# Syntheses and Structures of Two Metal-organic Frameworks Constructed from Zn/Ni and 3-Formyl-4-(pyridin-4-yl) Benzoic Acid Ligand (Postprint)

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## Abstract

Two metal-organic frameworks [(Zn0.5L) · (H2O)]n (1) and [(Ni0.5L) · (H2O)]n (2) constructed by the 3-formyl-4-(pyridin-4-yl) benzoic acid ligand (HL) were synthesized and characterized by single-crystal X-ray diffraction. 1 crystallizes in orthorhombic space group Pnna with a = 16.6152(8), b = 12.6825(6), c = 15.3908(8) Å, V = 3243.2(3) Å3, Z = 4, Mr = 511.12, Dc = 1.047 g/cm3, F(000) = 1048, = 1.144 mm-1, GOOF = 1.061, the final R = 0.0471 and wR = 0.1262 for 12168 observed reflections with I > 2 (I). 2 is isostructural to 1, which also crystallizes in orthorhombic space group Pnna with a = 16.6152(8), b = 12.6825(6), c = 15.3908(8) Å, V = 3243.2(3) Å3, Z = 4, Mr = 511.12, Dc = 1.047 g/cm3, F(000) = 1048, = 1.144 mm-1, GOOF = 1.061, the final R = 0.0471 and wR = 0.1262 for 12168 observed reflections with I > 2 (I). Additionally, thermogravimetric analysis, FT-IR spectroscopy and powder X-ray diffraction were discussed.

## Full Text

## Preamble

### Syntheses and Structures of Two Metal-Organic Frameworks Constructed from Zn/Ni and 3-Formyl-4-(pyridin-4-yl) Benzoic Acid Ligand

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## Abstract

Two metal-organic frameworks, [(Zn . L) • (H O)]  (1) and [(Ni . L) • (H O)]  (2), constructed from the 3-formyl-4-(pyridin-4-yl) benzoic acid ligand (HL), were synthesized and characterized by single-crystal X-ray diffraction. Compound 1 crystallizes in the orthorhombic space group Pnna with unit cell parameters a = 16.6152(8), b = 12.6825(6), c = 15.3908(8) Å, V = 3243.2(3) Å$^3$, Z = 4, M  = 511.12, Dc = 1.047 g/cm$^3$, F(000) = 1048,   = 1.144 mm $^1$, GOOF = 1.061, with final R = 0.0471 and wR = 0.1262 for 12168 observed reflections with I > 2 (I). Compound 2 is isostructural to 1, also crystallizing in orthorhombic space group Pnna with identical unit cell parameters: a = 16.6152(8), b = 12.6825(6), c = 15.3908(8) Å, V = 3243.2(3) Å$^3$, Z = 4, M  = 511.12, Dc = 1.047 g/cm$^3$, F(000) = 1048,   = 1.144 mm $^1$, GOOF = 1.061, and final R = 0.0471 and wR = 0.1262 for 12168 observed reflections with I > 2 (I). Additionally, thermogravimetric analysis, FT-IR spectroscopy, and powder X-ray diffraction were discussed.

**Keywords:** metal-organic frameworks; crystal structure; Zn; Ni; formyl
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## 1. Introduction

Metal-organic frameworks (MOFs) have attracted considerable attention over the past decades as a novel class of crystalline porous materials. MOFs are being actively investigated for diverse applications including gas storage and separation, catalysis, proton conduction, environmental monitoring, chemical sensing, ion exchange, drug delivery, and more. MOFs serve as excellent materials for organizing molecules in three-dimensional space, and installing complex functional moieties into MOF skeletons has led to rapid diversification of MOF structures.

