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Doubly Interpenetrating Three-Dimensional Framework Structure of *trans*-$[Cd(dppn)_2\{Ag(CN)_2\}_2]_n$ [dppn = 1,3-Di(4-pyridyl)propane]

Takayoshi Soma† and Toschitake Iwamoto‡

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan.
E-mail: soma@kitasato-u.ac.jp

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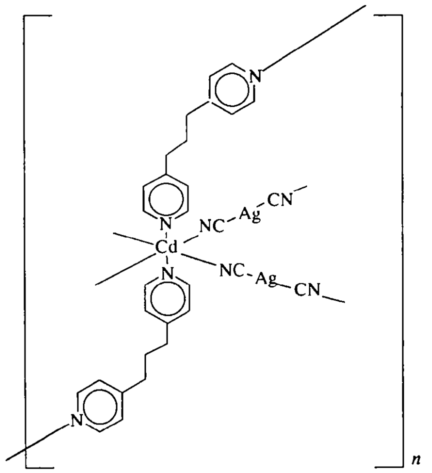
Abstract

In the title compound, poly[bis[μ-1,3-di(4-pyridyl)-propane-*N*:*N*′]cadmium(II)-bis-μ-[dicyanosilver(I)-*N*:*N*′]], $[Cd(C_{13}H_{14}N_2)_2\{Ag(CN)_2\}_2]_n$, the doubly interpenetrating three-dimensional framework structure is built by the stacking of considerably puckered two-dimensional $[Cd\{Ag(CN)_2\}_2]_n$ networks and the 1,3-di(4-pyridyl)-propane bridges from a Cd atom in one network, penetrating through the rhombus meshes of the adjacent networks, to two Ag atoms in the second next networks.

Comment

The two-dimensional (2D) network of $[Cd\{Ag(CN)_2\}_2]_n$ $\{= [Cd\text{–}(NC\text{–}Ag\text{–}CN\text{–}Cd_{1/4})_4]_n\}$, in which the Cd atom is successively linked to four other Cd atoms by the ambidentate $[Ag(CN)_2]^-$ anions, has given a variety of framework structures of $[CdL_2\{Ag(CN)_2\}_2]_n$ by using different *L* ligands, such as pyridine (py), 4-aminopyridine (4-ampy), 4-picoline (4-mepy) and 4,4′-bipyridine (bpy): the three-dimensional (3D) textile interwoven by the 2D networks of *trans*-$[Cd(py)_2\{Ag(CN)_2\}_2]_n$ including benzene or pyrrole guests in the meshes of the network (Soma & Iwamoto, 1996); the doubly interwoven 2D network of *trans*-$[Cd(4\text{-mepy})_2\{Ag(CN)_2\}]_n$ accommodating 4-mepy guests in the meshes of the network (Soma & Iwamoto, 1994); the 2D network of $[Cd(4\text{-ampy})_2\{Ag(CN)_2\}_2]_n$ embracing a pair of the one-dimensional chains of $[Cd\{Ag(CN)_2\}(mea)(4\text{-ampy})\{Ag(CN)_2\}]_n$ in the interlayer space (mea = 2-aminoethanol) (Soma & Iwamoto, 1996); the doubly interpenetrating 3D framework of *trans*-$[Cd(bpy)_2\{Ag(CN)_2\}_2]_n$ (Soma, Yuge & Iwamoto, 1994). The last structure is different from the others in involving the Ag atom in the trigonal three-coordination; the almost flat 2D networks of $[Cd\{Ag(CN)_2\}_2]_n$ stacked along the *a* axis are spanned by the bpy pillars extending from the Cd atom in one network to the Ag atoms in the second next networks to give the doubly interpenetrating 3D framework structure. The present complex, *trans*-$[Cd(dppn)_2\{Ag(CN)_2\}_2]_n$, (1) [dppn = 1,3-di(4-pyridyl)propane], gives the doubly interpenetrating 3D framework structure topologically the same as that observed for *trans*-$[Cd(bpy)_2\{Ag(CN)_2\}_2]_n$, (2), although the bridging ligand dppn in (1) has a flexible and longer skeleton in comparison with the bpy in (2).



