DALTON
COMMUNICATION

Highly stable copper(I)-olefin coordination polymers capable of co-existing with water and acid

Jing Zhang,[a] Ren-Gen Xiong,*[a] Jing-Lin Zuo,[a] Chi-Ming Che[b] and Xiao-Zeng You*[a]

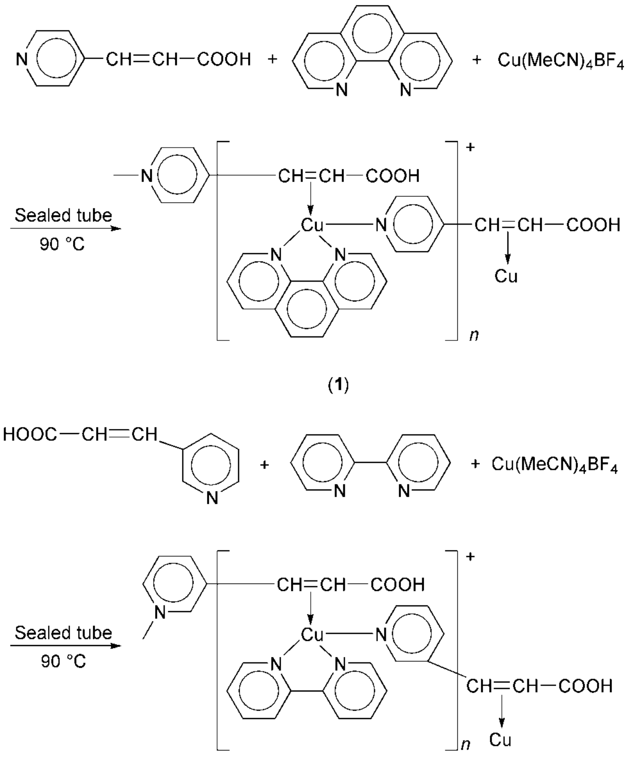
[a] *Coordination Chemistry Institute, The State Key Laboratory of Coordination Chemistry, Nanjing University, 210093, Nanjing, P. R. China. Fax: (+86) 25 3314502;*
E-mail: xyz@netra.nju.edu.cn
[b] *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong*

Received 26th June 2000, Accepted 28th July 2000

Under solvothermal conditions, the reactions of *trans*-3-(4-pyridyl)acrylic acid (4-HPYA) and 1,10-phenanthroline (phen), and *trans*-3-(3-pyridyl)acrylic acid (3-HPYA) and 2,2′-bipyridine (2,2′-bpy) with Cu(MeCN)$_4$BF$_4$ give rise to two unprecedented stable copper(I)–olefin coordination polymers, {[(phen)(4-HPYA)Cu(I)](BF$_4$)}$_n$ (1) and {[(2,2′-bpy)(3-HPYA)Cu(I)](BF$_4$)·H$_2$O}$_n$ (2), respectively.

Copper(I)–olefin complexes not only play an important role in biochemistry and modern organic chemistry, but they are involved in the copper-catalyzed addition of carbanions to α,β-unsaturated carbonyls and the copper-catalyzed cyclopropanation of alkenes by α-carbonyl diazoalkanes.[1] Ethylene, the smallest plant hormone, binds tightly to the copper receptor site, ETR 1, participating in a variety of stress response and developmental processes.[2] Since the pioneering work of Thompson and co-workers[3] demonstrated the first stable copper(I)–olefin complexes in which a tridentate ligand, hydrotris(3,5-dimethyl-1-pyrazolyl)borate [HB(3,5-Me$_2$PZ)$_3$], was used to stabilize the complexes, many copper(I)–olefin complexes have been reported in which bidentate ligands such as 2,2′-dipyridylamine,[4] 2,2-bipyridine[5] and 1,10-phenanthroline,[5] were used. An excellent example was shown by Doyle *et al.*[6] in which β-diketonate was introduced to chelate the copper(I)–olefin complex. Recently, a tridentate ligand, *N*-(3-indolylethyl)-*N*,*N*′-bis(6-methyl-2-pyridylmethyl)amine (Me$_2$IEP) and a macrocyclic ligand, *N*-[2-(1-naphthyl)ethyl]-1-aza-4,8-dithiacyclodecane, have been used to stablize copper(I)–η^2-indole[7] and copper(I)–η^2-naphthyl complexes. Moreover, Hoffmann *et al.* have successfully prepared a remarkably stable (up to 108 °C) copper(I)–ethylene complex in which iminophosphanamide derivatives were used as the chelating stabilizer to fix the ethylene.[8] However, it should be noted that all the complexes mentioned above are air-sensitive and molecular in nature. More recently, Schultz and co-workers have utilized crystal engineering strategies to synthesize a unique dense metal–organic layered framework containing η^2-copper(I)–olefinic bonds, in a monofumarate dicopper(I) complex.[9] They suggested that the high air stability of the copper(I)–olefin layered framework (up to 300 °C) may be due to the high concentration of bonding and exclusion of water in the lattice.

