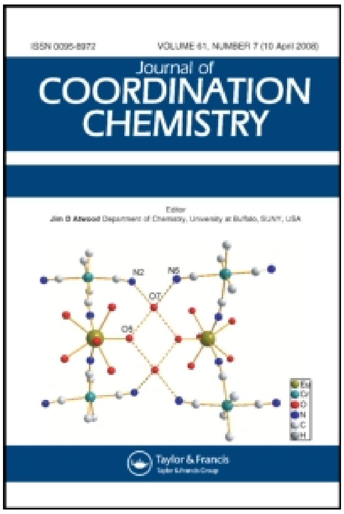

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses, structures and fluorescent properties of three copper cyanide coordination polymers based on N-heterocyclic ligands

Sheng-Wen Liang[a]; Xiang He[a]; Min Shao[b]; Ming-Xing Li[a]
[a] Department of Chemistry, College of Science, Shanghai University, Shanghai 200444, China [b] Instrumental Analysis and Research Center, Shanghai University, Shanghai 200444, China

To cite this Article Liang, Sheng-Wen , He, Xiang , Shao, Min and Li, Ming-Xing(2008) 'Syntheses, structures and fluorescent properties of three copper cyanide coordination polymers based on N-heterocyclic ligands', Journal of Coordination Chemistry, 61: 18, 2999 — 3007, First published on: 22 September 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970801995701

URL: http://dx.doi.org/10.1080/00958970801995701

Journal of Coordination Chemistry
Vol. 61, No. 18, 20 September 2008, 2999–3007

Syntheses, structures and fluorescent properties of three copper cyanide coordination polymers based on N-heterocyclic ligands

SHENG-WEN LIANG†, XIANG HE†, MIN SHAO‡ and MING-XING LI*†

†Department of Chemistry, College of Science, Shanghai University,
Shanghai 200444, China
‡Instrumental Analysis and Research Center, Shanghai University, Shanghai 200444, China

(*Received 22 February 2007; in final form 20 November 2007*)

Hydrothermal reactions of CuCN, $K_3[Fe(CN)_6]$ with 2,2′-bipyridine, 1,10-phenanthroline or 2,6-*bis*(1,2,4-triazolyl)pyridine (btp) afford three coordination polymers, $[Cu_7(CN)_7(bipy)_2]_n$ (**1**), $[Cu_2(CN)_2(phen)]_n$ (**2**) and $[Cu_3(CN)_3(btp)]_n$ (**3**). Complex **1** displays 1D polymeric ribbons which are assembled through Cu $\cdots$ Cu and π–π stacking interactions into a 3D framework. Complex **2** shows a 1D zigzag chain structure in which phen is a side ligand. In **3**, the copper cyanide 2D polymeric networks are connected by tridentate btp to form a 3D metal-organic framework. These coordination polymers exhibit strong fluorescent emissions in the solid state.

Keywords: Copper(I) cyanide; N-Heterocyclic ligand; Coordination polymer; Crystal structure; Fluorescence

1. Introduction

Coordination polymers have intriguing structural motifs and potential applications in functional materials [1–3]. Much effort has focused on design and controlled synthesis of coordination polymers. Transition metal cyanides have been studied extensively due to their importance in magnetism and other properties [4–6]. There has been a growing interest in copper(I) cyanide coordination polymers, with CuCN a good molecular building block in constructing metal-organic frameworks [7–10]. Cu(I) favors trigonal or tetrahedral coordination with cyanide and N-heterocyclic ligands [11, 12]. A series of copper(I) cyanide coordination polymers incorporating organodiimine ligands have been synthesized and structurally characterized [13, 14]. In our research on metal-organic frameworks and coordination polymers [15], three new copper cyanide coordination polymers based on N-heterocyclic ligands have been prepared hydrothermally. Herein, we report their syntheses, crystal structures, thermal stability and fluorescence.

