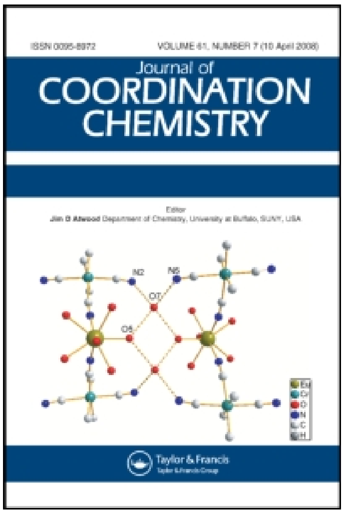


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, spectroscopic properties, and structures of copper(II) and manganese(II) complexes of pyridine-2,6-dicarboxylate and 1,10-phenanthroline

Xin Hu[a]; Yinping Li[a]; Yongjiang Wang[a]; Weijun Du[a]; Jixi Guo[b]
[a] College of Life Science and Chemistry, Xinjiang Normal University, Xinjiang, Urumqi, China [b] Institute of Applied Chemistry, Xinjiang University, Xinjiang, Urumqi, China

To cite this Article Hu, Xin , Li, Yinping , Wang, Yongjiang , Du, Weijun and Guo, Jixi(2009) 'Synthesis, spectroscopic properties, and structures of copper(II) and manganese(II) complexes of pyridine-2,6-dicarboxylate and 1,10-phenanthroline', Journal of Coordination Chemistry, 62: 21, 3438 — 3445, First published on: 22 September 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970903093686

URL: http://dx.doi.org/10.1080/00958970903093686

Journal of Coordination Chemistry
Vol. 62, No. 21, 10 November 2009, 3438–3445

Taylor & Francis
Taylor & Francis Group

Synthesis, spectroscopic properties, and structures of copper(II) and manganese(II) complexes of pyridine-2,6-dicarboxylate and 1,10-phenanthroline

XIN HU*†, YINPING LI†, YONGJIANG WANG†, WEIJUN DU† and JIXI GUO‡

†College of Life Science and Chemistry, Xinjiang Normal University, Urumqi, Xinjiang 830054, China
‡Institute of Applied Chemistry, Xinjiang University, Urumqi, Xinjiang 830046, China

(*Received 17 December 2008; in final form 11 March 2009*)

A binuclear copper(II) complex $[Cu(PDC)(phen)]_2 \cdot 2CH_3OH \cdot 1.5H_2O$ (**1**) and a seven-coordinate manganese(II) complex $[Mn(PDC)(phen)_2] \cdot CH_3OH$ (**2**) (PDC = pyridine-2,6-dicarboxylate, phen = 1,10-phenanthroline) have been synthesized hydrothermally and characterized by elemental analyses, spectroscopic studies (IR and UV), and single-crystal X-ray diffraction. In **1**, the binuclear copper(II) compound consists of two kinds of Cu(II) centers with five- and six-coordination environments by PDC and phen. The two Cu(II) ions are bridged by one PDC. In **2**, Mn(II) is seven-coordinate by two phen and one PDC.

Keywords: Binuclear copper(II) complex; UV spectra; Pyridine-2,6-dicarboxylate; Seven-coordinate manganese(II) complex

1. Introduction

Formation of metal/bi- or polycarboxylate assemblies are of interest [1–11]. A frequently used family of organic linkers consist of 1,4-benzenedicarboxylic acid, 1,3,5-benzenetricarboxylic, 1,2,4,5-benzenetetracarboxylic acid, pyridine-3,5-dicarboxylic acid, and pyridine-2,6-dicarboxylic acid. The versatile coordination modes of the carboxylates, as well as the chemical robustness, lead to the assembled frameworks exhibiting structural diversity and thermal stability [12]. Selection of appropriate multidentate ligands to link metal-organic frameworks is important for building low-dimensional coordination polymers and potential supramolecular complexes [13–17]. As a multidentate ligand, pyridine-2,6-dicarboxylic acid (H_2PDC) is usually tridentate as a bridging linker in design of metal-organic molecular assemblies [18, 19].

