Iron(III) complexes of 5,11,17,23-tetra-tert-butyl-24-hydroxy-26,27,28-tris(diethylcarbamoylmethoxy)calix[4]arene (I) and 5,11,17,23,29,35-hexa-tert-butyl-36,39-dihydroxy-37,38,40,41-tetrakis(diethylcarbamoylmethoxy)calix[6]arene (IV) have been synthesised, and a single crystal structure determination has been carried out on [Fe(II - H)][FeCl3]; the iron in the complex cation is bound to all seven O atoms of the calixarene with the shortest Fe–O distance to the phenolate O atom. The voltammetric properties of these complexes and the previously described Fe(III) complex of 5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-bis(diethylcarbamoylmethoxy)calix[4]arene (I) have been studied. The results suggest that the complexes of I and II undergo a reduction which is metal-centred, and an oxidation which is ligand-centred.

Introduction
The calixarene macrocyclic framework continues to attract attention as a starting point for the development of cation receptors. Amongst the many approaches available for elaborating calixarenes, amide functionalisation through O-alkylation has produced ionophores with high selectivities, particularly for alkali and alkaline earth metal cations, although complexation with the lanthanide cations, and to a lesser extent, d-block transition metal cations, has also been studied.

In particular, structural studies of iron complexes of amide-substituted calix[4]arenes have been reported, where the extent of substitution at the phenolic oxygen atoms influences the oxidation state of the iron species in the complex; thus an Fe(III) complex is isolated with the bis-substituted calix[4]arene (I), while an Fe(II) complex is obtained from reaction with the tetra-substituted calix[4]arene (II). The aim of the present work was to study the electrochemical properties of such species, while systematically varying the structure of the calixarene ligand. Reported here are the syntheses of the calix[6]arene amides IV and V together with voltammetric and UV/vis spectroscopic studies of iron complexes of I, II, and IV. The structure of the complex [Fe(II – H)][FeCl3] is also described.

Experimental
Syntheses

Ligand syntheses
5,11,17,23-Tetra-tert-butyl-24-hydroxy-26,27,28-tris(diethylcarbamoylmethoxy)calix[4]arene (I). The literature procedure for tri-substitution of p-tert-butylcalix[4]arene was used as follows. p-tert-Butylcalix[4]arene-toluene (1.14 g, 1.54 mmol) was added to a slurry of BaO (1.59 g, 2.36 mmol) and Ba(OH)2-8H2O (1.70 g, 5.4 mmol) in dmf (30 cm3) and stirred at room temperature for 1 h, under an inert atmosphere. A solution of 2-chloro-N,N-diethylacetamide (1.86 g, 15.4 mmol) in dmf (10 cm3) was then added dropwise, and the mixture stirred for 1 h, after which 1 M HCl (100 cm3) was added. The aqueous solution was extracted with dichloromethane (3 × 20 cm3). The dichloromethane extracts were combined, washed with water (2 × 20 cm3) and dried over MgSO4. The solvent was removed to give a pale yellow solid which was purified by column chromatography on silica, eluting the product with dichloromethane-toluene–methanol (8 : 1 : 1, v/v). Recrystallisation from petrol (bp 60–80 °C)–toluene gave the product as a white microcrystalline solid (0.35 g, yield 23%). (Found: C, 75.5; H, 9.11; N, 4.31.

C₆H₄NO₄ requires C, 75.3; H, 9.08; N, 4.25%). Mass spectrum (FAB): *m/z* 398 [M⁺]. 1010 [M⁺ – H + Na]. NMR (CDCl₃): δ 1.46 [s, 3H, CH₃], 1.37 [s, 18H, C(CH₃)₃], 3.45–3.65 (br m, 16H, NCH₂). 3.69 (s, 4H, OCH₂). 6.55 (d, *J* = 12 Hz, 2H, CH₂). 7.21 (s, 4H, ArH). 7.61 (d, *J* = 2.1 Hz, 4H, ArH). 13C, δ 12.87, 14.54 (CH₃CH₂). 31.29, 31.56 (CH₂CO). 29.92, 32.36 (CH₂), 34.16, 34.21 (CH₃CO). 40.11, 41.79 (CH₂CH₂). 58.80 (OCH₃). 72.18 (OCH₃). 123.30, 127.28, 127.88 (aromatic CH). 132.48, 132.72. 134.16, 145.79, 146.47, 152.30, 154.80 (aromatic C). 167.29 (C=O).

Complex syntheses

**Complex 2a, [Fe(II – H)](ClO₄)₃.** The calixarene II (0.15 g, 0.15 mmol) was dissolved in 1 : 1 dichloromethane–ethanol (2 ml). An approximately three fold excess of FeCl₃ was added, resulting in a deep green solution which was filtered. Upon slow evaporation the product precipitated as dark green rhombic crystals suitable for X-ray diffraction studies. (Yield: 70%). Mass spectrum (FAB): *m/z* 1043 [M⁺ – 2(ClO₄)³⁻].