---

*Corresponding author. Email: mx_li@mail.shu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970801995701

2. Experimental

2.1. *Materials and measurements*

Btp was prepared according to the literature method [16]. Other chemicals were of reagent grade and used as received without further purification. Elemental analyses (C, H, N) were performed on a Vario EL III elemental analyzer. Infrared spectra were recorded on a Nicolet A370 spectrometer by KBr pellet in the 400–4000 cm^{-1} region. TG-DSC analyses were completed on a Netzsch STA 449C thermal analyzer from 20 to 800°C at a heating rate of 10°C min^{-1} in air. Fluorescent spectra of crystalline samples were recorded on a Shimadzu RF-5301 PC spectrophotometer.

2.2. *Synthesis*

$[Cu_7(CN)_7(bipy)_2]_n$ (1): A mixture of CuCN (0.4 mmol), $K_3[Fe(CN)_6]$ (0.1 mmol), 2,2′-bipyridine (0.2 mmol) and 8 mL water was sealed in a 15-mL Teflon-lined reactor. The mixture was heated at 180°C for 48 h under autogenous pressure. Upon cooling to room temperature at a rate of 10°C h^{-1}, light yellow block crystals of **1** were harvested in 35% yield based on Cu. The crystals were washed thoroughly with 10 mL deionized water three times, with 2 mL ethanol twice, and dried in air. Anal. Calcd for $C_{27}H_{16}Cu_7N_{11}$ (%): C, 34.53; H, 1.72; N, 16.40. Found: C, 34.66; H, 1.73; N, 16.48. IR (KBr, cm^{-1}): 3066 w, 2131 s, 1597 s, 1469 m, 1439 s, 1153 w, 762 s, 734 w.

$[Cu_2(CN)_2(phen)]_n$ (2): A mixture of CuCN (0.4 mmol), $K_3[Fe(CN)_6]$ (0.2 mmol), 1,10-phenanthroline (0.2 mmol) and 10 mL water was sealed in a 25-mL Teflon-lined reactor. The mixture was heated at 170°C for 24 h under autogenous pressure. Upon cooling to room temperature at a rate of 10°C h^{-1}, orange prism-like crystals of **2** were collected in 55% yield based on Cu. These crystals were manually separated from a mixture of dark red needle crystals of $[Cu_6(CN)_6(phen)_4]_n$ [13]. The crystals were washed thoroughly with 10 mL deionized water three times and with 2 mL ethanol twice, and dried in air. Anal. Calcd for $C_{14}H_8Cu_2N_4$ (%): C, 46.80; H, 2.24; N, 15.59. Found: C, 46.86; H, 2.23; N, 15.63. IR (KBr, cm^{-1}): 3048 w, 2120 s, 1620 w, 1585 w, 1508 w, 1421 m, 1136 w, 842 s, 728 s.

$[Cu_3(CN)_3(btp)]_n$ (3): A mixture of CuCN (0.3 mmol), $K_3[Fe(CN)_6]$ (0.2 mmol), btp (0.3 mmol) and 10 mL water was sealed in a 15-mL Teflon-lined stainless-steel reactor. The mixture was heated at 140°C for 72 h under autogenous pressure. Upon cooling to room temperature at a rate of 10°C h^{-1}, colorless block crystals of **3** were harvested in 35% yield based on Cu. Anal. Calcd for $C_{12}H_7Cu_3N_{10}$ (%): C, 29.91; H, 1.46; N, 29.07. Found: C, 30.14; H, 1.48; N, 28.96. IR (KBr, cm^{-1}): 3138 w, 3098 m, 2113 s, 1606 s, 1588 w, 1513 s, 1455 s, 1241 s, 1048 s, 801 m, 764 w, 629 m.

2.3. *X-ray crystallography*

Well-shaped single crystals of **1**, **2** and **3** were selected for X-ray diffraction study. Data collections were performed with graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) on a Bruker Smart Apex-II CCD diffractometer at $T = 273(2)$ K.

