DOI: 10.1002/zaac.200801384

A Novel μ_2-(H_2O)-Bridged Double-Chain Coordination Polymer $[Cd(pc)(phen)(H_2O)]_n$ with Rhombic Grids (H_2pc = pamoic acid, phen = 1,10-phenanthroline)

Guang-Xi Han,[a] Yong-Juan Song,[a] Peng-Cheng Zhao,[b] Xia Chen,[a] and
Zheng-Bo Han*[a]

Keywords: Coordination chemistry; Polymerizations; Cadmium; Pamoic acid

Abstract. A novel coordination polymer $[Cd(pc)(phen)(H_2O)]_n$ (H_2pc = pamoic acid, phen = 1,10-phenanthroline) has been synthesized under hydrothermal conditions. Single crystal X-ray diffraction analysis reveals that the compound crystallizes in triclinic space group $P\bar{1}$. All the Cd^{II} atoms in the compound are hexacoordinate and are linked by pamoicate ligands to form a one-dimensional zigzag chain. Furthermore, two adjacent zigzag chains are connected by the μ_2-(H_2O) molecules to form a double-chain with rhombic grids. There exist intermolecular C–H···π contacts, π–π stacking and hydrogen-bonding interactions. Compound **1** displays strong fluorescent emission in the solid state at room temperature.

Introduction

In the past few years, low dimensional coordination polymers, generally including chain and layer structures, have received much attention owing to their interesting structural features and unique electro-conductivity, non-linear optical and photoluminescent properties, which are different from those of three-dimensional (3D) coordination polymers [1–7]. Particularly some possess photoluminescent properties, a feature that has contributed to d^{10} mental coordination polymers being investigated in the search for new materials. Many Cd^{II} coordination polymers assembled from different ligands and with different structures have been reported by us [8] and others [9–13], those complexes feature interesting supramolecular structures and most of them possess photoluminescent properties.

The hydrothermal method has been a promising technique in synthesizing novel coordination polymers [14]. On the other hand, the strategy for designing coordination polymers generally relies on the using of the multidentate N- and/or O-donor ligands that can act as bridges between metal atoms and form polymeric structures. In order to synthesize novel Cd^{II} complexes, different bridging ligand systems such as benzene dicarboxylic acid, pyrazinedicarboxylic acid, pyridinedicarboxylic acid and oxalic acid have successfully been used. Compared with other acids, pamoic acid is more difficult to form coordination polymers mainly because it is insoluble in many common solvents such as water, ethanol, ether or benzene, so that the coordination polymers formed by pamoic acid are less reported [15]. In this paper, we report the synthesis, crystal structure, and photoluminescence of a novel Cd^{II}-pamoate $[Cd(pc)(phen)(H_2O)]_n$ (**1**),that features an interesting double chain structure with rhombic grids.

Results and Discussion

Crystal Structure

X-ray analysis reveals that compound **1** features a novel μ_2-(H_2O)-bridged double-chain structure with repeated rhombic grids constructed by pamoate linkers, Cd^{II} atoms and phen ligands. Figure 1 shows the coordination environment of the Cd^{II} atom. Each Cd^{II} atom is hexacoordinate and surrounded by two nitrogen atoms of one phen ligand [Cd(1)–N(1) 2.341(3), Cd(1)–N(2) 2.320(3) Å], two carboxyl oxygen atoms of two different pc ligands [Cd(1)–O(2) 2.296(3), Cd(1)–O6(A) 2.240(3) Å] and two aqua ligands [Cd(1)–O(1W) 2.488(3), Cd(1)–O(1WA) 2.316(3) Å]. Thus, the Cd^{II} atom displays a distorted octahedral $[CdO_4N_2]$ coordination arrangement with a Cd–O1W–Cd bond angle of 108.3(1)°. The pc ligand adopts a bis(monodentate) bridging coordination mode (Scheme 1) to connect two Cd (II) atoms into a zigzag chain. One intriguing structural feature is that a pair of Cd^{II} atoms from two adjacent zigzag chains are linked together by two μ_2-H_2O molecules to form a double chain with the rhombic $[Cd_2(\mu_2\text{-}H_2O)_2]$ core. As we know, such bridging mode, in which two water molecules bridging two Cd^{II} atoms into a

---

* Dr. Z.-B. Han
Fax: +86-24-62202380
E-Mail: ceshzb@lnu.edu.cn
[a] College of Chemistry
Liaoning University
Shenyang 110036, P. R. China
[b] Department of Forensic Chemistry
China Criminal Police University
Shenyang 110015, P. R. China

dinuclear Cd^{II} subunit have been observed in Cd^{II} complexes [16].

