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Novel redox-active calixarenes

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Abstract

The synthesis of two redox-active calixarenes is described and their structure determined by a combination of mass spectrometry, infrared and $^{1}H/^{13}C$-NMR spectroscopy. A preliminary report of complexation with alkali and alkaline earth cations is presented also. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Calixarenes may be considered as three-dimensional building blocks for the design of new receptors which simultaneously possess a hydrophobic cavity suitable for the inclusion of small organic molecules and hydrophilic sites (e.g. hydroxyl groups) to coordinate cationic guests [1–4]. Calix-[4]-arene derivatives are generally conformationally mobile in solution and their binding capability is often improved by creating a well-defined cavity suitable for hosting small guests. This is achieved by covalent linking of two or more points of the skeleton by a chain of atoms as is illustrated by the family of calix crowns [2,3]. The combination of a calixarene and a polyether chain provides a hydrophobic cavity which is able to include organic substrates together with the metal complexing sites of a crown ether, thus creating receptors with high selective binding properties towards alkali and alkaline earth cations [5]. Calixarenes with diaza-oxa bridges are also able to coordinate softer ions and hence form complexes with mono-, di- or trivalent cations. Such ligands encapsulate the metal ion into an organic microenviroment which may prevent or at least reduce the interaction between the metal ion and solvent molecules. This produces complexes which may promote energy transfer from host to guest and hence display luminescent properties [6]. The incorporation of redox-active centres into a calix-[4]-arene host may also lead to a new class of molecular sensor and/or catalyst capable of detecting or catalysing redox reactions on a guest species [7,8]. The work reported below represents the first step in the design and synthesis of calix crowns potentially affording both photo- and redox-active properties.

2. Experimental

All reactions were carried out using anhydrous solvents unless otherwise stated. The solvents were dried by the usual procedures and stored under dinitrogen gas atmosphere and over activated molecular sieves. Chromatography columns were packed using Kieselgel 60 (70–230 mesh) or aluminium oxide type 507C neutral (100–125 mesh). ^{1}H- and ^{13}C-NMR spectra were recorded on either Bruker AM360 or Bruker AMX400 spectrometers. ^{1}H-NMR spectra were referenced to TMS as internal standard and ^{13}C-NMR spectra were referenced to the solvent signal at 77 ppm in $CDCl_3$ or 1.3 ppm in CD_3CN. ^{13}C DEPT spectra were recorded

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using the 135° pulse sequence, giving positive signals for CH_3 and CH, negative signals for CH_2 and no signal for quaternary (ipso) carbon atoms. Mass spectra were obtained using FAB with a thioglycerol or 3-NBA matrix on a Kratos MS890MS instrument at the ULIRS Mass Spectrometry Service King's College London or a V.G. Analytical ZAB-SE double focusing reverse geometry mass spectrometer at the School of Pharmacy, University of London, Brunswick Sq. Infra-red spectra were recorded as KBr discs using a Perkin Elmer FT-IR spectrometer (Paragon 1000). Cyclic voltammograms were recorded at 293K using an EG&G Model 273 potentiostat with Model 270 software controlled by a Viglen computer connected to a Hewlett–Packard Colour Plotter for graphical output. The cyclic voltammetry experiments were conducted in dry, nitrogen-purged CH_3CN or dry, nitrogen-purged propylene carbonate with 0.1 M Bu_4NClO_4 as supporting electrolyte, Ag | AgCl (sat. AgCl in 3 M NaCl) or Ag | $AgNO_3$ (0.01 M in acetonitrile) as the reference electrode and a Pt wire as both counter and working electrode. The scan rate was normally 100 mV s^{-1} with IR compensation applied during each scan.

1,1′-bis-Chlorocarbonylferrocene **2** was synthesised as described previously [9–11]. A sample of the calixarene, **1**, was kindly supplied by Professor J. Vicens (Strasbourg).

