



原位水热合成一个发光的烯炔铜(I)配合物

杜 楣 王锡森*

(南京大学化学化工学院, 南京 210093)

关键词: 烯炔铜(I)配合物; 荧光; 溶剂热合成

中图分类号: O614.121

文献标识码: A

文章编号: 1001-4861(2005)06-0941-04

A Luminescent Copper(I)-Olefin Complex Obtained Through *in situ* Hydrothermal Ligand Synthesis

DU Mei WANG Xi-Sen*

(School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093)

Abstract: The solvothermal reaction of 1-(Benzyl diallylamine)-2-naphtholallyl ether and CuCl yields a unexpected copper(I)-olefin complex, Cu₆Cl₆ (diallylamine) **1**, which bears twelve-membered ring oligomeric structure and displays red fluorescent emission in the solid state at room temperature. CCDC: 272088.

Key words: copper(I)-olefin complex ; fluorescent ; solvothermal synthesis

Comment

Copper-catalyzed addition of carbanions to α , β -unsaturated carbonyls and copper-catalyzed cyclopropanation of alkenes by R-carbonyl diazoalkanes involve copper(I)-olefin complexes as catalytically active species or resting state^[1]. Copper(I)-ethylene complexes may also participate in a variety of stress responses and developmental processes, as in the smallest plant hormone, an ethylene group binds tightly to the copper receptor site ETR^[2]. Recently the rational design and self-assembly of olefin-copper(I) coordination polymers with highly thermal stability and physical functions have achieved intensive interest^[3]. These polymers not only display general characters of metal-organic coordination polymer, but also remain Cu-olefin complex features, such as Cu- π coordinating bond labile. Due to these properties, the Cu(I)-olefin complexes have found wide applications in fluorescent

sensor^[3], olefin separation^[4] and chiral enantioseparation^[5].

In situ solvothermal ligand preparation not only provides a powerful synthesis method for organic ligands those are not readily accessible, but also represents a potential new direction for novel inorganic-organic hybrid network construction through crystal engineering. These reactions are often quite complicated and may involve *in situ* hydrolysis, oxidation and cycloaddition etc. The products generated under hydrothermal conditions cannot normally be obtained by direct mixing of solutions of metal ions and ligands^[6].

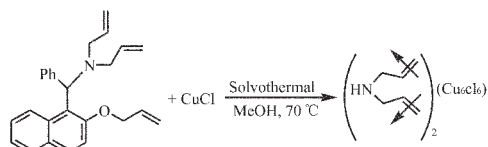
We have combined the above-mentioned synthetic strategies and designed 1-(Benzyl diallylamine)-2-naphtholallyl ether as a building block to construct a novel copper(I) complex with η^2 -olefin binding mode, Cu₆Cl₆ (diallylamine) (**1**) (Scheme 1) which, to the best of our knowledge, represents the first example of a copper(I)-olefin complex obtained through *in situ* hy-

收稿日期: 2005-03-30. 收修改稿日期: 2005-05-10.

*通讯联系人. E-mail: wxis@yahoo.com.cn

第一作者: 杜 楣, 女, 43 岁, 助工; 研究方向: 固体核磁共振。

drothermal ligand synthesis although this complex was obtained by alternating current electrochemical synthesis^[7]. Herein we report the synthesis, solid-state structure and fluorescent property of **1**.

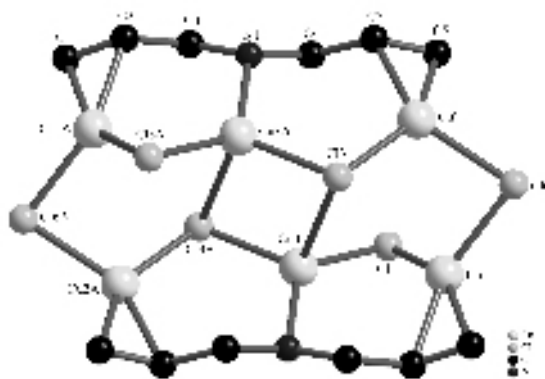
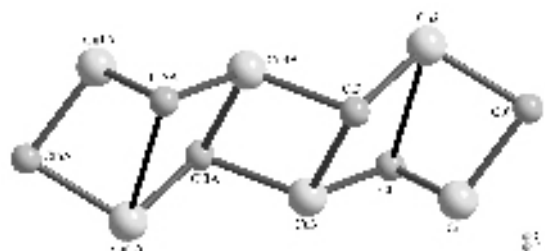


Scheme 1

Compound **1** was prepared under solvothermal conditions by the reaction of CuCl and ligand 1-(benzyl diallylamino)-2-naphtholallyl ether. EPR spectra of single crystal samples of **1** is silent, indicating that the valence of Cu atoms in **1** is monovalent. Under such condition, the ligand 1-(benzyl diallylamino)-2-naphtholallyl ether decomposes to 1-benzyl-2-naphtholallyl ether and diallylamine because there possibly exists a little HCl.

