Organic-Ligand-Supported Two-Dimensional Carbonyl-Bridged Copper(I) Polymers

Fu-Pei Liang,* Su-Ni Qin, Chun-Fang Jiang, Zhong Zhang, and Zi-Lu Chen

School of Chemistry and Chemical Engineering, Guangxi Normal University, Guilin 541004, Guangxi, People's Republic of China

Received July 2, 2007

Summary: Two carbonyl-bridged copper polymers, $[Cu_2(\mu\text{-}CO)L_2]_n$ (L = isonicotinate and nicotinate), have been synthesized by solvothermal reaction and structurally characterized. Both compounds contain a dicopper unit with one carbonyl bridge and two carboxylate bridges and have a two-dimensional network structure with carbonyl-bridged dicopper units as nodes and isonicotinate or nicotinate as connectors.

Introduction

Copper(I) carbonyl complexes have been extensively studied due to their importance in purification of industrial streams,[1] catalysis,[2] bioinorganic chemistry,[3] and understanding and refining the distinction between classical and nonclassical metal carbonyls.[4] The first evidence of copper(I) carbonyl complexes can be traced back to 150 years ago;[5] however, the crystal structure of this type of compounds was not reported until 1975, when M. I. Bruce et al. presented the structural characterization of the complex $\{Cu[HB(pz)_3](CO)\}$ ($HB(pz)_3^-$ = hydrotris(1-pyrazolyl)borate).[6] Since then, a variety of copper(I) carbonyls ranging from mononuclear species containing mono-,[7] di-, tri-, and tetracarbonyls[8] to di-,[9] tri-, and tetranuclear complexes,[10] and then to polymers[11] have been prepared and structurally characterized. Most of the structurally known copper(I) carbonyls are terminal CO-bonded species, and those with CO bridging two copper(I) atoms, which is believed to be of interest for metal-promoted CO activation, are extremely rare. Only three carbonyl-bridged dinuclear copper complexes, $[Cu_2(NN)_2(\mu\text{-}PhCO_2)(\mu\text{-}CO)][BPh_4]$ (NN = *N*,*N*,*N*′,*N*′-tetramethylpropylenediamine or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine)[12] and $[Cu_2(NN)_2(C_4O_4)(\mu\text{-}CO)]$ (NN = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine),[13] have been reported so far. All of these copper(I) carbonyls bear a dicopper skeleton with one carbonyl bridge and one carboxylate bridge (skeleton A) and are stabilized by additional chelating diamine ligands.

On the other hand, only a limited number of copper(I) coordination polymers containing a Cu−CO unit have been

---

* To whom correspondence should be addressed. E-mail: fliangoffice@yahoo.com.

[1] (a) Otmer, K. *Encyclopedia of Chemical Technology*, 4th ed.; J. Wiley: New York, 1993; Vol. 5, pp 110. (b) Peng, X. D.; Golden, T. C.; Pearlstein, R. M.; Pierantozzi, R. *Langmuir* **1995**, *11*, 534. (c) Capracotta, M. D.; Sullivan, R. M.; Martin, J. D. *J. Am. Chem. Soc.* **2007**, *128*, 13463.

[2] (a) Waugh, C. K. *Catal. Today* **1992**, *15*, 51. (b) Solomon, E. I.; Jones, P. M.; Maj, J. A. *Chem. Rev.* **1993**, *93*, 2623.

[3] (a) Hosler, J. P.; Kim, Y.; Shapleigh, J.; Gennis, R.; Alben, J.; Ferguson-Miller, S.; Babcock, G. *J. Am. Chem. Soc.* **1994**, *116*, 5515. (b) Kretzer, R. M.; Ghiladi, R. A.; Lebeau, E. L.; Liang, H.-C.; Karlin, K. D. *Inorg. Chem.* **2003**, *42*, 3016. (c) Zhou, L.; Powell, D.; Nicholas, K. M. *Inorg. Chem.* **2006**, *45*, 3840. (d) Kujime, M.; Kurahashi, T.; Tomura, M.; Fujii, H. *Inorg. Chem.* **2007**, *46*, 541.

