Available online at www.sciencedirect.com

SCIENCE DIRECT®

Inorganic Chemistry Communications 9 (2006) 72–74

INORGANIC CHEMISTRY COMMUNICATIONS

www.elsevier.com/locate/inoche

# Synthesis, crystal structures and luminescence properties of $\{[Cu(\mu\text{-}PhPPy_2)(CH_3CN)]ClO_4\}_2$ dimer and monodimensional polymer $[Cu_2(\mu\text{-}PhPPy_2)_2(\mu\text{-}SO_4)]_\infty$ ($PhPPy_2$ = bis(2-pyridyl)phenylphosphine)

Tianle Zhang [a,*], Chunguang Chen [a], Yu Qin [a], Xianggao Meng [b]

[a] *Department of Chemistry, Huazhong University of Science and Technology, 1037 Luoyu, Wuhan, Hubei 430074, PR China*
[b] *Department of Chemistry, Central China Normal University, Wuhan, Hubei 430079, PR China*

Received 21 September 2005; accepted 9 October 2005

## Abstract

A new binuclear complex, $\{[Cu(\mu\text{-}PhPPy_2)(CH_3CN)]ClO_4\}_2$ (**1**) is synthesized by a direct reaction of $[Cu(CH_3CN)_4]ClO_4$ with $PhPPy_2$. Dimeric cation of **1**, $[Cu(\mu\text{-}PhPPy_2)(CH_3CN)]_2^{2+}$, can be utilized as building block precursor to construct coordination polymer $[Cu_2(\mu\text{-}PhPPy_2)_2(\mu\text{-}SO_4)]_\infty$ (**2**) by replacement of coordinated acetonitrile molecules with bridging ligand ($SO_4^{2-}$). Both **1** and **2** exhibit strong green emissions in solid state at room temperature. Crystal structures of **1** and **2** have been determined by single crystal X-ray diffraction.

*Keywords:* Binuclear copper(I) complex; Polymer; Bis(2-pyridyl)phenylphosphine; Luminescence

There is a great interest in construction of supramolecular assemblies or polymers [1]. Recently, incorporation of bi- or polynuclear units, such as $Mo_2^{4+}$ [2a], $Rh_2^{4+}$ [2a], $Ru_2^{5+}$ [2b,2c], and $Cu_4I_4$ [3], into extended frameworks becomes a new area of supramolecular chemistry and material science, in which way synthetic materials may posses some novel properties due to metal–metal interactions and rigidity of dimeric or cluster units [3,4]. 2-pyridylphosphine ligands, especially $Ph_2PPy$ ((2-pyridyl)diphenylphosphine), have been extensively used to synthesize homo- or heterobinuclear complexes to study metal–metal bonding, due to their abilities to lock two metals together to enhance metal–metal interaction and stabilize metals at low oxidation states [5]. We are interested in utilization of 2-pyridylphosphines to prepare bi- or polynuclear low-valent transition metal complexes as building block precursors to construct supramolecular assemblies or polymeric materials exhibiting catalytic and photoluminescence properties. Although compared to $Ph_2PPy$, the coordination modes of $PhPPy_2$ are complicated, not only as monodentate [6], but also bidentate [7] and tridentate [6,8], leading to bi- or polynuclear complexes [6a,9], our previous results revealed that $PhPPy_2$ could be a suitable ligand to bond to transition metals adopting tetrahedral or square-planar geometry to form rigid binuclear complexes [9b]. In this paper, synthesis, crystal structures and luminescence properties of a binuclear copper(I) complex **1** and related polymer **2** are reported.

A direct reaction of $PhPPy_2$ with $[Cu(CH_3CN)_4]ClO_4$ quantitatively affords an air- and light-stable binuclear Cu(I) complex, $\{[Cu(\mu\text{-}PhPPy_2)(CH_3CN)]ClO_4\}_2$ (**1**). Single crystal X-ray crystallographic studies show that in solid state, two copper atoms are bridged by two *cis*-$PhPPy_2$ ligands (Fig. 1) [10]. Each copper atom adopts a distorted tetrahedral geometry, coordinated by one P and three N

---

[*] Corresponding author. Fax: +86 27 87543632.
*E-mail address:* tlzhang@mail.hust.edu.cn (T. Zhang).

