

A Novel Linking Schiff-Base Type Ligand (L: py-CH=N-C₆H₄-N=CH-py) and Its Zinc Coordination Polymers: Preparation of L, 2-Pyridin-3-yl-1*H*-benzimidazol, *trans*-[Zn(H₂O)₄L₂]·(NO₃)₂·(MeOH)₂, [Zn(NO₃)(H₂O)₂(L)]·(NO₃)·(H₂O)₂, and [Zn(L)(OBC)(H₂O)] (OBC = 4,4'-Oxybis(benzoate))

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Received February 14, 2005

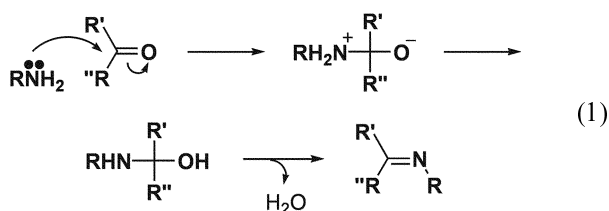
A long, bis(monodentate), linking Schiff-base ligand **L** (py-CH=N-C₆H₄-N=CH-py) was prepared from 1,4-phenylenediamine and 3-pyridinecarboxaldehyde by the Schiff-base condensation. Ligand **L** has two terminal pyridyl groups capable of coordinating to metals through their nitrogen atoms. In contrast, the same reaction between 1,2-phenylenediamine and 3-pyridinecarboxaldehyde produced a mixture of imidazol isomers (2-pyridin-3-yl-1*H*-benzimidazole), which are connected to one another by the N-H···N hydrogen bonding to form a tetramer. From Zn(NO₃)₂·6H₂O and ligand **L** under various conditions, one discrete molecule, *trans*-[Zn(H₂O)₄L₂]·(NO₃)₂·(MeOH)₂, and two 1-D zinc polymers, [Zn(NO₃)(H₂O)₂(L)]·(NO₃)·(H₂O)₂ and [Zn(L)(OBC)(H₂O)], were prepared. In ligand **L**, the N···N separation between the terminal pyridyl groups is 13.994 Å, with their nitrogen atoms at the meta positions (3,3') in a *trans* manner. The corresponding N···N separations in its compounds range from 13.853 to 14.754 Å.

Key Words : Linking Schiff-base ligand, Coordination polymer, Tetramer

Introduction

Coordination polymers, also known as metal-organic frameworks, have got continuous attraction due to their useful properties applicable to catalysis, chirality, conductivity, luminescence, spin crossover, and porosity.¹⁻⁶ Properties of linking ligands, such as various coordinating modes, variable lengths, and relative orientation of donor atoms, exert a crucial influence on constructing these polymers.

Schiff bases are imine compounds that contain a C=N bond in which the carbon atom is bonded to at least one aryl group. These compounds are prepared by the condensation of primary amines and ketones or aldehydes (eq. 1). The imines produced in eq. 1 typically decompose or polymerize unless at least one aryl group is bound to the nitrogen or carbon atom.⁷ A great number of metal complexes of the Schiff bases (acyclic or cyclic) have been prepared, and they have provided an enormously rich world of chemistry.^{8,9}



Whereas 4,4'-bipyridine-based bridging ligands have been used extensively in preparing various organic-inorganic networks¹⁰⁻¹² as well as pure organic networks,¹³ their 3,3'-bipyridine-based counterparts have not been explored to that

extent. Five types of 3,3'-bipyridine derivatives are now known: 3,3'-bipyridine (**L**¹),¹⁴⁻¹⁶ 1,2-bis(3-pyridyl)ethyne (**L**²),^{17,18} 1,4-bis(3-pyridyl)-2,3,5,6-tetrazene (**L**³),¹⁹ 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (**L**⁴),²⁰ and 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene (**L**⁵)^{21,22} (Chart 1). In particular, ligands **L**⁴ and **L**⁵ were prepared by the Schiff-base condensation reaction. Schiff-base ligands such as **L**⁴ and **L**⁵ should have an inherently long, rigid, bis(monodentate) character due to the presence of two pyridyl nitrogen-donor atoms and a conjugated π system; therefore, their employment in preparing coordination polymers may allow us to create novel open-framework structures. It is worth noting that Constable and co-workers recently developed a synthetic route to a new class of dinucleating ligands by