Postsynthetic modification (PSM) represents a powerful method for tuning MOF composition, functionality, and porosity, and is becoming increasingly important for developing MOFs with functional groups that can modify pores or introduce sophisticated properties. PSM is an attractive functionalization strategy, particularly because the organic components of MOFs can be prefabricated to contain specific reactive groups (tags), enabling rational covalent PSM through diverse organic reactions developed by chemists. New PSM approaches continue to be sought to enrich the diversity and complexity of MOFs and to achieve enhanced performance and novel functions. However, a dilemma exists in this research area: on one hand, the group chosen as a MOF tag should not coordinate to metal ions and must be stable enough to survive MOF synthesis conditions; on the other hand, most MOFs have limited chemical stability, so the tag must be sufficiently active to enable PSM under mild conditions without destroying the MOF structure.

A potential limitation in this field is the chemical lability of the aldehyde group, which could be incompatible with MOF synthetic reactions. Here we report the synthesis of aldehyde-tagged MOFs 1 and 2 through direct solvothermal reactions. MOFs 1 and 2 were constructed using the 3-formyl-4-(pyridin-4-yl) benzoic acid ligand and characterized by single-crystal X-ray diffraction, thermogravimetric analysis, FT-IR spectroscopy, and powder X-ray diffraction.

## 2. Experimental

### 2.1 Materials and Apparatus

The ligand 4-bromo-3-formylbenzoic acid (HL) was synthesized according to literature procedures. The 3-formyl-4-(pyridin-4-yl) benzoic acid ligand was prepared in 65% yield via palladium-catalyzed Suzuki coupling between 4-pyridylboronic acid and 4-bromo-3-formylbenzoic acid. All other chemicals were commercially available and used without further purification. FT-IR spectra (KBr pellet, 400–4000 cm$^{1}$ region) were recorded on a Nicolet Magna 750 FT-IR spectrometer. Thermogravimetric analysis (TGA) was performed under N atmosphere at a heating rate of 10 °C min$^{1}$ using a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance diffractometer with CuK radiation at 40 kV, 40 mA.

### 2.2 Syntheses of 1 and 2

**2.2.1 Synthesis of 1** A mixture of Zn(NO ) ·6H O (8.9 mg, 0.03 mmol), 3-formyl-4-(pyridin-4-yl) benzoic acid (6.8 mg, 0.03 mmol), DMF (1 mL), and EtOH (0.5 mL) in a capped vial was heated at 80 °C for 48 hours. Prismatic crystals of 1 were filtered, washed sequentially with MeOH and Et O, and dried at room temperature. Yield: 29.3 mg (69%) based on [(Zn . L) · (H O)] . Anal. Calcd. for [(Zn . L) · (H O)] : C, 56.38; H, 3.64; N, 5.06%. Found: C, 56.40; H, 3.57; N, 5.10%. FT-IR (KBr pellet, /cm$^{1}$): 472 (m), 642 (w), 766 (m), 780 (s), 815 (m), 837 (m), 946 (m), 1010 (m), 1098 (m), 1192 (m), 1224 (m), 1243 (m), 1296 (m), 1374 (s), 1424 (s), 1554 (m), 1618 (s), 1699 (s), 2750 (w), 2860 (w), 2974 (w), 3065 (w).

**2.2.2 Synthesis of 2** A mixture of Ni(NO ) ·6H O (8.7 mg, 0.03 mmol), 3-formyl-4-(pyridin-4-yl) benzoic acid (6.8 mg, 0.03 mmol), DMF (1 mL), and EtOH (0.5 mL) in a capped vial was heated at 80 °C for 48 hours. Blue prismatic crystals of 2 were filtered, washed sequentially with MeOH and Et O, and dried at room temperature. Yield: 25.9 mg (61%) based on [(Zn . L) · (H O)] . Anal. Calcd. for [(Zn . L) · (H O)] : C, 57.07; H, 3.68; N, 5.12%. Found: C, 57.10; H, 3.75; N, 5.20%. FT-IR (KBr pellet, /cm$^{1}$): 472 (m), 648 (w), 766 (m), 784 (s), 821 (m), 838 (m), 948 (m), 1010 (w), 1100 (m), 1193 (m), 1224 (m), 1250 (m), 1303 (w), 1386 (s), 1420 (s), 1438 (s), 1529 (m), 1549 (m), 1581 (s), 1610 (s), 1697 (s), 2756 (w), 2848 (w), 2933 (w), 3185 (w), 3409 (w).

