



A Two-Dimensional Supramolecular Layered Structure Constructed from Pyridine Carboxamide Molecule of 6-Bromo-*N*-(2-hydroxyphenyl)picolinamide

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In the course of our synthesis of luminescent materials based on benzoxazolyl-pyridine ligand, the 6-bromo-*N*-(2-hydroxyphenyl)picolinamide, C₁₂H₉N₂O₂Br (**III**), was obtained. It is a ring-opened structure of the initial 2-(6-bromopyridin-2-yl)benzo[*d*]oxazole ligand formed through a hydrolyzation reaction at the C-O bond of oxazole ring. It also could be seen as a condensation compound of *o*-aminophenol and 6-bromo-2-picolinic acid while these two aromatic ring parts show a little non-co-planar geometry in this crystal structure. Its asymmetric unit is just the whole pyridine-carboxamide molecule with *Z* = 8 in a unit cell. In the molecule, two intramolecular hydrogen bonding interactions could be found around the H_{acylamino}. Among the molecules, an aminophenol and an acylamino group of the neighbour molecule are fused *via* an obvious O-H...O hydrogen bond, thus a supramolecular chain structure is present. There is also π - π stacking interaction of pyridine and benzene rings between parallel stacking molecules. These hydrogen bonding and π - π stacking interactions, a supramolecular layer is constructed along the *ab* plane. In the unit cell, there are two supramolecular layers with ...ABAB... stacking model. Although the supramolecular connection fashion is same in these stacking layers, the directions of the molecular planes are different, exactly orthogonality, in A and B layer.

Keywords: Pyridine-carboxamide, 6-Bromo-*N*-(2-hydroxyphenyl)picolinamide, Supramolecular layers.

INTRODUCTION

The acylamino [-C(O)NH-] group, a key node and anchor in the first and second structures of proteins in the organism, is also an important ligand construction unit for coordination chemists¹. Up to date, it has been found that the acylamino group could present an anionic chelate model to many metal ions, such as copper², zinc³, silver⁴, iridium⁵ and so on, upon deprotonation of the carboxamide nitrogen atom. As a burgeoning class of multidentate ligands containing this group, pyridine carboxamides obviously have stronger coordination activity and could show more coordination fashion than those ligands containing acylamino group only, such as a neutral chelate model *via* N_{pyridyl} and O_{acylamino}^{6,7}, an anionic chelate model *via* N_{pyridyl} and N_{acylamino}⁸ and a dual chelate model *via* both of N_{pyridyl}, N_{acylamino} and O_{acylamino}^{9,10}. As a result of the presence of several N⁻ and O-coordinated sites, these ligands have also shown very good ability in the assembly of polynuclear complexes and received much attention along with its ability to stabilize metal ions in high oxidation states¹¹. Therefore, the pyridine carboxamide ligands have been widely

used to prepare a variety of metal complexes. Meanwhile, it is interesting that these complexes often show excellent characteristics in hydroxylation, epoxidation and asymmetric catalysts, NO deliver, molecular receptor, dendrimer synthesis and spin ground state control as well as magnetic interactions¹². In addition, these pyridine carboxamides can also been used as medicines themselves, such as C-Jun NH₂ terminal kinases inhibitors, IKK inhibitors and so on¹²⁻¹⁴.

Usually, pyridine carboxamides are prepared by condensation reactions from pyridyl-containing amine or carboxylic acid precursors, promoted by coupling agents such as 1,1'-carbonyldiimidazole, diphenoxy-phosphoryl azide or triphenyl phosphite¹. Matsushita *et al.*¹⁵ also reported that a series of smart cleavage reactions have been confirmed for constructing of the [-C(O)NH-] group as well the oxazole unit and two reaction conditions could be switched to obtain these two products. Of them, *N*-(2-hydroxyphenyl)picolinamide (**II**)^{15,16}, that is similar to the title compound except the absence of the bromine atom, has also been reported. In general, all the above-mentioned methods belong to the condensation reaction. While in this case, a new pyridine carboxamide

compound, 6-bromo-*N*-(2-hydroxyphenyl)picolinamide (**III**), is synthesized by a new route, a hydrolyzation ring-opened route, from corresponding oxazole compound.

EXPERIMENTAL

A mixture of europium nitrate (45 mg, 0.1 mmol), terephthalic acid (25 mg, 0.15 mmol), sodium hydroxide (12 mg, 0.3 mmol), 2-(6-bromopyridin-2-yl)benzo[*d*]oxazole (28 mg, 0.1 mmol) and ethanol/water (15 mL, 4:1 v/v) was heated at 398 K for 60 h in a sealed 25 mL Teflon-lined stainless steel vessel under autogenous pressure. The reaction mixture was then cooled slowly to room temperature, whereupon some yellow block crystals of (**III**) were obtained in a yield of 32 % (9 mg upon ligand). Anal. Calcd. for C₁₂H₉N₂O₂Br (%): C, 49.17; H, 3.09; N, 9.56; O, 10.92; found: C, 49.01; H, 3.46; N, 9.87; O, 11.26. Samples suitable for single-crystal X-ray diffraction were selected directly from the crop obtained from the reaction.

