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Syntheses, crystal structures and photoluminescent properties of two isophthalate-bridged complexes

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Abstract

Two interesting isophthalate-bridged coordination polymers, $[Cd_2(2,2'\text{-bpy})_2(ip)_2]_n$ (**1**) and $[Zn_2(2,2'\text{-bpy})_2(ip)_2]_n$ (**2**) (2,2′-bpy = 2,2′-bipyridine, ip = isophthalate) have been hydrothermally synthesized and structurally characterized. X-ray single-crystal diffraction analyses reveal that compound **1** contains a three-dimensional polymeric channel with tetra –Cd–ip– as building units and compound **2** forms a double-helical structure linked by $Zn_2O_4C_2$ cores. In **1**, one Cd(II) center is six-coordinated and the other is seven-coordinated, while the two Zn(II) centers in **2** are in different six-coordinated environments.

Keywords: 2,2′-Bipyridine; Cadmium(II) complex; Double-helix; Isophthalate; Polymeric tubes; Zinc(II) complex

1. Introduction

In the last few years, there has been a considerable interest in the design and elaboration of polymetallic molecular systems owing to their intriguing network topologies and potential functions as new classes of materials [1–3]. The most successful strategy for preparing these materials is the assembly reaction of a transition metal ion with two types of ligands, of which one acts as a terminal ligand and the other as a bridging ligand. Polynuclear d^{10} Zn(II) and Cd(II) complexes have been found to exhibit interesting structural and photoluminescent properties [4–6]. Although many Zn(II) and Cd(II) coordination polymers containing organic ligands with carboxylic groups have been prepared, those containing the isophthalate ligand are less considered [7–9]. We report here the preparation and crystal structures of two interesting coordination polymers constructed by cadmium(II) or zinc(II) centers, 2,2′-bipyridine and isophthalate, namely $[Cd_2(2,2'\text{-bpy})_2(ip)_2]_n$ (**1**) and $[Zn_2(2,2'\text{-bpy})_2(ip)_2]_n$ (**2**).

2. Experimental

2.1. General

Isophthalate, 2,2′-bipyridine and other chemicals were used as received. The IR spectra were recorded on a Magna 750 FT-IR spectrometer using KBr pellets. Elemental analyses were carried out on an elemental analyzer model Vario EL III. Fluorescent analyses were performed on an Edinburgh Instruments analyzer model FL920.

2.2. Syntheses of complexes

2.2.1. $[Cd_2(2,2'\text{-bpy})_2(ip)_2]_n$ (1)

The hydrothermal reactions of cadmium chloride with isophthalate and 2,2′-bipyridine in molar ratio 1:1:1 in 15 ml H_2O were carried out in a 30-ml autoclave with PTFE liners for 5 days at 180 °C. After cooling the reaction system at a rate of 5 °C/h to 30 °C, colorless prismatic crystals of complex **1** were isolated in 53%

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yield. *Anal.* Calc. for $C_{36}H_{24}N_4O_8Cd_2$: C, 49.96; H, 2.80; N, 6.47. Found: C, 49.37; H, 2.61; N, 6.37%. IR (KBr cm^{-1}): 411w, 538m, 656w, 671m, 690s, 729s, 926m, 1163m, 1281s, 1421s, 1581m, 1610s, 1693s.

2.2.2. *[Zn$_2$(2,2′-bpy)$_2$(ip)$_2$]$_n$ (**2**)*

The hydrothermal reaction of zinc chloride with isophthalate and 2,2′-bipyridine in molar ratio 1:1:1 in 15 ml H_2O were run in a 30-ml autoclave with PTFE liners for 5 days at 160 °C. Cooling the reaction system at a rate of 5 °C/h to 30 °C gave colorless prismatic crystals of complex **2** in 46% yield. *Anal.* Calc. for $C_{36}H_{24}N_4O_8Zn_2$: C, 56.06; H, 3.14; N, 7.26. Found: C, 55.87; H, 3.03; N, 7.05%. IR (KBr cm^{-1}): 417w, 654w, 719m, 735m, 750s, 1022w, 1315m, 1383s, 1443s, 1477w, 1570s, 1614s.

2.3. *X-ray crystallography*

Data collections of **1** and **2** were performed at 293 K on a Siemens Smart CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied by using the SADABS program for the Siemens area detector. The structures were solved with direct methods and all calculations were performed using the SHELXTL package. The positions of H atoms were generated geometrically. The structures were refined by full-matrix least-squares with anisotropic thermal parameters for all atoms. Details of the crystal data are listed in Table 1. Selected bond lengths and bond angles for **1** and **2** are listed in Tables 2 and 3, respectively.

