Inorg. Chem. **2007**, *46*, 5453–5455

Inorganic Chemistry
Communication

Unusual Oxidation of an N-Heterocycle Ligand in a Metal–Organic Framework

Zhangang Han,[†,‡] Yulong Zhao,[†] Jun Peng,*,[†] and Carlos J. Gómez-García[§]

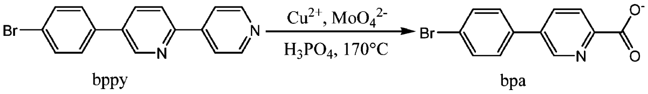
Key Laboratory of Polyoxometalate Science of Ministry of Education, Institute of Polyoxometalate Chemistry, Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, China, College of Chemistry & Material Science, Hebei Normal University, Shijiazhuang, Hebei 050016, China, and Instituto de Ciencia Molecular, Universidad de Valencia, Pol. La Coma, 46980 Paterna, Valencia, Spain

Received March 6, 2007

An in situ ligand reaction from the pyridine cycle to –COO$^-$ in the copper–organic framework is achieved under hydrothermal conditions. Compound $[Cu_2(bpa)_4]$ [**1**; bpa = 5-(4-bromophenyl)picolinic acid] exhibits a one-dimensional chain architecture based on weak Cu–O interactions. The mechanism of ligand transformation is discussed.

Recent studies have revealed that hydrothermal synthesis under pressure and at low temperatures (100−200°C) proves to be an effective method for in situ ligand synthesis. This strategy not only presents the opportunity to generate organic ligands that are difficult to synthesize but also represents a potential direction for the construction of new metal−organic frameworks (MOFs) through crystal engineering.[1] A variety of synthetic pathways were tested and completed successfully, including oxidation, reduction, and substitution reactions designed for preparing MOFs.[2] Examples of in situ ligand syntheses under hydrothermal conditions include hydrolysis of −CN and −COOR groups,[3] reduction of −COO$^-$,[4] hydroxylation,[5] C−C bond formation by reductive or oxidative coupling,[6] and cleavage and formation of disulfide bonds,[7] etc. In these examples, considerable attention has been placed on the investigation of copper complexes with organic N-heterocyclic ligands, which was mainly due to their attractive magnetic properties,[8] mixed-valence oxidation-state pairs, photoluminescence,[9] novel structural features, and biological relevance.[10] However, most of the exact mechanism of ligand transformation is not yet well-proven owing to the hydrothermal conditions. Chen and co-workers' experiments confirmed that coordination of bpy and phen to Cu ions is critical to their hydroxylation, which is also in agreement with the Gillard mechanism.[11]

Scheme 1. In Situ Generation of bpa from bppy



We report herein the in situ hydrothermal synthesis of 5-(4-bromophenyl)picolinic acid (bpa) from 5-(4-bromophenyl)-2-(pyridin-4-yl)pyridine (bppy) and its copper coordination polymer based on weak Cu^{II}−O interactions, formulated as $[Cu_2(bpa)_4]$ (**1**), which represents an unusual oxidation of a pyridine cycle of the ligand (see Scheme 1).

Crystals of **1** were obtained by hydrothermal reaction of $Cu(NO_3)_2$, Na_2MoO_4, H_3PO_4, and bppy. Single-crystal X-ray analysis[12] reveals that compound **1** consists of a one-dimensional chain architecture via weak Cu−O interactions.

---

* To whom correspondence should be addressed. E-mail: jpeng@nenu.edu.cn.

[†] Northeast Normal University.

[‡] Hebei Normal University.

[§] Universidad de Valencia.

(1) (a) Chen, X. M.; Tong, M. L. *Acc. Chem. Res.* **2006**, *40* (2), 162. (b) Zhang, X. M. *Coord. Chem. Rev.* **2005**, *249*, 1201. (c) Owen, R. E.; Xiong, R. G.; Wang, Z.; Wong, G. K.; Lin, W. *Angew. Chem., Int. Ed.* **1999**, *38*, 536. (d) Lu, J. Y. *Coord. Chem. Rev.* **200**3, *246*, 327.

(2) (a) Lu, J. Y.; Schauss, V. *Eur. J. Inorg. Chem.* **2002**, 1945. (b) Lu, J. Y.; Babb, A. M. *Inorg. Chem.* **2002**, *41*, 1339.