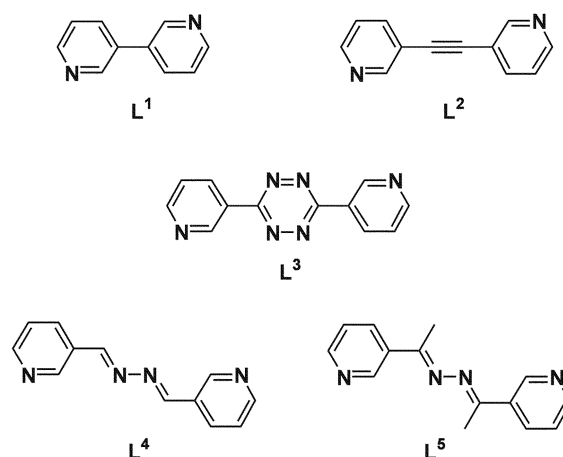
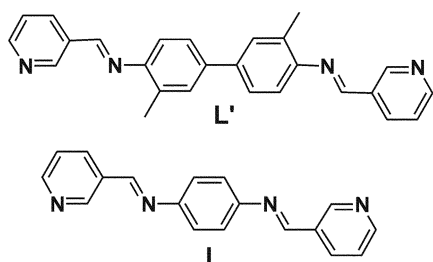


Chart 1

functionalizing 3,3'-bipyridine and its derivatives.²³

We have prepared several coordination polymers based on carboxylates or bipyridyls by hydrothermal or hydro(solvo) thermal reactions.²⁴⁻³⁰ We recently reported the preparation and structures of a 3,3'-bipyridine-based ligand (**L'**), a bis(monodentate) Schiff-base ligand containing two terminal pyridyl groups (py-CH=N-(CH₃)C₆H₃-(CH₃)C₆H₃-N=CH-py), and its Zn and Co coordination polymers ([ZnL'₂(NO₃)₂] and [CoL'_{1.5}(NO₃)₂]).³¹ As a continuation of our study, we set out to seek other Schiff-base type ligands based on the 3,3'-bipyridine. We report here the preparation and structures of another 3,3'-bipyridine-based ligand (**L**, *N,N'*-bis-pyridin-3-methylene-benzene-1,4-diamine, py-CH=N-C₆H₄-N=CH-py) and its zinc coordination polymers.



All solid chemicals were purified by recrystallization or sublimation, and all solvents were distilled and stored over molecular sieves. IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer. Elemental analyses were performed with EA1110 (CE instrument, Italy) at the Korea Basic Science Institute.

Preparation of ligand L. Ligand **L** was prepared by following the procedure used for the preparation of the **L'** ligand.²⁰ To 3-pyridinecarboxaldehyde (nicotinaldehyde, 5.0 mL, 50 mmol) in ethanol (50 mL) was added 1,4-phenylenediamine dihydrochloride (C₆H₄(NH₂)₂·2HCl, 4.53 g, 25 mmol). After the addition of dichloromethane (50 mL) and in turn two drops of formic acid, the mixture was stirred at room temperature for 24 h and then filtered. The resulting yellow crystalline solid was washed with a mixture of ethanol and hexane (v/v = 1 : 1; 3 × 10 mL), and dried in air to give ligand **L** (5.64 g, 19.7 mmol, 79%). Mp: 155-157 °C. IR (KBr, cm⁻¹): 3412, 2885, 1619, 1574, 1490, 1422, 1366, 880, 840, 800, 702, 560. Anal. Calcd for C₁₈H₁₄N₄ (*M_r* = 286.33): C, 75.44; H, 4.89; N, 19.56. Found: C, 74.82; H, 4.65; N, 20.53.

Preparation of 2-pyridin-3-yl-1*H*-benzoimidazol (1**).** Compound **1** was prepared in the same way as ligand **L**. To an ethanol solution (50 mL) containing 3-pyridinecarboxaldehyde and 1,2-phenylenediamine dihydrochloride (C₆H₄(NH₂)₂·2HCl, 4.53 g, 25 mmol) was added dichloromethane (50 mL) containing two drops of formic acid. The resulting mixture was stirred to give compound **1** (3.76 g, 19.3 mmol, 77%). Mp: 217-219 °C. IR (KBr, cm⁻¹): 3445, 1582, 1535, 1491, 1441, 1277, 1226, 1111, 1035, 958, 870, 816, 746, 704, 630. Anal. Calcd for C₁₂H₉N₃ (*M_r* = 195.22): C, 73.50; H, 4.62; N, 21.22. Found: C, 73.82; H, 4.65; N, 21.53.

