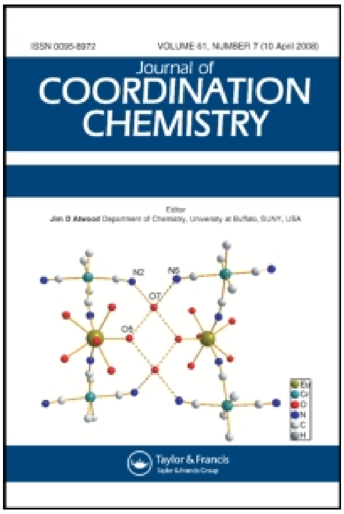

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A 2D coordination polymer with 4*8^2 topology constructed from a new <i>T</i>-shaped ligand: synthesis, crystal structure and photoluminescence

Shu Qiao[a]; Guo-Ping Yong[a]; Yu Xie[a]; Zhi-Yong Wang[a]
[a] Hefei National Laboratory for Physical Science at Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, China

To cite this Article Qiao, Shu , Yong, Guo-Ping , Xie, Yu and Wang, Zhi-Yong(2007) 'A 2D coordination polymer with 4*8^2 topology constructed from a new **<i>T</i>**-shaped ligand: synthesis, crystal structure and photoluminescence', Journal of Coordination Chemistry, 60: 23, 2559 — 2566, First published on: 22 September 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970701283729

URL: http://dx.doi.org/10.1080/00958970701283729

Journal of Coordination Chemistry
Vol. 60, No. 23, 1 December 2007, 2559–2566

A 2D coordination polymer with $4*8^2$ topology constructed from a new *T*-shaped ligand: synthesis, crystal structure and photoluminescence

SHU QIAO, GUO-PING YONG, YU XIE and ZHI-YONG WANG*

Hefei National Laboratory for Physical Science at Microscale and
Department of Chemistry, University of Science and
Technology of China, Hefei, Anhui 230026, China

(*Received 11 December 2006; in final form 29 March 2007*)

A cadmium(II) coordination polymer [CdL(H_2O)] (**1**) ($H_2L = 3,3$-*bis*(carboxymethyl)imidazo[1,2-*a*]pyridin-2-one) was synthesized under hydrothermal conditions and characterized by X-ray structure analysis. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.945(2)$ Å, $b = 8.0865(16)$ Å, $c = 13.114(3)$ Å, $\beta = 91.36(3)°$, $Z = 4$, and represents a 2D network with the $4*8^2$ topology constructed from combination of metal centers with a *T*-shaped geometry and ligands with *T*-shaped structure simultaneously. Compound **1** also exhibits strong photoluminescence at room temperature.

Keywords: 3,3-*Bis*(carboxymethyl)imidazo[1,2-a]pyridin-2-one; *T*-shaped ligand; Cadmium; Coordination polymer; Photoluminescence

1. Introduction

Rational design and construction of coordination polymers is of interest owing to their topologies and potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics, luminescence, and molecular sensing [1–3]. Many cadmium-polycarboxylate coordination polymers with extended frameworks have received much attention because of their interesting structures and excellent photoluminescent properties [4]. Heterocyclic carboxylic acids such as pyridine- [5], pyrazole- [6], and imidazole carboxylic acids [7] contain multioxygen and nitrogen atoms and can coordinate with metal ions in different ways resulting in formation of various metal–organic frameworks with specific topologies and useful properties. Organic ligands play crucial roles in the design and construction of desirable frameworks, because changes in flexibility, length, and symmetry of organic ligands can result in coordination polymers bearing diverse architectures and functions [8].

Many 2D networks with various structural motifs, including honeycomb, brick wall, rectangular grid, bilayer and herringbone have been documented and some 2D

---

*Corresponding author. Tel./Fax: +86-551-3603185. Email: zwang3@ustc.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970701283729

networks with 4*8^2 topologies have been reported [9]. Comparatively, less effort has been made in constructing 2D (6, 3) network [10] and 4*8^2 topology [11] by using three-connecting *T*-shaped ligands. Our previous work had shown that the *N*-containing polycarboxylate ligands could be used to construct novel coordination polymers [4d, 12]. Herein, we turn our attention to a novel *N*-containing polycarboxylate ligand, 3,3-*bis*(carboxymethyl)imidazo[1,2-*a*]pyridin-2-one [13], and report a coordination polymer [CdL(H_2O)] (**1**), with the 4*8^2 topology constructed from the *T*-shaped ligand.

