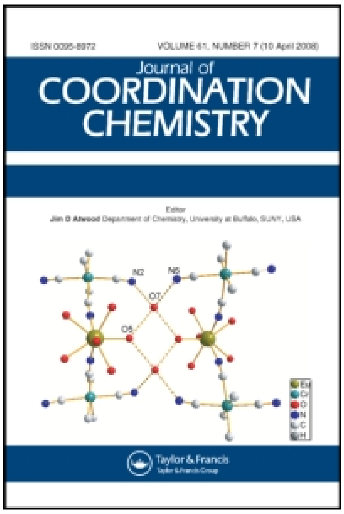

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Syntheses and structures of two zinc coordination polymers with a three-dimensional α-polonium cubic network and a two-dimensional (4,4) network

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Syntheses and structures of two zinc coordination polymers with a three-dimensional α-polonium cubic network and a two-dimensional (4,4) network

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Two unusual zinc coordination polymers $\{[Zn(bim)_3](NO_3)_2\cdot(H_2O)_4\}_n$ (**1**) and $\{[Zn(bte)_2(H_2O)_2](NO_3)_2\}_n$ (**2**) [bim = 1,2-bis(imidazol-1-yl)ethane, bte = 1,2-bis(1,2,4-triazol-1-yl)ethane] were synthesized and characterized. **1** possesses a double interpenetrating three-dimensional α-polonium cubic network and **2** consists of a two-dimensional (4,4) network.

Keywords: Zinc; Crystal structure; Three-dimensional network; Two-dimensional network; Bis(imidazole) ligand; Bis(triazole) ligand

1. Introduction

Coordination polymer materials have interesting physical and chemical properties and potential applications in selective guest adsorption, gas storage, ion exchange, nanoporous materials and magnetic materials [1–7]. The most commonly used organic connecting ligands are rigid building blocks containing pyridine units such as 4,4′-bipyridine and 4,4′-azobispyridine [8,9]. Flexible ligands have been used in recent years to obtain novel topologies not available from logical combinations of rigid building blocks. The simplest way to introduce flexibility into a ligand is by incorporating an alkyl chain into the spacer groups. For example, bis(2-benzimidazolyl)ethane [10], bis(2-benzimidazolyl)propane [10,11], 1,4-bis(benzimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene [12], 1,3-bis(pyrazol-1-yl)propane [13], 1,4-bis(imidazol-1-ylmethyl) benzene [14–16], bis(1,2,4-triazol-1-yl)methane [17,18] and 1,3-bis(1,2,4-triazol-1-yl) propane [19,20] have been used for the construction of novel topologies.

We have found that, besides linear pyridyl-like ligands, the flexible ligand 1,2-bis(1,2,4-triazol-1-yl)ethane (bte) [21] is also an effective organic bridging ligand for constructing coordination frameworks [22–24]. 1,2-Bis(imidazol-1-yl)ethane (bim)

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is similar to bte but has been rarely studied [25]. In this work, two novel coordination polymers $\{[Zn(bim)_3](NO_3)_2 \cdot (H_2O)_4\}_n$ (**1**) and $\{[Zn(bte)_2(H_2O)_2](NO_3)_2\}_n$ (**2**) were synthesized and characterized using bim and bte.

2. Experimental

2.1. *Materials and physical measurements*

All reagents were of analytical grade and used without further purification. 1,2-Bis(imidazol-1-yl)ethane (bim) and 1,2-bis(1,2,4-triazol-1-yl)ethane (bte) were prepared following a literature method [26]. Elemental analyses (C, H, N) were performed on a Perkin Elmer 240C instrument. IR spectra were obtained on a Nicolet 170SX FT-IR spectrophotometer in the 4000–400 cm^{-1} region using KBr pellets. Thermogravimetric data were collected on a Thermal Analyst 2100 TA instrument and SDT 2960 Simultaneous TGA-DTA instrument in flowing dinitrogen at a heating rate 10°C min^{-1}.

