Novel 1,3-Alternate Calix[4]thiacrown Ethers

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Received April 12, 2002

A series of novel 1,3-alternate calix[4]-*mono*-thiacrown and -*bis*-thiacrowns were synthesized within good yields. The three dimensional 1,3-alternate conformation was confirmed by X-ray crystal structure. From the results of two phase extraction and NMR studies on the ligand-metal complex, one can conclude that the calix[4]thiacrown ethers showed the very high selectivity for silver ion over other metal ions by an electrostatic interaction between sulfur atom and silver ion and by a π-metal complexation.

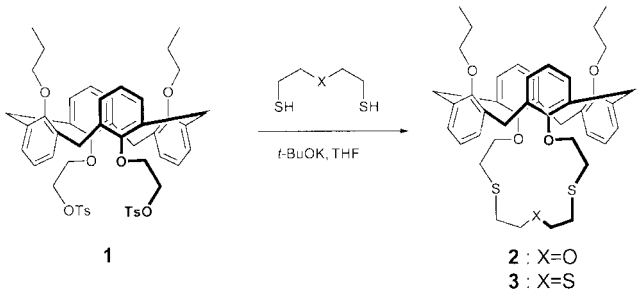
Keywords : Calix[4]thiacrown ether, Calix[4]-*bis*-thiacrown, Complexation, Picrate extraction.

Introduction

Much attention has recently been paid to the research dealing with supramolecular and assembled architectures using calixarene molecule.[1] 1,3-Alternate calix[4]arenes has been developed in synthetic strategies for constructing artificial systems with a precise disposition of atoms and functional groups.[2] In particular, 1,3-calix[4]crowns[3] and related aza-crown systems[4] which are linked to each other by a p-basic benzene tunnel have been reported. In spite of a number of synthetic and complexation studies on the thia-crown ethers,[5-8] calixthiacrown ethers in which the thiacrown ether is incorporated into the 1,3-alternate calix[4]arene have not been reported. It is possible that the calixthiacrown ether would result in an optimized structure for silver ion encapsulation due to (i) electrostatic interactions between the metal ion and both the sulfur atoms and oxygen electron donors, (ii) π-metal interactions between the metal ion and two rotated aromatic nuclei of the 1,3-alternate calixarene.[2] With this in mind, we report herein the synthesis of a series of novel calix[4]-*mono*-thiacrown and -*bis*-thiacrown, crystal structure and their complexing properties towards Ag^+.

Results and Discussion

As illustrated in Scheme 1, synthesis of **2** and **3** began with the condensation of 1,3-alternate calix[4]arene ditosylate **1**[4c] with 1.3 equivalent of 2-mercaptoethyl ether and 2-mercaptoethyl sulfide, respectively, using potassium *t*-butoxide in tetrahydrofuran (THF). With column-chromatographed purification, **2** and **3** were obtained in 45 and 47% yield, respectively. Presence of a singlet peak at 38.2 ppm (**2**) and 38.2 ppm (**3**) in ^{13}C NMR spectra for the methylene bridge carbons (Ar*C*H_2Ar) indicated that they are in the 1,3-alternate conformation. Variation of bases such as NaOH, NaH, and KH was not effective for the cyclization. For the preparation of symmetrical calix[4]-*bis*-dithiacrown ether



Scheme 1. Synthetic scheme for compounds **2** and **3**.

(**4**) and -*bis*-trithiacrown ether (**5**), the precursor **8** was synthesized as shown in Scheme 2. We, however, have encountered synthetic difficulty for **8** which was thought to be directly prepared from calix[4]arene and ethylene glycol monotosylate. Synthesis of **8** was finally successful by three-synthetic steps through alkylation of calix[4]arene followed by reduction and then tosylation. Alkylation of calix[4]arene using ethyl 2-bromoacetate was known,[9] but provided a mixture of four different conformational isomers in our experiment. According to TLC in ethyl acetate:hexanes (1 : 3) as eluent and product characterization, it is noteworthy that 1,2-alternate- (R_f = 0.6), 1,3-alternate- (R_f = 0.3) and cone-conformer (R_f = 0.2) were obtained as a solid in 2.0, 28.7 and 6.8% yield, respectively, while partial cone-conformer (R_f = 0.65) was oily and obtained in 31.6% yield. Reduction of **6** with LAH followed by tetra-tosylation using *p*-toluene-sulfoyl chloride yielded **8** retaining 1,3-alternate conformation which was proved by its NMR spectra. The 1,3-alternate conformation of **4** and **5** were also proven by an observation of a singlet peak of the Ar*C*H_2Ar at 38.2 ppm (**4**) and at 38.1 ppm (**5**) in ^{13}C NMR spectra, respectively. The solid-state structure of **4** as shown in Figure 1 strongly supports that the 1,3-alternate conformation is evident.

