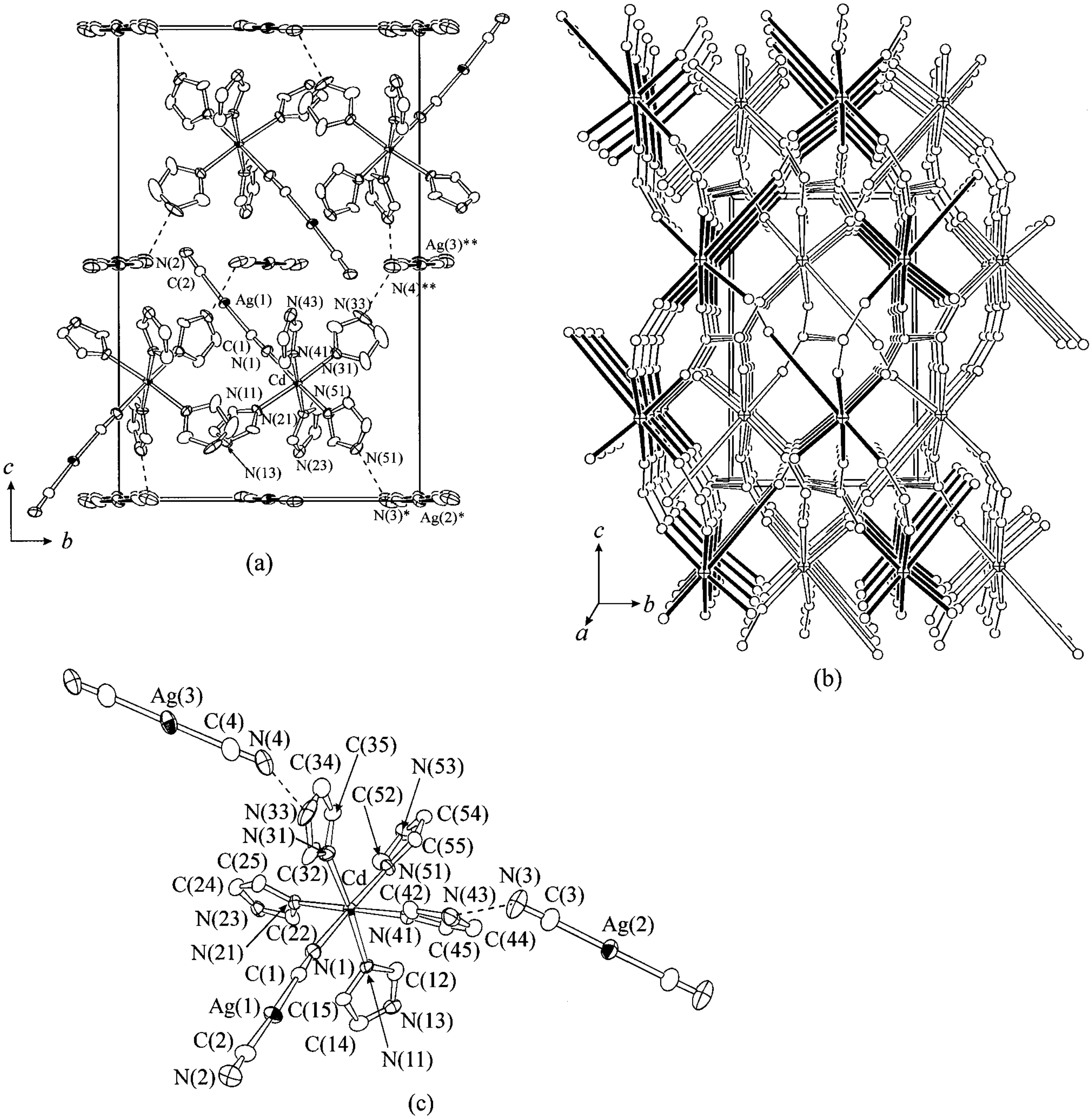

Figure 2. Structure of $[Cd(imH)_5\{Ag(CN)_2\}][Ag(CN)_2]$, **1b**: (a) array of the hydrogen-bonded $[Cd(imH)_5\{Ag(CN)_2\}]^+$ and $[Ag(CN)_2]^-$ viewed along the *a* axis (the counterpart generated by the inversion at Ag(2) is omitted for the sake of clarity); (b) the 3D network of the hydrogen bonds (thin lines) (only the coordination structure about Cd (circle with peripheries) and hydrogen-bonded N (open circle) are shown; the structure with open lines is generated by the inversion of that with solid lines); (c) asymmetric unit with atomic numbering.

layers of the anions extend along the [001] and [002] planes intercalating the layer of the cations across the *c* axis. The shank of the umbrella cation penetrates the anion layer with the distance between Ag(1) of the shank and Ag(2) of the discrete anion, 3.077(1) Å, being slightly longer than the interatomic distance in silver metal, 2.89 Å, similar to those observed in the previous multidimensional structures built of Cd^{2+} and $[Ag(CN)_2]^-$.[1-3]

Structure of $[Cd(N\text{-Meim})_4\{Ag(CN)_2\}]_n[Ag(CN)_2]_n$, 2. Among the three space groups *Cm*, *Cc*, and *C*2/*m* possible from the systematic absences, *C*2/*m* was finally chosen because it gave the most acceptable