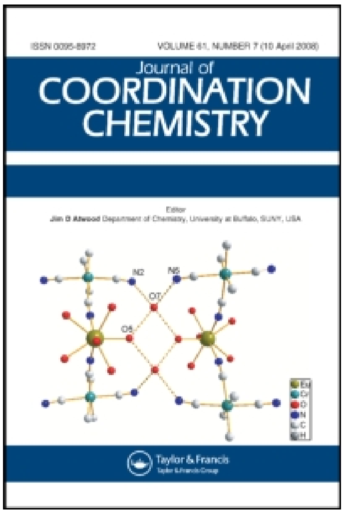
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

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

Synthesis and structural characterization of a yttrium coordination polymer formed by bridging of an acyclic polyether

Yong-Hong Wen[a]; Kun Zhang[a]; Shu-Sheng Zhang[a]
[a] College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao, P.R. China

To cite this Article Wen, Yong-Hong , Zhang, Kun and Zhang, Shu-Sheng(2008) 'Synthesis and structural characterization of a yttrium coordination polymer formed by bridging of an acyclic polyether', Journal of Coordination Chemistry, 61: 7, 1157 — 1164

To link to this Article: DOI: 10.1080/00958970701573145

URL: http://dx.doi.org/10.1080/00958970701573145

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Coordination Chemistry
Vol. 61, No. 7, 10 April 2008, 1157–1164

Synthesis and structural characterization of a yttrium coordination polymer formed by bridging of an acyclic polyether

YONG-HONG WEN, KUN ZHANG and SHU-SHENG ZHANG*

College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P.R. China

(*Received 17 December 2006; in final form 24 May 2007*)

The amide-type acyclic polyether, 1,2-ethylenedioxy-*bis*(*N*-pyridin-2-ylmethyl-benzamide) (**L**) was synthesized and characterized by EA, IR and ^{1}H NMR spectroscopy. The reaction of yttrium nitrate with **L** produced a rare chain structural coordination polymer $\{[Y(NO_3)_3L(H_2O)]\cdot(H_2O)\}_n$ (**1**) by use of the flexible ligand **L** as the building blocks. The structure of **1** was determined by X-ray crystallography and thermal analysis. In **1**, **L**, as a bidentate bridging spacer, binds two neighboring Y atoms to form a one-dimensional chain polymer. The chain polymer was further connected into the three-dimensional network by hydrogen bonding interactions.

Keywords: Acyclic polyether; Yttrium; Coordination polymer; Crystal structure

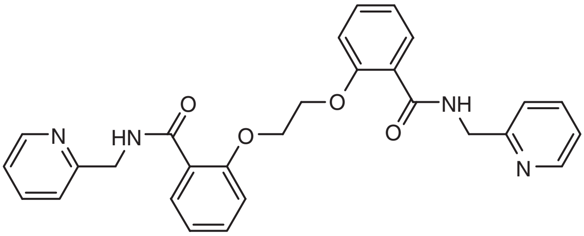
1. Introduction

Increasing attention has focused on acyclic polyether compounds, due to their complexing ability, selectivity to metal ions and their potential application in supramolecular chemistry [1–3]. Of particular interest are diamide-type acyclic polyethers that have been used for ion-selective electrodes and extractants for metal ions [4–9]. Structural investigations revealed that ring-like coordination structures were found in all the complexes of the diamide-type acyclic polyethers with rare earth ions (including yttrium), and these complexes were all mononuclear [10–15]. This is attributed to the preference of rare earth ions for high coordination numbers, favoring formation of condensed structures [16, 17], especially when flexible multidentate acyclic polyethers were used as ligands. In our ongoing studies of structures and properties of rare earth complexes with diamide-type acyclic polyethers, a new flexible acyclic polyether ligand 1,2-ethylenedioxy-*bis*(*N*-pyridin-2-ylmethyl-benzamide) (**L**, scheme 1), was synthesized. The reaction of yttrium nitrate with **L** did not yield the ring-like coordination structure, but a rare chain coordination polymer $\{[Y(NO_3)_3L(H_2O)]\cdot(H_2O)\}_n$ (**1**) by use of **L** as the building blocks. To the best of

---

*Corresponding author. Tel.: +86-532-84022750. Email: shushzhang@126.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701573145



Scheme 1. The structure of **L**.

our knowledge, **1** is the first example of a chain coordination polymer containing diamide-type acyclic polyethers as building blocks. Herein we report the synthesis and structural characterization of **1**.