3. Results and discussion

3.1. *Syntheses*

Dicarboxylates play an important role in the formation of coordination polymers. This kind of ligand is able to connect metal centers in many different manners, for example, linking the metal centers into either infinite chains or three-dimensional structures [10,11]. In this study, 2,2′-bipyridine was introduced as a co-ligand of isophthalate to react with different metal ions. The reaction of Cd(II) with 2,2′-bipyridine and isophthalate resulted in a three-dimensional polymer **1** with a channel structure, as expected. However, although the experimental conditions were nearly the same, the reaction of Zn(II) with 2,2′-bipyridine and isophthalate generated a one-dimensional polymer **2** with a double-helix structure. To the best of our knowledge, they are the first two examples of Zn(II) and Cd(II) coordination polymers containing both isophthalate and 2,2′-bipyridine ligands.

Table 1
Crystal data and refinement parameters of **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{36}H_{24}N_4O_8Cd_2$	$C_{36}H_{24}N_4O_8Zn_2$
Formula weight	865.39	771.33
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	21.4048(7)	9.3302(3)
b (Å)	9.3867(3)	11.2760(3)
c (Å)	33.486(1)	16.7809(5)
α (°)	90	100.118(2)
β (°)	103.73(1)	93.907(2)
γ (°)	90	110.630(2)
V (Å^3)	6535.7(4)	1610.28(8)
Z	8	2
D_{calc} (g cm^{-3})	1.759	1.591
Absorption coefficient (mm^{-1})	1.362	1.551
Crystal size (mm)	0.46 × 0.34 × 0.30	0.18 × 0.12 × 0.12
Reflections collected	10 854	6632
Unique reflections	5747	4164
R_{int}	0.0245	0.0520
Parameters	547	535
R_1 [a]	0.0362	0.0764
wR_2 [b]	0.0682	0.1384
S on F^2	1.190	1.244
Largest difference peak and hole (e Å^{-3})	0.538 and −0.451	0.419 and −0.658

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$, $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, $P = (2F_c^2 + F_o^2)/3$.

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

Cd(1)–O(1)	2.292(4)	Cd(2)–O(3B)	2.217(3)
Cd(1)–O(5)	2.369(4)	Cd(2)–O(4AA)	2.238(3)
Cd(1)–O(6)	2.414(3)	Cd(2)–O(8)	2.326(4)
Cd(1)–O(2)	2.422(3)	Cd(2)–N(4)	2.351(4)
Cd(1)–O(6A)	2.464(3)	Cd(2)–N(3)	2.360(4)
Cd(1)–N(1)	2.348(4)	Cd(2)–O(7)	2.362(3)
Cd(1)–N(2)	2.387(4)		
O(5)–Cd(1)–O(6)	54.4(1)	O(8)–Cd(2)–O(7)	55.4(1)
O(1)–Cd(1)–O(2)	55.3(1)	N(4)–Cd(2)–N(3)	69.9(1)
N(1)–Cd(1)–N(2)	69.2(2)	O(3B)–Cd(2)–N(3)	81.3(1)
O(1)–Cd(1)–O(6A)	84.6(1)	O(4AA)–Cd(2)–N(4)	85.1(1)
O(6)–Cd(1)–O(6A)	70.2(1)		

Symmetry transformations used to generate equivalent atoms: A, $-x, y, -z+1/2$; B, $-x, -y+1, -z$; AA, $x-1/2, y+1/2, z$.

3.2. *Crystal structure analyses*

3.2.1. *Crystal structure of complex 1*

X-ray single-crystal diffraction analyses reveal that compound **1** contains a three-dimensional polymeric channel with tetra –Cd–ip– as building units (Fig. 1). As shown in Fig. 2, four isophthalate ligands link four Cd(II) centers through bonding of Cd(II) and carboxylic groups (–Cd(1)–ip–Cd(2)–ip–Cd(1C)–ip–Cd(2C)–ip–) to form a nano-ring with a diameter of about

