Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Inorganic Chemistry Communications 6 (2003) 1017–1019

Inorganic Chemistry Communications

www.elsevier.com/locate/inoche

A photoluminescent polymeric chain complex: synthesis and structure of $[(PPh_3)_2Cu_2(\mu\text{-}I)_2(\mu\text{-}4,4'\text{-bpy})]_n$

Rong-Zhen Li [a], Dan Li [a,*], Xiao-Chun Huang [a,b], Zhi-Yu Qi [a], Xiao-Ming Chen [b]

[a] *Department of Chemistry, Shantou University, Shantou, Guangdong 515063, China*

[b] *School of Chemistry and Chemical Engineering, Sun Yat-Sen (Zhongshan) University, Guangzhou 510275, China*

Received 22 March 2003; accepted 27 April 2003

Abstract

The synthesis and crystal structure of a new one-dimensional mixed-ligand Cu(I) coordination polymer, $[(PPh_3)_2Cu_2(\mu\text{-}I)_2(\mu\text{-}4,4'\text{-bpy})]_n$ (4,4'-bpy = 4,4'-bipydine) are reported. The neutral polymer consists of $(PPh_3)_2Cu_2(\mu\text{-}I)_2(\mu\text{-}4,4'\text{-bpy})$ units bridged by 4,4'-bpy to construct an infinite chain architecture. Crystal data: $C_{23}H_{19}CuINP$, $M_r = 530.80$, Triclinic space group ($P\bar{1}$, No. 2), $a = 9.2279(8)$ Å, $b = 9.4014(8)$ Å, $c = 13.3663(12)$ Å, $\alpha = 107.445(2)°$, $\beta = 106.707(2)°$, $\gamma = 93.479(2)°$, $V = 1045.8(2)$ Å^3, $D_{calc} = 1.686$ g m^{-3}, $Z = 2$. The solid state of the complex is luminescent with a peak maximum at 535 nm, upon excitation at 300–400 nm at room temperature. The emission is assigned to Copper(I) to 4,4'-bpy charge transfer (MLCT).

Keywords: Copper(I); Coordination polymer; Structure; 4,4'-Bipyridine; Photoluminescence

1. Introduction

The self-assembly of large inorganic architectures has rapidly become one of the most exciting area in supramolecular chemistry. The crystal engineering of coordination polymers is becoming an increasing popular field of research, and offers the promise of deliberately designing new materials with novel electronic, optical, magnetic and catalytic properties [1–6]. While a larger number of copper(I) complexes have been found to be photoluminescence with different emitting excited state [7,8], luminescent Cu(I) polymers are less common [9,10]. 4,4'-Bipyridine (4,4'-bpy) is well-known used as a linear ligand to bridge metal centers to form one-, two- and three-dimensional polymeric networks. [11–15] We report herein the synthesis and crystal structure of a new one dimensional mixed-ligand Cu(I) complex $[(PPh_3)_2Cu_2(\mu\text{-}I)_2(\mu\text{-}4,4'\text{-bpy})]_n$ with photoluminescent properties.

2. Experimental

2.1. General

The chemicals and reagents for syntheses were obtained commercially and used without further purification. Infrared spectra were recorded in the range of 4000–400 cm^{-1} on a Nicolet Magna 750 spectrometer. Elemental analyses were carried out using a Perkin–Elmer 2400C instrument. Ultraviolet and photoluminescence analyses were performed on a UV-1100 spectrometer and a Perkin–Elmer LS 55 luminescence Spectrometer, respectively.

2.2. Preparation of $[(PPh_3)_2Cu_2(\mu\text{-}I)_2(\mu\text{-}4,4'\text{-bpy})]_n$

Crystals of the title complex were prepared by multilayer diffusion method. To a dichloromethane solution (10 ml) of $[CuIPPh_3]_4$ (0.45 g, 0.25 mmol) in a glass tube was carefully added a buffer layer of THF/CH_2Cl_2 (20 ml). A solution of 4,4'-bipyridine (0.23 g, 1.2 mmol) in THF (10 ml) was introduced dropwise to form a third layer. Yellow block crystals suitable for X-ray diffrac-

---

[*] Corresponding author. Tel: +86-754-290-3154; fax: +86-754-251-0505.