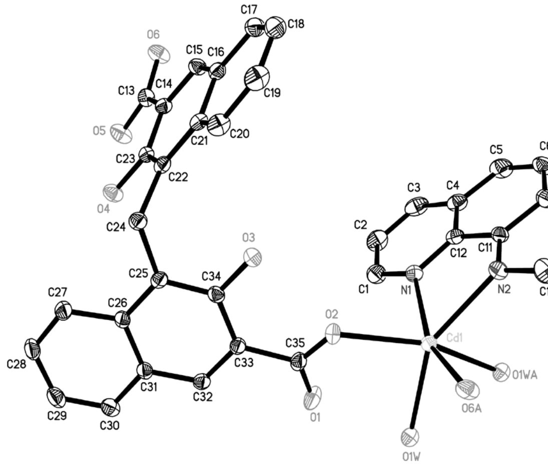
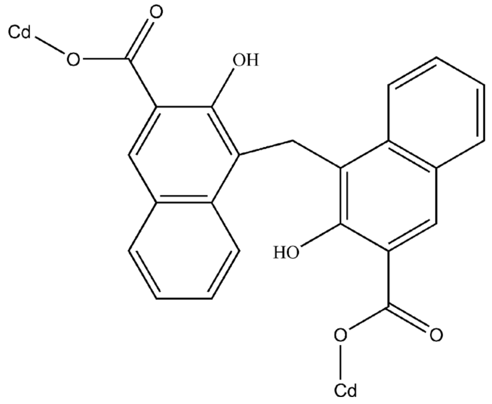


Figure 1. OPTEP view of coordination environment (30 % probability level).



Scheme 1. Coordination mode of the pc ligand.

Comparing with the previously reported double-chain structure that results from two μ_2-H_2O molecules as bridges, $[Cd(C_4O_4)(dpa)(H_2O)]$ (dpa = 2,2-dipyridylamine) [16a], in which the Cd^{II} atom is hexacoordinated and adopts a slightly distorted octahedral coordination environment bonded to two nitrogen atoms from dpa ligands and two oxygen atoms from two squarate ligands and two water molecules. Two cadmium ions are linked through two bridging water molecules to form a $[Cd(dpa)(H_2O)]_2$ dimeric fragment in the equatorial plane with bond lengths of Cd(1)–O(1W) 2.330(2), Cd(1)–O(1WA) 2.384(2) Å, Cd(1)–N(1) 2.296(2) and Cd(1)–N(3) 2.276(2) Å. The squarate ligand adopts a $\mu_{1,2}$-binding mode to connect the neighboring $[Cd(dpa)(\mu_2\text{-}OH_2)]_2$ fragments at the axial sites with bond lengths of Cd(1)–O(1) 2.240(2), Cd(1)–O(2) 2.269(2) Å, constructing a linear, ladderlike MOF along the *a* axis. In this work, Cd–O1W bond lengths, 2.488(3) and 2.316(3) Å, fall in the normal range.

Interestingly, two pc ligands and two Cd^{II} atoms as well as two phen ligands form a rhombic grid unit with the diagonal lengths of 14.449(2) and 12.023(3) Å. The pc ligands and dinuclear cadmium atoms occupy the corners of the rhombic grid and two phen ligands fill in the void space of it (Figure 2). Calculation using PLATON [17] revealed that there exist intermolecular π–π, C–H···π and hydrogen-bonding interactions (Table 1). The intermolecular π–π stacking interactions link the double-chains to form a two-dimensional layer along the *bc* plane (Figure 3). These intermolecular interactions enhance the stability of the compound. Although the formula of **1** is similar to that $\{[Cd(pc)(phen)](DMF)\}_n$ [15a] its architecture is different from the latter, in which pamoate connectors interlink the Cd^{II} ions to form an undulating layered coordination framework along the ac plane. These layers are decorated with perpendicular phen terminals, being outward in the same orientation. Furthermore, pairs of the neighboring layers are arranged in a head-to-head fashion to form a zipper-like interdigitated stacking. The difference of the structure between compound **1** and $\{[Cd(pc)(phen)](DMF)\}_n$ mainly because of the different synthesizing conditions. Compound **1** was synthesized under hydrothermal conditions, whereas $\{[Cd(pc)(phen)](DMF)\}_n$ was prepared with the presence of DMF through solution evaporation.

