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Synthesis, characterisation and metal complexation reactions of two calix[4]arene derivatives functionalised with pendant benzamide arms

John McGinley [a,*], Vickie McKee [b], John M.D. Walsh [a]

[a] *Department of Chemistry, National University of Ireland Maynooth, Maynooth, Co. Kildare, Ireland*
[b] *Department of Chemistry, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK*

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ABSTRACT

Two calix[4]arene derivatives (**3** and **4**) functionalised at the lower rim with pendant benzamide arms were successfully synthesised and characterised, with the X-ray crystal structure of **3** being determined. Only **4** took part in some metal ion complexation reactions, namely those involving metal(II) acetate salts, with metals salts containing other anions not being complexed.

1. Introduction

Calix[4]arene scaffolds are among the most versatile building blocks in supramolecular chemistry and are widely used for creating selective extractants, catalysts and sensor materials as well as cationic, anionic and neutral binding materials [1–8]. As part of our research, we have previously reported the design of calix[4]arene Schiff base derivatives as potential ligands for fluorescence studies [9] as well as functionalising calix[4]arenes at the lower rim, so that they are capable of binding metal ions [10–14]. In extending this theme, we are targeting the attachment of functional groups, which do not contain imine functionalities, to the lower rim of our calix[4]arene scaffolds. We have reported our observations of the reactions of three Schiff base ligands with various MX_2 salts (M = Cu, Ni or Zn; X = chloride, perchlorate or acetate) which resulted in the cleavage of the imine bond and formation of metal–amine complexes [15]. We have also reported the metal complexation reactions of *N*-(2-aminoethyl)-2-hydroxy-5-nitrobenzamide, an amine which contains an amide functional group [16]. Herein, we report the synthesis, characterisation and metal complexation reactions of two calix[4]arenes functionalised with *N*-(2-aminoethyl)-2-methoxy-5-nitrobenzamide (**3**) and *N*-(2-aminoethyl)-2-hydroxy-5-nitrobenzamide (**4**), respectively (see Scheme 1).

2. Experimental

2.1. Materials and methods

^1H and ^{13}C NMR (δ ppm; *J* Hz) spectra were recorded on a Bruker Avance 300 MHz NMR spectrometer using saturated $CDCl_3$ solutions with Me_4Si reference, unless indicated otherwise, with resolutions of 0.18 Hz and 0.01 ppm, respectively. Infrared spectra (cm^{-1}) were recorded as KBr discs or liquid films between KBr plates using a Perkin Elmer System 2000 FT-IR spectrometer. Melting point analyses were carried out using a Stewart Scientific SMP 1 melting point apparatus and are uncorrected. Microanalysis was carried out at the Microanalytical Laboratory of either University College, Dublin, the National University of Ireland Cork or the National University of Ireland Maynooth. Electrospray (ESI) mass spectra were collected on an Agilent Technologies 6410 Time of Flight LC/MS. Complexes were dissolved in acetonitrile–water (1:1) solutions containing 0.1% formic acid, unless otherwise stated. The interpretation of mass spectra was made with the help of the program “Agilent Masshunter Workstation Software”. Standard Schlenk techniques were used throughout. Starting materials were commercially obtained and used without further purification. The calix[4]arene derivative (**1**) [17] has been reported previously.

Caution! Although not encountered in our experiments, perchlorate salts of metal ions are potentially explosive and should be manipulated with care and used only in small quantities.

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[*] Corresponding author.
E-mail address: john.mcginley@may.ie (J. McGinley).

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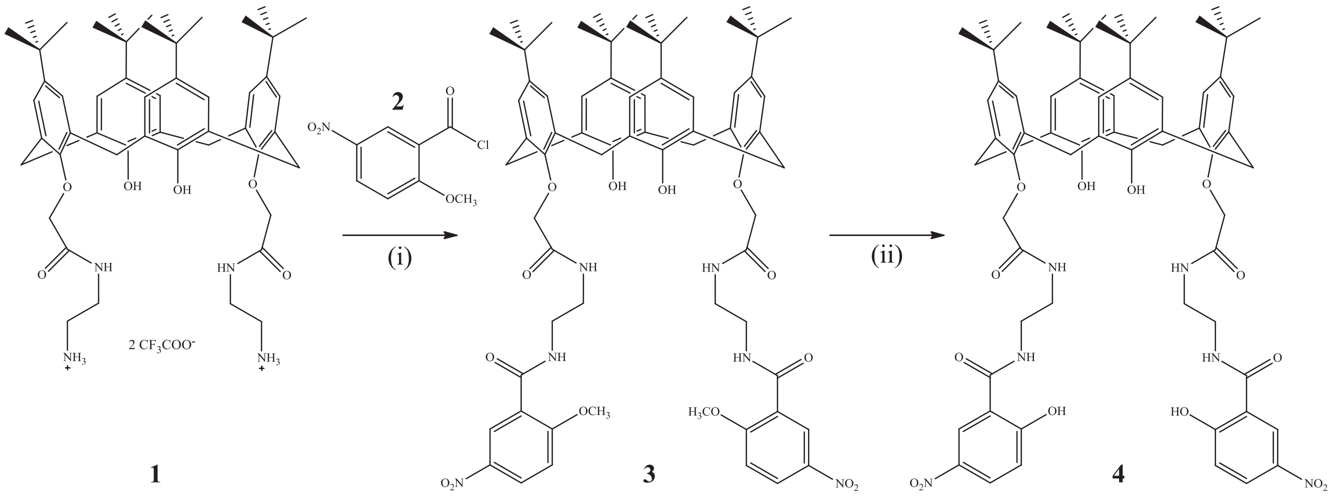