2. Experimental

2.1. *Materials and general methods*

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses were carried out with an Elementar Vario EL III microanalyser. The FTIR spectra were recorded with a Bruker Vector 22 spectrophotometer in the 4000–400 cm^{-1} region. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AV300 and AV400 spectrometer, respectively. The emission spectrum for the solid sample was recorded at room temperature with a Hitachi 850 fluorescence spectrophotometer. Thermogravimetric analysis was performed under N_2 with a heating rate of 10°C min^{-1} with a Shimadzu TGA-50H TG analyzer.

Caution: $Cd(ClO_4)_2 \cdot 6H_2O$ is potentially explosive and should be used with care.

2.2. *Synthesis of 3,3-bis(carboxymethyl)imidazo[1,2-a]pyridin-2-one(H_2L)*

A solution of KOH (33.6 g, 0.6 mol) in water (75 mL) was added dropwise to an ice-bath cooled solution of chloroacetic acid (28.4 g, 0.3 mol) in water (75 mL). To the resulting alkaline solution, 2-aminopyridine (9.4 g, 0.1 mol) was slowly added, and the mixture was heated under reflux at 86°C for 30 h. HCl (6 N, 53 mL) was added to neutralize the solution, which was concentrated under boiling conditions and then cooled (ice-bath) to remove KCl. After the mother liquor (pH = 2–3) was allowed to stand in the refrigerator for three days, the desired acid (H_2L) separated out and was collected by filtration. The solid was recrystallized from hot ethanol/water (1 : 1), and the colorless product was then collected by filtration and air-dried. Yield: 5.75 g (23%, based on 2-aminopyridine). Anal. Calcd for $C_{11}H_{10}N_2O_5$(%): C, 52.80; H, 4.03; N, 11.20. Found: C, 52.48; H, 4.05; N, 10.93. ^{1}H NMR (300 MHz, D_2O, 25°C): 8.77 (d, $^3J_{H,H} = 6.8$ Hz, 1 H, 5-H), 8.48 (dd, $^3J_{H,H} = 6.8$, 8.4 Hz, 1 H, 6-H), 7.67 (m, 2 H, 7-H, 8-H), 3.44 (s, 4 H, CH_2). ^{13}C NMR (100 MHz, D_2O, 25°C): 175.5, 172.0, 153.2, 147.9, 136.2, 120.4, 111.6, 69.8, 42.5. IR data (KBr, cm^{-1}): 3434m, 3077m, 2972m, 2876w, 2792w, 2683w, 1771s, 1708m, 1649s, 1580m, 1519s, 1414m, 1185s, 807m, 598m, 440m.

2.3. *Synthesis of [CdL(H_2O)] (1)*

The mixture of $Cd(ClO_4)_2 \cdot 6H_2O$ (0.15 mmol) with H_2L (0.15 mmol) was placed in a heavy-walled Pyrex tube containing *N*,*N*-Diethylformamide (DEF) (0.3 mL)

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

Compound	**1**
Empirical formula	$C_{11}H_{10}CdN_2O_6$
Formula weight	378.61
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	11.945(2)
b (Å)	8.0865(16)
c (Å)	13.114(3)
β (°)	91.36(3)
V (Å^3)	1266.3(4)
Z	4
$F(000)$	744
ρ_{calcd}(g cm^{-3})	1.986
T (K)	293(2)
μ (mm^{-1})	1.752
Goodness-of-fit on F^2	0.962
Reflections collected	7269
Independent reflections (R_{int})	2969 (0.0722)
Observed reflections	2247
Final R_1, wR_2 [$I>2\sigma(I)$]	0.0370, 0.0908
Final R_1, wR_2 [all data]	0.0495, 0.0963

