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Structural Isomers of a Potential Linking Ligand Containing a Pyridyl and a Carboxylate Terminals: (*n*-py)–CH=N–C_6H_4–CH_2–COOH} (*n* = 3, 4)

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Coordination polymers currently receive much attention due to their desirable properties applicable to a wide variety of fields, such as ion exchange, host–guest chemistry, adsorption–desorption, luminescence, magnetism, biomedicine, catalysis, and gas storage.[1-9] Many factors influence the topology of such polymers, including the preferred geometry of a metal, coordination modes of linking ligands, the nature of solvents used, the acidity of a reaction mixture, and synthetic methods adopted (layer-diffusion, hydrothermal, solvothermal, hydro(solvo)thermal, or microwave heating method). In particular, the judicious choice of appropriate linking ligands is crucial to the successful preparation of desired polymers, and bis(pyridy)- or multicarboxylate-type linking ligands have been commonly used.[10-12]

Recently, several asymmetric linking ligands possessing a carboxylate and a pyridyl or an imidazole were employed to prepare coordination polymers, in which both *d*- and *f*-block metals coexist as nodes within their frameworks.[13-21] We also recently prepared several pyridyl–carboxylate-type linking ligands (L1–L6 in Chart 1) and their coordination polymers.[22-31] Ligands L1 and L2 contain an amide (–C(O)–NH–) fragment, whereas ligands L3–L6 possess an imine (–C=N–) fragment. In particular, the π conjugation is interrupted in ligands L1–L4.

As a continuation of our research, we prepared two relatively long potential linking ligands by Schiff-base condensation. They contain pyridyl–carboxylate terminals and are structural isomers due to the different positions of the nitrogen atoms in the pyridyl terminals. We herein report the preparation and structures of these compounds: (*n*-py)–CH=N–C_6H_4–CH_2–COOH} (*n* = 3 (**1**), 4 (**2**)).

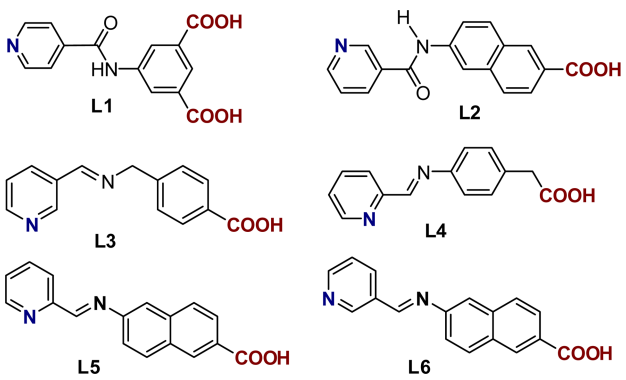


Chart 1. Pyridyl–carboxylate-type linking ligands prepared by our group.

Experimental Section

All solid chemicals were purified by recrystallization, and methanol was distilled and stored under argon. Infrared (IR) samples were prepared as KBr pellets, and their spectra were obtained in the range 400–4000 cm^{-1} on a Nicolet 320 FTIR spectrophotometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on an 500 MHz Varian Inova spectrometer at the Cooperative Center for Research Facilities (CCRF) in Sungkyunkwan University.

Synthesis of Compounds 1 and 2. Both compounds were prepared in the same way. At room temperature, 4-(aminophenyl)acetic acid (1.00 g, 6.6 mmol) was dissolved in hot methanol (30 mL), and then 3-pyridinecarboxaldehyde (0.71 g, 6.6 mmol) was added slowly. The mixture was refluxed for 3 h and then cooled slowly to room temperature. The resulting yellow powder was filtered, washed with methanol (10 mL × 3), and vacuum-dried for 30 min. Finally, the yellow powder in methanol was heated in a 24 mL Teflon-lined vessel at 75 °C for 12 h, and then slowly air-cooled. The resulting yellow crystals were isolated to give compound **1** (1.42 g, 5.91 mmol, 89.0% yield). mp 193–195 °C. ^1H NMR (500 MHz, CD_3SOCD_3) δ 9.06 (d, 1H, pyridine N–C*H*), 8.71 (s, 1H, imine C*H*=N), 8.69 (d, 1H, pyridine N–C*H*), 8.33 (m, 1H, aromatic), 7.57 (m, 1H, aromatic), 7.34–7.25 (m, 4H, aromatic), 3.60 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3SOCD_3) δ 172.7 (*C*OOH), 158.2 (*C*=N, imine), 151.9, 150.4, 149.5, 134.9, 133.5, 131.6, 130.3, 124.1, 121.0, 40.3 (*C*H_2). IR (KBr, cm^{-1}): 3450 (OH), 3066, 2899, 2721, 1903, 1715, 1622 (C=N), 1579, 1503, 1420, 1350, 1235, 1186, 1113, 1031, 986, 895, 809, 695, 643, 562, 520, 451.