2.2. *Synthesis of $\{[Zn(bim)_3](NO_3)_2 \cdot (H_2O)_4\}_n$ (1)*

An aqueous solution (10 cm^3) of bim (0.75 mmol, 0.121 g) was added slowly to an aqueous solution (10 cm^3) of $Zn(NO_3)_2 \cdot 6H_2O$ (0.25 mmol, 0.075 g) with stirring for 10 min. The mixture was filtered and the filtrate left at room temperature. After 1 month, well-shaped, colorless, single crystals of **1** were obtained. Yield: 68%. Anal. Calcd. for $C_{24}H_{38}N_{14}O_{10}Zn$(%): C, 38.54; H, 5.12; N, 26.22. Found: C, 38.37; H, 5.15; N, 26.01. IR absorption bands (KBr, cm^{-1}): 3434m, 3133m, 1628w, 1516m, 1462w, 1385vs, 1289m, 1238m, 1111m, 1092s, 1030w, 934w, 833w, 748w, 683w, 660m, 633w.

2.3. *Synthesis of $\{[Zn(bte)_2(H_2O)_2](NO_3)_2\}_n$ (2)*

A solution of bte (0.60 mmol, 0.098 g) in 10 cm^3 methanol was added slowly to an aqueous solution (10 cm^3) of $Zn(NO_3)_2 \cdot 6H_2O$ (0.30 mmol, 0.089 g). The mixture was stirred at room temperature for 30 min and filtered. The filtrate was allowed to stand at room temperature for 2 weeks, and well-shaped, colorless, single crystals of **2** were obtained. Yield: 56%. Anal. Calcd. for $C_{12}H_{20}N_{14}O_8Zn$(%): C, 26.03; H, 3.64; N, 35.42. Found: C, 25.92; H, 3.66; N, 35.36. IR absorption bands (KBr, cm^{-1}): 3442w, 3116m, 3090w, 3006w, 1535m, 1518m, 1384s, 1273m, 1216m, 1138m, 1012m, 1004w, 895m, 825w, 696m, 650m.

2.4. *Crystal structure determination*

Single crystals of **1** and **2** with approximate dimensions 0.50 × 0.40 × 0.25 and 0.58 × 0.30 × 0.24 mm, respectively, were selected for lattice parameter determination and collection of intensity data using a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Intensities were collected by the ω scan technique. The structures were solved by direct methods and refined with full-matrix least-squares techniques using SHELXTL-97 [27]. Crystal data collection and refinement details are given in table 1. Bond lengths and angles are given

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

	1	**2**
Empirical formula	$C_{24}H_{38}N_{14}O_{10}Zn$	$C_{12}H_{20}N_{14}O_8Zn$
Formula weight	748.05	553.79
Temperature (K)	293(2)	193.15
Wavelength (Å)	0.71073	0.71073
Crystal system	Trigonal	Monoclinic
Space group	$P\bar{3}$	$P2_1/c$
A (Å)	18.982(4)	8.640(4)
B (Å)	18.982(4)	12.357(6)
C (Å)	7.9137(18)	10.268(5)
α (°)	90.00	90.00
β (°)	90.00	100.898(6)
γ (°)	120.00	90.00
V (Å)	2469.5(10)	1076.5(9)
Z	3	2
$F(000)$	1170	568
ρ (g cm^{-3})	1.509	1.709
μ (mm^{-1})	0.821	1.216
Crystal size (mm)	0.50 × 0.40 × 0.25	0.58 × 0.30 × 0.24
θ range for data collection (°)	3.28 to 27.47	3.28 to 27.48
Index ranges	$-24 \le h \le 24$, $-19 \le k \le 24$, $-10 \le l \le 8$	$-11 \le h \le 11$, $-16 \le k \le 15$, $-13 \le l \le 13$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Independent reflections	3659 [R(int) = 0.0416]	2402 [R(int) = 0.0240]
Goodness of fit S	1.082	1.078
Final R_1 and wR_2 [$I > 2\sigma(I)$]	0.0786, 0.1723	0.0352, 0.0749
R_1 and wR_2 indices (all data)	0.0851, 0.1768	0.0384, 0.0765
Largest diff. peak and hole (e Å^{-3})	0.721 and −0.608	0.368 and −0.275

in table 2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) (e-mail: deposit@ccdc.cam.ac.uk) as supplementary material and the CCDC reference numbers for **1** and **2** are 228277 and 228278, respectively.