and H_2O (0.3 mL). The tube was frozen in liquid N_2, sealed under vacuum, and then heated at 120°C for 48 h. The products were filtered, washed with ethanol, and then air-dried. The air-stable colorless transparent crystals were obtained in 50% yield (based on H_2L). Anal. Calcd for $C_{11}H_{10}CdN_2O_6$(%): C, 34.86; H, 2.64; N, 7.39. Found: C, 33.72; H, 3.01; N, 7.01. IR data (KBr cm^{-1}): 3422vs, 3041vw, 1706s, 1632vs, 1582s, 1562s, 1498vs, 1412s, 1349m, 1299w, 1236w, 1141m, 1083w, 769m, 700w, 611w, 513w.

2.4. *X-ray crystallographic study*

Single crystals were mounted to collect diffraction data at room temperature (293 K) on a Siemens SMART CCD diffractometer equipped with Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved using direct methods with the SHELXTL97 [14] program. Data were corrected for absorption with SADABS [15]. Refinements were performed by full-matrix least-squares analysis with $I > 2\sigma(I)$ to the final $R_1 = 0.0370$ and $wR_2 = 0.0908$ ($w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$). Hydrogen atoms from water were located from E-map and the others were added at idealized positions. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Selected crystallographic data and structure refinement for **1** are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Description of the structure*

Single-crystal X-ray structural analysis reveals that **1** crystallizes in monoclinic $P2_1/n$ space group with the asymmetric unit containing one Cd atom, one L^{2-} ligand and

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

Cd(1)–O(1)	2.234(2)	Cd(1)–O(4)#4	2.346(2)
Cd(1)–O(2)	2.592(2)	Cd(1)–O(6)	2.259(3)
Cd(1)–O(3)#4	2.343(2)	Cd(1)–N(1)#2	2.204(2)
O(1)–Cd(1)–O(2)	53.09(8)	O(2)–Cd(1)–N(1)#2	163.35(8)
O(1)–Cd(1)–O(3)#4	101.86(9)	O(3)#4–Cd(1)–O(4)#4	55.73(8)
O(1)–Cd(1)–O(4)#4	135.40(9)	O(3)#4–Cd(1)–O(6)	148.39(9)
O(1)–Cd(1)–O(6)	98.53(10)	O(3)#4–Cd(1)–N(1)#2	102.65(9)
O(1)–Cd(1)–N(1)#2	112.53(9)	O(4)#4–Cd(1)–O(6)	92.93(9)
O(2)–Cd(1)–O(3)#4	89.66(9)	O(4)#4–Cd(1)–N(1)#2	110.10(9)
O(2)–Cd(1)–O(4)#4	86.05(8)	O(6)–Cd(1)–N(1)#2	91.37(10)
O(2)–Cd(1)–O(6)	83.52(9)		

Symmetry codes: #2 $-x+1/2$, $y+1/2$, $-z+1/2$; #4 $x-1/2$, $-y-1/2$, $z-1/2$.

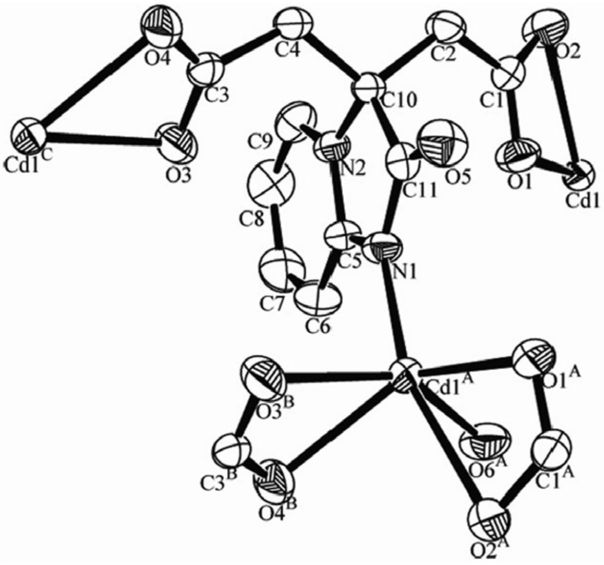

Figure 1. ORTEP drawing at the 50% probability level showing the Cd(II) coordination environment and *T*-shaped ligand in **1**. Hydrogen atoms are omitted for clarity. Symmetry code: A $= -x+1/2$, $y+1/2$, $-z+1/2$; B $= -x$, $-y$, $-z$; C $= x-1/2$, $-y-1/2$, $z-1/2$.