Scheme 1. Preparation of **3** and **4**. Reaction conditions: (i) **2**, Et_3N, DCM, Ar, 0 °C and (ii) BBr_3, DCM.

2.2. Synthesis of **2**

2-Methoxy-5-nitrobenzoic acid (1.0 g, 5.1 mmol) was heated to reflux under a guard tube in thionyl chloride (16 mL) for 4 h. The solution was allowed to cool and the volatiles were removed under reduced pressure to leave an off white solid (**2**). Yield quantitative. m.p.: 84–88 °C (lit: 82–83 °C) [18]. IR (KBr, cm^{-1}): 3115, 3076, 1776, 1755, 1609, 1490, 1287, 1261, 1103, 1002, 750. ^1H NMR ($CDCl_3$): $\delta_H = 4.07$ (s, 3H, OCH_3), 7.14 (d, 1H, ArH, $J = 9.2$ Hz), 8.47 (dd, 1H, ArH, $J = 9.2$ and 2.6 Hz), 9.56 (d, 1H, ArH, $J = 2.6$ Hz).

2.3. Synthesis of **3**

A suspension of (**1**) (0.84 g, 0.78 mmol) and dry triethylamine (4 mL) in dry dichloromethane (30 mL) was cooled to 0 °C under an argon atmosphere. A solution of **2** (0.84 g, 3.90 mmol) in dichloromethane (10 mL) was added dropwise through the septum whilst maintaining cooling. After addition the solution was allowed to rise to room temperature and the stirring was continued for 11 h. The volatiles were removed under reduced pressure. The residue was taken up in methanol (30 mL) and the insolubles were isolated by filtration. The off white solid was dissolved in chloroform (80 mL) and washed with 1 M sodium hydroxide solution (2 × 40 mL), 1 M hydrochloric acid solution (2 × 40 mL) and saturated brine solution (3 × 40 mL). The organic layer was dried over magnesium sulphate, the inorganic salts removed by filtration and the solvent removed under reduced pressure. The residue was treated with acetone (15 mL) to precipitate a white solid. The solid was removed by filtration, washed with acetone and dried in an oven at 75 °C to give **3**. A second crop was obtained from the mother liquor by cooling in a freezer at −20 °C overnight. Yield 46% (0.43 g, 0.36 mmol). m.p.: 160–164 °C. *Anal.* Calc. for $C_{68}H_{82}N_6O_{14}$: C, 67.63; H, 6.85; N, 6.96. Found: C, 67.81; H, 6.64; N, 6.83%. IR (KBr, cm^{-1}): 2958, 1655, 1615, 1522, 1485, 1343, 1282, 1192, 1125, 1088, 1016, 874, 823, 749. ^1H NMR ($CDCl_3$): $\delta_H = 1.03$ (s, 18H, *t*-Bu), 1.20 (s, 18H, *t*-Bu), 3.24 (d, 4H, $ArCH_2Ar$, $J = 13.2$ Hz), 3.70 (m, 4H, $NHCH_2CH_2NHOCPh$), 3.78 (m, 4H, $NHCH_2CH_2NHOCPh$), 3.98 (s, 6H, OCH_3) 4.05 (d, 4H, $ArCH_2Ar$, $J = 13.2$ Hz), 4.66 (s, 4H, OCH_2CO), 6.78 (d, 2H, ArH, $J = 9.1$ Hz), 6.85 (s, 4H, ArH), 6.88 (s, 4H, ArH), 7.92 (s, 2H, OH), 8.08 (m, 2H, $NHCH_2CH_2NHOCPh$), 8.14 (dd, 2H, ArH, $J = 9.1$ & 2.8 Hz), 9.00 (d, 2H, ArH, $J = 2.8$ Hz), 9.12 (m, 2H, $NHCH_2CH_2NHOCPh$). ^{13}C NMR ($CDCl_3$): $\delta_C = 29.9$, 30.5, 30.9, 32.8, 33.1, 37.0, 39.8, 55.6, 73.7, 110.4, 120.9, 124.3, 125.2, 125.9, 126.8, 127.0, 131.4, 140.5, 141.9, 147.6, 147.7, 148.0, 160.5, 162.4, 168.3.