2. Experimental

2.1. *Materials and methods*

2-Hydroxy-*N*-(2-pyridinylmethyl) benzamide was synthesized according to a method previously described [18]. Other chemicals were of analytical reagent grade and used directly without further purification. The C, H and N contents were determined by using an Elementar Vario EL III analyzer. Infrared spectra were recorded from KBr pellets on a Nicolet 510P FT-IR spectrometer. An ^{1}H NMR spectrum was recorded on a Bruker 500 MHz with TMS as an internal standard. Thermogravimetric analysis was recorded on a Mettler TG-50 thermal analyzer under an atmosphere of nitrogen at a heating rate of 10°C min^{-1}.

2.2. *Synthesis of 1,2-ethylenedioxy*-bis*(*N*-pyridin-2-ylmethyl-benzamide) (L)*

1,2-Dichloroethane (0.99 g, 0.01 mol) was added dropwise to 50 mL of DMF solution containing 2-hydroxy-*N*-(2-pyridinylmethyl) benzamide (4.56 g, 0.02 mol), K_2CO_3 (3 g, 0.02 mol) and KI (0.5 g), and the mixture was stirred at 55°C for 48 h. After cooling to room temperature, the mixture was filtered. DMF was removed from the filtrate under reduced pressure, and the residue was washed by column chromatography (silica gel, $C_2H_5OH : CH_3CO_2C_2H_5 = 1 : 5$) resulting in a colorless solid. Yield: 62%. m.p. 167 ~ 168°C Anal. Calcd for $C_{28}H_{26}N_4O_4$ (%): C, 69.70; H, 5.43; N, 11.61. Found: C, 69.56; H, 5.48; N, 11.57. Main IR bands (KBr, cm^{-1}): 3317 (m), 1634 (s), 1599 (m), 1571 (m), 1536 (m), 1239 (s), 1113 (m), 755 (m). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 8.92 (1H, s), 8.12 (2H, d), 7.43 (2H, m), 7.16 (1H, d), 7.10 (1H, t), 6.98 (1H, d), 6.87 (1H, t), 4.63 (2H, d), 4.63 (2H, d).

2.3. *Synthesis of* $\{[Y(NO_3)_3L(H_2O)] \cdot (H_2O)\}_n$ *(1)*

To an ethanol solution (10 mL) of yttrium nitrate (0.07938 g, 0.2 mmol) was added an ethanol solution (10 mL) of **L** (0.10 g, 0.2 mmol) and the mixture was stirred for 5 h at room temperature. The precipitated solid was filtered, washed with ethanol and dried *in vacuo* over P_2O_5 for 48 h. Yield: 71%. Anal. Calcd for $C_{28}H_{30}N_7O_{15}Y$ (%): C, 42.38; H, 3.81; N, 12.36. Found: C, 42.29; H, 3.87; N, 12.30. IR (KBr, cm^{-1}): 3384 (m), 3348 (m), 1611 (s), 1600 (s), 1561 (m), 1509 (m), 1483 (s), 1226 (s), 1111 (m), 754 (m). Recrystallization of **1** from a DMF-ethanol (1 : 20, v/v) solution afforded colorless single crystals suitable for X-ray diffraction analysis.

2.4. *X-ray crystallography*

Single crystal X-ray diffraction data of **1** were collected using a Bruker SMART 1000 CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using ω scan mode at 293(2) K. Intensity data were corrected for *Lp* factors and empirical absorption. The structure was solved by direct methods and expanded by using Fourier differential techniques with SHELXL-97 [19]. All non-hydrogen atoms were located with successive difference Fourier syntheses. The structure was refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Atomic scattering factors and anomalous dispersion corrections were taken from International tables for X-ray crystallography [20].

3. Results and discussion

3.1. *Synthesis, spectroscopy and thermal analysis*

The flexible ligand **L** was prepared by reaction of 2-hydroxy-*N*-(2-pyridinylmethyl) benzamide and 1,2-dichloroethane in DMF solution under the basic condition of potassium carbonate and with potassium iodide as a catalyst. The self-assembly reaction of yttrium nitrate with **L** produced the chain structural coordination polymer **1** in high yield.

Compared with the IR spectrum of **L**, the IR spectrum of **1** shows a carbonyl C=O stretching vibration shift by 34 cm^{-1} towards lower wavenumber, indicating that only carbonyl oxygen atoms take part in coordination to the metal ion. This agrees with the structural analysis.

