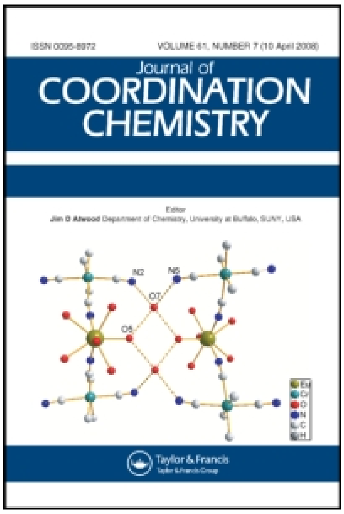

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Hydrothermal synthesis and characterization of a zigzag neodymium-2,2'-bipyridine-3,3'-dicarboxylate-isonicotinate coordination polymer

Ming Hu[a]; Jingya Yao[a]; Haiquan Su[a]
[a] Department of Chemistry, Inner Mongolia University, Hohhot 010021, P.R. China

To cite this Article Hu, Ming , Yao, Jingya and Su, Haiquan(2010) 'Hydrothermal synthesis and characterization of a zigzag neodymium-2,2'-bipyridine-3,3'-dicarboxylate-isonicotinate coordination polymer', Journal of Coordination Chemistry, 63: 10, 1744 — 1751, First published on: 11 June 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.490294

URL: http://dx.doi.org/10.1080/00958972.2010.490294

Journal of Coordination Chemistry
Vol. 63, No. 10, 20 May 2010, 1744–1751

Hydrothermal synthesis and characterization of a zigzag neodymium-2,2′-bipyridine-3,3′-dicarboxylate-isonicotinate coordination polymer

MING HU*, JINGYA YAO and HAIQUAN SU

Department of Chemistry, Inner Mongolia University, Hohhot 010021, P.R. China

(*Received 5 January 2010; in final form 25 February 2010*)

A new neodymium(III) coordination polymer, $\{[\mathrm{Nd(bpdc)(iso)(H_2O)_2}]\cdot(\mathrm{H_2O})_{2.25}\}_n$ (**1**), was synthesized by treating neodymium oxide with 2,2′-bipyridine-3,3′-dicarboxylic acid (H_2bpdc), and isonicotinic acid (Hiso) under hydrothermal conditions. Single-crystal X-ray diffraction shows that **1** is a 1-D zigzag chain and extends to 2-D network structure through π–π interactions and hydrogen bonds. Thermogravimetric analysis of **1** displays a considerable thermal stability. The variable-temperature magnetic susceptibility of **1** was measured.

Keywords: Neodymium; Coordination polymer; Hydrothermal synthesis; Crystal structure

1. Introduction

Self-assembly of lanthanide coordination polymers has become the subject of many current studies [1–5] due to their photoluminescence [1, 2], magnetism [2, 3], microporosity [4], and gas adsorption [5]. The self-assembly of metal ions and suitable ligands has proved to be an effective method for formation of 1-D to 3-D structures [6, 7]. The nature of the lanthanide coordination polymer is controlled by a subtle interplay between metal and ligand interactions and steric hindrance between ligands [7].

The 2,2′-bipyridine-3,3′-dicarboxylic acid (H_2bpdc) is a diverse bridging ligand and has drawn considerable attention in photochemistry and crystal engineering [8–16]. With 2,2′-bipyridyl and dicarboxyl functional groups, bpdc exhibits bis(monodentate) [8], tridentate [9, 10, 12], bis(bidentate) [10, 11, 15], pentadentate [16], or even hexadentate [16] bridging modes to facilitate formation of transition metal coordination polymers. Some transition metal coordination polymers constructed from H_2bpdc have been synthesized recently [17]. As a linker to construct coordination polymers, bpdc is an inflexible ligand while twists along the central C–C bond form diverse structures from the bipyridyl and carboxylate groups, indicating ligand-directed assembly [10]. Hiso as another pyridine carboxylic acid has also been used to construct coordination polymers [18]. The two ligands should display high reactivity to lanthanides since carboxylate has a strong affinity to Ln^{3+}, which have larger radii and higher

---

*Corresponding author. Email: hm988@126.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.490294

coordination numbers than transition metals. Some lanthanide coordination polymers with mixed carboxylate have recently been observed [19]. In this study, we selected H_2bpdc, Hiso ligands and neodymium oxide to assemble coordination polymer **1** under hydrothermal conditions, forming a 2-D network structure based on the 1-D zigzag chains through π–π interactions and hydrogen bonds. To the best of our knowledge, there are only few reports on lanthanide-2,2′-bipyridine-3,3′-dicarboxylate coordination compounds [20] and there have been no reports on lanthanide coordination polymers with mixed 2,2′-bipyridine-3,3′-dicarboxylic acid, and another pyridine carboxylic acid.