Table 1. Crystal data and structure refinement for **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{27}H_{16}Cu_7N_{11}$	$C_{14}H_8Cu_2N_4$	$C_{12}H_8Cu_3N_{10}$
Formula weight	939.29	359.32	482.90
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	*Pbca*	$P2(1)/n$
a (Å)	8.6585(1)	8.2739(8)	14.1682(14)
b (Å)	9.4173(2)	15.5840(15)	6.8770(7)
c (Å)	10.8453(3)	20.704(2)	16.1200(16)
α (°)	102.214(2)	90.0	90
β (°)	95.596(2)	90.0	111.482(1)
γ (°)	115.843(1)	90.0	90
V (Å^3)	759.56(3)	2669.5(4)	1461.5(3)
Z	1	8	4
D_{Calc} (Mg m^{-3})	2.053	1.788	2.195
Absorption coefficient (mm^{-1})	4.844	3.178	4.346
F(000)	458	1424	7135
Crystal size (mm^3)	0.20 × 0.10 × 0.10	0.40 × 0.30 × 0.30	0.30 × 0.25 × 0.12
Unique reflections	2691 [$R_{\mathrm{int}} = 0.0314$]	2364 [$R_{\mathrm{int}} = 0.0221$]	2563 [$R_{\mathrm{int}} = 0.0164$]
Data/restraints/parameters	2691/0/205	2364/0/182	2563/0/226
R [$I > 2\sigma(I)$]	$R_1 = 0.0286$, $wR_2 = 0.0655$	$R_1 = 0.0234$, $wR_2 = 0.0604$	$R_1 = 0.0245$, $wR_2 = 0.0648$
R (all data)	$R_1 = 0.0412$, $wR_2 = 0.0710$	$R_1 = 0.0301$, $wR_2 = 0.0625$	$R_1 = 0.0281$, $wR_2 = 0.0664$
Goodness-of-fit on F^2	1.029	1.056	1.046

Determinations of the crystal system, orientation matrix and cell dimensions were performed according to established procedures. Lorentz polarization and absorption corrections were applied. The structures were solved by direct method with SHELXS-97 and refined by full-matrix least squares on F^2 with SHELXL-97 [17]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at their calculated position. The crystal data and structure refinement results are summarized in table 1.

3. Results and discussion

3.1. *Synthesis and IR spectra*

Complexes **1**, **2** and **3** were prepared by hydrothermal reactions of CuCN with 2,2′-bipy, 1,10-phen or btp in the presence of $K_3[Fe(CN)_6]$. Here $K_3[Fe(CN)_6]$ acts as a cyanide source [16]. Preparation of **1**, **2** and **3** without $K_3[Fe(CN)_6]$ failed. We previously reported the double helical copper cyanide coordination polymer $[Cu_3(CN)_3(phen)]_n$ [15]. Trying to prepare this complex under similar hydrothermal condition, only changing the volume of water from 8 mL to 10 mL and the reactor volume from 15 mL to 25 mL, a new complex **2** was prepared unexpectedly.

IR absorptions in the region of 2200–2000 cm^{-1} are due to CN^- stretching vibrations [18]. The characteristic strong absorptions of cyanide for **1**, **2** and **3** appear at 2131, 2120, and 2113 cm^{-1} respectively. All cyanide groups with a single vibration peak indicates that they are bound to copper in one coordination mode. There also exist characteristic absorption bands of bipy, phen and bpt in the IR spectra of **1**–**3**. The formulas have been confirmed by elemental analysis data and X-ray structural analysis.

3.2. *Description of structures*

3.2.1. Structure of $[Cu_7(CN)_7(bipy)_2]_n$ (1). X-ray structural analysis revealed that **1** has a one-dimensional ribbon polymeric structure. The molecular structure and packing diagram are illustrated in figure 1. Selected bond lengths and angles are listed in table 2.