Thermogravimetric (TG) and differential thermogravimetric analysis (DTA) for coordination **1** are presented in figure 1. The first mass loss of 5.00% in the range 40–150°C corresponds to two water molecules per formula unit. Two endothermic peaks at 97.7 and 120°C are the loss of crystal water and coordinated water, respectively. Then decomposition of the ligand occurs, including two main exothermic processes: a weight loss corresponding to pyridinylmethyl group at 231.1°C, and another weight loss corresponding to pyridin-2-ylmethylaminomethoxylphenoxy moiety at 301.2°C.

3.2. *X-ray crystal structure*

A summary of the key crystallographic data and structural refinement for **1** is presented in table 1. Selected bond distances and angles are given in table 2. The molecular

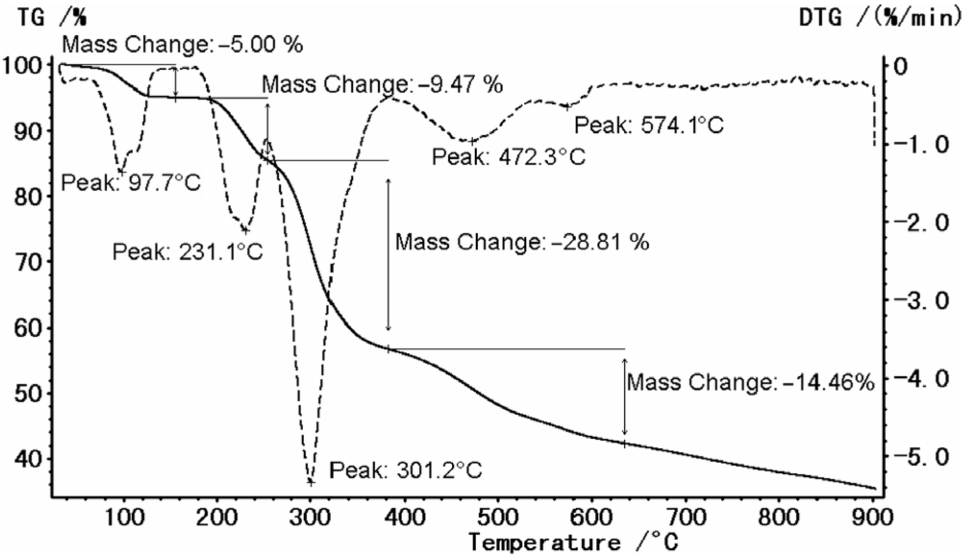


Figure 1. The thermal analysis curves of **1**.

Table 1. A summary of crystallographic data and structural refinement for **1**.

Formula	$C_{28}H_{30}N_7O_{15}Y$
Formula weight	793.50
Temperature (K)	293 (2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	10.2222(11)
b	13.8563(16)
c	26.712(3)
β	106.330(4)
V (Å^3)	3630.9(7)
Z	4
D_{Calcd} (g cm^{-3})	1.452
Absorption coefficient (mm^{-1})	1.682
F (000)	1624
Crystal size (mm)	0.07 × 0.13 × 0.27
θ ranges (°)	1.6–26.0
Reflections collected	20,101
Independent reflections	7142 ($R_{\text{int}} = 0.063$)
GOF	1.107
Final R indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0687$ $wR_2 = 0.1989$

$^a w = 1/[\sigma^2(F_o^2) + (0.1210P)^2 + 0.3295P]$, $P = (F_o^2 + 2(F_c^2))/3$.

structure of **1** with atomic numbering is shown in figure 2. Figure 3 shows the molecular packing in the unit cell.

The single-crystal X-ray diffraction analysis of **1** revealed that each Y is nine-coordinate with nine oxygen donor atoms, six of which are from three bidentate nitrate groups, two from carbonyl groups in two ligands and the remaining one from a