Hydro(solvo)thermal method is good for synthesis of extended coordination networks and new materials [20–23], generating species that are difficult to obtain by routine synthetic methods. It is very difficult to assess the role of each reagent used [20], as some reagents control formation of product in ways that are difficult to predict.

---

*Corresponding author. Email: huxin81387429@yahoo.com.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970903093686

Herein, we describe a binuclear copper complex [Cu(PDC)(phen)]$_2 \cdot 2CH_3OH \cdot 1.5H_2O$ (**1**) and a mononuclear manganese complex [Mn(PDC)(phen)$_2$]$\cdot CH_3OH$ (**2**), synthesized by hydrothermal methods and characterized by elemental analyses, spectroscopic studies (IR and UV), and single-crystal X-ray diffraction. The copper compound is asymmetric with each Cu center in a unique coordination environment. The manganese compound is seven-coordinate.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals used in these syntheses were of reagent grade and used as purchased. Infrared (IR) spectra were recorded on a BRUKER EQUINOX-55 spectrophotometer from 400 to 4000 cm^{-1} using KBr pellets. Elemental analyses were performed on a Perkin-Elmer 2400 elemental analyzer. UV spectra were determined in methanol with concentration (1.0×10^{-4} M) using a HITACHI UV-3310 spectrometer with 1 cm quartz cell in the range 200–800 nm at room temperature.

2.2. *Synthesis of [Cu(PDC)(phen)]$_2$•2CH$_3$OH•1.5H$_2$O (1)*

A mixture of pyridine-2,6-dicarboxylic acid (1 mmol), 1,10-phenanthroline (1 mmol), Cu(OAc)$_2 \cdot H_2O$ (1 mmol), NaOH (2 mmol), and 8 mL methanol were placed in a 23 mL Teflon lined stainless steel reactor. The vessel was heated to 120°C for 3 days and then cooled at 5°C h^{-1} to room temperature; blue crystals were obtained by filtration. Anal. Calcd for $C_{40}H_{33}Cu_2N_6O_{11.5}$: C, 52.86; H, 3.67; N, 9.25. Found: C, 53.47; H, 3.32; N, 9.36.

2.3. *Synthesis of [Mn(PDC)(phen)$_2$]•CH$_3$OH (2)*

Compound **2** was prepared similarly to **1** by using Mn(OAc)$_2 \cdot 4H_2O$ (1 mmol), NaOH (2 mmol), pyridine-2,6-dicarboxylic acid (1 mmol), 1,10-phenanthroline (1 mmol), and 8 mL methanol. Colorless crystals were obtained by filtration. Anal. Calcd for $C_{33}H_{27}MnN_5O_6$: C, 61.49; H, 4.22; N, 10.87. Found: C, 60.84; H, 4.18; N, 10.70.

2.4. *X-ray crystallography*

Suitable single crystals of **1** and **2** were mounted on a Rigaku R-axis Spider II diffractometer equipped with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. The unit cell parameters were determined by least squares refinements of all reflections in both cases. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogens were located from the difference map and then added geometrically. All calculations were performed using the *SHELXTL-97* program package [24–26]. Crystal data and experimental details for **1** and **2** are provided in table 1. Selected bond distances and angles are listed in table 2.

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

Identification code	**1**	**2**
Empirical formula	$C_{40}H_{33}Cu_2N_6O_{11.5}$	$C_{33}H_{27}MnN_5O_6$
Formula weight	908.80	644.54
Temperature (K)	153(2)	153(2)
Crystal system	Monoclinic	Monoclinic
Wavelength (Å)	0.71073	0.71073
Space group	*C*2/*c*	*I*2/*a*
Unit cell dimensions (Å, °)		
a	33.963(7)	13.775(3)
b	15.220(3)	11.340(2)
c	14.676(3)	18.451(6)
α	90	90
β	106.76(10)	92.84(10)
γ	90	90
Volume (Å^3, Z)	7264.2(3), 8	2878.7(12), 4
Crystal size (mm^3)	0.59 × 0.41 × 0.32	0.56 × 0.52 × 0.42
Calculated density (g cm^{-3})	1.662	1.487
F(000)	3720	1332
θ range for data collection (°)	3.00–27.48	3.16–25.50
Limiting indices	$-44\le h\le 41$; $-19\le k\le 19$; $-18\le l\le 19$	$-16\le h\le 15$; $-13\le k\le 13$; $-22\le l\le 22$
Reflections collected	8294	2685
Independent reflections	7587 [R(int) = 0.0237]	2611 [R(int) = 0.0158]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	8294/4/561	2685/0/208
Goodness-of-fit on F^2	1.018	1.077
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0308$, $\omega R_2 = 0.0784$	$R_1 = 0.0322$, $\omega R_2 = 0.0955$
R indices (all data)	$R_1 = 0.0272$, $\omega R_2 = 0.0765$	$R_1 = 0.0316$, $\omega R_2 = 0.0950$

