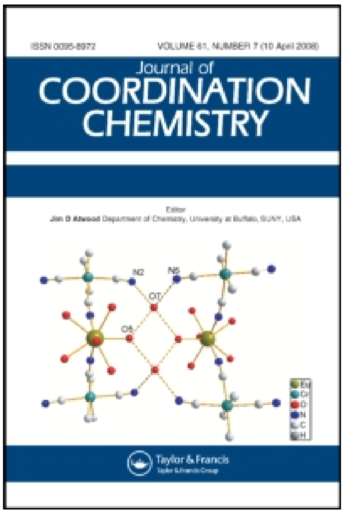


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses, crystal structures, and fluorescence of two complexes constructed by *N*'-(pyridin-2-ylmethylene)-2-(*1H* -1,2,4-triazol-1-yl)acetohydrazide

Xiao-Wei Hou[a]; Wei-Na Shi[a]; De-Gang Ding[ab]; Yao-Ting Fan[a]; Hong-Wei Hou[a]
[a] Department of Chemistry, Zhengzhou University, Zhengzhou 450052, P. R. China [b] Quality Examination and Management, Zhengzhou College of Animal Husbandry Engineering, Zhengzhou 450011, P. R. China

To cite this Article Hou, Xiao-Wei , Shi, Wei-Na , Ding, De-Gang , Fan, Yao-Ting and Hou, Hong-Wei(2010) 'Syntheses, crystal structures, and fluorescence of two complexes constructed by *N*'-(pyridin-2-ylmethylene)-2-(*1H* -1,2,4-triazol-1-yl)acetohydrazide', Journal of Coordination Chemistry, 63: 23, 4104 — 4112

To link to this Article: DOI: 10.1080/00958972.2010.531391

URL: http://dx.doi.org/10.1080/00958972.2010.531391

Journal of Coordination Chemistry
Vol. 63, No. 23, 10 December 2010, 4104–4112

Taylor & Francis
Taylor & Francis Group

Syntheses, crystal structures, and fluorescence of two complexes constructed by *N′*-(pyridin-2-ylmethylene)-2-(*1H*-1,2,4-triazol-1-yl)acetohydrazide

XIAO-WEI HOU†, WEI-NA SHI†, DE-GANG DING†‡, YAO-TING FAN*† and HONG-WEI HOU†

†Department of Chemistry, Zhengzhou University, Zhengzhou 450052, P. R. China
‡Quality Examination and Management, Zhengzhou College of Animal Husbandry Engineering, Zhengzhou 450011, P. R. China

(*Received 20 April 2010; in final form 22 September 2010*)

Two new binuclear complexes, $Cd_2(HL)_2(NO_3)_4 \cdot (CH_3OH)_2$ (**1**) and $Cu_2(L)_2(ClO_4)_2$ (**2**), based on *N′*-(pyridin-2-ylmethylene)-2-(*1H*-1,2,4-triazol-1-yl)acetohydrazide (HL) and Cd(II) and Cu(II) salts have been synthesized and characterized by single crystal X-ray diffraction. Hydrogen bonds and π–π interactions extend both binuclear molecules, a 3-D supramolecular framework for **1** and 1-D staggered chains for **2**. Fluorescence of both complexes is discussed.

Keywords: Triazole derivative; Transition metal ion; Crystal structure; Fluorescence

1. Introduction

Design and self-assembly of metal coordination compounds based on Schiff-base ligands have received attention because of structural diversity and potential applications as functional materials in fluorescence, selective catalysis, magnetic, and nonlinear optical materials [1–6]. Some mono-, bi-, and poly-nuclear complexes of transition metals with Schiff-base derivatives have been reported [7–12], which exhibit fluorescence, electrochemical, and magnetic properties [7, 8, 11, 12]. Homobimetallic systems display more biological activity than corresponding monometallic analogues [12, 13]. Binuclear complexes can also serve as simple models for multi-metal-centered catalysts and multielectron-transfer reagents, in which a ligand structure maintains two metal centers in close proximity but in different compartments separated by an intervening group [9, 14]. However, construction of complexes with predicted structures and properties is still a challenge since there are many factors influencing the formation and structure of the complexes such as the structural characteristics of the ligand, the coordination environment of metal ions, counterions and reaction conditions, etc.