Table 3
Selected bond lengths(Å) and bond angles(°) for **2**

Zn(1)–O(8A)	2.009(6)	Zn(2)–O(3B)	1.983(7)
Zn(1)–O(1)	2.056(7)	Zn(2)–O(6)	2.038(6)
Zn(1)–O(7)	2.062(7)	Zn(2)–N(4)	2.051(9)
Zn(1)–N(1)	2.125(8)	Zn(2)–N(3)	2.139(9)
Zn(1)–N(2)	2.170(8)	Zn(2)–O(5)	2.355(8)
Zn(1)–O(2)	2.425(7)	Zn(2)–O(4B)	2.463(8)
O(1)–Zn(1)–O(2)	58.1(2)	N(4)–Zn(2)–N(3)	77.7(3)
N(1)–Zn(1)–N(2)	75.5(3)	O(3B)–Zn(2)–O(4B)	57.8(3)
O(7)–Zn(1)–N(1)	88.6(3)	O(6)–Zn(2)–O(5)	59.6(3)
O(8A)–Zn(1)–N(1)	103.1(3)		

Symmetry transformations used to generate equivalent atoms: A, $-x+1$, $-y$, $-z+1$; B, x, $y+1$, z.

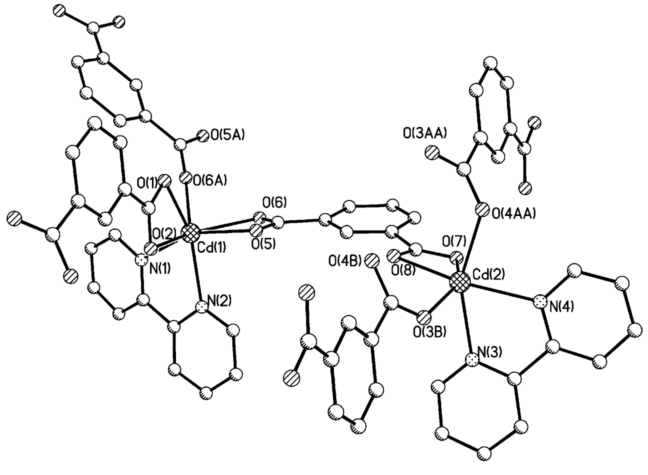


Fig. 1. Metal coordination in $[Cd_2(2,2'\text{-bpy})_2(ip)_2]_n$.

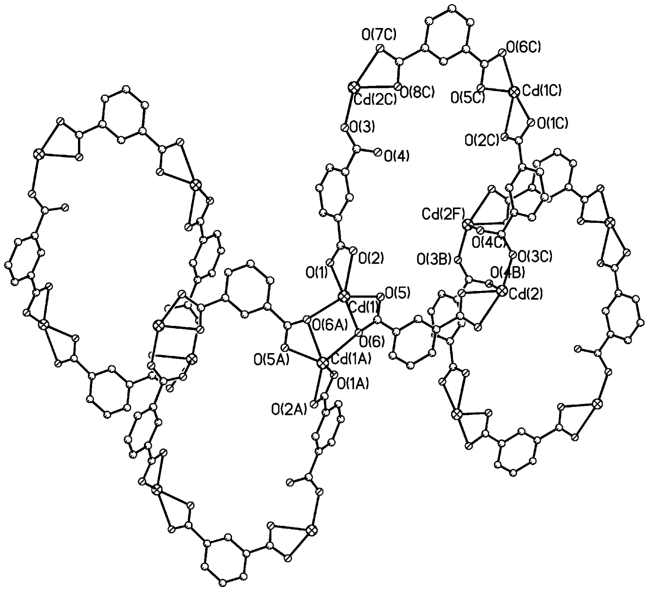


Fig. 2. View of the cavities with 2,2′-bipyridine omitted in complex **1** (along *b* axis).