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

Y1–O1W	2.304(5)	Y1–O8	2.487(6)
Y1–O1a	2.283(4)	Y1–O9	2.479(5)
Y1–O4	2.282(4)	Y1–O11	2.426(5)
Y1–O5	2.442(5)	Y1–O12	2.408(5)
Y1–O6	2.429(5)		
O1W–Y1–O4	75.55(17)	O1a–Y1–O8	76.56(16)
O1W–Y1–O5	75.95(18)	O1a–Y1–O1W	82.00(17)
O1a–Y1–O6	124.77(16)	O4–Y1–O5	124.84(17)
O1W–Y1–O6	84.83(18)	O1a–Y1–O9	75.45(16)
O1W–Y1–O8	131.76(19)	O4–Y1–O11	76.01(18)
O8–Y1–O9	50.69(18)	O4–Y1–O9	75.76(16)
O8–Y1–O11	68.91(18)	O1a–Y1–O4	145.41(15)
O8–Y1–O12	71.16(19)	O5–Y1–O9	143.61(17)
O1W–Y1–O9	82.36(18)	O5–Y1–O6	51.89(17)
O1W–Y1–O11	147.30(19)	O6–Y1–O9	154.14(17)
O1W–Y1–O12	148.19(18)	O6–Y1–O11	74.35(18)

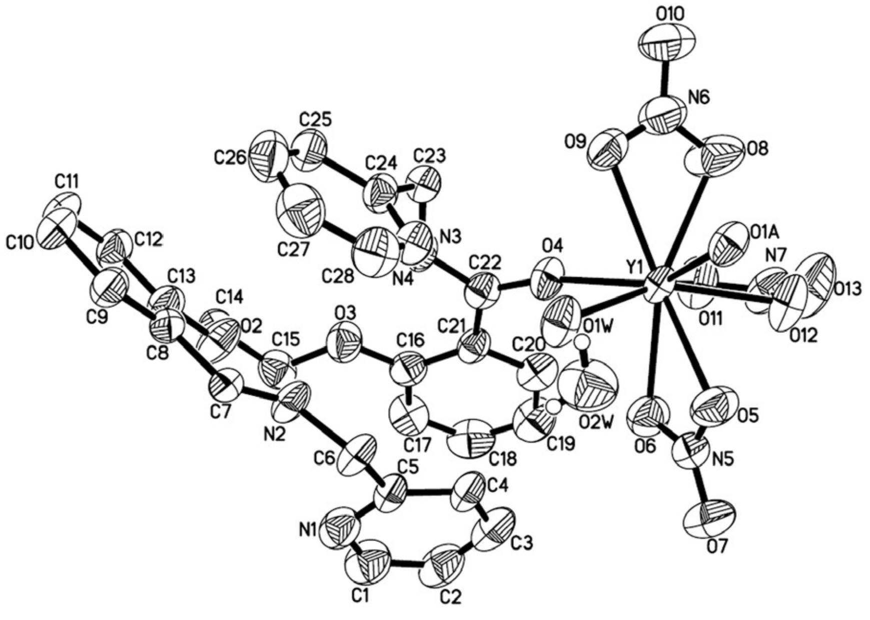


Figure 2. The molecular structure of **1** with atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. The partial H atoms were omitted for clarity.

water molecule. The Y–O distances (table 2) can be divided into two sets: the longer ones vary from 2.408(5) Å to 2.487(6) Å for the nitrate groups and the shorter ones vary from 2.282(4) Å to 2.304(5) Å for the carboxylate groups and water. The short distances of two Y–O (C=O) bonds suggest the strong complexing ability of the carboxylate to Y. The coordination geometry around Y is a mono-capped distorted square antiprism (figure 2). In **1**, **L** is a bidentate bridging spacer binding two neighboring Y atoms, forming a one-dimensional chain polymer along the *a* axis (figure 4). Individual chains

