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Coordination Polymers Self-Assembling from Cadmium(II) Ions and Flexible Pyridine-Based Bridging Ligands

Makoto Fujita,* Masaru Aoyagi,† and Katsuyuki Ogura††

Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki 444-8585

†The Graduate University for Advanced Studies, Myodaiji, Okazaki 444-8585

††Department of Applied Chemistry, Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522

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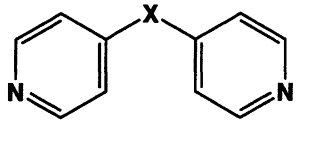
This paper describes coordination polymers assembled from cadmium nitrate and flexible bridging ligands, py–X–py (py = 4-pyridyl, **1a**: X = CH_2, **1b**: X = C(=CH_2), **1c**: X = CH_2CH_2). The X-ray structure analysis of these complexes showed that their infinite topologies are quite different from each other, despite the structural similarity of ligands **1a**—**1c**. Upon treatment with $Cd(NO_3)_2$, **1a** gave an infinite two-dimensional sheet structure with a stoichiometry of ML_2 (M and L denote metal and ligand, respectively). Ligand **1b** also afforded an infinite polymer possessing the same ML_2 composition. However, the polymer structure is characterized by one-dimensionally bounded macrocyclic frameworks where adjacent Cd ions are linked by two ligand molecules. Interestingly, ligand **1c** gave an infinite polymer of M_2L_3 composition whose structure was shown to be a unique one-dimensional framework having macrocyclic frameworks (M_2L_2) linked together by the third L molecules.

Interest in coordination polymers formed from metal ions and bridging ligands has been driven by the expectation of developing new materials with unique electronic, magnetic, or optic properties, catalytic activities, or enclathration abilities.[1—5] Such polymers have been previously designed by employing rigid ligands (e.g.; 4,4′-bipyridine).[3a,6] In contrast, flexible ligands have been seldom employed[7,8] probably due to difficulties in predicting the self-assembling network structures. For engineering crystals, the accumulation of the knowledge about the coordination networks has become a subject of special attention in current chemistry. Therefore, we have been studying the complexation of pyridine-based flexible ligands with transition metals and have found inclusion properties of some networks.[3a] Here we report the complexation of Cd(II) ions with simple flexible ligands, py–X–py (**1**, py = 4-pyridyl), where the spacer X is an sp^3 carbon (**a**: CH_2), sp^2 carbon (**b**: C(=CH_2)), or two sp^3 carbons (**c**: CH_2CH_2) (Chart 1). Despite very similar basic skeletons, these ligands are found to give completely different infinite structures featuring one- or two-dimensional (1D or 2D) coordination frameworks. A part of the present work has been already communicated.[9]



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a: X = CH_2

b: X = C(=CH_2)

c: X = CH_2CH_2

Chart 1. Formulas **1a**—**c**.

Results and Discussion

The Crystal Structure of Bis(4-pyridyl)methane (1a) with Cadmium Nitrate. It has been shown that 4,4′-bipyridine gives 2D grid structures upon complexation with metal ions.[3a,6] One of the simplest modification of the bipyridine framework is the insertion of a methylene unit between two pyridyl groups (i. e., ligand **1a**). We found that complexation of **1a** with Cd^{2+} gives a 2D network structure essentially the same as those formed from 4,4′-bipyridine. Thus, complexation of **1a** (100 mM, 1 M = 1 mol dm^{-3}) and cadmium nitrate (50 mM) in H_2O–EtOH (4 : 1) provides suitable crystals for X-ray analysis with a formula of $[Cd(\mathbf{1a})_2](NO_3)_2$ (**2a**). The diffraction study of **2a** gave an infinite 2D structure, shown in Fig. 1. Cadmium ion takes an octahedral geometry with four equatorial pyridyl groups and two axial nitrate ions. The Cd–O bond distance (2.37 Å) is shorter than those reported so far (2.49 Å)[3a] because of less distorted geometry about the cadmium center. The included angle of two pyridyl groups (C(5)–C(6)–C(7)) is very close to an ideal sp^3 angle (110.9°). The network topology is the same to that of the infinite grid prepared from 4,4′-bipyridine and cadmium nitrate although the geometry of each macrocyclic unit is significantly deformed from an ideal square: adjacent Cd–Cd distance is 11.2 Å, while diagonal Cd–Cd distances are 14.7 and 16.8 Å. The 2D sheets stack on each other with the interlayer separation of 4.9 Å. The shortest face-to-face distance between two pyridine rings across the layers is 3.5 Å, indicative of π-π stacking interaction. Relevant X-ray data for **2a** are summarized in Tables 1, 2, and 3.