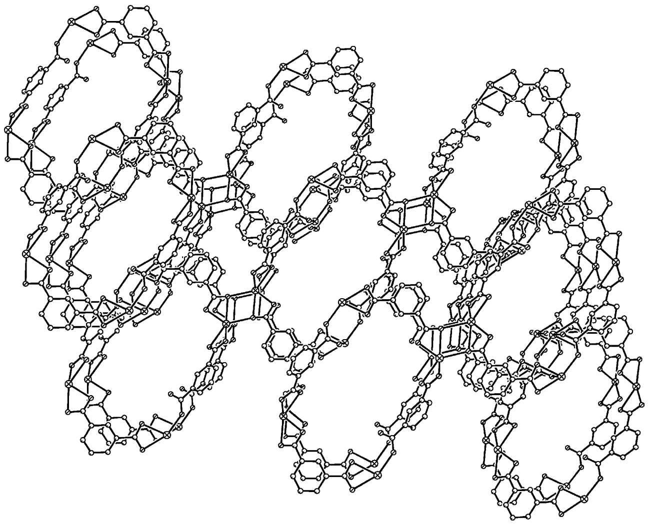
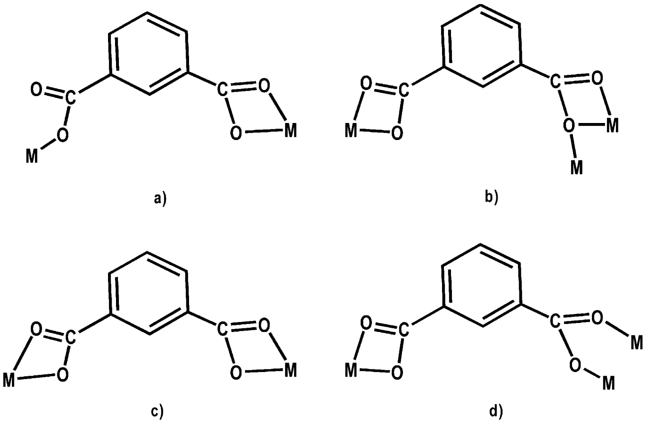


Fig. 3. Three-dimensional packing diagram with 2,2′-bipyridine omitted of complex **1** along *b* axis.

14.4 Å. The connections between neighboring rings via Cd–O bonds generate a three-dimensional network structure with nano-channels, as shown in Fig. 3. Comparing with the phthalate ligand, the isophthalate ligand possesses a wider coordination angle (~120° vs 60°) for its two carboxylic group positions. As a novel result, isophthalate ligands link four Cd(II) centers to generate a nano-ring in complex **1**. In contrast, the phthalate ligand can solely cooperate with a linear ligand such as 4,4′-bipyridine to form a ring structure [12–17]. There are two types of Cd(II) coordination environments: Cd(1) (type I) is seven-coordinated by two nitrogen atoms from 2,2′-bipyridine and five oxygen atoms from isophthalate ligands, while Cd(2) (type II) is six-coordinated by two nitrogen atoms from 2,2′-bipyridine and four oxygen atoms from isophthalate ligands. Two coordination modes (Scheme 1(a) and (b)) of the isophthalate ligand are present in the structure of complex **1**. In mode *a*, one carboxylate group acts as a chelating ligand and the other as a mono-dentate one to bond to two Cd(II) centers, while both carboxylate groups in mode *b* act as chelating ligands to coordinate to three Cd(II) centers.



Scheme 1. Coordination modes of the ip ligand.

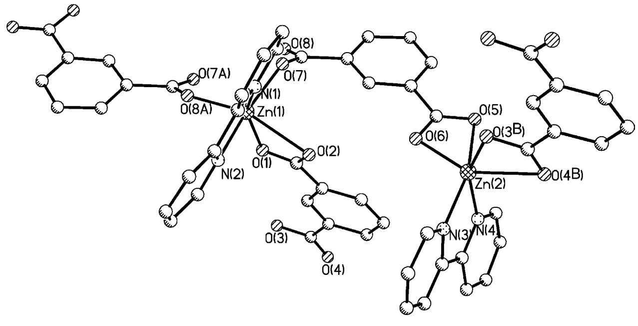


Fig. 4. Metal coordination in $[Zn_2(2,2'\text{-bpy})_2(ip)_2]_n$.

3.2.2. *Crystal structure of complex 2*

The structure of **2** contains a double-helical structure with tetra –Zn–ip– as building units. There are two coordination modes (Scheme 1(c) and (d)) of the isophthalate ligand that differ from those in complex **2**. In mode *c*, both carboxylic groups of isophthalate act as a chelating ligands and connecting two Zn(II) centers, while one carboxylic group in mode *d* acts as a chelate and the other acts as a bridge, together linking three Zn(II) centers. The phthalate ligand exhibits similar various coordination modes. It can form a polymeric chain, while it seldom forms a double-helix due to steric hindrance effects (due to neighboring carboxylic groups) [15]. All Zn(II) centers are six-coordinated by two nitrogen atoms from 2,2′-bipyridine and four oxygen atoms from isophthalate ligands (Fig. 4). The most striking feature of complex **2** is its double-helix structure generated by the connection of differently coordinated Zn atoms via isophthalate ligands, as shown in Fig. 5. The top helix (–Zn2G–ip–Zn1G–ip–Zn2E–ip–Zn1E–ip–Zn2C–ip–Zn1C–ip–Zn2A–ip–Zn1A–ip–) is a Λ-helical chain, while the bottom helix (–Zn2B–ip–Zn1B–ip–Zn2D–ip–Zn1D–ip–Zn2F–ip–Zn1F–ip–Zn2H–ip–Zn1H–ip–) is a Δ-helical chain. This is a novel structure found in the Zn(II) coordination polymers.