convergence at every stage of the refinement. As shown in Figure 3, the octahedral Cd is equatorially coordinated with the four *N*-Meim ligands like a propeller, similar to the Cd in **1a**, but the −NCAgCN− shaft extends a 1D chain linking the propellers successively along the *a* axis on the [001] plane. The discrete $[Ag(CN)_2]^-$ anions on the [002] plane fill the gap formed by the *C*-base-centered packing of the propellers. Eventually the layers of the 1D chains and the discrete anions are alternately stacked along the *c* axis. The axial elongation of the Cd octahedron is again observed for **2**: Cd−N(1) = 2.387(5) Å; Cd−N(11) = 2.320(3) Å.

Similar 1D structures are seen in $[Zn(en)_2\{Ag(CN)_2\}_2][Ag(CN)_2]$ as an almost straight chain[6] and in $[Cu(o\text{-phen})_2\{Ag(CN)_2\}][Ag(CN)_2]$ as a zigzag chain,[7] although complex **2** does not contain discrete $[Ag(CN)_2]^-$. There are a number of known 2D and 3D structures containing the −[Cd−NCAgCN−] unit as a constituent of their frameworks.[1-3,9]

Structure of $[Cd(2\text{-MeimH})_4\{Ag(CN)_2\}]_n[Ag(CN)_2]_n\cdot nH_2O$, 3. The centrosymmetric space group *Pnnm* was chosen because the noncentrosymmetric *Pnn*2 possible from the systematic absences gave negative thermal parameters for a number of