---

*Corresponding author. Email: yt.fan@zzu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.531391

As a ligand with multiple coordination sites, 1,2,4-triazole is a good linker in generation of structurally versatile metal–organic coordination compounds [15–17]. Taking into account the above factors, *N′*-(pyridin-2-ylmethylene)-2-(*1H*-1,2,4-triazol-1-yl)acetohydrazide (HL) is selected as a Schiff-base ligand for the construction of bi-nuclear complexes based on its two major characteristics: First, the imino moieties can be coordinated to metal ions and the amino groups may act as donors in hydrogen-bonding interactions. Second, π–π interactions among pyridyl rings may be formed.

Two new coordination compounds $Cd_2(HL)_2(NO_3)_4 \cdot (CH_3OH)_2$ (**1**) and $Cu_2(L)_2(ClO_4)_2$ (**2**) have been synthesized and characterized by single-crystal X-ray diffraction analysis, elemental analysis, and infrared (IR). In addition, the fluorescence spectra of both compounds were also measured in DMF at room temperature.

2. Experimental

2.1. *Reagents and measurements*

All chemicals employed were commercially available and used without purification. IR spectra were recorded from 4000 to 400 cm^{-1} on a Tensor 27 OPUS FT-IR spectrometer with KBr pellets. ^{1}H NMR spectra were recorded at room temperature on Bruker DPX 400 spectrometers. Emission spectra were recorded on a HITACHI F-4500 fluorescence spectrophotometer.

2.2. *Synthesis of ligand HL*

The ligand was synthesized by the condensation of 2-(*1H*-1,2,4-triazol-1-yl)acetohydrazide (40 mmol) and 2-pyridinecarboxaldehyde (40 mmol) in the presence of glacial acetic acid in methanol. After refluxing the methanolic solution for 12 h, the mixture was allowed to cool to room temperature and then the solid products were filtered off. The resulting products were used without further purification. Yield: 66%. ^{1}H NMR (400 MHz, DMSO-d$_6$, 25°C) δ: 11.969(d, 1H), 8.596–8.607(d, 1H), 8.531–8.560(d, 1H), 8.089(s, 1H) 8.066(m, 2H), 7.984(m, 1H), 7.476(m, 1H), 5.540(s, 2H).

2.3. *Synthesis of* $Cd_2(HL)_2(NO_3)_4 \cdot (CH_3OH)_2$ *(1)*

A methanol solution (4 mL) of HL (11.5 mg, 0.05 mmol) was added dropwise to an aqueous solution of $Cd(NO_3)_2 \cdot 4H_2O$ (15.4 mg, 0.05 mmol), giving a clear solution. The resulting solution was allowed to stand at room temperature. Crystals suitable for X-ray diffraction were obtained 1 day later. Yield: 56%. Anal. Calcd for $C_{11}H_{14}CdN_8O_8$ (%): C, 26.49; H, 2.83; N, 22.47; Found (%): C, 26.46; H, 2.85; N, 22.49.

2.4. *Synthesis of* $Cu_2(L)_2(ClO_4)_2$ *(2)*

The procedure was similar to that of **1** except for the replacement of $Cd(NO_3)_2 \cdot 4H_2O$ with $Cu(ClO_4)_2 \cdot 6H_2O$. Crystals suitable for X-ray diffraction were obtained 1 day later.

Yield: 69%. Anal. Calcd for $C_{10}H_9ClCuN_6O_5$ (%): C, 30.62; H, 2.31; N, 21.43; Found (%): C, 30.65; H, 2.29; N, 21.41.