Preparation of *trans*-[Zn(H₂O)₄L₂](NO₃)₂(MeOH)₂

(**2**). A methanol solution (3 mL) containing Zn(NO₃)₂·6H₂O (59 mg, 0.2 mmol) was layered onto the top of a chloroform solution (3 mL) containing ligand **L** (114 mg, 0.4 mmol). The resulting solution was allowed to stand at room temperature for 3 days. The crystalline product was filtered, washed with hexane (3 × 10 mL), and then air-dried to give crystals of compound **2** (0.030 g, 0.033 mmol, 16%). Mp: 155-157 °C. IR (KBr, cm⁻¹): 3519, 2362, 1658, 1610, 1490, 1421, 1197, 1110, 1042, 972, 884, 836, 699, 643, 558, 453. Anal. Calcd for C₃₈H₄₄N₁₀O₁₂Zn (*M_r* = 898.20): C, 50.83; H, 4.90; N, 15.60. Found: C, 49.85; H, 4.53; N, 15.99.

Preparation of [Zn(NO₃)(H₂O)₂(L)]·(NO₃)·(H₂O)₂ (3**).** This polymer was prepared analogously to compound **2**. An acetonitrile solution (3 mL) containing Zn(NO₃)₂·6H₂O (59 mg, 0.2 mmol) was layered onto the top of a dichloromethane solution (3 mL) containing ligand **L** (114 mg, 0.4 mmol) to give crystals of polymer **3** (0.040 g, 0.073 mmol, 24.3%). Mp: 131-133 °C. IR (KBr, cm⁻¹): 3474, 1623, 1494, 1382, 1199, 1103, 1051, 977, 887, 838, 702, 646, 561. Anal. Calcd for C₁₈H₂₂N₆O₁₀Zn (*M_r* = 547.79): C, 50.84; H, 4.90; N, 15.60. Found: C, 51.00; H, 4.12; N, 16.20.

Preparation of [Zn(L)(OBC)(H₂O)] (4**).** A mixture of Zn(NO₃)₂·6H₂O (12 mg, 0.040), ligand **L** (0.018 g, 0.063 mmol), OBCH₂ (4,4'-oxybis(benzoic acid), 0.016 g, 0.062 mmol), dichloromethane (2 mL), acetonitrile (3 mL), and benzene (1 mL) was heated in a 23-mL Teflon-lined reaction vessel at 55 °C for 3 days, and then cooled to room temperature by air-cooling. The crystalline product was collected by filtration, washed with acetone (3 × 5 mL) and ethanol (3 × 5 mL), and then air-dried to give yellow crystals of polymer **4** (2 mg, 0.003 mmol, 7.5%). Mp: 165-167 °C. IR (KBr, cm⁻¹): 3433, 2131, 1601, 1557, 1497, 1381, 1239, 1159, 1101, 878, 831, 788, 699, 653, 457. C₃₂H₂₄N₄O₆Zn (*M_r* = 625.92): C, 61.40; H, 3.83; N, 8.95. Found: C, 60.71; H, 3.84; N, 8.88.

X-ray structure determination. All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. Details on crystal data and refinement details are given in Table I. No absorption corrections were made for organic compounds (**L** and **1**), but empirical absorption corrections were made with ψ -scan data for zinc compounds **2-4**. All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. All calculations were carried out with the SHELXTL programs.³²

A yellow crystal of **L** (a block, 0.55 × 0.44 × 0.16 mm) was used for crystal- and intensity-data collection. The unit-cell parameters and systematic absences indicated two possible space groups: *P*2₁ and *P*2₁/*m*. The structural analysis converged only in *P*2₁. All hydrogen atoms were generated in ideal positions and refined in a riding model. A yellow crystal of compound **1** (a block, 0.40 × 0.36 × 0.32 mm) was used, and all hydrogen atoms were located and refined isotropically.

A brown crystal of compound **2** (a block, 0.58 × 0.56 × 0.24 mm) was used. The unit-cell parameters indicated a triclinic unit cell with the two possible space groups: *P*1 and