For the preparation of compound **2**, 4-(aminophenyl)acetic acid (1.00 g, 6.6 mmol) and 4-pyridinecarboxaldehyde (0.71 g, 6.6 mmol) were used. Data for compound **2**: (1.45 g, 6.04 mmol, 91.0% yield). mp 222–224 °C. ^1H NMR (500 MHz, CD_3SOCD_3) δ 8.74 (d, 2H, pyridine N–C*H*), 8.71 (s, 1H, imine C*H*=N), 7.85 (d, 2H, aromatic), 7.83 (d, 2H, aromatic), 7.31 (d, 2H, aromatic), 3.61 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR

Table 1. X-ray data collection and structure refinement

Compound	**1**	**2**
Empirical formula	$C_{14}H_{12}N_2O_2$	$C_{14}H_{12}N_2O_2$
Formula weigh	240.26	240.26
Temperature, K	296(2)	296(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
Crystal size	0.32 × 0.30 × 0.02	0.08 × 0.03 × 0.02
Crystal shape	plate	block
a, Å	13.6677(3)	27.801(1)
b, Å	5.8548(1)	4.6608(2)
c, Å	14.7813(3)	22.206(1)
α, deg	90	90
β, deg	91.127(1)	124.983(7)
γ, deg	90	90
V, Å^3	1182.60(4)	2357.5(3)
Z	4	8
D_{cal}, g cm^{-3}	1.349	1.354
μ, mm	0.092	0.093
F(000)	504	1008
θ range (º)	1.49–28.56	1.79–28.41
T_{max}	0.9982	0.9982
T_{min}	0.9711	0.9926
No. of reflns measured	39696	19121
No. of reflns unique	2988	2944
No. of reflns with $I > 2\sigma(I)$	1885	1564
No. of params	167	167
Max., in Δρ (e Å^{-3})	0.208	0.178
Min., in Δρ (e Å^{-3})	–0.218	–0.185
GOF on F^2	1.042	1.000
$R1^a$	0.0539	0.0506
$wR2^b$	0.1072	0.0989

$^aR = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|]$, $^bwR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

(125 MHz, CD_3SOCD_3) δ 172.6 (*C*OOH), 158.8 (*C*=N, imine), 150.5, 149.0, 142.5, 134.0, 130.3, 122.2, 121.1, 40.3 (*C*H$_2$). IR (KBr, cm^{-1}): 3439 (OH), 3047, 2939, 2801, 1963, 1704, 1604 (C=N), 1560, 1510, 1421, 1378, 1131, 1055, 1015, 965, 903, 819, 735, 644, 608, 550, 492, 440.

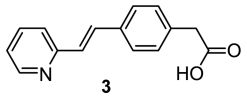
X-ray Structure Determination. All X-ray data were collected on a Bruker Smart APEX2 diffractometer equipped with a Mo X-ray tube (CCRF).[32] Absorption corrections were made on the basis of the Laue symmetry of equivalent reflections with SADABS programs.[33] All calculations were carried out with SHELXTL programs.[34] All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. The COOH hydrogen atoms were located in the difference Fourier maps and refined freely. The remaining hydrogen atoms were generated in idealized positions and refined in a riding model.

A yellow crystal of compound **1**, shaped as a plate of approximate dimensions 0.32 × 0.30 × 0.02 mm^3, was used for crystal- and intensity-data collection. A yellow crystal of compound **2** (a block, 0.08 × 0.03 × 0.02 mm^3) was used. Details on crystal data, intensity collection, and refinement details are given in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC 948700 and 948701 contain the supplementary crystallographic data for compounds **3** and **4**, and respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Results and Discussion

Preparation. Two potential linking ligands were prepared by Schiff-base condensation of an aminocarboxylic acid and a pyridinecarboxaldehyde (Scheme 1). Both compounds have a pyridyl (a *N*-donor) and a carboxylate (an *O*-donor) terminals, as well as an intervening benzyl imine group (–CH=N–C$_6$H$_4$–CH$_2$–) between the terminals. These two compounds are structural isomers due to the different nitrogen positions in the pyridyl terminals. In addition, the preparation and structure of (2-py)–CH=N–C$_6$H$_4$–CH$_2$–COOH (**3**), which is a structural isomer of compounds **1** and **2**, was previously reported by our group.[26] The above synthetic method was also used for the preparation of other pyridyl–carboxylate-type ligands.[22,26-29] Moreover, the Suzuki–Miyaura cross-coupling reaction was employed to prepare the interesting pyridyl–carboxylate-type ligands, *trans*-3-(4-pyridyl)propenoic acid, 4-(4-pyridyl)benzoic acid, and *trans*-3-(4-(4-pyridyl)phenyl)propenoic acid, which contain only carbon-containing intervening groups.[35]