(3) (a) Li, W.; Owen, R. E.; Xiong, R. G.; Wang, Z. *J. Am. Chem. Soc.* **1998**, *120*, 13272. (b) Lin, W. B.; Wang, Z. Y.; Ma, L. *J. Am. Chem. Soc.* **1999**, *121*, 11249. (c) Evans, O. R.; Lin, W. B. *Chem. Mater.* **2001**, *13*, 3009.

(4) Feng, Y. H.; Han, Z. G.; Peng, J.; Hao, X. R. *J. Mol. Struct.* **2005**, *734*, 171.

(5) (a) Zhang, X. M.; Tong, M. L.; Chen, X. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1029. (b) Zhang, X. M.; Tong, M. L.; Gong, M. L.; Lee, H. K.; Luo, L.; Li, K. F.; Tong, Y. X.; Chen, X. M. *Chem.*−*Eur. J.* **2002**, *8*, 3187. (c) Tao, J.; Zhang, Y.; Tong, M. L.; Chen, X. M.; Yuen, T.; Lin, C. L.; Huang, X. Y.; Li, J. *Chem. Commun.* **2002**, 1342.

(6) (a) Liu, C. M.; Gao, S.; Kou, H. Z. *Chem. Commun.* **2001**, 1670. (b) Evans, R.; Lin, W. *Cryst. Growth Des.* **2001**, *1*, 9.

(7) (a) Han, L.; Bu, X.; Zhang, Q.; Feng, P. *Inorg. Chem.* **2006**, *45*, 5736. (b) Humphrey, S. M.; Mole, R. A.; Rawson, J. M.; Wood, P. T. *Dalton Trans.* **2004**, 1670.

(8) Lo, S. M. F.; Chui, S. S. Y.; Shek, L. Y.; Lin, Z.; Zhang, X.; Wen, G.; Williams, I. D. *J. Am. Chem. Soc.* **2000**, *122*, 6293.

(9) (a) Ford, P. C.; Cariati, E.; Bourassa, J. *Chem. Rev.* **1999**, *99*, 3625. (b) Chen, C. M.; Mao, Z.; Miskowski, V. M.; Tse, M. C.; Chan, C. K.; Cheung, K. K.; Phillips, D. L.; Leung, K. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 4084.

(10) (a) Iwata, S.; Ostermeier, C.; Ludwig, B.; Michel, H. *Nature* **1995**, *376*, 660. (b) Ferguson-Miller, S.; Babcock, G. T. *Chem. Rev.* **1996**, *96*, 2889.

(11) Gillard, R. D. *Coord. Chem. Rev.* **1975**, *16*, 67.

10.1021/ic700432p CCC: $37.00

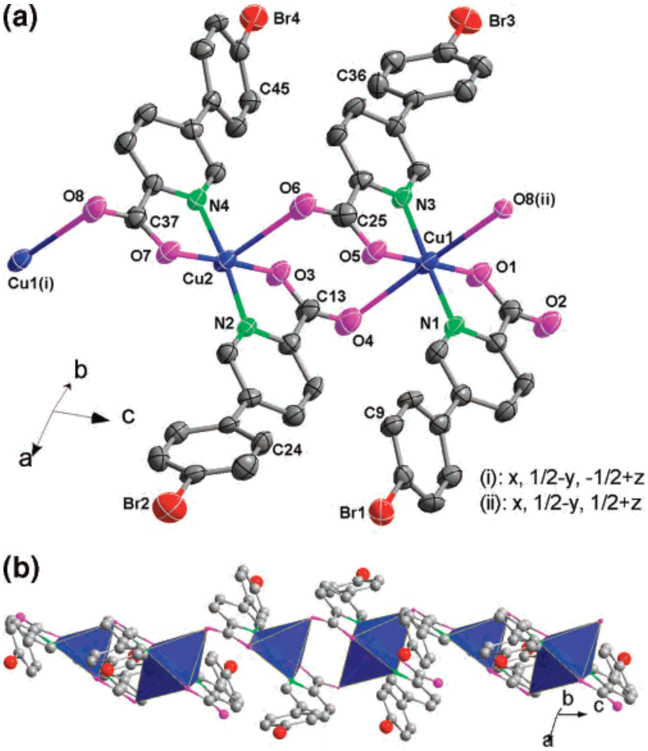


Figure 1. (a) Coordination environment of the Cu atoms in **1** with thermal ellipsoids set at 30% probability. (b) Polyhedral view of the chainlike structure formed via weak Cu–O interactions. All H atoms are omitted for clarity.