2.4. Synthesis of **4**

3 (0.050 g, 0.041 mmol) was dissolved in dry dichloromethane (10 mL) and the solution was cooled to 0 °C under a flow of nitrogen. A 1 M solution of boron tribromide in dichloromethane (0.065 mL) was added dropwise to the cooled flask. The solution was allowed to rise to room temperature and stirring was continued for a further 12 h. The solution was cooled to 0 °C and water (2 mL) was added dropwise. The solution was stirred for a further 30 min after which the biphasic solution was transferred to a separating funnel. The aqueous layer was removed and the organic layer was washed with 1 M hydrochloric acid solution (2 mL) and saturated brine solution (2 mL). The organic layer was dried over sodium sulphate, filtered and the solvent removed under reduced pressure. The residue was dissolved in methanol (3 mL) and produced immediate precipitation of a white solid. The solid was removed by filtration, washed with methanol and dried in an oven at 75 °C to give **4**. Yield 33% (0.016 g, 0.013 mmol). m.p.: >250 °C. LC/TCOF-MS: $(M+Na)^+$ requires: 1201.5468 g, found: 1201.5526 g. IR (KBr, cm^{-1}): 3362, 2960, 1667, 1651, 1607, 1524, 1484, 1341, 1300, 1205, 1126, 1039, 872, 839. ^1H NMR ($CDCl_3$): $\delta_H = 1.08$ (s, 18H, *t*-Bu), 1.14 (s, 18H, *t*-Bu), 3.36 (d, 4H, $ArCH_2Ar$, $J = 13.2$ Hz), 3.78 (m, 8H, $NHCH_2CH_2NH$), 4.09 (d, 4H, $ArCH_2Ar$, $J = 13.2$ Hz), 4.65 (s, 4H, OCH_2CO), 6.79 (d, 2H, ArH, $J = 9.3$ Hz), 6.84 (s, 4H, ArH), 6.94 (s, 4H, ArH), 8.02 (dd, 2H, ArH, $J = 9.3$ and 2.3 Hz), 8.22 (s, 2H, OH), 8.55 (br s, 2H, $NHOCCH_2$), 8.64 (d, 2H, ArH, $J = 2.3$ Hz), 9.61 (br s, 2H, NHOCPh), 13.48 (s, 2H, OH). ^{13}C NMR ($CDCl_3$): $\delta_C = 30.0$, 30.5, 31.0, 32.8, 33.2, 37.6, 38.2, 73.5, 112.3, 117.7, 122.4, 124.5, 125.4, 125.8, 128.0, 131.7, 137.7, 142.1, 147.5, 147.5, 147.9, 166.0, 168.2, 169.0.

2.5. Metal complex titrations

Metal complexation reactions were performed with either **3** or **4** in either d_6-DMSO or a d_6-DMSO/H_2O mixture using stoichiometric equivalents of metal salt solutions. The metal salts used were either M^IX or $M^{II}X_2$: M = Na, Ag, Zn, Hg and X = perchlorate, chloride or acetate.

2.6. Crystal structure determination

Crystallographic Data for **3**: data were collected at 150(2) K on a Bruker APEX II CCD diffractometer. The structure was solved by direct methods and refined on F^2 using all the reflections [18]. Hydrogen atoms were placed at calculated positions and refined using a riding model, except for those on the water molecules which were not included in the model. *Crystal data:* $C_{69}H_{84}Cl_2N_6\ O_{18}$, $M = 1356.32$, monoclinic, $a = 25.8174(18)$, $b = 12.9239(9)$, $c = 23.2764(16)$ Å, $\beta = 109.574(1)°$,$U = 7317.6(9)$ Å^3, space group $P2_1/c$, $Z = 4$, μ(Mo Kα) = 0.159 mm^{-1}, ρ_{calc} = 1.231 mg m^{-3}. 62 134 data (14 360 unique, $R_{int} = 0.0452$) were measured in the range $1.67 < \theta < 26.00°$. $R_1(I > 2\sigma(I)) = 0.0727$ and wR_2 (all data) = 0.2458. Goodness of fit on $F^2 = 1.056$. CCDC No. 801435.