1387-7003/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2005.10.012

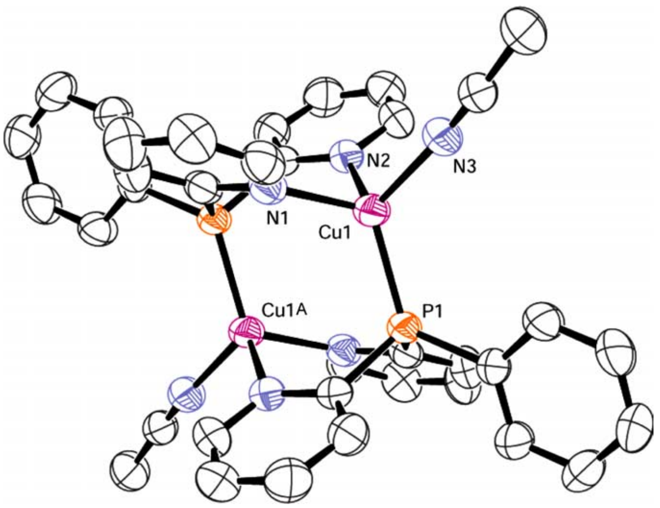

Fig. 1. Molecular structure of **1**. $ClO_4^-$ anions are omitted for clarity. Selected bond lengths (Å) and angles (°) Cu(1)–P(1) 2.1908(9), Cu(1)–N(1) 2.073(3), Cu(1)–N(2) 2.047(3), Cu(1)–N(3) 2.026(3), N(1)–Cu(1)–N(3) 100.70(13), N(1)–Cu(1)–N(2) 94.38(11), N(2)–Cu(1)–N(3) 104.31(13), P(1)–Cu(1)–N(1) 118.25(8), P(1)–Cu(1)–N(2) 115.94(9), P(1)–Cu(1)–N(3) 119.36(9).

atoms, two of which are from pyridyl groups of another $PhPPy_2$ ligand, and one from acetonitrile molecule. This coordination mode of $PhPPy_2$ is similar to that observed in $[(PhPPy_2)_2PdCuCl_2]ClO_4$ [9b]. Bond lengths of Cu–P and Cu–N (from pyridyl groups), and related bond angles are normal. A distance of Cu–N (from acetonitrile) is 2.026(3) Å, shorter than that found in $[Cu_3(dpmp)_2(CH_3CN)_2(\mu\text{-}Cl)_2]ClO_4$ (2.13(1) Å) [11]. The Cu...Cu distance is 3.691 Å. At this value, no Cu...Cu interaction is expected. Interestingly, two copper atoms are collinear with two coordinated acetonitrile molecules.

In our synthetic strategy to coordination polymers and supramolecular assemblies with controllable structures, bridging ligands with specific geometries are chosen as linkers to connect bi- or polynuclear units. In $\{[Cu(\mu\text{-}PhPPy_2)(CH_3CN)]ClO_4\}_2$ molecule, $PhPPy_2$ groups are non-labile, while coordinated acetonitrile molecules are possibly easy to be exchanged by various linkers, which could allow the construction of high-order architectures. While adding $CuSO_4$ in methanol to a solution of **1** in acetonitrile, a deep blue-green solution was obtained, from which polymer **2** crystallized as a pale green-yellow blocks in moderate yield (62.5%). Polymer **2** is not soluble in common organic solvents, such as dichloromethane, acetonitrile and methanol. IR data indicated that anion metathesis reaction occurred and the bands for coordinated acetonitrile molecules disappeared. X-ray diffraction studies confirm this, and reveal that the dimeric cations, $[Cu(\mu\text{-}PhPPy_2)]_2^{2+}$, are connected by sulfate anions to form a zigzag chain (Fig. 2) [12]. The angle of S–O–Cu is 177.1(10)°, just slightly deviated from perfect linearity [13]. Two copper centers are still collinear with two oxygen atoms from coordinated sulfate anions.