2.5. *Single crystal structure determination*

A single crystal suitable for X-ray diffraction was mounted on a glass fiber. All data were collected at 291(2) K on a Rigaku Saturn 724 CCD diffractometer using graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and expanded using Fourier techniques [18]. The non-hydrogen atoms were refined anisotropically. Hydrogens were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed using the SHELXL-97 program [19]. Table 1 shows crystal data and processing parameters of **1** and **2**. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structure of 1*

X-ray diffraction analysis reveals that **1** crystallizes in the space group *P2₁/c* and each asymmetric unit contains a Cd(II), a HL (scheme 1), two coordinated nitrates, and a free methanol (figure 1a). As shown in figure 1a, the Cd(II) is eight-coordinate, connected to N6, N3#1 (#1: $-x$, $-y+1$, $-z$), N5, O1, O2, O3, O5, and O6. The carbonyl oxygen weakly coordinates to Cd(II) with a distance of 2.673(9) Å [20]. The Cd–N and Cd–O bond lengths are within normal ranges [20–22]. Every ligand is

Table 1. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{11}H_{14}CdN_8O_8$	$C_{10}H_9ClCuN_6O_5$
Formula weight	498.70	392.22
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*P2₁/c*	*P2₁/c*
Unit cell dimensions (Å, °)		
a	14.646(3)	14.314(3)
b	9.3218(19)	11.288(2)
c	13.855(3)	8.8432(18)
B	108.49(3)	100.60(3)
Volume (Å^3), *Z*	1793.9(6), 4	1404.5(5), 4
Calculated density (Mg m^{-3})	1.847	1.855
Goodness-of-fit on F^2	1.063	1.069
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0255$, $wR_2 = 0.0636$	$R_1 = 0.0496$, $wR_2 = 0.1345$
θ range (°)	2.81–25.5	1.45–27.89
Largest difference peak and hole (e A^{-3})	0.411 and −0.344	0.880 and −0.580

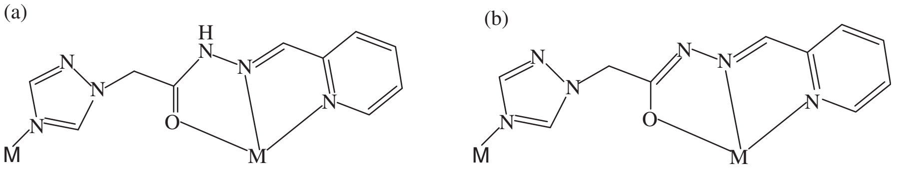
$R_1 = \Sigma\|F_o|F_c\|/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$.

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

1[a]			
Cd(1)–N(3)#1	2.272(2)	Cd(1)–O(5)	2.361(2)
Cd(1)–N(6)	2.366(2)	Cd(1)–N(5)	2.376(2)
Cd(1)–O(2)	2.3814(19)	Cd(1)–O(6)	2.556(2)
Cd(1)–O(3)	2.561(2)	N(3)#1–Cd(1)–O(5)	91.72(8)
N(3)#1–Cd(1)–N(6)	154.44(8)	O(5)–Cd(1)–N(6)	92.63(8)
N(3)#1–Cd(1)–N(5)	136.66(7)	O(5)–Cd(1)–N(5)	85.09(8)
N(6)–Cd(1)–N(5)	68.84(7)	N(3)#1–Cd(1)–O(2)	85.32(7)
O(5)–Cd(1)–O(2)	172.23(7)	N(6)–Cd(1)–O(2)	93.13(7)
N(5)–Cd(1)–O(2)	92.13(7)	N(3)#1–Cd(1)–O(6)	84.21(7)
O(5)–Cd(1)–O(6)	51.43(7)	N(6)–Cd(1)–O(6)	78.94(7)
N(5)–Cd(1)–O(6)	124.15(7)	O(2)–Cd(1)–O(6)	135.07(7)
N(3)#1–Cd(1)–O(3)	80.37(8)	O(5)–Cd(1)–O(3)	135.05(7)
N(6)–Cd(1)–O(3)	78.79(7)	N(5)–Cd(1)–O(3)	129.70(7)
O(2)–Cd(1)–O(3)	51.50(7)	O(6)–Cd(1)–O(3)	83.67(7)
2[b]			
N(3)–Cu(1)#1	1.944(3)	Cu(1)–N(5)	1.922(3)
Cu(1)–N(3)#1	1.944(3)	Cu(1)–O(1)	1.988(2)
Cu(1)–N(6)	2.030(3)	Cu(1)–O(2)	2.430(4)
N(5)–Cu(1)–N(3)#1	167.83(12)	N(5)–Cu(1)–O(1)	79.11(10)
N(3)#1–Cu(1)–O(1)	93.60(9)	N(5)–Cu(1)–N(6)	81.54(11)
N(3)#1–Cu(1)–N(6)	104.39(11)	O(1)–Cu(1)–N(6)	159.79(10)
N(5)–Cu(1)–O(2)	90.15(16)	N(3)#1–Cu(1)–O(2)	100.56(15)
O(1)–Cu(1)–O(2)	97.73(11)	N(6)–Cu(1)–O(2)	88.08(11)

[a] Symmetry code in 1: $1-x$, $-y+1$, $-z$.