The ratio of **4** and **5** to silver ion was assessed by high-resolution mass spectrometry. FAB-MS molecular ion peak of 913 and 945 *m/z* indicate 1 : 1 complex of **4**·Ag^+ and **5**·Ag^+, respectively. No other mass fragmentation (*e.g.* 1 : 2 or 2 : 1) complexes were observed.

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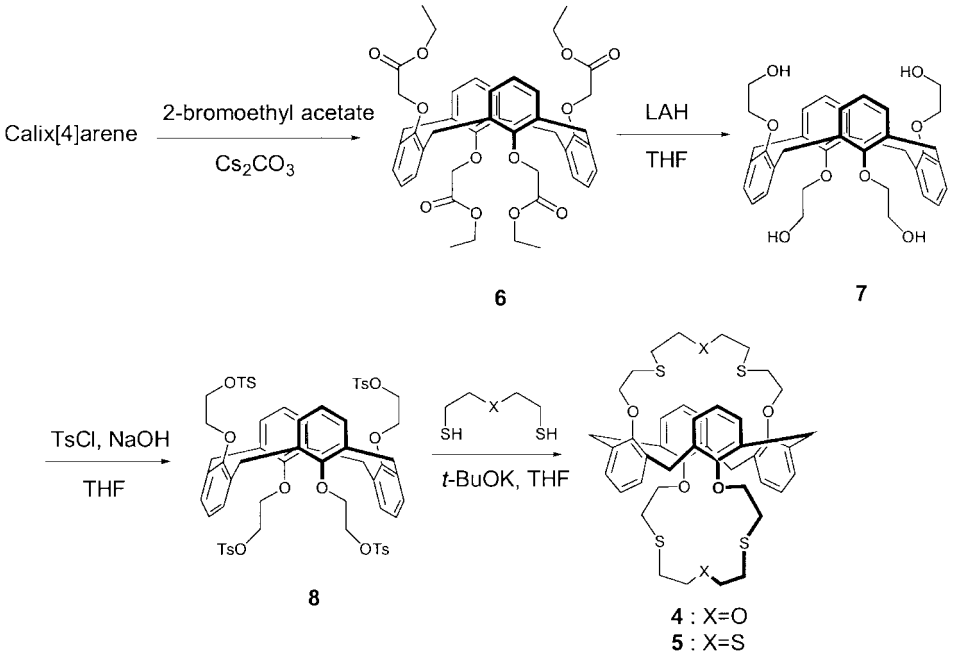


Scheme 2. Synthetic scheme for compounds **4** and **5**.

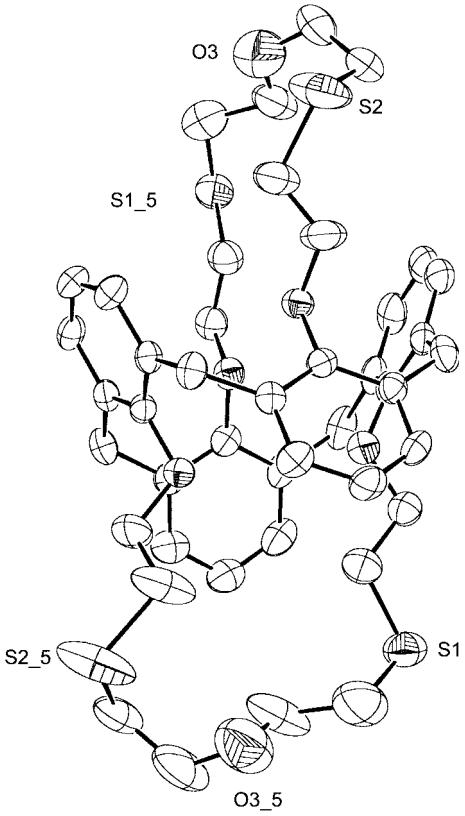


Figure 1. X-ray crystal structure of **4**. Hydrogen atoms are omitted for clarity.

