

Communication

Synthesis, characterization and crystal structure of a novel 3D network triorganotin(IV) polymer containing two types of macrocycles

Handong Yin *, Hongyun Wang, Daqi Wang

Department of Chemistry, Liaocheng University, Liaocheng 252059, China

Received 23 October 2007; received in revised form 28 November 2007; accepted 4 December 2007

Available online 8 December 2007

Abstract

A novel triorganotin(IV) complex **1** has been synthesized and structurally characterized by elemental analysis, FT-IR, NMR (^1H , ^{119}Sn) spectra and X-ray crystallography. This complex displays a 3D network structure, which contains two types of chair form macrocycles.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Organotin; Macrocycles; Coordination polymer; Crystal structure

1. Introduction

In the past decade, the design and synthesis of multidimensional coordination polymers and metal-organic framework materials (MOFs) have been an attractive area due to their intriguing topological structures as well as their unique application as functional materials [1–6]. As we know organotin complexes are attracting more and more attention due to their wide industrial applications and anti-tumor activities [7]. The chemistry of novel organotin(IV) polymers based on covalent interactions [8–12] or supramolecular contacts (such as hydrogen bonding and/or π – π stacking interactions) [13–16] has been actively investigated too, but most of the reported polymeric systems are, 1D chain or 2D network structures, and some of them are constructed through supramolecular contacts. So far, few multidimensional organotin coordination polymers based on covalent interactions have been studied.

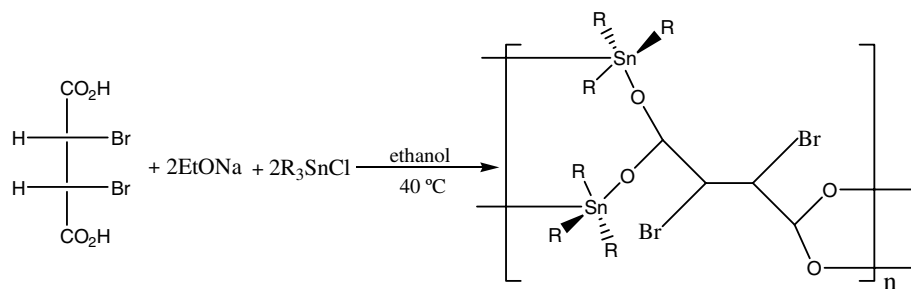
The above considerations stirred our interest in the synthesis of multidimensional organotin coordination polymers. So we selected an interesting ligand: meso-2,3-dibromosuccinic acid (H_2dbsa). This ligand was chosen

for the following reasons: first, the carboxy groups in this ligand can form strong covalent bonds with the organotin moiety, thus providing sufficient thermodynamic stability for them to be stable in the solid state; second, H_2dbsa is a multiple chelate ligand with two carboxy groups, so it has a rich coordination chemistry and can help to construct multidimensional coordination polymers by acting as a multidentate bridging linker; third, the conformational flexibility of this ligand will allow for the formation of various and interesting coordination polymers; fourth, H_2dbsa is a simple linear ligand without a complicated inner structure, which makes it easy to analyze the electronic and steric influence of the organic substituents attached to the tin atom on the coordination polymers.

Recently, we began to treat H_2dbsa with organotin compounds with the hope of obtaining interesting coordination polymers by the assembly of this ligand with different organotin compounds. As a result, we obtained the complex **1** by the reaction of H_2dbsa , sodium ethoxide and tri-*n*-butyltin chloride in dry ethanol. The reaction procedure is shown in Scheme 1. The structure analysis for complex **1** reveals that it is a 3D network polymer linked by the Sn–O bonds, and the related monomeric compound, bis(tributyltin) meso-2,3-dibromosuccinate, was described in a patent as an antifouling agent without the crystal

* Corresponding author. Tel./fax: +86 6358239121.

E-mail address: handongyin@lcu.edu.cn (H. Yin).

Scheme 1. R = ⁿBu.

structure [17]. It is noteworthy that complex **1** contains two types of macrocycles: one is six-tin 24-membered macrocycles, the other is six-tin 36-membered macrocycles. Such large macrocyclic structures appearing in a multidimensional organotin polymeric systems based on covalent interactions are rare, although organotin macrocycles have been extensively studied for their potential industrial applications and biological activities [18]. To the best of our knowledge, complex **1** is the first 3D network triorganotin(IV) polymer, which contains two types of six-tin nuclear macrocycles.