In this work we have combined the above-mentioned synthetic strategies and designed *trans*-3-(4-pyridyl)acrylic acid (4-HPYA) and *trans*-3-(3-pyridyl)acrylic acid (3-HPYA) as building blocks to construct two novel one-dimensional copper(I) polymers with η^2-olefin binding mode, *catena*-(1,10′-phenanthroline)[*trans*-3-(4-pyridyl)acrylic acid]copper(I) tetrafluoroborate {[(phen)(4-HPYA)Cu(I)](BF$_4$)}$_n$, (1) and *catena*-(2,2′-bipyridine)[*trans*-3-(3-pyridyl)acrylic acid]copper(I) tetrafluoroborate monohydrate {[(2,2′-bpy)(3-HPYA)Cu(I)](BF$_4$)·H$_2$O}$_n$, (2). To the best of our knowledge, these represent the first examples of stable copper(I)–olefin complexes capable of co-existing with organic acid and water (Scheme 1).



Scheme 1

Golden yellow crystals of **1** were obtained by treating 4-HPYA, 1,10-phenanthroline and Cu(MeCN)$_4$(BF$_4$) under solvothermal reaction conditions.† The IR spectrum of complex **1** shows a very strong peak at 1082 cm^{-1}, indicating the existence of a typical BF$_4^-$ anion. A broad peak at *ca.* 3200–3400 cm^{-1} and two peaks at 1702 cm^{-1} (s) and 1612 cm^{-1} (m) suggest that the carboxylic acid group of 4-HPYA in **1** is protonated.[10]

Golden yellow crystals of **2** were also obtained by treating 3-HPYA, 2,2′-bipyridine and Cu(MeCN)$_4$(BF$_4$) under solvothermal reaction conditions.† The IR spectrum of complex **2** clearly shows a very strong peak at 1072 cm^{-1}, indicating the existence of a typical BF$_4^-$ anion. A broad peak at *ca.* 3400 cm^{-1} and two peaks at 1712 cm^{-1} (s) and 1596 cm^{-1} (s) suggest that the carboxylic acid group of 3-HPYA in **2** is protonated[10] and probably water persists in **2**.

Complex **1** possesses high thermal stability, as evidenced from a melting point analysis of crystals, which only exhibited color darkening at 225 °C while complex **2** has a relatively low thermal stability, darkening at 122 °C, probably due to the existence of water in the lattice of **2**. The EPR results of both **1** and **2** are silent, indicating that they are cuprous.