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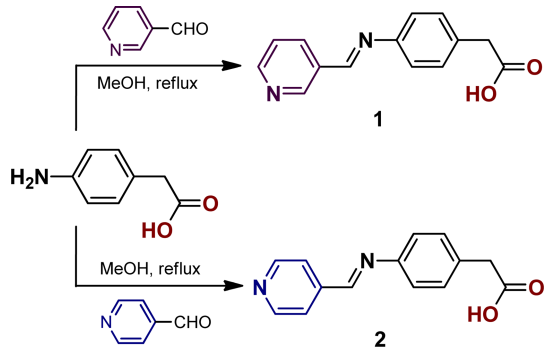
A mixture of 4-(aminophenyl)acetic acid and 3-pyridinecarboxaldehyde in the mole ratio of 1:1 was refluxed in

Table 2. Selected bond lengths (Å) and bond angles (º)

Compound **1**					
O1–C14	1.318(2)	O2–C14	1.197(2)	N2–C6	1.254(2)
N2–C7	1.423(2)	O1–HO1	1.00(3)		
C6–N2–C7	119.8(2)	N2–C6–C2	123.2(2)	C14–O1–HO1	106(2)
Compound **2**					
O1–C14	1.311(2)	O2–C14	1.202(2)	N2–C6	1.257(2)
N2–C7	1.422(2)	O1–HO1	1.07(3)		
C6–N2–C7	120.3(2)	N2–C6–C3	122.6(2)	C14–O1–HO1	109(1)



Scheme 1. Preparation of compounds **1** and **2**.

methanol for 3 h to produce compound **1** in 89.0% yield. Compound **2**, which contains the 4-pyridyl terminal group, was prepared in the same way by using 4-pyridinecarboxaldehyde in place of 3-pyridinecarboxaldehyde. Both products were characterized by ^{1}H NMR, ^{13}C{^{1}H} NMR, IR, and X-ray diffraction.

The IR spectra of the products display a characteristic C=N stretching band at 1622 (compound **1**) or 1604 (compound **2**) cm^{-1}. The C=N stretching bands of Schiff bases appear typically in the range of 1680–1600 cm^{-1}.[36-38] In ^{1}H NMR spectra, the methylene (–CH_2–) protons appears as a singlet at 3.60 (compound **1**) or 3.61 (compound **2**) ppm. In the ^{13}C{^{1}H} NMR spectrum of compound **1**, the chemical shifts of the carboxylate carbon (–*C*OOH) and the imine carbon (–*C*H=N–) are 172.7 and 158.2 ppm, respectively. In the case of compound **2**, the corresponding peaks appear at 172.6 and 158.8 ppm.

Crystal Structures. The molecular structure of compound **1** with the atom-labeling scheme is given in Figure 1, which clearly shows both the pyridyl and the carboxylate terminals. The methylene fragment interrupts the π conjugation system, and therefore this compound may be flexible in bonding to metals. The aromatic rings are significantly twisted from

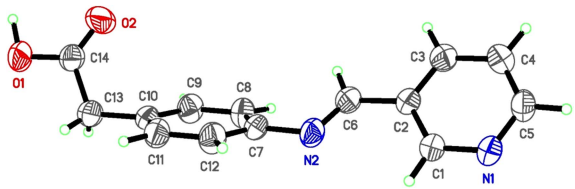


Figure 1. Ortep drawing of compound **1**. Displacement ellipsoids for non-hydrogen atoms exhibit 40% probability level.

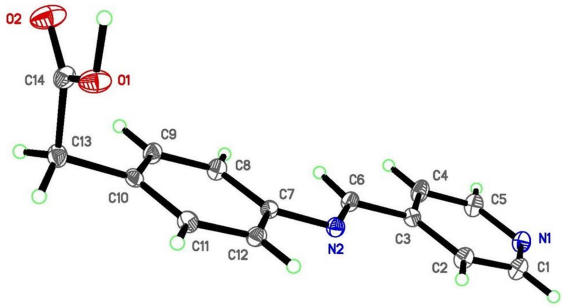


Figure 3. Ortep drawing of compound **2** with the 40% atomic displacement parameters.