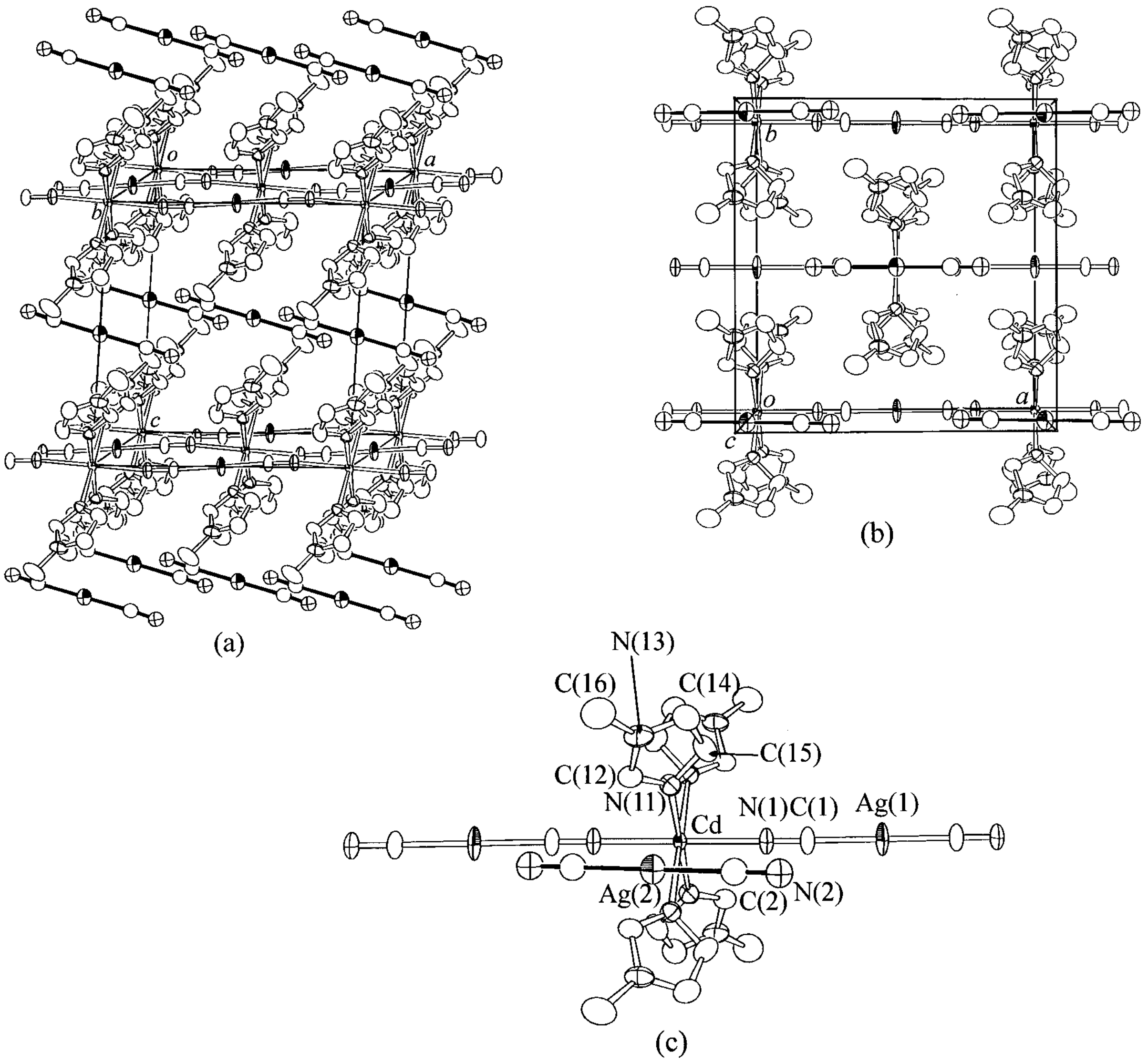

Figure 3. Structure of [Cd(N-Meim)$_4${Ag(CN)$_2$}]$_n$[Ag(CN)$_2$]$_n$, **2**: (a) view along the *b* axis; (b) view along the *c* axis; (c) asymmetric unit with atomic numbering.

atoms in the refinement processes. As shown in Figure 4, the crystal comprises the cationic 1D chain $-$[Cd(2-MeimH)$_4$$-$NCAgCN$-$]$_n$, the discrete [Ag(CN)$_2$]$^-$ anion, both being similar to those observed in **2**, and the water of crystallization. The structural similarity between **2** and **3** is also seen in the *a* and *b* dimensions of the unit cell and the layer structure stacked along the *c* axis, but the *c* dimension of **3** is longer by *ca.* 1.1 Å than twice that of **2** to be compared with. Although the relative arrangements of the 1D chains running along the respective *a* axes are similar, the arrangements and orientations of the discrete [Ag(CN)$_2$]$^-$ anions are different between **2** and **3**. In **3**, the central Ag is squeezed out to the position between the Cd atoms at z = *ca.* 0.26 and 0.74 with the [Ag(CN)$_2$]$^-$ molecular axis on the mirror plane inclined against the *a* axis by *ca.* 73.1°.