2. Results and discussion

2.1. Spectroscopic studies

The main feature in the IR spectra of complex **1** is the absence of bands in the region 3120–2980 cm⁻¹, which appear in the free ligand as CO₂H stretching vibrations, thus indicating metal-ligand bonding through these sites. The typical absorptions for Sn–C, Sn–O, vibrations in complex **1** are located in the normal range of similar organotin complexes [19,20]. The ¹H NMR spectra show the expected integration and peak multiplicities. In the spectra of the free ligand, the resonances observed at δ ≈ 10.50 ppm, which are absent in the spectra of the complex, indicate removal of the CO₂H proton and formation of Sn–O bond. This conclusion accords well with the IR data. The ¹¹⁹Sn NMR spectrum of complex **1** exhibits one signal at +69 ppm within the range corresponding to coordination number 4, +200 to –60 ppm [21]. Therefore it can reasonably be assumed that the structure of compound **1** in solution is likely different from that observed in the solid state.

2.2. Description of crystal structure

The coordination environment of the Sn atom is shown in Fig. 1. For clarity, the β, γ and δ carbon atoms of the butyl groups and the hydrogen atoms have been omitted. All the tin atoms in complex **1** possess the same coordination environment. The coordination about the tin atom is only slightly distorted from a regular trigonal bipyramidal geometry, with the equatorial plane occupied by three

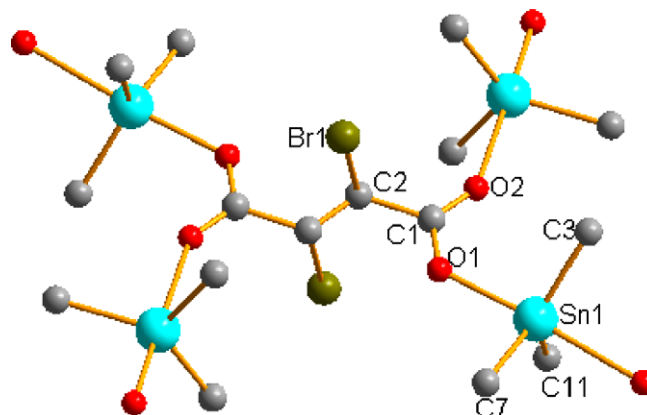


Fig. 1. The coordination environment of the Sn atom in **1**, for clarity, the β, γ and δ carbon atoms of the butyl groups and the hydrogen atoms have been omitted. Key bond lengths (Å) and angles (°): Sn(1)–C(11) 2.093(10), Sn(1)–C(7) 2.130(8), Sn(1)–C(3) 2.147(9), Sn(1)–O(1) 2.182(5), Sn(1)–O(2)[#1] 2.559(5); C(11)–Sn(1)–C(7) 116.3(4), C(11)–Sn(1)–C(3) 123.4(3), C(7)–Sn(1)–C(3) 118.9(4), C(11)–Sn(1)–O(1) 95.3(3), C(7)–Sn(1)–O(1) 89.0(3), C(3)–Sn(1)–O(1) 97.1(3), C(11)–Sn(1)–O(2)[#1] 87.7(3), C(7)–Sn(1)–O(2)[#1] 85.7(3), C(3)–Sn(1)–O(2)[#1] 84.8(3), O(1)–Sn(1)–O(2)[#1] 174.7(2). Symmetry code: $x - y + 1, x, -z + 2$.

n-butyl groups and the axial positions shared by two coordinated oxygen atoms from the ligand. Associated with the Sn(1)–O(1) distance [2.182(5) Å] and Sn(1)–O(2)#1 (symmetry code: $x - y + 1, x, -z + 2$) distance [2.559(5) Å] are close to the reported [(ⁿBu₃Sn)₂(2,5-pdc)]_n [22] and [Me₂Sn(pca)Cl]₃ [23] respectively, and much shorter than the sum of the van der Waals radii of Sn and O (3.68 Å) [24]. The angle O(1)–Sn(1)–O(2)#1 174.7(2)° is close to a linear arrangement. The sum of the angles subtended at the tin atom in the equatorial plane is 358.6° for Sn(1), so that the atoms Sn(1), C(3), C(7) and C(11) are almost in the same plane. The Sn–C distances [2.093(10)–2.147(9) Å] are equal within experimental error and close to the single-bond value for trigonal bipyramidal tin.