DOI: 10.1039/b005101m

The X-ray crystal structure analysis of complexes **1** and **2** illustrated that both Cu(I) ions are coordinated in a distorted tetrahedral geometry,‡ which is defined by three nitrogen atoms (two from phen and one from 4-HPYA) and the C–C moiety of the olefin of 4-HPYA (Fig. 1) in **1** while **2** is defined by three nitrogen atoms (two from 2,2′-bipy and one from 3-HPYA) and the C–C moiety of the olefin of 3-HPYA (Fig. 2). Both 4-HPYA and 3-HPYA act as a neutral bidentate spacers to link two Cu(I) ions *via* the N atom and olefin moiety to give rise to a 1D coordination polymer, as depicted in Fig. 3a and b, respectively. The C–C bond distances (1.359(12) Å for **1** and 1.373(5) Å for **2**) of the coordinated olefin, are comparable to those found in [Cu(2,2-bipy)(C$_2$H$_4$)]·ClO$_4$ [1.360(13)–1.346(18) Å],[5] [Cu(phen)(C$_2$H$_4$)]·ClO$_4$ [1.361(22) Å],[5] [Cu$_2$(HB(3,5-Me$_2$Pz)$_3$(C$_2$H$_4$)Cl] [1.347(5) Å], [Cu(C$_2$H$_4$)(2,2′-dipyridylamine)] [1.359(7) Å],[4] [Cu$_2$(O$_2$CCH=CHCO$_2$)] [1.371(14) Å][9] and [Bu$^t_2$P(NSiMe$_3$)$_2$-κ^2*N*]Cu(η^2-C$_2$H$_4$) [1.362(6) Å].[8] However, they are slightly longer than those found in [Cu(HB(3,5-Me$_2$Pz)$_3$)(C$_2$H$_4$)] [1.329(9) Å],[3] and [Cu$_2$(COT)(hfacac)$_2$] [(1.31(1)–1.33(1) Å] (COT = cycloocta-1,3,5,7-tetraene, hfacac = hexafluoroacetylacetone).[6]

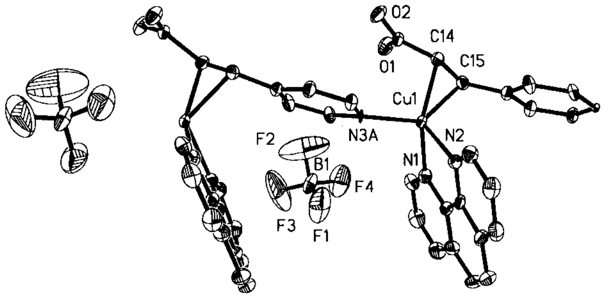


Fig. 1 An ORTEP diagram of the asymmetric unit of **1** (30% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Cu(1)–N(1) 2.020(7), Cu(1)–N(2) 2.173(7), Cu(1)–N(3 Å) 1.981(6), Cu(1)–C(14) 2.041(8), Cu(1)–C(15) 2.086(8), C(14)–C(15) 1.359(12); N(1)–Cu(1)–N(2) 80.2(3), N(3A)–Cu(1)–N(1) 106.6(3), C(14)–Cu(1)–C(15) 38.4(3), N(2)–Cu(1)–C(15) 111.8(3), N(1)–Cu(1)–C(14) 139.4(3), N(3A)–Cu(1)–C(14) 101.1(3), N(3A)–Cu(1)–C(15) 135.1(3).

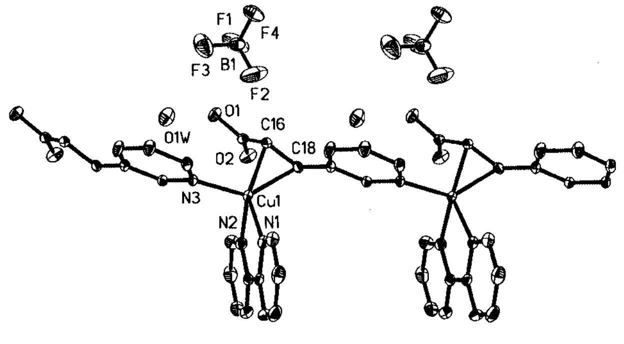


Fig. 2 An ORTEP diagram of the asymmetric unit of **2** (30% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Cu(1)–N(1) 2.060(3), Cu(1)–N(2) 2.119(3), Cu(1)–N(3) 2.025(3), Cu(1)–C(16) 2.047(4), Cu(1)–C(18) 2.128(4); N(1)–Cu(1)–N(2) 78.89(13), N(3)–Cu(1)–N(2) 106.41(13), C(16)–Cu(1)–N(3) 99.26(14), C(18)–Cu(1)–N(3) 137.09(14), C(18)–Cu(1)–N(2) 105.31(14), C(16)–Cu(1)–N(1) 142.02(14), C(18)–Cu(1)–C(16) 38.35(15).