There are two crystallographically independent metal atom centers: Cu1 presenting an octahedral coordination and Cu2 with a square-pyramidal coordination (see Figure 1a). Cu1 is primarily coordinated to two O atoms and two N atoms of two bpa ligands in the equatorial plane, namely, Cu(bpa)$_2$. The bond lengths are Cu–N, 1.960(4) and 1.965(4) Å, and Cu–O, 1.928(3) and 1.942(3) Å. In the axial positions, Cu1 weakly interacts[13] with the O4 and O8 atoms [2.778(5) and 2.798(5) Å, respectively] from two other bpa ligands (the sum of the van der Waals radii of Cu and O is 2.92 Å),[14] leading to an axially distorted octahedral geometry for Cu1. The basal plane of Cu2 is defined by two N and two O atoms of two bpa ligands: Cu–N, 1.960(4) and 1.966(4) Å; Cu–O, 1.921(3) and 1.929(3) Å. The apical position is occupied by an O6 atom from another bpa with a bond length of 2.719(5) Å. Furthermore, Cu1 octahedra and Cu2 square pyramids alternately connect organic bpa ligands via weak Cu–O interactions extended along the *c* axis to form a one-dimensional stucture (Figure 1b).

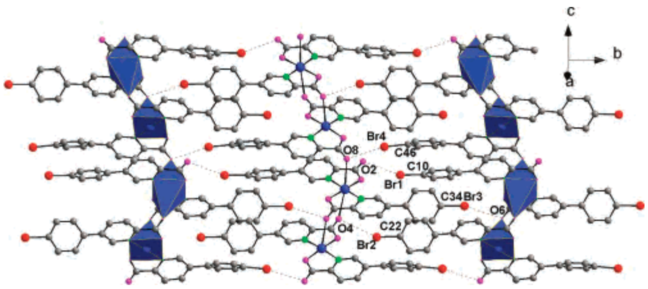


Figure 2. Two-dimensional structural view showing the intermolecular halogen bond C–Br···O interaction in **1**.

A series of crystal structures reported show that intermolecular halogen bonding (C–X···O, X = Cl, Br, or I) is a kind of useful synthon in the control of the stacking of crystalline lattices.[15–17] In compound **1**, the halogen Br···O bond lengths ranging from 3.163(4) to 3.168(3) Å, shown in Figure 2, are shorter than the sum of the van der Waals radii (1.85 Å for Br and 1.52 Å for O). The angles of the C–Br···O bonds are in the range of 151.5(1)–167.1(1)°. Thus, the O atoms meet the corresponding Br atoms roughly in line with the C–Br bond, which is consistent with an n → σ^* electron donation from O to Br.

It is surprising that compound **1** and the in situ synthesis of bpa are simultaneously generated under the hydrothermal reaction conditions. Many investigation results have pointed out that metal ions can promote the hydrolysis of polynitrogen heterocycles: Lerner and Lippard[18] first found that Cu^{II} in aqueous media promoted the hydrolysis of 2,4,6-tris-(2-pyridyl)-1,3,5-triazine (tptz) to a bis(2-pyridylcarbonyl)-amide anion (bpca); a similar hydrolysis reaction was also observed by Paul et al. upon reacting RhCl$_3$·3H$_2$O with tptz in refluxing ethanol–water;[19] Miguel et al. reported a series of complexes with Cu^{II}-assisted hydrolysis of tptz;[20] Bu et al. characterized Cu^{II}-promoted hydrolysis of 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (DPTZ) to 2,5-bis(2-pyridyl)-1,3,4-oxodiazole and *N*,*N*′-bis(α-hydroxyl-2-pyridyl)ketazine.[21] In all of these cases, none involves the ring opening of a