E-mail address: dli@stu.edu.cn (D. Li).

doi:10.1016/S1387-7003(03)00170-9

tion analysis were obtained on interdiffusion of the reactants in 2 weeks. Polycrystalline $[(PPh_3)_2Cu_2(\mu\text{-}I)_2(\mu\text{-}4,4'\text{-bpy})]_n$ was synthesized by the direct reaction of CuI with PPh_3 and 4,4′-bpy. To a suspension of CuI (0.19 g, 1 mmol) in 10 ml CH_2Cl_2 were added PPh_3 (0.53 g, 2 mmol) and 0.20 g 4,4′-bpy (1 mmol). Yellow precipitates were formed rapidly. Solid $[(PPh_3)Cu(\mu\text{-}I)_2(\mu\text{-}4,4'\text{-bpy})]_n$ was obtained by filtration after washing with diethyl ether and dried in vacuo. Anal. Calcd for $C_{23}H_{19}CuINP$: C, 52.12%; H, 3.40%; N, 2.60%. Found: C, 52.04%; H, 3.61%; N, 2.64%. IR(KBr pellets), v/cm^{-1}: 519s, 694vs, 749vs, 1093s, 1433vs, 1481s (PPh_3); 810s, 1000m, 1047w, 1219s, 1406s, 1599s (4,4′-bpy).

2.3. X-ray structure determination

A yellow crystal (0.43 mm × 0.34 mm × 0.13 mm) was chosen for X-ray crystallography determination. Crystal data: $C_{23}H_{19}CuINP$, $Mr = 530.80$, Triclinic space group ($P\bar{1}$, No. 2), $a = 9.2279(8)$ Å, $b = 9.4014(8)$ Å, $c = 13.3663(12)$ Å, $\alpha = 107.445(2)°$, $\beta = 106.707(2)°$, $\gamma = 93.479(2)°$, $V = 1045.8(2)$ Å^3, $D_{calc} = 1.686$ g m^{-3}, $Z = 2$, 6637 reflections collected, 4988 unique, ($R_{int} = 0.0219$), Final R indices $[I \geq 2\sigma(I)]$ $R_1 = 0.0325$, $wR_2 = 0.0935$. Data collections ($4.43 < \theta < 28.28$) were performed at 293 K on a Siemens R3m diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. The structure was solved with direct methods and refined by full matrix least squares (SHELXTL) [16].

3. Results and discussion

Single crystal crystallography has revealed the title complex is a neutral compound that consists of $(PPh_3)_2Cu_2(\mu\text{-}I)_2$ units (Fig. 1) bridging by 4,4′-bpy to construct an infinite chain architecture (Fig. 2). Selected bond distances and angles are listed in Table 1. It is compared well with its chloride analogues $[(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-}4,4'\text{-bpy})]_n$ and $[(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-pyz})]_n$ (pyz = pyrazine) reported by Lu et al. [15] and Henary et al. [9], respectively, as well as a Ag(I) analogue $[(PPh_3)_2Ag_2(\mu\text{-}I)_2(\mu\text{-}4,4'\text{-bpy})]_n$ by Vittal et al. [17]. The two pyridine rings in the title complex are almost coplanar, similar to those in $[(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-pyz})]_n$ [9]. The four-coordination Cu(I) was completed by one N from 4,4′-bpy, one P from triphenylphosphine and two iodine atoms to form a distorted tetrahedron geometry. Unlike the short Cu–Cu distances of 2.65–2.88 Å in $Cu_4I_4L_4$ (L = nitrogen containing heterocyclic ligands) cubic clusters [8], the Cu⋯Cu distance in the title polymer is 3.143 Å indicating no Cu–Cu interaction existing.

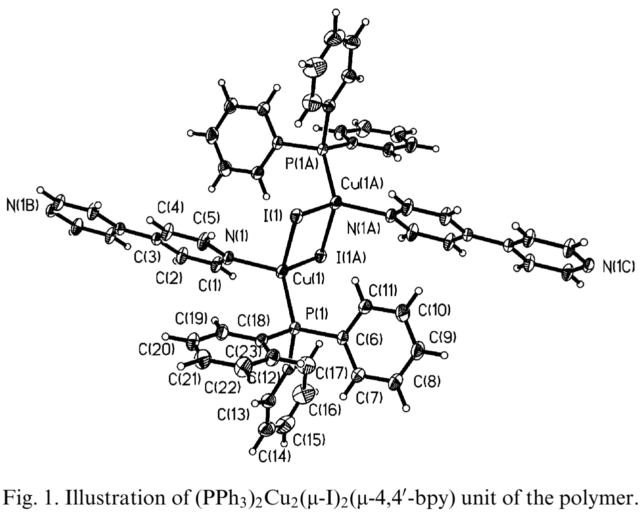

Fig. 1. Illustration of $(PPh_3)_2Cu_2(\mu\text{-}I)_2(\mu\text{-}4,4'\text{-bpy})$ unit of the polymer.