Crystal Structure of 1,1-Bis(4-pyridyl)ethene (1b) with

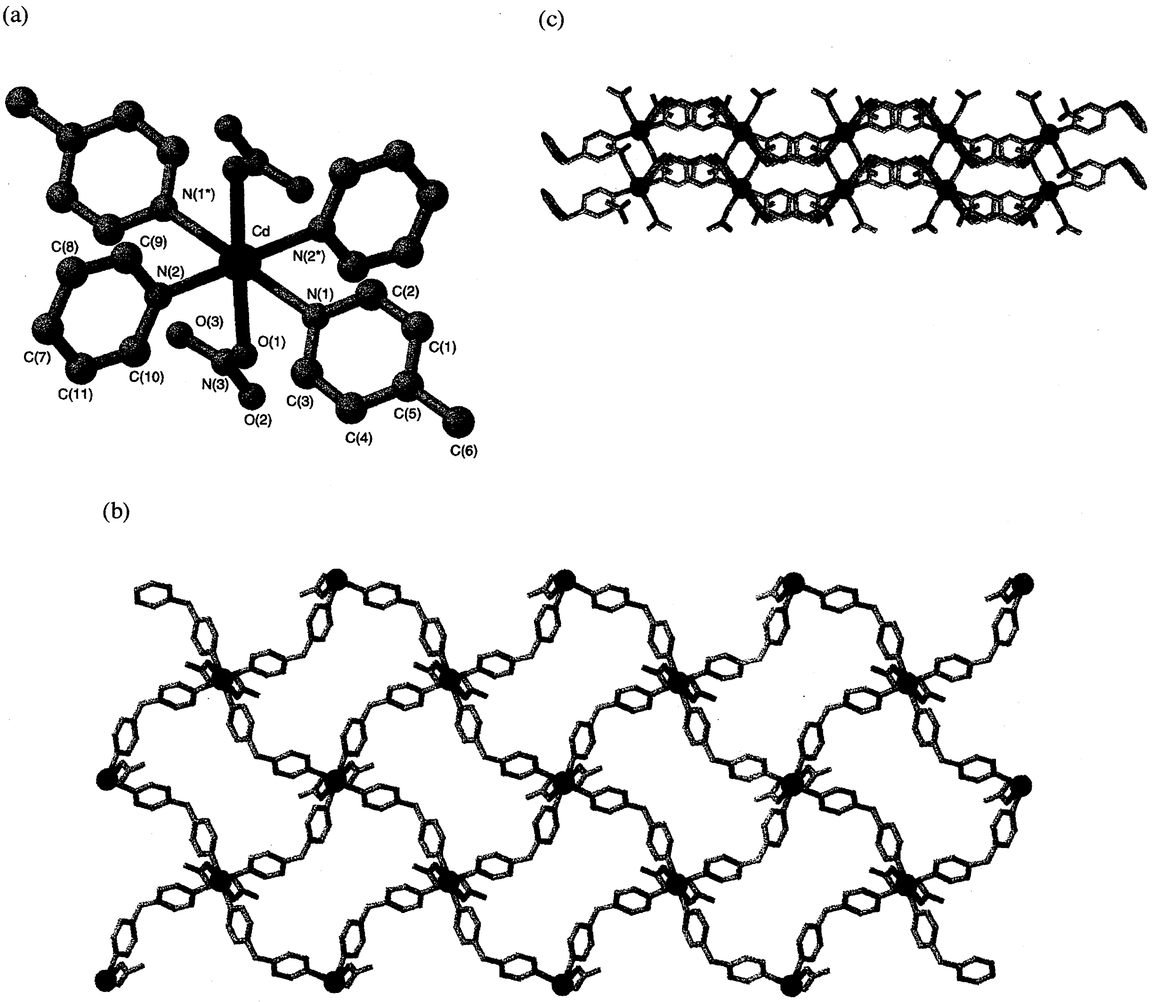

Fig. 1. (a) crystal structure of **2a**; (b) infinite network structure; (c) side view of two layers.

Cadmium Nitrate. When ligand **1b** was complexed with cadmium nitrate in water–ethanol, we again obtained crystals with a formula of $[Cd(\mathbf{1b})_2](NO_3)_2$ (**2b**), whose structure was determined by X-ray analysis. The crystal structure showed that **1b** has a 1D chain structure composed of dinuclear macrocycle units (Fig. 2, Tables 1, 4, and 5). The major structural difference between ligands **1a** and **1b** is the included angle of two pyridine rings [an sp^3 angle for **1a** whereas an sp^2 angle (122.3°) for **1b**]. Apical ligands are somewhat distorted [O(17)–Cd(1)–O(17*) 151.8°, Cd(1)–O(17) 4.6 Å]. It is interesting that, despite this small difference, the infinite structure of **2b** is quite different from that of **2a**. That is, a one-dimensional coordination polymer was formed that involves dinuclear macrocyclic framework as a unit.[10] The distance between adjacent Cd atoms is 10.8 Å. In the crystal, all one-dimensional polymers align along the a axis. The nearest Cd(II)–Cd(II) distance across the chain is 13.6 Å.

