DOI: 10.1002/zaac.201300223

Syntheses, Structures, and Catalytic Activities of Copper(I) Complexes with the Ligand 2(4,5-Diphenyl-1H-imidazol-2-yl)pyridine

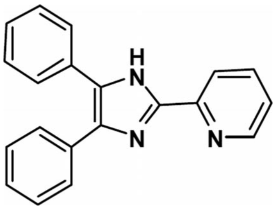
Hua Yang,[a,b] Yonglu Liu,[c] and Dao-Dao Hu*[a]

Keywords: Copper; Structures; Catalysis; IR spectroscopy; X-ray diffraction

Abstract. Two copper(I) complexes of compositions $[Cu(HL)I]_2{\cdot}EtOH$ (**1**) and $[Cu(HL)_3]I{\cdot}MeOH$ (**2**) were synthesized via the reactions of HL [HL = 2(4,5-diphenyl-1*H*-imidazol-2-yl)pyridine] and CuI in EtOH and MeOH, respectively, under solvothermal conditions. The complexes were characterized by X-ray single crystal diffraction, IR spectroscopy, and elemental analysis. Compounds **1** and **2** are catalytically active towards ketalization reaction, giving various ketals under mild conditions.

Introduction

The coordination chemistry of Cu^I complexes has attracted intense attention in recent years.[1–4] The most important factors are: (i) development of biologically active Cu^I precursors, which serve as 1e shuttles, alternating between Cu^I and Cu^{II}, and facilitating a series of biological reactions;[5–7] (ii) application of Cu^I complexes as favorable alternatives to the polypyridine Ru^{II} compounds that have been extensively utilized in molecular solar energy conversion devices and for molecular sensing;[8–11] (iii) employment of Cu^I complexes as inexpensive and environmentally benign catalysts to catalyze a variety of organic reactions.[12–14] While pyrazolates,[15] bis(pyrazolyl)borate,[16] derivatives of phenanthroline,[17] imidazole,[18] and pyridine[19] are widely used as ligands to construct Cu^I complexes, 2(4,5-diphenyl-1*H*-imidazol-2-yl)pyridine (HL, Scheme 1),[20] which is a combination of imidazole and pyridine, has never been employed to prepare Cu^I complexes. The use of HL has previously given a handful of Pd^{II},[21] Ru^{II},[22] Ni^{II},[23] and Ti^{IV}[20] complexes. It was assumed that a number of Cu^I complexes might be available and reactions of Cu^I and HL were conducted, which yielded the complexes $[Cu(HL)I]_2{\cdot}EtOH$ (**1**) and $[Cu(HL)_3]I{\cdot}MeOH$ (**2**). Herein, we report the syntheses, structures, and catalytic activity of these two complexes.



Scheme 1. The structure of the ligand HL.

Results and Discussion

Synthesis of Complexes 1 and 2

Complexes **1** and **2** were prepared under solvothermal conditions in sealed reaction vessels. Treatment of HL with two equiv. of CuI in EtOH led to $[Cu(HL)I]_2{\cdot}EtOH$ (**1**). Complex **1** was readily isolated as yellow needle crystals with moderate yield.

When the reaction solvent was changed to MeOH, a new complex $[Cu(HL)_3]I{\cdot}MeOH$ (**2**) was obtained, suggesting that the solvent may play an important role in the preparation of **1** and **2**. We thus conducted the reaction in a 1:1 mixture of MeOH and EtOH, and both the microcrystals of **1** and **2** were found in the reaction vessel.

We have also explored the preparation of **1** and **2** under atmospheric pressure at room temperature, and failed to obtain any product. It seems that solvothermal technique is a good method to prepare **1** and **2**.

Structure Descriptions of Complexes 1 and 2

Partially labeled plots of complexes **1** and **2** are shown in Figure 1 and Figure 2, respectively. The crystallographic data of the complexes are listed in Table 1.

---

* Prof. Dr. D.-D. Hu
E-Mail: daodaohu@snnu.edu.cn
[a] School of Materials Science and Engineering
Shaanxi Normal University
Xi'an, Shaanxi, 710062, P. R. China
[b] College of Chemistry and Chemical Engineering
Yan'an University
Yan'an, Shaanxi, 716000, P. R. China
[c] Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry
Chemical Engineering and Materials Science
Soochow University
Suzhou, 215123, P. R. China

Supporting information for this article is available on the WWW under **http://dx.doi.org/10.1002/zaac.201300223** or from the author.