3. Results and discussion

3.1. *X-ray structure of 1*

The molecular view of $[Cu(PDC)(phen)]_2 \cdot 2CH_3OH \cdot 1.5H_2O$ (**1**) with atomic-numbering scheme is shown in figure 1. Selected bond distances and angles are listed in table 2. The asymmetric unit of **1** contains two copper(II) ions, two PDC, two phen, two methanol, and 1.5 waters (figure 1). One methanol and one water are disordered over two sites.

Single-crystal structure analysis reveals that there are two distinguishable copper ions in **1**. In this binuclear molecule, the two PDC ligands differ considerably in their interaction with copper(II). One PDC is tetradentate linking two Cu(II) ions (scheme 1a). The other is tridentate to another Cu(II) (scheme 1b). The two copper(II) atoms are bridged by O7 from tetradentate PDC. Cu1 is five-coordinate by two phen molecules and one PDC in distorted square-pyramidal geometry and Cu2 is in a distorted octahedral geometry with two PDC units (figure 1).

Cu1 is five-coordinate with two phen ligands (N1, N2, N3, N4) and one oxygen (O7) from PDC ligand. Since the angular structural index parameter, $\tau = (\beta - \alpha)/60$, is evaluated by the two largest angles ($\alpha < \beta$) in the five-coordinate geometry, where α and β are the bond angles involving the *trans* donors in the basal plane, $\tau = 0$ and 1 for ideal square pyramidal and trigonal bipyramidal geometries, respectively [27]. In **1**, the largest angle around Cu1 is N(4)–Cu(1)–N(1) (175.46(5)°, β) and the second largest is O(7)–Cu(1)–N(2) (146.78(5)°, α). The value of τ (0.20) indicates square-pyramidal