3. Results and discussion

In the preparation of coordination polymers **1** and **2**, we found that the final products were independent of the metal/ligand molar ratio. Coordination polymer $\{[Zn(bim)_3](NO_3)_2 \cdot (H_2O)_4\}_n$ (**1**) with a Zn/bim molar ratio of 1 : 3 was obtained on mixing $Zn(NO_3)_2 \cdot 6H_2O$ and bim in either a 1 : 3 or a 1 : 2 molar ratio in aqueous solution. Coordination polymer $\{[Zn(bte)_2(H_2O)_2](NO_3)_2\}_n$ (**2**) with a Zn/bte molar ratio of 1 : 2 was assembled when mixing $Zn(NO_3)_2 \cdot 6H_2O$ and bte in either a 1 : 2 or a 1 : 3 molar ratio in methanol/H_2O.

X-ray analysis shows that **1** is composed of a $[Zn(bim)_3]_n^{2n+}$ macrocation, disordered NO_3^- anions and lattice water molecules. There are two independent zinc centers and two independent bim ligands. Each zinc atom is located on position $\bar{3}$ with octahedral geometry (figure 1). Each zinc atom is coordinated by six imidazole nitrogen atoms from six individual bim ligands. N–Zn–N bond angles are close to 90° [89.24(11), 89.64(11), 90.38(11) and 90.74(11)° for Zn(1); 89.30(10) and 90.70(10)° for Zn(2)]. The ethane groups in bim are disordered. Each bim ligand adopts the *anti* conformation. The dihedral angle between N(1) and N(3) imidazole rings of one bim ligand

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

Complex 1			
Zn(1)–N(1)	2.181(3)	Zn(1)–N(1)$^{\#1}$	2.181(3)
Zn(1)–N(1)$^{\#2}$	2.181(3)	Zn(1)–N(5)	2.205(3)
Zn(1)–N(5)$^{\#1}$	2.205(3)	Zn(1)–N(5)$^{\#2}$	2.205(3)
Zn(2)–N(3)	2.193(3)	Zn(2)–N(3)$^{\#3}$	2.193(3)
Zn(2)–N(3)$^{\#4}$	2.193(3)	Zn(2)–N(3)$^{\#5}$	2.193(3)
Zn(2)–N(3)$^{\#6}$	2.193(3)	Zn(2)–N(3)$^{\#7}$	2.193(3)
N(1)$^{\#1}$–Zn(1)–N(1)	90.74(11)	N(1)$^{\#1}$–Zn(1)–N(5)	89.64(11)
N(1)–Zn(1)–N(5)	89.24(11)	N(5)–Zn(1)–N(5)$^{\#1}$	90.38(11)
N(1)$^{\#1}$–Zn(1)–N(5)$^{\#2}$	179.62(11)	N(1)$^{\#2}$–Zn(1)–N(5)	179.62(10)
N(1)–Zn(1)–N(5)$^{\#1}$	179.62(10)	N(3)–Zn(2)–N(3)$^{\#3}$	90.70(10)
N(3)$^{\#3}$–Zn(2)–N(3)$^{\#4}$	89.30(10)	N(3)–Zn(2)–N(3)$^{\#4}$	180.00(17)
N(3)$^{\#5}$–Zn(2)–N(3)$^{\#6}$	180.00(16)	N(3)$^{\#3}$–Zn(2)–N(3)$^{\#7}$	180.00(14)
Complex 2			
Zn(1)–N(3)	2.1758(17)	Zn(1)–N(3)$^{\#1}$	2.1758(17)
Zn(1)–N(6)$^{\#2}$	2.1419(17)	Zn(1)–N(6)$^{\#3}$	2.1419(17)
Zn(1)–O(1)	2.1145(16)	Zn(1)–O(1)$^{\#1}$	2.1145(16)
N(3)–Zn(1)–N(3)$^{\#1}$	180.0	N(6)$^{\#2}$–Zn(1)–N(6)$^{\#3}$	180.0
N(6)$^{\#2}$–Zn(1)–N(3)	89.38(7)	N(6)$^{\#3}$–Zn(1)–N(3)$^{\#1}$	90.62(7)
O(1)–Zn(1)–O(1)$^{\#1}$	180.00(6)	O(1)–Zn(1)–N(3)	91.45(7)
O(1)$^{\#1}$–Zn(1)–N(3)	88.55(7)	O(1)–Zn(1)–N(6)$^{\#2}$	90.10(7)
O(1)–Zn(1)–N(6)$^{\#2}$	89.90(7)		