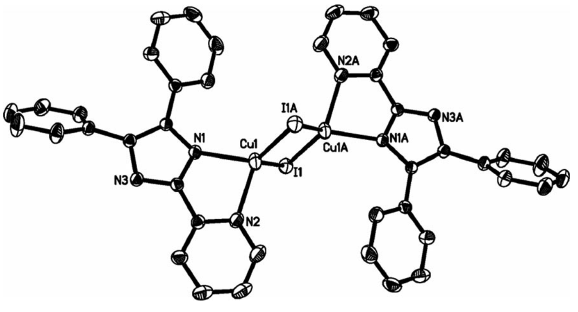


Figure 1. Solid state structure of **1** showing the atom labeling scheme. Hydrogen atoms are omitted for clarity.

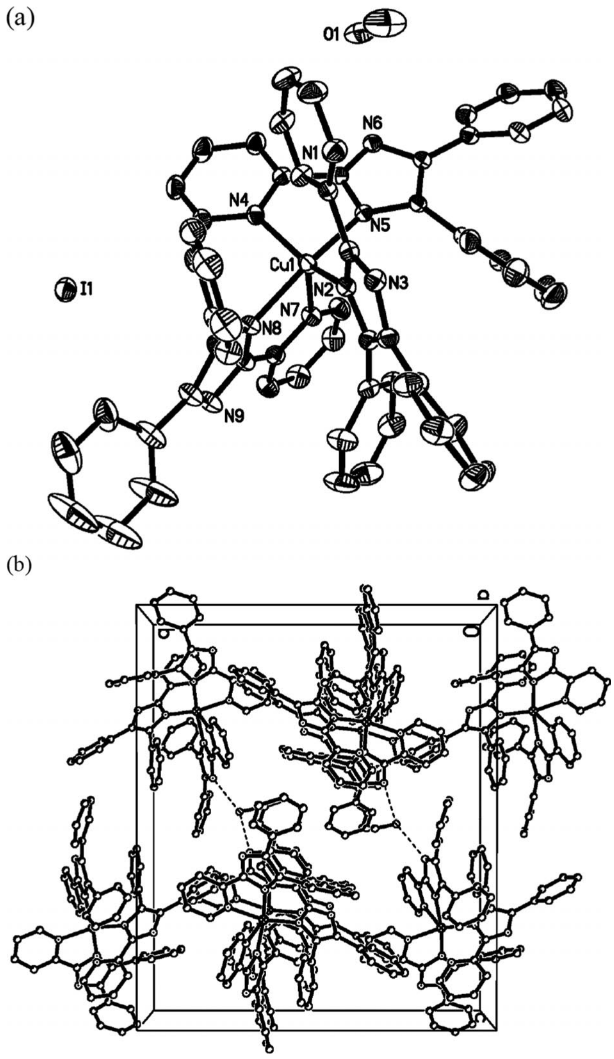


Figure 2. (a) Solid state structure of **2** showing the atom labeling scheme. Hydrogen atoms and solvent molecules are omitted for clarity. (b) Crystal packing diagram of complex **2**. Hydrogen contacts are represented by dotted lines.

Structure of [Cu(HL)I]$_2$·EtOH (1)

X-ray crystallographic analysis reveals that **1** crystallizes in the monoclinic $P2_1/n$ space group. It has a centrosymmetrical dimeric structure (Figure 1). The two Cu^I ions are linked by a pair of iodide bridges and have a similar tetra-coordinate environment. The arrangement around each central Cu^I atom is best described as a distorted tetrahedron. The Cu^I ion is bound to one nitrogen atom from imidazole ring, one pyridine nitrogen atom, and two bridging I$^-$ ions. The Cu–N distances [2.145 (3) and 2.093(3) Å] fall in the normal range of those previously reported iodide-bridged Cu^I complexes containing Cu–N bonds [2.005(3)–2.119(3) Å for Cu–N(imine) bonds and 2.049(3)–2.173(3) Å for Cu–N(pyridyl) bonds].[24–27] The Cu–I distances [2.6065(10) and 2.6248(7) Å] are congruent with the published values.[24–27]

Table 1. Crystal data and structure refinements for **1** and **2**.