The water O on the mirror plane is within hydrogen-bond distance to the N-end of the discrete anion, $O^{viii}\cdots N(2) = 2.81(3)$ Å, and to the pyrrole N of the 2-MeimH, $O^{x}\cdots N(23) = 2.90(1)$ Å. The occupancy of O has been refined to 1.14(1) to support the stoichiometric result in the chemical analysis.

Discussion. Delicate similarities and differences in crystal structure are observed among the present four complexes with the similar chemical compositions CdL$_4$·2Ag(CN)$_2$ for **1a**, **2**, and **3** but different in the substituent on the imidazole ring of L; **3** has a water of crystallization additionally. As for **1b** with the composition CdL$_5$·2Ag(CN)$_2$, similarity is seen in its layer structure to the three others. The layers of discrete [Ag(CN)$_2$]$^-$ anions and the respective Cd complex cations are alternately stacked along the *c* axis in the structures of **1b**, **2**, and **3**; **1a** also has the analogous layered array of the propellers stacked along both *b* and *c* axes. The layered crystal structure involving dicyanoargentate(I) appears to be rather common even for a single complex salt such as Na[Ag(CN)$_2$][17] or K$_2$Na[Ag(CN)$_2$]$_3$.[18]

The imidazole ligands examined in the present work are capable of supplying equatorial tetracoordination to the octahedral Cd atom in the crystal structures given under the applied experimental conditions; the stability constant K = [CdL$_4$]/[Cd·L^4] is *ca.* 7.6 in log K for L = imH.[19]

As for the CdL$_4$ complexes **1a**, **2**, and **3**, the Ag atoms in the Ag(CN)$_2$ moieties, both ligand and discrete anion, are surrounded by four imidazole rings. In **1a**, the respective molecular complexes are interlocked at the monodentate shaft $-$NCAgCN by the pillow of four imH rings, two each from the two Cd atoms separated by *b*/2 or *c*/2 from the shaft; the hydrogen bond

---

(17) Range, K.-J.; Kühnel, S.; Zabel, M. *Acta Crystallogr.* **1989**, *C45*, 1419.
(18) Zabel, M.; Kühnel, S.; Range, K.-J. *Acta Crystallogr.* **1989**, *C45*, 1619.
(19) *Stability Constants. Part I: Organic Ligands*; The Chemical Society: London, 1957; p 11.