In **1**, the asymmetric structural unit contains four crystallographically independent copper(I) atoms. Cu(1) is planar, trigonally coordinated by bipy and a cyanide group. Bond angle C(3)–Cu(1)–N(5) is 131.47(14)°. Cu(2) is planar, trigonally coordinated by three bridging cyanide groups. Bond angles N(1)–Cu(2)–N(2), N(1)–Cu(2)–C(4) and N(2)–Cu(2)–C(4) are 117.98(12), 124.72(13), 115.85(13)°, respectively. Both Cu(3) and Cu(4) are two-coordinate with bridging cyanide groups. Bond angles C(2)–Cu(3)–N(3) and N(4)–Cu(4)–N(4A) are 169.70(16), 179.997(1)°, respectively. Other bond lengths and angles are as expected.

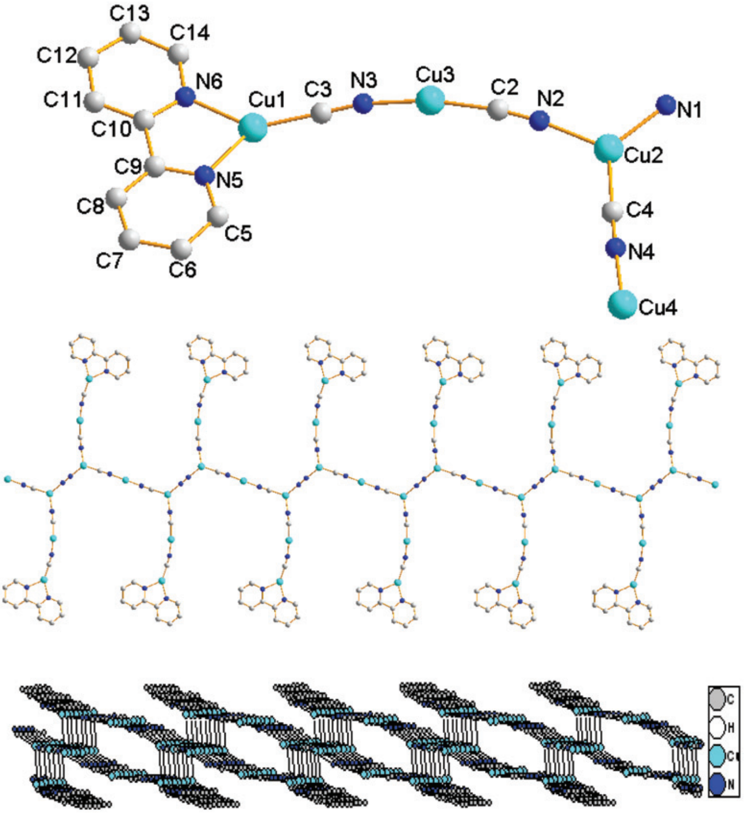

Figure 1. Asymmetric structural unit and ribbon polymeric structure of **1.**

In **1**, all cyanide groups are μ_2-bridges. The structure of **1** is a one-dimensional polymeric ribbon with 2,2′-bipyridine coordinated along both sides. The π–π stacking interactions between parallel 2,2′-bipyridine aromatic rings are of three types with plane-to-plane separation of 3.319, 3.363 and 3.378 Å. There exist obvious Cu ··· Cu interactions between different ribbons. The Cu ··· Cu distances vary from 2.891 to 2.941 Å. Through the Cu ··· Cu and π–π stacking interactions, the ribbons are further connected to form a three-dimensional framework.

3.2.2. Structure of $[Cu_2(CN)_2(phen)]_n$ (2).

Complex **2** shows one-dimensional zigzag chain polymeric structure. The molecular structure and packing diagram are illustrated in figure 2. Selected bond lengths and angles are listed in table 3.