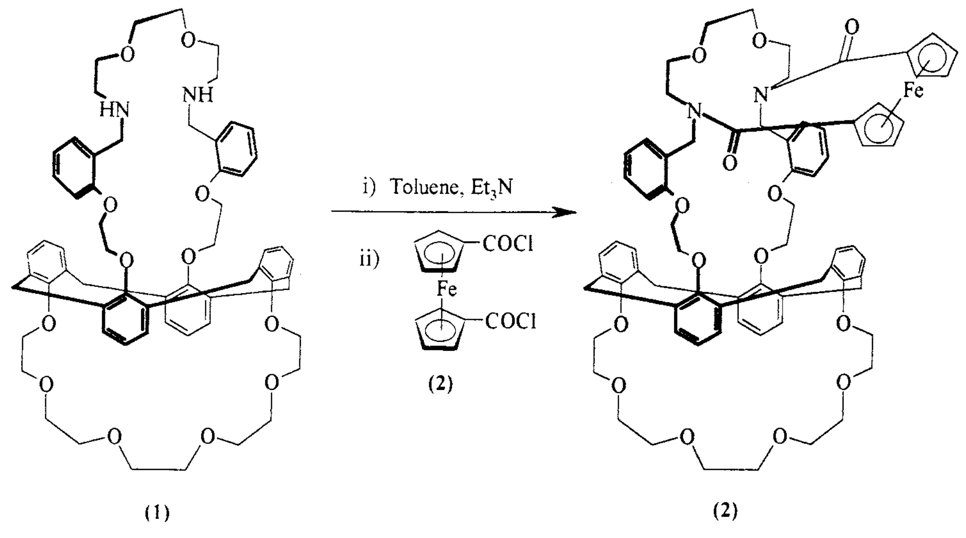
2.1. Synthesis

*2.1.1. Synthesis of cryptand, **3***

A 500 ml three-necked flask equipped with a mechanical stirrer was flushed with nitrogen and charged with dry toluene (50 ml). A solution of 1,1′-bis-chlorocarbonylferrocene (**2**, 90 mg, 0.29 mmol) dissolved in dry toluene (50 ml) and a solution containing the cryptand (**1**, 300 mg, 0.29 mmol) and triethylamine (0.4 ml, 2.9 mmol) in dry toluene (50 ml) were added dropwise and simultaneously by automatic syringe to the vigorously stirred toluene solvent at room temperature. After stirring overnight, the orange mixture was filtered through a fluted paper (to remove Et_3NHCl) and the filtrate was evaporated to leave an orange solid. The solid was dissolved in dichloromethane (50 ml), washed with water (2 × 20 ml), dried and the solvent evaporated. The orange solid was redissolved in dichloromethane and chromatographed on neutral alumina with a mixture of dichloromethane/0.2% methanol. The orange band was collected and evaporated to give 0.11 g, (31%) of an orange powder, m.p. > 250° (d), ms (FAB), 1277 ($M+1$). Elemental analysis, found: C, 68.83; H, 6.87; N, 2.15%; Calc. for $C_{74}H_{80}N_2O_{14}Fe.H_2O$: C, 68.62; H, 6.38; N, 2.16%. IR (KBr, cm^{-1}), 3435 (br, OH str); 1616 (amide, C=O); 1243 (aromatic, C–O str); 1096 (aliphatic C–O str). The ^1H-NMR spectrum was poorly resolved but split into three regions: δ (ppm); 6.7–7.5 (20H, aromatic H); 4.0-5.3 (10H, mainly cp); 2.7–4.0 (50H, $OCH_2 + NCH_2 + C–CH_2$). There was also a broad peak at 1.7 ppm (4H) corresponding to two molecules of water. ^{13}C (tetrachloroethane, δ ppm): 37.8, 38.0 (Ar–CH_2–Ar); 42.7(br), 47.9, 49.3, 49.9 (NCH_2); 68.1,69.3, 69.6 (centre of three signals), 70.6, 70.7, 70.8, 70.9, 71.0, 71.6, 71.8, 73.0, 76.9, 82.6, (OCH_2 and ferrocene-C); 120.7, 120.9, 122.4, 122.6, 122.8, 123.0, 124.9, 125.3, 126.1, 127.2, 127.7, 128.0, 129.6, 129.7, 130.0 (two signals?), 130.2, 133.3, 133.4, 133.6, 133.9, 134.0, 134.2, (aromatic CH and ipso-C); 155.8, 156.2, 156.3, 156.7 (ipso aromatic C–O); 170.0, 171.5 (C=O).