2. Experimental

2.1. *General remarks*

H_2bpdc was synthesized according to reference [21]. All other materials were purchased commercially and used as received without purification. Infrared (IR) spectra in KBr disks were recorded with a Magna 750 Fourier transform infrared (FT-IR) spectrophotometer. C, H, and N elemental analyses were determined with a Perkin Elmer 240 elemental analyzer. Thermogravimetric analyses were performed under air on a Rigaku thermogravimetric differential thermal analyzer at a heating rate of $10^\circ\mathrm{C\,min^{-1}}$ from room temperature to 800°C. Variable-temperature magnetic susceptibilities were measured on a SQUID MPMS-7 magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

2.1.1. X-ray crystallographic study. X-ray single-crystal data collection was performed with a Bruker Smart 1000 CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Semi-empirical absorption corrections were applied using SADABS. The structures were solved by direct methods and refined by full-matrix least squares on $|F|^2$ using the SHELXTL-97 program. All non-hydrogen atoms were refined anisotropically. The hydrogens were set in calculated positions and refined as riding with a common fixed isotropic thermal parameter. The crystallographic data of **1** are listed in table 1.

2.2. *Synthesis*

2.2.1. Preparation of $\{[Nd(bpdc)(iso)(H_2O)_2]\cdot(H_2O)_{2.25}\}_n$ (1). A mixture of Nd_2O_3 (0.25 mmol), H_2bpdc (0.5 mmol), Hiso (0.5 mmol), and H_2O (10 mL) was stirred for 0.5 h in air, then transferred and sealed in a 25 mL stainless-steel container with a Teflon liner, which was heated at 160°C for 72 h, then cooled to 100°C over 48 h and kept for 48 h, and then cooled to 20°C in 48 h. Purple crystals were obtained by filtration, washed with ethanol and water in 50% yield (based on Nd). Elem Anal. for **1**, Calcd C 36.92, H 3.16, and N 7.18; found C 36.80, H 3.18, and N 7.12. IR (KBr pellet): $\nu = 3400(s), 1576(s), 1553(s), 1461(m), 1407(s), 1173(m), 1067(m), 711(m), 694(m)\,\mathrm{cm^{-1}}$.

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

Empirical formula	$C_{18}H_{18.50}N_3NdO_{10.25}$
Formula weight	585.10
Temperature (K)	294(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.376(3)
b	10.018(3)
c	12.443(4)
α	67.121(4)
β	87.832(5)
γ	81.136(5)
Volume (Å^3), Z	1063.6(5), 2
Calculated density (mg m^{-3})	1.827
Absorption coefficient (mm^{-1})	2.503
F(000)	579
θ range for data collection (°)	1.78–26.40
Limiting indices	$-7 \le h \le 11$; $-12 \le k \le 12$; $-15 \le l \le 15$
Reflections collected	6072
Independent reflections	4287 [R(int) = 0.0305]
Data/restraints/parameters	4287/18/298
Goodness-of-fit on F^2	1.029
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0356$, $wR_2 = 0.0722$
R indices (all data)	$R_1 = 0.0483$, $wR_2 = 0.0767$

3. Results and discussion

3.1. *General characterization*

Compound **1** is stable in air and insoluble in water or in common organic solvents. The IR spectrum of **1** shows characteristic bands of carboxylate at 1576, 1553 cm^{-1} for asymmetric stretching, and at 1407 cm^{-1} for symmetric stretching. The broadband at 3400 cm^{-1} in **1** is assigned to water [22].