In **2**, the asymmetric structural unit consists of two crystallographically independent copper(I) atoms, two cyanide groups, and one phen. Cu(1) is tetrahedrally coordinated by phen and two bridging cyanides. Bond angles N(3)–Cu(1)–C(14) and N(3)–Cu(1)–N(1) are 115.84(9), 108.32(7)°, respectively. Cu(2) is two-coordinate by bridging cyanide groups in a nonlinear fashion. Bond angle N(4)–Cu(2)–C(13) is 173.75(11)°. All cyanide groups are μ_2-bridges linking Cu(I) atoms to form a 1D zigzag chain in which phen is a side ligand.

Adjacent zigzag chains cross mutually, while pairs of chains are parallel to each other, different than the double helical structure of $[Cu_3(CN)_3(phen)]_n$ [15]. There exist π–π stacking interactions between parallel phen aromatic rings with plane-to-plane separation of 3.473 Å, by which the zigzag chains are assembled into a three-dimensional supramolecular framework.

3.2.3. Structure of $[Cu_3(CN)_3(btp)]_n$ (3).

Complex **3** is a three-dimensional coordination polymer. The molecular structure and packing diagram are illustrated in figure 3. Selected bond lengths and angles are listed in table 4.

The asymmetric structural unit consists of three crystallographically independent copper(I) atoms, three cyanides and a btp ligand. Both Cu(1) and Cu(2) atoms are in distorted tetrahedral coordination environments, coordinated to a triazole N atom of btp and three bridging cyanide groups. Bond lengths Cu(1)–N(8) and Cu(2)–N(3A) are 2.062(2), 2.030(2) Å respectively. Cu(3) is in a trigonal coordination environment, coordinating to a triazole N and two bridging cyanides. Bond length Cu(3)–N(7) is 2.024(2) Å. Btp is tridentate coordinating to three Cu(I) atoms through three triazole N atoms, while N(4) and pyridyl N(6) are uncoordinated.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu(1)–N(5)	2.048(3)	Cu(2)–C(4)	1.915(3)
Cu(1)–N(6)	2.016(3)	Cu(3)–C(2)	1.833(3)
Cu(1)–C(3)	1.844(4)	Cu(3)–N(3)	1.828(3)
Cu(2)–N(1)	1.923(3)	Cu(4)–N(4)	1.858(4)
Cu(2)–N(2)	1.966(3)		
C(3)–Cu(1)–N(5)	131.47(14)	N(1)–Cu(2)–C(4)	124.72(13)
C(3)–Cu(1)–N(6)	142.83(15)	N(2)–Cu(2)–C(4)	115.85(13)
N(5)–Cu(1)–N(6)	80.74(11)	C(2)–Cu(3)–N(3)	169.70(16)
N(1)–Cu(2)–N(2)	117.98(12)	N(4)–Cu(4)–N(4A)	179.997(1)