[4] (a) Lupinetti, A. J.; Jonas, V.; Thiel, W.; Strauss, S. H.; Frenking, G. *Chem.−Eur. J.* **1999**, *5*, 2573. (b) Strauss, S. H. *J. Chem. Soc., Dalton Trans.* **2000**, 1.

[5] (a) Leblanc, F. *C. R. Acad. Sci. Paris* **1850**, *30*, 483. (b) Berthelot, M. *Ann. Chim. Phys.* **1856**, *346*, 477.

[6] Churchill, M. R.; DeBoer, B. G.; Rotella, F. J.; Abu Salah, O. M.; Bruce, M. I. *Inorg. Chem.* **1975**, *14*, 2051.

[7] (a) Kläul, W.; Lenders, B.; Hessner, B.; Evertz, K. *Organometallics* **1988**, *7*, 1357. (b) Kitajima, M.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277. (c) Ardizzoia, G. A.; Beccalli, E. M.; La Monica, G.; Masciocchi, N.; Moret, M. *Inorg. Chem.* **1992**, *31*, 2706. (d) Reger, D. L.; Collins, J. E.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **1996**, *15*, 2029. (e) Kiani, S.; Long, J. R.; Stavropoulos, P. *Inorg. Chim. Acta* **1997**, *263*, 357. (f) Imai, S.; Fujisawa, K.; Kobayashi, T. Shirasawa, N.; Fujii, H.; Yoshimura, T.; Kitajima, N.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 3066. (g) Conry, R. R.; Ji, G.-Z.; Tipton, A. A. *Inorg. Chem.* **1999**, *38*, 906. (h) Shimazaki, Y.; Nogami, T.; Tani, F.; Odani, A.; Yamauchi, O. *Angew. Chem., Int. Ed.* **2001**, *40*, 3859. (i) Dias, H. V. R.; Singh, S. *Inorg. Chem.* **2004**, *43*, 5786. (j) Dias, H. V. R.; Goh, T. K. H. H. *Polyhedron* **2004**, *23*, 273. (k) Chou, C.-C.; Su, C.-C.; Yeh, A. *Inorg. Chem.* **2005**, *44*, 6122. (l) Dias, H. V. R.; Singh, S.; Flores, J. A. *Inorg. Chem.* **2006**, *45*, 8859. (m) Hill, L. M. R.; Gherman, B. F.; Aboelella, N. W.; Cramer, C. J.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2006**, 4944. (n) Kanishita, A.; Osako, T.; Tachi, Y.; Teraoka, J.; Itoh, S. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1729.

[8] (a) Rack, J. J.; Webb, J. D.; Strauss, S. H. *Inorg. Chem.* **1996**, *35*, 277. (b) Polyakov, O. G.; Ivanova, S. M.; Gaudinski, C. M.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *Organometallics* **1999**, *18*, 3769. (c) Ivanova, S. M.; Ivanov, S. V.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorg. Chem.* **1999**, *38*, 3756.