(I)

As the *ORTEP*II drawings (Johnson, 1976) in Figs. 2 and 3 show, the 2D network $[Cd\{Ag(CN)_2\}_2]_n$ of (1) has a distorted rhombus mesh cornered by Cd and edged by an –NCAgCN– span similar to those previously observed for the $[CdL_2\{Ag(CN)_2\}_2]_n$ structures (Soma & Iwamoto, 1994, 1996; Soma *et al.*, 1994). The 2D network stacked along the *a* axis is considerably puckered. The dppn spanning the 2D networks from Cd to Ag is twisted at the trimethylene skeleton taking a *trans–gauche* conformation along the linkage of C14—C31—C32—C33—C23 to give a dihedral angle of

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† Current address: Department of Chemistry, School of Science, Kitasato University, Kitasato, Sagamihara, Kanagawa 228, Japan.

‡ Current address: Department of Fundamental Science, College of Science and Engineering, Iwaki Meisei University, Chyuohdai Iino, Iwaki, Fukushima 970, Japan.

45.5° between the two pyridyl rings, the bend angle of N11—C32—N21 being 138°. The dppn ligands extend from the Cd atom in one network, penetrating through the meshes of the adjacent networks above and beneath, to the Ag atoms in the second next networks with a Cd–dppn–Ag span distance of 14.26 Å. Thus, a pair of the 3D latticeworks interpenetrate to form a doubly interpenetrating 3D framework structure with a topology the same as in (2).

As shown in Fig. 3, the 3D latticeworks are arranged with the shortest and the longest interlayer distances of 3.66 and 10.60 Å between the 2D networks of the independent pair; the expanded interlayer space is filled by the dppn ligands. Although the 3D framework of (1) is geometrically more distorted than that of (2), the respective bond distances and angles are not unusual. The Ag—N21 distance of 2.516 (6) Å is longer by about 0.06 Å than that of (2), 2.463 (3) Å. The bond angles in the 2D network are comparable with those in (2); *e.g.* Cd—N2—C2: (1) 154.2 (6), (2) 157.9 (4)°; C1—Ag—C2: (1) 153.5 (2); (2) 153.6 (2)°.

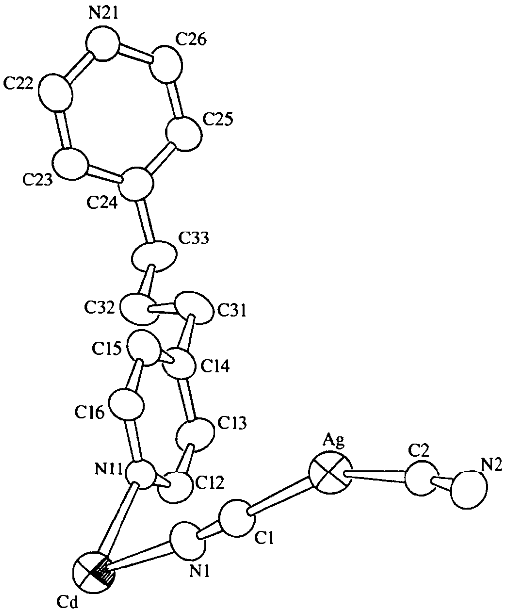

Fig. 1. Asymmetric unit of *trans*-$[Cd(dppn)_2\{Ag(CN)_2\}_2]_n$, (1), showing the atomic notations; displacement ellipsoids are drawn at the 30% probability level; H atoms have been omitted for clarity.