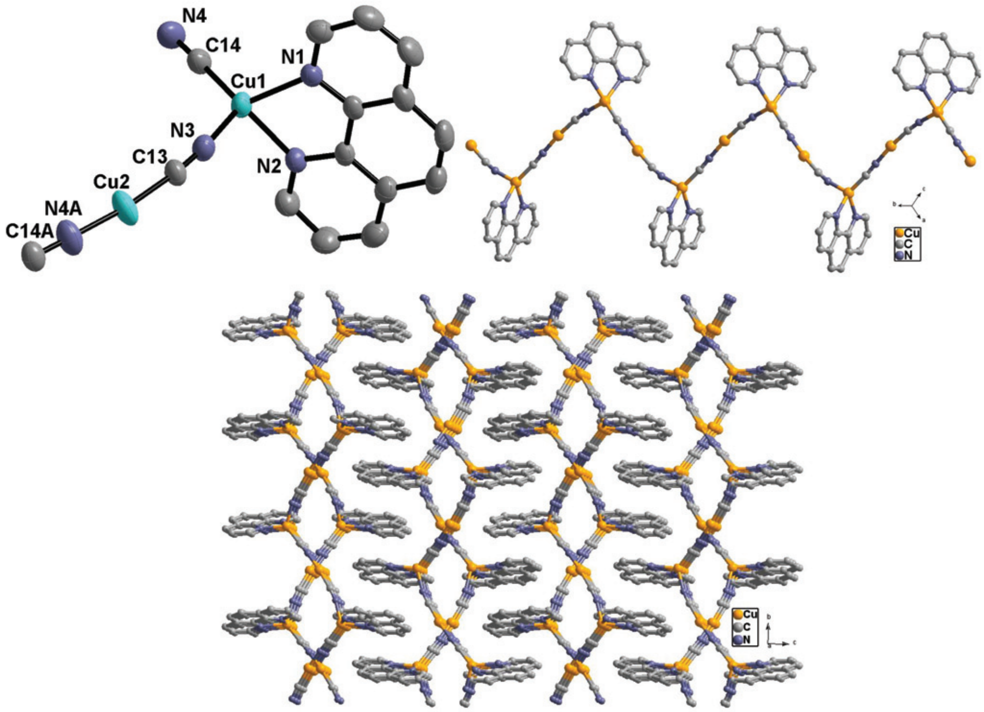

Figure 2. Views of the zigzag chain structure and packing diagram of **2.**

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Cu(1)–N(1)	2.1197(18)	Cu(1)–C(14)	1.877(2)
Cu(1)–N(2)	2.0765(19)	Cu(2)–N(4)	1.829(2)
Cu(1)–N(3)	1.999(2)	Cu(2)–C(13)	1.831(2)
N(1)–Cu(1)–N(2)	79.28(7)	C(14)–Cu(1)–N(3)	115.84(9)
N(1)–Cu(1)–N(3)	108.32(7)	N(4)–Cu(2)–C(13)	173.75(11)
N(2)–Cu(1)–N(3)	99.93(8)		

The three cyanides adopt different coordination modes. Two tridentate cyanide groups link Cu(1) and Cu(2) to form a dimer. Such dimers are further linked with Cu(3) to form a 1D copper cyanide chain. The third cyanide is a bidentate bridge, connecting the 1D copper cyanide chains to generate a 2D polymeric network composed of Cu(I) and cyanides in a 1:1 ratio. The copper cyanide 2D layers are further connected by tridentate btp ligands to form a 3D metal-organic framework. Generally, btp possesses seven potential N-donors making it appealing for coordination polymers; however, only two btp complexes have been documented to date [19, 20].

3.3. *Thermal stability and fluorescence*

Thermal stability is an important property for metal-organic frameworks. Complex **1** is stable to 270°C. An endothermic maximum at 280.9°C without weight-loss indicates