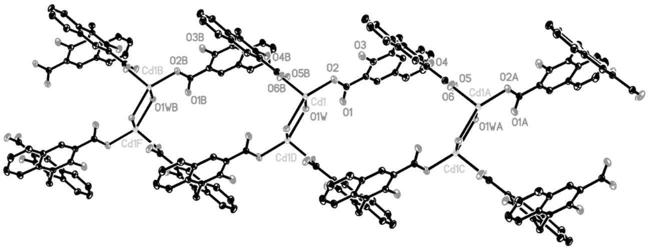


Figure 2. View of the 1D double-chain structure of 1 viewed along the *a*-axis.

XRPD patterns and TGA

The simulated and experimental XRPD patterns of **1** are shown in Figure 4. Their peak positions are in good agreement with each other, indicating the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples [18]. The thermal stability of **1** was examined by TGA in a dry nitrogen atmosphere from 40 to 900 °C. Complex **1** was stable up to ca. 300 °C and then began to decompose upon further heating (Figure 5).

Photoluminescent Properties

Photoluminescence properties of **1** are shown in Figure 6. In the solid state, strong photoluminescent emission bands at 460 and 530 nm (λ_{ex} = 380 nm) are observed. There is no obvious emission observed for free H_2pc under the same experimental conditions. Therefore, the fluorescent emissions of **1** may be attributed to the charge transition of pc^{2-} to Cd^{II} atoms (LMCT) [19].

Table 1. Significant intermolecular interactions found in the X-ray structure of **1**.

D–H···A	D–H	H···A	D···A	∠D–H···A	Symmetry operations for A
O(1W)–H(1B···O(5)	0.85	1.949	2.602(2)	132.69	1+*x*, –1+*y*, *z*
O(3)–H(3B)···O(2)	0.82	1.862	2.598(3)	148.70	*x*, *y*, *z*
C(3)–H(3A)···Cg(1)	0.93	2.637	3.537(4)	163.02	–*x*, –*y*,1–*z*
C(5)–H(5A)···*Cg*(2)	0.93	2.939	3.804(5)	155.20	–*x*, –*y*,1–*z*
C(6)–H(6A)···*Cg*(4)	0.93	3.183	3.422(3)	96.93	1–*x*, –*y*, 1–*z*
Cg(1)···*Cg*(2)	–	–	3.732(4)	–	–*x*, –*y*, –*z*
Cg(3)···*Cg*(3)	–	–	3.708(6)	–	1–*x*, –*y*, 1–*z*

Cg(1): C(25), C(26), C(31)–C(34); *Cg*(2): C(26)–C(31); *Cg*(3): C(4)–C7, C11, C12; *Cg*(4): C16–C21.

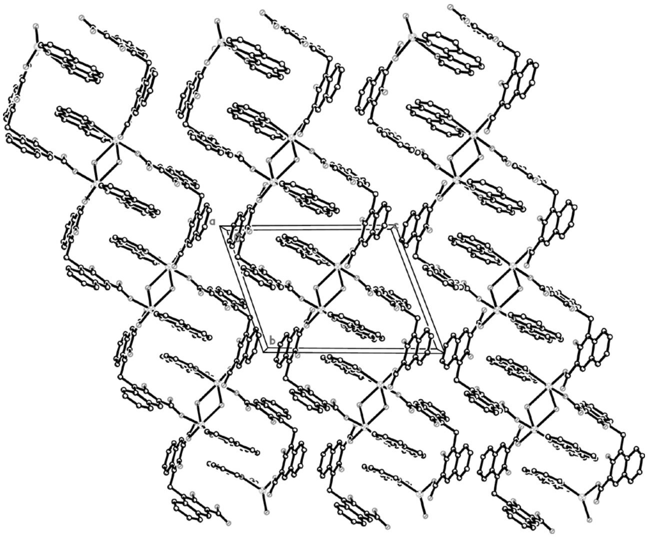


Figure 3. Two dimensional layer structure showing the π–π stacking interactions.