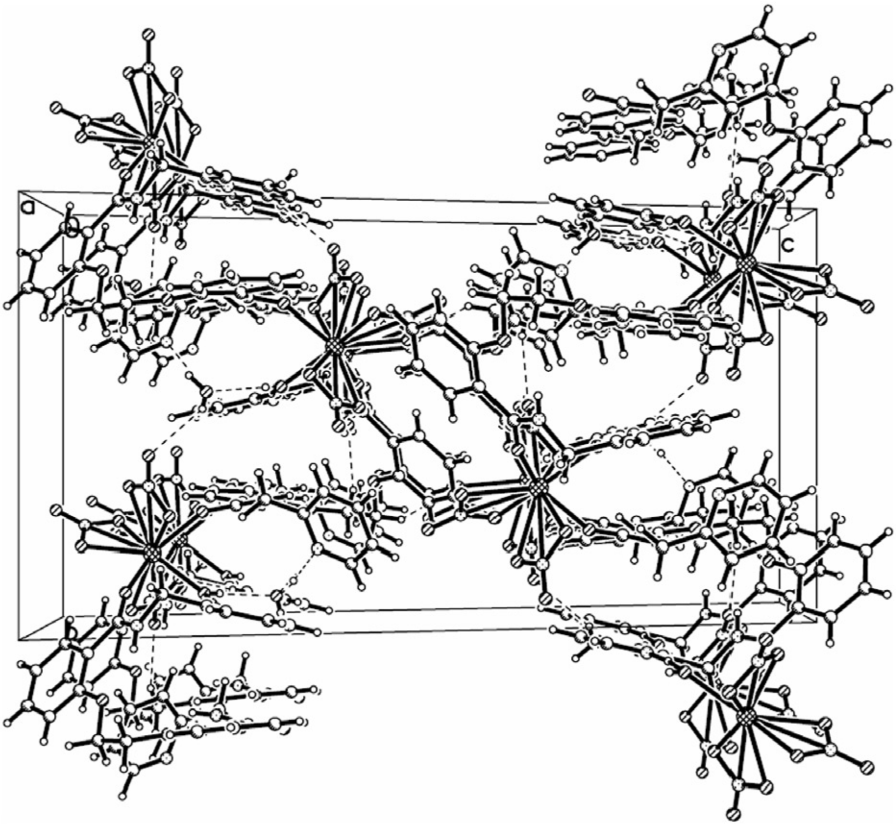


Figure 3. A view of the crystal packing down the *a* axis for **1**.

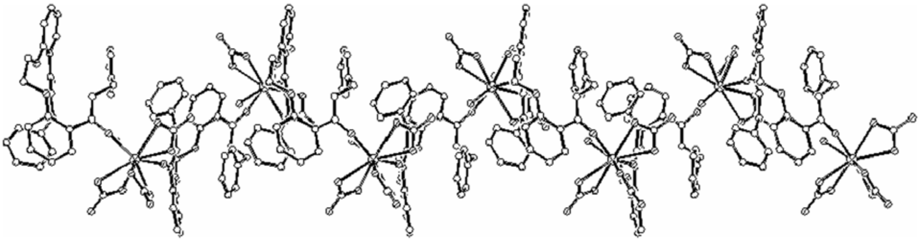


Figure 4. The one-dimensional chain polymeric structure of **1**, along the *a* axis.

Table 3. Hydrogen bonds (Å, °) for **1**.

D–H···A	D–H	H···A	D···A	D–H···A
O1W–H11W···O2W	0.58(6)	2.17(6)	2.750(9)	178(9)
O2W–H12W···N1	0.89(10)	2.04(10)	2.880(10)	157(9)^{a}
O2W–H22W···O10	0.61(6)	2.57(5)	3.096(10)	146(6)^{b}
C6–H6A···O9	0.9717	2.5156	3.334(7)	141.79^{b}
C14–H14A···O7	0.9701	2.3700	3.255(9)	151.31^{c}
C15–H15B···O11	0.9709	2.5389	3.388(9)	146.04^{d}
C25–H25A···O5	0.9302	2.5704	3.478(9)	165.27^{c}

Symmetry code: a = $1-x$, $-1/2+y$, $1/2-z$; b = $1-x$, $1/2+y$, $1/2-z$; c = $1+x$, y, z; d = $1-x$, $-y$, $-z$.

were connected into the two-dimensional network by intermolecular hydrogen bonds, viz C6–H6A ⋯ O9, C14–H14A ⋯ O7, C15–H15B ⋯ O11, C25–H25A ⋯ O5. The uncoordinated water molecules as hydrogen bond donors and acceptors form three intermolecular hydrogen bonds, viz O2W–H12W ⋯ N1, O2W–H22W ⋯ O10, O1W–H11W ⋯ O2W, and connect the structure into the three-dimensional network (figure 3 and table 3).

Figures 2 and 4 show that two ether oxygen atoms of **L** do not coordinate with the metal; such coordination for diamide-type acyclic polyethers is very rare. To our knowledge, **1** is the first example. The nitrogen atoms in pyridine rings were also uncoordinated. Many complexes of diamide-type acyclic polyethers with rare earth ions, including yttrium, have been studied. In all these complexes, both carbonyl oxygen atoms and ether oxygen atoms bind to the metal, forming ring-like coordination structures [6, 10–15]. A similar structure has been reported by Zhang and co-workers [21], where reaction of (((2′-benzylaminoformyl)phenoxyl)methyl)propane (**L**′) with europium nitrate gave a one-dimensional chain coordination polymer $[Eu(NO_3)_3L' (CH_3CO_2C_2H_5)]_n$ (**2**). In **1** and **2**, the central ions (Y and Eu) have similar coordination geometry. The amide-type tripodal ligand **L**′ also showed a bidentate bridging mode to two neighboring metal ions, and the remaining arm was uncoordinated.