Symmetry codes: **1** $^{\#1}$ $-x+y, -x+1, z$; $^{\#2}$ $-y+1, x-y+1, z$; $^{\#3}$ $-y, x-y, z$; $^{\#4}$ $-x, -y, -z$; $^{\#5}$ $-x+y, -x, z$; $^{\#6}$ $x-y, x, -z$; $^{\#7}$ $y, -x+\mathrm{y}, -z$; **2** $^{\#1}$ $-x+2, -y+1, -z+1$; $^{\#2}$ $-x+2, y-1/2, -z+3/2$; $^{\#3}$ $x, -y+3/2, z-1/2$.

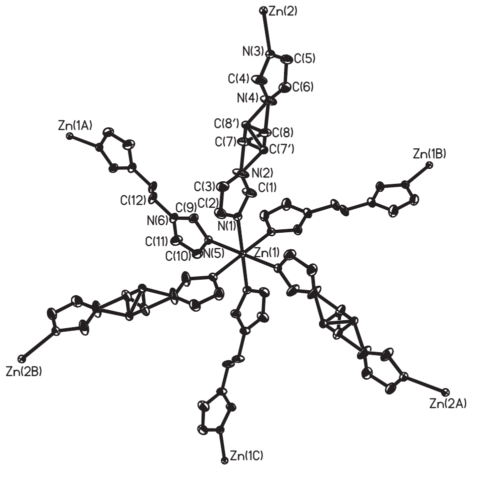

Figure 1. The coordination environment of the zinc centers in **1**.

is 2.86(40)°. Two imidazole ring planes of the bim ligand containing the N(5) atom are essentially coplanar due to the center of symmetry. Each bim ligand bridges two adjacent zinc atoms, building up polymers into an open three-dimensional α-polonium cubic network [28] (figure 2). Zn$\cdots$Zn separations across the bridging bim ligand are 12.274 Å for Zn(1)$\cdots$Zn(1) and 12.109 Å for Zn(1)$\cdots$Zn(2), similar to the corresponding metal–metal separation in $[\mathrm{Cu(bim)}_{2.5}](\mathrm{ClO}_4)_2 \cdot 2\mathrm{MeOH}$ (12.55 Å) [25]. There are double interpenetrating α-polonium cubic networks in the crystal (figure 3) and channels approximately 4×4 Å are formed in which lie disordered NO_3^- anions and lattice water molecules.

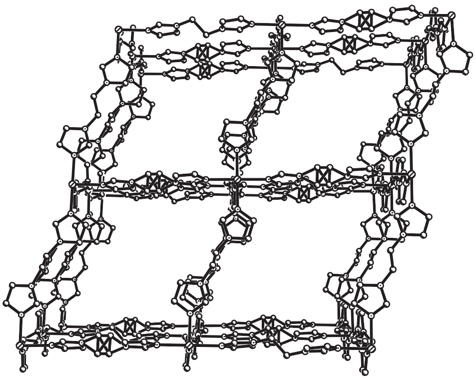

Figure 2. The three-dimensional α-polonium cubic network in **1**.