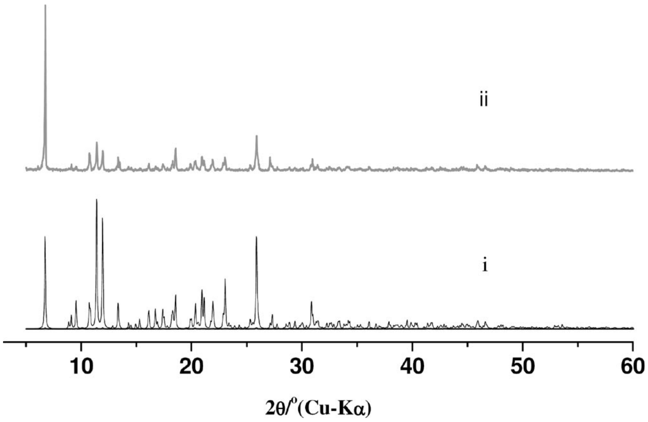


Figure 4. Simulated (i) and experimental (ii) X-ray powder diffraction patterns for **1**.

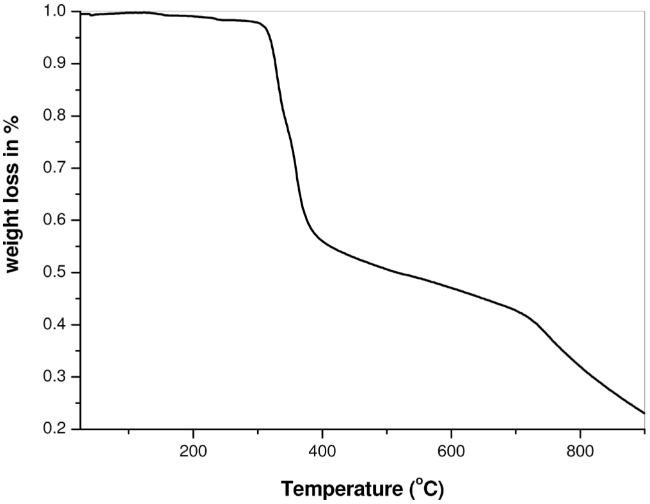


Figure 5. TGA curve of **1**.

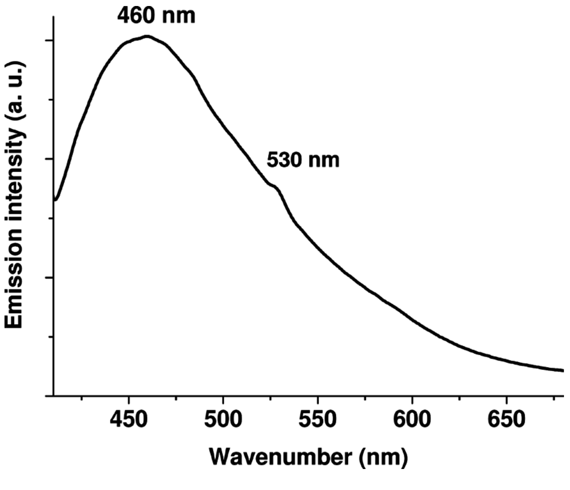


Figure 6. . The photoluminescence spectra of **1** in the solid state at room temperature.

Experimental Section

Materials and Methods

All reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Perkin–Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the 4000–400 cm^{-1} range with a Nicolet 5DX spectrometer. The emission spectra were recorded with a Perkin–Elmer LS50B fluorescence spectrophotometer.

Hydrothermal Synthesis

[Cd(pc)(phen)(H$_2$O)]$_n$: A mixture of Cd(CH$_3$COO)$_2$·2H$_2$O (0.133g, 0.5 mmol), pamoic acid (0.194 g, 0.5 mmol), phen (0.09g, 0.5 mmol),

Table 2. Crystallographic data for **1**.