The network structure is illustrated in Fig. 2. It consists of infinite ribbons extending through the cell in the a, b, c three directions leading to a 3D network structure polymer, as indicated in Fig. 3. The tri-*n*-butyltin(IV) groups are situated in special positions in the polymer and are linked by a carboxylate; each dbsa ligand in complex **1**, in turn,

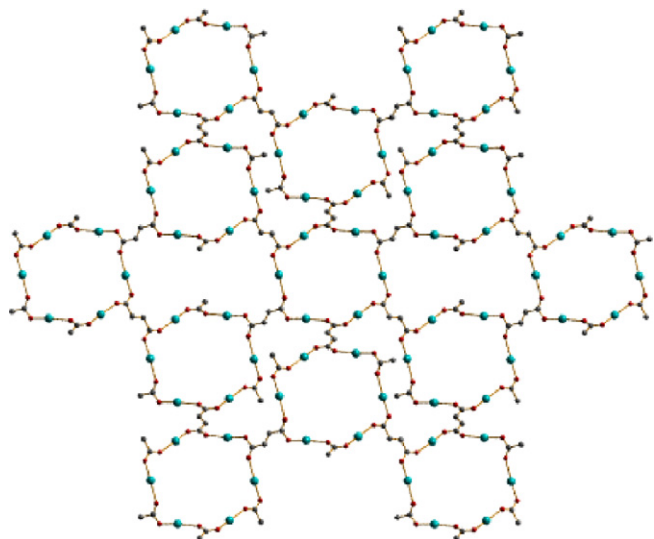


Fig. 2. The network structure of **1**, for clarity, only the atoms on the lattice were shown.

employs its two bidentate carboxylic groups to coordinate to four metal centers. Thus, six ligands are linked by six metal centers into a chair form 24-membered macrocycle (Fig. 4a), which is further linked to 12 nearest-neighbor Sn centers by six independent dbsa ligands to give rise to a 3D network structure with another chair form 36-membered macrocycle (Fig. 4b). The two types of cavities can be evaluated by the transannular Sn···Sn and O···O distances, which are 11.125–13.131 and 11.227–16.442 Å, respectively. Similar cavities have been found within the polymeric crystal structures of microporous metal-organic frameworks formed between 2,5-pyridinedicarboxylic acid and Sn center [25].

2.3. Thermogravimetric analysis

To study the stability of complex **1**, thermogravimetric analysis (TGA) was performed in the temperature range of 50–500 °C under N₂ atmosphere. The TGA curve of complex **1** exhibit one continuous weight loss stages in

the range of 150–356 °C (Fig. 5). In general, complex **1** exhibit good thermal stability [26].

In summary, using a flexible ligand, meso-2,3-dibromosuccinic acid, a new triorganotin(IV) coordination polymer has been synthesized and characterized via X-ray single-crystal diffraction analysis, elemental analysis, FT-IR and NMR(¹H, ¹¹⁹Sn) spectroscopy. The structure of the coordination polymer reveal that the ligand acts as linker to connect four metal centers to give rise to a 3D network structure. The ligand can bond more than one organotin moiety, which will increase the opportunities for the higher structural dimensionalities assembly, so the selection of organic ligands with appropriate coordination sites is the key to forming metal-organic coordination polymers with fascinating structures. Other organotin coordination polymers based on the H₂dbsa and diorganotin(IV) are currently investigated in our laboratory too.