3. Results and discussion

3.1. Synthesis of calix[4]arene derivatives

The synthesis of the calix[4]arene derivatives **3** and **4** is depicted in Scheme 1. The preparation of **1** has been previously reported by Chen and Chen [17]. 2-Methoxy-5-nitrobenzoyl chloride (**2**) can be obtained from 2-methoxy-5-nitrobenzoic acid, as reported by de Paulis et al. [19]. We obtained the carboxylic acid from the commercially available methyl 2-methoxy-5-nitrobenzoate. In the presence of Et_3N under argon, the reaction of **1** with **2** afforded the product **3** in 46% yield. In the ^1H NMR spectrum of **3**, the methylene protons appear as a pair of doublets, indicating the calix[4]arene adopts a cone conformation. There are also two signals for the two NH groups, which appear as two multiplets at 8.08 and 9.12 ppm, respectively, indicating that the reaction was successful. Furthermore, a singlet at 3.98 ppm corresponds to the presence of the methoxy group on the aromatic ring containing the nitro group. We converted **3**–**4** by the reaction of **3** with BBr_3 in DCM. The ^1H NMR spectrum of **4** showed that there was no signal at 3.98 ppm for the methoxy groups, as had been the case in **3**, but that there was a new signal at 13.48 ppm which was assigned to the presence of the new hydroxy groups.

3.2. Description of crystal structure

Small colourless crystals of **3**, suitable for an X-ray crystallographic study, were obtained from dichloromethane. The structure confirmed the cone conformation of the calix[4]arene (Fig. 1) while also showing that **3** formed an inclusion complex with one molecule of DCM sitting in the upper cavity. Four molecules of water (not shown) are also included in the lattice.

The DCM molecule sits in the cavity with the H atoms interacting with the π systems of two of the aromatic rings, with hydrogen-bonding distances of 2.548 and 2.616 Å to the centroids of the rings. This type of inclusion interaction between DCM and a calix[4]arene has been previously reported [20–22]. The X-ray analysis of **3** revealed that several intramolecular hydrogen bonds, with N(2A)–H(2A)···O(6A), N(2C)–H(2C)···O(6C), N(1C)–H(1C)···O(1C), N(1C)–H(1C)···O(1D), O(1B)–H(1B)···O(1C) and O(1D)–H(1D)···O(1A) distances of 2.664(4), 2.678(3), 2.605(3), 2.967(3), 2.739(3) and 2.710(3) Å, respectively, cause the calix[4]arene skeleton to be in a cone conformation and the methoxy group to be locked into a six-membered ring conformation with the amide NH. The odd orientations of the "tails" are explained by the π–π stacking in the lattice (Fig. 2). The structure consists of double layers perpendicular to the *a* axis with the *tert*-butyl groups of the calix[4]arene rings on the outside. Within each layer the molecules interact forming short (6 ring) π–π stacks. The π–π interactions between each of the six rings are 3.545, 3.704, 3.604, 3.704 and 3.545 Å, respectively. As a result, each calix[4]arene unit interacts with three neighbouring calix[4]arenes. Two of the *tert*-butyl groups are disordered and were modelled with 50:50 and 60:40% occupancies of two orientations.

3.3. Metal complexation reactions

Due to the relatively poor solubility of metal salts in $CDCl_3$, metal complexation studies for **3** were performed in d_6-DMSO using ^1H NMR spectroscopy as the analytical technique. The ^1H NMR spectrum of calix[4]arene **3** was first obtained in the deuterated solvent. Then an excess of the appropriate metal salt solution (M^IX or $M^{II}X_2$: M = Na, Ag, Zn, Hg and X = chloride, perchlorate or acetate) in d_6-DMSO was added to the ligand. In the case of silver(I) acetate, the metal salt was added as an aqueous solution because of the very limited solubility of the silver(I) salt in d_6-DMSO. The ^1H NMR spectrum of the mixture was obtained and then compared with the corresponding spectrum of the starting material.

In all cases, no shift of the calix[4]arene peaks were detected. Considering the number of potential binding sites on the ligand, this is a surprising result. There are numerous examples in the literature of this type of complexation of metal ions by ligands containing amide functional groups [12,23–25]. In addition to the amides' oxygens, the amide nitrogen (if deprotonated) also has the potential to bind metal ions. We then repeated the same metal complexation reactions with **4** to determine if we could get binding of metal ions to occur. The hydroxy derivative, **4**, which possesses a labile proton, has upon deprotonation the potential to function as an anionic ligand. To this end metal salt titrations with some sodium(I), silver(I) and zinc(II) salts were performed, using a similar method to that for **3**.