The X-ray crystal structure analysis of complex **1** illustrated that there are a unique Cu₆Cl₆ cluster and three different coordination spheres copper atoms in compound **1**^[8]. Cu1 possesses a trigonal planar coordination environment formed by two halide atoms and a C=C bond moiety in diallylamine that was in situ synthesized. Similarly, Cu2 was surrounded by two chloride atoms and C=C to give a trigonal pyramid whereas the coordination environment of Cu3 can be best described as tetrahedral which formed from three chloride atoms and one nitrogen atom of diallylamine. Thus, the ligand diallylamine acts as a tridentate spacer which links three Cu(I) ions by using one N atom and two olefin moiety to give rise to a olefin-copper(I) polymer, as shown in Fig.1. The Cl atom adopts a bidentate (or tridentate) bridging mode to link two (or three) Cu atoms to form a dimer (Cl3-Cu3-Cl3A-Cu3A) and six-membered ring (Cu1-Cl6-Cu2-Cl3-Cu3-Cl5), respectively, all the Cu atoms was connected together by the Cl atom in compound **1** to form a twelve-membered ring which can be regarded as five Cu₂Cl₂ dimer adjoined to each other sharing one Cu atom and Cl atom (Fig.2). Furthermore, it can be found from crystal packing view of **1** that one of Cl atoms from the six-membered ring (one part of twelve-membered ring) still takes part in the weak coordination of Cu(I) atom which comes from another twelve-

membered ring to result in the formation of 2D network, as shown in Fig.3.

Fig.1 Crystal structure of complex **1**Fig.2 Simplified twelve-membered ring representation of compound **1**

The black lines stand for pseudo-linking line.

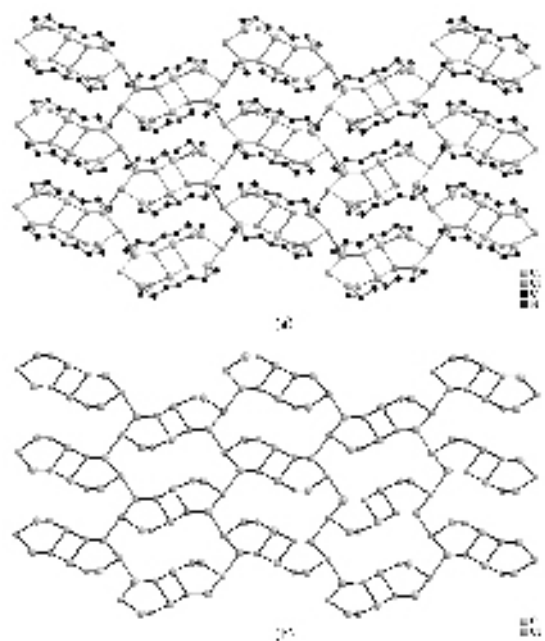


Fig.3 (a) 2D network representation of compound **1** through weak Cu-Cl interaction (red line); (b) Simplified 2D representation of compound **1** in which each twelve-membered ring is connected by weak Cu-Cl interaction and the diallylamine ligand is abbreviated

The C-C double bond distances (0.134 4(6) ~ 0.135 4(6) nm) are slightly longer than those found in [Cu(HB(3,5-Me₂PZ)₃(C₂H₄))] (0.132 9(9) nm)^[9a], [Cu₂(COT)(hfacac)₂] (0.131(1)~0.133(1) nm)^[9b], but slightly shorter than those found in [Cu₂Cl₂(C₅H₈)] (C₅H₈=2-methylbutadiene) (0.135 8(7) nm)^[9c], [CuCl-(C₅H₈O)] (C₅H₈O=1-penten-3-one) (0.138 3(8) nm)^[9d] and [CuCl(C₄H₆O₂)](C₄H₆O₂=methylpropenoate) (0.137 0(8) nm)^[9e]. It is interesting to note that the C-C bond lengths of the coordinated olefin in the two copper(I) π -complexes, Cu₄Cl₄L (0.133(2) nm) and Cu₄Br₄L (0.134(2) nm) (L=C₇H₈, 1,4-pentadiene), containing a Cu₄X₄ cubane core are slightly shorter than that of **1**^[9f] while those of the copper(I) π -complex Cu₄Br₄L (0.134 6(2) ~ 0.144 2 nm) (L=TTT) are slightly longer than that of **1**^[9h]. Finally, the lengthening of the C-C double bond may be typical of ethylene ligands that are η^2 -bonded to low valant electron-rich transition metals^[10].