	1	**2**
Empirical formula	$C_{44}H_{40}Cu_2I_2N_6O_2$	$C_{61}H_{49}CuIN_9O$
Formula weight	1065.70	1114.53
Temperature /K	293(2)	293(2)
Wavelength /Å	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a /Å	8.8653(18)	11.160(2)
b /Å	24.173(5)	20.155(4)
c /Å	10.406(2)	23.688(5)
α /°	90	90
β /°	108.67(3)	90.53(3)
γ /°	90	90
Volume /Å^3	2112.7(7)	5328.2(18)
Z	2	4
ρ /mg·m^{-3}	1.675	1.389
$F(000)$	1052	2272
Crystal size /mm	0.37× 0.28 × 0.27	0.27 × 0.25 × 0.23
Theta range /°	2.23 to 28.41	1.72 to 28.30
Limiting indices	$-11 \le h \le 11$ $-32 \le k \le 32$ $-13 \le l \le 10$	$-12 \le h \le 14$ $-26 \le k \le 26$ $-31 \le l \le 31$
Reflections collected / unique	20588 / 5285	49077 / 13206
Data / restraints / parameters	5285 / 0 / 250	13206 / 7 / 660
GooF on F^2	1.036	0.917

Structure of [Cu(HL)$_3$]I·MeOH (2)

X-ray crystallographic analysis reveals that **2** crystallizes in the monoclinic space group $P21/c$. It consists of one Cu^I ion, three HL ligands, one I$^-$ ion to balance the positive charge, and one solvent methanol molecule (Figure 2a). The Cu^I ion displays distorted square-pyramid arrangement. It is coordinated by two pyridine nitrogen atoms (N4 and N7) and three imine nitrogen atoms (N2, N5, and N8) from three HL ligands, with Cu–N bond lengths being 1.999(4) and 2.050(4) Å.

Noticeable intermolecular N–H···O contacts from NH groups of the HL ligands (donors) to the oxygen atoms of solvent MeOH molecules (acceptors) are determined (Figure 2b).

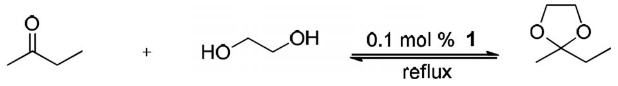
Catalytic Activities of 1 and 2

As the central copper atoms of **1** and **2** show the 1+ oxidation state, they may exhibit Lewis acid catalytic properties.

We found that **1** and **2** are catalytically active in ketal formation.[28] Ketalization is an important method to protect the carbonyl group in organic synthesis and drug design.[29] The reaction requires a Lewis acid catalyst to activate the oxygen of the carbonyl group, allowing glycol to substitute the ketone group.

The initial experiment was performed for the reaction of 2-butanone and ethylene glycol in toluene and catalyst loading is 0.1 %. Our results are summarized in Table 2. As can be seen from Table 2, when the reaction was performed at 90 °C for 12 h, the product 2-ethyl-2-methyl-1,3-dioxolane was obtained in 35 % yield. When the reaction time was prolonged to 24 h, 42 % yield of the product was obtained. It seems that higher temperature facilitates the reaction. As the reactions were conducted at 100, 110, and 120 °C, respectively, 52 %, 85 %, and 90 % yields of the products were achieved.

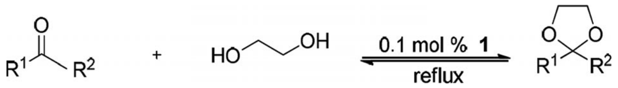
Table 2. Conversion yields for the ketalization of 2-butanone catalyzed by **1**.



Entry	Time /h	T /°C	Conversion /%
1	12	90	35
2	24	90	42
3	24	100	52
4	24	110	85
5	24	120	90

Next, the scope of the catalysis was probed and several ketones were screened. The results are given in Table 3. The ketalization of cyclohexanone with ethylene glycol proceeded in 94 % yield, whereas only low yields of ketalization products for acetophenone and benzophenone were observed.

Table 3. Conversion yields for the ketalization of various ketones catalyzed by **1**.[a)]

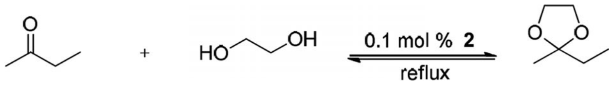


Entry	Ketone	Conversion /%
1	acetophenone	18
2	benzophenone	2
3	cyclohexanone	94

a) Reaction conditions: 110 °C at 24 h.

The catalytic activity of **2** (Table 4) toward ketalization of 2-butanone with ethylene glycol is even better than that of **1**. When the reaction was conducted at 90 °C, 85 % yield of the product was obtained. As the temperature was increased to 120 °C, nearly 100 % yield of the product was achieved, which indicates that the ketone could be completely protected under the relatively mild condition.

Table 4. Conversion yields for the ketalization of 2-butanone catalyzed by **2**.