From the metal titrations carried out, the only cases where interactions occur with the ligand is when metal acetate salts are used. This is surprising since it was postulated that the removal of the methyl moiety would afford favourable binding characteristics similar to that shown by *N*-(2-aminoethyl)-2-hydroxy-5-nitrobenzamide [16], where both chloride and perchlorate metal salts bind with ease. The ^1H NMR spectra suggest that the sodium(I) acetate interacts with **4** in a 2:1 metal to ligand ratio, while both the zinc(II) and silver(I) acetate salts interact in a 1:1 metal to ligand ratio. A summary of the ^1H NMR spectral data of the metal acetate titrations is presented in Table 1. The exchange of cations is fast on the NMR time-scale, as only the average signal for both the starting calix[4]arene derivative and the metal complex is observed. This type of interaction has been previously observed [11].

A suggestion that zinc(II) acetate was effecting an alteration of **4** in solution was the observed change in the solution colour. The original ligand solution exhibited a very pale yellow colour which alters on contact with the zinc(II) acetate solution to give a much stronger yellow colour. On addition of excess zinc(II) acetate, additional changes in the ^1H NMR spectrum were not observed. The most noticeable difference after the addition of the zinc(II) solution is the disappearance of the signal in **4** at 13.94 ppm. This suggests that the zinc ion must be binding to the *ortho*-hydroxy benzamide moiety in an *O*,*O*-bidentate fashion analogous to that displayed in the X-ray crystal structure of bis-*O*,*O*′-(*N*-(2-aminoethyl)-2-hydroxy-5-nitrobenzamide)-copper(II) perchlorate dihydrate [16]. Evidence that the calix[4]arene's pendant arm is functioning with only one site of deprotonation is the continued presence of the amide protons, whose representative signals are observed at 9.38 and 9.02 ppm in the ^1H NMR spectrum of **4** and which have diverged on addition of the zinc(II) solution to 10.29 and 8.76 ppm, respectively. The increased difference in their resonance positions would suggest that only one of the amide functional groups is participating in binding the zinc(II) ion. This suggests that the zinc(II) ion is binding in a 1:1 metal to ligand ratio, with the pendant arms working in tandem to provide an *O*,*O*,*O*,*O*-tetradentate coordination site. This type of coordination mode with *ortho*-hydroxy benzamides and zinc(II) salts have been reported previously [26]. A proposed structure of the zinc(II) calix[4]arene complex is displayed in Fig. 3.

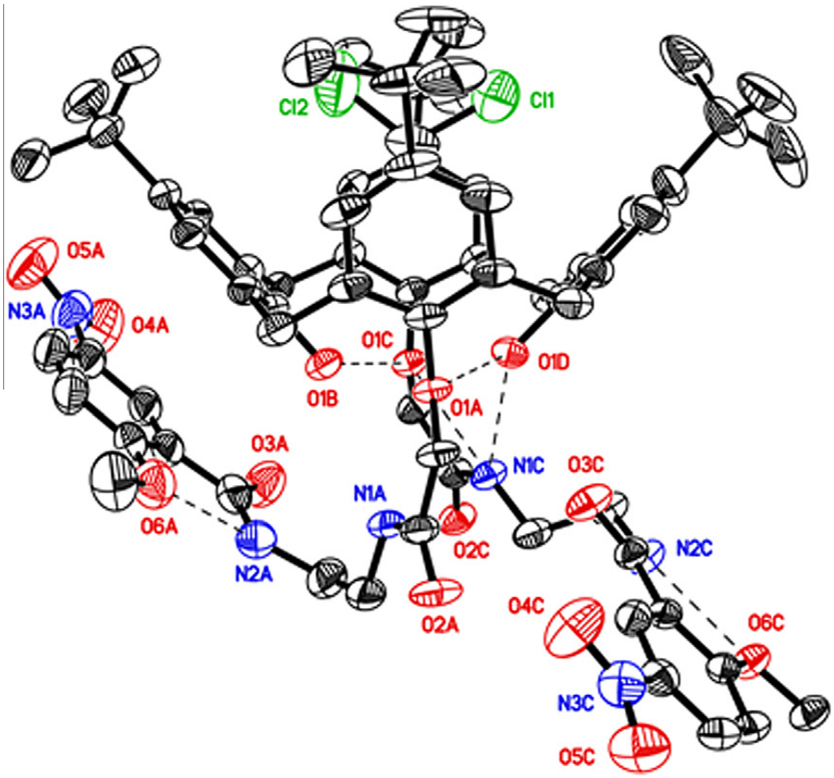

Fig. 1. Molecular structure of **3** with displacement ellipsoids at the 50% probability level. H-bonds are shown as dashed lines; hydrogen atoms and the disorder of the *tert*-butyl groups omitted for clarity.