[9] (a) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* **1981**, *20*, 3382. (b) Gagne, R. R.; Kreh, R. P.; Dodge, J. A.; Marsh, R. E.; McCool, M. *Inorg. Chem.* **1982**, *21*, 254. (c) Villacorta, G. M.; Lippard, S. J. *Inorg. Chem.* **1987**, *26*, 3672. (d) Patch, M. G.; Choi, H.-K.; Chapman, D. R.; Bau, R. McKee, V.; Reed, C. A. *Inorg. Chem.* **1990**, *29*, 110. (e) Karlin, K. D.; Tyeklár, Z.; Farooq, A.; Haka, M. S.; Ghosh, P.; Cruse, R. W.; Gutneh, Y.; Hayes, J. C.; Toscano, P. J.; Zubieta, J. *Inorg. Chem.* **1992**, *31*, 1436. (f) Schindler, S.; Szalda, D. J.; Creutz, C. *Inorg. Chem.* **1992**, *31*, 2255. (g) Solari, E.; Latronico, M.; Blech, P.; Floriani, C. *Inorg. Chem.* **1996**, *35*, 4526. (h) Lopes, C.; Håkansson, M.; Jagner, S. *Inorg. Chem.* **1997**, *36*, 3232. (i) Mahapatra, S.; Kaderli, S.; Llobet, A.; Neuhold, Y.-M.; Palanche, T.; Halfen, J. A.; Young Junior, V. G.; Kaden, T. A.; Que Junior, L.; Zuberbühler, A. D.; Tolman, W. B. *Inorg. Chem.* **1997**, *36*, 6343. (j) Polyakov, O. G.; Nolan, B. G.; Fauber, B. P.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **2000**, *39*, 1735. (k) Costas, M.; Xifra, R.; Llobet, A.; Sola, M.; Robles, J.; Parella, T.; Stoeckli-Evans, H.; Neuburger, M. *Inorg. Chem.* **2003**, *42*, 4456.

[10] (a) Geerts, R. L.; Huffman, J. C.; Folting, K.; Lemmen, T. H.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 3503. (b) Floriani, C.; Fiaschi, P.; Chiesi-Villa, A.; Guastini, C.; Zanazzi, P. F. *J. Chem. Soc., Dalton Trans.* **1988**, 1607. (c) Singh, K.; Long, J. R.; Stavropoulos, P. *Inorg. Chem.* **1998**, *37*, 1073.

[11] (a) Doyle, G.; Eriksen, K. A.; van Engen, D. *Inorg. Chem.* **1983**, *22*, 2892. (b) Håkansson, M.; Jagner, S. *Inorg. Chem.* **1990**, *29*, 5241. (c) Kitagawa, S.; Matsuyama, S.; Munakata, M.; Emori, T. *J. Chem. Soc., Dalton Trans.* **1991**, 2869. (d) Dell'Amico, D. B.; Alessio, R.; Calderazzo, F.; Pina, F. D.; Englert, U.; Pampaloni, G.; Passarelli, V. *J. Chem. Soc., Dalton Trans.* **2000**, 2067. (e) Dell'Amico, D. B.; Calderazzo, F.; Labella, L.; Lorenzini, F.; Marchetti, F. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1868. (f) Wiles, A. B.; Pike, R. D. *Organometallics* **2006**, *25*, 3282.

[12] (a) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Guastini, C. *J. Am. Chem. Soc.* **1981**, *103*, 185. (b) Pasquali, M.; Floriani, C.; Venturi, G.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **1982**, *104*, 4092.

[13] Doyle, G.; Eriksen, K. A.; Modrick, M.; Ansell, G. *Organometallics* **1982**, *1*, 1613.

10.1021/om700662h CCC: $37.00

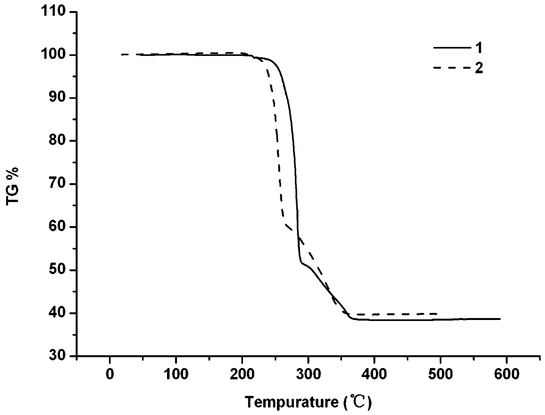

Figure 1. TGA traces of **1** and **2**.

structurally characterized. All reported copper(I) carbonyl polymers with polydentate ligands, either with N-containing bridging ligands such as diazabicyclo[2.2.2]octane, piperazine, *N*,*N*′-dimethypiperazine, and 1,2-di-2-pyridylethylene[11c,f] or with polyoxygen anions such as ethyl sulfonate, hydrogen sulfate, and trichloroacetate,[11a,d,e] exhibit chain structures. Only [CuCl(CO)]$_n$, a compound without a supporting organic ligand, shows a hexagonal honeycomb layer structure,[11b] and it represents the only reported two-dimensional copper(I) carbonyl polymer.