one coordinated water molecule. Cd1 adopts a distorted octahedral coordination environment surrounded by one water oxygen [Cd1–O6 = 2.259(3) Å], four carboxylate oxygen atoms [Cd1–O = 2.234(2), 2.343(2), 2.346(2), 2.592(2) Å] and one nitrogen atom [2.204(2) Å] from three L^{2-} ligands (figure 1). Each L^{2-} ligand uses two carboxylate groups to coordinate two Cd atoms in chelating fashion, while using a nitrogen to link the third Cd atom. As a result, L^{2-} can be described as a three-connecting *T*-shaped building block.

The crystal structure of **1** consists of a 2D network based on the three-connecting *T*-shaped ligand. Four arms (two acetate groups and two imidazo[1,2-*a*]pyridin-2-one rings) from two different L^{2-} ligands bridge two Cd atoms to form a four-membered metallacycle with a Cd $\cdots$ Cd distance of 6.52 Å. The Cd atom can also be taken as a three-connecting node with a *T*-shaped geometry if one coordinated water molecule is

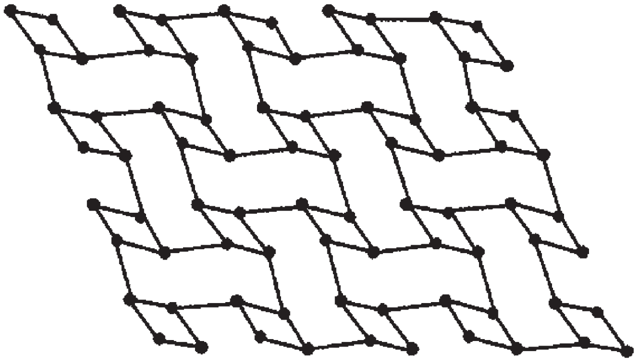

Figure 2. Schematic representation of the 4^*8^2 topology in **1**.

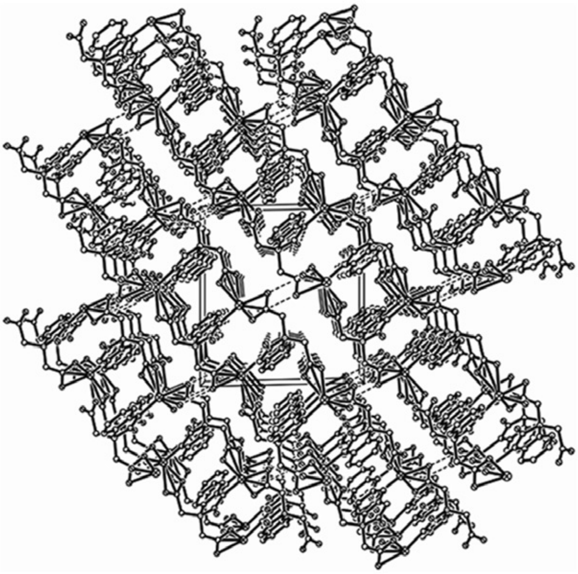

Figure 3. 3D supramolecular network of **1** formed by interlayer O–H $\cdots$ O interactions.

disregarded (the aqua ligand does not bridge). Each four-membered metallacycle connects four neighboring ones via four three-connecting nodes (two Cd1 atoms and two C10 atoms), resulting in the formation of the 2D network. Four L^{2-} ligands, each using two of their three arms, are connected by four three-connecting Cd atoms to form an eight-membered metallacycle. Accordingly, each four-membered ring is surrounded by four eight-membered rings, and each eight-membered ring neighbors upon four four-membered and four eight-membered rings. Namely the 2D network has a 4^*8^2 topology (figure 2).

