

Carboxylate Selective Calix[6]arene Ruthenium Complex

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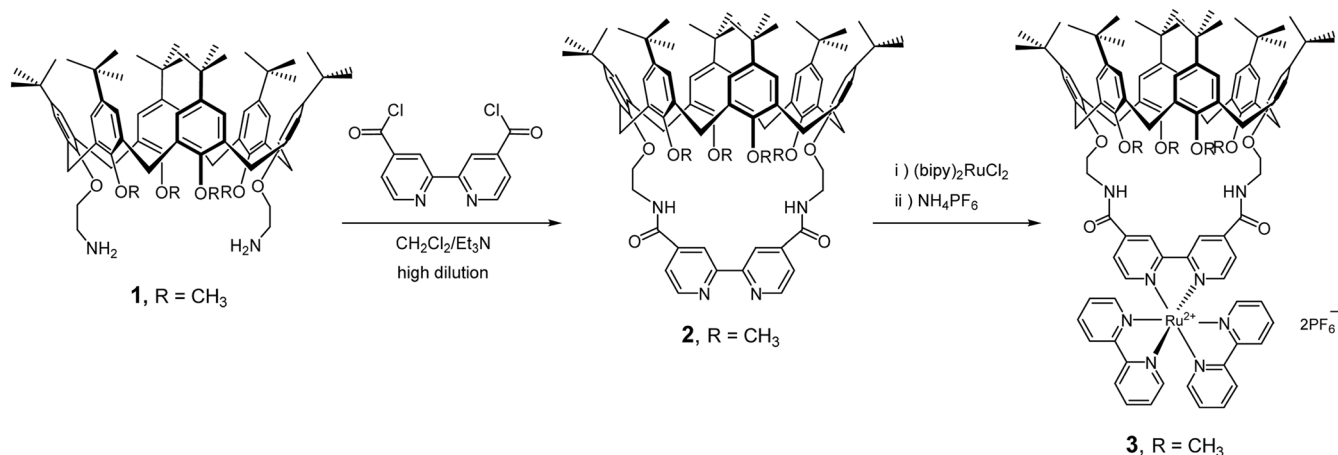
Anions play an important fundamental role in biological and chemical processes, and considerable attention has been focused on the design of host molecules that can recognize and sense anion species selectively.^{1,2} Over the last 30 years there has been a considerable research interest in transition metal bipyridine complexes, especially those of ruthenium.^{3,4} This is attributed predominantly due to the chemical stability, redox properties, excited state reactivity and luminescence⁵ emission that the coordination complexes exhibit. Beer and coworkers^{6,7} reported the several anion selective calix[4]arene complex with ruthenium,⁸ but calix[6]arene ruthenium complex was not reported yet, presumably due to the difficulties of modifying of calix[6]arene. Redox-active⁹⁻¹² and photoactive¹³ calix[6]arene ruthenium(II) complex could be an attractive candidate to be utilized as an electrochemical receptor for anions. Here we reported the synthesis of a novel calix[6]arene ruthenium(II) bipyridyl anion receptor and its electrochemical and binding properties in the presence of anions are investigated.

Results and Discussion

Synthesis. The key step for synthesizing ligand **3** is a bridge reaction of two amines in **2** with a bipyridyl unit as shown in Scheme 1. Bridge reaction was conducted in dilute solution in 38% yield. The ruthenium(II) bipyridyl calix[6]arene complex **3** was prepared by refluxing $[\text{RuCl}_2(\text{bipy})_2] \cdot 2\text{H}_2\text{O}$ with **2** in a mixture of EtOH, H_2O and acetic acid, followed by the precipitation of the hexafluorophosphate

complex on addition of ammonium hexafluorophosphate. ^1H NMR spectrum of **2** showed the characteristics of bipyridine¹⁴ such as two doublets and a singlet at δ 8.69, 7.63 and 8.09 and a broad triplet at δ 7.87 for the amide N-H protons. Much complicated aromatic spectral features were observed for the ligand **3** due to the ruthenium complex and a singlet at δ 9.18 for the amide protons was observed.