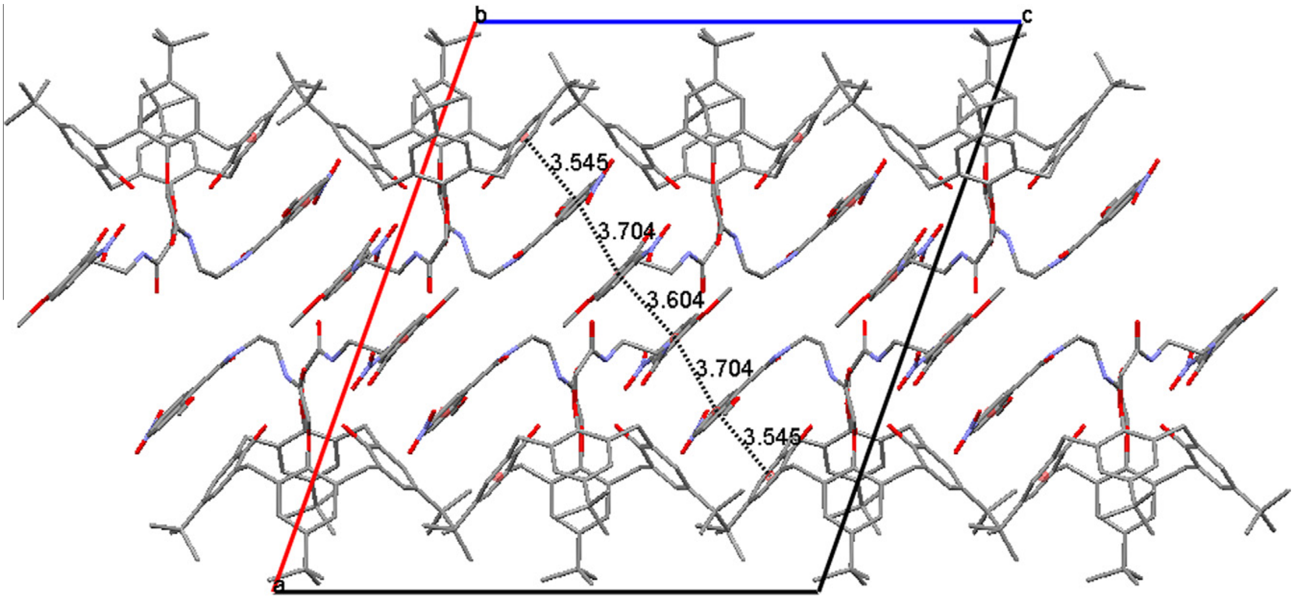

Fig. 2. Partial packing diagram for **3** viewed down the *b* axis, to illustrate π–stacking interactions. Distances shown are centroid-centroid distances in Å. The DCM and water molecules have been omitted for clarity.

Suggestive complexation of the ligand with sodium acetate was again provided by a similar colour change to that observed on addition of zinc(II) acetate. Titrations were carried out in an identical manner to that for the zinc(II) acetate complexation. Similar to the binding studies on zinc(II) acetate, the phenolic proton signal present at 13.94 ppm in the ^{1}H NMR spectrum of **4** is not observed in the ^{1}H NMR spectrum of the sodium complex. Furthermore, the two signals for the amide protons are still present in the ^{1}H NMR spectrum of the metal complex solution. They shift in a similar manner to that observed for the zinc(II) complex with the amide protons' signals diverging to 11.27 and 8.80 ppm, respectively. In an identical manner to that postulated for the complexed zinc(II) ion, it is proposed that the sodium(I) ion is bound in a bidentate *O*,*O*-coordination mode, with additional solvent molecules, either water or d_6-DMSO, filling the metal ion's coordination sphere. This would imply that the sodium(I) ion complexes to **4** in a metal to

Table 1
Summary of ^1H NMR spectral data of **4** in d_6-DMSO[a] and d_6-DMSO/H_2O[b] and corresponding chemical shift of the ligand's signals on addition of various equivalents of metal acetates.

4	**4** and 2 eq. NaO_2CCH_3[a]	**4** and 1 eq. $Zn(O_2CCH_3)_2$[a]	**4** and 1 eq. AgO_2CCH_3[b]
13.94 (s, 2H, ArO*H*)	–	–	–
9.38 (br s, 2H, N*H*OCPh)	11.27	10.29	10.89
9.02 (br s, 2H, N*H*OCCH2)	8.79	8.76	8.92
8.67 (d, 2H, Ar*H*, *J* = 2.5 Hz)	8.58	8.61	8.51
8.33 (s, 2H, O*H*)	8.47	8.38	8.28
7.97 (dd, 2H, Ar*H*, *J* = 9.2 and 2.5 Hz)	7.72	7.85	7.69
7.10 (s, 4H, Ar*H*)	7.13	7.12	7.03
6.87 (d, 2H, Ar*H*, *J* = 9.2 Hz)	6.19	6.58	6.28
6.79 (s, 4H, Ar*H*)	7.08	7.04	6.88