The diffuse-reflectance UV-VIS spectrum of **1** shows only a low-energy band at *ca.* 429 nm, which can be assigned to the metal-to-ligand charge transfer (MLCT) band^[11]. The strong red emission spectrum of **1** in the solid state at room temperature is shown in Fig.4, with a maximum peak at *ca.* 622 nm (λ_{exc} =363 nm). A clear bathochromic shift occurs in **1** relative to [Cu₄I₄(py)] (λ_{emax} =580 nm) and [Cu(3,4-bpyBr)] (λ_{emax} =580 nm)^[11], which is probably due to π -back-donation from the filled metal D π orbital to the vacant anti-bonding π^* orbital of the coordinated olefin^[12].

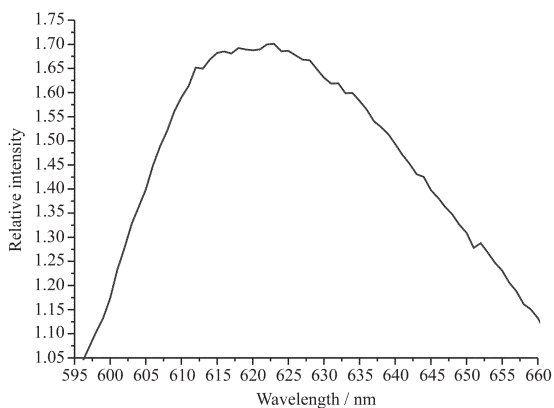


Fig.4 Fluorescent emission spectra of Cu₆Cl₆(diallylamine) in the solid state at room temperature (λ_{exc} =363 nm)

In conclusion, the solvothermal synthesis technique provides a powerful synthetic method to give organometallic compounds, which are not readily ac-

cessible through classical solution synthesis.

Experimental

Preparation of compound **1**. CuCl (3.0 mmol) and 1-(Benzyl diallylamine)-2-naphtholallyl ether (1.0 mmol) were placed in a thick Pyrex tube (*ca.* 20 cm in length). After addition of 2 mL of MeOH, the tube was frozen with liquid N₂, evacuated under vacuum, and sealed with a torch. The tube was then placed into oven at 70 °C for 2 days to give pale-yellow block crystals. Anal. Found: C, 45.24; H, 2.76; N, 6.45. Calcd: C, 45.39; H, 2.86; N, 6.62. IR (KBr, cm⁻¹): 3 442(br w), 2 961(w), 1 621(s), 1 561(w), 1 479(s), 1 388(m), 1 357(w), 1 319(w), 1 305(w), 1 266(w), 977(w), 949(w), 934(w), 778(m), 746(w), 736(w), 695(w), 528(w), 428(w).

Acknowledgement: This work was supported by The Major State Basic Research Development Program (Grant No. G2000077500), Distinguished Young Scholar Fund to R.-G. Xiong (No.20225103), the National Natural Science Foundation of China and the Natural Science Foundation of JiangSu (BK2003204) as well as 20030284001(SRFDP).

References:

- [1] (a)Hallnemo G, Olsson T, Ullenius C. *J. Organomet. Chem.*, **1985**,**282**:133~138
(b)Mori S, Nakamura E. *Chem. Eur. J.*, **1999**,**5**:1534~1543
(c)Diaz-Requejo M M, Nicasio M C, Perez P. *J. Organometallics*, **1998**,**17**:3051~3057
(d)Diaz-Requejo M M, Belderrain T R, Nicasio M C, et al. *Organometallics*, **1999**,**18**:2601~2609
(e)Striejewske W S, Conry R R. *Chem. Commun.*, **1998**:555~566
(f)Shimazaki Y, Yokoyama H, Yamauki O. *Angew. Chem., Int. Ed.*, **1999**,**38**:2401~2403
(g)Diaz-Requejo M M, Belderrain T, Perez P J. *Chem. Commun.*, **2000**:1853~1854
- [2] (a)Schaller G E, Bleecker A B. *Science*, **1995**,**270**:1809~1813
(b)Rodriguez F I, Esch J J, Hall A E, et al. *Science*, **1999**, **283**:996~998
(c)Ecker J R. *Science*, **1995**,**268**:667~671
- [3] (a)Zhang J, Xiong R G, Zuo J L, et al. *Chem. Commun.*, **2000**: 1495~1496
(b)Zhang J, Xiong R G, Zuo J L, et al. *J. Chem. Soc., Dalton. Trans.*, **2000**:2898~2900
(c)Zhang J, Xiong R G, Chen X T, et al. *Organometallics*,