We present herein the syntheses and structures of two unprecedented two-dimensional copper(I) carbonyl polymers, [$Cu_2(\mu$-CO)L_2]$_n$ (L = isonicotinate (INA, **1**), nicotinate (NA, **2**)). Both compounds display a new dicopper skeleton with one carbonyl bridge and two carboxylate bridges (skeleton B). Furthermore, they are the first example of a coordination polymer containing carbonyl-bridged copper units, as well as the first example of an organic-ligand-supported two-dimensional copper(I) carbonyl polymer.

Results and Discussion

Solvothermal synthesis has been extensively used to produce metal coordination compounds;[14] however, as far as we know, such a synthetic approach has never been used in the preparation of copper(I) carbonyls. By a solvothermal synthesis procedure, we obtained successfully two new copper(I) carbonyl polymers. Reaction of $Cu(MeCO_2)_2$, $Mo(CO)_6$, and isonicotinic acid or nicotinic acid in a molar ratio of 3:2:5 in a mixed solvent of H_2O and THF at 60 °C for 3 days afforded crystals of **1** or **2** in moderate yield. The two compounds have been characterized by elemental analysis, IR spectroscopy, thermal analysis, and X-ray single-crystal structural analysis. The phase purities of the two compounds were confirmed by similarities between their simulated and experimental powder X-ray diffraction (Figures S1 and S2). The infrared spectra of the compounds show a strong peak at 1950 cm^{-1} for **1** and 1946 cm^{-1} for **2**, corresponding to the vibration of the bridging CO. A series of peaks at 1604, 1592, 1546, 1392 cm^{-1} and 1615, 1591, 1565, 1390 cm^{-1} for **1** and **2**, respectively, due to the vibrations related to the organic ligands, are observed. **1** and **2** are quite stable in air. The thermal analyses of **1** and **2** in air atmosphere (Figure 1) show that both complexes decompose in two separate stages.

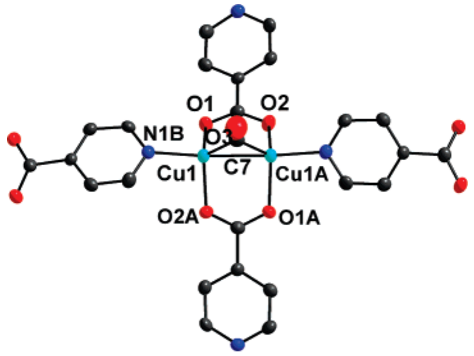

Figure 2. View of the coordination environment of copper in **1**. Selected bond lengths (Å) and angles (deg): Cu1−O1 2.065(3); Cu1−O2A 2.055(3); Cu1−N1B 2.000(4); Cu1−C7 1.915(7); Cu1−Cu1A 2.4036(11); C7−O3 1.131(9); O1−Cu1−C7 114.65(12); O1−Cu1−O2A 112.50(14); N1B−Cu1−O2A 98.25(14); N1B−Cu1−C7 118.6(2). Symmetry codes: (A) $-x+2$, y, $-z+3/2$; (B) $x+1/2$, $-y+1/2$, $-z+1$.