**Complex 2b, [Fe(II – H)](ClO₄)₂.** The calixarene II (0.15 g, 0.15 mmol) was dissolved in 1 : 1 dichloromethane–ethanol (2 ml). An approximately three fold excess of FeCl₃ was added, resulting in a deep green solution which was filtered. Upon slow evaporation the product precipitated as dark green crystals. (Yield: 80%). Mass spectrum (FAB): *m/z* 988 [M⁺ | Fe].

**Complex 3a, [Fe(II – H)](ClO₄)₂.** The calixarene II (0.15 g, 0.15 mmol) was dissolved in 1 : 1 dichloromethane–ethanol (2 ml). An approximately three fold excess of FeCl₃ was added, resulting in a deep green solution which was filtered. Upon slow evaporation the product precipitated as dark green crystals. (Yield: 80%). Mass spectrum (FAB): *m/z* 1043 [M⁺ – 2(ClO₄)³⁻].

**Complex 4, [Fe(IV – H)](ClO₄)₂.** The calixarene IV (0.14 g, 0.10 mol) was dissolved in 1 : 1 dichloromethane–ethanol (2 ml). An approximately three fold excess of Fe(ClO₄)₂·6H₂O was added, resulting in a deep green solution which was filtered. Upon slow evaporation the product precipitated as dark green crystals, often contaminated with a red amorphous precipitate. (Yield: 40–50%). Mass spectrum (FAB): *m/z* 1480 [M⁺ – 2(ClO₄)⁻ – H⁺].
The iron atom environment in 2b. r is the iron–oxygen atom distance (Å); other entries in the matrix are the angles (°) subtended at the metal by the relevant atoms at the head of the row and column.

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Crystal refinement data for 2b. [Fe(II − H)](FeCl₄)₂H₂O = C₆H₆FeCl₄Fe₂N₂O₄, M = 1455.6. Monoclinic, space group P2₁/n (C₁₀, no. 14), a = 19.25887(1), b = 14.765(1), c = 25.914(2) Å, β = 100.6811(1)°, V = 7475 Å³. D(=4) = 1.29 g cm⁻³. h mosaic = 9.1 cm⁻¹; specimen: 0.45 × 0.45 × 0.45 mm (rhomb); = Tmin = 0.67, 0.83. |Å|/|Å| = 0.60(4) e Å⁻³. CCDC reference number 165283. See http://www.rsc.org/suppdata/dt/b1/b104963c/ for crystallographic data in CIF or other electronic format.

Results and discussion

Ligand syntheses

The required calix[4]arene ligands I, II, and III were synthesised according to literature methods.9,10 The trisamide ligand II has been synthesised previously by adding the amide groups to a monoalkylated calix[4]arene derivative, followed by removal of the original substituent to give the trisamide. In this work, II was synthesised by adapting the published procedure for trialkylation of calix[4]arenes,11 giving the required trisamide in modest yield. The synthesis of calix[6]arene derivative IV was serendipitous; under conditions expected to give the hexa-substituted calix[6]arene, a tetra-substituted product (by FAB MS) was obtained in significant and reproducible yield. The cause of this has not been clarified, but the synthesis provides a convenient route to this tetra-substituted product. The ¹H NMR of the product is extremely complicated, and is consistent with the molecule assuming a number of different rigid conformations in solution. Variable temperature NMR studies were used, but it was not possible to determine the substitution pattern of the calix[6]arene, although previous work with different alkylating agents indicated that a 1,2,4,5-substitution pattern was likely.12 Metathylation of the remaining phenol groups of IV gave V which was readily characterised by ¹H and ¹³C NMR. The number of signals and integration of peaks in the ¹H NMR was found to be consistent with 1,2,4,5-substitution. From these studies, it was concluded that IV also has the 1,2,4,5-substitution pattern. The complex NMR spectra obtained for IV are presumably due to slow conformational change on the NMR timescale, caused by hydrogen bonds involving the unsubstituted phenol groups, although it is notable that the related bridged calix[6]arene tetraamide, where the remaining phenol groups are linked by a polyether bridge, is also conformationally restricted.13