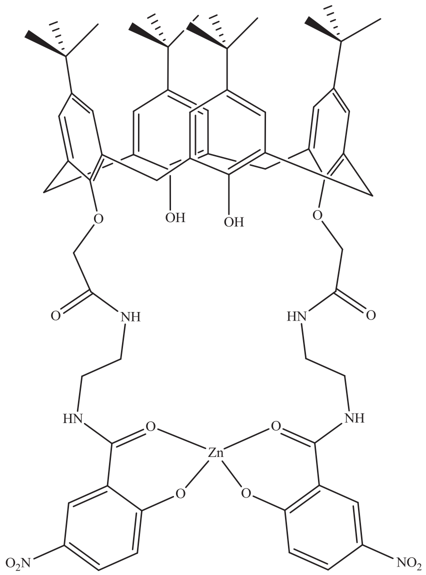

Fig. 3. Proposed structure of **4** with one equivalent of zinc(II) acetate.

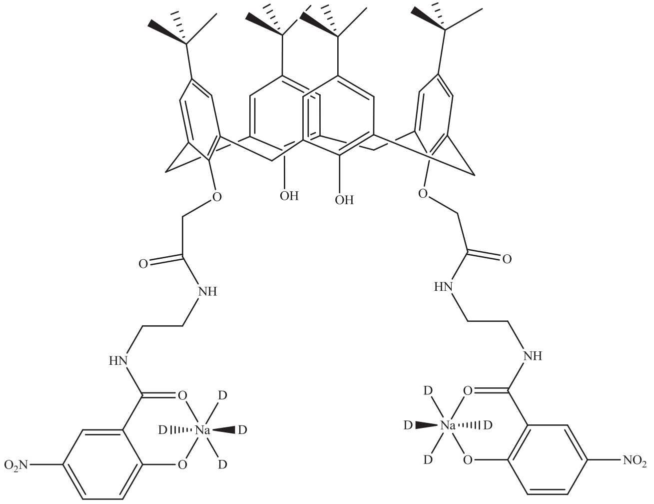

Fig. 4. Proposed structure of **4** with two equivalents of sodium(I) acetate, with D representing donor solvent molecules.

ligand ratio of 2:1, suggesting that each pendant arm binds one sodium ion apiece, as displayed by the proposed structure in Fig. 4.

Solubility issues with the silver acetate salt in d_6-DMSO meant that an aqueous solution of silver(I) acetate was used in the metal salt titrations with **4**. From the experimental set up (identical to the zinc(II) and sodium(I) titrations except for the solvent) and chemical shift of the ligand's signals in the ^1H NMR spectrum, it is suggested that the ligand interacts with the silver(I) ion in a 1:1 metal to ligand ratio, although solubility issues prevented a thorough investigation of this complexation process. The intensification of the yellow colour in the sample was also noted. The signal of the phenolic hydrogen on the pendant arm, observed in the ^1H NMR spectrum of the ligand at 13.94 ppm, had, like in all previous cases, disappeared. Given that the silver ion possesses a +1 charge, this would suggest that the silver ion is shared between the ligands, thus forming a long chain polymer. Formation of coordination polymers have been observed before with ligands binding silver(I) ions [27]. Support for this theory also comes in the physical appearance of the NMR sample. As the acetate solution was added upon completion of the addition of one full equivalent of silver(I) acetate, a yellow solid was formed in sample tube, though this may be simply a result of the calix[4]arene's decreased solubility in the new solvent mixture. Attempts were made to redissolve this solid, but to no avail. Prior to the formation of this precipitate the ^1H NMR spectrum of the metal to ligand mixture showed that many of the signals representing the protons on the pendant arms had altered to give a very broad appearance, again supporting the theory that polymer formation had occurred. The amide protons that were present in the ^1H NMR spectrum of **4** at 9.38 and 9.02 ppm have shifted to 10.89 and 8.92 ppm upon addition of one metal salt equivalent. This conveys that the metal, as in the two previous cases, sits in an *O*,*O*-bidentate coordination sphere. It is difficult to envisage a simple polymeric structure that accounts for the loss of both phenolic protons.