Interestingly, both coordinated olefinic bonds in **1** [1.359(12) Å] and in **2** [1.373(5) Å] are longer than free ethylene [1.337(2) Å], probably suggesting that the coordination of copper(I) could potentially activate the olefinic bond. This could find useful application in catalysis.[8] The Cu–N and Cu–O bond lengths of complex **1** and **2** are normal and lie within the distances expected for Cu(I) complexes. Moreover, Cu–C bond distances [2.041(8)–2.086(8) Å for **1** and 2.047(4)–2.128(4) Å for **2**] are comparable to those found in other reported copper(I) organometallic compounds.

It is notable that in complex **1** the H atom of the carboxylic acid group of 4-HPYA is hydrogen bonded to one of the fluoro atoms of BF$_4^-$ with a hydrogen bond distance of 3.087 Å while in complex **2** there are two kinds of hydrogen bond: H–O–H···F–BF$_3^-$ (2.858 Å) and 3-HPYA···H–O–H (2.607 Å). Moreover, there are the stabilizing π–π interactions (about 3.73 Å for **1** and 3.50 Å for **2**) of adjacent strands, clearly suggesting that the π–π stacking of neighboring strands plays an important role in the stable copper(I)–olefin complexes. As far as we are aware, **1** and **2** are the first examples of 1D Cu(I)–olefin coordination polymers containing protonated organic acid ligands and water through hydrogen bonding and π–π stacking stabilization, similar to weak hydrogen bonds of the C–H$_{\mathrm{aromatic}}$···F–C type in organic crystalline solids capable of stabilizing the secondary structure of biomolecules such as DNA.[11,12] Attempts to synthesize neutral {[(phen)(4-PYA)Cu(I)]}$_n$, and [Cu(I)(2,2′-bipy)(3-PYA)]$_n$ were unsuccessful.

In conclusion, the rational design of building blocks and the flexible combination of copper(I) in the supramolecular system provides a robust routine for the construction of coordination polymers supported by a metal–olefin bond.

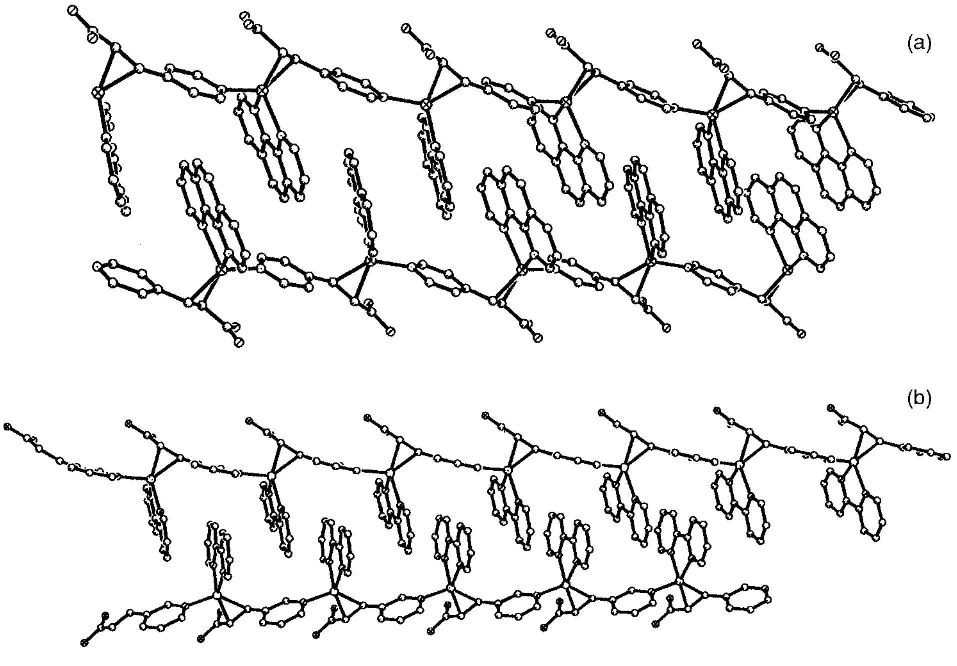


Fig. 3 (a) An extended 1D chain representation of **1** showing π–π stacking between adjacent strands. (b) An extended 1D representation of **2** showing π–π stacking between adjacent strands.