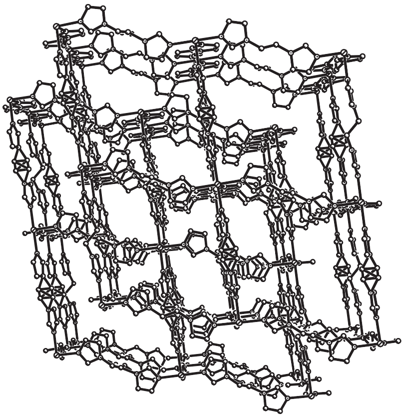

Figure 3. The double-interpenetrating three-dimensional α-polonium cubic network in **1**.

The crystal structure of **2** consists of a two-dimensional (4,4) network, which is clearly different from the open three-dimensional α-polonium cubic network in **1**. The key factor governing the structural topologies of **1** and **2** is the metal/ligand molar ratio (1 : 3 in **1** and 1 : 2 in **2**).

The coordination geometry of zinc(II) in **2** is distorted octahedral (figure 4), in which the equatorial plane has four exodentate nitrogen atoms at the 4-position of the triazole rings from four different bte ligands and the axial positions are occupied by two water molecules. Each bridging bte ligand links two Zn(II) atoms and each Zn(II) atom bonds four bte ligands to form a two-dimensional (4,4) network containing square $Zn_4(bte)_4$ units (figure 5). The Zn···Zn separation across the bridging bte ligand is 8.003 Å, similar to the corresponding metal–metal separation of 8.369 Å in $[Zn(dca)_2(bte)_2]_n$ [22]. The two-dimensional network structure consists of puckered rhombus grids with dimensions of 8.003 × 8.003 Å. The most intriguing feature of the structure is that the basic two-dimensional grid is puckered (figure 6), unlike that observed in previous grid-like structures in which the basic grids are usually coplanar or *quasi*-coplanar [29,30]. The puckered shape of the basic grid in **2** occurs because

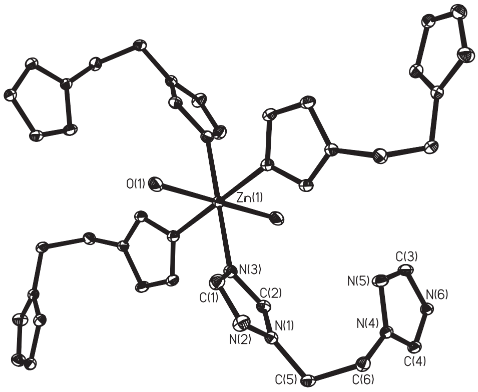

Figure 4. ORTEP drawing of the coordination environment of zinc(II) in **2**, and the atom numbering scheme.

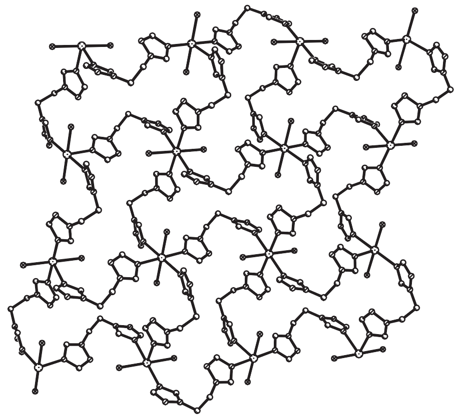

Figure 5. View of the two-dimensional (4,4) network in **2** along the *a* direction.