Single crystal X-ray diffraction analysis of compound

III: Yellow block crystals of C₁₂H₉N₂O₂Br belong to the monoclinic crystal system: *a* = 12.4800 (16) Å, *b* = 8.4343 (13) Å, *c* = 21.939 (3) Å, β = 95.201 (13)°, *V* = 2299.8 (6) Å³, *M* = 293.12, *d_x* = 1.693 mg/m³, *Z* = 8, *F*(000) = 1168, space group *C2/c*. Diffraction data were collected with ω scan mode at 293(2) K on an Oxford Xcalibur Gemini ultra CCD diffractometer (MoK_α, λ = 0.7107 Å) using the CrysAlis PRO¹⁷ software from a single crystal of 0.32 × 0.23 × 0.13 mm. Crystallographic and refinement data are given in Table-1. Empirical absorption were applied using multi-scan ABSCOR¹⁸. The structure was solved using direct methods and refined by full-matrix least-squares techniques with the programme package SHELXS97¹⁹. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added at calculated positions and refined using the riding model with *U*_{iso} = 1.2 times of that *U*_{eq} of the bounded atoms. The CIF file containing full information on the studied structure was deposited with CCDC under No. 965699. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/conts/retrieving.html> [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk].

RESULTS AND DISCUSSION

Here we report the structure of the title pyridine carboxamide compound **III**, which features a supra-molecular layered structure constructed *via* hydrogen bonding interactions in its crystal. The asymmetric unit of **III** just contains one molecule (Fig. 1). This molecule could be regarded as a bromine substituted *N*-(2-hydroxyphenyl)picolinamide (**II**)^{15,16}, or a derivant of *N*-phenyl-2-pyridinecarboxamide (**I**)²⁰ after a bromine and a hydroxyl substitution. The crystal structure of the compound **I** has been reported by Zhuang *et al.*²⁰ previously, but the crystal structure data of compound **II** has not been released yet. Thus, for studying the substituting effect around pyridine or benzene ring, it is worthy to compare and analysis the differences of the crystal structure data between compound **I** and **III**. Similar to that of compound **I**, the central [-C(O)NH-] group of compound **III** act as a good linkage

TABLE-1
CRYSTALLOGRAPHIC DATE AND REFINEMENT
PARAMETERS FOR COMPOUND **III**

| Parameter | Value |
|---|---|
| Empirical formula | C ₁₂ H ₉ N ₂ O ₂ Br |
| Molecular mass | 293.12 |
| Crystal system | Monoclinic |
| Space group | <i>C2/c</i> |
| <i>a</i> , <i>b</i> , <i>c</i> , Å | 12.4800 (16), 8.4343 (13), 21.939 (3) |
| β, (°) | 95.201 (13) |
| <i>V</i> , (Å ³) | 2299.8 (6) |
| <i>Z</i> | 8 |
| <i>D_x</i> , (g/m ³) | 1.693 |
| μ, (mm ⁻¹) | 3.57 |
| <i>F</i> (000) | 1168 |
| Crystal size, mm | 0.32 × 0.23 × 0.13 |
| θ Data collection range, (°) | 3.3-25.5 |
| Intervals of reflection indices | -14 ≤ <i>h</i> ≤ 15, -10 ≤ <i>k</i> ≤ 7, -20 ≤ <i>l</i> ≤ 26 |
| Measured/Independent reflections | 4547/2132 [<i>R</i> _{int} = 0.043] |
| Observed reflections [<i>I</i> > 2σ(<i>I</i>)] | 1533 |
| Parameters | 155 |
| Goodness of fit on <i>F</i> ² , <i>S</i> | 1.058 |
| <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> 1 = 0.0617, <i>wR</i> 2 = 0.1675 |
| <i>R</i> indices (all data) | <i>R</i> 1 = 0.0900, <i>wR</i> 2 = 0.1837 |
| Weighting scheme | <i>w</i> = 1/[σ ² (<i>F</i> _o) ² + (0.0963 <i>P</i>) ² + 4.5317 <i>P</i>] where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3 |
| Residual electron density (max/min), e/Å ⁻³ | -0.38/0.59 |
| CCDC | 965699 |
| Symmetry code: (i) <i>x</i> + 1/2, <i>y</i> - 1/2, <i>z</i> | |

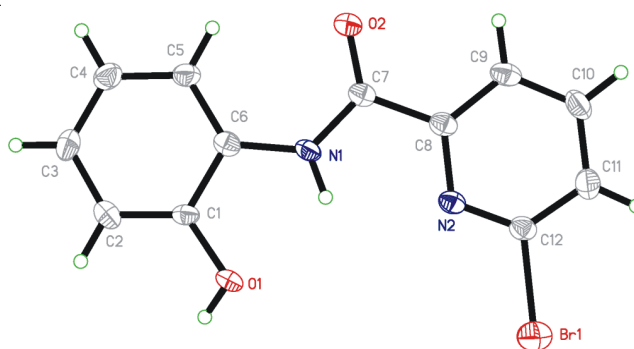


Fig. 1. Symmetric molecule structure of (**III**), with displacement ellipsoids drawn at the 30 % probability level and H atoms shown as small spheres of arbitrary radii