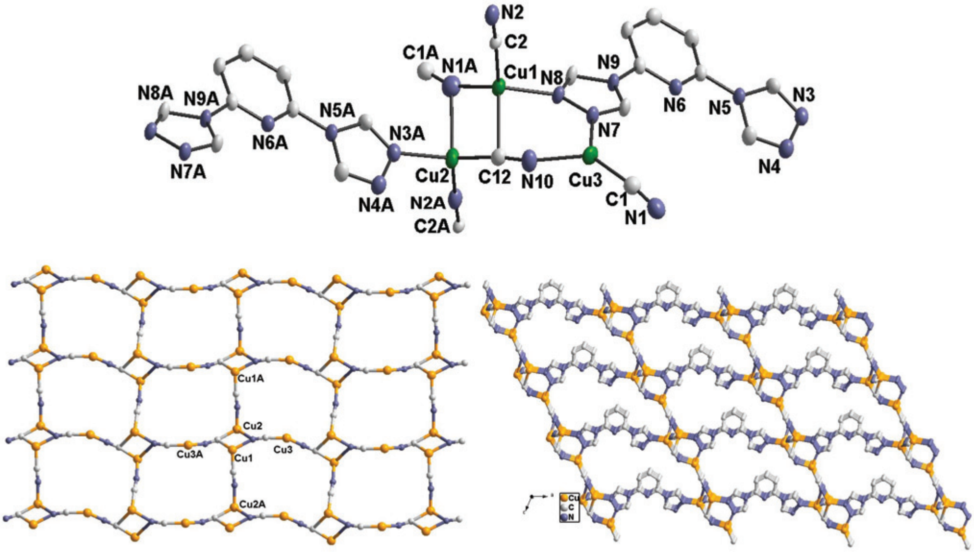

Figure 3. Asymmetric structural unit and coordination network of **3.**

Table 4. Selected bond lengths (Å) and angles (°) for **3**.

Cu(1)–C(2)	1.931(3)	Cu(2)–C(12)	1.926(3)
Cu(1)–N(1)	1.980(3)	Cu(2)–N(2)	1.951(3)
Cu(1)–N(8)	2.062(2)	Cu(2)–N(3)	2.030(2)
Cu(1)–C(12)	2.342(3)	Cu(2)–N(1)	2.422(3)
Cu(3)–C(1)	1.862(3)	Cu(3)–N(7)	2.024(2)
Cu(3)–N(10)	1.960(3)		
N(1)–Cu(1)–N(8)	118.22(11)	N(10)–Cu(3)–N(7)	98.49(10)
C(2)–Cu(1)–C(12)	109.03(11)	C(1)–Cu(3)–N(10)	129.82(12)
N(1)–Cu(1)–C(12)	106.90(12)	C(1)–Cu(3)–N(7)	131.05(11)

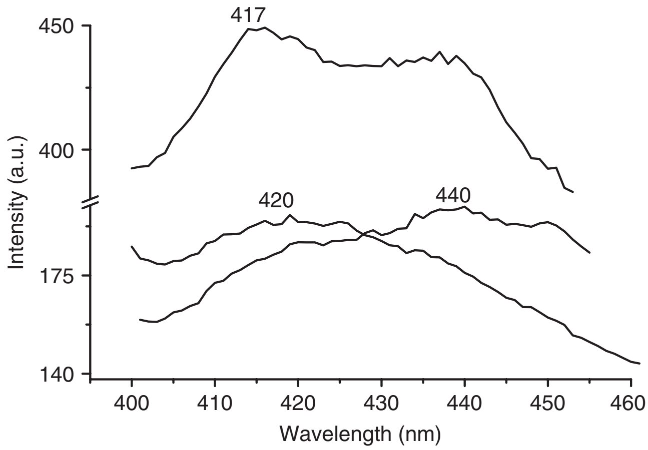

Figure 4. Fluorescent emission spectra of **1**–**3**.

a phase transfer process. This is also observed in $[Cu_3(CN)_3(phen)]_n$ (299.4°C) [15]. In the temperature range of 280–700°C, the complex decomposed continuously with the final thermal stable residue CuO (Found 60.04%, Calcd 59.28%). Similar to **1**, complex **2** is stable to 260°C and exhibiting an endothermic maximum at 279.4°C. In the range of 260–800°C, the complex decomposed continuously with 51.25% CuO residue left (Calcd 44.28%).

The complexes **1**–**3** are strong blue fluorescent emitters in the solid state under excitations. Photo-excitations of **1**, **2** and **3** with 355 nm light give emission peaks with maxima at 440, 420, and 417 nm, respectively. Generally, metal-to-ligand charge transfer (MLCT) is the lowest electronic excited state for fluorescent emission of copper(I) cyanide complexes [21, 22], and **1**–**3** may be assigned to the electron transferred from Cu(I) to the π^* orbital of cyanide [23, 24].

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC-636041 for **1**, CCDC-619855 for **2** and CCDC-619856 for **3**. Copies of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2IEZ, UK. Email: deposit@ccdc.cam.ac.uk.