There exist strong O–H $\cdots$ O hydrogen bonds between coordinating water molecules and L^{2-} in an undulating 2D layer [O6 $\cdots$ O5 = 2.741(4) Å]. The whole 3D supramolecular network (figure 3) is consolidated by inter-layer strong O–H $\cdots$ O hydrogen bond interactions [O6 $\cdots$ O2 = 2.669(3) Å] (table 3).

Table 3. Hydrogen bonds (Å and °) for **1**.

D–H···A	D···A	∠(D–H···A)
O(6)–H(02)···O(2)^{i}	2.669(3)	164.4
O(6)–H(01)···O(5)	2.741(4)	175(4)

Symmetry codes: (i) $-x$, $-y$, $-z$.

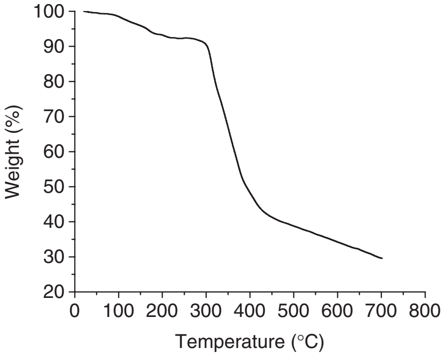

Figure 4. TGA curve for **1**.

3.2. *Thermal analysis*

The thermal behaviour of **1** was examined by thermogravimetric analysis (TGA) under N_2 with the heating rate of 10°C min^{-1} (figure 4). The TGA result indicates that **1** does not decompose up to 122°C. Due to the loss of one coordinating water molecule, the first weight loss of 5.61% occurs from 122 to 193°C, which is consistent with the calculated value 4.75%. The second weight loss starts at ca 296°C, which is ascribed to loss of L^{2-}.

3.3. *Photoluminescent property*

The emission spectrum of **1** in the solid state at room temperature is presented in figure 5, showing a shoulder peak with maximum intensity at 410 nm ($\lambda_{ex} = 270$ nm). Compared to the free ligand (figure 5a), **1** shows significantly stronger photoluminescence, probably due to coordination of L^{2-} to the metal ions, increasing the ligand conformational rigidity [16]; nonradiative decay of the intraligand excited state is thereby reduced. The metallacycles of **1** built by *T*-shaped L^{2-} ligands cause significant enhancement to the rigidity of the ligand. Compound **1** may be an excellent candidate for potential photoactive materials, since this condensed material is thermally stable and insoluble in water and common organic solvents.

4. Conclusions

A 2D coordination polymer, [CdL(H_2O)], with the 4*8^{2} topology, has been synthesized by solvothermal method and structurally characterized by X-ray structural analysis. **1** exhibits strong photoluminescence at room temperature.

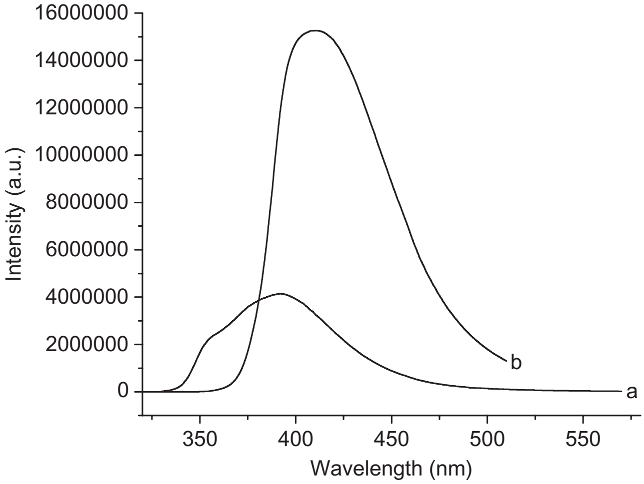

Figure 5. The emission spectrum of the free H_2L (a) and **1** (b) at room temperature.

Supplementary material

CCDC 615856 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; or Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20472078).