[b] Symmetry code in 2: #1 $-x$, $-y+2$, $-z+1$.



HL L⁻

Scheme 1. Coordination mode of HL and L⁻.

tetradentate bridging two Cd(II) atoms in NNO donor set and monodentate (scheme 1a), and two nitrates are bidentate chelating. Two four-membered rings, formed by Cd(II) and two nitrates, are almost coplanar with mean deviation being 0.0225 Å, and two five-membered rings, which are built by Cd(II), N4, N5, N6, C4, C5, C6, and O1, are also coplanar with mean deviation being 0.0301 Å. Furthermore, the four-membered ring is nearly perpendicular to the five-membered ring with dihedral angle of 93.5°.

In **1**, two HL ligands bridge two Cd(II) atoms giving a dimetal ring, and the two triazol rings are parallel at *ca* 5.825 Å. Each $[Cd_2(HL)_2(NO_3)_4](CH_3OH)_2$ links four $[Cd_2(HL)_2(NO_3)_4](CH_3OH)_2$ molecules through intermolecular hydrogen bonds to result in a 2-D lamellar framework lying in the *bc* plane (figure 1b). As shown in figure 1b, free methanol molecules play an important role in the formation of hydrogen bonds. The uncoordinated N4 and O8 donate hydrogens to O8 and O2#1 (#1: $-x$, $-y+1$, $-z$),

