

# A new carboxylate anion selective cobaltocenium calix[4]arene receptor

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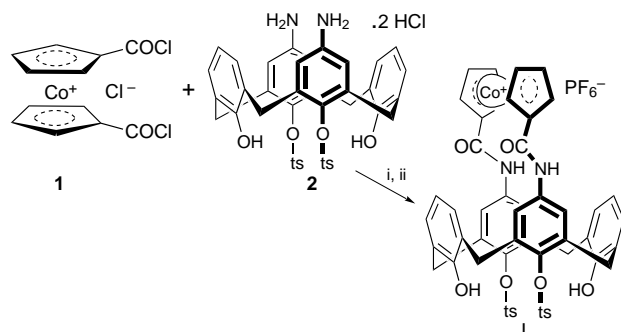
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**A new upper-rim cobaltocenium bridged calix[4]arene receptor L is synthesised and by virtue of its unique topology exhibits remarkable carboxylate anion selectivity.**

The synthesis of positively charged or neutral electron-deficient abiotic receptor molecules designed to non-covalently bind<sup>1</sup> and sense<sup>2</sup> anions of biochemical, medical and environmental importance is an area of intense current research activity. As a consequence of their inimitable upper- and lower-rim topologies the calixarenes<sup>3</sup> are attractive host molecules to modify and so create unique cavities for the recognition of target guest species. Although this has been exploited for the recognition of metal cations,<sup>4</sup> in contrast calixarene anion receptors are still relatively rare.<sup>5</sup> We report here the synthesis of a new upper-rim cobaltocenium-bridged calix[4]arene receptor L which by virtue of its topology exhibits remarkable carboxylate anion selectivity.

The condensation of 1,1'-bis(chlorocarbonyl)cobaltocenium chloride **1**<sup>6</sup> with the upper-rim bis-amine-substituted calix[4]arene derivative **2**<sup>7</sup> in dry acetonitrile in the presence of triethylamine initially gave a crude product which after silica column chromatography and addition of ammonium hexafluorophosphate afforded L as a yellow powder in 38% yield (Scheme 1).



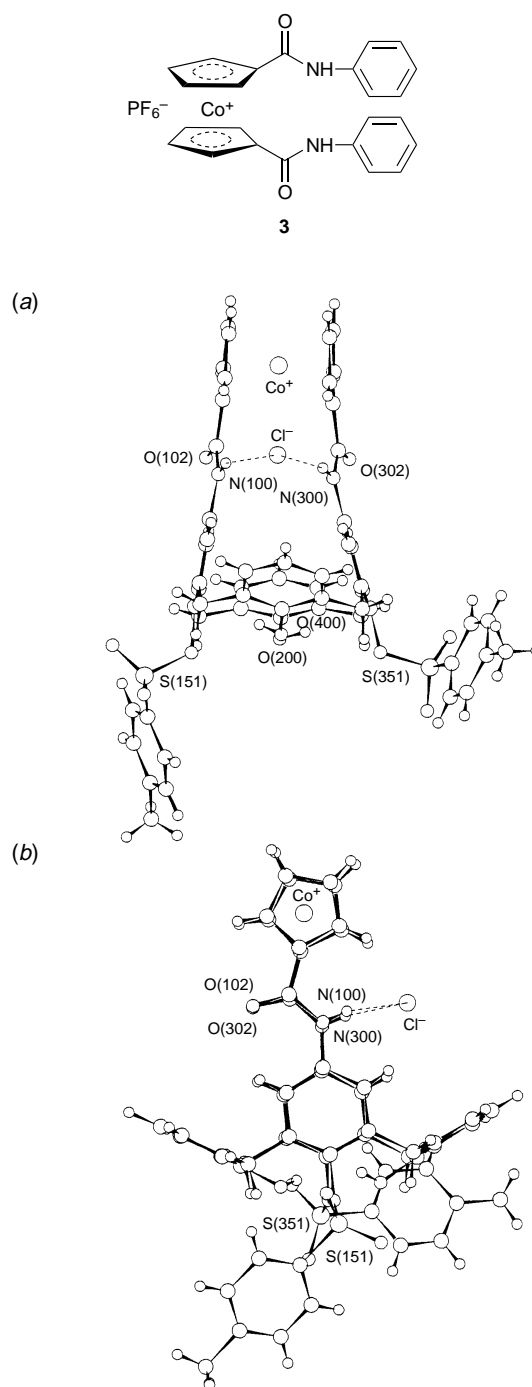
**Scheme 1** Reagents: i, MeCN–thf–py; ii, NH<sub>4</sub>PF<sub>6</sub>; ts = O<sub>2</sub>SC<sub>6</sub>H<sub>4</sub>Me-*p*

**Table 1** Stability constant data in (CD<sub>3</sub>)<sub>2</sub>SO

Anion	K <sup>a</sup> /dm <sup>3</sup> mol <sup>-1</sup>	
	L	<b>3</b>
Cl <sup>-</sup>	70	35
Br <sup>-</sup>	— <sup>b</sup>	—
NO <sub>3</sub> <sup>-</sup>	125	—
HSO <sub>4</sub> <sup>-</sup>	40	—
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	6 380	320
MeCO <sub>2</sub> <sup>-</sup>	41 520	1560
PhCO <sub>2</sub> <sup>-</sup>	38 400	—
PhCH <sub>2</sub> CO <sub>2</sub> <sup>-</sup>	22 270	—
C <sub>10</sub> H <sub>17</sub> CO <sub>2</sub> <sup>-</sup>	19 750	—

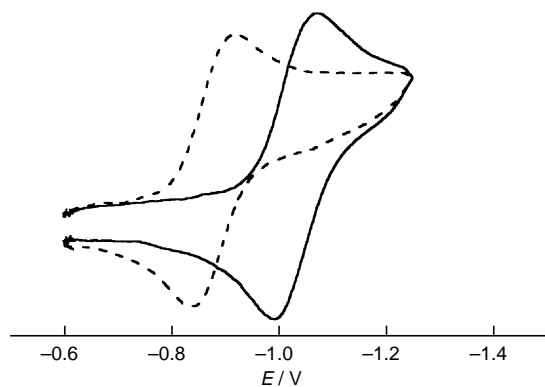
<sup>a</sup> Errors estimated to be ≤10%. <sup>b</sup> Very weak binding, a stability constant value could not be calculated in this solvent.