The anion binding property was investigated from the ^1H NMR titration in CD_3CN and $\text{DMSO}-d_6$. The ^1H NMR spectrum of **3** shows dramatic changes in the presence of anions such as carboxylate particularly in CD_3CN . The chemical shift of amide proton was shifted from δ 8.0 to 11.5 in the presence of 1 equivalent of acetate drastically and then saturated upon addition of further acetate, indicating that ligand **3** bind with acetate very strongly and 1:1 stoichiometry. But most carboxylates such as acetate, benzoate, and phenyl acetate showed a similar change. For the comparison of several carboxylate binding abilities toward ligand **3**, $\text{DMSO}-d_6$ was used as a solvent. Table 1 summarized the stability constants from the EQNMR¹⁵ calculation. The stability constants of acetate showed the highest at 6190 and that of benzoate was the lowest at 360, indicating that the basicity of carboxylate could be the major force for the anion binding. It was expected that the large calix[6]arene receptor might be bound strongly with the large anion such as benzoate, but not in this case. The relative magnitudes followed the order $\text{CH}_3\text{CO}_2^- > \text{PhCH}_2\text{CO}_2^- > \text{H}_2\text{PO}_4^- > \text{Cl}^- > \text{PhCO}_2^-$. In acetonitrile solution, K_a values were too high to compare the relative binding strength. A similar trend was



Scheme 1. Synthesis of ruthenium complex **3**.

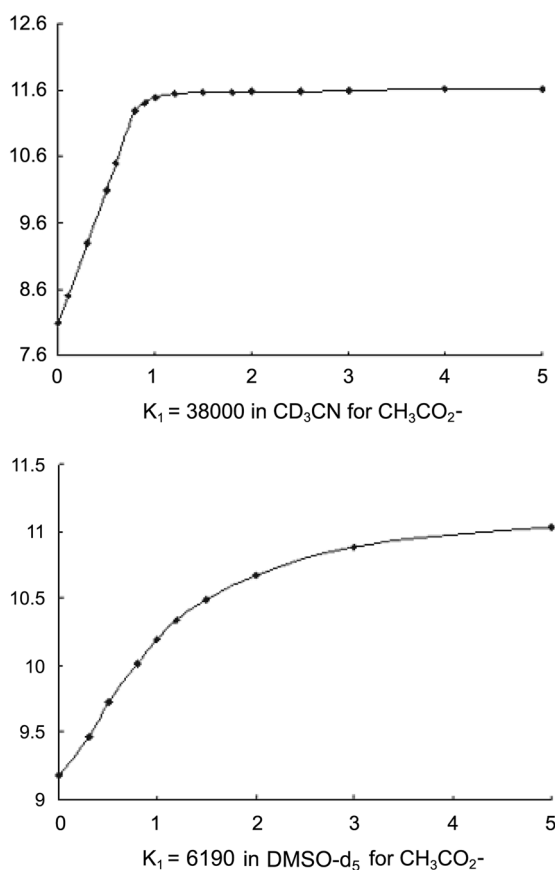


Figure 1. ^1H NMR titration data for **3** in CD_3CN and $\text{DMSO}-d_6$.

Table 1. Stability constants (K_a) and cathodic shifts of ruthenium complex **3** in the presence of anions

Anion	$K_a/\text{dm}^3\text{mol}^{-1}$	ΔE^b (mV)
CH_3CO_2^- ^c	6190	132
PhCO_2^-	360	96
H_2PO_4^-	1570	ppt
Cl^-	640	76
$\text{PhCH}_2\text{CO}_2^-$	3600	98

^aNMR titration was conducted in $\text{DMSO}-d_6$. ^bThe cathodic shift was carried out in CH_3CN . ^cTetrabutylammonium salts. Errors estimated to be <10%.

observed from the electrochemical property as shown in Table 1.

In summary, a novel calix[6]arene ruthenium complex **3** was synthesized by the bridge reaction of the corresponding amine and bipyridine unit and followed by the metalation. A high binding stability for the acetate was observed and a further application of ligand **3** are in progress.

Experimental

Bipyridine bridged of 5,11,17,23,29,35-hexa-tert-butyl-37,40-bis(aminoethoxy)-38,39,41,42-tetramethoxycalix[6]arene (2). To a solution of 300 mL of CH_2Cl_2 with 0.5 mL (3.6 mmol) of Et_3N , 1.1 g of **1**¹⁶ (1.0 mmol) in 100 mL of CHCl_3 and 0.32 g (1.3 mmol) acid chloride of bis

