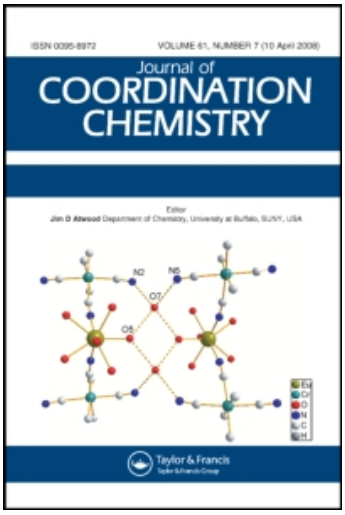

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Metallic macrocycle with a 1,3-alternate calix[4]arene salicylideneamine ligand

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Metallic macrocycle with a 1,3-alternate calix[4]arene salicylideneamine ligand

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The calix[4]arene-based podand which incorporates two salicylideneamine units in 1,3-alternate positions of the lower rim has been prepared and subjected to complexation studies with transition metal ions. The nickel and copper complexes form a 2:2 stoichiometric metallic macrocyclic framework.

Keywords: Calixarene; Schiff base; Salen; Metallic complex; Crystal structure

1. Introduction

Calixarenes have attracted much attention in recent years for their unique structural and chemical diversity, which allow their use in the synthesis of various molecular architectures [1]. Calixarenes have advantage over other members of the family due to easy accessibility, well-defined structures, variable conformation, and easy modification [2]. Research in coordination chemistry of calixarenes has shown the ability of these compounds as selective binders, carriers, and also as building blocks for the construction of supermolecules [3, 4]. Calix[4]arenes are the lowest oligomers in the series and are readily available, and numerous metal complexes have been prepared and structurally authenticated. The relatively rigid organic backbone of calix[4]arenes provides a platform for the assembly of several metal centers in close proximity. The vast majority of these metallocalix[4]arene derivatives exist as either mono- or binuclear complexes, retaining the cone-like conformation of the parent ligands. Recently, metal complexes containing larger ring systems such as calix[6]arene and calix[8]arene have attracted attention [5–7]. Schiff bases have been employed widely in the formation of metal complexes and in the study of inclusion phenomena, owing to their easy preparation, remarkable stability, and high versatility. The fusion of the Schiff base and calixarene properties into a unique entity can give an interesting and versatile system with very peculiar coordination properties. Several works have demonstrated the introduction of Schiff base at the lower or upper rim of calixarenes and used them mostly as cation or anion receptors and carriers [8–12]. Although calixarene Schiff bases in

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ion recognition, extraction, and transportation have long been established, study of preparation and crystal structures of transition metal complexes of calixarene Schiff bases has not yet been investigated in detail. The synthesis and coordination properties of a family of calixsalen-type macrocycles have received limited study [13]. As part of an ongoing program investigating coordination environments afforded by calixarenes [14], herein we report design of 1,3-alternate Schiff-base ligands with calix[4]arene as a platform for the construction of transition metal complexes.

2. Experimental

2.1. *Reagents and instruments*

All reagents and solvents of analytical grade were commercially available and used as received. Further purification and drying by standard methods and distillation were employed prior to use when necessary. Evaporation of organic solvents was carried out with a rotary evaporator in conjunction with a water aspirator. *p-tert*-Butylcalix[4]arene was prepared according to the published methods.