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

Complex **1**			
Cu(1)–O(7)	1.9675(11)	Cu(2)–N(5)	1.9136(13)
Cu(1)–N(4)	1.9841(13)	Cu(2)–N(6)	1.9772(13)
Cu(1)–N(1)	1.9940(13)	Cu(2)–O(3)	2.0624(11)
Cu(1)–N(2)	2.0728(14)	Cu(2)–O(1)	2.0948(11)
Cu(1)–N(3)	2.1663(13)	Cu(2)–O(5)	2.2404(12)
		Cu(2)–O(7)	2.3805(11)
O(7)–Cu(1)–N(4)	94.20(5)	O(3)–Cu(2)–O(1)	159.35(5)
O(7)–Cu(1)–N(1)	90.11(5)	N(5)–Cu(2)–O(5)	113.00(5)
N(4)–Cu(1)–N(1)	175.46(5)	N(6)–Cu(2)–O(5)	77.91(5)
O(7)–Cu(1)–N(2)	146.78(5)	O(3)–Cu(2)–O(5)	98.36(5)
N(4)–Cu(1)–N(2)	93.67(5)	O(1)–Cu(2)–O(5)	91.03(5)
N(1)–Cu(1)–N(2)	81.93(5)	N(5)–Cu(2)–O(7)	94.68(5)
O(7)–Cu(1)–N(3)	117.45(5)	N(6)–Cu(2)–O(7)	74.39(5)
N(4)–Cu(1)–N(3)	80.54(5)	O(3)–Cu(2)–O(7)	89.06(4)
N(1)–Cu(1)–N(3)	98.72(5)	O(1)–Cu(2)–O(7)	91.15(4)
N(2)–Cu(1)–N(3)	95.67(5)	O(5)–Cu(2)–O(7)	152.15(4)
N(5)–Cu(2)–O(3)	80.07(5)	N(5)–Cu(2)–N(6)	169.07(5)
N(6)–Cu(2)–O(3)	99.52(5)	N(5)–Cu(2)–O(1)	79.33(5)
N(6)–Cu(2)–O(1)	100.42(5)		
Complex **2**			
Mn–N(3)	2.2287(19)	Mn–N(1A)	2.3064(15)
Mn–O(1)	2.2792(12)	Mn–N(2)	2.3507(14)
Mn–O(1A)	2.2792(12)	Mn–N(2A)	2.3507(14)
Mn–N(1)	2.3064(15)		
N(3)–Mn–O(1)	70.62(3)	N(3)–Mn–N(1A)	91.18(3)
N(3)–Mn–O(1A)	70.62(3)	O(1A)–Mn–N(1)	85.29(5)
O(1)–Mn–O(1A)	141.23(6)	O(1A)–Mn–N(1A)	95.50(5)
N(3)–Mn–N(2)	141.31(3)	N(3)–Mn–N(1)	91.18(3)
O(1)–Mn–N(2A)	137.92(5)	O(1)–Mn–N(1)	95.50(5)
O(1A)–Mn–N(2A)	77.05(5)	N(1A)–Mn–N(1)	177.65(7)
N(1A)–Mn–N(2A)	71.07(5)	N(1)–Mn–N(2A)	107.00(5)
N(1A)–Mn–N(2)	107.00(5)	N(1)–Mn–N(2)	71.07(5)
N(3)–Mn–N(2A)	141.31(3)	N(2A)–Mn–N(2)	77.39(7)
O(1)–Mn–N(2)	77.05(5)	O(1)–Mn–N(1A)	85.29(5)
O(1A)–Mn–N(2)	137.92(5)		

geometry around Cu1. The basal plane is defined by N1, N2, N4, and O7 (root mean square (rms) deviation 0.273 Å) and the apical position is occupied by N3. The coordination geometry around Cu2 is a distorted octahedron with two tridentate PDC ligands. Each Cu2 has distorted [CuO_4N_2] octahedral coordination geometry with the apical positions taken up by O5 and O7. The apical Cu–O distances (2.240(12) Å for Cu(2)–O(5); 2.381(11) Å for Cu(2)–O(7)) are considerably longer than the equatorial ones and the geometry quite distorted from ideal octahedron. The axial elongation could be attributed to the Jahn–Teller distortion of copper(II). The basal atoms (Cu2, N5, N6, O1, and O3) are non-planar with rms deviation of 0.296 Å. The maximum deviation of any equatorial atom from the mean plane around Cu2 is 0.0937 Å. The bond angle of O(3)–Cu(2)–O(1) is 159.35°, deviating from ideal value of 180°. The N(5)–Cu(2)–O(3), N(6)–Cu(2)–O(3), N(6)–Cu(2)–O(1), and O(1)–Cu(2)–O(7) angles are 80.07(5)°, 99.52(5)°, 100.42(5)°, and 91.15(5)°, respectively, implying geometry around Cu2 is distorted.