3.2. *Structural description*

A crystal of **1** was structurally characterized by X-ray single-crystal diffraction and selected bond lengths and angles of **1** are listed in table 2. Hiso and H_2bpdc are deprotonated to form anion (iso) and dianion (bpdc). In **1**, each Nd^{3+} is nine-coordinate and the coordination geometry is a distorted tricapped trigonal prism. The coordination environment around Nd^{3+} have six oxygens (O1, O3, O1A, O2A, and O4B) from three carboxylates of three different bpdc, two oxygens (O5 and O6) from one carboxylate of iso and another two oxygens (O7 and O8) of coordinated water (figure 1). The mean Nd–O (carboxylate) bond length is 2.526 Å and the mean Nd–O (water) distance is 2.482 Å; the O–Nd–O bond angles range from 50.36° to 145.36°, close to those found in other Nd(III) complexes [23]. The carboxylate groups of bpdc adopt two types of coordination modes, one is chelating-bridging tridentate to connect two Nd^{3+} ions (an oxygen is μ_2-O mode), another is also a bridging bidentate mode to connect two Nd^{3+} ions, while the carboxylate group of iso adopts a chelating bidentate mode to one Nd^{3+}. The nitrogens of the pyridyl motif in bpdc

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

Nd(1)–O(1)	2.581(3)	Nd(1)–O(1)$^{\#2}$	2.564(3)
Nd(1)–O(2)$^{\#2}$	2.617(3)	Nd(1)–O(3)	2.418(3)
Nd(1)–O(4)$^{\#1}$	2.359(3)	Nd(1)–O(6)	2.564(3)
Nd(1)–O(5)	2.582(3)	Nd(1)–O(7)	2.473(3)
Nd(1)–O(8)	2.490(3)		
O(4)$^{\#1}$–Nd(1)–O(3)	75.45(11)	O(4)$^{\#1}$–Nd(1)–O(7)	75.97(11)
O(3)–Nd(1)–O(7)	122.84(12)	O(4)$^{\#1}$–Nd(1)–O(8)	76.07(11)
O(3)–Nd(1)–O(8)	76.70(10)	O(7)–Nd(1)–O(8)	139.52(11)
O(4)$^{\#1}$–Nd(1)–O(1)$^{\#2}$	121.19(10)	O(3)–Nd(1)–O(1)$^{\#2}$	145.36(10)
O(7)–Nd(1)–O(1)$^{\#2}$	91.61(12)	O(8)–Nd(1)–O(1)$^{\#2}$	78.61(10)
O(4)$^{\#1}$–Nd(1)–O(6)	144.31(12)	O(3)–Nd(1–O(6)	111.23(11)
O(7)–Nd(1)–O(6)	71.26(11)	O(8)–Nd(1)–O(6)	139.36(11)
O(1)$^{\#2}$–Nd(1)–O(6)	74.04(10)	O(4)$^{\#1}$–Nd(1)–O(1)	144.47(11)
O(3)–Nd(1)–O(1)	84.19(10)	O(7)–Nd(1)–O(1)	139.18(11)
O(8)–Nd(1)–O(1)	71.04(10)	O(1)$^{\#2}$–Nd(1)–O(1)	64.91(10)
O(6)–Nd(1)–O(1)	70.34(10)	O(4)$^{\#1}$–Nd(1)–O(5)	106.54(12)
O(3)–Nd(1)–O(5)	69.45(10)	O(7)–Nd(1)–O(5)	72.94(11)
O(8)–Nd(1)–O(5)	143.79(11)	O(1)$^{\#2}$–Nd(1)–O(5)	124.40(10)
O(6)–Nd(1)–O(5)	50.36(11)	O(1)–Nd(1)–O(5)	92.67(11)
O(4)$^{\#1}$–Nd(1)–O(2)$^{\#2}$	71.18(10)	O(3)–Nd(1)–O(2)$^{\#2}$	137.90(10)
O(7)–Nd(1)–O(2)$^{\#2}$	72.60(11)	O(8)–Nd(1)–O(2)$^{\#2}$	71.00(10)
O(1)$^{\#2}$–Nd(1)–O(2)$^{\#2}$	50.49(9)	O(6)–Nd(1)–O(2)$^{\#2}$	110.86(11)
O(1)–Nd(1)–O(2)$^{\#2}$	109.18(9)	O(5)–Nd(1)–O(2)$^{\#2}$	144.87(11)
Nd(1)$^{\#2}$–O(1)–Nd(1)	115.09(10)		

Symmetry transformations used to generate equivalent atoms: $^{\#1}-x+2,\ -y+2,\ -z+1$; $^{\#2}-x+1,\ -y+2,\ -z+1$.