Crystal Structure of 1,2-Bis(4-pyridyl)ethane (1c) with Cadmium Nitrate. For infinite structures from octahedral cadmium(II) and pyridine-based bridging ligands, network topologies of **2a** and **2b** are considered to be major patterns as far as four pyridyl groups occupy equatorial positions of Cd(II) ion. However, we encountered an unprecedented infinite pattern from $Cd(NO_3)_2$ and **1c**. Thus, complexation of these components in water–ethanol afforded single crystals of **2c** with a formula of $[Cd(\mathbf{1c})_{1.5}](NO_3)_2$. X-Ray analysis of complex showed a T-shaped assembly of three pyridyl groups on Cd atom taking a heptacoordinated geometry (Fig. 3).[11] The details of coordination angles and bond distances are described in a previous report.[10] The symmetry operation of this structure provided a unique one-dimensional coordination polymer: Two molecules of **1c** bridge two Cd(II) atoms giving a cyclic closed structure, which is linked to the next one by another **1c** molecule (Tables 6 and 7). The crystal packing of **2c** is interesting: i. e., the 1D polymers align parallel with each other to make a molecular sheet stacked orthogonally on the next sheet with interplanar separation of 4.76 Å.

Conclusions

Network structures formed from $Cd(NO_3)_2$ and flexible ligands **1a**—**c** were examined by single crystal X-ray analysis. Despite the structural similarity, these three ligands gave completely different one- or two-dimensional coordination polymers. No obvious relation between ligand structures and the network structures was observed. The structural variation is due to the flexibility of the ligand and the irregularity of

Table 1. Selected Crystal Data for **2a**—**2c**

Compound	**2a**	**2b**	**2c**
Crystal data			
Chemical formula	$C_{22}H_{20}N_6O_6Cd$	$C_{24}H_{20}N_6O_6Cd$	$C_{18}H_{18}N_5O_6Cd$
Formula weight	576.85	600.87	512.78
Crystal size/mm	0.2 × 0.3 × 0.4	0.35 × 0.20 × 0.15	0.30 × 0.35 × 0.20
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$ (#14)	*Pcan* (#60)	$P2_1/n$ (#14)
a/Å	7.4142(7)	10.766(5)	12.529(4)
b/Å	16.770(2)	13.631(3)	17.186(5)
c/Å	9.669(3)	17.085(7)	9.531(3)
α/°	90.00	90.00	90.00
β/°	109.72(1)	90.00	92.49
γ/°	90.00	90.00	90.00
V/Å^3	1131.8(3)	1074(1)	2050(1)
Z	2	4	4
D_{calcd}/g cm^{-3}	1.69	1.59	1.66
F(000)	580	1207	1027
Data collection			
Radiation/Å	Mo $K\alpha$, 0.71070	Mo $K\alpha$, 0.71073	Mo $K\alpha$, 0.71073
μ(Mo $K\alpha$)/cm^{-1}	10.19	11.544	11.029
Total data	2074	2843	5326
Unique data	2074	2508	4717
Observed data	1782 (F>4.0($\sigma(F)$))	2224 (F>3.0($\sigma(F)$))	3713 (F)>3.0($\sigma(F)$))
Refinement			
No. of reflections	1784	2224	3713
No. of parameters	161	188	311
R	0.056	0.041	0.034
R_w	0.065	0.050	0.036

Table 2. Fractional Atomic Coordinates and B(iso) for **2a**

Atom	x/a	y/b	z/c	B(iso)
Cd	1.0000	0.0000	1.0000	1.79(2)
O(1)	0.7674(5)	0.0642(2)	1.0801(4)	2.97(9)
O(2)	0.7256(7)	0.1527(3)	1.2275(5)	4.7(1)
O(3)	0.9102(6)	0.0535(3)	1.3179(5)	4.0(1)
N(1)	1.7687(6)	0.4560(3)	1.2760(4)	2.03(9)
N(2)	1.1480(6)	0.1227(3)	0.9987(5)	2.09(9)
N(3)	0.8022(6)	0.0906(3)	1.2106(5)	2.35(10)
C(1)	1.6888(7)	0.3747(3)	1.0602(6)	2.3(1)
C(2)	1.8195(7)	0.4101(3)	1.1817(6)	2.3(1)
C(3)	1.5806(7)	0.4676(3)	1.2456(6)	2.1(1)
C(4)	1.4415(6)	0.4347(3)	1.1256(5)	2.2(1)
C(5)	1.4941(6)	0.3868(3)	1.0303(5)	1.9(1)
C(6)	1.3476(7)	0.3499(3)	0.8949(6)	2.3(1)
C(7)	1.2794(7)	0.2700(3)	0.9313(5)	1.9(1)
C(8)	1.1200(8)	0.2647(3)	0.9764(6)	2.6(1)
C(9)	1.0594(8)	0.1912(3)	1.0078(6)	2.5(1)
C(10)	1.3047(7)	0.1281(3)	0.9566(6)	2.3(1)
C(11)	1.3724(7)	0.1993(3)	0.9237(6)	2.5(1)