References

[1] (a) S.R. Batten, R. Robson. *Angew. Chem. Int. Ed.*, **37**, 1460 (1998); (b) A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M.A. Withersby, M. Schröder. *Coord. Chem. Rev.*, **183**, 117 (1999); (c) B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001).

[2] (a) M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi. *Acc. Chem. Res.*, **34**, 319 (2001); (b) O.R. Evans, W. Lin. *Acc. Chem. Res.*, **35**, 511 (2002); (c) C. Janiak. *Dalton Trans.*, 2781 (2003); (d) S. Kitagawa, R. Kitaura, S.-i. Noro. *Angew. Chem. Int. Ed.*, **43**, 2334 (2004); (e) D. Maspoch, D. Ruiz-Molina, J. Veciana. *J. Mater. Chem.*, **14**, 2713 (2004).

[3] (a) N.G. Pschirer, D.M. Ciurtin, M.D. Smith, U.H.F. Bunz, H.C. zur Loye. *Angew. Chem. Int. Ed.*, **41**, 583 (2002); (b) G.S. Papaefstathiou, Z. Zhong, L. Geng, L.R. MacGillivray. *J. Am. Chem. Soc.*, **126**, 9158 (2004); (c) J.S. Seo, D. Whang, H. Lee, S.I. Jun, J. Oh, Y.J. Jeon, K. Kim. *Nature*, **404**, 982 (2000); (d) Z. Ni, A. Yassar, T. Antoun, O.M. Yaghi. *J. Am. Chem. Soc.*, **127**, 12752 (2005).

[4] (a) J.C. Dai, X.T. Wu, Z.Y. Fu, S.M. Hu, W.X. Du, C.P. Cui, L.M. Wu, H.H. Zhang, R.Q. Sun. *Chem. Commun.*, 12 (2002); (b) J. Tao, X. Yin, Z.B. Wei, R.B. Huang, L.S. Zheng. *Eur. J. Inorg. Chem.*, 125 (2004); (c) S. Skoulika, P. Dallas, M.G. Siskos, Y. Deligiannakis, A. Michaelides. *Chem. Mater.*, **15**, 4576 (2003); (d) G.P. Yong, S. Qiao, Z.Y. Wang, Y. Cui. *Inorg. Chim. Acta*, **358**, 3905 (2005); (e) J. Fan, H.F. Zhu, T. Okamura, W.Y. Sun, W.X. Tang, N. Ueyamab. *New J. Chem.*, **27**, 1409 (2003); (f) W.G. Lu, L. Jiang, X.L. Feng, T.B. Lu. *Cryst. Growth Des.*, **6**, 564 (2006).

[5] (a) P. Ayyappan, O.R. Evans, W.B. Lin. *Inorg. Chem.*, **40**, 4627 (2001); (b) M.L. Tong, S. Hu, J. Wang, S. Kitagawa, S.W. Ng. *Cryst. Growth Des.*, **5**, 837 (2005); (c) Y. Xu, L. Han, Z.Z. Lin, C.P. Liu, D.Q. Yuan, Y.F. Zhou, M.C. Hong. *Eur. J. Inorg. Chem.*, 4457 (2004); (d) B. Zhao, P. Cheng, Y. Dai, C. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang, G.L. Wang. *Angew. Chem. Int. Ed.*, **42**, 934 (2003).

[6] L. Pan, N. Ching, X.Y. Huang, J. Li. *Chem. Eur. J.*, **7**, 4431 (2001).

[7] (a) Y.L. Liu, V. Kravtsov, R.D. Walsh, P. Poddar, H. Srikanth, M. Eddaoudi. *Chem. Commun.*, 2806 (2004); (b) M.T. Caudle, J.W. Kampf, M.L. Kirk, P.G. Rasmussen, V.L. Pecoraro. *J. Am. Chem. Soc.*, **119**, 9297 (1997); (c) E. Shimizu, M. Kondo, Y. Fuwa, R.P. Sarker, M. Miyazawa, M. Ueno, T. Naito, K. Maeda, F. Uchida. *Inorg. Chem. Commun.*, **7**, 1191 (2004); (d) P. Angaridis, J.W. Kampf, V.L. Pecoraro. *Inorg. Chem.*, **44**, 3626 (2005); (e) P. Mahata, S. Natarajan. *Eur. J. Inorg. Chem.*, 2156 (2005); (f) J.Y. Lu, Z.H. Ge. *Inorg. Chim. Acta*, **358**, 828 (2005); (g) Z.F. Fei, D.B. Zhao, T.J. Geldbach, R. Scopelliti, P.J. Dyson, S. Antonijevic, G. Bodenhausen. *Angew. Chem. Int. Ed.*, **44**, 5720 (2005); (h) W.G. Lu, L. Jiang, X.L. Feng, T.B. Lu. *Cryst. Growth Des.*, **6**, 564 (2006).