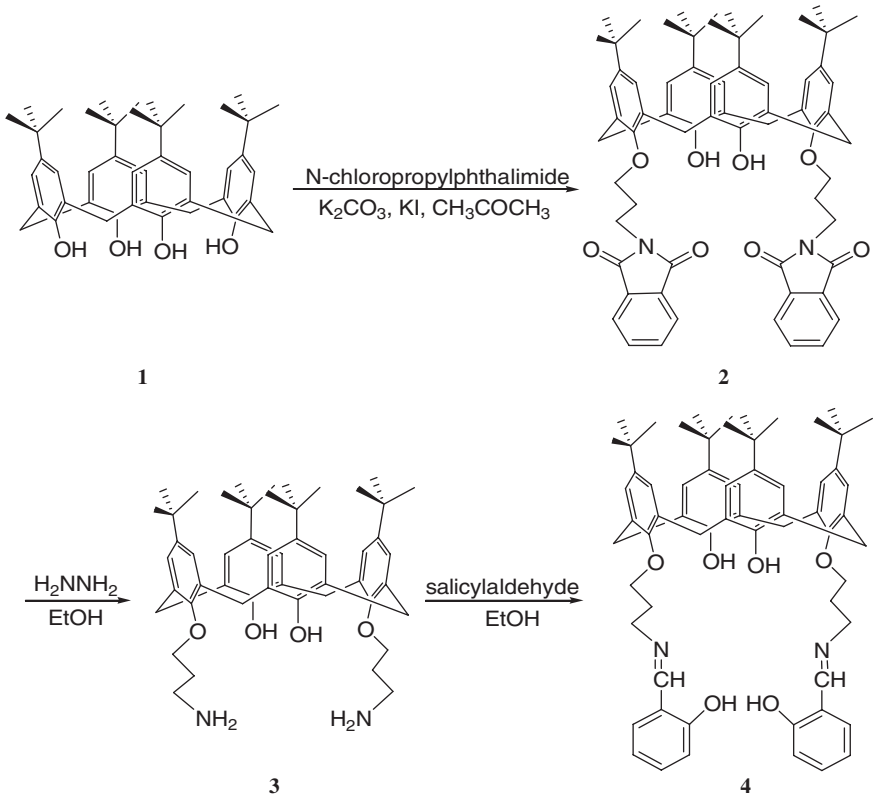
Melting points were taken on a hot-plate microscope apparatus and were uncorrected. ^{1}H NMR spectra were recorded with a Bruker AV-600 spectrophotometer (600 MHz for ^{1}H NMR). IR spectra were obtained on a Bruker Tensor27 spectrometer (KBr disc). X-ray data were collected on a Bruker Smart APEX-2 diffractometer.

2.2. *Synthesis of 5,11,17,23-tetra-p-butyl-25,27-di(phthalimidopropyl)-26, 28-dihydroxycalix[4]arene (2)*

A suspension of **1** (scheme 1, 5.0 mmol, 3.24 g) and anhydrous potassium carbonate (20 mmol, 2.76 g), potassium iodide (0.5 g, 3.0 mmol) in dry acetone (150 mL) was heated to reflux under nitrogen for 2 h. Then, *N*-chloropropylphthalimide (15.0 mmol, 3.35 g) was added. The reaction mixture was refluxed for 4 days. After removal of solvent, the residue was extracted with 100 mL of methylene chloride. The organic layer was washed with water and evaporated to dryness. The resulting precipitates were collected and recrystallized to give pure solid **2**; white solid, yield: 55%. m.p.: 220–222°C IR (KBr) υ: 3430(s), 2960(m), 2867(m), 1772(w), 1712(vs), 1634(w), 1480(m), 1384(m), 1190(w). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.89 (s, 18H, $C(CH_3)_3$), 1.20 (s, 18H, $C(CH_3)_3$), 2.36 (*t*, $J = 5.7$ Hz, 4H, CH_2), 3.24 (d, $J = 13.2$ Hz, 4H, $ArCH_2Ar$), 4.02–4.05 (m, 8H, NCH_2, CH_2O), 4.24 (d, $J = 13.2$ Hz, 4H, $ArCH_2Ar$), 6.73 (s, 4H, ArH), 6.99 (s, 4H, ArH), 7.19 (s, 2H, ArOH), 7.55–7.57 (m, 4H, ArH), 7.68–7.69 (m, 4H, ArH). Anal. Calcd. for $C_{66}H_{74}N_2O_8$: C, 77.47; H, 7.29; N, 2.74. Found: C, 77.19; H, 7.36; N, 2.89.