*2.1.2. Reduction of **3** to **4***

Fresh $LiAlH_4$ (50 mg, 1.3 mmol) was added to a stirred solution of (**3**, 100 mg, 0.08 mmol) in a mixture of dichloromethane (18 ml) and THF (3 ml) [12]. The colour of the solution changed rapidly from deep orange to light yellow and the mixture was then treated with water (0–3 ml) in THF (2 ml) and filtered. Evaporation of the filtrate gave 80 g (81%) of an orange solid, m.p. > 250° d. Mass spectrum (FAB) = 1250 ($M+1$,



(1) (2)

and base peak); elemental analysis, found: C, 69.39; H, 7.80,; N, 1.90%; Calc. for $C_{74}H_{84}N_2O_{12}Fe \cdot 2H_2O$: C, 69.15; H, 6.90; N, 2.18%. IR (KBr, cm^{-1}): 3423 (br, adventitious H_2O), 2922–2864 (C–H str), 1451 (CH_2, def), 1249 (aromatic C–O str), 1095, 1047 (aliphatic C–O str). The ^1H-NMR although simplified relative to **3** could again be resolved only into three broad regions: 6.7–7.5 (20H, aromatic); 3.8–4.2 (ca. 10H, mainly cp); 3.0–3.8 (54H, $OCH_2 + NCH_2 + CCH_2$). ^{13}C (CD_2Cl_2, δ ppm): 36.4, 37.9 (Ar–CH_2–Ar); 52.0, 52.5, 54.9 (N–CH_2); 68.7, 70.7, 71.0, 71.1, 71.3, 71.4, 71.5, 72.0, 72.1, 72.4 (O–CH_2); 68.2,68.5, 72.7 (all br. Fc–CH); 85.2 (Fc-ipso); 131.7, 131.1, 130.6, 128.1, 122.8 (two signals), 122.3, 121.1, 112.7, 112.1 (aromatic CH); 133.9, 133.5, 129.4, 113.7 (aromatic ipso-C); 156.4 (two signals?), 158.1 (ipso aromatic C–O).

3. Results and discussion

The calixarene, **1**, capped with a bis-aza-oxa-crown was reacted with **2** in toluene and in the presence of triethylamine gave the redox-active cryptand, **3**, in a 31% yield. The compound was characterised by elemental analysis, mass spectrometry, IR and $^1H/^{13}C$-NMR. The ^1H-NMR spectrum showed three distinct regions (aromatic, cyclopentadiene and $OCH_2 + NCH_2 + CCH_2$) with the correct relative integrations of 20:8:52. In addition, a water peak was in evidence at 1.7 ppm which was probably occluded within the structure. The ^{13}C spectrum showed also all the relevant peaks in the correct chemical shift regions (C=O, aromatic, cp, OCH_2, NCH_2 and CCH_2) and the complexity of the spectrum suggested a lack of symmetry within the molecule. It is now well-established that amide cryptands containing ferrocene may exist in *cis* or *trans* configuration [13] although the *trans* form usually predominates both in solution and in the solid state [14]. High temperature NMR (to 120°C in tetrachlorodideuterioethane) had very little effect on the spectrum and hence the *trans* structure is apparently very rigid. The IR spectrum showed a strong tertiary amide carbonyl at 1616 cm^{-1} together with aromatic (ca. 1240 cm^{-1}) and aliphatic (1095 and 1050 cm^{-1}) C–O stretching vibrations and both aromatic (3050 cm^{-1}) and aliphatic (2931, 2874 cm^{-1}) C–H stretching vibrations. In addition, there was a strong broad band at 3435 cm^{-1} again indicative of water complexed within the structure.