Entry	Time /h	T /°C	Conversion /%
1	12	90	85
2	24	90	90
3	24	100	93
4	24	110	99.8

As the reactions were conducted under aerobic conditions, it is possible that the oxidation of Cu^{I} to Cu^{II} occurred, and Cu^{II} may also serve as the catalyst. To test this assumption, the ketalization reaction of 2-butanone with ethylene glycol catalyzed by $HL+Cu(OH)_2$, was conducted. It was found that the yield of ketalization reaction catalyzed by Cu^{II} is much lower than that of complex **1** catalyzed reaction, indicating that Cu^{I} species is the main catalyst of the reaction (see for details Supporting Information).

Conclusions

Two Cu^{I} complexes were prepared under solvothermal conditions in different solvent. They were able to catalyze the ketalization reaction of several ketones, affording various ketals under mild conditions.

Experimental Section

Materials and Instruments: All reagents used in the synthesis were of analytical grade. Elemental analyses for carbon, hydrogen, and nitrogen atoms were performed with a Carlo-Erba EA1110 CHNO-S microanalyzer. Infrared spectra (4000–400 cm^{-1}) were recorded by using KBr pellets with a Nicolet MagNa-IR500 FT-IR spectrometer. Crystal determination was performed with a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å).

X-ray Crystallography: The single crystals were placed in a Bruker SMART APEX II CCD diffractometer. The diffraction data were obtained by using graphite monochromated Mo-K_α radiation with a ω–2θ scan technique at room temperature. The structure was solved by direct methods with SHELX-97. A full-matrix least-squares refinement on F^2 was carried out by using SHELXL-97. The collected crystal data for the two structures are shown in Table 1.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-868930 (**1**) and CCDC-873502 (**2**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Synthesis of $[CuI(HL)]_2$·EtOH (1): A mixture of CuI (0.0380 g, 0.20 mmol), HL (0.0296 g, 0.1 mmol), and ethanol (1.2 mL) was sealed in an 8 mL Pyrex-tube, which was heated to 120 °C for 4 d, and then cooled to room temperature. Purple crystals were collected by filtration. Yield: 45 %. Elemental analysis: $C_{44}H_{40}Cu_2I_2N_6O_2$: calcd. C 49.59, H 3.78, N 7.89 %; found: C 49.26, H 3.98, N 8.17 %. **IR** (KBr, selected data): $\tilde{\nu}$ = 3396 (s), 3258 (s), 1659 (m), 1479 (m), 1452 (m), 1384 (m), 744 (m), 696 (s), 635 (m) cm^{-1}.

Synthesis of $[Cu(HL)_3]I\cdot MeOH$ (2): A mixture of CuI (0.0380 g, 0.20 mmol), HL (0.0296 g, 0.1 mmol), and methanol (1.2 mL) was sealed in an 8 mL Pyrex-tube, which was heated to 120 °C for 2 d, and then cooled to room temperature. Purple crystals were collected by filtration. Yield: 46 %. Elemental analysis: $C_{61}H_{49}CuIN_9O$: calcd. C 65.74, H 4.43, N 11.31 %; found: C 65.8, H 4.01, N 11.55 %. **IR** (KBr, selected data): $\tilde{\nu}$ = 3423 (s), 3061 (m), 1613 (m), 1473 (s), 1384 (m), 1250 (m), 1155 (m), 984 (s), 770 (m), 694 (s), 613 (m) cm^{-1}.

Ketalization Reaction Catalyzed by 1 or 2: Ethylene glycol (70 mmol), ketone (70 mmol), and catalyst (0.07 mmol) were introduced into 80 mmol of toluene, the latter was used as a solvent. The reaction was refluxed at 110 °C under Dean-Stark conditions for 24 h. The catalyst was isolated by filtration. All product yields were determined by ^1H NMR (Supporting Information).

Supporting Information (see footnote on the first page of this article): Selected bond lengths and angles of complexes **1** and **2**; ^1H NMR spectra of the catalysis reactions.

Acknowledgements

The authors appreciate the financial support of Department of Education of Shaanxi Province (2013JK0664).