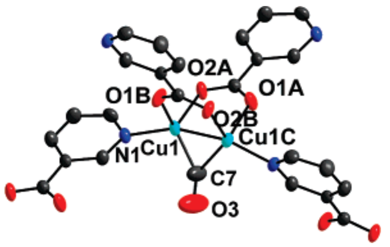

Figure 3. View of the coordination environment of copper in **2**. Selected bond lengths (Å) and angles (deg): Cu1−O1B 2.064(4); Cu1−O2A 2.045(4); Cu1−N1 1.989(4); Cu1−C7 1.894(8); Cu1−Cu1C 2.384(2); C7−O3 1.118(10); O1B−Cu1−C7 114.19(16); O1B−Cu1−O2A 102.67(17); N1−Cu1−O2A 108.49(17); N1−Cu1−C7 110.7(2). Symmetry codes: (A) $x-1/2$, $y+1/2$, z; (B) $-x+1/2$, $y+1/2$, $-z+1/2$; (C) $-x$, y, $-z+1/2$.

Compound **1** begins to decompose at 226 °C and loses 47.8% of its weight in the first stage in the range 226−288 °C and 13.7% in the second stage in the range 228−365 °C. The decomposition of **2** starts at 213 °C. It loses 39.5% of its weight in the first stage in the range 213−266 °C and 20.7% in the second stage in the range 266−355 °C. The remaining weights of 38.5% and 39.8% for **1** and **2**, respectively, correspond to the final residual of CuO (calc 39.8%).

The single-crystal X-ray structural analyses reveal that compound **1** crystallizes in the orthorhombic space group *Pbcn*, while compound **2** crystallizes in monoclinic *C*2/*c*. Both complexes have a two-dimensional network consisting of dimeric copper units bridged by a carbonyl and two carboxylate groups. Figures 2 and 3 show the coordination structures of the dimeric copper units of **1** and **2**, respectively. The copper ions are all four-coordinated by the carbon atom of the bridging carbonyl, the pyridyl nitrogen atom of a INA or NA ligand, and two carboxylate oxygen atoms from two organic ligands. Taking no account of the Cu−Cu interaction, the coordination geometry about the copper atom may be represented as a distorted tetrahedron. The Cu−O distances of 2.065(3), 2.055(3) Å for **1** and 2.064(4), 2.045(4) Å for **2**, as well as the Cu−C distances of 1.915(7) and 1.894(8) Å for **1** and **2**, respectively, are all longer compared to those found for the carbonyl-bridged dinuclear copper complexes with only one carboxylate bridge reported previousy,[12,13] which can be ascribed apparently to the increasing steric interaction between bridging ligands with the increase of the ligand bridge from skeleton A to B. Additionally, the Cu−C elongation can also be attributed to the electronic

---

[14] (a) Kesanli, B.; Lin, W. *Coord. Chem. Rev.* **2003**, *246*, 305. (b) Gao, H.-L.; Yi, L.; Zhao, B.; Zhao, X.-Q.; Cheng, P.; Liao, D.-Z.; Yan, S.-P. *Inorg. Chem.* **2006**, *45*, 5980. (c) Rowsell, J. L. C.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 1304. (d) Quellette, W.; Prosvirin, A. V.; Chieffo, V.; Dunbar, K. R.; Hudson, B.; Zubieta, J. *Inorg. Chem.* **2006**, *45*, 9346. (e) Cheng, L.; Zhang, W.-X.; Ye, B.-H.; Lin, J.-B.; Chen, X.-M. *Inorg. Chem.* **2007**, *46*, 1135.

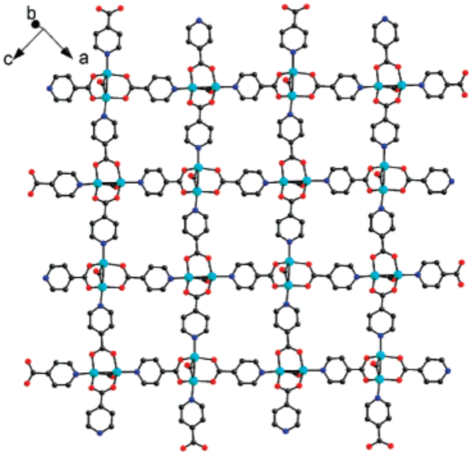

Figure 4. View of the two-dimensional network of **1**.