Mono- or polynuclear copper(I) complexes and polymers have been extensively studied due to their fascinating luminescence properties [3,14,15]. At room temperature, both **1** and **2** exhibit intense green emissions with bands around 531 and 535 nm in solid state, respectively. The spectra of polymer **2** is shown in Fig. 3. It is unreasonable to assign the observed luminescence to intraligand $PhPPy_2$ $\pi \rightarrow \pi^*$, as the energy gap between the two emission maxima is on the order of 7480 $cm^{-1}$ ($\lambda_{max}^{emi} = 380$ nm for free $PhPPy_2$). This emission band might be assigned as metal to ligand charge transfer (MLCT), mainly arising from

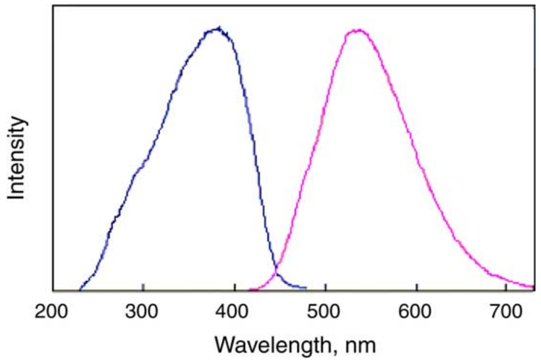

Fig. 3. Excitation and emission spectra of **2** in solid state at room temperature: emission spectrum ($\lambda_{max} = 531$ nm); excitation spectrum ($\lambda_{max} = 375$ nm).

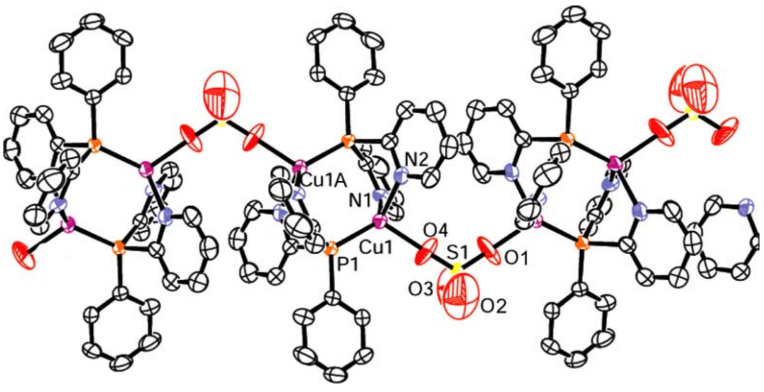

Fig. 2. Crystal structure of **2**. Selected bond lengths (Å) and angles (°): Cu(1)–P(1) 2.1792(17), Cu(1)–N(1) 2.084(6), Cu(1)–N(2) 2.059(6), Cu(1)–O(4) 2.024(7), N(1)–Cu(1)–P(1) 123.30(15), N(2)–Cu(1)–P(1) 120.50(17), N(2)–Cu(1)–N(1) 92.7(2), O(4)–Cu(1)–N(1) 101.8(4), O(4)–Cu(1)–N(2) 98.2(4), O(4)–Cu(1)–P(1) 115.4(3), S(1)–O(4)–Cu(1) 177.1(10), O(4)–S(1)–O(1) 114.3(9), O(3)–S(1)–O(2) 103.5(16).

Cu(I) → $PhPPy_2$ as no noticeable change was observed while the replacement of coordinated acetonitrile molecules by sulfate anions occurred [14a].