Attempts to detect complexation with metal cations by NMR met with little success. For example, a 1:1 molar ratio mixture of **3** with $Ba(CF_3SO_3)_2$ in $CDCl_3$/CD_3CN gave an ^1H-NMR spectrum which was similar, though not identical, to the parent cryptand. Heating the complex mixture to 50°C produced a sharp spectrum which was clearly different to that of **3** but the shifts associated with each resonance signal were impossible to assign with any confidence.

Cyclic voltammetry (CV) was used to give a clearer indication of complexation. In propylene carbonate as solvent the cryptand gave a pseudo-reversible wave (E_c–$E_a \approx 150$ mV) with a redox potential of 630 mV relative to Ag | AgCl (Fig. 1a). Because the ferrocene content of the cryptand was low, however (ca. 15% by weight) the current response (± 10 μA) was also low and hence the CV data of the complexes was often difficult to interpret. A range of cations was used, all as their

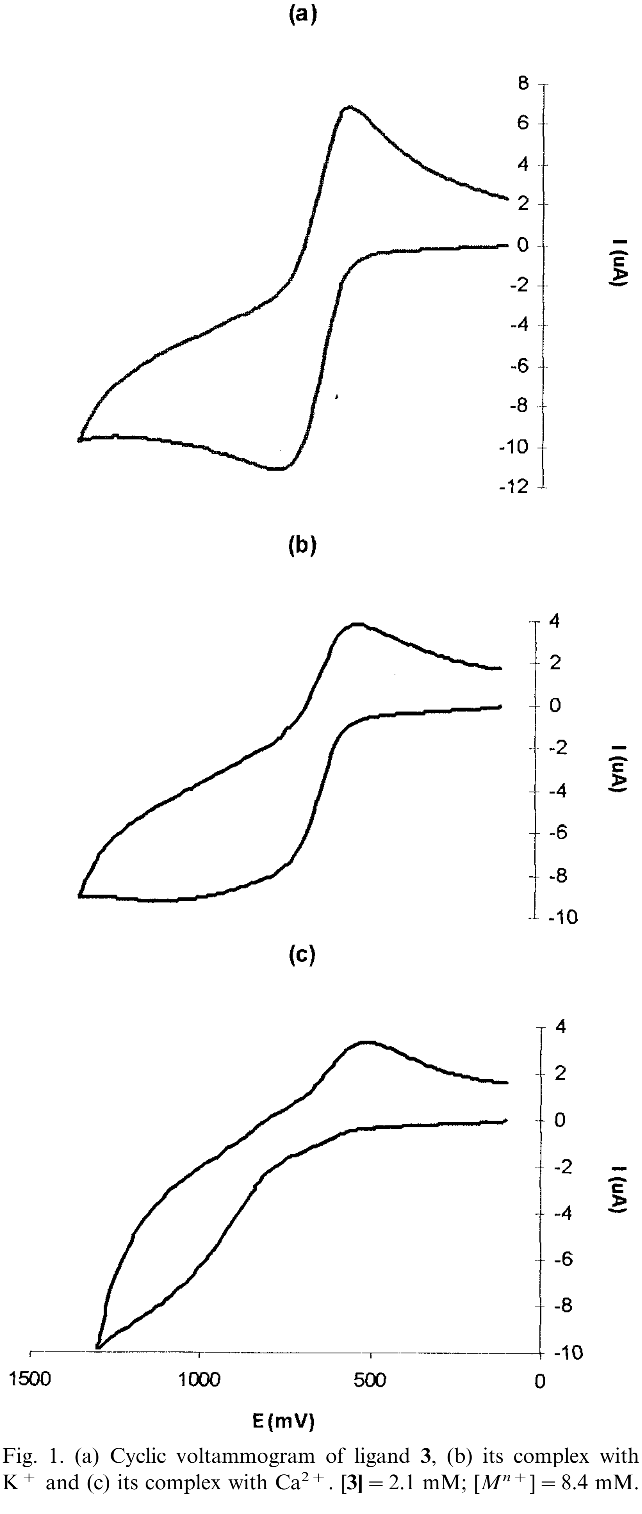
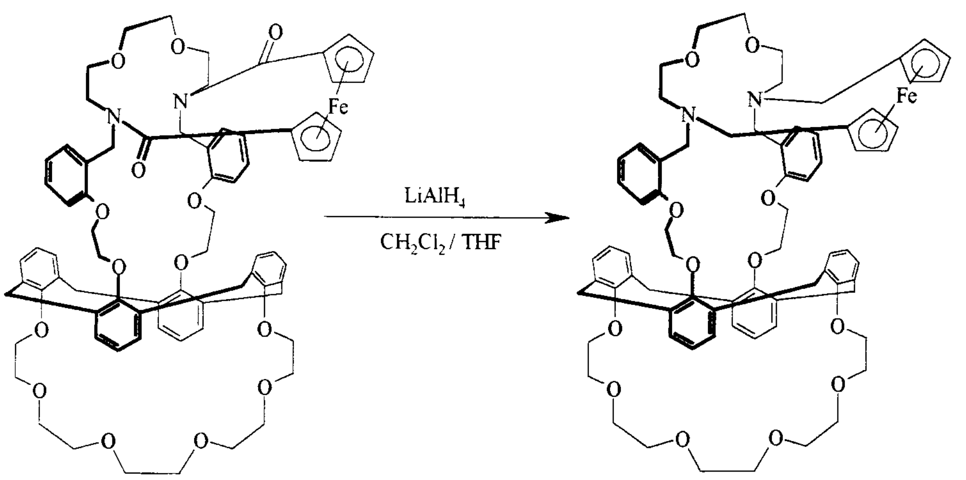