## 2.3 Crystallographic Measurements

Single-crystal XRD data for 1 and 2 were collected on a Bruker APEX-II CCD diffractometer with graphite-monochromated CuK  radiation (  = 1.54178 Å) at 123(2) K. The structures were solved by direct methods using SHELXS-2014 and refined with SHELXL-2014 via OLEX 2.032. All non-hydrogen atoms were refined anisotropically using full-matrix techniques, while hydrogen atoms were geometrically fixed at calculated positions, attached to their parent atoms, and treated as riding atoms. Contributions from highly disordered solvent molecules to the scattering were removed using the SQUEEZE routine of PLATON (Spek, A. L. J. Appl. Crystallogr. 2003, 36, 7), after which structures were refined again using the generated data. For 1 (CCDC-1547814), the final refinement converged at R = 0.0471 and wR = 0.1262 (w = 1/[ $^2(Fo^2) + (0.1071P)^2$], where P = $(Fo^2 + 2Fc^2)/3$), S = 1.061, (Δ/ )max = 0.001, (Δ )max = 0.199 and (Δ )min = -0.288 e/Å$^3$. For 2 (CCDC-1547815), the final refinement converged at R = 0.0471 and wR = 0.1262 (w = 1/[ $^2(Fo^2) + (0.1071P)^2$], where P = $(Fo^2 + 2Fc^2)/3$), S = 1.061, (Δ/ )max = 0.001, (Δ )max = 0.199 and (Δ )min = -0.288 e/Å$^3$.

The selected bond lengths and bond angles are given in Tables 1 and 2, respectively.

**Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for 1**

| Dist. | | Dist. |
|---|---|---|
| Zn(1)-O(1)#1 | 2.0457(15) | Zn(1)-O(1) |
| Zn(1)-O(2)#1 | 2.3223(17) | Zn(1)-O(2) |
| Zn(1)-N(1)#2 | 2.0599(19) | Zn(1)-N(1)#3 |

| Angle | | Angle |
|---|---|---|
| O(1)#1-Zn(1)-O(1) | 148.50(10) | O(1)#1-Zn(1)-O(2)#1 |
| O(1)-Zn(1)-O(2)#1 | 94.56(6) | O(1)-Zn(1)-O(2) |
| O(1)#1-Zn(1)-O(2) | 94.56(6) | O(1)#1-Zn(1)-N(1)#2 |
| O(1)-Zn(1)-N(1)#3 | 97.80(7) | O(1)-Zn(1)-N(1)#2 |
| O(1)#1-Zn(1)-N(1)#3 | 101.34(7) | N(1)#2-Zn(1)-O(2)#1 |
| N(1)#3-Zn(1)-O(2) | 155.33(7) | N(1)#3-Zn(1)-O(2)#1 |
| N(1)#2-Zn(1)-O(2) | 91.73(7) | N(1)#2-Zn(1)-N(1)#3 |
| O(2)-Zn(1)-O(2)#1 | 79.84(9) | |

Symmetry transformations: #1 -x+1/2, -y+1, z; #2 -x+1, y+1/2, z+1/2; #3 x-1/2, -y+1/2, z+1/2; #4 x+1/2, -y+1/2, z-1/2

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

| Dist. | | Dist. |
|---|---|---|
| Ni(1)-O(1) | 2.056(3) | Ni(1)-O(2) |
| Ni(1)-O(2)#1 | 2.157(3) | Ni(1)-N(1)#2 |
| Ni(1)-N(1)#3 | 2.030(4) | Ni(1)-O(1)#1 |