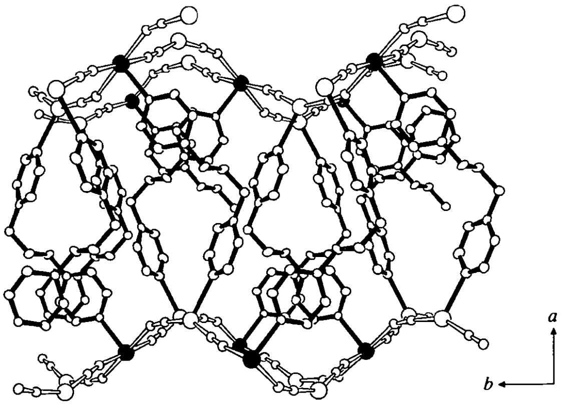

Fig. 2. View of the framework structure of (1); Cd and Ag atoms are shown as shaded and open circles, respectively. C and N atoms are shown as smaller open circles. Two-dimensional networks are drawn with open bonds and the dppn pillars with solid bonds.

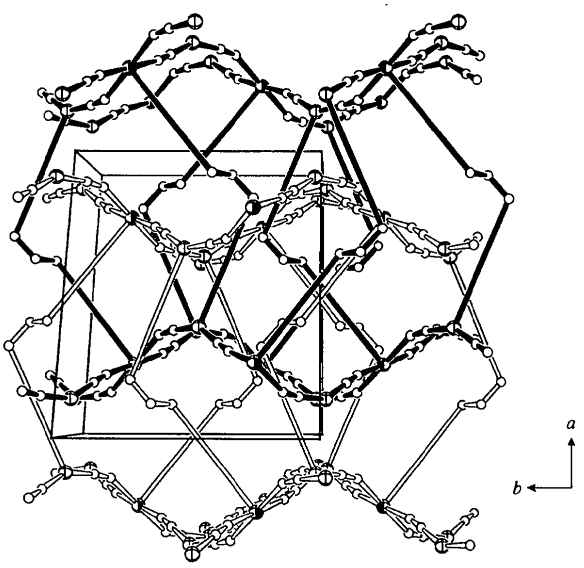

Fig. 3. Ball-and-stick model of the doubly interpenetrating frameworks with a sketch of the unit cell; one of the 3D lattices is shown with solid bonds and the other with open bonds; the dppn span is shown only with the central trimethylene unit.

As has been exemplified for the interpenetrating 3D framework structures of $[Cd(mea)(daptn)\{Ni(CN)_4\}]_n$ and $[Cd(mea)(dahxn)\{Ni(CN)_4\}]_n.nH_2O$ (daptn = 1,5-diaminopentane and dahxn = 1,6-diaminohexane; Yuge, Nishikiori & Iwamoto, 1996), the multiplicity of interpenetration is much influenced by the skeletal length of the bridging diaminoalkane. The double interpenetration in the former structure becomes the triple one in the latter upon the increase of a methylene unit in the diaminoalkane skeleton. The topological identity of (1) involving the flexible dppn spans with (2) involving the rigid bpy spans appears to be deduced from the flexibility of both $[Cd\{Ag(CN)_2\}_2]_n$ network and dppn bridge. The stacking of the puckered networks generates an interlayer space great enough to accommodate the dppn ligand twisted at the trimethylene linkage between the two pyridyl rings.

Experimental

To an aqueous solution containing 1.14 g (5 mmol) of $CdCl_2.2.5H_2O$, 1.99 g (10 mmol) of $K[Ag(CN)_2]$ and 0.40 g (2 mmol) of dppn, appropriate amounts of citric acid and 2-aminoethanol were added to adjust the pH to 10 in a final volume of 200 ml. After excess dppn was filtered off, the filtrate was allowed to stand in a refrigerator at 278 K; colourless block crystals of the title compound were obtained after a few days.