Table 3. Selected Intramolecular Bond Lengths (Å) and Angles (°) for **2a**

Cd–O(1)	2.374(3)	C(1)–C(2)	1.380(7)
Cd–N(1)	2.381(4)	C(1)–C(5)	1.388(7)
Cd–N(2)	2.334(4)	C(3)–C(4)	1.381(7)
O(1)–N(3)	1.278(5)	C(4)–C(5)	1.375(7)
O(2)–N(3)	1.224(6)	C(5)–C(6)	1.522(7)
O(3)–N(3)	1.243(6)	C(6)–C(7)	1.515(7)
N(1)–C(2)	1.341(6)	C(7)–C(8)	1.394(6)
N(1)–C(3)	1.339(6)	C(7)–C(11)	1.386(7)
N(2)–C(9)	1.341(7)	C(8)–C(9)	1.381(7)
N(2)–C(10)	1.357(6)	C(10)–C(11)	1.374(7)
O(1)–Cd–N(1)	77.1(1)	Cd–N(1)–C(2)	121.0(3)
O(1)–Cd–N(2)	89.8(1)	Cd–N(1)–C(3)	122.1(3)
N(1)–Cd–N(2)	85.3(1)	Cd–N(2)–C(9)	120.9(3)
Cd–O(1)–N(3)	123.5(3)	Cd–N(2)–C(10)	120.8(3)

coordination geometry on Cd atoms (octahedral vs. pentagonal bipyramidal). From Cd ions and larger ligands, we have already observed a heptacoordinated Cd ion and the formation of infinite ladder and brick structures.[8] These examples demonstrate that the prediction of infinite topology is very difficult, but 1D or 2D (not 3D) structure is preferred in the polymer formation. The unfavorable formation of 3D structure can be explained in terms of high entropy price required in its formation. On the other hand, 1D and 2D structures are comparable in their thermodynamic stability: 1D structure is favored in entropy but unfavored in enthalpy because the macrocyclic unit is slightly strained, whereas 2D structure is favored in enthalpy (no ring strain) but not in entropy (no freedom of atoms because of the network structure). Due to this thermodynamic balance, appearance of 1D and 2D

Table 4. Fractional Atomic Coordinates and *U*(iso) for **2b**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)
Cd(1)	0.87903(2)	0.00000	0.25000	0.035
N(2)	0.7199(2)	0.0305(2)	0.1561(1)	0.039
C(3)	0.7152(2)	0.1164(2)	0.1177(2)	0.046
C(4)	0.6090(2)	0.1520(3)	0.0816(2)	0.045
C(5)	0.4988(2)	0.0986(2)	0.0862(1)	0.034
C(6)	0.5035(3)	0.0077(2)	0.1245(2)	0.039
C(7)	0.6156(3)	−0.0233(2)	0.1571(2)	0.041
N(8)	1.0418(2)	−0.0706(2)	0.3245(2)	0.046
C(9)	1.0523(3)	−0.0577(3)	0.4023(2)	0.052
C(10)	1.1588(3)	−0.0780(3)	0.4449(2)	0.047
C(11)	1.2638(2)	−0.1123(2)	0.4048(1)	0.035
C(12)	1.2529(2)	−0.1280(2)	0.3245(2)	0.039
C(13)	1.1410(2)	−0.1077(3)	0.2869(2)	0.044
C(14)	1.3810(2)	−0.1366(2)	0.4476(2)	0.036
C(15)	1.3785(2)	−0.1922(3)	0.5121(2)	0.049
N(16)	0.8781(2)	−0.2010(2)	0.1660(2)	0.045
O(17)	0.8234(3)	−0.1723(2)	0.2268(2)	0.070
O(18)	0.9431(3)	−0.1400(3)	0.1316(2)	0.081
O(19)	0.8654(4)	−0.2854(3)	0.1424(3)	0.087

Table 5. Selected Intramolecular Bond Lengths (Å) and Angles (°) for **2b**

Cd(1)–N(2)	2.383(3)	Cd(1)–N(8)	2.370(3)
Cd(1)–O(17)	2.456(4)	N(2)–C(3)	1.343(5)
N(2)–C(7)	1.341(4)	C(3)–C(4)	1.388(4)
C(4)–C(5)	1.394(4)	C(6)–C(5)	1.401(4)
C(14)–C(5)	1.487(4)	C(6)–C(7)	1.395(4)
N(8)–C(9)	1.346(5)	N(8)–C(13)	1.344(4)
C(10)–C(9)	1.386(5)	C(11)–C(10)	1.402(4)
C(11)–C(12)	1.394(4)	C(11)–C(14)	1.495(4)
C(12)–C(13)	1.393(4)	C(14)–C(15)	1.338(5)
N(16)–O(17)	1.257(5)	N(16)–C(18)	1.236(5)
N(16)–O(19)	1.228(5)		
N(2)–Cd(1)–N(8)	164.5(1)	N(2)–Cd(1)–O(17)	83.3(2)
N(8)–Cd(1)–O(17)	83.0(2)	Cd(1)–N(2)–C(3)	120.5(2)
Cd(1)–N(8)–C(9)	122.6(3)	C(3)–N(2)–C(7)	116.7(3)
C(9)–N(8)–C(13)	117.0(3)		

structures is unpredictable.