Upon to date, there have been a number of Cu(I) polymers reported [16], but synthetic strategies to coordination polymers, especially low-dimensional polymers with designed architectures, and structure–property relationship of polymers still remain to be further investigated. Due to the rigidity and linear geometry for **1**, $\{Cu(\mu\text{-}PhPPy_2)(CH_3CN)ClO_4\}_2$, could be an excellent building block precursor for the construction of supramolecular assemblies or coordination polymers. Work in this area is in progress.

## References

[1] (a) S. Kitagawa, R. Kitaura, S. Noro, Angew. Chem., Int. Edn. 43 (2004) 2334;
(b) O.R. Evans, W. Lin, Acc. Chem. Res. 35 (2002) 511;
(c) S.R. Seidel, P.J. Stang, Acc. Chem. Res. 35 (2002) 972;
(d) M. Fujita, M. Tominaga, A. Hori, B. Therrien, Acc. Chem. Res. 38 (2005) 371.

[2] (a) F.A. Cotton, C. Lin, C.A. Murillo, Proc. Natl. Acad. Sci. USA 99 (2002) 4810;
(b) P. Angaridis, J.F. Berry, F.A. Cotton, C.A. Murillo, X. Wang, J. Am. Chem. Soc. 125 (2003) 10327;
(c) G. Arribas, M.C. Barral, R. González-Prieto, R. Jiménez-Aparicio, J.L. Priego, M.R. Torres, F.A. Urbanos, Inorg. Chem. 44 (2005) 5770.

[3] S. Hu, M.-L. Tong, J. Chem. Soc., Dalton Trans. (2005) 1165.

[4] (a) F.A. Cotton, C. Lin, C.A. Murillo, Acc. Chem. Res. 34 (2001) 759;
(b) Z. Peng, Angew. Chem., Int. Edn. 43 (2004) 930;
(c) S.-L. Zheng, M. Messerschmidt, P. Coppens, Angew. Chem., Int. Edn. 44 (2005) 4614;
(d) Y. Fuma, M. Ebihara, S. Kutsumizu, T. Jawamura, J. Am. Chem. Soc. 126 (2004) 12238;
(e) F.A. Cotton, P. Lei, C. Lin, C.A. Murillo, X. Wang, S.-Y. Yu, Z.-X. Zhang, J. Am. Chem. Soc. 126 (2004) 1518.

[5] (a) P. Espinet, K. Soulantica, Coord. Chem. Rev. 193-195 (1999) 499;
(b) Z.Z. Zhang, H. Cheng, Coord. Chem. Rev. 147 (1996) 1.

[6] (a) P. Espinet, P. Gómez-Elipe, F. Villafañe, J. Organomet. Chem. 450 (1993) 145;
(b) G.R. Newkome, D.W. Ecans, F.R. Fronczek, Inorg. Chem. 26 (1987) 3500.

[7] (a) P. Espinet, R. Hernando, G. Iturbe, F. Villafañe, A.G. Orpen, I. Pascual, Eur. J. Inorg. Chem. (2000) 1013;
(b) Y. Xie, C.L. Lee, Y. Yang, S.J. Rettig, B.R. James, Can. J. Chem. 70 (1992) 751;
(c) G.F. Zhang, J. Zhao, G.R. Sieber, E. Herdtweck, F.E. Kühn, Polyhedron 21 (2002) 1737.

[8] R.P. Schtte, S.J. Rettig, A.M. Joshi, B.R. James, Inorg. Chem. 36 (1997) 5809.

[9] (a) J.A. Casares, P. Espinet, J.M. Martin-Alvarez, V. Santos, Inorg. Chem. 43 (2004) 189;
(b) T. Zhang, Y. Qin, D. Wu, C. Wang, C. Liu, J. Coord. Chem. 58 (2005) 1485.