Table 1. X-ray Data Collection and Structure Refinement Details

	L	1	2	3	4
Empirical formula	C ₁₈ H ₁₄ N ₄	C ₁₂ H ₉ N ₃	C ₃₈ H ₄₄ N ₁₀ O ₁₂ Zn	C ₁₈ H ₂₂ N ₆ O ₁₀ Zn	C ₃₂ H ₂₄ N ₄ O ₆ Zn
Formula weight	286.33	195.22	898.20	547.79	625.92
Temperature, K	293(2)	293(2)	293(2)	293(2)	
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
a, Å	11.604(1)	10.147(1)	8.604(2)	8.3839(9)	14.673(5)
b, Å	4.773(1)	11.492(2)	9.935(2)	8.2773(7)	11.017(3)
c, Å	12.861(1)	17.774(3)	12.525(2)	16.645(2)	17.219(5)
α, deg			81.60(1)		
β, deg	92.330(9) ^o	103.931(9)	71.64(1)	99.14(1)	97.94(2)
γ, deg			78.87(2)		
V, Å ³	711.8(2)	2011.6(6)	992.8(3)	1140.4(2)	2757(1)
Z	2	8	1	2	4
d _{cal} , g cm ⁻³	1.336	1.289	1.502	1.595	1.508
μ, mm ⁻¹	0.083	0.080	0.696	1.144	0.946
F(000)	300	816	468	564	1288
T _{min}			0.5926	0.7285	0.5254
T _{max}			0.8774	0.9239	0.8514
2θ range (°)	3.5-50	3.5-50	3.5-50	3.5-50	3.5-50
scan type	ω	ω	ω	ω	ω
No. of reflns measured	1434	3733	3679	2129	4958
No. of reflns unique	1363	3521	3431	1985	4753
No. of reflns with I > 2σ(I)	983	2404	3241	1788	3317
No. of params refined	200	343	298	206	484
Max., in Δρ (e Å ⁻³)	0.206	0.228	1.143	0.761	0.431
Min., in Δρ (e Å ⁻³)	-0.1763	-0.141	-0.618	-0.333	-0.341
GOF on F ²	1.064	1.020	1.057	1.063	1.052
R ^a	0.0549	0.0437	0.0569	0.0371	0.0480
wR ₂ ^b	0.1634	0.0962	0.1570	0.1020	0.1112

$$^a R = \sum ||F_o| - |F|| / \sum |F_o|, ^b wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]^{1/2}$$

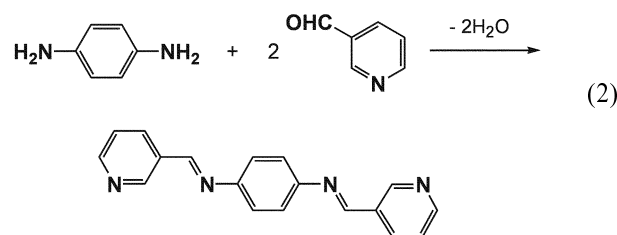
P-1. The structure analysis converged only in *P*-1. The hydrogen atoms in aqua ligands and co-crystallized methanol were located and refined isotropically. The remaining hydrogen atoms were generated in ideal positions. A yellow crystal of polymer **3** (a block, 0.44 × 0.32 × 0.32 mm) was used. The unit-cell parameters and systematic absences indicated two possible space groups: *Pc* and *P2/c*. The structural analysis converged only in *P2/c*. All hydrogen atoms were located and refined isotropically. A yellow crystal of polymer **4** (a block, 0.50 × 0.18 × 0.16 mm) was used, and all hydrogen atoms were located. Selected bond lengths and angles are shown in Table 2.

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center: 262364 (**L**), 262365 (**1**), 262366 (**2**), 262367 (**3**), and 262368 (**4**). Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Results and Discussion

Preparation of ligand **L**. A long, bis(monodentate)

ligand (**L**) of the Schiff-base type, which contains two terminal pyridyl groups, was prepared by the condensation of diamine (1,4-phenylenediamine) and aldehyde (3-pyridinecarboxaldehyde) (eq. 2). Ligand **L** has the 3,3'-positional orientation of two nitrogen-donor atoms in the two terminal pyridyl groups. The C=N stretching frequencies of Schiff bases are known to appear in the range 1680-1603 cm⁻¹, and therefore the absorption band at 1619 cm⁻¹ in the IR spectrum of ligand **L** can be assigned to the C=N bond.^{7,9}



The N...N separation between the two terminal pyridyl groups in **L** is 13.994 Å, which is somewhat larger than that (10.729 Å) in **L**⁴ (py-CH=N-N=CH-py) previously reported

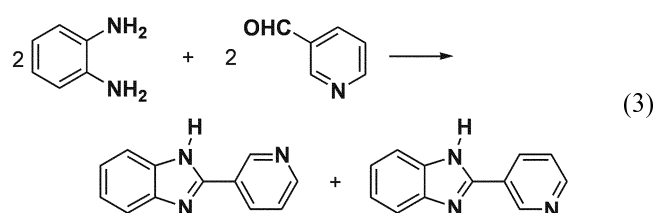
Table 2. Selected Bond Lengths (Å) and Angles (deg)