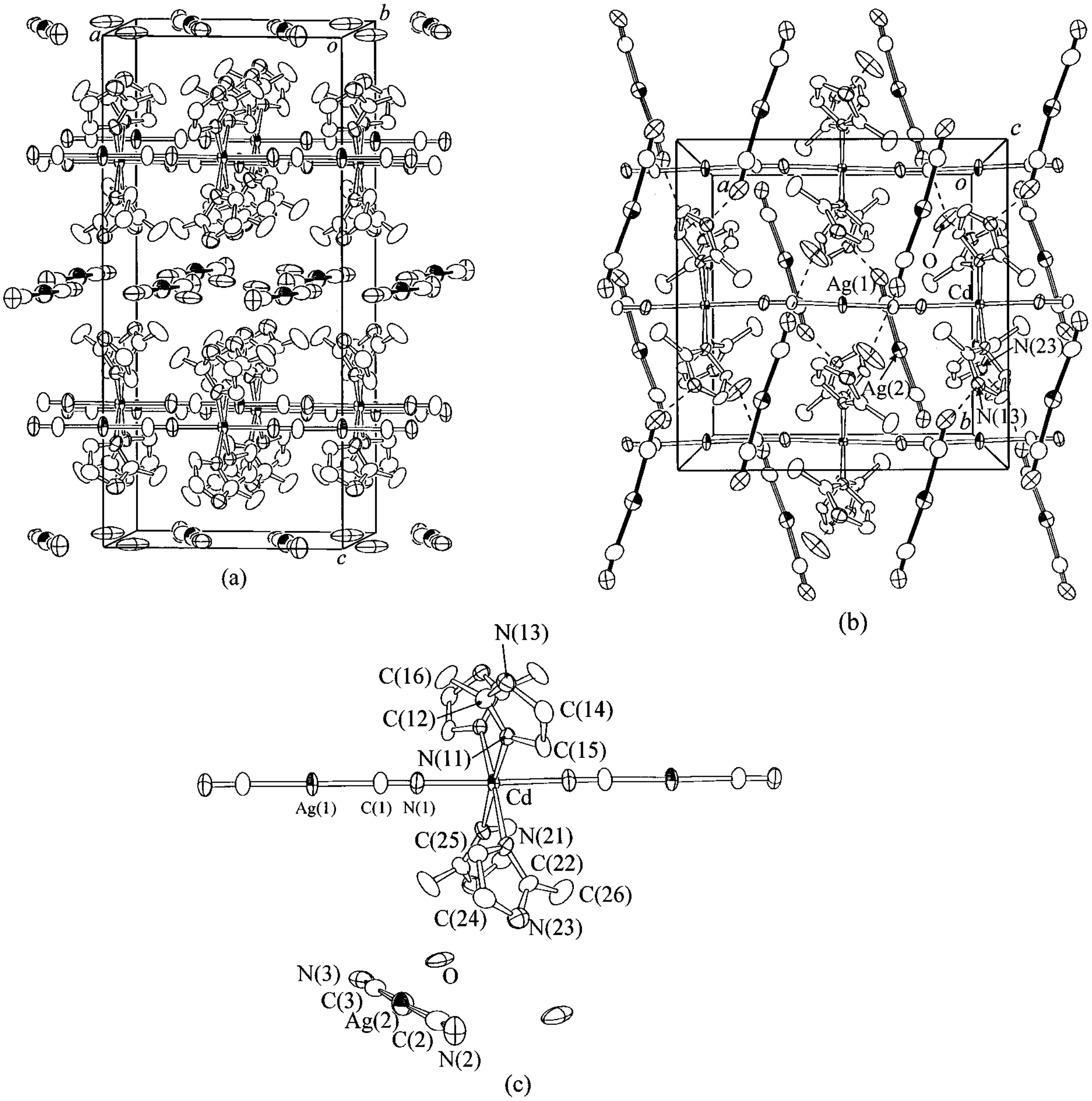

Figure 4. Structure of $[Cd(2\text{-}MeimH)_4\{Ag(CN)_2\}]_n[Ag(CN)_2]_n\cdot nH_2O$, **3**: (a) view along the *b* axis; (b) view along the *c* axis (hydrogen bonds shown with broken lines); (c) asymmetric unit with atomic numbering.

between the pyrrole H of imH and the unbridged N-end of the shaft reinforces the interlocking. With respect to the calculated density as an index for crystal packing, **1a** with tetracoordination by the nonsubstituted imH ligands has the greatest among the four complexes.

The interlocking in **2** is similar to that in **1a** between the monodentate moiety and the *N*-Meim rings along the *b* axis. No hydrogen-bond formation is observed in **2** because the pyrrole H is blocked by the CH_3 in *N*-Meim. This blocking forces the orientation of the imidazole ring to twist by *ca.* 32° against the shaft of the propellers so that the discrete rod anion $[NCAgCN]^-$ is arrayed slantwise on the mirror plane at $y = {}^1/_2$ with the closer approach of the CN groups to the CH_3 groups of *N*-Meim's.