3.3. *Fluorescent analyses*

As shown in Figs. 6–8, complex **1** exhibits intense photoluminescence at 435.0 nm upon photo-excitation at 357.4 nm, while complex **2** exhibits intense photoluminescence at 439.9 nm upon photo-excitation at 380 nm. In contrast, the free ligand 2,2′-bipyridine emits at 535.0 nm on excitation at 347.0 nm in the solid state. The luminescence spectra for complexes **1** and **2** are likely assigned to intraligand ππ* transitions [18,19]. Since hydrothermal products are usually stable, the

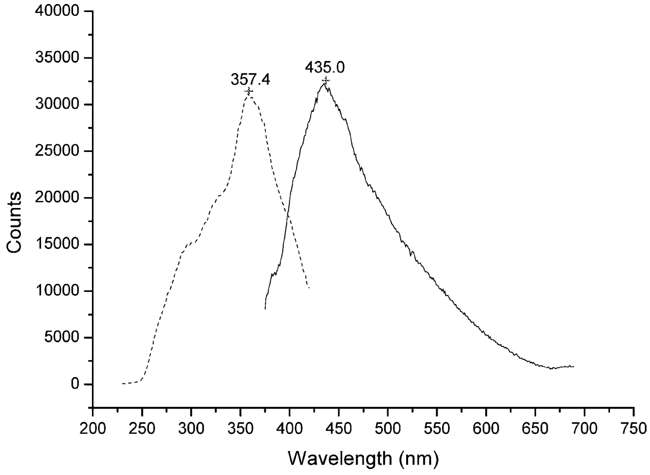


Fig. 6. Excitation spectrum (. . .) and emission spectrum (—) of **1** in the solid state.

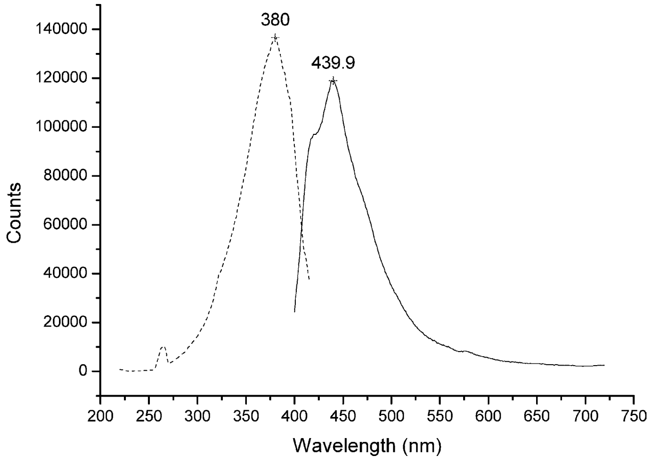


Fig. 7. Excitation spectrum (. . .) and emission spectrum (—) of **2** in the solid state.

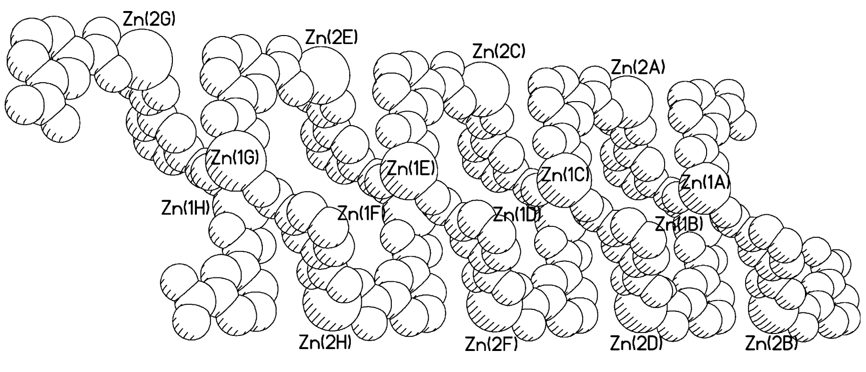


Fig. 5. View of double-helix with isophthalate omitted in complex **2** along *a* axis.