Empirical formula	$C_{35}H_{24}CdN_2O_7$
Formula weight	696.96
Wavelength /Å	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions:	
a /Å	9.900(3)
b /Å	11.316(2)
c /Å	14.205(3)
α /°	67.78(1)
β /°	79.95(2)
γ /°	69.53(2)
V /Å^3	1378.5(6)
Z	2
D_c /g·cm^{-3}	1.679
μ /mm^{-1}	0.851
F(000)	704
Crystal size /mm	0.37 × 0.32 × 0.27
θ Range for data collection /°	1.55 to 27.50
Reflections collected	7286
Independent reflections(R_{int})	6203 (0.0412)
Max. and min. transmission	0.8059,0.7448
T /K	293(2)
Goodness-of-fit on F^2	1.092
Data/restraints/parameters	6203 / 0 / 406
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0400$, $wR_2 = 0.0999$
R indices (all data)	$R_1 = 0.0557$, $wR_2 = 0.1132$
Largest diff. peak and hole /e·Å^{-3}	0.546, –0.920

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

NaOH (0.04 g, 1 mmol), Et_3N (0.05 mL) and H_2O (10 mL) was put in a 23 mL Teflon reactor and stirred for 30 min in air at room temperature, then kept under autogenous pressure at 160 °C for 5 d. The mixture was cooled to room temperature at a rate of 5 °C·h^{-1}. Yellow block-like crystals of **1** were isolated by filtration, washed with distilled water, and dried in air (yield ca. 35 % based on Zn^{II}). The initial and final pH value of the reaction mixture is 8.5 and 7.0, respectively. $C_{35}H_{24}CdN_2O_7$: calcd.: C 60.31; H 3.47; N 4.02; found: C 60.25; H 3.29; N 4.38. **IR** (KBr): $\tilde{\nu}$ = 3435 (vs), 1637 (s), 1550 (m), 1451 (s), 1391 (s), 1369 (s), 1328 (m), 746 (s) cm^{-1}.

X-ray Crystallography

Crystallographic data of **1** were collected at room temperature with a Bruker P4 diffractometer with Mo-K_α radiation (λ = 0.71073 Å) and graphite monochromator using the ω-scan mode. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL [20]. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically. Crystallographic data and experimental details for structural analysis are summarized in Table 2. Selected bond lengths and angles are listed in Table 3. CCDC-670654 contains the supplementary crystallographic data for this paper. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int code +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk].

Table 3. Selected bond lengths /Å and angles /deg. for **1**.

1			
Cd(1)–O(6)#1	2.240(3)	Cd(1)–O(2)	2.296(3)
Cd(1)–O(1W)	2.316(3)	Cd(1)–N(2)	2.320(3)
Cd(1)–N(1)	2.341(3)	Cd(1)–O(1W)#2	2.488(3)
O(2)–Cd(1)–O(1W)#2	147.65(10)	O(1 W)–Cd(1)–O(1W)#2	71.72(10)
O(6)#1–Cd(1)–O(2)	104.59(11)	O(6)#1–Cd(1)–O(1W)	86.60(10)
O(2)–Cd(1)–O(1W)	87.12(10)	O(6)#1–Cd(1)–N(2)	86.67(11)
O(6)#1–Cd(1)–N(1)	158.31(11)	O(2)–Cd(1)–N(2)	126.50(11)
O(1W)–Cd(1)–N(2)	146.29(10)	O(2)–Cd(1)–N(1)	85.19(11)

Symmetry transformations used to generate equivalent atoms: #1 x–1, y+1, z; #2 –x+1, –y+1, –z+1.

Conclusions

In conclusion, a novel Cd^{II} coordination polymer [Cd(pc)(phen)(H_2O)]$_n$ (**1**) has been successfully synthesized, in which Cd^{II} atoms are hexacoordinate with nitrogen and oxygen atoms from pc groups and phen ligands. The pc ligand adopts a bis(monodentate) coordination mode to connect two Cd^{II} atoms to form a zigzag single-chain. Then the adjacent single-chains are linked by the μ_2-H_2O molecules to form a double-chain with repeated rhombic grids. In addition, the compound is stabilized by intermolecular π–π, C–H···π stacking and hydrogen-bonding interactions. Compound **1** displays strong fluorescent emission in the solid state at room temperature.

Acknowledgement

This work was granted financial support from *National Natural Science Fundation of China* (Grant 20871063) and the *Program for Liaoning Excellent Talents in University* (RC-05-11).

References

[1] C.-T. Chen, K. S. Suslick, *Coord. Chem. Rev.* **1993**, *128*, 293.

[2] a) X.-M. Zhang, M.-L. Tong, X.-M. Chen, *Angew. Chem. Int. Ed.* **2002**, *41*, 1029. b) Z.-B. Han, X.-N. Cheng, X.-M. Chen, *Cryst. Growth Des.* **2005**, *5*, 695.

[3] A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini, M. A. Novak, *Angew. Chem. Int. Ed.* **2001**, *40*, 1760.