Ether-amide type acyclic ligand **L** and tripodal ligand **L**′ have very similar structures with ethylene and propylene connecting salicylamides with benzyl groups and 2-pyridinylmethyl groups at nitrogen atoms, respectively, despite the difference in arm number. So it is possible for these ligands to provide the same building blocks that can self-assemble into structures with the same coordination modes. Although the reason for formation of specific coordination modes cannot be explained, this possibility of assembling large coordination polymers with fexible amide-type acyclic polyethers as building blocks are significant for predetermined synthesis of new ligands to form the novel structures and/or unique properties for complexes.

Supplementary material

Crystallographic data for the structural analysis of **1** has been deposited with the Cambridge Crystallographic Data Center. CCDC reference number 623905 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was supported by the program for New Century Excellent Talents in University (No. NCET-04-0649) and the Outstanding Adult-young Scientific Research Encouraging Foundation of Shandong Province, China (No. 2006BS03049).

References

[1] L. Cornin. *Annu. Rep. Prog. Chem., Sect. A*, **100**, 323 (2004).
[2] J.M. Lehn. *Supramolecular Chemistry*, VCH Publisher, New York (1995).
[3] W. Liu, X. Li, Y. Wen, M. Tan. *Dalton Trans.*, 640 (2004).
[4] M. Güggi, E. Pretsch, W. Simon. *Anal. Chim. Acta*, **91**, 107 (1977).
[5] S.J. West, S. Ozawa, K. Seller, S.S. Tan, W. Simon. *Anal. Chem.*, **64**, 533 (1992).
[6] X. Li, Y. Wen, W. Liu, S. Liu, M. Tan, K. Yu. *J. Coord. Chem.*, **56**, 1537 (2003).
[7] J.C.G. Bunzli, J.M. Pfefferle, B. Amman, G. Chapuis, F.J. Zuniga. *Helv. Chim. Acta*, **67**, 196 (1984).
[8] Y. Wen, Z. Qin, W. Liu. *J. Radioanal. Nucl. Chem.*, **250**, 285 (2001).
[9] Y.H. Wen, S. Lahiri, Z. Qin, X.L. Wu, W.S. Liu. *J. Radioanal. Nucl. Chem.*, **253**, 263 (2002).
[10] L. Fan, W. Liu, X. Gan, N. Tang, M. Tan, W. Jiang, K. Yu. *Polyhedron*, **19**, 779 (2000).
[11] S. Liu, W. Liu, M. Tan, K. Yu, G. Tan. *Helv. Chim. Acta*, **80**, 586 (1997).
[12] W. Jiang, W. Liu, M. Tan, K. Yu. *J. Coord. Chem.*, **55**, 309 (2002).
[13] S. Liu, W. Liu, M. Tan, K. Yu. *J. Coord. Chem.*, **39**, 105 (1996).
[14] S. Liu, W. Liu, M. Tan, K. Yu. *Polyhedron*, **16**, 1491 (1997).
[15] L. Fan, W. Liu, S. Liu, M. Tan. *J. Coord. Chem.*, **48**, 33 (1999).
[16] L.P. Wu, M. Munakata, T.K. Sona, M. Maekawa, Y. Suenaga. *Inorg. Chim. Acta*, **249**, 183 (1996).
[17] J.A. Seddon, A.R.W. Jackson, R.A. Kresinski, W.G. Platt. *Polyhedron*, **15**, 1899 (1996).
[18] Y. Wen, Y. Yu, K. Zhang, X. Li, S. Zhang. *Acta Cryst. Sect. E*, **62**, 3782 (2006).
[19] G.M. Sheldrick. *SHELXS-97, Program for X-ray Crystal Structure Solution*, Göttingen University, Germany (1997).
[20] A.J.C. Wilson. *International Tables for X-ray Crystallography*, Vol. C, Kluwer Academic Publishers, Dordrecht (1992); Tables 6.1.1.4 (pp. 500–520) and 4.2.6.8 (pp. 219–222), respectively.
[21] J. Zhang, Y. Tang, N. Tang, M.-Y. Tan, W.-S. Liu, K.-B. Yu. *J. Chem. Soc., Dalton Trans.*, 832 (2002).