Experimental

Materials. Compound **1a**[12] and bis(4-pyridyl) ketone[13] (precursor of **1b**) were prepared according to reported procedures. Compound **1c** and $Cd(NO_3)_2 \cdot 4H_2O$ are commercially available.

Preparation of 1b. Butyllithium (2.2 mmol, 1.7 M in hexane) was added to a tetrahydrofuran (THF, 10 mL) solution of methyltriphenylphosphonium bromide (0.71 g, 2.0 mmol) at −78 °C and the solution was stirred for 1.5 h at room temperature. To this solution was added a THF (2 mL) solution of bis(4-pyridyl) ketone (0.386 g, 2.0 mmol) at −78 °C. After 20 h at room temperature, the resulting mixture was extracted with 1 M HCl aqueous solution (20 mL×5). The combined aqueous layers are neutralized by K_2CO_3 and extracted again with dichloromethane (20 mL×5). The organic layers were combined, dried over anhydrous Na_2SO_4, and evaporated. The residue was purified by column chromatography on silica gel to give **1b** as colorless crystals: Mp 50 °C; ^1H NMR ($CDCl_3$) $\delta = 8.62$ (d, $J = 5.9$ Hz, 4 H), 7.21 (d, $J = 5.9$ Hz, 4H), 5.77 (s, 2 H); IR (KBr) 1593, 1514, 1412, 836, 590 cm^{-1}. HRMS. Found: *m*/*z* 183.0912. Calcd for $C_{12}H_{10}N_2$, M, 183.0921.

Table 6. Fractional Atomic Coordinates and *U*(iso) for **2c**

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)
Cd(1)	−0.42049(2)	−0.23874(2)	−0.35530(3)	0.039
N(2)	−0.3195(3)	−0.3282(2)	−0.4774(4)	0.044
C(3)	−0.3227(3)	−0.3338(2)	−0.6179(4)	0.047
C(4)	−0.2596(3)	−0.3850(3)	−0.6893(5)	0.049
C(5)	−0.1875(3)	−0.4330(2)	−0.6168(4)	0.042
C(6)	−0.1823(3)	−0.4251(3)	−0.4714(5)	0.052
C(7)	−0.2488(4)	−0.3738(3)	−0.4070(5)	0.053
N(8)	−0.5724(3)	−0.3151(2)	−0.3488(4)	0.048
C(9)	−0.6367(3)	−0.3141(3)	−0.2408(4)	0.051
C(10)	−0.7351(3)	−0.3512(3)	−0.2432(5)	0.050
C(11)	−0.7717(3)	−0.3902(2)	−0.3640(4)	0.043
C(12)	−0.7051(4)	−0.3915(3)	−0.4760(5)	0.064
C(13)	−0.6062(4)	−0.3545(3)	−0.4642(5)	0.068
C(14)	−0.8814(3)	−0.4274(2)	−0.3729(5)	0.047
C(15)	−0.8818(3)	−0.5098(2)	−0.3092(5)	0.047
N(16)	−0.2806(3)	−0.1484(2)	−0.3552(4)	0.045
C(17)	−0.2966(3)	−0.0724(2)	−0.3847(5)	0.049
C(18)	−0.2139(3)	−0.0208(3)	−0.4041(5)	0.052
C(19)	−0.1094(3)	−0.0473(3)	−0.3934(5)	0.051
C(20)	−0.0931(3)	−0.1248(3)	−0.3605(6)	0.055
C(21)	−0.1796(3)	−0.1731(3)	−0.3421(5)	0.052
C(22)	−0.0163(4)	0.0054(3)	−0.4240(6)	0.064
N(23)	−0.5408(3)	−0.1411(2)	−0.5482(4)	0.050
O(24)	−0.4850(3)	−0.1958(2)	−0.5924(4)	0.064
O(25)	−0.5416(3)	−0.1330(2)	−0.4168(4)	0.064
O(26)	−0.5888(3)	−0.0969(3)	−0.6290(5)	0.084
N(27)	−0.3921(3)	−0.2599(3)	−0.0599(3)	0.060
O(28)	−0.3454(4)	−0.3033(3)	−0.1433(4)	0.081
O(29)	−0.4471(3)	−0.2053(2)	−0.1133(4)	0.067
O(30)	−0.3852(4)	−0.2700(3)	0.0668(4)	0.099

Crystallization of 2a. An aqueous solution (0.8 mL) of cadmium nitrate (0.05 mmol) was combined with an ethanol (0.2 mL) solution of **1a** (0.1 mmol). Initially formed fine precipitate (very small amount) was filtered and the clear filtrate was allowed to stand at room temperature for one day to give single crystals of **2a** (33%): IR (KBr) 1605, 1423, 1386, 1013, 626, 563 cm^{-1}. Found: C, 45.89; H, 3.21; N, 14.60%. Calcd for $C_{22}H_{20}N_6O_6Cd$: C, 45.81; H, 3.21; N, 14.57%.