---

(12) Crystal data of **1**: C$_{48}$H$_{28}$Br$_4$Cu$_2$N$_4$O$_8$, M_r = 1235.45, monoclinic, space group $P2(1)/c$, a = 15.837(3) Å, b = 14.029(3) Å, c = 20.124(4) Å, β = 109.93(3)°, V = 4203.1(15) Å^3, Z = 4, F(000) = 2424, D_{calcd} = 1.952 Mg m^{-3}. The final statistics based on F^2 are GOF = 0.947, R1 = 0.0475, and wR2 = 0.0854 for $I > 2\sigma(I)$. The structure was solved by direct methods using *SHELXS-97* and refined by full-matrix least squares on F^2. All non-H atoms were anisotropically refined. H atoms were located from difference maps and refined with isotropic temperature factors. CCDC 629772 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(13) (a) Debord, J. B. D.; Haushalter, R. C.; Meyer, L. M.; Rose, D. J.; Zapf, P. J.; Zubieta, J. *Inorg. Chem. Acta* **1997**, *256*, 165. (b) Han, Z. G.; Ma, H. Y.; Peng, J.; Chen, Y. H.; Wang, E. B.; Hu, N. H. *Inorg. Chem. Commmun.* **2004**, *7*, 182.

(14) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(15) (a) Han, Z. G.; Zhao, Y. L.; Peng, J.; Tian, A. X.; Liu, Q.; Ma, J. F.; Wang, E. B.; Hu, N. H. *CrystEngComm* **2005**, *7*, 380. (b) Corradi, E.; Meille, S. V.; Messina, M. T.; Metrangolo, P.; Resnati, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 1782. (c) Han, Z. G.; Zhao, Y. L.; Peng, J.; Tian, A. X.; Feng, Y. H.; Liu, Q. *J. Solid State Chem.* **2005**, *178* (5), 1386.

(16) Vangala, V. R.; Nangia, A.; Lynch, V. M. *Chem. Commun.* **2002,** 1304.

(17) Chu, Q. L.; Wang, Z.; Huang, Q.; Yan, C.; Zhu, S. Z. *J. Am. Chem. Soc.* **2001**, *123*, 11069.

(18) (a) Lerner, E. I.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 5397. (b) Lerner, E. I.; Lippard, S. J. *Inorg. Chem.* **1977**, *16*, 1546.

(19) (a) Paul, P.; Tyagi, B.; Bhadbhade, M. M.; Suresh, E. *J. Chem. Soc., Dalton Trans.* **1997**, 2273. (b) Paul, P.; Tyagi, B.; Bilakhiya, A. K.; Bhadbhade, M. M.; Suresh, E. *J. Chem. Soc., Dalton Trans.* **1999**, 2009. (c) Paul, P.; Tyagi, B.; Bilakhiya, A. K.; Bhadbhade, M. M.; Suresh, E.; Ramachandraiah, G. *Inorg. Chem.* **1998**, *37*, 5733.

(20) (a) Castro, I.; Faus, J.; Julve, M.; Amigó, J. M.; Sletten, J.; Debaerdemaeker, T. *J. Chem. Soc., Dalton Trans.* **1990**, 891. (b) Cantarero, A.; Amigó, J. M.; Faus, J.; Julve, M.; Debaerdemaeker, T. *J. Chem. Soc., Dalton Trans.* **1988**, 2033. (c) Faus, J.; Julve, M.; Amigó, J. M.; Debaerdemaeker, T. *J. Chem. Soc., Dalton Trans.* **1989**, 1681.

(21) Bu, X. H.; Liu, H.; Du, M.; Zhang, L.; Guo, Y. M.; Shionoya, M.; Ribas, J. *Inorg. Chem.* **2002**, *41* (7), 1855.

pyridyl ring itself. As is well-known, the oxidation of pyridyl rings is more difficult than that of phenyl rings. The precursor bppy molecule consists of a bromophenyl and two pyridyl groups. However, in crystal **1**, a pyridyl ring was replaced by a carbonyl group. As an aromatic group, the cleavage of a 2-pyridin-4-yl group should be much more difficult than that of the single C−C bond between the two pyridyl groups in bppy. In addition, no other possible carboxyl source was present in the reaction mixture. To the best of our knowledge, this is the first example of pyridine cycle oxidation to $-COO^-$ reported in MOFs including multifunctional pyridine-containing ligands.