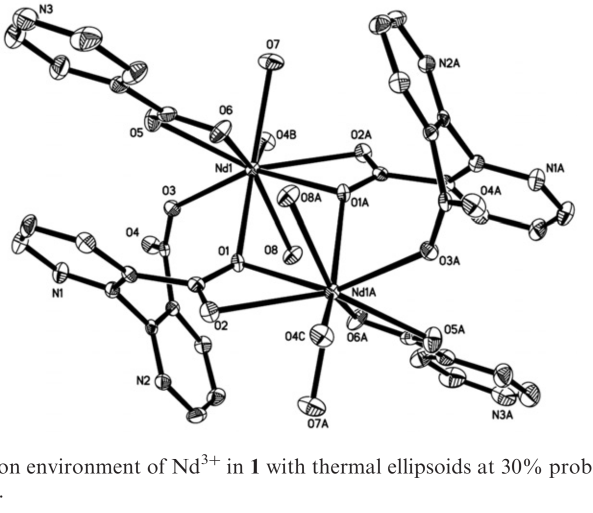

Figure 1. Coordination environment of Nd^{3+} in **1** with thermal ellipsoids at 30% probability; all hydrogens are omitted for clarity.

and iso are uncoordinated. The coordination environment shows that there are three bpdc and one iso linking each Nd^{3+}.

In **1**, the dinuclear portion of $[Nd_2(bpdc)_2(iso)_2(H_2O)_4]_n$ is centrosymmetric and linked by bridging bidentate carboxylate of bpdc; a 1-D infinite zigzag chain is then formed (figure 2). In each dinuclear motif, there are two bpdc and two iso ligands coordinating two Nd^{3+}, with the Nd $\cdots$ Nd distance of 4.341 Å. Adjacent Nd^{3+} ions are linked by carboxylate oxygens of the chelating-bridging tridentate bpdc ligands,

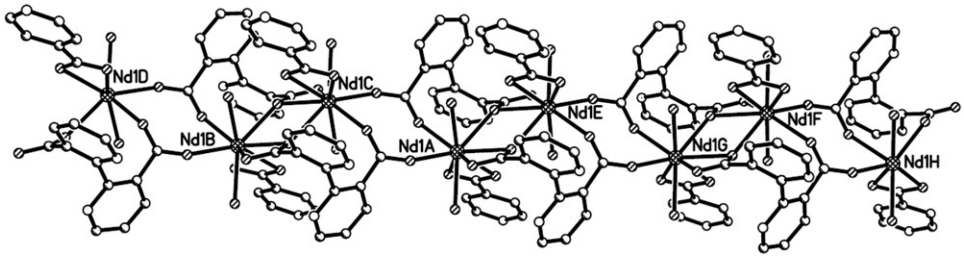

Figure 2. 1-D zigzag chain of **1** viewed along the *b*-axis; all hydrogens are omitted for clarity.

in which one oxygen is a μ_2-O. The two bipyridyl rings of bpdc are present along the central C–C bond with dihedral angles of 59.63°; two carboxylates and linking pyridyl rings of bpdc are not coplanar, showing 53.80° and 45.57° twist from the connected groups. The carboxylate groups and linking pyridyl rings of iso ligands are twisted a little, with dihedral angles of 4.85°.