Ligand L					
N1-C2	1.309(8)	N1-C1	1.330(9)	N2-C6	1.242(7)
N2-C7	1.409(7)	N3-C13	1.235(7)	N3-C10	1.418(7)
N4-C16	1.318(9)	N4-C15	1.335(9)		
C13-N3-C10	112.9(4)	C16-N4-C15	109.3(5)	N2-C6-C5	116.1(4)
N3-C13-C14	115.0(4)				
Compound 1					
N1-C7	1.348(2)	N1-C1	1.395(3)	N2-C7	1.308(2)
N2-C6	1.415(2)	N4-C19	1.318(2)	N4-C13	1.383(3)
N5-C19	1.370(2)	N5-C18	1.380(2)		
C7-N1-C1	106.4(2)	C7-N2-C6	104.1(2)	N2-C7-N1	114.1(2)
C19-N4-C13	105.0(2)	C19-N5-C18	106.7(2)	N4-C19-N5	113.0(2)
Compound 2					
Zn1-O1	2.074(2)	Zn1-N1	2.158(3)	Zn1-O2	2.162(3)
O1-Zn1-N1	90.2(1)	O1-Zn1-O2	91.6(1)	N1-Zn1-O2	89.8(1)
Polymer 3					
Zn1-O1	2.069(3)	Zn1-N1	2.096(2)	Zn1-O2	2.256(2)
N2-C6	1.268(4)				
O1-Zn1-N1	90.4(1)	O1-Zn1-O2	88.5(1)	N1-Zn1-O2	92.9(1)
Polymer 4					
Zn1-O4	1.974(3)	Zn1-O6	1.979(3)	Zn1-O1	2.003(3)
Zn1-N1	2.072(3)				
O4-Zn1-O6	103.6(2)	O4-Zn1-O1	117.2(1)	O6-Zn1-O1	92.0(2)
O4-Zn1-N1	132.6(1)	O6-Zn1-N1	106.0(2)	C23-O3-C26	120.6(3)

by the Loye's group.²⁰ In other words, our synthesis has a net effect of inserting a phenylene unit (-C₆H₄-) into the central N-N bond in the Loye's ligand, making the pyridyl N...N separation larger.

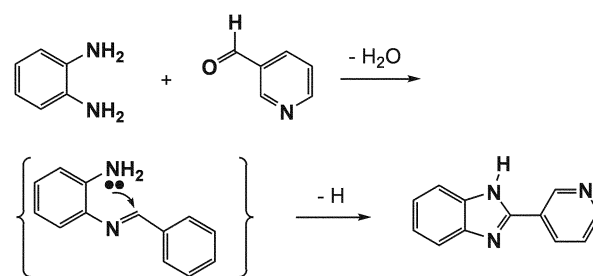
A hydrogen-bonded tetramer forming a 16-membered rectangle. On the basis of the successful preparation of ligand L, which has an approximate coordination angle of 180°, we tried to prepare its structural isomer, starting from 1,2-phenylenediamine in place of 1,4-phenylenediamine under the same reaction conditions. Inconsistent with our expectation, this reaction did not give a free ligand; instead, it produced a tetrameric compound **1** that could not be employed in preparing coordination polymers.

1,2-Phenylenediamine reacted with 3-pyridinecarboxyaldehyde to give a mixture of imidazole isomers (2-pyridin-3-yl-1*H*-benzoimidazole), whose diffraction study revealed that they differ in the relative orientations between the imidazole ring N-H bond and the pyridine ring N atom, and can be regarded as conformational isomers (eq. 3). The IR spectrum of compound **1** displays an absorption band at



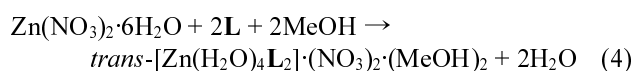
1582 cm⁻¹, which can be assigned to the C=N bond. For Schiff bases, the presence of hydrogen bonding is known to induce a low-frequency shift of the C=N stretching,⁷ which can explain the lower C=N frequency of compound **1** relative to ligand L.