Crystal data

$[Ag_2Cd(CN)_4(C_{13}H_{14}N_2)_2]$
$M_r = 828.57$
Monoclinic
$C2/c$
$a = 18.676\,(5)$ Å
$b = 12.553\,(4)$ Å
$c = 16.657\,(3)$ Å
$\beta = 130.134\,(8)^\circ$
$V = 2985\,(1)$ Å^3
$Z = 4$
$D_x = 1.84$ Mg m^{-3}
$D_m = 1.83\,(1)$ Mg m^{-3}
D_m measured by flotation in mesitylene–bromoform

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 17.89$–21.65°
$\mu = 2.02$ mm^{-1}
$T = 293$ K
Prism
$0.25 \times 0.25 \times 0.20$ mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.621$, $T_{\max} = 0.665$
4752 measured reflections
3782 independent reflections

2812 reflections with $F > 4\sigma(F)$
$R_{\rm int} = 0.007$
$\theta_{\max} = 29.97^\circ$
$h = 0 \rightarrow 26$
$k = 0 \rightarrow 17$
$l = -23 \rightarrow 17$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.0574$
$wR = 0.0488$
$S = 0.930$
2812 reflections
188 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o) + 0.001F_o^2]$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.57$ e Å^{-3}
$\Delta\rho_{\min} = -0.57$ e Å^{-3}

Extinction correction: *SHELX76* (Sheldrick, 1976)
Extinction coefficient: 0.00089 (6)
Scattering factors from *SHELX76* for C, H, N; *International Tables for X-ray Crystallography* (Vol. IV) for Ag, Cd

Table 1. *Selected geometric parameters (Å, °)*

Cd—N1	2.347 (8)	C14—C15	1.41 (1)
Cd—N2$^{\rm i}$	2.386 (5)	C14—C31	1.50 (1)
Cd—N11	2.372 (6)	C15—C16	1.38 (1)
Ag—C1	2.119 (10)	N21—C22	1.36 (1)
Ag—C2	2.107 (8)	N21—C26	1.34 (1)
Ag$^{\rm ii}$—N21	2.516 (6)	C22—C23	1.375 (9)
N1—C1	1.15 (1)	C23—C24	1.40 (1)
N2—C2	1.13 (1)	C24—C33	1.519 (8)
N11—C12	1.341 (8)	C24—C25	1.39 (1)
N11—C16	1.349 (7)	C25—C26	1.369 (9)
C12—C13	1.40 (1)	C31—C32	1.51 (1)
C13—C14	1.394 (8)	C32—C33	1.55 (1)
N1—Cd—N11	86.9 (2)	C15—C14—C31	121.8 (5)
N1—Cd—N2$^{\rm i}$	91.1 (2)	C14—C15—C16	120.2 (6)
N11—Cd—N2$^{\rm i}$	91.7 (2)	N11—C16—C15	122.8 (6)
C1—Ag—C2	153.5 (3)	Ag$^{\rm ii}$—N21—C22	125.3 (5)
C1—Ag—N21$^{\rm iii}$	94.5 (3)	Ag$^{\rm ii}$—N21—C26	117.8 (2)
C2—Ag—N21$^{\rm iii}$	111.9 (3)	C22—N21—C26	115.8 (6)
Cd—N1—C1	172.0 (5)	N21—C22—C23	124.0 (9)
Ag—C1—N1	179.0 (5)	C22—C23—C24	119.6 (10)
Ag—C2—N2	172.3 (8)	C33—C24—C23	122.5 (9)
Cd—N11—C12	121.8 (4)	C33—C24—C25	121.6 (8)
Cd—N11—C16	120.2 (5)	C23—C24—C25	116.0 (6)
C12—N11—C16	117.7 (6)	C24—C25—C26	120.6 (9)
N11—C12—C13	122.6 (5)	N21—C26—C25	124.1 (10)
C12—C13—C14	120.3 (6)	C14—C31—C32	110.9 (9)
C13—C14—C15	116.3 (6)	C31—C32—C33	113.1 (9)
C13—C14—C31	121.8 (6)	C32—C33—C24	114.6 (6)

Symmetry codes: (i) $x, -y, z - \frac{1}{2}$; (ii) $-\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$; (iii) $-\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$.

All non-H atoms were refined anisotropically. All H atoms fixed at the calculated positions with the isotropic displacement parameters $B_{\rm iso} = 6.0$ Å^2 were included in F_c calculations.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *SHELX76*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELX76*. Molecular graphics: *ORTEPII*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1010). Services for accessing these data are described at the back of the journal.

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