Crystallization of 2b. An aqueous solution (0.6 mL) of cadmium nitrate (15 mg, 0.05 mmol) was combined with an ethanol (0.4 mL) solution of **1b** (18 mg, 0.1 mmol). Fine precipitate (very small amount) was filtered and the clear filtrate was allowed to stand at room temperature for one day to give single crystals of **2b** (45%): IR (KBr) 1605, 1419, 1384, 1312, 1013, 604 cm^{-1}. Found: C, 47.51; H, 3.19; N, 13.74%. Calcd for $C_{24}H_{20}N_6O_6Cd$: C, 47.97; H, 3.35; N, 13.99%.

Crystallization of 2c. An ethanol solution (0.4 mL) of **1c** (0.2 mmol) was combined with an aqueous solution (1.6 mL) of $Cd(NO_3)_2$ (0.1 mmol). The mixture was allowed to stand for 3 d at room temperature, giving **2c** as colorless single crystals (39%): IR (KBr) 1611, 1434, 1385, 1016, 833, 815 cm^{-1}. Found: C, 42.16; H, 3.36; N, 13.51%. Calcd for $C_{18}H_{18}N_5O_6Cd$: C, 42.08; H, 3.53; N, 13.63%.

Crystallographic Analysis. X-Ray measurement of **2a** was made on a Rigaku Raxis IV area detector with graphite monochromated Mo *Kα* radiation. The data were collected to a maximum

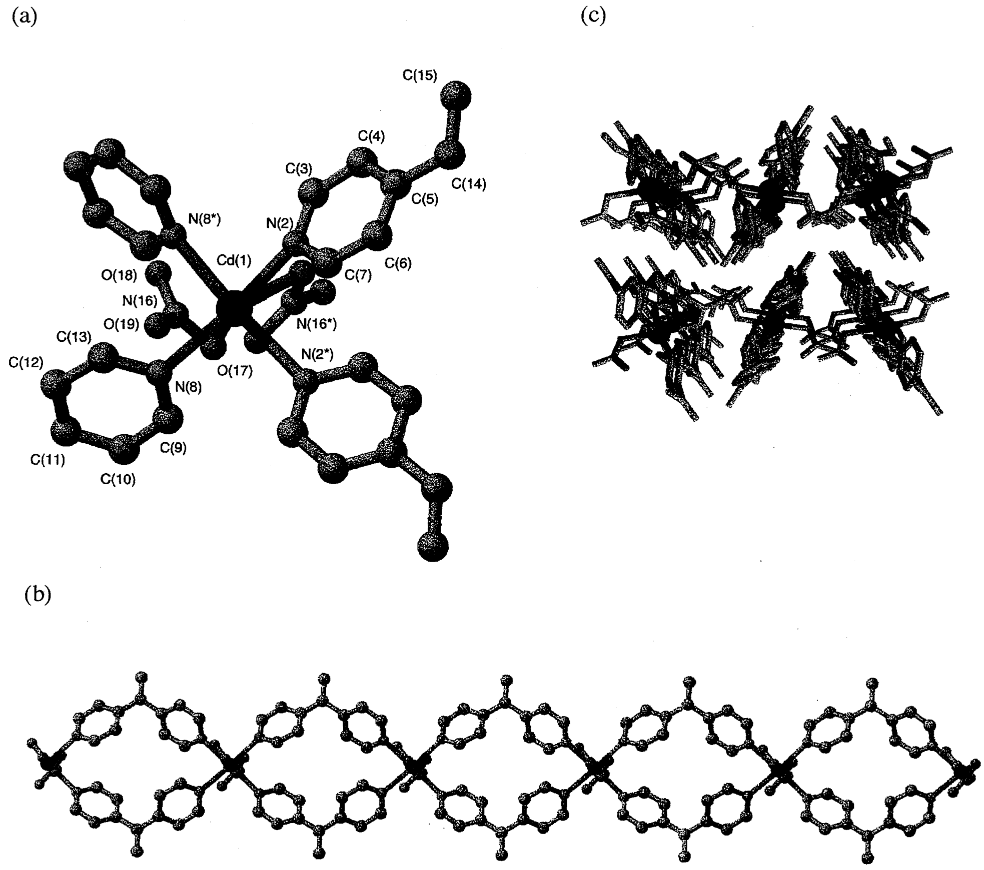

Fig. 2. (a) crystal structure of **2b**; (b) infinite crystal structure; (c) view of crystal packing along *a* axis.