The preparation of compound **1** seems to involve two steps. The first step is the Schiff-base condensation, and the second step is the intramolecular nucleophilic attack of the amino group at the imino carbon to bring about the C-N coupling (Scheme 1). The imino (or azidomethine, C=N) carbon is partially positively charged, and therefore is susceptible to nucleophilic attack, intermolecular or intramolecular.⁹ In particular, the intramolecular reactions give 5- or 6-membered heterocycles. The starting compound (1,2-phenylenediamine) has two amino groups on the adjacent carbons, and the unreacted amino group in the first step attacks the imino carbon in the intermediate to give the

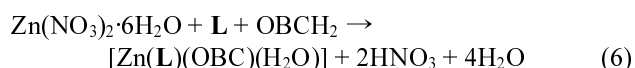
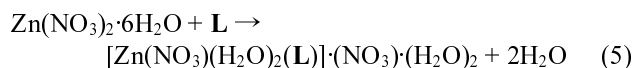
**Scheme 1**

final product (compound **1**), which contains a 5-membered imidazol ring.

Preparation of zinc compounds. One discrete molecule and two 1-D coordination polymers of zinc were prepared from zinc nitrate and ligand **L** under various conditions. A methanol solvate compound, *trans*-[Zn(H₂O)₄L₂](NO₃)₂·(MeOH)₂ (**2**·(MeOH)₂), was prepared by layering a methanol solution containing Zn(NO₃)₂·6H₂O onto the top of a chloroform solution containing ligand **L** (eq. 4). X-ray diffraction study revealed that compound **2** is a discrete molecule, not a coordination polymer. The nitrate groups act as counterions in compound **2**. A closely related 1-D cobalt coordination polymer [Co(H₂O)₄(pyrazine)]·(NO₃)₂·(H₂O)₂ was reported very recently.³³



An acetonitrile solution containing Zn(NO₃)₂·6H₂O was layered onto the top of a dichloromethane solution containing ligand **L** to give crystals of the 1-D zinc polymer [Zn(NO₃)(H₂O)₂(L)]·(NO₃)·(H₂O)₂ (**3**) (eq. 5). Another 1-D zinc polymer [Zn(L)(OBC)(H₂O)] (**4**) could be prepared under solvothermal conditions (eq. 6). Heating Zn(NO₃)₂·6H₂O, ligand **L**, and OBCH₂ in a mixture of solvents (CH₂Cl₂:CH₃CN:C₆H₆ = 2:3:1, v/v) in a Teflon-lined reaction vessel at 55 °C for 3 days produced the polymeric compound **4**. Polymer **4** contains two potential linking ligands (**L** and OBC²⁻), but only the OBC ligands link the metals to give a polymer structure. Both polymers **3** and **4** are insoluble in common organic solvents and water, and stable in air.



Structure. The molecular structure of ligand **L** with the atom-numbering scheme is shown in Figure 1, in which two pyridyl groups are linked by a diimine moiety (-CH=N-C₆H₄-N=CH-) and have their nitrogen atoms at the meta positions (3,3'). The two terminal pyridyl rings are essentially parallel to each other (their dihedral angle = 0.4(4)°), and the pyridyl nitrogen atoms are oriented in a *trans* manner.

The molecular structure of compound **1** is presented in Figure 2. The asymmetric unit contains two isomers of benzoimidazole, which differ in the relative orientations between the imidazole ring N-H bond and the pyridine ring

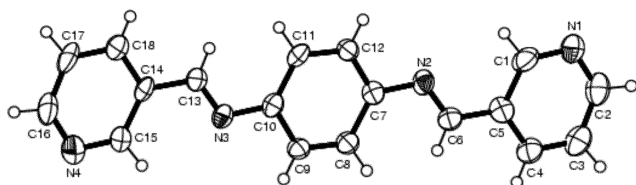


Figure 1. ORTEP drawing of ligand **L**¹ with 50% probability thermal ellipsoids.

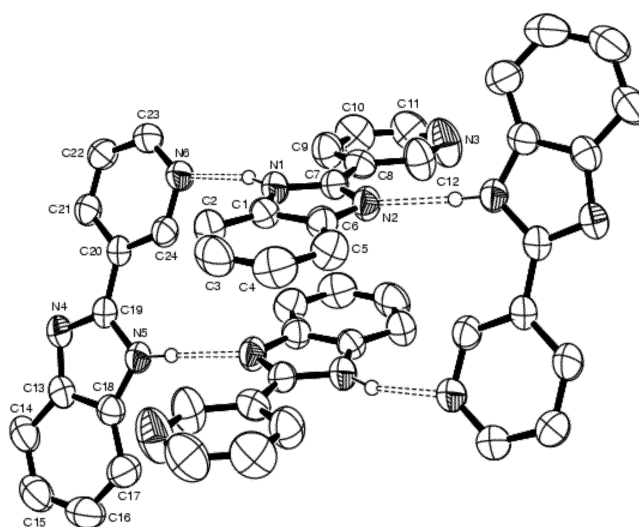


Figure 2. ORTEP drawing of compound **1**.