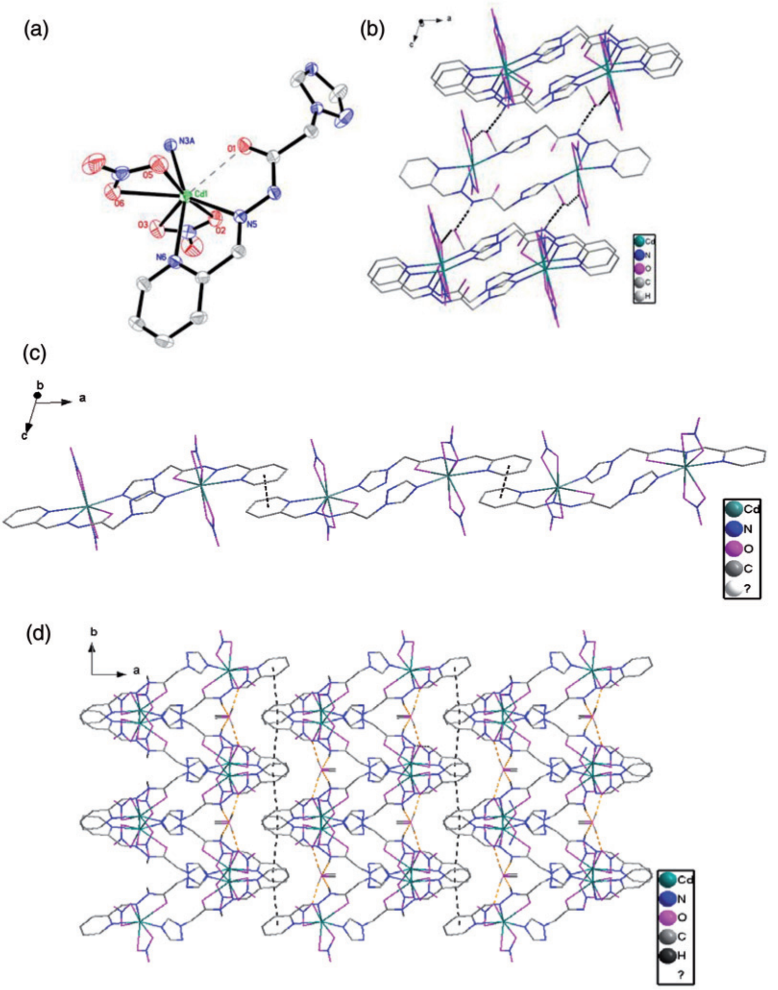


Figure 1. (a) Coordination of Cd(II) in **1** with ellipsoids at 30% probability level, hydrogens and methanol are omitted for clarity; (b) the hydrogen bonds in **1** leading to lamellar framework of **1**, fractional hydrogens are omitted for clarity; (c) the π–π interactions in **1**, hydrogens are omitted for clarity; (d) 3-D framework of **1** generated through hydrogen bonds and π–π interactions, fractional hydrogens are omitted for clarity.

Table 3. Distance (Å) and angles (°) of hydrogen bonding for **1**.

D–H···A	Distance of D···H	Distance of H···A	Distance of D···A	Angle of D–H–A
O(8)–H(8)···O(2)#2	0.85	2.05	2.832(3)	153.2
N(4)–H(4A)···O(8)	0.86	1.89	2.740(3)	170.3

Symmetry code: #2 x, $-y+1/2$, $z-1/2$.

respectively, forming two sorts of hydrogen bonds. All hydrogen bonding distances and angles are summarized in table 3. These 2-D layers are interconnected by a stable π–π interactions among pyridine rings with the closest interplane C···C and centroid···centroid distances of 3.88 and 4.22 Å, respectively (figure 1c), above the

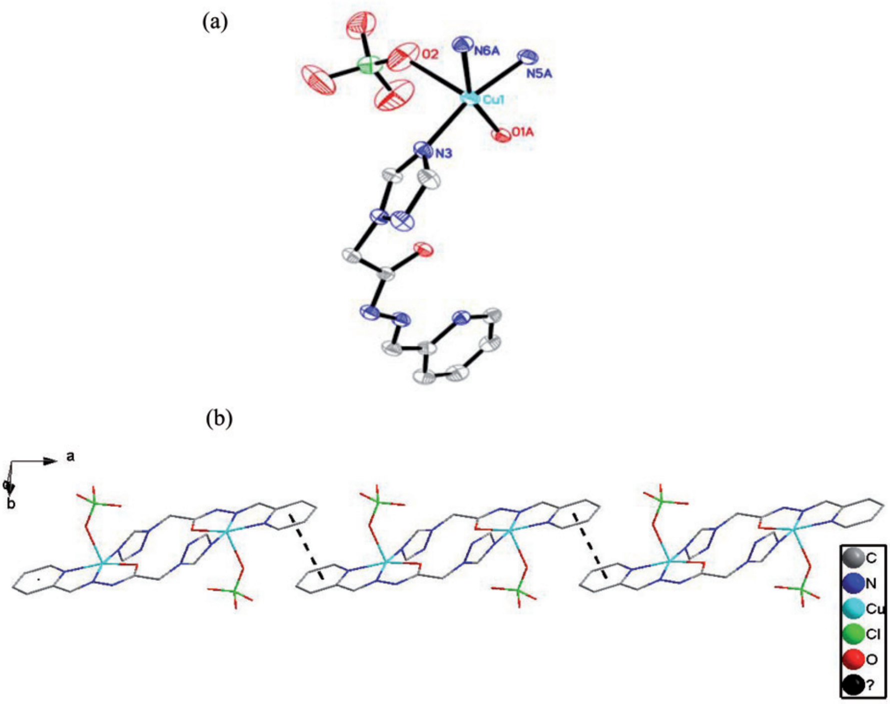


Figure 2. (a) Coordination of Cu(II) in **2** with ellipsoids at 30% probability and (b) the 1-D chain of **2** showing π–π interactions. Hydrogens are omitted for clarity.

optimal distances for π-stacking [23]. By linkage of these interplane π–π interactions, a 3-D framework is formed (figure 1d).