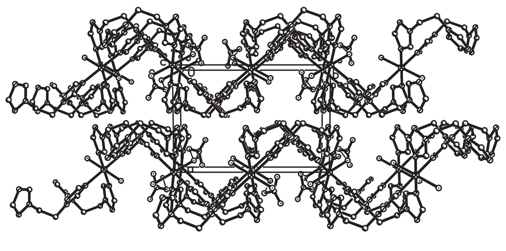

Figure 6. View of the tightened packed structure in **2** along the *c* direction; only two layers are shown for clarity.

the bte ligand exhibits a *gauche* conformation in **2**. The dihedral angle between N(3) and N(6) triazole ring planes is 33.0°. The bte ligand has twisted during coordination with a torsion angle N(1)–C(5)–C(6)–N(4) of 68.4(2)°. Hydrogen-bonding interactions exist between hydrogen atoms of the coordination water molecules and oxygen atoms of the nitrate anions [O(1)–H(1WA)···O(2) (x, $-y+1/2$, $z-1/2$), 2.743(3) Å; O(1)–H(1WB)···O(3), 2.926(3) Å; O(1)–H(1WB)···O(4), 2.988(3) Å].

Thermogravimetric analyses (TGA) were performed to determine the thermal stability of complexes **1** and **2**. Thermal analysis of **1** shows that the lattice water molecule was lost in a continuous fashion (Obsd. 9.4%; Calcd., 9.6%) from 20 to 105°C. The $\{[Zn(bim)_3](NO_3)_2\}_n$ framework did not lose weight upon further heating to 210°C, but began to decompose above this temperature. Thermal analysis of **2** shows that the coordinated water molecules were lost in a continuous fashion (Obsd. 6.3%; Calcd. 6.5%) from 110 to 170°C, followed by the bte ligand.

In summary, assembly of $Zn(NO_3)_2 \cdot 6H_2O$ with bim or bte resulted in two unusual zinc coordination polymers: $\{[Zn(bim)_3](NO_3)_2 \cdot (H_2O)_4\}_n$ (**1**) with a three-dimensional α-polonium cubic network and $\{[Zn(bte)_2(H_2O)_2](NO_3)_2\}_n$ (**2**) with a two-dimensional (4,4) network. The different motifs of **1** and **2** show that the properties of the ligands are key to self-assembly of the coordination polymers. Small changes in the ligands can generate very different topologies; rationalization of the resulting topologies is still difficult. The syntheses of **1** and **2** enrich the supramolecular chemistry of the flexible ligands 1,2-bis(imidazol-1-yl)ethane and 1,2-bis(1,2,4-triazol-1-yl)ethane and provide useful information for crystal engineering.