The anion coordination properties of L were investigated by <sup>1</sup>H NMR anion titration experiments in (CD<sub>3</sub>)<sub>2</sub>SO solution with various tetrabutylammonium halide, nitrate, dihydrogen phos-



**Fig. 1** Structure of the chloride complex of L

phate, hydrogen sulfate and carboxylate salts. Substantial downfield perturbations of the receptor's amide and cyclopentadienyl protons were observed especially with carboxylate anionic guests, suggesting anion binding is taking place at the upper-rim vicinity of the receptor. It is noteworthy that with benzoate and  $\beta$ -naphthylcarboxylate anions large upfield perturbations of the receptor's aryl calix[4]arene protons of 0.6 ppm were also seen. Stability constants were calculated from the resulting titration curves using EQNMR<sup>8</sup> and these values are presented in Table 1 which includes stability constant data for acyclic receptor **3**. The receptor **L** exhibits remarkable thermodynamic stability and selectivity preferences for carboxylate anions, in particular for acetate over  $\text{H}_2\text{PO}_4^- \gg \text{NO}_3^- > \text{Cl}^- > \text{HSO}_4^- > \text{Br}^-$ . In comparison **3** forms a much weaker complex with the acetate anion (Table 1). These novel anion coordination properties may be attributable to the upper-rim rigidly held cobaltocenium bridging unit of **L** creating a unique and ideal bidentate amide (CO–NH) hydrogen-bond donor environment of complementary topology for recognising bidentate anions such as carboxylates. The X-ray crystal structure of the chloride complex of **L** corroborates this postulation<sup>‡</sup> [Fig. 1(a), (b)]. As is clearly shown particularly in Fig. 1(a) the calix[4]arene has the typical flattened cone conformation with  $C_2$  distortion. The angles made by the four phenyl rings and the plane of the four methylene carbon atoms are 106.8, 28.4, 98.9 and 29.8°. The two angles  $> 90^\circ$  illustrate



**Fig. 2** Cyclic voltammograms of **L** in MeCN in the absence (---) and presence (—) of 3 equiv.  $\text{NBu}_4\text{O}_2\text{CMe}$

**Table 2** Electrochemical data for **L**<sup>a</sup>

Anion	$\Delta E^b/\text{mV}$
$\text{Cl}^-$	60
$\text{NO}_3^-$	20
$\text{HSO}_4^-$	10
$\text{H}_2\text{PO}_4^-$	130
$\text{MeCO}_2^-$	155
$\text{PhCO}_2^-$	140
$\text{PhCH}_2\text{CO}_2^-$	150
$\text{C}_{10}\text{H}_{17}\text{CO}_2^-$	135

<sup>a</sup> Obtained in acetonitrile solution containing  $0.1 \text{ mol dm}^{-3}$   $\text{NBu}_4\text{PF}_6$  as supporting electrolyte. <sup>b</sup> Cathodic shift perturbations of cobaltocenium/cobaltocene redox couple of **L** produced by presence of anions (up to 5 equiv.) added as their tetrabutylammonium salts.

that the tops of the two phenyl rings of the calixarene are pulled together so that the cobaltocenium bridge can be formed [Fig. 1(b)]. However, despite being attached to the upper rim of the calixarene, the two cyclopentadiene rings are almost coplanar intersecting at an angle of  $7.6^\circ$ . The Co–C distances are in the range 2.04(1)–2.10(1) Å. In addition to the cobaltocenium linkage as shown in the Figure, the two N–H groups form hydrogen bonds to the chloride anion  $\text{Cl}(1)\cdots\text{N}(100)$  3.287,  $\text{N}(300)$  3.298 Å.

Electrochemical anion recognition studies in acetonitrile solutions reveal **L** to electrochemically sense carboxylate anions through substantial cathodic shift perturbations of up to  $\Delta E = 155 \text{ mV}$  of the reversible cobaltocenium–cobaltocene redox couple (Fig. 2, Table 2) at 0.85 V. Thus **L** is a first-generation prototype amperometric selective sensing reagent for carboxylate anionic guest species.

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## Footnotes

<sup>†</sup> Visiting scholar from Chonnam National University, Republic of Korea.

<sup>‡</sup> Crystal data for  $\text{Cl}\cdot\text{MeCN}$ ,  $\text{C}_{56}\text{H}_{47}\text{ClCoN}_3\text{O}_{10}\text{S}_4$ ,  $M = 1080.5$ , orthorhombic, space group  $Pbca$ ,  $a = 15.401(12)$ ,  $b = 17.418(13)$ ,  $c = 31.43(4)$  Å,  $U = 10\,578$  Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.362 \text{ Mg m}^{-3}$ , 15 659 reflections measured ( $R_{int} = 0.065$ ), 6660 independent reflections refined on  $F^2$  to  $R$  of 0.0871. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/322.

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