The coordination of the metal ion will cause some decrease of the electron density on the aromatic ring, hence activating the ligand. It is reasonable to postulate that an intermediate complex bppy−CuL_n may be formed during the conversion of bppy into bpa. As shown by a previous investigation, Cu^{II} can act as an oxidant under hydrothermal conditions, especially at neutral or basic pH.[1,2,22,23] However, the reaction reported here was performed under moderate acidic conditions, and the Cu centers in $[Cu_2(bpa)_4]$ still remained in the +2 oxidation state. Therefore, Cu^{II} is not a strong oxidant under the reaction conditions. A crystalline phase besides **1** was also observed, which was identified as a Keggin-type phosphomolybdate. As is well-known, polyoxometalates (POMs) are a kind of very important doubly functional reagent with oxidative and catalytic properties and have been shown to be of general interest as oxidative catalysts for heterogeneous and homogeneous phase oxidation reactions, such as iodosobenzene,[24] hydroperoxdide,[25] periodate,[26] *N*-oxide,[27] and oxydehydrogenation reactions,[28] and most recently the oxygenation of hydrocarbons.[29] During the course of reiterative experiments, we found that the absence of Cu^{2+} or MoO_4^{2-} in the reactions did not lead to the pba-containing products;[15a] no bpa was observed under the same hydrothermal conditions when other nitrates, such as cobalt and/or silver nitrate salts, instead of copper nitrate salt were used.[30] These experimental results indicated that both Keggin-type POMs and Cu^{2+} were necessary for the successful synthesis of **1**. Considering all of the points mentioned above, it is possible that a combination of several factors together, including the presence of valence-changeable POM and Cu^{2+} ions and the hydrothermal conditions of high temperature and pressure, leads to the oxidation of bppy to bpa. Further work to clarify this point is underway.

The magnetic measurement of compound **1** is in agreement with the presence of two Cu^{2+} ions per formula. Thus, the $\chi_m T$ product at room temperature is ca. 0.8 emu K mol^{-1}, as expected for two noninteracting Cu^{2+} ions ($S = {}^1/_2$). When the temperature is lowered, the $\chi_m T$ product remains constant down to low temperatures, indicating the absence of significant magnetic interactions between the Cu^{II} ions in the title compound.

In summary, an unusual oxidation of the pyridine ring is achieved in crystal **1**. The inorganic components in the reaction solution show interesting catalytic properties. This current work not only opens a new perspective for the application of pyridyl-based ligands in metal−organic chemistry but also may serve as a new bridge between coordination chemistry and synthetic organic chemistry.

Acknowledgment. This work was financially supported by the National Natural Science Foundation of China (Grant 20671016).

Supporting Information Available: Experimental section, a CIF file, IR of **1**, and ^1H NMR of bppy. This material is available free of charge via the Internet at http://pubs.acs.org.

IC700432P

---

(22) Gillard, R. D.; Hall, D. P. J. *Chem. Commun.* **1988**, 1163.

(23) Zhang, X. M.; Wu, H. S.; Chen, X. M. *Eur. J. Inorg. Chem.* **2003**, 2959.

(24) Weiner, H.; Hayashi, Y.; Finke, R. G. *Inorg. Chem.* **1999**, *38*, 2579.

(25) Mizuno, N.; Nozaki, C.; Kiyoto, I.; Misono, M. *J. Am. Chem. Soc.* **1998**, *120*, 9267.

(26) Zhang, X.; Sasaki, K.; Hill, C. L. *J. Am. Chem. Soc.* **1996**, *118*, 4809.

(27) Neumann, R.; Khenkin, A. M.; Dahan, M. *Angew. Chem.* **1995**, *107*, 1740; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1587.

(28) Neumann, R.; Levin, M. *J. Am. Chem. Soc.* **1992**, *114*, 7278.

(29) Khenkin, A. M.; Neumann, R. *Angew. Chem.* **2000**, *112*, 4254; *Angew. Chem., Int. Ed.* **2000**, *39*, 4088.

(30) Han, Z. G.; Zhao, Y. L.; Peng, J.; Ma, H. Y.; Liu, Q.; Wang, E. B.; Hu, N. H.; Jia, H. Q. *Eur. J. Inorg. Chem.* **2005**, *2*, 264.