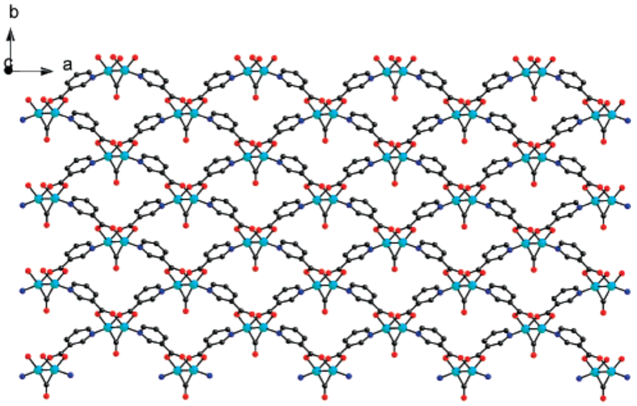

Figure 5. View of the two-dimensional network of **2**.

effect relating to the back-bonding of Cu to the CO ligand. The weaker back-bonding of Cu to CO, as indicated by the higher CO stretching frequencies compared to that in the compounds in refs 12 and 13, leads to a longer Cu−C separation in compounds **1** and **2**. Consistent with the trend of the Cu−C bond elongation, the C−O distances of the CO ligands in the two compounds are shorter than those in the complexes mentioned above. The Cu−Cu distances are very short due to a triple bridging interaction between the two copper atoms: Cu1−Cu1A = 2.4036(11) Å in **1**, Cu1−Cu1C = 2.384(2) Å in **2**. These distances are considerably shorter than that in copper metal (2.55 Å), indicating the existence of a copper−copper bonding interaction.[13,15]

Both INA and NA function as a μ_3-bridging ligands. Connection of each dimeric copper unit to four adjacent dimeric copper units via four INA or NA ligands forms a two-dimensional network of **1** or **2**, as shown in Figures 4 and 5. Differences between the structures of the two-dimensional networks of **1** and **2** due to the difference of the positions of the coordination sites in INA and NA are obvious. Viewed along the *b*-axis, compound **1** exihibts a square grid network with grid dimensions of 9.803 × 9.803 Å. The dimeric copper units in the network are not located in one plane but approximately 1.7 Å apart. The adjacent dicopper units are perpendicularly oriented to each other along the Cu−Cu direction. The bridging carbonyl ligands orient alternatively in two opposite directions parallel to the crystallographic *b*-axis, that is, perpendicular to the plane on which the dicopper unit lies. Compound **2** displays a rhombohedral grid network in the *a,b*-plane with grid dimensions of approximately 8.0 × 8.0 Å. All dimeric copper units are in one plane and are parallel to each other in the Cu−Cu orientation running in the direction of the *a*-axis. The bridging carbonyl ligands are also parallel to each other, and each points to the center of a rhombohedral grid in the direction of the inverted *b*-axis.

Table 1. Crystal and Structure Refinement Data for Complexes 1 and 2

	1	2
empirical formula	$C_{13}H_8Cu_2N_2O_5$	$C_{13}H_8Cu_2N_2O_5$
fw	399.29	399.29
cryst syst	orthorhombic	monoclinic
space group	*Pbcn*	*C*2/*c*
a (Å)	13.728(3)	13.668(14)
b (Å)	7.050(2)	8.401(9)
c (Å)	13.559(3)	12.406(13) A
β (deg)	90	96.961(13)
V (Å^3)	1312.2(6)	1414(2)
Z	4	4
calcd density (mg·m^{-3})	2.021	1.876
absorp coeff (mm^{-1})	3.267	3.031
T (K)	298(2)	298(2)
θ range (deg)	2.97 to 25.01	2.85 to 25.00
limiting indices (*h*, *k*, *l*)	−16, 15; −6, 8; −13, 16	−16, 16; −9, 9; −12, 14
no. of reflns collected	6186	3517
no. of indep reflns	1160 [R_{int} = 0.0606]	1242 [R_{int} = 0.0481]
R (data with $I > 2\sigma(I)$)	$R_1 = 0.0328$ $wR_2 = 0.0746$	$R_1 = 0.0381$ $wR_2 = 0.0859$
goodness-of-fit on F^2	0.999	1.040
F(000)	792	792
no. of restraints/params	0/101	6/101
largest peak and hole (e·Å^{-3})	0.363, −0.325	0.692, −0.612