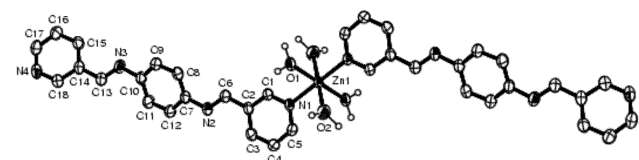


Figure 3. ORTEP drawing of compound **2**.

N atom, and are linked to each other by the N-H···N hydrogen bonds. Two dimer units are connected further by another N-H···N hydrogen bonds to eventually form a tetrameric 16-membered rectangle with dimensions of 7.88 × 4.28 Å based on the N···N separations. Both benzoimidazole rings in the asymmetric unit are essentially planar with an average atomic displacement of 0.0083 (N1, N2, C1-C7) or 0.0046 (N4, N5, C13-C19) Å, and their dihedral angle is 63.85(3)°. The dihedral angle between the benzoimidazole and pyridine ring is 5.1(1) or 6.6(1)°.

The molecular structure of compound **2** is shown in Figure 3, which clearly shows ligand **L** to act simply as a monodentate ligand. The asymmetric unit of compound **2** consists of only half of the formula unit with the other half generated by crystallographic inversion. The Zn metal is coordinated by two Schiff base ligands (**L**) and four aqua ligands. The nitrate groups are not bound to the metal and act as counterions. The geometry of the Zn metal can be described as a distorted octahedron, in which the aqua ligands form an equatorial plane. The N···N separation between the two pyridyl groups is 14.754 Å

Figure 4 shows the local coordination of the zinc center in polymer **3**. The Zn metal lies on the crystallographic 2-fold rotation (C₂) axis, which explains why this crystal has the Z value of 2 instead of 4. In addition, the N3 and O3 atoms in the nitrate ligand also lie on the C₂ axis. The coordination sphere of zinc can be described as a pseudo-octahedron, in which equatorial sites are occupied by two oxygens of the chelating nitrate ligand and two nitrogens of the Schiff-base ligands, and axial sites are occupied by two aqua ligands.

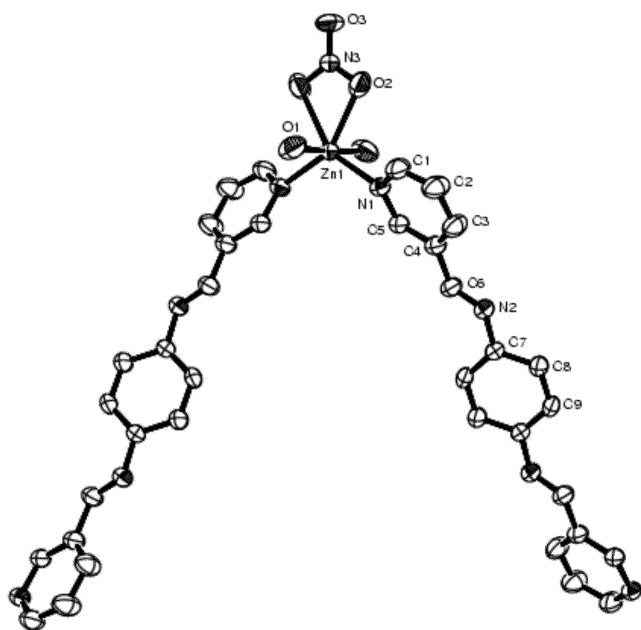


Figure 4. Local coordination environment of zinc in polymer 3.

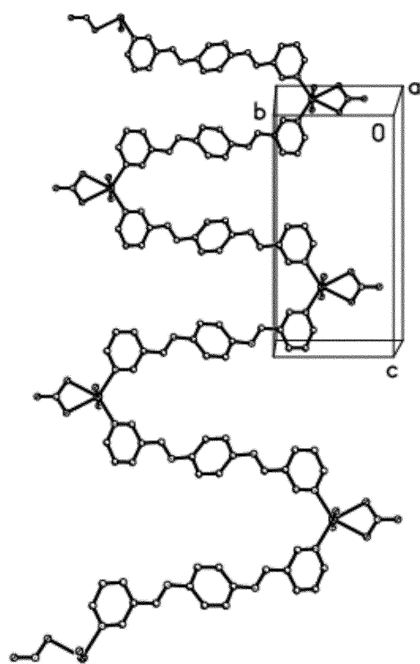


Figure 5. Projection of polymer 3 along the *a*-axis, showing a 1-D zigzag chain.