References

[1] W. Y. Lo, C. H. Lam, V. W. W. Yam, N. Y. Zhu, K. K. Cheung, S. Fathallah, S. Messaoudi, B. Guennic, S. Kahlal, J. F. Halet, *J. Am. Chem. Soc.* **2004**, *126*, 7300–7310.
[2] O. Green, B. A. Gandhi, J. N. Burstyn, *Inorg. Chem.* **2009**, *48*, 5704–5714.
[3] A. Listorti, G. Accorsi, Y. Rio, N. Armaroli, O. Moudam, A. Gegout, B. Delavaux-Nicot, M. Holler, J. F. Nierengarten, *Inorg. Chem.* **2008**, *47*, 6254–6261.
[4] A. Y. Kovalevsky, M. Gembicky, P. Coppens, *Inorg. Chem.* **2004**, *43*, 8282–8289.
[5] L. M. Mirica, X. Ottenwaelder, T. D. P. Stack, *Chem. Rev.* **2004**, *104*, 1013–1045.
[6] W. Kaim, J. Rall, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 43–60.
[7] M. Fontecave, J. L. Pierre, *Coord. Chem. Rev.* **1998**, *170*, 125–140.
[8] H. M. Rowe, W. Xu, J. N. Demas, B. A. DeGraff, *Appl. Spectrosc.* **2002**, *56*, 167–173.
[9] D. A. Chang-Yen, Y. Lvov, M. J. McShane, B. K. Gale, *Sens. Actuators B* **2002**, *87*, 336–345.
[10] P. Y. Chen, T. J. Meyer, *Chem. Rev.* **1998**, *98*, 1439–1478.
[11] C. A. Kelly, G. J. Meyer, *Coord. Chem. Rev.* **2001**, *211*, 295–315.
[12] W. Jin, X. Li, B. Wan, *J. Org. Chem.* **2011**, *76*, 484–491.
[13] F. A. Luzzio, *Tetrahedron* **2001**, *57*, 915–945.
[14] Z. P. Han, Y. H. Li, *Inorg. Chem. Commun.* **2012**, *15,* 73–76.
[15] H. V. R. Dias, H. V. K. Diyabalanage, M. G. Eldabaja, O. Elbjeirami, M. A. Rawashdeh-Omary, M. A. Omary, *J. Am. Chem. Soc.* **2005**, *127*, 7489–7501.
[16] M. A. Omary, M. A. Rawashdeh-Omary, H. V. K. Diyabalanage, H. V. R. Dias, *Inorg. Chem.* **2003**, *42*, 8612–8614.
[17] D. G. Cuttell, S. M. Kuang, P. E. Fanwick, D. R. McMillin, R. A. Walton, *J. Am. Chem. Soc.* **2002**, *124*, 6–7.
[18] T. McCormick, W. L. Jia, S. N. Wang, *Inorg. Chem.* **2006**, *45*, 147–155.
[19] D. H. Lee, L. Q. Hatcher, M. A. Vance, R. Sarangi, A. E. Milligan, A. A. N. Sarjeant, C. D. Incarvito, A. L. Rheingold, K. O. Hodgson, B. Hedman, *Inorg. Chem.* **2007**, *46*, 6056–6068.
[20] Y. Zhao, M. S. Lin, Z. Chen, H. Pei, Y. H. Li, Y. M. Chen, X. F. Wang, L. Li, Y. Y. Cao, Y. Zhang, W. Li, *RSC Adv.* **2012**, *2*, 144–150.
[21] A. O. Eseola, W. Li, O. G. Adeyemi, N. O. Obi-egbedi, J. A. O. Woods, *Polyhedron* **2010**, *29*, 1891–1901.
[22] K. Pachhunga, B. Therrien, K. A. Kreisel, G. P. A. Yap, M. R. Kollipara, *Polyhedron* **2007**, *26*, 3638–3644.
[23] A. O. Eseola, M. Zhang, J. F. Xiang, W. W. Zuo, Y. Li, J. A. O. Woods, W. H. Sun, *Inorg. Chim. Acta* **2010**, *363*, 1970–1978.
[24] S. C. Sheu, M. J. Tien, M. C. Cheng, T. I. Ho, S. M. Peng, Y. C. Lin, *J. Chem. Soc., Dalton Trans.* **1995**, 3503–3510.
[25] H. Oshio, T. Watanabe, A. Ohto, T. Ito, H. Masuda, *Inorg. Chem.* **1996**, *35*, 472–479.
[26] G. F. Manbeck, W. W. Brennessel, C. M. Evans, R. Eisenberg, *Inorg. Chem.* **2010**, *49*, 2834–2843.
[27] C. X. Jia, *Acta Crystallogr. Sect. E* **2011**, *67*, m1059.
[28] H. H. Fei, D. L. Rogow, S. R. J. Oliver, *J. Am. Chem. Soc.* **2010**, *132*, 7202–7209.
[29] B. K. Banik, M. Chapa, J. Marquez, M. Cardona, *Tetrahedron Lett.* **2005**, *46*, 2341–2343.

Received: April 29, 2013
Published Online: October 2, 2013