When the CH_3 group is displaced to the 2-position in **3**, the array of the imidazole rings are more twisted owing to the steric repulsion between the CH_3 group and the shaft $-CN-$: the angles are *ca.* 49 and *ca.* 39°, greater than that in **2** (*ca.* 32°), about the Cd$-$N(11) and Cd$-$N(21) bonds, respectively. The interlocking along the *b* axis in **3** is preserved similarly to those in **1a** and **2**. The discrete anion with the hydrogen-bonded water is extremely slanted on the mirror plane at $z = 0$ and ${}^1/_2$ with inclinations of 73.1° against the 1D chains at $z = {}^1/_4$ and ${}^3/_4$. However, the anion is surrounded by four 2-MeimH rings from four Cd atoms separated by $\pm a/4$ and $\pm b/4$, respectively.

The umbrella cation $[Cd(imH)_5{-}NCAgCN]^+$ and the discrete anion $[Ag(CN)_2]^-$ in **1b** are three-dimensionally linked through the hydrogen bonds among pyrrole H and unbridged N atoms of both the monodentate and the discrete $[Ag(CN)_2]^-$. As shown in Figure 2a, an umbrella is linked to four neighboring ones. The direct connections are from the N-end of the $-NCAgCN$ shank to the pyrrole H of the rib imH in the first neighbor [N(2)$\cdots$N(13^{iii}) = 2.86(2) Å] and from the rib N(13) to the corresponding shank-end of the second neighbor. Indirect double linkings through the discrete anions are from the two ribs to the top and the rib of the third neighbor [N(43)$\cdots$2.93(1) Å$\cdots$N(3)$\cdots$2.97(2) Å$\cdots$N(53)*; N(33)$\cdots$3.09(2) Å$\cdots$N(4)$\cdots$2.96(1) Å$\cdots$N(23)*] and from the top N(53) and the rib N(23) to the corresponding two ribs of the fourth neighbor. The unit of the apparent 2D network thus formed is linked to that generated by the inversion at the position of *e.g.* Ag(2) through another N-end of the discrete $[Ag(2)(CN)_2]^-$ anion to give a complex 3D lattice with interpenetration of the hydrogen bonds.

Concluding Remarks. The ambidentate behavior of dicyanoargentate(I) is influenced by the stereospecific properties of the imidazole ligands in the present series of the complexes. The five-membered aromatic ring of imH without substituents is favorable to the formation of molecular complex **1a**; the packing of the discrete propellers is reinforced by the hydrogen bond between the pyrrole H of the imH blade and the unbridged N of the $Ag(CN)_2$ shaft; there is no room for the discrete $[Ag(CN)_2]^-$ in the compact packing. The presence of the discrete anion is evident in the structure of **1b** in that the octahedral coordination of $[Cd(imH)_5]^{2+}$ is satisfied by the additional ligation of the monodentate −NCAgCN. As the number of pyrrole H atoms and unbridged N-end sites of CN increases, the sites for hydrogen bond increase to give the hydrogen-bonded 3D structure. The blocking of a pyrrole H by a CH_3 group in **2** forbids hydrogen-bond formation in the crystal structure, resulting in loose packing of the CdL_4 moieties. The combination of the 1D linkage of $-[CdL_4-NCAgCN-]_n$ and the discrete anion is favorable to reducing void spaces by the accommodation of the discrete anion in the interchain space. Although the CH_3 group at the 2-position of 2-MeimH in **3** is less favorable to the packing of CdL_4 moieties than in **2**, the ability to form hydrogen bonds is recovered; the water of crystallization contributes to filling up the void space along with the discrete anion.

Supporting Information Available: Tables of detailed crystallographic and experimental data, anisotropic thermal parameters, H atom coordinates, and bond distances and angles (9 pages). Ordering information is given on any current masthead page.

IC950629G