[10] *Dimer* **1**: UV–Vis($CH_3CN$) $\lambda$, nm: 211, 235, 310; IR(KBr disk), $\nu$, $cm^{-1}$: 2020($CH_3CN$), 1145, 1086, 626($ClO_4^-$); *Anal.* Calcd. for $C_{18}H_{16}N_3O_4PClCu$: C, 46.17; H, 3.44; N, 8.97, Found: C, 46.03; H, 3.51; N, 9.02. *Crystal data for* **1** *at 292 K*: Monoclinic, $P2_1/n$, $a = 8.7492(8)$ Å, $b = 9.8287(8)$ Å, $c = 23.0359(19)$ Å, $\beta = 91.540(2)°$, $V = 1980.2(3)$ Å$^3$, $Z = 4$, $\rho = 1.571$ Mg/m$^{-3}$, abs. coeff. = 1.348 mm$^{-1}$, $F(000) = 952$, $\theta$ range: 1.77–26.00°, $R_1 = 0.0473$, $wR_2 = 0.1336$ $[I > 2\sigma(I)]$; $R_1 = 0.0564$, $wR_2 = 0.1410$ (all data), $S = 1.036$.

[11] D. Li, H.-K. Yip, C.-M. Che, Z.-Y. Zhou, T.C.W. Mak, S.-T. Liu, J. Chem. Soc., Dalton Trans. (1992) 2445.

[12] *Polymer* **2**: Pale yellow-green crystals become powder when exposed to air due to partial loss of solvated molecules. IR(KBr disk), $\nu$, $cm^{-1}$: 1165, 1046, 617($SO_4^{2-}$). *Crystal data for* **2** ($C_{32}H_{26}N_4O_4P_2SCu_2 \cdot 2\text{-}CH_3OH \cdot H_2O$) *at 293 K*: Orthorhombic, Pbcn, $a = 10.056(2)$ Å, $b = 20.966(5)$ Å, $c = 17.043(4)$ Å, $\beta = 90.00°$, $V = 3593.3(14)$ Å$^3$, $Z = 4$, $\rho = 1.537$ Mg/m$^{-3}$, abs. coeff. = 1.384 mm$^{-1}$, $F(000) = 1704$, $\theta$ range: 1.94–25.00 °, $R_1 = 0.0688$, $wR_2 = 0.1967$ $[I > 2\sigma(I)]$; $R_1 = 0.1033$, $wR_2 = 0.2412$ (all data), $S = 1.160$.

[13] C. Tamasi, R. Cini, J. Chem. Soc., Dalton Trans. (2003) 2928.

[14] (a) P.C. Ford, E. Cariati, J. Bourassa, Chem. Rev. 99 (1999) 3625;
(b) H.V.R. Dias, H.V.K. Diyabalanage, M.A. Rawashdeh-Omary, M.A. Franzman, M.A. Omary, J. Am. Chem. Soc. 125 (2003) 12072;
(c) V.W.-W. Yam, Acc. Chem. Res. 35 (2002) 553;
(d) C.-M. Che, Z. Mao, V.M. Miskowski, M.-C. Tse, C.-K. Chan, K.-K. Cheung, D.L. Phillips, K.-H. Leung, Angew. Chem., Int. Edn. 39 (2000) 4084.

[15] (a) D. Fortin, M. Drouin, M. Turcotte, P.D. Harvey, J. Am. Chem. Soc. 119 (1997) 531;
(b) E. Fournier, F. Lebrun, M. Drouin, A. Decken, P.D. Harvey, Inorg. Chem. 43 (2004) 3127;
(c) M. Henary, J.L. Wootton, S.I. Khan, J.I. Zink, Inorg. Chem. 36 (1997) 796.

[16] (a) X.-C. Huang, J.-P. Zhang, X.-M. Chen, J. Am. Chem. Soc. 126 (2004) 13218;
(b) J.-P. Zhang, S.-L. Zheng, X.-C. Huang, X.-M. Chen, Angew. Chem., Int. Edn. 43 (2004) 206;
(c) X.-M. Zhang, R.-Q. Fang, H.-S. Wu, J. Am. Chem. Soc. 127 (2005) 7670;
(d) D. Li, T. Wu, X.-P. Zhou, R. Zhou, X.-C. Huang, Angew. Chem., Int. Edn. 44 (2005) 4175.