Acknowledgements

Financially supported by the Research Foundation for Returned Chinese Scholars Overseas of Chinese Education Ministry (7A14219), and the Development Foundation of Shanghai Education Commission (03AK35).

References

[1] S.R. Seidel, P.J. Stang. *Acc. Chem. Res.*, **35**, 972 (2002).
[2] C.N.R. Rao, S. Natarajan, R. Vaidhyanathan. *Angew. Chem., Int. Ed.*, **43**, 1466 (2004).
[3] O.M. Yaghi, M.O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim. *Nature*, **423**, 705 (2003).
[4] M. Ohba, H. Okawa. *Coord. Chem. Rev.*, **198**, 313 (2000).
[5] H.Z. Kou, B.C. Zhou, S. Gao, R.J. Wang. *Angew. Chem. Int. Ed.*, **42**, 3288 (2003).
[6] A.M. Chippindale, S.J. Hibble, A.R. Cowley. *Inorg. Chem.*, **43**, 8040 (2004).
[7] X. He, C.Z. Lu, C.D. Wu, L.J. Chen. *Eur. J. Inorg. Chem.*, **12**, 2491 (2006).
[8] K. Park, I. Yoon, J. Seo, J. Lee, J. Kim, K.S. Choi, O. Jung, S.S. Lee. *Crystal Growth & Design*, **5**, 1707 (2005).
[9] D.J. Chesnut, D. Plewak, J. Zubieta. *J. Chem. Soc., Dalton Trans.*, 2567 (2001).
[10] D. Kim, J. Koo, C.S. Hong, S. Oh, Y. Do. *Inorg. Chem.*, **44**, 4383 (2005).
[11] E. Colacio, R. Kivekas, F. Lloret, M. Sunberg, J. Suarez-Varela, M. Bardaji, A. Laguna. *Inorg. Chem.*, **41**, 5141 (2002).
[12] D.J. Chesnut, J. Zubieta. *Chem. Commun.*, 1707 (1998).
[13] X. He, C.Z. Lu, D.Q. Yuan, S.M. Chen, J.T. Chen. *Eur. J. Inorg. Chem.*, **11**, 2181 (2005).
[14] J.H. Yu, J.Q. Xu, Q.X. Yang, L.Y. Pan, T.G. Wang, C.H. Lu, T.H. Ma. *J. Mol. Struct.*, **658**, 1 (2003).
[15] S.W. Liang, M.X. Li, M. Shao, Z.X. Miao. *Inorg. Chem. Commun.*, **9**, 1312 (2006).
[16] R.H. Wiley, A.J. Hart. *J. Org. Chem.*, **18**, 1368 (1953).

[17] G.M. Sheldrick, *SHELX*-97 *Program for Crystal Structure Solution and Refinement*, University of Göttingen, Germany (1997).
[18] H.L. Shyu, H.H. Wei, Y. Wang. *Inorg. Chim. Acta*, **258**, 81 (1997).
[19] Y. Wang, B. Ding, P. Cheng, D.Z. Liao, S.P. Yan. *Inorg. Chem.*, **46**, 2002 (2007).
[20] Y.Q. Huang, B. Ding, H.B. Song, B. Zhao, P. Ren, P. Cheng, H.G. Wang, D.Z. Liao, S.P. Yan. *Chem. Commun.*, 4906 (2006).
[21] J.P. Lang, Q.F. Xu, Z.N. Chen, B.F. Abrahams. *J. Am. Chem. Soc.*, **125**, 12682 (2003).
[22] J.D. Lin, Z.H. Li, T. Li, J.R. Li, S.W. Du. *Inorg. Chem. Commun.*, **9**, 675 (2006).
[23] C.P. Cui, S.M. Hu, J.J. Zhang, W.X. Du, X.T. Wu. *Inorg. Chem. Commun.*, **8**, 704 (2005).
[24] X. Liu, G. Guo, A. Wu, L. Cai, J. Huang. *Inorg. Chem.*, **44**, 4282 (2005).