carboxylic bipyridine in 100 mL of CH_2Cl_2 prepared by refluxing in 20 mL (0.27 mol) of SOCl_2 for 3 days were added slowly over the period of 5 h while the solution heated to reflux under nitrogen atmosphere. After refluxing the mixture over night, the solvents were removed and the residue was purified by column chromatography (eluant; $\text{CH}_2\text{Cl}_2:\text{MeOH} = 10:1$) to yield 0.5 g (38%) of **2**. ^1H NMR (CD_2Cl_2) δ 8.69 (d, 2H, BpH, $J = 4.8$ Hz), 8.09 (s, 2H, BpH), 7.87 (broad s, 2H, NH), 7.63 (d, 2H, BpH, $J = 4.9$ Hz), 7.07, 6.98 and 6.62 (three s, 12H, ArH), 4.35, 3.68, 3.38 and 3.24 (two pair of d, 12H, ArCH_2Ar), 4.07 and 3.94 (two t, 8H, $-\text{OCH}_2\text{CH}_2-$), 2.81 (s, 12H, $-\text{OCH}_3$), 1.16 and 1.04 (two s, 54H, $-\text{C}(\text{CH}_3)_3$). ^{13}C NMR (CD_2Cl_2) δ 167.38 ($-\text{CONH}-$), 157.17, 153.99, 152.35, 150.84, 146.79, 146.14, 144.18, 133.78, 126.15, 126.02, 121.72 and 120.06 (Bp and Ar), 71.75 ($-\text{OCH}_2-$), 60.58 ($-\text{OCH}_3$), 41.45 ($-\text{CH}_2\text{N}-$), 34.42, 34.27, 31.46, 31.42 and 30.44 (ArCH_2Ar and $-\text{C}(\text{CH}_3)_3$). MAS-FAB m/z : 1346 $[\text{M}+\text{Na}]^+$. Anal. Calcd for $\text{C}_{86}\text{H}_{106}\text{N}_4\text{O}_8$: C, 78.06; H, 8.02; N, 4.24. Found: C, 74.93; H, 8.85; N, 3.92.

Bipyridine Ru-complex of bis(aminoethoxy)-calix[6]-arene (3). A solution of 0.4 g (0.27 mmol) of **2** in 35 mL of EtOH, 5 mL of H_2O and 1 mL of acetic acid mixture and 0.14 g (0.27 mmol) of $[\text{RuCl}_2(\text{bipy})_2]\cdot 2\text{H}_2\text{O}$ was refluxed for 1 h. The solvent was removed and the residue was purified by column (eluant; $\text{MeOH}:\text{Acetic acid} = 8:1$). Chloride anion was replaced with PF_6^- anion by dissolving in $\text{H}_2\text{O}/\text{MeOH}$ (50/40 mL) and precipitate with NH_4PF_6 . The precipitate was collected and extracted with CH_2Cl_2 in distilled water. The organic layer was separated and removed the solvent. The product was dried under vacuum for 2 days to give 0.3 g (50%) of **3**. ^1H NMR (CD_3CN) δ 9.00 (s, 2H, BpH), 8.49 (dd, 4H, BpH), 8.08 (m, 4H, BpH), 8.04 (s, 2H, $-\text{CONH}$), 7.84 (dd, 4H, BpH), 7.64 (d, 2H, BpH), 7.48 (d, 2H, BpH), 7.42 (t, 2H, BpH), 7.25 (t, 2H, BpH), 7.1-6.7 (six s, 12H, ArH), 4.5-3.1 (three pair of d, 12H, ArCH_2Ar), 4.1-3.7 (m, 8H, $-\text{OCH}_2\text{CH}_2\text{N}-$), 3.07-2.76 (two s, 12H, $-\text{OCH}_3$), 1.09, 1.05 and 1.03 (three s, 54H, $-\text{C}(\text{CH}_3)_3$). ^{13}C NMR (CD_3CN) δ 164.18 ($-\text{CO}-$), 157.64, 157.29, 157.13, 153.99, 152.65, 152.05, 151.49, 146.44, 146.00, 154.94, 143.47, 138.57, 138.46, 133.77, 133.47, 133.21, 133.17, 133.03, 132.90, 128.25, 128.13, 126.23, 125.98, 125.82, 124.84, 124.79 and 122.80 (Bp and Ar), 71.12 ($-\text{OCH}_2-$), 60.29 ($-\text{OCH}_3$), 41.53 ($-\text{CH}_2\text{N}-$), 34.47, 34.19, 31.15, 29.61, 29.33 and 29.22 (ArCH_2Ar and $-\text{C}(\text{CH}_3)_3$). MAS-FAB m/z : 1882 $[\text{M}-\text{PF}_6]^+$. Anal. Calcd for $\text{C}_{106}\text{H}_{212}\text{N}_8\text{O}_8\text{RuF}_{12.5}\text{H}_2\text{O}$: C, 60.14; H, 6.24; N, 5.29. Found: C, 60.18; H, 6.46; N, 5.09.

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