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References

[1] R. Robson, B.F. Abrahams, S.R. Batten, R.W. Gable, B.F. Hoskins, J. Liu, *Supramolecular Architecture*, p. 526, American Chemical Society, Washington, DC (1992).
[2] M.C. Hong, Y.J. Zhao, W.P. Su, R. Cao, M. Fujita, Z.Y. Zhou, A.S.C. Chan, *Angew. Chem. Int. Ed. Engl.* **39**, 2468 (2000).
[3] C.Y. Su, Y.P. Cai, C.L. Chen, F. Lissner, B.S. Kang, W. Kaim, *Angew. Chem. Int. Ed. Engl.* **41**, 3371 (2002).
[4] M.L. Tong, H.K. Lee, X.M. Chen, R.B. Huang, T.C.W. Mak, *J. Chem. Soc., Dalton Trans.* 3657 (1999).
[5] L.Z. Wang, Z.R. Qu, H. Zhao, X.S. Wang, R.G. Xiong, Z.L. Xue, *Inorg. Chem.* **42**, 3969 (2003).
[6] P. Yin, S. Gao, L.M. Zheng, Z.M. Wang, X.Q. Xin, *J. Chem. Soc., Chem. Commun.* 1076 (2003).
[7] J. Fan, W.Y. Sun, T.A. Okamura, W.X. Tang, N. Ueyama, *Inorg. Chem.* **42**, 3168 (2003).
[8] B.L. Li, G. Yin, H.Q. Cao, Y.J. Liu, Z. Xu, *Inorg. Chem. Commun.* **4**, 451 (2001).
[9] B.L. Li, J.P. Lang, J.G. Ding, Y. Zhang, *Inorg. Chem. Commun.* **6**, 141 (2003).
[10] G.A.N. Albada, W.J.J. Smeets, N. Veldman, A.L. Spek, J. Reedijk, *Inorg. Chim. Acta* **290**, 105 (1999).
[11] G.A.V. Albada, W.J.J. Smeets, A.L. Spek, J. Reedijk, *Inorg. Chim. Acta* **288**, 220 (1999).
[12] C.Y. Su, Y.P. Cai, C.L. Chen, B.S. Kang, *Inorg. Chem.* **40**, 2210 (2001).
[13] A.M. Schuitema, M. Engelen, I.A. Koval, S. Gorter, W.L. Driessen, J. Reedijk, *Inorg. Chim. Acta* **324**, 57 (2001).
[14] B.F. Hoskins, R. Robson, D. Slizys, *J. Am. Chem. Soc.* **119**, 2952 (1997).
[15] B.F. Hoskins, R. Robson, D. Slizys, *Angew. Chem. Int. Ed. Engl.* **36**, 2336 (1997).
[16] H.Y. Shen, D.Z. Liao, Z.H. Jiang, S.P. Yan, G.L. Wang, X.K. Yao, H.G. Wang, *Acta Chem. Scand.* **53**, 387 (1999).
[17] Effendy, F. Marchetti, C. Pettinari, R. Pettinari, B.W. Skelton, A.H. White, *Inorg. Chem.* **42**, 112 (2003).
[18] L.F. Tang, Z.H. Wang, J.F. Chai, W.L. Jia, Y.M. Xu, J.T. Wang, *Polyhedron* **19**, 1949 (2000).
[19] G.A.V. Albada, R.C. Guijt, J.G. Haasnoot, M. Lutz, A.L. Spek, J. Reedijk, *Eur. J. Inorg. Chem.* 121 (2000).

[20] Q.H. Zhao, H.F. Li, X.F. Wang, Z.D. Chen, *New J. Chem.* **26**, 1709 (2002).
[21] B.Z. Li, X. Zhu, B.L. Li, Y. Zhang, *J. Mol. Struct.* **691**, 159 (2004).
[22] B.L. Li, B.Z. Li, X. Zhu, L.M. Zhu, Y. Zhang, *Acta Cryst.* **C59**, 350 (2003).
[23] B.L. Li, Z. Xu, Z.B. Cao, L.M. Zhu, K.B. Yu, *Transition Met. Chem.* **24**, 622 (1999).
[24] B.L. Li, J.Z. Zou, C.Y. Duan, Y.J. Liu, X.W. Wei, Z. Xu, *Acta Cryst.* **C55**, 165 (1999).
[25] L.P. Wu, Y. Yamagiwa, T. Kuroda-Sowa, T. Kamikawa, M. Munakata, *Inorg. Chim. Acta* **256**, 155 (1997).
[26] J. Torres, J.L. Lavandera, P. Cabildo, R.M. Claramunt, J. Elguero, *J. Heterocycl. Chem.* **25**, 771 (1988).
[27] G.M. Sheldrick, *SHELX-97: Program for Crystal Structure Analysis*, University of Göttingen, Germany (1997).
[28] M.L. Tong, J. Ru, Y.M. Wu, X.M. Chen, H.C. Chang, K. Mochizuki, S. Kitagawa, *New J. Chem.* **27**, 779 (2003).
[29] K. Biradha, M. Fujita, *J. Chem. Soc.*, *Dalton Trans.* 3805 (2000).
[30] K. Biradha, Y. Hongo, M. Fujita, *Angew. Chem. Int. Ed. Engl.* **39**, 3843 (2000).