One nitrate ion exists outside the coordination sphere as a counterion, and therefore the formal oxidation state of zinc is +2. There are two co-crystallized water molecules per monomer unit of this coordination polymer. Figure 5 shows a packing diagram along the *a*-axis and demonstrates a one-dimensional polymeric structure of **3**. The linear ligands connect Zn metals in the *bc*-direction to form a 1-D zigzag chain. The Zn...Zn separation in this chain is 18.153 Å, and the N...N separation between the two pyridyl groups is 14.751 Å. All hydrogen atoms in the aqua ligands and co-crystallized water molecules participate in intermolecular

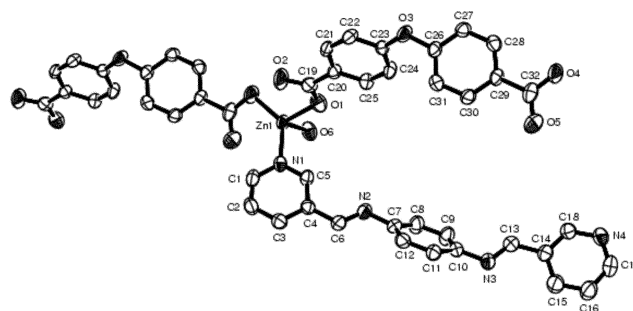


Figure 6. Local coordination environment of zinc in polymer 4.

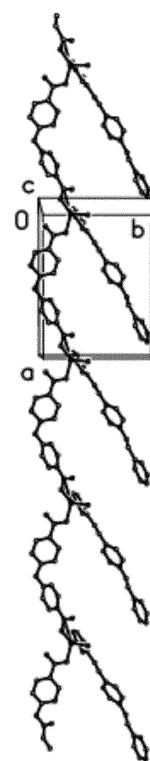


Figure 7. Projection of polymer 4 along the *c*-axis, showing a 1-D chain.

hydrogen bonds of either the O-H...O or O-H...N type.

Figure 6 shows the local coordination of the zinc metal in polymer 4. The coordination sphere of zinc can be described as a pseudo-tetrahedron, which consists of two oxygen atoms of two OBC ligands, one nitrogen atom of the monodentate Schiff-base ligand (**L**), and one oxygen atom of the aqua ligand. The Zn-N bond length is 2.072(3) Å and Zn-O bond lengths are 1.974(3)-2.003(3) Å. The bond angle (C23-O3-C26) around the ether oxygen O3 in the OBC ligand is 120.6(3)°. Two aryl rings in OBC ligand are nearly orthogonal with a dihedral angle of 81.2(2)°. The projection of polymer 4 along the *c*-axis demonstrates its one-dimensional structure (Figure 7). The one-dimensional chain is formed by the bridging OBC ligands linking Zn metals in the [110] direction, with the Zn...Zn separation of 14.673 Å and the N...N separation of 13.853 Å. As is the case for compound **2**, ligand **L** does not act as a linking

agent but does serve simply as a monodentate ligand. Both hydrogen atoms in the aqua ligand participate in intermolecular hydrogen bonds of either the O-H...O or O-H...N type. The crystal structure of **4** suggests that the OBC ligand has a greater linking ability than ligand **L**.

In summary, we prepared a novel Schiff-base type ligand (**L**, py-CH=N-C₆H₄-N=CH-py) from 1,4-phenylenediamine and 3-pyridinecarboxaldehyde by the Schiff-base condensation reaction. Ligand **L** has two terminal pyridyl groups that can provide coordinating nitrogen atoms. On the other hand, the same reaction employing 1,2-phenylenediamine in place of 1,4-phenylenediamine produced a mixture of imidazol isomers, four of which are connected by the N-H...N hydrogen bonds to form a rectangular tetramer. From Zn(NO₃)₂·6H₂O and ligand **L** under various conditions, one discrete molecule, *trans*-[Zn(H₂O)₄L₂](NO₃)₂(MeOH)₂, and two 1-D zinc polymers, [Zn(NO₃)(H₂O)₂(L)](NO₃)(H₂O)₂ and [Zn(L)(OBC)(H₂O)], were prepared. The N...N separation between two pyridyl groups in **L** is 13.994 Å, which varies from 13.853 to 14.754 Å in its compounds, reflecting a flexibility of the framework of this ligand.

Acknowledgement. This work was supported by the Korea Research Foundation (Grant No. KRF-2003-015-C00309).

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