| Angle | | Angle |
|---|---|---|
| O(1)-Ni(1)-O(1)#1 | 157.4(2) | O(1)#1-Ni(1)-O(2)#1 |
| O(1)#1-Ni(1)-O(2) | 99.36(13) | O(1)-Ni(1)-O(2)#1 |
| O(1)-Ni(1)-O(2) | 63.00(13) | O(2)#1-Ni(1)-O(2) |
| N(1)#2-Ni(1)-O(1)#1 | 97.81(15) | N(1)#3-Ni(1)-O(1) |
| N(1)#2-Ni(1)-O(1) | 96.93(15) | N(1)#3-Ni(1)-O(1)#1 |
| N(1)#3-Ni(1)-O(2)#1 | 158.51(14) | N(1)#2-Ni(1)-O(2)#1 |
| N(1)#2-Ni(1)-O(2) | 158.51(14) | N(1)#3-Ni(1)-O(2) |
| N(1)#3-Ni(1)-N(1)#2 | 98.1(2) | |

Symmetry transformations: #1 -x+1/2, -y+1, z; #2 x-1/2, -y+1/2, z+1/2; #3 -x+1, y+1/2, z+1/2; #4 x+1/2, -y+1/2, z-1/2

## 3. Results and Discussion

### 3.1 Synthesis and Characterization of 1 and 2

As illustrated in Scheme 1, the 3-formyl-4-(pyridin-4-yl) benzoic acid ligand was synthesized in 65% yield from 4-bromo-3-formylbenzoic acid via palladium-catalyzed Suzuki coupling with 4-pyridylboronic acid. Compounds 1 and 2 were obtained through solvothermal reactions of Zn(II) and Ni(II) ions with 3-formyl-4-(pyridin-4-yl) benzoic acid, respectively. Phase purity was confirmed by comparing experimental and simulated X-ray powder diffraction patterns. After removal of guest solvents by solvent exchange followed by thermal activation under vacuum at 80 °C, both 1 and 2 retained their framework structures, as evidenced by powder XRD [Figure 1: see original paper]. The IR spectra of 1 and 2 [Figure 2: see original paper] show strong bands at approximately 1690 cm $^{1}$, characteristic of aldehyde (C=O) stretching vibrations. Thermogravimetric analysis [Figure 3: see original paper] reveals that both materials release solvent molecules upon heating to 200 °C, with framework decomposition beginning at approximately 350 °C.

### 3.2 Structural Descriptions

Compound 1 crystallizes in the orthorhombic space group Pnna, with the asymmetric unit comprising half a Zn(II) ion and one 3-formyl-4-(pyridin-4-yl) benzoic acid ligand. The Zn ion adopts a distorted octahedral coordination environment provided by nitrogen atoms from pyridine moieties of two ligands (Zn-

N bond length = 2.0599(19) Å) and two chelated carboxylate groups from two ligands (Zn–O bond lengths ranging from 2.0457(15) to 2.3223(17) Å) [Figure 4a: see original paper]. The Zn–N and Zn–O bond lengths are consistent with those reported for Zn(II)-based coordination polymers. Each ligand bridges two Zn(II) centers [Figure 4b: see original paper], resulting in each Zn being linked by four ligands and each ligand connecting two Zn centers to generate a three-dimensional diamondoid network. Two such 3D networks interpenetrate to form the final framework structure.

Isostructural with 1, compound 2 also crystallizes in orthorhombic space group Pnna, featuring Ni–N bond lengths of 2.030(4) Å and Ni–O bond lengths ranging from 2.056(3) to 2.157(4) Å. These metric parameters fall within the ranges reported for Ni(II)-based coordination polymers. The framework exhibits twofold interpenetration, as shown in [Figure 5: see original paper].

## 4. Conclusion

In summary, we have successfully synthesized two new metal-organic frameworks based on zinc and nickel with the 3-formyl-4-(pyridin-4-yl) benzoic acid ligand. Both compounds have been thoroughly characterized by single-crystal and powder X-ray diffraction, FT-IR spectroscopy, and thermogravimetric analysis. The presence of reactive aldehyde groups in these MOFs provides a versatile and convenient handle for postsynthetic modification, and further studies in this direction are currently underway.

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*Note: Figure translations are in progress. See original paper for figures.*