Two neighboring $[Nd_2(bpdc)_2(iso)_2(H_2O)_4]_n$ dinuclear motifs are connected by the bridging bidentate carboxylates of bpdc in the form of four Nd^{3+}–O (carboxylate) bonds to construct a 1-D infinite zigzag chain. Two adjacent Nd^{3+} ions of different dinuclear motifs are 5.906 Å apart. In the 1-D zigzag chains of **1**, there are hydrogen bonds between coordinated carboxylate oxygens (O6), coordinated water (O7 and O8), lattice water (O9), and nitrogens (N2 and N3) of pyridyl rings, the O8 ⋯ O6, O8 ⋯ O9, O7 ⋯ N2, and O7 ⋯ N3 distances are 2.677, 2.906, 2.900, and 2.807 Å, respectively; the corresponding angles of hydrogen bonds are 167.81°, 159.81°, 165.35°, and 161.18°, respectively. Hydrogen bonds also exist among lattice water (O9, O10), carboxylate oxygen (O2), and nitrogen (N1) of pyridyl rings of the bpdc, the lengths of O9 ⋯ O10, O2 ⋯ O10, and O10 ⋯ N1 are 2.870, 2.968, and 3.025 Å, respectively, with corresponding ∠DHA 170.97°, 167.63°, and 154.04°, respectively. At the same time, there are π–π interactions between iso rings in neighboring 1-D zigzag chains at 3.448 Å [24, 25]. Thus, a 2-D supramolecular network structure along the *b*-axis is constructed with adjacent chains pulled together by π–π interactions of iso ligands and hydrogen bonds, the dimensions of channels are 9.376 × 12.944 Å based on distances of Nd^{3+} ions and are occupied by lattice water (figure 3). Although the nitrogens of bipyridyl of bpdc and iso ligands do not coordinate to Nd^{3+}, they are important in the structure since they participate in the formation of hydrogen bonds with water molecules.

3.3. *Thermal stability of 1*

Thermogravimetric analysis of **1** was performed in air showing that lattice water is removed initially at 102°C with weight loss of 7.2% (Calcd 6.9%); coordinated water is then lost when the temperature reaches 224°C (total weight loss for lattice and coordinated water molecules is 13.6%, Calcd 13.1%). The very strong exothermal peak at 510°C suggests that the complex is completely decomposed (31.0%) to Nd_2O_3 (Calcd 29.3%). Consequently, compound **1** shows considerable thermal stability, indicating that the high coordination numbers and coordination environment of neodymium have

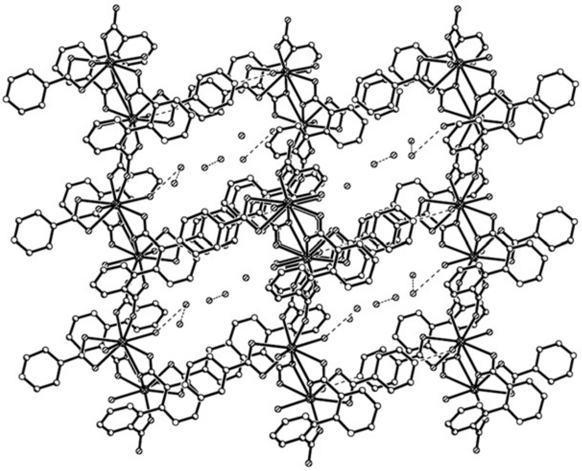

Figure 3. The 2-D supramolecular network structure of **1** along the *b*-axis.

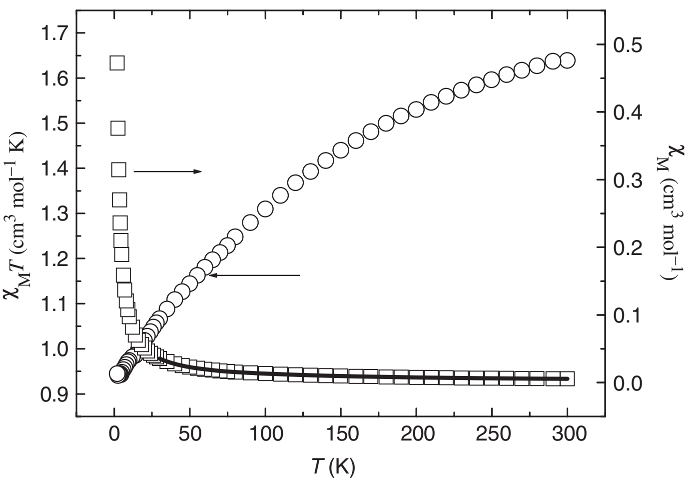

Figure 4. Plot of temperature dependence of the $\chi_M T$ (○) and χ_M (□) of **1**.

profound effects on the overall framework rigidity and thermal stability. The hydrogen bonds and π–π interactions also play a role in stabilizing the network structure.