[4] 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.* **2001**, *40*, 3201.

[5] A. Kamiyama, T. Noguchi, T. Kajiwara, T. Ito, *Angew. Chem. Int. Ed.* **2000**, *39*, 3130.

[6] Y. Li, E. Wang, H. Zhang, G. Luan, C. Hu, N. Hu, H. Jia, *J. Solid State Chem.* **2002**, *163*, 10.

[7] a) W.-S. You, E.-B. Wang, L. Xu, C.-W. Hu, G.-Y. Luan, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2000**, *56*, 289. b) L. Xu, E. Wang, C. Hu, R. Huang, *Transition. Met. Chem.* **2001**, *26*, 563.

[8] a) Y. Ma, Z. Han, Y. He, L. Yang, *Chem. Commun.* **2007**, 4107. b) Z.-B. Han, Y. Ma, Z.-G. Sun, W.-S. You, *Inorg. Chem. Commun.* **2006**, *9*, 844.

[9] a) J. H. Yang, W. Li, S. L. Zheng, Z. L. Huang, X. M. Chen, *Aust. J. Chem.* **2003**, *56*, 1175. b) S. L. Zheng, J. H. Yang, X. L. Yu, X. M. Chen, W. T. Wong, *Inorg. Chem* **2004**, *43*, 830. c) S. L. Zheng, M. L. Tong, S. D. Tan, Y. Wang, J. X. Shi, Y. X. Tong, H. K. Lee, X. M. Chen, *Organometallics* **2001**, *20*, 5319.

[10] a) Q.-R. Fang, G.-S. Zhu, Z. Jin, M. Xue, X. Wei, D.-J. Wang, S.-L. Qiu, *Angew. Chem. Int. Ed.* **2006**, *45*, 6126. b) Q. Shi, Y. Sun, L. Sheng, K. Ma, M. Hu, X. Hu, S. Huang, *Cryst. Growth Des.* **2008**, *8*, 3401.

[11] C.-D. Wu, W. Lin, *Inorg. Chem.* **2005**, *44*, 1178.

[12] Q. Ye, X.-S. Wang, H. Zhao, R.-G. Xiong, *Tetrahedron: Asymmetry* **2005**, *16*, 1595.

[13] T. K. Maji, K. Uemura, H.-C. Chang, R. Matsuda, S. Kitagawa, *Angew. Chem. Int. Ed.* **2004**, *43*, 3269.

[14] T. Ezuhara, K. Endo, Y. Aoyama, *J. Am. Chem. Soc.* **1999**, *121*, 3279.

[15] a) M. Du, C.-P. Li, X.-J. Zhao, Q. Yu, *Cryst. Eng. Commun.* **2007**, *9*, 1011. b) J.-J. Wang, M.-L. Yang, H.-M. Hu, G.-L. Xue, D.-S. Li, Q.-Z. Shi, *Inorg. Chem. Commun.* **2007**, *10*, 269. c) Q. Shi, Y. Sun, L. Sheng, K. Ma, M. Hu, X. Hu, S. Huang, *Cryst. Growth Des.* **2008**, *8*, 3401.

[16] a) Q.-Y. Liu, Y.-L. Wang, L. Xu, *Eur. J. Inorg. Chem.* **2006**, 4843. b) C. H. Wei, K. B. Jacobson, *Inorg. Chem.* **1981**, *20*, 356. c) N. Nakasuka, S. Azuma, M. Tanaka, *Acta Crystallogr., Sect. C* **1986**, *42*, 1736. d) E. Dubler, G. Haenggi, H. Schmalle, *Inorg. Chem.* **1990**, *29*, 2518. e) S. I. Nishikiori, *J. Coord. Chem.* **1996**, *37*, 23. f) H. Aghabozorg, N. Ilaie, M. Heidari, F. Manteghi, H. Pasdar, *Acta Crystallogr., Sect. E* **2008**, *64*, ,1351.

[17] A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Untrecht University, Utrecht, the Netherlands, 1999.

[18] A. Gilbert, J. Baggott, *Essentials of Molecular Photochemistry*; CRC Press:Boca Raton, FL, 1991; pp 87–89.

[19] a) W.-G. Lu, L. Jiang, X.-L. Feng, T.-B. Lu, *Cryst. Growth Des.* **2006**, *6*, 564.

[20] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

Received: December 17, 2008