- 2001,20**:4118~4121
- (d)Zhang J, Xiong R G, Chen X T, et al. *Organometallics*, **2002,21**:235~238
- (e)Qu Z R, Chen Z F, Zhang J, et al. *Organometallics*, **2003,22**:2814~2816
- (f)Xie Y R, Wang X S, Zhao H, et al. *Organometallics*, **2003,22**:4396~9398
- (g)Li Y H, Wang X S, Zhao H, et al. *Inorg. Chem.*, **2004,43**:712~715
- (h)Xue X, Wang X S, Xiong R G, et al. *Angew. Chem., Int. Ed.*, **2002,41**:2944~2946
- (i)Young D M, Geiser U, Schultz A J, et al. *J. Am. Chem. Soc.*, **1998,120**:1331~1332
- (j)Ye Q, Wang X S, Zhao H, et al. *Chem. Soc. Rev.*, **2005,34**:208~225
- [4] (a)Blytas G C, Li N N, Calo J M. in *Separation and Purification Technology*, Eds. Dekker, New York, **1992**.19.
- (b)Suzuki T, Nobel R D, Koval C A. *Inorg. Chem.*, **1997,36**:136~140
- (c)Wang K, Stiefel E I. *Science*, **2001,291**:106~109
- [5] (a)Cavallo L, Cucciolito M E, Martino A De, et al. *Chem. Eur. J.*, **2000,6**:1127~1139
- (b)Frayse S, Zelewsky A. *Von New J. Chem.*, **2001,25**:1374~1375
- [6] (a)Xiong R G, You X Z, Abrahams B F, et al. *Angew. Chem., Int. Ed.*, **2001,40**:4422~4425
- (b)Xiong R G, Zhang J, Chen Z F, et al. *J. Chem. Soc., Dalton. Trans.*, **2001**:780~782
- (c)Xiong R G, Xue X, Zhao H, et al. *Angew. Chem. Int. Ed.*, **2002,41**:3800~3803
- [7] Filinchuk Y E, Glowiak T, Mys'kiv M G. *Pol. J. Chem.*, **1999,73**:1283~1291
- [8] $C_6H_{11}Cl_3Cu_3N$, $M_r=394.13$, Orthorhombic, space group, *Pccn*, $a=1.520\ 08(13)$ nm, $b=1.902\ 16(16)$ nm, $c=0.757\ 69(7)$ nm, $\alpha=\beta=\gamma=90^\circ$, $V=2.190\ 8(3)$ nm³, $Z=8$, $T=296(2)$ K, $\rho_{\text{cal}}=2.390$ g·cm⁻³, Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm), $\mu=6.452$ mm⁻¹, $R_1=0.039\ 0$, $wR_2=0.119\ 1$ for 1 855 observed reflections from 2 821 independent, GOF=1.079. CCDC: 272088.
- [9] (a)Thompson J S, Harlow R L, Whitney J F. *J. Am. Chem. Soc.*, **1983,105**:3522~3527
- (b)Doyle G, Eriksen K A, Engen D. *Van Organometallics*, **1985,4**:830~835
- (c)Hakansson M, Jagner S. *Organometallics*, **1991,10**:1317~1319
- (d)Hakansson M, Jagner S. *J. Organomet. Chem.*, **1987,336**:279~285
- (e)Hakansson M, Jagner S. *J. Organomet. Chem.*, **1989,361**:269~276
- (f)Hakansson M, Jagner S, Clot E, et al. *Inorg. Chem.*, **1992,31**:5389~5394
- [10](a)Iael S D, Ibers J A. *Adv. Organomet. Chem.*, **1976,14**:33~41
- (b)Mingos D M. In *Comprehensive Organometallic Chemistry*. Wilkinson G, Stone F G A, Abel E W Eds. Pergamon Press: New York, **1982**.Vol.3,1~88
- [11](a)Fun H K, Raj S S S, Xiong R G, et al. *J. Chem. Soc., Dalton Trans.*, **1999**:1711~1712
- (b)Kyle K R, Ryu C K, DiBenedetto J A, et al. *J. Am. Chem. Soc.*, **1991,113**:2954~2965
- (c)Henary M, Wootton J L, Khan S I, et al. *Inorg. Chem.*, **1997,36**:796~801
- (d)Miller M T, Gantzel P K, Karpishin T B. *J. Am. Chem. Soc.*, **1999,121**:4292~4293