2.3. *Synthesis of 5,11,17,23-tetra-p-butyl-25,27-di(aminopropyl)-26, 28-dihydroxycalix[4]arene (3)*

To a solution of **2** (2.93 mmol) in 50 mL of ethanol was added hydrated hydrazine (80%, 205 mmol, 10 mL) and the mixture was refluxed for 12 h. After cooling to



Scheme 1. Synthesis of *p-tert*-butylcalix[4]arene salen ligand.

room temperature, 300 mL of water was added to the solution and mixture was extracted with methylene dichloride. The organic layer was dried with $MgSO_4$ and evaporated to give white solid as **3**: yield: 88%. m.p.: >230°C IR(KBr) υ: 3420(s), 2960(s), 2867(m), 1632(w), 1480(s), 1384(m), 1209(m). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.87 (s, 18H, $C(CH_3)_3$), 1.20 (s, 18H, $C(CH_3)_3$), 2.12 (s, 4H, NH_2), 2.22 (*t*, $J = 5.7$ Hz, 4H, CH_2), 3.19–3.24 (m, 4H, CH_2), 3.30 (d, $J = 13.2$ Hz, 4H, $ArCH_2Ar$), 4.05 (*t*, $J = 5.7$ Hz, 4H, OCH_2), 4.23 (d, $J = 13.2$ Hz, 4H, $ArCH_2Ar$), 6.71 (s, 4H, ArH), 6.97 (s, 4H, ArH). Anal. Calcd for $C_{50}H_{70}N_2O_4$: C, 78.70; H, 7.33; N, 3.67. Found: C, 78.45; H, 7.58; N, 3.41.

2.4. *Synthesis of 5,11,17,23-tetra-p-butyl-25,27-di(salicylideneaminopropyl)-26, 28-dihydroxy calix[4]arene (4)*

The mixture of **3** (1.0 mmol, 0.762 g) and salicylaldehyde (2.5 mmol, 0.306 g) in 20 mL of ethanol was stirred at room temperature for 6 h. The precipitate was filtered and washed with cold ethanol to give **4**: yield: 87%, m.p.: 179–180°C. IR (KBr) υ: 3380(m), 2956(s), 2867(m), 1634(s), 1484(s), 1360(w), 1278(m), 1206(m), 1152(m), 871(m), 781(s). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.03 (s, 18H, $C(CH_3)_3$), 1.29 (s, 18H, $C(CH_3)_3$), 2.40 (*t*, $J = 5.7$ Hz, 4H, CH_2), 3.34 (d, $J = 13.2$ Hz, 4H, $ArCH_2Ar$), 4.09 (*t*, $J = 5.1$ Hz,

4H, NCH_2), 4.152 (*t*, $J = 5.7$ Hz, 4H, OCH_2), 4.27 (d, $J = 13.2$ Hz, 4H, $ArCH_2Ar$), 6.824 (*t*, $J = 7.5$ Hz, 2H, ArH), 6.88 (s, 4H, ArH), 6.96 (d, $J = 8.4$ Hz, 2H, ArH), 7.06 (s, 4H, ArH), 7.15 (d, $J = 7.8$ Hz, 2H, ArH), 7.29 (*t*, $J = 7.5$ Hz, 2H, ArH), 7.91 (s, 2H, ArOH), 8.56 (s, 2H, CH=N), 13.51 (s, 2H, ArOH). Anal. Calcd for $C_{64}H_{78}N_2O_6$: C, 79.14; H, 8.09; N, 2.88. Found: C, 78.97; H, 8.06; N, 2.97.

2.5. *General procedure for the synthesis of transition metal complexes of (4)*

To nickel acetate or copper acetate hydrate (0.03 mmol) in methanol (15 mL) was added **4** (0.03 mmol) in chloroform (10 mL) and the solution was stirred at room temperature for 2 days. The precipitate was filtered, washed with cold methanol, and dried in air to give the complexes. **5a**: Nickel complex, yellow solid, yield: 65%, m.p.: $>250^\circ$C; IR 3416(m), 2930(m), 1615(vs), 1542(m), 1483(s), 1452(s), 1291(m), 1204(m), 1152(w), 756(s) cm^{-1}; UV: 326, 425 nm. **5b**: Copper complex, greenish yellow solid, yield: 84%, m.p.: $>250^\circ$C; IR 3423(m), 2962(m), 1621(vs), 1549(m), 1479(s), 1451(s), 1277(m), 1197(m), 1010(m), 753(s) cm^{-1}; UV: 272, 291, 365 nm.