Picrate extraction[10] for selected alkali, alkaline earth, and transition metal ions using **2**-**5** as hosts has been carried out. Percentage extractability (%)[10] for silver ion was recorded as 97.5, 80.1, 17.2, and 7.5, respectively. None of other metal ions were extracted. Calix[4]-*mono*-thiacrown showed better binding ability than the calix[4]-*bis*-thiacrown ether. This is attributable to the fact that although calix-*bis*-crowns have two cavities able to simultaneously capture two metal ions, they have been shown to have even worse extractability than calix-*mono*-crowns due not only to electrostatic repulsion between the two metal ions, but also to an induced conformation change that does not favor binding of the second metal.[11,3c] This extractability is consistent with the result of silver ion-induced chemical shift change upon the complexation.

Silver ion induced chemical shift changes have been determined by ^{1}H NMR as shown in Table 1. The -OC($\boldsymbol{H_g}$)$_2$-C($\mathbf{H}_f$)$_2$SC($\boldsymbol{H_e}$)$_2$- of **2** showed down-field shift changes, indicating silver ion is entrapped by the thiacrown ether linkage. In addition, importantly, Ar-$\boldsymbol{H_a}$ (*para* carbon) also revealed 0.48 ppm down-field shifting upon the complexation, implying the considerable π-metal interaction. In contrast, in the case of **4** and **5**, only a little change of chemical shift was observed, which is in accordance with the results of two-phase extraction that the extractability decreased in order of **2** > **3** > **4** > **5**. ^{1}H NMR study for **3**·$\mathbf{Ag}^+$ could not be described in this paper due to peak broadening. Investigation of silver ion oscillation through the symmetrical calix[4]thiacrown tube is in progress in our lab and will be reported soon.

Experimental Section

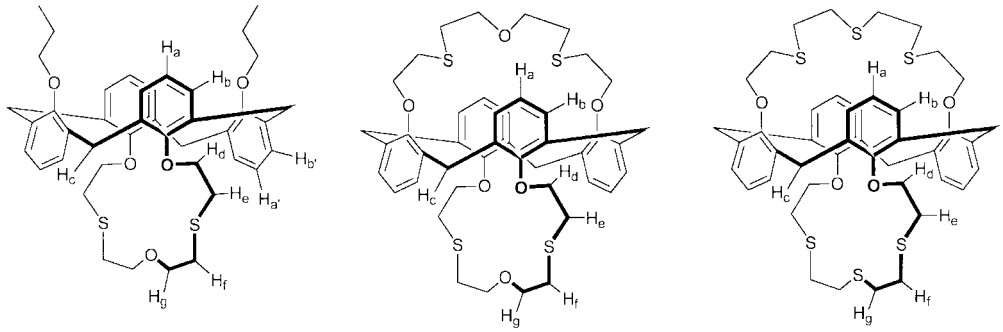
Unless specified otherwise, reagent-grade reactants and solvents were obtained from chemical suppliers and used as received. Dry solvents were prepared as follows: tetrahydrofuran was freshly distilled from sodium metal ribbon or chunks.

Table 1. Metal picrate extraction by calix[4]arene thiacrown ethers **2-4** and **5**

Ligand	Extractability (%) for cations[a]								
	Na^+	K^+	Rb^+	Cs^+	NH_4^+	Ag^+	Pb^{2+}	Sr^{2+}	Ba^{2+}
2	0.00	0.00	0.00	0.00	0.00	97.46	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	80.11	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	17.23	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	7.59	0.00	0.00	0.00

[a]The average value of three independent determinations. The experimental values deviate from the reported values by an average of ±10%.

Table 2. Ag^+-induced change in ^{1}H-NMR chemical shifts of lariat calixthiacrown ethers **2**, **4** and **5**



2 **4** **5**

Ligand	Induced chemical shift (ppm)[a]								
	a	b	a'	b'	c	d	e	f	g
2	+0.213	+0.145	+0.488	+0.181	+0.104	+0.217	+1.266	+0.982	+0.554
4	+0.006	+0.007	–	–	-0.002	+0.017	+0.023	+0.026	+0.015
5	+0.015	+0.014	–	–	+0.001	+0.007	+0.057	+0.022	+0.022

[a]Induced chemical shift (ppm) = (new chemical shift value of the complex)– (chemical shift of the ligand); the (+) and (–) imply down-field- and up-field-shifted signs on metal-ion complexation, respectively.