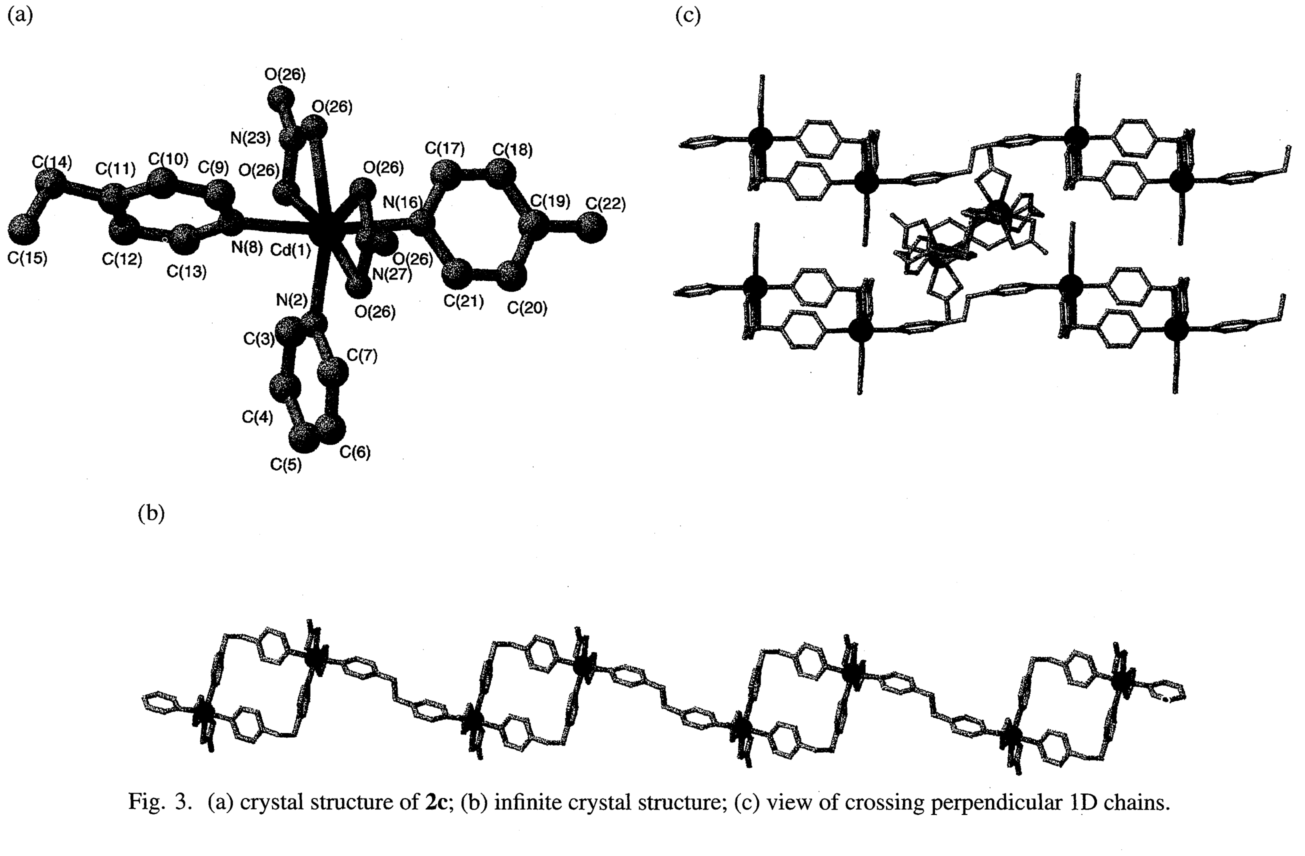

Fig. 3. (a) crystal structure of **2c**; (b) infinite crystal structure; (c) view of crossing perpendicular 1D chains.

Table 7. Selected Intramolecular Bond Lengths (Å) and Angles(°) for **2c**

Cd(1)–N(2)	2.333(4)	Cd(1)–N(8)	2.315(4)
Cd(1)–N(16)	2.342(4)	Cd(1)–O(24)	2.479(4)
Cd(1)–O(25)	2.423(4)	Cd(1)–O(28)	2.457(5)
Cd(1)–O(29)	2.414(4)	N(2)–C(3)	1.341(6)
N(2)–C(7)	1.341(6)	N(8)–C(9)	1.334(6)
N(8)–C(13)	1.345(7)	N(16)–C(17)	1.350(6)
N(16)–C(21)	1.335(6)	N(23)–O(24)	1.256(6)
N(23)–O(25)	1.261(6)	N(23)–O(26)	1.221(6)
N(27)–O(28)	1.253(6)	N(27)–O(29)	1.258(6)
N(27)–O(30)	1.220(5)		
N(2)–Cd(1)–N(8)	116.6(4)	N(2)–Cd(1)–N(16)	117.3(4)
N(2)–Cd(1)–O(24)	84.5(2)	N(2)–Cd(1)–O(25)	136.1(2)
N(2)–Cd(1)–O(28)	85.2(2)	N(2)–Cd(1)–O(29)	137.2(2)
N(8)–Cd(1)–O(28)	90.5(2)	N(8)–Cd(1)–O(29)	88.6(2)
N(16)–Cd(1)–O(24)	91.0(2)	N(16)–Cd(1)–O(25)	88.0(2)
N(16)–Cd(1)–O(28)	92.2(2)	N(16)–Cd(1)–O(29)	88.6(2)