3. Results and discussion

3.1. *Synthesis and characterization of ligand*

We planned to introduce salen at the lower rim of calixarenes by formation of the Schiff base. Therefore, we needed to synthesize amino calixarene to be condensated with a suitable aldehyde derivative. The tetraamino and diamino derivatives at the lower rim of *p-tert*-butylcalix[4]arene were prepared according to the procedures reported in the literature with some change. The calixarene salicylideneamine ligand is prepared in three steps by the reactions depicted in scheme 1. First, phthalimide is incorporated by *O*-alkylation on the lower rim of calix[4]arene according to a literature method. The reaction is carried out by refluxing a mixture of *p-tert*-butylcalix[4]arene with *N*-(3-chloropropyl)phthalimide in the system of K_2CO_3/KI/acetone for 4 days. After workup, the 1,3-disubstituted calixarene phthalimide **2** is obtained in 55% yield. Then the phthalic protecting group is removed by hydrazinolysis of phthalimido in **2** to give the calixarene diamino derivative **3**, which is condensed with salicylaldehyde in ethanol at room temperature to give the 1,3-alternate calixarene salen ligand (**4**) in 87% yield.

The ^{1}H NMR spectrum of **4** (Supplementary material) shows singlets at 1.03 and 1.29 ppm for the *t*-butyl protons in the ratio of 1 : 1, two doublets at 3.34 and 4.27 for the methylene bridge protons, indicating that **4** exists in a *cone*-conformation. There is only one signal of hydroxyl at 13.51 ppm and one signal of methine (CH=N) at 8.56 ppm, suggesting that the two salicylideneimine groups are magnetically equivalent. Two propylene chains display one triplet at 4.15 ppm for OCH_2 and one triplet at 4.09 ppm for NCH_2 groups, also showing that salicylideneimine groups are in the same position.

Complexation reactions were carried out by stirring methanol solution of **4** with transition metal acetate at room temperature for 10 h. The resulting precipitates were collected and pure complexes **5a** and **5b** were characterized by UV–Vis and IR spectroscopy and X-ray single crystal analysis. Comparing the IR spectra of **4** with

that of complexes, the CH=N absorption at 1634 cm^{-1} in **4** shifts to 1614–1625 cm^{-1} in complexes, showing that nitrogen of imine are coordinated to metal ions. The UV–Vis spectra also support this observation. The UV–Vis spectrum of ligand **4** show an absorption peak at 316 for CH=N which shifts to 358–415 nm in spectra of the complexes.

3.2. *Crystal structure*

The molecular structure of complexes has been established by single crystal X-ray diffraction analysis of nickel and copper complexes (**5a** and **5b**). Single crystals of **5a** and **5b** were formed when a chloroform/methanol solution was allowed to slowly evaporate for a couple of weeks. Both compounds crystallize in the triclinic system, *P*-ī space group (details are in table 1). Perspective views with the atomic-numbering scheme are shown in figures 1 and 2, respectively. Compounds **5a** and **5b** have very similar noncentrosymmetric 40-member metallocyclic frameworks from linkage of two Ni or Cu ions and two calixarene salicylideneamine ligands. The calixarenes still exist in cone conformation, in agreement with the NMR data. The calixarene

Table 1. Crystal data and structure refinement details of the complexes.

	5a	**5b**
Empirical formula	$C_{128}H_{152}N_4Ni_2O_{12}$	$C_{255}H_{307}Cu_4N_8O_{24}$
Formula weight	2055.92	4122.30
Temperature (K)	296(2) K	296(2) K
Wavelength (Å)	0.71073	0.71073 A
Crystal system, space group	Triclinic, *P*ī	Triclinic, *P*ī
Unit cell dimensions (Å, °)		
a	18.946(8)	15.420(16)
b	20.239(9)	18.240(19)
c	43.39(2)	29.07(3)
α	76.549(7)	78.005(15)
β	85.031(9)	78.474(16)
γ	70.524(7)	78.474(16)
Volume ($Å^3$)	15255(12)	7335(13)
Z	4	1
Calculated density ($g\,cm^{-3}$)	0.895	0.933
Absorption coefficient (mm^{-1})	0.293	0.338
F(000)	4399	2201
Crystal size (mm^3)	0.2 × 0.2 × 0.3	0.20 × 0.20 × 0.20
θ range for data collection	1.45–29.97	1.5–27.5
hkl ranges	−24–24, −26–25, −56–56	−19–19, −19–23, −37–37
Reflections collected/unique	135,457/69,320 [*R*(int) = 0.1122]	64,176/32,718 [*R*(int) = 0.074]
Completeness to *θ* = 27.50	94.4%	
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	69320/3327/2884	16636/0/993
Goodness-of-fit on F^2	0.949	0.98
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0869$, $wR_2 = 0.1718$	$R_1 = 0.0776$, $wR_2 = 0.1857$
R indices (all data)	$R_1 = 0.2889$, $wR_2 = 0.1867$	
Largest difference in peak and hole ($e\,Å^{-3}$)	0.553 and −0.304	0.42 and −0.32