Examining the results of the metal complex titrations with **4**, it becomes clear that the ligand binds exclusively to metal acetates. An explanation for this trend can be found by the relative basicity of the respective counterions, namely the acetate, perchlorate and chloride anions. Using known pK_a values determined in DMSO for analogous compounds, it is possible to show why the acetate salts are the only ones to bind to **4**. Ligand **4** has a *para*-nitrophenol moiety on its pendant arm and will have an approximate pK_a of 10.8 in DMSO [23]. In reality, the pK_a of **4** will probably be even lower, as the presence of the amide *ortho* to the hydroxyl would also contribute toward the stability of the conjugate base (i.e. the phenoxide), thus enhancing the acidity of the phenol and lowering the pK_a even further. Acetic acid, whose conjugate base is the acetate anion, has a pK_a of 12.3 in DMSO [28]. This would suggest that the acetate anion is more basic than the ligand (**4**), specifically the nitrophenol moiety. From this information it can be proposed that the acetate anion, a sufficiently strong base, is able to deprotonate the nitrophenol moiety to give the corresponding phenoxide. The charged species, being a much stronger donor, is now able to bind to the metal cation, in a way that the neutral ligand could not. Evidence of the crucial role of the counterion in facilitating metal binding arises when the acetate salts are compared with their chloride and perchlorate counterparts. Hydrochloric acid (pK_a of 1.8 in DMSO (−8.0 in H_2O)) [28] and perchloric acid (pK_a of −10 in H_2O) [28] are both stronger acids than acetic acid, meaning that both the chloride and perchlorate anions would be weaker bases than the acetate anion. This suggests that the chloride or perchlorate anions are not sufficiently strong to remove the proton from the nitrophenol moiety. Failure to deprotonate means that the neutral ligand is not a strong enough ligand to bind to the metal cation.

Using the three separate metals also rules out that the acetate anion is functioning as a 'naked anion' and that no complexation

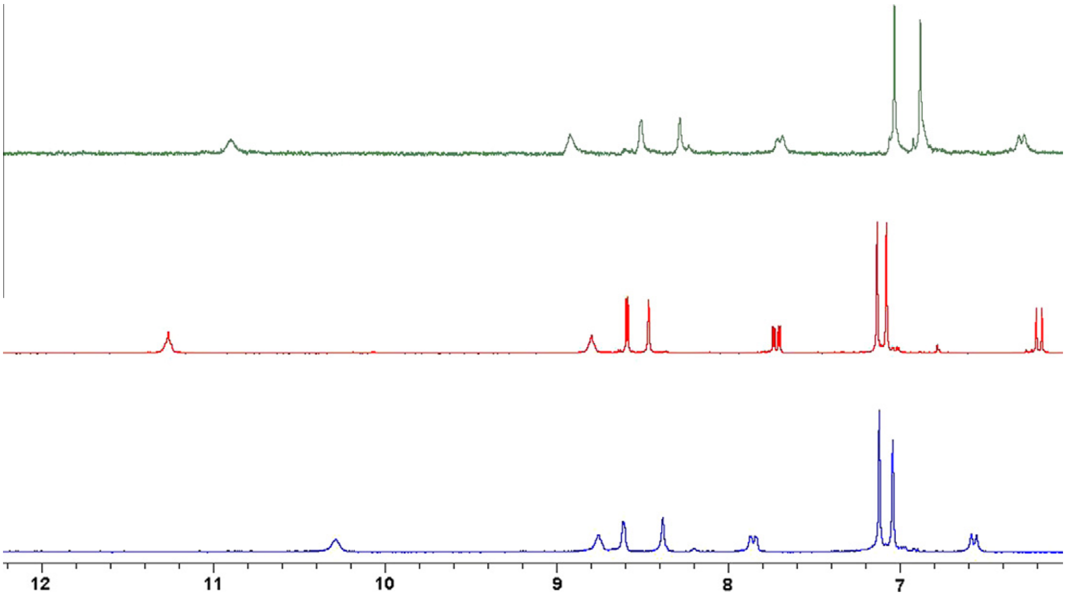

Fig. 5. Partial ^{1}H NMR spectra of **4** with zinc(II) acetate (blue trace), sodium(I) acetate (red trace) and silver(I) acetate (green trace) with *x*-axis scale in ppm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the metal cation is occurring. By comparing the three ^{1}H NMR spectra of the metal titrations it can be seen that obvious variations occur in the spectra though accurate comparison between the silver complex and the zinc and silver derivatives is dubious. This suggests that the metal ion is forming a coordination complex with the charged ligand. Partial ^{1}H NMR spectra of the three acetate titrations are shown in Fig. 5, displaying how emphatic the differences between the metals are.

4. Conclusion

Two new calix[4]arene derivatives are reported, each containing several metal ion binding sites. Only one of them (**4**), however, showed any sign of metal ion binding, but this binding was selective for metal acetate salts. Further investigations are currently underway to synthesise and characterise completely these metal ion complexes.

Acknowledgements

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Appendix A. Supplementary material

CCDC 801435 contains the supplementary crystallographic data for **3**·DCM·4H_2O. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.04.028.

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