Fig. 1. (a) Cyclic voltammogram of ligand **3**, (b) its complex with K^+ and (c) its complex with Ca^{2+}. [**3**] = 2.1 mM; [M^{n+}] = 8.4 mM.

trifluoromethane sulphonate salts which were either purchased from Aldrich or prepared from the corresponding metal carbonate and triflic acid [15]. Addition of Na^+, even in excess, caused only slight perturbations of the CV wave. There was a slight broadening of the CV wave of the cryptand on addition of K^+ (Fig. 1b) but a distinct wave due to the complex was not observed. Anodic shifts with Ca^{2+} (Fig. 1c), Sr^{2+} and Ba^{2+} were more discernible but the corresponding reduction wave of the cyclic voltammogram was not observed suggesting that the association constants for complex formation were low, i.e. the oxidised complex dissociated before reduction could occur. This in turn suggests that the cations are bound loosely to the carbonyl groups of the cryptand rather than being encapsulated within the calixarene. Taking into account the anodic shifts alone, a trend in the $\Delta E_{1/2}$ values is discernible (Table 1) from Ca^{2+} to Ba^{2+} in line with the charge densities of the respective cations [15]. Definitive evidence on the stoichiometry of the complexes however, is not available.



(3)

(4)

The cryptand, **3**, was then reduced by Gokel's procedure to **4** which was again characterised by mass spectrometry, elemental analysis, IR and $^1H/^{13}C$-NMR. The elemental analysis was not perfect and despite rigorous drying under high vacuum it was obvious from the infrared data that water was still occluded within the molecule. The IR spectrum showed that the amide carbonyl groups had been reduced, and the mass spectrum and NMR data were consistent with the proposed structure. The pseudo-reversible redox wave of **4** ($E_c - E_a = 120$ mV) appears at 360 mV relative to Ag | AgCl some 270 mV less positive than the wave from **3**. As expected therefore, the amine was easier to oxidise than the amide but showed no detectable complex formation with phenol. Complex formation of **3** and **4** with a variety of guest species is currently being investigated by luminescence spectroscopy.

Table 1

ΔE_a values[a] (mV) and charge/radius (c/r) ratios for the complexes of **3** with Ca^{2+}, Sr^{2+} and Ba^{2+} in propylene carbonate solvent

Cations	Ca^{2+}	Sr^{2+}	Ba^{2+}
c/r	2.020	1.780	1.490
ΔE_a (mV)	284	258	225

[**3**] = 2.1 mM; [M^{2+}] = 8.4 mM.

[a] ΔE_a, change in anodic potential on complexation with metal cations.

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