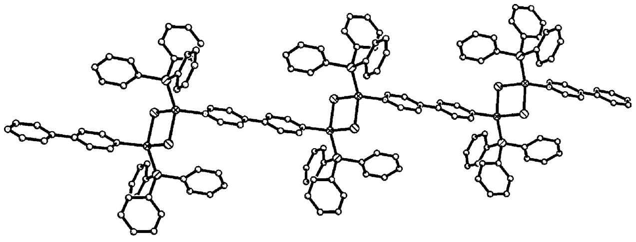

Fig. 2. View of the infinite chain architecture.

Table 1
Selected bond lengths (Å) and angles (°) for $[(PPh_3)_2Cu_2(\mu\text{-}I)_2(\mu\text{-}4,4'\text{-bpy})]_n$

Cu(1)–N(1)	2.079(2)
Cu(1)–P(1)	2.2434(8)
Cu(1)–I(1A)	2.6650(5)
Cu(1)–I(1)	2.7393(5)
I(1)–Cu(1A)	2.6650(5)
N(1)–Cu(1)–P(1)	120.04(7)
N(1)–Cu(1)–I(1A)	103.75(7)
P(1)–Cu(1)–I(1A)	114.74(2)
N(1)–Cu(1)–I(1)	101.15(7)
P(1)–Cu(1)–I(1)	107.13(2)
I(1A)–Cu(1)–I(1)	108.91(1)
Cu(1A)–I(1)–Cu(1)	71.10(1)

The N(1)–Cu(1)–P(1) and averaging values of N(1)–Cu(1)–I are 120.04(7)° and 102.45°. The P(1)–Cu(1)–I(1) and P(1)–Cu(1)–I(1A) are 107.13(2) and 114.74(2), respectively. The Cu(1)–N(1) distances of 2.079(2) Å and Cu(1)–P(1) of 2.2434(8) Å are comparable with those in its chloride analogues [14,16]. The Cu–I distances of 2.6650(5)–2.7393(5) Å are slightly longer than those of 2.499(3)–2.565(3) Å in the related chain complex $[Cu_2I_2(PPh_3)_2(C_4H_5N_3)]_n$ ($C_4H_5N_3$ = 2-aminopyrimidine) [18].

The solid state of the polymer is luminescent upon excited with UV light. Fig. 3 illustrates the emission spectrum of the complex with a peak maximum at 535 nm, upon excitation at 300–400 nm at room temperature. We have reported that the emission ($\lambda_{max}^{em} = 483$

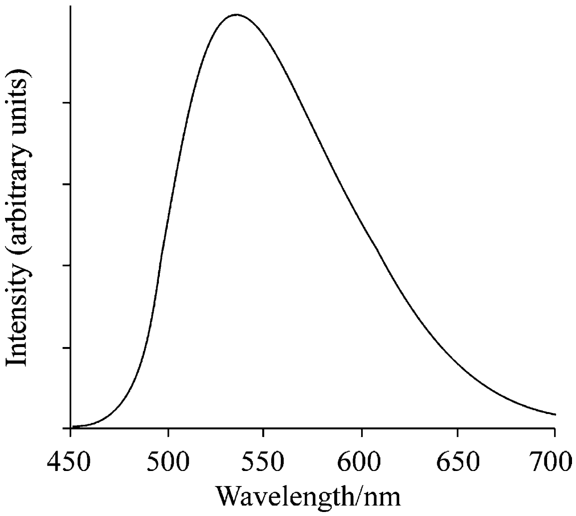

Fig. 3. Emission spectrum excited at 350 nm of the solid polymer at room temperature.

nm) of $[Cu_2(PPh_3)_4(CH_3CN)_2(\mu\text{-}4,4'\text{-bpy})](BF_4)_2$ originates from phosphine-intraligand transition, a red-shift of free triphenylphosphine ($\lambda_{max}^{em} = 450$ nm) [19]. Therefore emission of the polymer from phosphine can probably be ruled out. Intraligand emissive excited state has also been found in complexes with nitrogen-containing heterocyclic ligands [20,21], but this is not the case in our polymer for 4,4′-bpy does not emit at room temperature. Emission bands of various polynuclear CuX systems (X represents the halogen) were shown to depend on $(CuX)_n$ core structure [8]. Extensive experimental studies and molecular orbital calculations have been carried out on the $Cu_4I_4L_4$ system with Cu–Cu bonding [22,23]. These cubic complexes displays two different emission bands, e.g., 438 and 619 nm for L = pyridine. The higher energy band has been ascribed to a halide to ligand charge transfer (XLCT) excited state and lower energy band to a cluster-centered excited state (a combination of copper d–s transition and iodide to copper charge transfer XMCT). Likewise, excited states involving Cu–Cu interactions can be eliminated because of the distance between the copper atoms in the title polymer. The lowest excited state in the Cu(I) polymer is assigned as a Cu(I) to 4,4′-bpy metal-to-ligand charge transfer (MLCT) excited state in comparison with a dimeric complex $[(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(pyridine)_2]$ [9] with emission peak maximum at 510 nm. Similar assignment was also made in the $[(PPh_3)_2Cu_2(\mu\text{-}Cl)_2(\mu\text{-}pyz)]_n$ polymer on the basis of resonance Raman experiments [9].