Note: Weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.1660P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3'$.

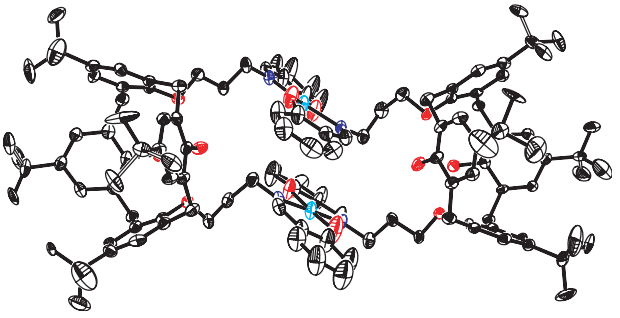


Figure 1. The crystal structure of **5a**.

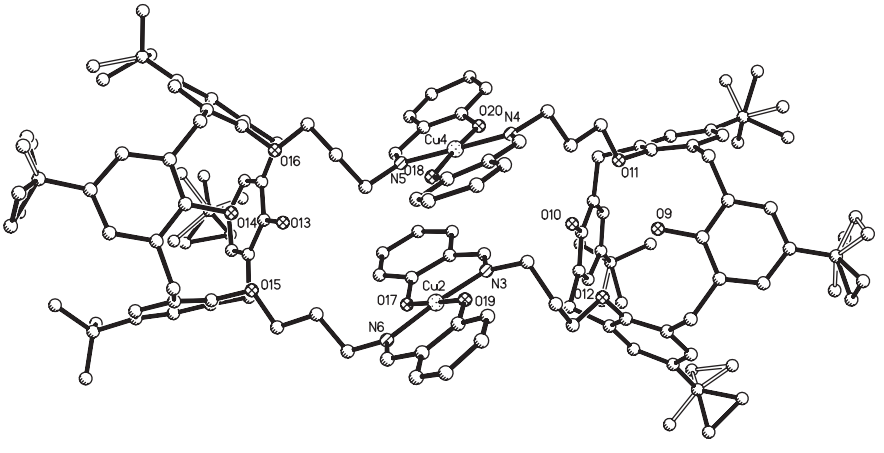


Figure 2. The crystal structure of **5b**.

salicylideneamine ligand in **5a** is a dianion tetradentate ligand connecting two Ni atoms via phenolic oxygen and imino nitrogen from two salicylideneimine groups. Two Ni(II) ions link two calixarene salicylideneamine ligands to form a 40-member metallocyclic framework. Each nickel in the dimeric complex **5a** is coordinated by two phenolic oxygens and two imino nitrogens to give square-planar geometry. The Ni–O distances range from 1.814(2) to 1.850(2) Å, and Ni–N distances are from 1.878(3) to 1.935(3) Å, respectively.

Due to the disorder of *t*-butyl groups, the quality of crystal **5b** is not good. The structure of **5b** is similar to that of **5a** and two Cu(II)'s connect two calixarene salicylideneamine ligands via the phenolic oxygens and imino nitrogens of the salicylideneamine groups resulting in a 40-member metallocyclic framework. The four Cu–O distances fall in the range of 1.869(3)–1.932(2) Å and the Cu–N bond lengths are from 1.966(3) to 2.010(2) Å.

Supplementary material

Single crystal X-ray diffraction data are deposited with CCDC (Deposition numbers **5a**: CCDC 688287; **5b**: CCDC 688288).