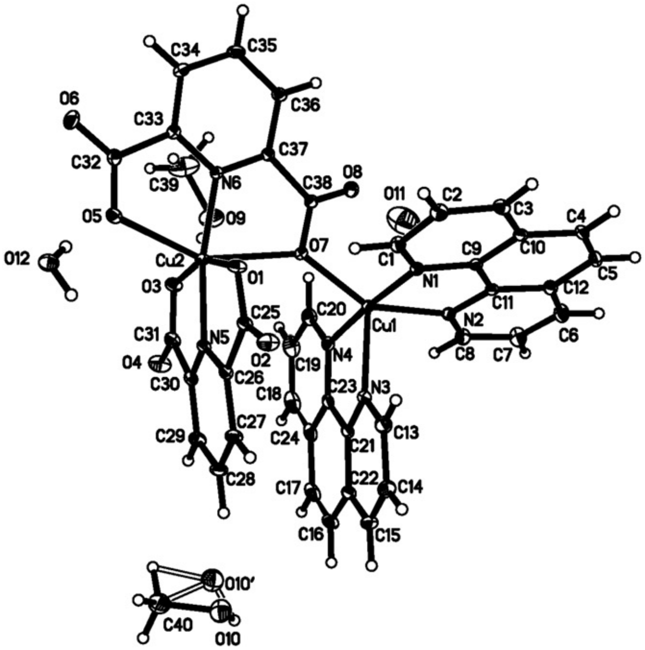
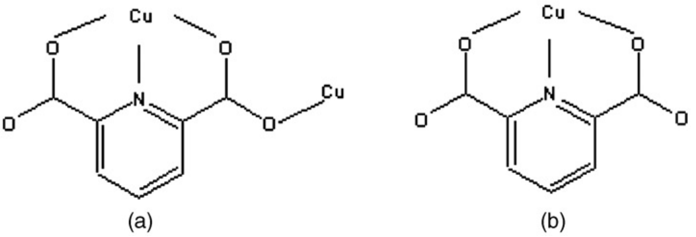


Figure 1. Molecular structure of **1** with atom numbering scheme (30% thermal ellipsoids).



Scheme 1. Coordination modes of PDC.

3.2. *X-ray structure of 2*

The X-ray crystal structure of [Mn(PDC)(phen)$_2$] $\cdot$ CH$_3$OH (**2**) is shown in figure 2 and selected bond lengths and angles are listed in table 2. The asymmetric unit consists of tridentate PDC, two bidentate phen's and one methanol. The Mn center resides on a two-fold axis, through Mn, N(3), and C(16) so that the phen groups are *cis* to each other. The best equatorial pentagonal plane is defined by O(1), O(1A), N(2), N(2A), N(3), and Mn (rms deviation of the fitted atoms 0.296 Å). The five angles in this plane are approximately evenly distributed (70.62(3), 70.62(3), 77.05(5), 77.05(5), and 77.39(7) for N(3)–Mn–O(1A), O(1)–Mn–N(3), O(1A)–Mn–N(2A), O(1)–Mn–N(2), and N(2A)–Mn–N(2), respectively). N(1) and N(1A) are apical with equal bond lengths (table 2); the N(1)–Mn–N(1A) angle is 177.65(7)°. The axial Mn–N bond length of 2.306 Å is between the equatorial ones (2.229 Å, 2.350 Å). There are several reports of seven-coordinate pentagonal bipyramidal manganese(II) [28, 29]. Macrocyclic ligands

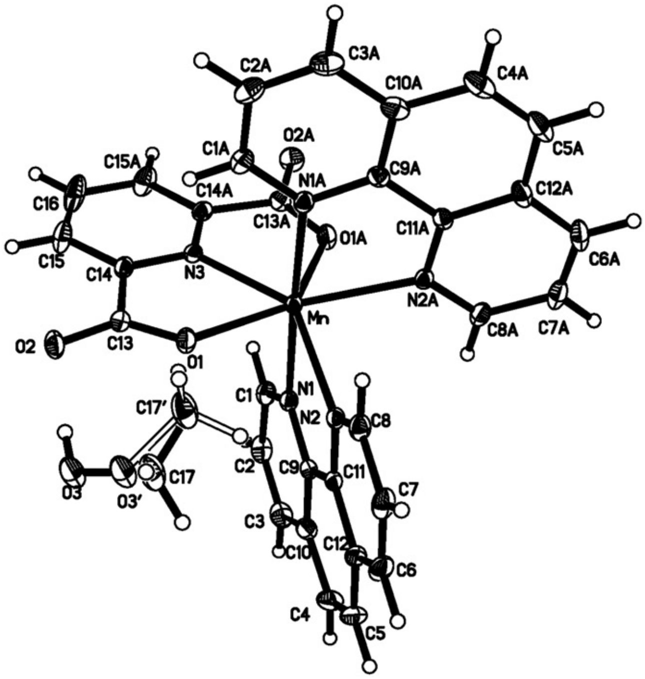


Figure 2. Molecular structure of **2** with atom numbering scheme (30% thermal ellipsoids). The symmetry element names end in "A" ($-x$, y, $0.5-z$).

or rigid, resonance-stabilized planar ligands have been employed to enforce pentagonal planar coordination [30]. The PDC ligand uses three atoms to coordinate to the Mn(II) to form two, five-membered chelate rings, leaving space to accommodate four other donors. Steric crowding of the four, five-membered chelate rings may prevent dimerization of the monomeric units in solid state.