Synthesis. 25,27-Bis-(propyloxy)calix[4]-*mono*-dithiacrown-5 (2): To a refluxed solution of *t*-BuOK (0.448 g, 3.99 mmol) in THF (100 mL) was added dropwise a solution of **1** (1.00 g, 1.10 mmol) and 2-mercapto ethyl ether (0.184 g, 1.33 mmol) in THF (50 mL) for 2 h under nitrogen, and the reaction mixture was refluxed for an additional 24 h. After cooling to room temperature, 10% HCl (10 mL) was added and the solvent (THF) was removed under reduced pressure. The reaction mixture was extracted with CH_2Cl_2 (3×50 mL), washed with water and then dried over anhyd. $MgSO_4$. The crude product was chromatographed on silica gel using ethyl acetate and *n*-hexane (1 : 2) as eluent, and recrystallized from CH_2Cl_2/*n*-hexane (1 : 30, *v*/*v*) to give a white crystalline solid in 45% yield (0.35 g). Mp 256-259 °C. IR (KBr pellet): 2920, 1472, 1231, 1190, 1101, 821 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.19-6.75 (m, 12H, Ar-*H*), 3.80 (s, 8H, ArCH_2Ar), 3.69 (t, 4H, O$CH_2$$CH_2$S), 3.49 (t, 4H, O$CH_2$$CH_2$-$CH_3$), 3.35 (t, 4H, SCH$_2$$CH_2$O), 2.63 (t, 4H, OCH$_2$$CH_2$S), 2.17 (t, 4H, S$CH_2CH_2$O), 1.29-1.24 (m, 4H, OCH$_2$$CH_2CH_3$), 0.69 (t, 6H, OCH$_2CH_2$$CH_3$). ^{13}C NMR ($CDCl_3$): 134.0, 133.7, 129.0, 128.7, 122.4, 122.2, 73.5, 71.5, 68.7, 38.2, 33.3, 32.5, 22.5, 10.1 ppm. MS (FAB, *m/z*): 721 (M^++Na), 698 (M^+), 119.

25,27-Bis-(propyloxy)-*mono*-calix[4]trithiacrown-5 (3): General procedures are same as for **2**. A white crystalline solid with 47% yield. Mp 168-171 °C. IR (KBr pellet): 2919, 1457, 1220, 1112, 1011, 719 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.11-6.79 (m, 12H, Ar-*H*), 3.87 (s, 8H, ArCH_2Ar), 3.50 (t, 4H, O$CH_2$$CH_2$S), 3.37 (t, 4H, O$CH_2$$CH_2$$CH_3$), 2.69 (m, 8H, SC$H_2CH_2$S), 2.06 (t, 4H, OCH$_2CH_2$S), 1.16-1.05 (m, 4H, OCH$_2$CH_2CH$_3$), 0.58 (t, 6H, OCH$_2$CH$_2$CH_3). ^{13}C NMR ($CDCl_3$): δ 134.2, 133.6, 129.1, 128.7, 122.6, 121.8, 71.5, 67.5, 38.2, 33.7, 31.8, 30.7, 22.5, 10.1 ppm. MS (FAB, *m/z*): 738 (M^++Na), 715 (M^+), 87.

Calix[4]-*bis*-dithiacrown-5 (4): General procedures are same as for **2** except using 2.46 equivalents of **8**. A white crystalline solid with 29% yield. Mp 232-234 °C. IR (pellet): 2919, 1459, 1215, 1089, 996, 766 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.05 (d, 8H, Ar-*H*), 6.90 (t, 4H, Ar-*H*) 3.89 (s, 8H, ArCH_2Ar), 3.63 (t, 8H, ArOCH_2CH$_2$S), 3.41 (t, 8H, SCH$_2$CH_2O), 2.63 (t, 8H, ArOCH$_2$CH_2S), 2.07 (t, 8H, SCH_2CH$_2$O). ^{13}C NMR ($CDCl_3$): δ 156.4, 134.0, 128.8, 122.7, 73.3, 68.8, 38.2, 33.5, 32.8 ppm. MS (FAB, *m/z*) : 827 (M^++Na), 805 (M^+), 154.