connecting a benzene ring and a pyridine ring system, which derives from *o*-aminophenol and 6-bromo-2-picolinic acid, respectively. Though all atoms of this molecule are almost coplanar, some dihedral angles could not be omitted among three conjugated partitions of the [-C(O)NH-] group and two ring systems of benzene and pyridine. The dihedral angle of the [-C(O)NH-] and benzene ring is 5.616° in this case, smaller than that in the compound **I** of 14.796°²⁰. The dihedral angle of the [-C(O)NH-] and pyridine ring is 3.435° in this case, also smaller than that in the compound **I** of 14.023°²⁰. These changes illustrate that the conjugation of the compound **III** should be better than that of (**I**) and should be induced by the substitution of a bromine or a hydroxyl at pyridine or benzene

ring. These changes could also be found in other -Br or -NO₂ substituted compounds^{21,22}. In addition, these substitution also make the bond lengths more equalization, that should reflect the expansion of the conjugation. The bond length of C-C between [-C(O)NH-] and pyridine is shorter here than that of (**I**), 1.4986 vs 1.5023 Å, similar to that of C-N between [-C(O)NH-] and benzene with 1.4060 vs 1.4102 Å²⁰. While the C-O and C-N bonds both elongate in this case, 1.2312 vs. 1.2238 Å and 1.3443 vs. 1.3438 Å, respectively.

As shown in Fig. 2, there are three obvious hydrogen bond interactions. The hydrogen-bonding data (Table-2) are in the range of ordinary examples and have been examined by the PLATON program^{23,24}. Two of them, hydrogen bonds of N1-H...O1 and N1-H...N2, are intramolecular. The other one, O1-H...O2i [symmetry code: (x + 1/2, y - 1/2, z)], is intermolecular and connects two neighbour molecules through an aminophenol and an acylamino group, so that a supra-molecular chain structure is formed. There is also π - π stacking interaction, which fused the adjacent supra-molecular chains to construct a supramolecular layer along the ab plane. The π - π stacking interaction is an offset face-to-face fashion concerning to adjacent pyridine (ring A) and benzene rings (ring B). The pyridine ring A (N2-C8-C9-C10-C11-C12) [symmetry code: (x, y, z)] is almost parallel (angel 5.717°) to the benzene ring B (C1-C2-C3-C4-C5-C6) [symmetry code: (-x, 1 - y, -z)] with a separation of about 3.3828 Å. Comparing with the previously reported case²⁵, the π - π stacking interaction should be strong here. In the unit cell, there are two supramolecular layers with ...ABAB... stacking model (Fig. 3). Although the supra-molecular connection fashion is same in these stacking layers, the directions of the molecular planes are different, exactly perpendicular each other, in A and B layer.

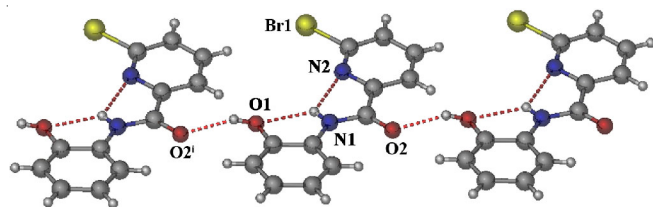


Fig. 2. Supramolecular chain for (**III**) constructed via hydrogen bonding interactions, which shown as dash line

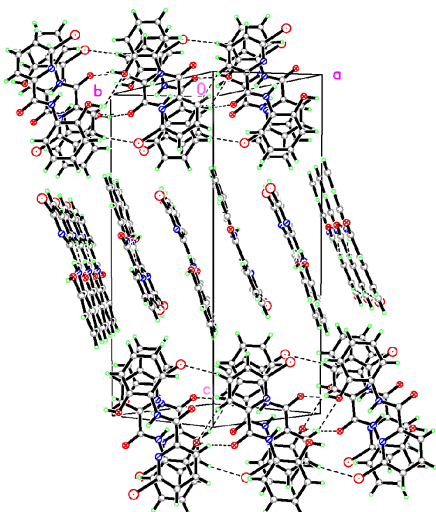


Fig. 3. A packing diagram for (**III**), viewed along the [110] direction

TABLE-2
HYDROGEN-BOND GEOMETRY (Å, °)

| D-H...A | D-H | H...A | D...A | D-H...A |
|--------------|------|-------|-----------|---------|
| O1-H1A...O2i | 0.82 | 2.00 | 2.709 (5) | 145 |
| N1-H1B...O1 | 0.86 | 2.19 | 2.609 (5) | 110 |
| N1-H1B...N2 | 0.86 | 2.21 | 2.660 (6) | 112 |

Conclusion

In summary, a pyridine-carboxamide compound, C₁₂H₉N₂O₂Br (**III**), has been synthesized and structurally characterized. It is a ring-opened structure of the initial 2-(6-bromopyridin-2-yl)benzo[d]oxazole ligand formed through a hydrolyzation reaction at the C-O bond of oxazole ring.

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