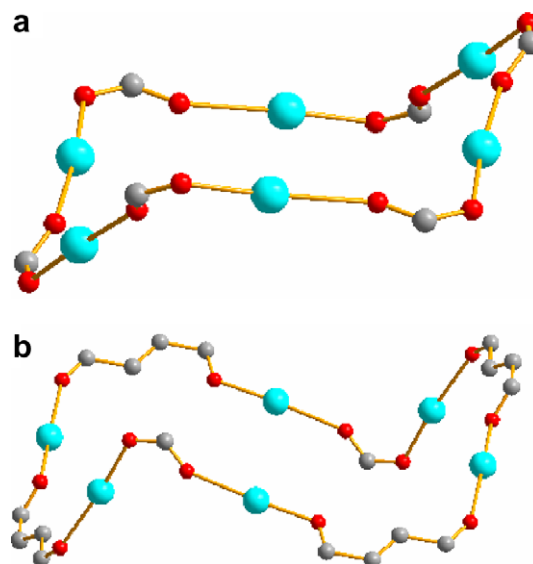


Fig. 4. (a) The chair form 24-membered macrocycle. (b) The chair form 36-membered macrocycle, for clarity, only the atoms on the macrocycle were shown.

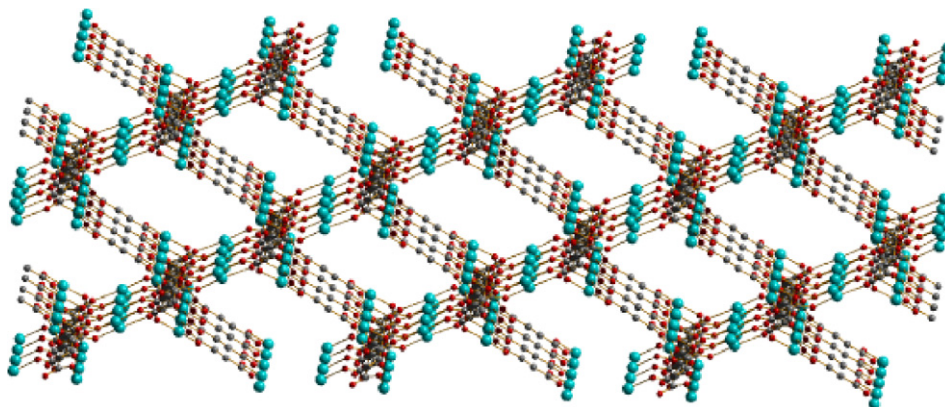


Fig. 3. The 3D network structure of **1** (viewed along the *a* axis), for clarity, only the atoms on the lattice were shown.

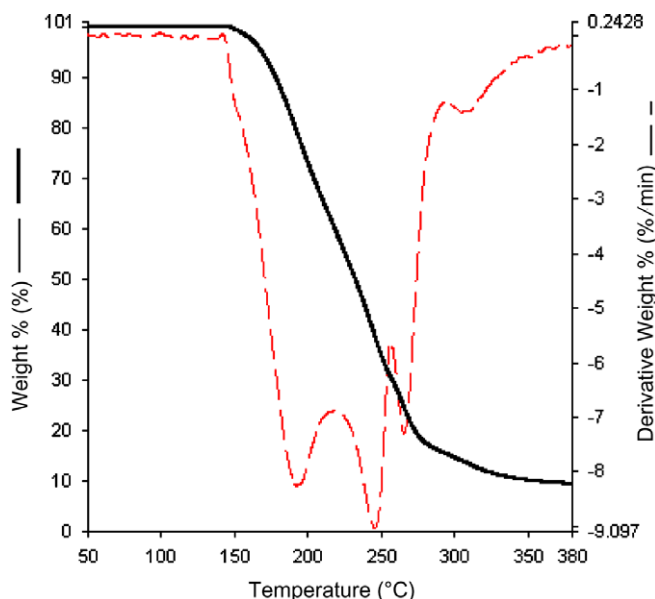


Fig. 5. TGA curve of 1.

3. Experimental details

3.1. Materials and measurements

Tri-*n*-butyltin chloride and meso-2,3-dibromosuccinic acid were purchased from Aldrich. Analytical grade solvents were dried before use. The melting points were obtained with Kofler micromelting point apparatus and are uncorrected. Infrared-spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. ^1H and ^{119}Sn NMR spectra were recorded on a Varian Mercury Plus 400 spectrometer operating at 400 MHz. The chemical shifts were given in ppm in CDCl_3 solvent. Elemental analyses were performed with a PE-2400II apparatus. TGA was carried out with a Perkin–Elmer Pyris-1 instrument with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from 50 to $500\text{ }^\circ\text{C}$ and with a $20.0\text{ cm}^3\text{ min}^{-1}$ nitrogen gas flow.