[8] (a) X.H. Bu, W. Chen, S.L. Lu, R.H. Zhang, D.Z. Liao, W.M. Bu, M. Shionoya, F. Brisse, J. Ribas. *Angew. Chem. Int. Ed.*, **40**, 3201 (2001); (b) D.N. Dybtsev, H. Chun, K. Kim. *Angew. Chem. Int. Ed.*, **43**, 5033 (2004); (c) X.L. Wang, C. Qin, E.B. Wang, L. Xu, Z.M. Su, C.W. Hu. *Angew. Chem. Int. Ed.*, **43**, 5036 (2004).

[9] (a) S.A. Barnett, A.J. Blake, N.R. Champness, J.E.B. Nicolson, C.J. Wilson. *J. Chem. Soc. Dalton Trans.*, 567 (2001); (b) S.Y. Wan, J. Fan, T.-a. Okamura, H.F. Zhu, X.M. Ouyang, W.Y. Sun, N. Ueyama. *Chem. Commun.*, 2520 (2002); (c) D.L. Long, A.J. Blake, N.R. Champness, C. Wilson, M. Schröder. *Chem. Eur. J.*, **9**, 2026 (2002); (d) D.L. Long, A.J. Blake, N.R. Champness, M. Schröder. *Chem. Commun.*, 1369 (2000); (e) J. Fan, C. Slebodnick, D. Troya, R. Angel, B.E. Hanson. *Inorg. Chem.*, **44**, 2719 (2005); (f) P.X. Yin, J. Zhang, J.K. Cheng, Z.J. Li, Y.G. Yao. *Inorg. Chem. Commun.*, **9**, 541 (2006).

[10] M.S. Wang, G.C. Guo, L.Z. Cai, W.T. Chen, B. Liu, A.Q. Wu, J.S. Huang. *Dalton Trans.*, 2230 (2004).

[11] (a) Y.L. Lu, J.Y. Wu, M.C. Chan, S.M. Huang, C.S. Lin, T.W. Chiu, Y.H. Liu, Y.S. Wen, C.H. Ueng, T.M. Chin, C.H. Hung, K.L. Lu. *Inorg. Chem.*, **45**, 2430 (2006); (b) J. Fan, M.H. Shu, T.-a. Okamura, Y.Z. Li, W.Y. Sun, W.X. Tang, N. Ueyama. *New J. Chem.*, **27**, 1307 (2003).

[12] (a) G.P. Yong, Z.Y. Wang, Y. Cui. *Eur. J. Inorg. Chem.*, 4317 (2004); (b) G.P. Yong, Z.Y. Wang, J.T. Chen. *J. Mol. Struc.*, **707**, 223 (2004).

[13] S. Qiao, G.P. Yong, Y. Xie, Z.Y. Wang. *Acta Cryst.*, **62**, 4634 (2006).

[14] G.M. Sheldrick. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany (1997).

[15] G.M. Sheldrick. *SHELXS-97, Program for X-ray Crystal Structure Solution*, University of Göttingen, Göttingen, Germany (1997).

[16] (a) S.L. Zheng, J.H. Yang, X.L. Yu, X.M. Chen, W.T. Wong. *Inorg. Chem.*, **43**, 830 (2004); (b) L.Y. Zhang, J.P. Zhang, Y.Y. Lin, X.M. Chen. *Cryst. Growth Des.*, **6**, 1684 (2006).