Acknowledgements

This work was supported by The Major State Basic Research Development Program (Grant No. G2000077500), the Distinguished Young Scholar Fund to C. M. Che from the National Natural Science Foundation of China (NSF29929001) and the National Nature Science Foundation of China. X. R. G. thanks Prof. Fun Hoong-Kun (X-Ray Crystallography Unit, School of Physics, Universiti Sains Malaysia) for help in X-ray crystallographic determination and solutions of the compounds.

Notes and references

† Compound **1**: Samples of 1 mmol of Cu(MeCN)$_4$BF$_4$, 1 mmol of 1,10-phen and 1 mmol of 4-HPYA were placed in a thick Pyrex tube (*ca.* 20 cm long). After addition of 0.1 ml of water and 2.5 ml of *n*-butanol, the tube was frozen with liquid N$_2$, evacuated under vacuum and sealed with a blowtorch. The tube was heated at 90 °C for two days to give golden yellow rod shaped crystals (pure phase) in 55% yield based on 4-HPYA. IR (KBr, cm^{-1}), 3400 (br, w), 1702 (m), 1610 (m), 1561 (s), 1381 (vs), 1115 (w), 1082 (vs), 972 (w), 828 (w) and 621 (w). Anal. Calc. For $C_{20}H_{15}BCuF_4N_3O_2$: C, 50.08; H, 3.15; N, 8.76; Found, C, 50.14; H, 3.21; N, 8.90%.

Compound **2**: Samples of 1 mmol of Cu(MeCN)$_4$BF$_4$, 1 mmol of 2,2′-bpy and 1 mmol of 3-HPYA were placed in a thick Pyrex tube (*ca.* 20 cm long). After addition of 0.1 ml of water and 2.5 ml of *n*-butanol, the tube was frozen with liquid N$_2$, evacuated under vacuum and sealed with a blowtorch. The tube was heated at 90 °C for two days to give golden yellow rod shaped crystals (pure phase) in 45% yield based on 3-HPYA. IR (KBr, cm^{-1}): 3392 (m), 3224 (m), 1712 (vs), 1569 (s), 1565 (w), 1441 (m), 1375 (m), 1281 (w), 1168 (s), 1072 (vs), 998 (sh, m), 830 (w), 762 (s), 735 (w) and 595 (w). Anal. Calc. For $C_{18}H_{17}BCuF_4N_3O_3$: C, 45.64; H, 3.62; N, 8.87; Found, C, 45.58; H, 3.70; N, 8.90%.

‡ Crystal data for **1**: $C_{20}H_{15}BCuF_4N_3O_2$, $M_r = 479.70$, monoclinic, space group *C2/c*, $a = 28.4958(1)$, $b = 10.2352(2)$, $c = 14.8060(2)$ Å, $\beta = 117.203(1)°$, $U = 3840.68(9)$ Å^3, $Z = 8$, $T = 293(2)$ K, μ(Mo-Kα) = 1.199 mm^{-1}, 134001 reflections measured, 4709 unique ($R_{int} = 0.0920$) which were used in all calculations. The $wR(F^2)$ was 0.3125, $R1$=0.1067. [The relatively high R value is probably due to ghost peaks (Q1(3.07), Q2(2.44) and Q3(2.09 e Å^{-3}) located near the Cu atom, C19 and C20 (the distances of Cu–Q(1), C(19)–Q3 and C(20)–Q2 as well as Q2–Q3 are *ca.* 1.689, 1.138, 1.039 and 0.764 Å, respectively].