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References

[1] (a) V. Bohmer. *Angew. Chem. Int. Ed. Engl.*, **34**, 713 (1995); (b) A. Ikeda, S. Shinkai. *Chem. Rev.*, **97**, 173 (1997).
[2] (a) S.M. Biros, J. Rebek Jr. *Chem. Soc. Rev.*, **36**, 93 (2007); (b) M.D. Pluth, K.N. Raymond. *Chem. Soc. Rev.*, **36**, 161 (2007); (c) S.J. BaDalgarno, P.K. Thallapally, L.J. Barbour, J.L. Atwood. *Chem. Soc. Rev.*, **36**, 236 (2007); (d) L. Baldini, A. Casnati, F. Sansone, R. Ungaro. *Chem. Soc. Rev.*, **36**, 254 (2007).
[3] (a) A.J. Petrella, C.L. Raston. *J. Organomet. Chem.*, **689**, 4125 (2004); (b) J.L. Atwood, L.J. Barbour, M.J. Hardie, C.L. Raston. *Coord. Chem. Rev.*, **222**, 3 (2001); (c) C. Wieser, C.B. Dieleman, D. Matt. *Coord. Chem. Rev.*, **165**, 93 (1997).
[4] C. Redshaw. *Coord. Chem. Rev.*, **244**, 45 (2003).
[5] (a) P.C. Leverd, D. Rinaldo, M. Nierlich. *Eur. J. Inorg. Chem.*, 2021 (2001); (b) P.C. Leverd, M. Nierlich. *Eur. J. Inorg. Chem.*, 1733 (2000); (c) L.N. Puntus, A.S. Chauvin, S. Varbanou, J.C.G. Bunzli. *Eur. J. Inorg. Chem.*, 2071 (2003).
[6] (a) O. Seneque, M. Campion, M. Giogi, Y.L. Mest, O. Reinaod. *Eur. J. Inorg. Chem.*, 1817 (2004); (b) U. Darbost, X.S. Zeng, M.-N. Rager, M. Giorgi, I. Jabin, O. Reinaod. *Eur. J. Inorg. Chem.*, 4371 (2004).
[7] A.E. Wetherby, L.R. Goeller, A.G. Dipasquale, A.L. Rheingold, C.S. Weinert. *Inorg. Chem.*, **46**, 7579 (2007).
[8] (a) T. Rojsajjakul, S. Veravong, G. Tumcharene, R. Seangprasertkij-Magee, T. Tuntulani. *Tetrahedron*, **53**, 4669 (1997); (b) G.T. Hwang, B.H. Kim. *Tetrahedron*, **58**, 9019 (2002); (c) A. Yilmaz, S. Memon, M. Yilmaz. *Tetrahedron*, **58**, 7735 (2002).
[9] (a) R. Seangprasertkij, Z. Asfari, F. Arnaud, J. Vicens. *J. Org. Chem.*, **59**, 1741 (1994); (b) H. Halouani, I. Dumazet-Bonnamour, M. Perrin, R. Lamartine. *J. Org. Chem.*, **69**, 6921 (2004).
[10] S. Tamburini, P. Tomasin, P.A. Vigato, A. Casnati, L. Domiano. *Inorg. Chim. Acta*, **254**, 209 (1997).
[11] M. Amato, F. Ballistreri, A. Pappalardo, G. Tomaselli, R. Toscano, D. Williams. *Eur. J. Org. Chem.*, 3562 (2005).
[12] Z. Liang, Z.L. Liu, Y.H. Gao. *Tetrahedron Lett.*, **48**, 3587 (2007).
[13] (a) Z.M. Li, C. Jablonski. *Chem. Commun.*, 1531 (1999); (b) Z.M. Li, C. Jablonski. *Inorg. Chem.*, **39**, 2456 (2000); (c) S. Srimurugan, B. Viswanathan, T.K. Varadarajan, B. Varghese. *Tetrahedron Lett.*, **46**, 3151 (2005); (d) J. Gao, J.H. Reibenspies, R.A. Zingaro, F.R. Woolley, A.E. Martell, A. Clearfield. *Inorg. Chem.*, **44**, 232 (2005).
[14] (a) J. Han, Y.H. Cai, L. Liu, C.G. Yan, Q. Li. *Tetrahedron*, **63**, 2275 (2007); (b) Y.Y. Wang, Y.H. Cai, C.G. Yan. *Supramol. Chem.*, **19**, 467 (2007).