2θ value of 51.4°. A total of 9 oscillation images are exposed for 12 min. The crystal-to-detector distance was 120 mm. The detector swing angle was 6°. The data were corrected for Lorentz and polarization effects. Calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Data of **2b** and **2c** were collected on a MAC Science MXC 18. The radiation used was Mo $K\alpha$ monochromatized by a crystal of graphite. Cell constants were obtained from a least squares refinement of 22 reflections with $31° < 2\theta < 34°$. Intensity data in the range $3° < 2\theta < 55°$ were collected at room temperature using the ω–2θ scan technique. Correcting for absorption was not applied. The calculations were performed with the Crystan GM 6.2.1 crystallographic software package of MAC Science Co., Ltd. Crystal data, data collection, structure solution and refinement for **2a**—**2c** are summarized in Table 1.[14)]

References

1) a) R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins, and J. Liu, "ACS Symposium Series 499, Supramolecular Architecture," ed by T. Bein, ACS, Washington D. C. (1992), Chap. 19; b) A. F. Wells, "Three-Dimensional Nets and Polyhedra," Wiley, New York (1977), Chaps. 5—8.

2) a) T. Iwamoto (Chap. 2), J. Liplowski (Chap. 3), J. Hanotier, and P. de Radzitzky (Chap. 4), "Inclusion Compounds," ed by J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, Academic Press, London (1984), Vol. 1, Chaps. 2—4, pp. 29—134; b) T. Iwamoto, "Inclusion Compounds," ed by J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, Academic Press, London (1991), Vol. 5, Chap. 6, pp. 177—212.

3) a) M. Fujita, Y. J. Kwon, S. Washizu, and K. Ogura, *J. Am. Chem. Soc.*, **116**, 1151 (1994); b) G. B. Gardner, D. Venkataraman, J. S. Moore, and S. Lee, *Nature*, **374**, 792 (1995); c) O. M. Yaghi, G. Li, and H. Li, *Nature*, **378**, 703 (1995).

4) a) H. O. Stumpf, L. Ouahab, Y. Pei, D. Grandjean, and O. Kahn, *Science*, **261**, 447 (1993); b) K. Inoue and H. Iwamura, *J. Am. Chem. Soc.*, **116**, 3173 (1994); c) H. O. Stumpf, L. Ouahab, Y. Pei, P. Bergerat, and O. Kahn, *J. Am. Chem. Soc.*, **116**, 3866 (1994).

5) a) S. Kitagawa, S. Matsuyama, M. Munakata, and T. Emori, *J. Chem. Soc., Dalton Trans.*, **1991**, 2869; b) S. Kitagawa, M. Munakata, and T. Tanimura, *Chem. Lett.*, **1991**, 623; c) S. Takahashi, M. Kariya, T. Yatake, K. Sonogashira, and N. Hagihara, *Macromolecules*, **11**, 1063 (1978); d) K. Toriumi, Y. Wada, T. Mitani, S. Bandow, M. Yamashita, and Y. Fuji, *J. Am. Chem. Soc.*, **111**, 2341 (1989).

6) a) R. W. Gable, B. F. Hoskins, and R. Robson, *J. Chem. Soc., Chem. Commun.*, **1990**, 1677; b) S. Subramanian and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, **34**, 2127 (1995); c) P. Losier and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, **35**, 2779 (1996).

7) D. M. L. Goodgame, S. Menzer, A. M. Smith, and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, **34**, 574 (1995).

8) M. Fujita, Y.-J. Kwon, O. Sasaki, K. Yamaguchi, and K. Ogura, *J. Am. Chem. Soc.*, **117**, 7287 (1995).

9) M. Fujita, Y.-J. Kwon, M. Niyazawa, and K. Ogura, *J. Chem. Soc., Chem. Commun.*, **1994**, 1977.

10) M. Fujita, M. Aoyagi, and K. Ogura, *Inorg. Chim. Acta*, **246**, 53 (1996).

11) a) N. G. Charles, E. A. H. Griffith, P. F. Rodesiler, and E. L. Amma, *Inorg. Chem.*, **22**, 2717 (1983); b) A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *J. Chem. Soc., Dalton Trans.*, **1972**, 1608.

12) I. Tabushi, S. Kugimiya, M. G. Kinnaird, and T. Sasaki, *J. Am. Chem. Soc.*, **107**, 4192 (1985).

13) F. L. Minn, C. L. Trichilo, C. R. Hurt, and N. Filipescu, *J. Am. Chem. Soc.*, **92**, 3600 (1970).

14) Detailed crystallographic data for **2a**—**c** are deposited as Document No. 71043 at the Office of the Editor of Bull. Chem. Soc. Jpn.