Supplementary material

Crystallographic data for the title complex have been deposited at the Cambridge Crystallographic Data Centre with the deposition number of CCDC 200365. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) or from the corresponding author on request.

Acknowledgements

D. Li is grateful to the National Natural Science Foundation of China (29901004, 20271031) and Natural Science Foundation of Guangdong Province of China (021240) for financial support.

References

[1] R. Robson, J. Chem. Soc., Dalton Trans. (2000) 3735.
[2] C.B. Aakeröy, A.M. Beatty, D.S. Leinen, Angew. Chem., Int. Ed. Engl. 38 (1999) 1815.
[3] G.M. Whiteside, E.E. Simanek, J.P. Mathias, C.T. Seto, D.N. Chin, M. Mammen, D.M. Gordon, Acc. Chem. Res. 28 (1995) 37.
[4] S.W. Keller, S. Lopez, J. Am. Chem. Soc. 121 (1999) 6306.
[5] S.-L. Zheng, M.-L. Tong, X.-M. Chen, S.W. Ng, J. Chem. Soc., Dalton Trans. (2002) 360.
[6] A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M.A. Withersby, M. Schroder, Coord. Chem. Rev. 183 (1999) 117.
[7] V.W.-W. Yam, K.K.-W. Lo, Chem. Soc. Rev. 28 (1999) 323.
[8] P.C. Ford, E. Cariati, J. Bourassa, Chem. Rev. 99 (1999) 3625.
[9] M. Henary, J.L. Wootton, S.I. Khan, J.I. Zink, Inorg. Chem. 36 (1997) 796.
[10] H.-K. Fun, S.S.S. Raj, R.-G. Xiong, J.-L. Zuo, Z. Yu, X.-L. Zhu, X.-Z. You, J. Chem. Soc., Dalton Trans. (1999) 1711.
[11] S.R. Batten, B.F. Hoskins, R. Robson, Angew. Chem., Int. Ed. Engl. 34 (1995) 820.
[12] M. Fujita, Y.J. Kwon, O. Sasaki, K. Yamaguchi, K. Ogura, J. Am. Chem. Soc. 117 (1995) 7287.
[13] O.M. Yaghi, G. Li, Angew. Chem., Int. Ed. Engl. 34 (1995) 207.
[14] K. Biradha, A. Mondal, B. Moulton, M.J. Zaworotko, J. Chem. Soc., Dalton Trans. (2000) 3837.
[15] J. Lu, G. Crisci, T. Niu, A.J. Jacobon, Inorg. Chem. 36 (1997) 5140.
[16] G.M. Sheldrick, SHELX97, Program for X-ray Crystal Structure Solution and Refinement, Göttingen University, Germany, 1997.
[17] J.T. Sampanthar, J.J. Vittal, Cryst. Eng. 3 (2000) 117.
[18] Q.-H. Jin, X.-M. Lu, H.-J. Zhu, X.-P. Ji, Chin. J. Chem. 18 (2000) 928.
[19] D. Li, Z.-Y. Qi, Q. Feng, R.-Z. Li, X.-L. Feng, J.-W. Cai, Acta Chim. Sinica 60 (2002) 1637.
[20] D. Li, R.-Z. Li, Z. Ni, Z.-Y. Qi, X.-L. Feng, J.-W. Cai, Inorg. Chem. Commun. 6 (2003) 469.
[21] Q. Feng, D. Li, Y.-G. Yin, X.-L. Feng, J.-W. Cai, Acta Chim. Sinica 60 (2002) 2167.
[22] K.R. Kyle, C.K. Ryu, J.A. DiBenedetto, P.C. Ford, J. Am. Chem. Soc. 113 (1991) 2954.
[23] M. Vitale, W.E. Palke, P.C. Ford, J. Phys. Chem. 96 (1992) 8329.