3.3. *Spectroscopic properties*

Infrared spectrum of **1** shows two strong carboxylate bands at 1633–1596 $\mathrm{cm^{-1}}$ for the symmetric vibration and 1428–1360 $\mathrm{cm^{-1}}$ for the asymmetric vibration [31]. For **2**, typical asymmetric and symmetric stretching bands of carboxylates are at 1623–1589 $\mathrm{cm^{-1}}$ and 1422–1376 $\mathrm{cm^{-1}}$. The IR bands attributable to the presence of phen in **1** (3064 m, 3050 m, 1271 m, 856 m, and 727 m) and in **2** (3058 m, 2925 m, 1276 m, 1044 m, 863 s, and 730 m) are also observed [32].

The UV absorption spectra of pyridine-2,6-dicarboxylic acid (L), **1** and **2** (10^{-4} M) in MeOH are shown in figure 3. The free ligand L exhibits absorption bands at 227 and 268 nm (with molar absorption coefficients in $\mathrm{dm^3 \cdot mol^{-1} \cdot cm^{-1}}$), indicating π–π^* electronic transitions [33], originating from the pyridyl groups of pyridine-2,6-dicarboxylic acid; these bands are red-shifted upon coordination in **1** and **2**.

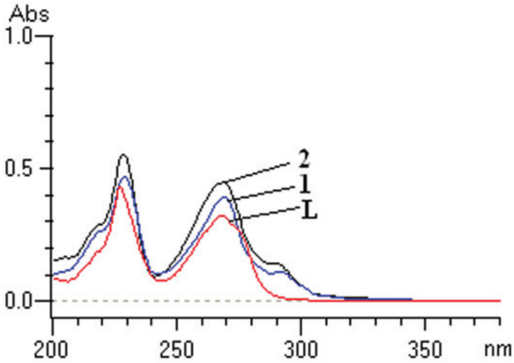


Figure 3. UV spectra of **1**, **2**, and H_2PDC (L) in methanol (*ca.* 10^{-4} M).

4. Conclusion

In this article, a new binuclear copper(II) and a seven-coordinate manganese(II) compound have been synthesized and characterized. Although the two compounds were synthesized from a similar reaction system, the structures are very different because of the different metal centers and the steric demands of ligands.

Supplementary material

CCDC reference numbers: 676787 and 676788. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Scientific Research Foundation in Xinjiang Educational Institutions (XJEDU2007S24) and the Young Scholar Science Foundation of Xinjiang Normal University.

References

[1] C. Pettinari, F. Marchetti, A. Drozdov, J.A. McCleverty, T.J. Meyer (Eds.). *Comprehensive Coordination Chemistry II*, Vol. 6, p. 1240, Elsevier, Amsterdam (2004).
[2] H.L. Gao, C. Cheng, B. Ding, W. Shi, H.B. Song, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang. *J. Mol. Struct.*, **738**, 105 (2005).
[3] Y.G. Huang, D.Q. Yuan, Y.Q. Gong, F.L. Jiang, M.Ch. Hong. *J. Mol. Struct.*, **872**, 99 (2008).
[4] S.K. Ghosh, P.K. Bharadwaj. *Inorg. Chem.*, **44**, 3156 (2005).
[5] S. Konar, P.S. Mukherjee, M.G.B. Drew, J. Ribas, N.R. Chaudhuri. *Inorg. Chem.*, **42**, 2545 (2003).
[6] Y. Li, N. Hao, Y. Lu, E. Wang, Z. Kang, C. Hu. *Inorg. Chem.*, **42**, 3119 (2003).
[7] H.L. Gao, B. Ding, L. Yi, P. Cheng, D.Z. Liao, Sh. Yan, Z.H. Jiang. *Inorg. Chem. Commun.*, **8**, 151 (2005).