3.4. *Magnetic susceptibility of 1*

The variable-temperature magnetic susceptibility of **1** was measured on 1 kOe from 2 to 300 K. The $\chi_M T$ for the [Nd^{3+}] unit at 300 K is 1.64 cm^3 K^{-1} mol^{-1}, which is just equal to the calculated value for noninteracting Nd^{3+} free ion in ground level of $^4I_{9/2}$ [26]. The $\chi_M T$ values of **1** fall while temperature declining, reaching a minimum value of 0.94 cm^3 K^{-1} mol^{-1} at 2 K (figure 4). The data in the range between 30 and 300 K can be well fitted to the Curie–Weiss law with $C = 1.53$ cm^3 K^{-1} mol^{-1} and $\theta = -14.88$ K.

However, the decline of $\chi_M T$ at low temperature probably results primarily from the splitting of ligand field of Nd^{3+} [27].

4. Conclusion

A new example of lanthanide coordination polymer with H_2bpdc and Hiso was self-assembled by the hydrothermal method. The bpdc adopt chelating-bridging tridentate and bridging bidentate mode and iso ligands show a chelating bidentate mode, connecting Nd^{3+} ions to form a 1-D infinite zigzag chain. A 2-D supramolecular network structure is constructed with the chains pulled together by π–π interactions and hydrogen bonds. Compound **1** exhibits a considerable thermal stability and the variable-temperature magnetic susceptibility of **1** was discussed.

Supplementary material

Cambridge Crystallographic Data Centre (CCDC): 685724 (for **1**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the CCDC, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44 1223-336-033; or Email: deposit@ccdc.cam.ac.uk

Acknowledgments

This work is supported by Inner Mongolia Natural Science Foundation of China (no. 20080404MS0205) and Program for New Century Excellent Talents in University (NCET-04-0261).

References

[1] N.M. Shavaleev, R. Scopelliti, F. Gumy, J.G. Bunzli. *Inorg. Chem.*, **48**, 2908 (2009).

[2] Z.R. Pan, Y. Song, Y. Jiao, Z.J. Fang, Y.Z. Li, H.G. Zheng. *Inorg. Chem.*, **47**, 5162 (2008).

[3] O. Roubeau, R. Clerac. *Eur. J. Inorg. Chem.*, 4325 (2008).

[4] S. Kitagawa, R. Matsuda. *Coord. Chem. Rev.*, **25**, 2490 (2007).

[5] K.M. Thomas. *Dalton Trans.*, 1487 (2009).

[6] C.B. Dyith, L.J. Barbour, M. Makha, C.L. Raston, A.N. Sobolev. *Chem. Commun.*, **6**, 950 (2006).

[7] (a) H.L. Gao, L. Yi, B. Ding, H.S. Wang, P. Cheng, D.Z. Liao, S.P. Yan. *Inorg. Chem.*, **45**, 481 (2006); (b) S.K. Ghosh, P.K. Bharadwaj. *Inorg. Chem.*, **43**, 2293 (2004).

[8] G.Y.S.K. Swamy, K. Chandramohan, N.V. Lakshmi, K. Ravikumar. *Z. Kristallogr.*, **213**, 191 (1998).

[9] Z.J. Zhong, X.Z. You, Q.C. Yang. *Polyhedron*, **13**, 1951 (1994).

[10] X.M. Zhang, H.S. Wu, X.M. Chen. *Eur. J. Inorg. Chem.*, 2959 (2003).

[11] B.L. Wu, H.Q. Zhang, H.Y. Zhang, Q.A. Wu, H.W. Hou, Y. Zhu, X.Y. Wang. *Aust. J. Chem.*, **56**, 335 (2003).

[12] M.L. Tong, G. Yang, X.M. Chen. *Aust. J. Chem.*, **53**, 607 (2000).

[13] M.W. Perkovic. *Inorg. Chem.*, **39**, 4962 (2000).

[14] P.X. Xie, Y.J. How, B.W. Zhang, F. Wu, W.J. Tian, J.C. Shen. *J. Chem. Soc., Dalton Trans.*, 4217 (1999).

[15] B.L. Wu, H.Q. Zhang, H.Y. Zhang, Q.A. Wu, H.W. Hou, Y. Zhu, X.Y. Wang. *Synth. React. Inorg. Met. Org. Chem.*, **34**, 313 (2004).