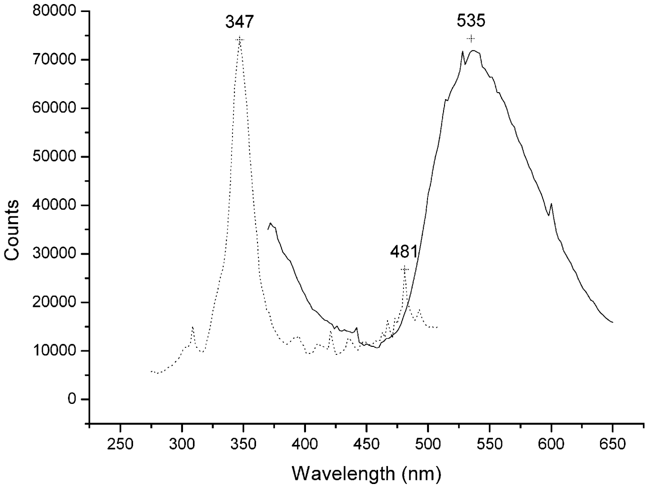


Fig. 8. Excitation spectrum (...) and emission spectrum (—) of 2,2′-bipyridine in the solid state.

above complexes may be promising as blue-light emitting materials.

4. Supplementary material

Crystallographic data of complexes **1** and **2** have been deposited at the Cambridge Crystallographic Data Center (CCDC) CCDC No. 189000 and 188999. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] S.R. Batten, R. Robson, Angew. Chem., Int. Ed. 37 (1998) 1460.
[2] (a) O.M. Yaghi, H. Li, C. Davis, D. Richardson, T.L. Groy, Acc. Chem. Res. 31 (1998) 474;
(b) M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke, O.M. Yaghi, J. Solid State Chem. 152 (2000) 3.
[3] P.J. Hagrman, D. Hagrman, J. Zubieta, Angew. Chem., Int. Ed. 38 (1999) 2639.
[4] P.C. Ford, E. Cariati, J. Bourassa, Chem. Rev. 99 (1999) 3625.
[5] J. Tao, M.-L. Tong, J.-X. Shi, X.-M. Chen, S.W. Ng, Chem. Commun. 2 (2000) 2043.
[6] W. Clegg, D.R. Harbron, C.D. Homan, P.A. Hunt, J.R. Little, B.P. Straughan, Inorg. Chim. Acta 186 (1991) 51.
[7] A.D. Burrows, R.W. Harrington, M.F. Mahon, C.E. Price, J. Chem. Soc., Dalton Trans. (2000) 3845.
[8] S.A. Bourne, J.-J. Lu, B. Moulton, M.J. Zaworotko, Chem. Commun. (2001) 861.
[9] X.S. Tan, D.-F. Xiang, W.-X. Tang, K.-B. Yu, Polyhedron 16 (1997) 1441.
[10] R.H. Groeneman, L.R. MacGillivray, J.L. Atwood, Inorg. Chem. 38 (1999) 208.
[11] A.D. Burrows, D.M.P. Mingos, S.E. Lawrence, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (1999) 1295.
[12] Q.Y. Liu, P. Liu, J. Wang, Y. Chen, Chin. J. Struct. Chem. 21 (2002) 509.
[13] H.X. Zhang, B.S. Kang, A.W. Xu, Z.N. Chen, Z.Y. Zhou, A.S.C. Chan, K.B. Yu, C. Ren, J. Chem. Soc., Dalton Trans. (2001) 2559.
[14] S.G. Baca, Y.A. Simonov, N.V. Gerbeleu, M. Gdaniec, P.N. Bourosh, G.A. Timco, Polyhedron 20 (2001) 831.
[15] A.D. Burrows, R.W. Harrington, M.F. Mahon, C.E. Price, J. Chem. Soc., Dalton Trans. (2000) 3845.
[16] Y. Zhang, J. Li, Q. Su, Q. Wang, X. Wu, J. Mol. Struct. 516 (2000) 231.
[17] P. Lightfoot, A. Snedden, J. Chem. Soc., Dalton Trans. (1999) 3549.
[18] N.W. Alcock, P.R. Barker, J.M. Haider, M.J. Hannon, C.L. Painting, Z. Pikramenon, E.A. Plummer, K. Rissanen, P. Saarenketo, J. Chem. Soc., Dalton Trans. (2000) 1447.
[19] J.P. Collin, I.M. Dixon, J.P. Sauvage, J.A.G. Williams, F. Barigelletti, L. Flamigni, J. Am. Chem. Soc. (1999) 5009.