[8] Y.C. Liang, R. Cao, M.C. Hong, D.F. Sun, Y.J. Zhao, J.B. Weng, R.H. Wang. *Inorg. Chem. Commun.*, **5**, 366 (2002).
[9] E.E. Sileo, A.S. Araujob, G. Rigottic, O.E. Piroc, E.E. Castellanob. *J. Mol. Struct.*, **644**, 67 (2003).
[10] C.N.R. Rao, S. Natarajan, R. Vaidhyanathan. *Angew. Chem. Int. Ed.*, **43**, 1466 (2004).
[11] Q. Yue, J. Yang, G.H. Li, G.D. Li, W. Xu, J.S. Chen, S.N. Wang. *Inorg. Chem.*, **44**, 5241 (2005).
[12] W.X. Chen, S.T. Wu, L.S. Long, R.B. Huang, L.S. Zheng. *Cryst. Growth Des.*, **7**, 1171 (2007).
[13] C. Janiak. *J. Chem. Soc., Dalton Trans.*, **21**, 3885 (2000).
[14] M. Geraghty, M. McCann, M. Casey, M. Curran, M. Devereux, V. McKee, J. Mcrea. *Inorg. Chim. Acta*, **277**, 257 (1998).
[15] M. Devereux, M. McCann, J.F. Cronin, G. Ferguson, V. McKee. *Polyhedron*, **18**, 2141 (1999).
[16] Y.Q. Zheng, Z.P. Kong. *Inorg. Chem. Commun.*, **6**, 478 (2003).
[17] Y.Q. Guo, H.Y. An, Y.Q. Li, E.B. Wang, X.L. Wang, L. Xu, C.W. Hu. *Inorg. Chim. Acta*, **357**, 4582 (2004).
[18] W.Z. Wang, X. Liu, D.Z. Liao, Z.H. Jiang, S.P. Yan, G.L. Wang. *Inorg. Chem. Commun.*, **4**, 327 (2001).
[19] K.Y. Choi, H. Ryu, Y.M. Lim, N.D. Sung, U.S. Shin, M. Suh. *Inorg. Chem. Commun.*, **6**, 412 (2003).
[20] F.C. Liu, Y.F. Zeng, J.P. Zhao, B.W. Hu, E. Carolina Sañudo, J. Ribas, X.H. Bu. *Inorg. Chem.*, **46**, 7698 (2007).
[21] Z.B. Han, X.N. Cheng, X.M. Chen. *Cryst. Growth Des.*, **5**, 695 (2005).
[22] S.H. Feng, R.R. Xu. *Acc. Chem. Res.*, **34**, 239 (2001).
[23] K.S. Min, M.P.J. Suh. *Solid State Chem.*, **152**, 183 (2000).
[24] G.M. Sheldrick. *SHELXS-97*, *Program for X-ray Crystal Structure Determination*, Göttingen University, Germany (1997).
[25] G.M. Sheldrick. *SHELXL-97, Program for X-ray Crystal Structure Refinement*, Göttingen University, Germany (1997).
[26] G.M. Sheldrick. *SHELXTL*, *Version V*, Siemens Industrial Automation Inc., Madison, Wisconsin, USA (1997).
[27] W. Addison, T.N. Rao, J. Rijn, G.C. Verschoor. *J. Chem. Soc., Dalton Trans.*, 71349 (1984).
[28] S. Brooker, V. McKee. *J. Chem. Soc., Dalton Trans.*, **8**, 2397 (1990).
[29] S. Brooker, V. McKee. *Acta Cryst. C*, **49**, 441 (1993).
[30] Z.M. Sun, P.K. Gantzel, D.N. Hendrickson. *Polyhedron*, **17**, 1511 (1998).
[31] C.Z. Xie, B.F. Zhang, X.W. Liu, X.Q. Wang, H.Z. Kou, G.Q. Shen, D.Z. Shen. *Inorg. Chem. Commun.*, **7**, 1037 (2004).
[32] I. Castro, M. Luisa Calatayud, J. Sletten, F. Lloret, M. Julve. *Inorg. Chim. Acta*, **287**, 173 (1999).
[33] W. Barnum. *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).