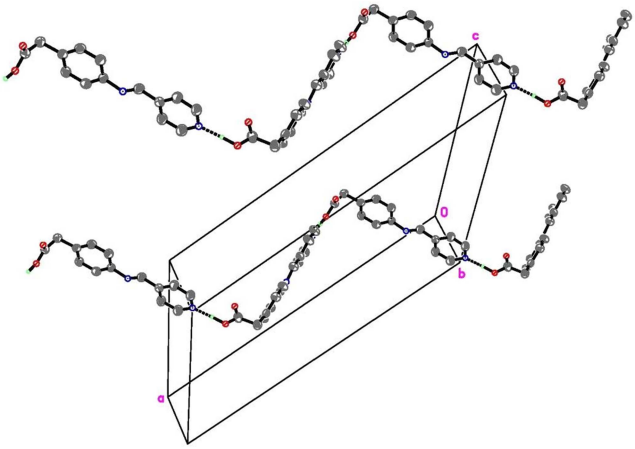


Figure 4. A 1-D zigzag network formed by O–H···N hydrogen bonds of compound **2**.

each other with a dihedral angle of the 3-pyridyl ring (N1, C1–C5) and the phenyl ring (C7–C12) of 48.87(5)°. The C2–C6–N2–C7 torsion angle is 178.4(2)°. The N2–C6 bond length (1.254(2) Å) clearly indicates a C=N double bond, which has been formed during the reaction. The N1···O1 and N1···O2 separations are 11.942(2) and 10.342(2) Å, respectively. As shown in Figure 2, molecules of compound **1** are connected by the strong intermolecular hydrogen bonds of the O–H···N type (Table 3). These H-bonds lead to a 1-dimensional zigzag network approximately along the *a*-axis (Figure 2).

Figure 3 shows the molecular structure of compound **2**, a structural isomer of compound **1**. Two planar 6-membered rings (4-pyridyl and phenyl rings) are essentially coplanar the dihedral angle of 3.0(1)°, which is quite different from

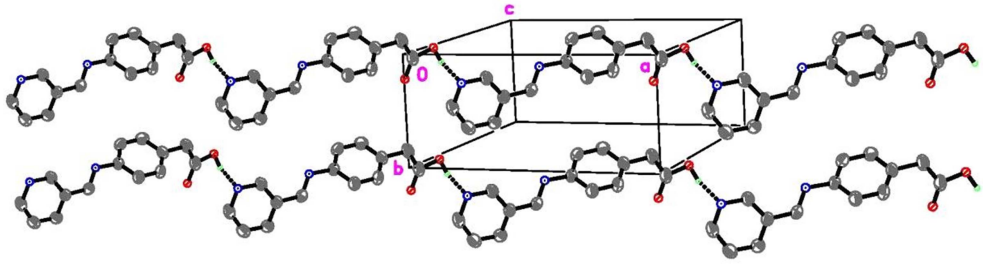


Figure 2. A 1-D network formed by O–H···N hydrogen bonds of compound **1**.

Table 3. Hydrogen bonds for compounds **1** and **2** (Å and °)

D–H···A	D–H	H···A	D···A	D–H–A
Compound **1**				
O1–HO1···N1#1	1.00(3)	1.70(3)	2.680(2)	164(3)
Compound **2**				
O1–HO1···N1#2	1.07(3)	1.57(3)	2.636(2)	173(2)

Symmetry transformations used to generate equivalent atoms: #1 = x + 1, y, z; #2 = x + 1/2, y + 3/2, z + 1/2.

that (48.87(5)°) found for compound **1**. The reason for the difference in the dihedral angles for compounds **1** and **2** is not clear. The torsion angle of C3–C6–N2–C7 is 179.8(2)°. The N2–C6 bond length (1.257(2) Å) corresponds to a C=N double bond. The N1···O1 and N1···O2 separations are 11.446(2) and 11.586(2) Å, respectively. Figure 4 shows a 1-dimensional hydrogen-bonded network in which the molecules are connected in the [101] direction by the O–H···N hydrogen bonds (Table 3). Whereas compounds **1** and **2** form a 1D network by intermolecular O–H···N hydrogen bonds, compound **3** forms a dimeric unit linked by a pair of symmetry-equivalent O–H···N hydrogen bonds.[26]

In summary, we prepared two new potential linking ligands by the simple and straightforward Schiff-base condensation: {(*n*-py)–CH=N–C_6H_4–CH_2–COOH} (n = 3 (**1**), 4 (**2**)). Both compounds contain a pyridyl terminal and a carboxylate terminal, and they are expected to be flexible due to the presence of an intervening methylene fragment that interrupts the π conjugation. Compounds **1** and **2** are structural isomers due to the different positions of the nitrogen atoms in the pyridyl terminal groups. Both compounds form a 1D network by intermolecular O–H···N hydrogen bonds.

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