Calix[4]-*bis*-trithiacrown-5 (5): A white crystalline solid with 28% yield. Mp 316-318 °C (dec.). IR (pellet): 2916, 1459, 1216, 1093, 1007, 769 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.07 (d, 8H, Ar-*H*), 6.92 (t, 4H, Ar-*H*) 3.88 (s, 8H, ArCH_2Ar), 3.49 (t, 8H, ArOCH_2CH$_2$S), 2.62 (br-s, 16H, SCH_2CH_2S),

Table 3. Crystal data for the X-ray diffraction studies on **4**

formula	$C_{44}H_{52}O_6S_4$
f.w.	805.2
crystal system	tetragonal
space group	$P4_12_12$
a (Å)	11.3452(7)
b (Å)	11.3452(8)
c (Å)	32.210(3)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	4145.9(6)
Z	4
F(000)	1712
calculated density (g cm^{-3})	1.290
radiation (Å) (Mo-Kα)	0.71073
no. of reflcns for measd	25
2θ range (°)	12.921-18.329
μ (mm^{-1})	0.276
temperature (K)	300
crystal size (mm)	0.5 × 0.3 × 0.5
color	colorless
diffractometer	Enraf-Nonius CAD-4
data collection method	w/2θ scans
absorption correction	psi-scan
no. of unique reflcns	3652
no. of observed reflcns. ($I_o \geq 2\ I_o$)	1955
θmax	25.0
hkl range	0 13; 0 13; 0 38
interval (count)	200
R_{int}	0.2244
no. of patameters	273
R & R_w	0.0888 & 0.2309
GOF	1.281
$(\Delta/\sigma)_{max}$	0.073
$(\Delta\rho)_{max}$ (e/Å^3)	0.427
$(\Delta\rho)_{min}$ (e/Å^3)	-0.344
extinction correction	0000

1.95 (t, 8H, OCH_2CH_2S). ^{13}C NMR ($CDCl_3$): δ 156.1, 133.7, 128.3, 122.6, 67.4, 38.1, 33.5, 31.5, 30.5 ppm. MS (FAB, *m/z*): 859 (M^++Na), 837 (M^+), 154.

25,26,27,28-Tetra(ethyl acetoethoxy)calix[4]arene (6): To a refluxing suspension of calix[4]arene (2.00 g, 4.53 mmol) and Cs_2CO_3 (8.87 g, 27.0 mmol) in dry acetone (150 mL) was added dropwise a solution of ethyl 2-bromoacetate (6.05 g, 36.2 mmol) in dry acetone (50 mL) over 3 h under nitrogen atmosphere. The reaction mixture was refluxed for an additional 24 h. After cooling to room temperature, the salt was filtered off and the solvent (acetone) was removed *in vacuo*. The reaction mixture was extracted with CH_2Cl_2 (3 × 50 mL), washed twice with water, dried over anhyd. $MgSO_4$, and the solvent was removed *in vacuo*. The crude product was chromatographed on silica gel using ethyl acetate and *n*-hexane (1 : 5) as eluent. Recrystallization from CH_2Cl_2/*n*-hexane (1 : 30, *v*/*v*) gave a white crystalline solid **6** in 29% yield (1.02 g). Mp 118-119 °C (lit.[9] 111-112 °C). IR (KBr pellet): 2921, 1771, 1439, 1181, 1092, 1048, 760 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.16 (d, 8H, Ar-*H*), 6.71 (t, 4H, Ar-*H*), 4.23 (q, 8H, OCH_2CH_3), 4.04 (s, 8H, $ArCH_2Ar$), 3.78 (s, 8H, $ArOCH_2$), 1.33 (t, 12H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 169.5, 155.4, 133.4, 130.3, 122.8, 69.6, 60.7, 35.5, 14.1 ppm.

25,26,27,28-Tetra(2-hydroxyethoxy)calix[4]arene (7): To a suspension of LAH (0.172 g, 4.68 mmol) in THF (100 mL) was added dropwise a solution of **6** (0.901 g, 1.17 mmol) in THF (50 mL) and the mixture was stirred at room temperature overnight. Excess LAH was destroyed by the addition of water, and the solvent (THF) was removed *in vacuo*. The crude product was extracted with CH_2Cl_2 (3 × 50 mL), washed with water, and dried over anhyd. $MgSO_4$. Recrystallization from CH_2Cl_2/*n*-hexane (1 : 30, *v*/*v*) gave a white crystal of **7** in 98% yield (0.69 g). Mp 264 °C (dec.). IR (KBr pellet): 3342, 2932, 1454, 1199, 1087, 1036, 925, 889, 822, 627 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.10 (d, 8H, Ar-*H*), 6.95 (t, 4H, Ar-*H*), 3.96 (s, 8H, $ArCH_2Ar$), 3.61 (t, 8H, $ArOCH_2CH_2OH$), 3.25 (t, 8H, $ArOCH_2CH_2OH$). ^{13}C NMR ($CDCl_3$): δ 156.1, 133.3, 130.5, 122.7, 71.4, 60.8, 38.1 ppm. MS (FAB, *m/z*): 601 (M^+), 163, 119.