[16] B.L. Wu, D.Q. Yuan, F.L. Jiang, R.H. Wang, L. Han, Y.F. Zhou, M.C. Hong. *Eur. J. Inorg. Chem.*, 2695 (2004).

[17] (a) X.L. Chen, Y.J. Yao, H.M. Hu, S.H. Chen, F. Fu, Z.X. Han, T. Qin, M.L. Yang, G.L. Xue. *Inorg. Chim. Acta*, **362**, 2686 (2009); (b) Z.M. Chen, D.P. Li, H.Q. Li, D.Z. Kuang. *Chin. J. Inorg. Chem.*, **11**, 1907 (2008).

[18] (a) X.J. Gu, D.F. Xue. *Inorg. Chem.*, **45**, 9257 (2006); (b) Y.C. Qiu, Z.H. Liu, J.X. Mou, H. Deng, M. Zeller. *CrystEngComm.*, **12**, 277 (2010).

[19] (a) Z.Q. Ming, Y.X. Miao, S.F. Si. *J. Coord. Chem.*, **62**, 833 (2009); (b) Y.H. Wen, X.H. Wu, S. Bi, S.S. Zhang. *J. Coord. Chem.*, **62**, 1249 (2009); (c) H.Y. Wu, N. Wang, S.T. Yue, Y.L. Liu. *J. Coord. Chem.*, **62**, 2511 (2009); (d) X.M. Lin, X.X. Zhou, H.C. Fang, R.H. Zeng, X. Xiao, Y.P. Cai. *J. Coord. Chem.*, **62**, 2796 (2009).

[20] (a) X.Q. Song, W. Dou, W.S. Liu, J.X. Ma. *Inorg. Chem. Commun.*, **10**, 419 (2007); (b) C.Z. Zhang, H.Y. Mao, J. Wang, H.Y. Zhang, J.C. Tao. *Inorg. Chim. Acta*, **360**, 448 (2007); (c) M. Hu, Q.L. Wang, G.F. Xu, G.R. Deng, G.M. Yang, M. Yu, Y.H. Zhang. *Inorg. Chim. Acta*, **360**, 1684 (2007); (d) M. Hu, Q.L. Wang, G.F. Xu, G.R. Deng, G.M. Yang. *Inorg. Chem. Commun.*, **10**, 381 (2007); (e) G.S. Guo, Y.C. Liu, J. Zhang, H.Y. Guo. *J. Rare Earths*, **26**, 633 (2008); (f) W.G. Lu, K. Yang, L. Jiang, X.L. Feng, T.B. Lu. *Inorg. Chim. Acta*, **362**, 5259 (2009); (g) X.X. Xu, X.X. Liu, T. Sun, X. Zhang, E.B. Wang. *J. Coord. Chem.*, **62**, 2755 (2009).

[21] S. Dholakia, R.D. Gillard, F.L. Wimmer. *Polyhedron*, **4**, 791 (1985).

[22] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th Edn, Wiley & Sons, New York (1997).

[23] (a) R. Vaidhyanathan, S. Natarajan, C.N.R. Rao. *Inorg. Chem.*, **41**, 4496 (2002); (b) A. Mondry, P. Starynowicz. *Eur. J. Inorg. Chem.*, 1859 (2006).

[24] (a) C.C. Wang, C.H. Yang, G.H. Lee. *Eur. J. Inorg. Chem.*, 820 (2006); (b) C.H. Yang, C.M. Chou, G.H. Lee, C.C. Wang. *Inorg. Chem. Commun.*, **6**, 135 (2003).

[25] A.J. Blake, S.J. Hill, P. Hubberstey, W. Li. *J. Chem. Soc., Dalton Trans.*, 913 (1997).

[26] O. Kahn. *Molecular Magnetism*, VCH Publishers, New York (1993).

[27] (a) X.M. Chen, Y.L. Wu, Y.X. Tong, Z.M. Sun, D.N. Hendrickson. *Polyhedron*, **16**, 4265 (1997); (b) D.X. Jia, Y. Zhang, J. Dai, Q.Y. Zhu, W. Lu, W.J. Guo. *Inorg. Chem. Commun.*, **8**, 588 (2005); (c) B.Q. Ma, D.S. Zhang, S. Gao, T.Z. Jin, C.H. Yan, G.X. Xu. *Angew. Chem. Int. Ed.*, **39**, 644 (2000).