3.2. Synthesis of complex 1

The reaction was carried out under nitrogen atmosphere by use of standard Schlenk techniques. The meso-2,3-dibromosuccinic acid (0.276 g, 1 mmol) was added to the solution of dry ethanol (60 mL) together with sodium ethoxide (0.136 g, 2 mmol), and the mixture was stirred for 10 min. Tri-*n*-butyltin chloride (0.326 g, 2 mmol) was then added to the mixture, and the reaction was allowed to continue for 12 h at $40\text{ }^\circ\text{C}$. After cooling down to room temperature, the solution was filtered. The solvent was gradually removed from the filtrate by evaporation under vacuum until solid product was obtained. The solid was then crystallized from the mother liquor. Colorless crystals were formed. M.p. $147\text{--}149\text{ }^\circ\text{C}$. Yield, 73%. Anal. Calc. for $\text{C}_{14}\text{H}_{28}\text{BrO}_2\text{Sn}$: C, 39.38; H, 6.61. Found: C, 39.51; H, 6.52%. ^1H NMR (CDCl_3): δ 0.896 (t, 9H, CH_3), 1.300–

1.689 (m, 18H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 4.604 (s, 1H, CH), ppm. ^{119}Sn NMR (CDCl_3): δ +69 ppm. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$ 1619, $\nu_{\text{s}}(\text{COO})$ 1437, $\nu(\text{Sn–C})$ 577, $\nu(\text{Sn–O})$ 483.

3.3. X-ray structures determination of complex 1

Crystal data for 1: $\text{C}_{14}\text{H}_{28}\text{BrO}_2\text{Sn}$, $M = 426.96$, trigonal, space group $R\bar{3}$, $a = 27.497(2)$, $b = 27.497(2)$, $c = 12.8751(15)\text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$; $V = 8430.5(14)\text{ \AA}^3$, $Z = 18$, $D_c = 1.514\text{ Mg m}^{-3}$, $\lambda = 0.71073\text{ \AA}$, $T = 298(2)\text{ K}$, $\mu(\text{Mo K}\alpha) = 3.492\text{ mm}^{-1}$, $F(000) = 3834$, $\text{GoF} = 1.088$. Data were collected on a Bruker SMART CCD 1000 diffractometer using a colorless block of dimensions $0.42 \times 0.40 \times 0.39\text{ mm}^3$ by the area-detector method ($1.48 \leq \theta \leq 25.00$). Of a total of 10248 collected reflections, 3300 were independent ($R_{\text{int}} = 0.0370$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R_1[I > 2\sigma(I)] = 0.0499$ and $wR_2 = 0.1539$ (all data); largest peak and hole in the final difference map 0.968 and -0.619 e \AA^{-3} .

Acknowledgement

We thank the National Natural Science Foundation of China (20771053) and the Natural Science Foundation of Shandong Province (2005ZX09) for financial support.

Appendix A. Supplementary material

CCDC 659932 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.12.002](https://doi.org/10.1016/j.jorganchem.2007.12.002).

References

- [1] J.L.C. Rowsell, A.R. Millward, K.S. Park, O.M. Yaghi, *J. Am. Chem. Soc.* 126 (2004) 5666.
- [2] M.L. Tong, X.M. Chen, S.R. Batten, *J. Am. Chem. Soc.* 125 (2003) 16170.
- [3] C.F. Wang, J.L. Zuo, B.M. Bartlett, Y. Song, J.R. Long, X.Z. You, *J. Am. Chem. Soc.* 128 (2006) 7162.
- [4] L. Pan, E.B. Woodlock, X. Wang, *Inorg. Chem.* 39 (2000) 4174.
- [5] P.J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem., Int. Ed.* 38 (1999) 3268.
- [6] E.Q. Gao, S.Q. Bai, Z.M. Wang, C.H. Yan, *J. Am. Chem. Soc.* 125 (2003) 4984.
- [7] (a) O. Lentzen, C. Moucheron, A. Kirsch-De Mesmaeker, *Metallotherapeutic Drugs and Metal-Based Diagnostic Agents*, Wiley, New York, 2005; (b) L. Pellerit, L. Nagy, *Coord. Chem. Rev.* 224 (2002) 111; (c) M. Gielen, *Coord. Chem. Rev.* 151 (1996) 41; (d) M. Nath, S. Pokharia, R. Yadav, *Coord. Chem. Rev.* 215 (2001) 99; (e) M. Gielen, *Tin-Based Antitumor Drugs NATO ASI series*, vol. H37, Springer, Berlin, 1990; (f) A.K. Saxena, F. Huber, *Coord. Chem. Rev.* 95 (1989) 109; (g) M. Gielen, *Appl. Organomet. Chem.* 16 (2002) 481.