In conclusion, 2-D coordination polymers with a new carbonyl-bridged dicopper skeleton supported by two organic bridging ligands have been successfully synthesized by solvothermal reaction. The new carbonyl-bridged dicopper skeleton is of substantial interest for structural models in understanding the mechanism of copper-promoted activation of CO and other small molecules, and the results could have important implications in the construction of microporous coordination polymers with reactive or catalytic sites. Further synthesis of analogues with other organic bridging ligands and the properties and utility of these types of compounds are the subject of ongoing study.

Experimetal Section

Materials and Methods. All the starting materials were purchased commercially as reagent grade and used without further purification. Elemental analyses were performed on a Perkin-Elmer 2400 II elemental analyzer. IR spectra were obtained in KBr pellets on a Nicolet 360 FTIR spectrometer in the range 4000−400 cm^{-1}. Thermogravimetric analyses were carried out in air using a Perkin-Elmer Thermal TGA7 at a heating rate of 10 °C·min^{-1}.

Synthesis of 1. Isonicotinic acid (0.0308 g, 0.25 mmol) was dissolved in water (3 mL), and the pH of the solution was adjusted to ca. 6 with NaOH solution (0.5 M), to which $Mo(CO)_6$ (0.0264 g, 0.1 mmol) dissolved in THF (10 mL) and $Cu(CH_3COO)_2{\cdot}H_2O$ (0.0300 g, 0.15 mmol) dissolved in water (2 mL) were added. The resulting solution was transferred and sealed in a 25 mL Teflon-lined stainless steel vessel, heated at 60 °C for 3 days, and then cooled to room temperature. Light green crystals of **1** were harvested in a yield of 38% based on Cu. Anal. Calcd for **1**, $C_{13}H_8Cu_2N_2O_5$: C, 39.10; H, 2.02; N, 7.01. Found: C, 38.76; H, 2.09; N, 7.11. IR (KBr, cm^{-1}): 1950s, 1604s, 1592s, 1546s, 1392s, 774m, 696m.

Synthesis of 2. The compound was prepared by the same method described for **1** using nicotinic acid (0.0308 g, 0.25 mmol) instead

---

(15) Kölmel, C.; Ahlrichs, R. *J. Phys. Chem.* **1990**, *94*, 5536.

of isonicotinic acid. Yield: 45%. Anal. Calcd for **2**, $C_{13}H_8Cu_2N_2O_5$: C, 39.10; H, 2.02; N, 7.01. Found: C, 38.89; H, 1.97; N, 7.24. IR data (KBr, cm^{-1}): 1946s, 1615s, 1591s, 1565s, 1390s, 755m.

Single-Crystal Structure Determination. Suitable single crystals of complexes **1** and **2** were selected and mounted in air onto thin glass fibers. X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer at 298(2) K using Mo Kα radiation ($\lambda = 0.71073$ Å) by the $\varphi-\omega$ scan mode. The program SAINT was used for integration of the diffraction profiles. The structures were solved by direct methods using the SHELXS-97 program package and refined against F^2 by full-matrix least-squares methods with SHELXL-97. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were set in calculated positions and refined as riding atoms. Crystallographic data and processing parameters are listed in Table 1.

Acknowledgment. We are grateful for financial support from the National Natural Science Foundation of China (No. 20461001) and Guangxi Natural Science Foundation (No. 0639031).

Supporting Information Available: CIF files giving X-ray crystallographic data and PXRD patterns for complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700662H