Crystal data for **2**: $C_{18}H_{17}BCuF_4N_3O_3$, $M_r = 473.70$, orthorhombic, space group *Pbca*, $a = 7.0050(3)$, $b = 19.8147(8)$, $c = 27.2050(10)$ Å, $V = 3776.1(3)$ Å^3, $Z = 8$, $T = 293(2)$ K, μ(Mo-Kα) = 1.222 mm^{-1}, 25221 reflections measured, 4687 unique ($R_{int} = 0.1267$) which were used in all calculations. The $wR(F^2)$ was 0.1276, $R1$=0.0626. CCDC reference number 186/2116. See http://www.rsc.org/suppdata/dt/b0/b005101m/ for crystallographic files in .cif format.

1 G. Hallnemo, T. Olsson and C. Ullenius, *J. Organomet. Chem.*, 1985, **282**, 133; S. Mori and E. Nakamura, *Chem. Eur. J.*, 1999, **5**, 1534; M. M. Diaz-Requejo, M. C. Nicasio and P. J. Perez, *Organometallics*, 1998, **17**, 3051; M. M. Diaz-Requejo, T. Belderrain, M. C. Nicasio, F. Prieto and P. J. Perez, *Organometallics*, 1999, **18**, 2603.

2 G. E. Schaller and A. B. Bleecker, *Science*, 1995, **270**, 1809; F. I. Rodriguez, J. J. Esch, A. E. Hall, B. M. Binder, G. E. Schaller and A. B. Bleecker, *Science*, 1999, **283**, 996; J. R. Ecker, *Science*, 1995, **268**, 667.

3 J. S. Thompson, R. L. Harlow and J. F. Whitney, *J. Am. Chem. Soc.*, 1983, **105**, 3522; J. S. Thompson and J. F. Whitney, *J. Am. Chem. Soc.*, 1983, **105**, 5488.

4 J. S. Thompson and J. F. Whitney, *Inorg. Chem.*, 1984, **23**, 2813; J. S. Thompson and R. M. Swiatek, *Inorg. Chem.*, 1985, **24**, 110.

5 H. Masuda, N. Yamamoto, T. Taga, K. Machida, S. Kitagawa and M. Munakata, *J. Organomet. Chem.*, 1987, **322**, 121; M. Munakata, S. Kitagawa, S. Kosomo and A. Asahara, *Inorg. Chem.*, 1986, **25**, 2622.

6 G. Doyle, K. A. Eriksen and D. Van Engen, *Organometallics.*, 1985, **4**, 830.

7 W. S. Striejewske and R. R. Conry, *Chem. Commun.*, 1998, 555; Y. Shimazaki, H. Yokoyama and O. Yamauki, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 2401.

8 B. F. Straub, F. Eisenträger and P. Hofmann, *Chem. Commun.*, 1999, 2507.

9 D. M. Young, U. Geiser, A. J. Schultz and H. Wang, *J. Am. Chem. Soc.*, 1998, **120**, 1331.

10 T. M. Reineke, M. Edaoudi, M. Fehr, D. Kelley and O. M. Yaghi, *J. Am. Chem. Soc.*, 1999, **121**, 165.

11 V. R. Thalladi, H.-H. Weiss, D. Bläser, R. Boese, A. Nangia and G. R. Desiraju, *J. Am. Chem. Soc.*, 1998, **120**, 8702; T. A. Evans and K. R. Seddon, *Chem. Commun.*, 1997, 2024; M. L. Renak, G. P. Bartholomew, S. Wang, P. J. Ricatto, R. J. Lachicotte and G. C. Bazan, *J. Am. Chem. Soc.*, 1999, **121**, 7787.

12 N. Yoshida, H. Oshio and T. Ito, *Chem. Commun.*, 1998, 63; M. Lämsä, J. Huuskonen, K. Rissanen and J. Pursiainen, *Chem. Eur. J.*, 1998, **4**, 84; D. Ranganathan, V. Haridas, R. Gilardi and I. L. Karle, *J. Am. Chem. Soc.*, 1998, **120**, 10793.

13 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.