25,26,27,28-Tetra(2-*p*-tosylethoxy)calix[4]arene (8): To a solution of **7** (1.00 g, 1.83 mmol) and *p*-toluenesulfonyl chloride (2.79 g, 14.6 mmol) in THF (150 mL) was added dropwise a solution of NaOH (3.66 g, 91.5 mmol) in water (5 mL) over 3 h under nitrogen atmosphere at 0 °C, and stirred for 30 min to ensure a homogeneous solution. The solution was warmed to room temperature and stirred for additional 24 h. After removing the solvent (THF), the reaction mixture was extracted with CH_2Cl_2 (3 × 50 mL), washed with water and dried over anhyd. $MgSO_4$. Removal of the solvent gave a white solid which was recrystallized from a mixture of CH_2Cl_2/*n*-hexane (1 : 30) to give the tetratosylate **8** in 79% yield (1.74 g). Mp 197-199 °C. IR (KBr pellet): 2926, 1598, 1461, 1361, 1176, 1094, 991, 925, 823, 768, 662 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.78 (d, 8H, CH_3Ar-*H*), 7.37 (d, 8H, CH_3Ar-*H*), 6.92 (d, 8H, Ar-*H*), 6.60 (t, 4H, Ar-*H*) 3.65 (s, 8H, $ArCH_2Ar$), 3.64 (t, 8H, $ArOCH_2CH_2O$), 3.50 (t, 8H, $ArOCH_2CH_2O$), 2.47 (s, 12H, Ar-CH_3). ^{13}C NMR ($CDCl_3$): δ 155.2, 145.0, 133.5, 129.9, 129.5, 127.920, 123.1, 67.7, 67.5, 37.0, 21.6 ppm. MS (FAB, *m/z*): 1239 (M^++Na), 1216 (M^+), 154.

Mass spectroscopy of complex. A mixture of **4** (20 mg) dissolved in $CHCl_3$ (10 mL) and excess AgOTf (at least 5 equivalent) was stirred for 1 h. After filtration of the precipitated excess AgOTf, the filtrate was evaporized *in vacuo* to give a white solid complex **4**·Ag^+OTf^-.

^{1}H NMR of complexes. Samples of metal picrate complexes were prepared for ^{1}H NMR as follows. A mixture of ligand (20 mg) and excess metal picrate (at least 5 equivalents) in $CDCl_3$ (3 mL) was stirred for 1 hr. After filtration of the excess metal picrate, the proton-NMR (400 MHz) spectra of the filtrate was obtained.

Two-phase extraction. The picrate concentration in the organic layer was analyzed with a UV-vis spectrometer. Metal picrate was prepared by reacting picric acid and metal

carbonate.[12] To obtain an association constant (K_a) and a stoichiometric coefficient between the extractant and metal picrate, an aqueous solution (2.0 cm^3) containing 0.20 mM metal picrate and chloroform solutions of the same volume according to the extractant concentration (0.1 mM) were mixed and equilibrated by shaking for 30 min at 25 °C. Concentrations of picrate anion extracted from the aqueous phase into the organic layer were determined by UV spectrophotometry (λ_{max} = 373 nm).

Determination of the X-ray crystal structure. A crystal of approximately $0.5 \times 0.3 \times 0.5$ mm was obtained by the slow evaporation of solvent from a solution of **4** in methanol. The crystal was mounted and aligned on an Enraf-Nonius Cad-4 diffractometer[13] and accurate monoclinic cell parameters were refined from setting angles of 25 reflections. MoKα radiation, using the $\omega/2\theta$ scan technique at room temperature. The data were collected for L-p, decay and empirical absorption corrections, and 3298 reflections were assumed as observed by applying the condition $F_o \geq 4\sigma$ (F_o) and space group $P4_12_12$ with Z = 4. The structure was solved by direct methods and was refined by a program for the refinement of crystal structures.[13] All hydrogen atoms were placed in their calculated positions and allowed to ride on their parent carbon atoms.

Acknowledgment. This work was supported by Grant (KCS-KOSEF-2001-05) from Korean Chemical Society and Korea Science & Engineering Foundation. We also thank KBSI in Daejeon for instrumental supporting (600 MHz NMR and High Resolution Tandem Mass Spectrometry).

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