3.2. *Crystal structure of 2*

The structural study reveals that the asymmetric unit of **2** contains a Cu(II), a L^-, and a coordinated perchlorate ion. Unlike the cadmium complex, Cu(II) is close to square pyramidal from the coordination of the NNO donor set of L^- (figure 2a). The square base is formed by a carbonyl oxygen (O1), pyridyl nitrogen (N6), triazol nitrogen (N3#1) (#1: $-x$, $-y+2$, $-z+1$), and imine nitrogen (N5). The O2 from perchlorate occupies the axial position. The axial Cu–O bond length (2.430 Å) is substantially longer than the basal Cu–N, O lengths (1.922–2.030 Å) [24, 25]. The variation of the bond angles (79.11–104.39°) indicates significant distortion from ideal square pyramidal geometry.

In the crystal structure of **2**, each HL loses a proton to maintain the electric charge balance, different from ligands of **1**. Every ligand is tetradentate bridging two Cu(II) atoms in NNO donor set and monodentate fashion (scheme 1b). Two L^- also bridge two Cu(II) atoms giving a bimetallic ring. Adjacent $[Cu_2(L)_2(ClO_4)_2]$ are linked by π–π interactions among pyridine rings (centroid–centroid distance is 3.82 Å) forming 1-D staggered chain (figure 2b).

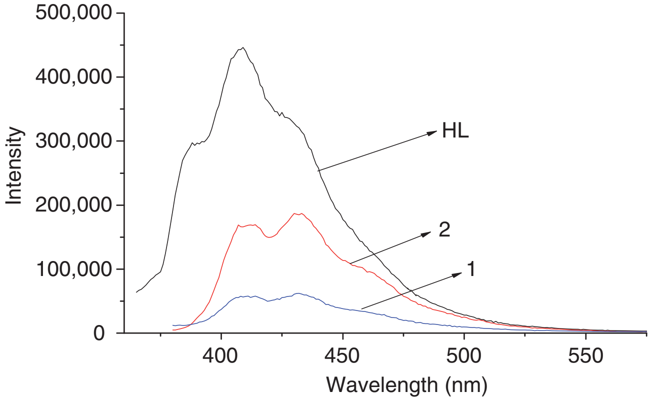


Figure 3. Emission spectra of **1**, **2**, and HL in DMF.

The crystal structures of both **1** and **2** are different from those reported in other binuclear complexes of Cd(II) and Cu(II), in which only powder samples were obtained and characterized by elemental analyses and FAB mass spectra [9–11].

3.3. *IR and fluorescent spectra*

IR spectra of **1**, **2**, and free HL have been measured from 4000 to 400 cm^{-1}. The IR spectrum of the ligand contains a strong C=O absorption at 1699 cm^{-1} and a N–H absorption at 3200 cm^{-1}. Several significant changes are observed in spectra of the corresponding metal compounds. In **1**, containing the neutral form of the ligand, the N–H absorption band is almost unaffected by complex formation, whereas the C=O absorption is shifted by *ca* 17 cm^{-1} to lower wavenumbers indicating bonding of the ligand to the metal ion through the carbonyl oxygen. The N–H and C=O absorptions are absent in **2** which contains deprotonated ligands indicating ligand enolization, followed by hydroxyl proton loss during complexation with the metal. In addition, a broad band is centered at 3411–3484 cm^{-1} in **1** due to O–H of the methanol.

The fluorescence spectra of **1**, **2**, and HL were measured in 10^{-5} mol L^{-1} DMF at room temperature (figure 3). HL exhibits a strong fluorescence emission at 425 nm with excitation at 301 nm. In contrast with fluorescence spectra of HL, partial fluorescence quenching phenomena are observed in both **1** and **2** with two weak fluorescence emissions at 409 and 431 nm for **1**, 407 and 433 nm for **2** upon excitation at 301 nm. The maximum emission wavelength of HL at 425 nm is red-shifted about 6–8 nm owing to the formation of complex. The fluorescence quenching behavior is similar to that reported by Wang *et al.* [7].

4. Conclusion

Two new binuclear complexes have been synthesized by self-assembling Schiff-base HL (HL = *N′*-(pyridin-2-ylmethylene)-2-(*1H*-1,2,4-triazol-1-yl)acetohydrazide) with Cd(II) and Cu(II) salts. Compound **1** exhibits a 3-D architecture constructed by intermolecular hydrogen bonds and π–π interactions, while in **2** adjacent $[Cu_2(L)_2(ClO_4)_2]$ molecules are linked by π–π interactions forming 1-D staggered chains. Partial fluorescence quenching phenomena are also observed for both **1** and **2** in DMF at room temperature.