- [8] (a) S. Bhandari, C.G. Frost, C.E. Hague, M.F. Mahon, K.C. Molloy, J. Chem. Soc., Dalton Trans. (2000) 663;
(b) A. Goodger, M. Hill, M.F. Mahon, J. McGinley, K.C. Molloy, J. Chem. Soc., Dalton Trans. (1996) 847;
(c) M. Hill, M.F. Mahon, K.C. Molloy, J. Chem. Soc., Dalton Trans. (1996) 1857;
(d) S. Bhandari, M.F. Mahon, J.G. McGinley, K.C. Molloy, C.E.E. Roper, J. Chem. Soc., Dalton Trans. (1998) 3425.
- [9] R. Wang, M. Hong, J. Luo, R. Cao, J. Weng, Eur. J. Inorg. Chem. (2002) 2082.
- [10] A. Galani, M.A. Demertzis, M. Kubicki, D. Kovala-Demertzi, Eur. J. Inorg. Chem. (2003) 1761.
- [11] H. Preut, F. Huber, M. Gielen, Acta Crystallogr., Sect. C 46 (1990) 2071.
- [12] S.W. Ng, Z. Kristallogr., New Cryst. Struct. 213 (1998) 157.
- [13] F.L. Lee, E.J. Gabe, L.E. Khoo, W.H. Leong, G. Eng, F.E. Smith, Inorg. Chim. Acta 166 (1989) 257.
- [14] R. Xiong, J. Zuo, X. You, H. Fun, S.S.S. Raj, Organometallics 19 (2000) 4183.
- [15] F. Huber, B. Mundus-Glowacki, H. Preut, J. Organomet. Chem. 365 (1989) 111.
- [16] (a) S.W. Ng, S.S.S. Raj, H. Fun, I.A. Razak, J.M. Hook, Acta Crystallogr., Sect. C 56 (2000) 966;
(b) S.W. Ng, J. Holecek, Acta Crystallogr., Sect. C 54 (1998) 750;
(c) S.W. Ng, V.G. Kumar, G. Xiao, A. van der Helm, J. Holecek, A. Lycka, Heteroatom Chem. 2 (1991) 495.
- [17] F. Hiroshi, N. Yoshio, K. Teiichi. Jpn. Tokkyo Koho (1970) JP 45031553.
- [18] S.K. Duboy, U. Roy, Appl. Organomet. Chem. 17 (2003) 3.
- [19] T.A. George, J. Organomet. Chem. 31 (1971) 233.
- [20] J.R. May, W.R. McWhinnie, R.C. Poller, Spectrochim. Acta A 27 (1971) 969.
- [21] J. Holeček, A. Lyčka, K. Handlír, M. Nádvorník, Collect. Czech. Chem. Commun. 55 (1990) 1193.
- [22] H.D. Yin, F.H. Li, CH.H. Wang, Inorg. Chim. Acta 360 (2007) 2797.
- [23] C.L. Ma, Y.F. Han, R.F. Zhang, D.Q. Wang, Dalton Trans. (2004) 1832.
- [24] A. Bondi, J. Phys. Chem. 68 (1964) 441.
- [25] C.L. Ma, J.K. Li, R.F. Zhang, D.Q. Wang, J. Organomet. Chem. 691 (2005) 1713.
- [26] C.L. Ma, G.R. Tian, R.F. Zhang, Inorg. Chem. Commun. 9 (2006) 882.