Supplementary material

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Center (CCDC 773558 and 773559). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +(1223)336-033; Email: teched@chemcrys.cam.ac.uk).

Acknowledgments

We gratefully acknowledge the financial support of the National Natural Science Foundation of China (Nos. 20871106 and 91010008).

References

[1] S. Yamada. *Coord. Chem. Rev.*, **190**, 537 (1999).
[2] E.C. Niederhoffer, J.H. Timmons, A.E. Martell. *Chem. Rev.*, **84**, 137 (1984).
[3] R.D. Archer, B. Wang. *Inorg. Chem.*, **29**, 39 (1990).
[4] P.G. Lacroix. *Eur. J. Inorg. Chem.*, 339 (2001).
[5] J. Tisato, F. Refosco, F. Bandoli. *Coord. Chem. Rev.*, **135**, 325 (1994).
[6] W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen. *J. Am. Chem. Soc.*, **112**, 2801 (1990).
[7] Q.H. Wang, W. Weng, J.M. Liu, L.Z. Cai, G.C. Guo. *J. Coord. Chem.*, **59**, 485 (2006).
[8] Z.L. Fang, Q.X. Nie. *J. Coord. Chem.*, **63**, 2328 (2010).
[9] N.V. Kulkarni, M.P. Sathisha, S. Budagumpi, G.S. Kurdekar, V.K. Revankar. *J. Coord. Chem.*, **63**, 1451 (2010).
[10] T.M.A. Ismail. *J. Coord. Chem.*, **58**, 141 (2005).
[11] S. Budagumpi, G. Kurdekar, G.S. Heded, N.H. Bevinahalli, V.K. Revankar. *J. Coord. Chem.*, **63**, 1430 (2010).
[12] M.K. Singh, N.K. Kar, R.A. Lal, M. Asthana. *J. Coord. Chem.*, **62**, 2893 (2009).
[13] D.G. McCollum, C. Fraser, R. Ostrander, A.L. Rheingold, B. Bosnich. *Inorg. Chem.*, **33**, 2383 (1994).
[14] F.R. Keene, J.A. Smith, J.G. Collins. *Coord. Chem. Rev.*, **253**, 2021 (2009).
[15] W. Ouellette, B.S. Hudson, J. Zubieta. *Inorg. Chem.*, **46**, 4887 (2007).
[16] D.G. Ding, M.L. Zhang, L.C. Li, Y.T. Fan, H.W. Hou. *J. Coord. Chem.*, **62**, 2675 (2009).
[17] D.G. Ding, L.X. Xie, Y.T. Fan, H.W. Hou, Y. Xu. *Solid State Chem.*, **182**, 1443 (2009).
[18] G.M. Sheldrick. *SHELXS-97*, *Programs zur Verfeinerung von Kristallstrukturen*, University of Göttingen, Göttingen, Germany (1997).
[19] G.M. Sheldrick. *SHELXS-97*, *Programs zur Lösung von Kristallstrukturen*, University of Göttingen, Göttingen, Germany (1997).
[20] S.L. Li, Y.Q. Lan, J.F. Ma, J. Yang, G.H. Wei, L.P. Zhang, Z.M. Su. *Cryst. Growth Des.*, **8**, 675 (2008).
[21] R.H. Cui, Y.H. Xu, Z.H. Jiang. *Inorg. Chem. Commun.*, **12**, 933 (2009).

[22] C.D. Wu, P. Ayyappan, O.R. Evans, W. Lin. *Cryst. Growth Des.*, **7**, 1690 (2007).

[23] F.H. Zeng, J. Ni, Q.G. Wang, Y.B. Ding, S.W. Ng, W.H. Zhu, Y.S. Xie. *Cryst. Growth Des.*, **10**, 1611 (2010).

[24] B.B. Ding, Y.Q. Weng, Z.W. Mao, C.K. Lam, X.M. Chen, B.H. Ye. *Inorg. Chem.*, **44**, 8836 (2005).

[25] R.T. Stibrany, J.A. Potenza, H.J. Schugar. *Inorg. Chim. Acta*, **243**, 33 (1996).