Metal complexation

Iron complexation by the partly substituted calixarenes is clearly indicated by the rapid formation of an intensely coloured solution (purple for I, green for II and IV) when an iron salt is added to a dichloromethane–ethanol solution of the calixarene. As reported previously, III also forms an intense green solution initially, fading to a pale green solution over 24 h, from which the colourless iron(III) complex crystallises.9 Careful addition of an iron(III) perchlorate solution to dichloromethane–ethanol solutions of the calixarenes I, II and IV shows an increase in a broad absorbance in the visible region (I, 580 nm; II, IV, 800 nm), characteristic of a phenolate–iron(III) charge transfer band,16 up to 1:1 metal:ligand ratio, after which no further changes are observed. This is consistent with the formation of a 1:1 complex in solution for all the calixarenes studied. The complexes are readily isolated by allowing the solutions to evaporate slowly, and macroanalytical and FAB MS data were consistent with the formulation of the products as [Fe(I − 2H)](ClO₄)₂ (I), [Fe(II − H)]ClO₄ (II) and [Fe(IV − H)](ClO₄)₂ (IV). Attempts to study the complexation process in more polar solvents such as dmf and dmso were unsuccessful, and it appears that iron complexation does not occur under these conditions. Addition of a base is often required to induce metal complexation with ionisable calixarenes.17 In the present case, addition of triethylamine to the various reaction mixtures resulted in rapid precipitation of an amorphous brown solid which did not contain a significant proportion of the calixarene (presumably the solid is ‘iron hydroxide’ as no attempt was made to perform the reactions under strictly anhydrous conditions).

Reaction of trisamide II with iron(III) chloride rather than the perchlorate, resulted in the isolation of complex 2b. This complex formed crystals appropriate for a single crystal X-ray study, the results of which are consistent with the formulation [Fe(II − H)](FeCl₄)₂H₂O, one formula unit, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. Macroanalytical data indicate that the solvent water molecule is lost upon drying of the product. The structure of the complex cation is shown in Fig. 1, and pertinent bond distances and angles are listed in Table 1. The calix[4]arene assumes a distorted cone conformation, although, given the dihedral angle between phenyl ring 4 and the phenol O(41) Å, the dihedral angle between the parent C₆H₆N₂O₄ planes are 84.74(9), 87.41(5), 85.11°. J. Chem. Soc., Dalton Trans., 2001, 3073–3077 3075

Electrochemical studies

The metal complexes 1, 2a, 3 and 4 dissolve readily in acetonitrile and dichloromethane, and the electrochemical
Also observed for ferrocene under the same conditions. A reduction process is consistent results. The voltammograms of I and 2a were more readily studied, and the results reported here will focus on these systems.

Representative cyclic voltammograms of I and 2a in acetonitrile are shown in Fig. 2. The complex 2a undergoes a reduction at $E_{1/2} = 0.15$ V (vs. Fc/Fc); varying the scan rate showed that the process is diffusion controlled, with changes in the oxidation and reduction potentials of less than 15 mV. The separation between the oxidation and reduction potentials at a scan rate of 200 mV s$^{-1}$ is 90 mV, compared with 75 mV for ferrocene under the same conditions. A reduction process is also observed for I in acetonitrile (Fig. 2); in this case the $E_{1/2}$ is $-0.73$ V, and the process is somewhat less reversible, with a peak separation of 105 mV at a scan rate of 200 mV s$^{-1}$, increasing to 195 mV at 1000 mV s$^{-1}$. The behaviour in dichloromethane solvent is comparable to that observed in acetonitrile, albeit with poorer reversibility; for I, the $E_{1/2}$ is $-0.77$ V, and for 2a, $-0.25$ V (vs. Fc/Fc).

To examine this process further, controlled potential bulk electrolys of the solutions was performed. During this procedure the solutions became colourless, and UV/vis spectroscopy confirmed that the peak at 580 nm for 1, and 800 nm for 2a were no longer present. This observation is consistent with the reduction of iron(III) to iron(II).18 When performed in acetonitrile or dichloromethane solvents the reduction was irreversible, indicating that the complex may have dissociated or precipitated. It was found that the complexes could be dissolved in dmf, and the resulting solutions were sufficiently stable (as judged by the UV/vis spectra) for bulk electrolysis experiments (although the solutions were colourless after 24 h indicating gradual dissociation of the complexes). In this solvent the bulk reduction process was reversible, and given that the complexes could not be synthesised in this solvent, it seems likely that the iron(III) complex is reduced without significant dissociation of the resulting iron(II) complex. These measurements show that the trisamide iron(III) complex 2a, is more readily reduced than the bisamide complex 1, consistent with increased stability of the higher metal oxidation state with increased number of phenolate O donor atoms.16

Cyclic voltammetry also shows that the two complexes undergo oxidation processes, although this aspect of the electrochemistry was not studied in detail. A thorough study of the anodic oxidation of I in dichloromethane solvent has recently been reported,19 showing that the calixarene undergoes two irreversible oxidations (with a minor, unassigned oxidation peak also observed in cyclic voltammograms) followed by chemical reactions to give electrochemically active species (an ECE-type mechanism); preparative coulometry produced the mono- and di-calixquinones resulting from oxidation of the unsubstituted phenol groups. In the present case, the complex 2a was found to undergo an irreversible oxidation at 1.1 V (Fig. 3) in acetonitrile, after which a new reduction wave was observed, albeit overlapping with the process assigned to the iron(III) reduction, at approximately $-0.3$ V. This is consistent with a chemical reaction step following the initial oxidation, as observed for the uncomplexed calixarene I.

It is interesting to note that the cyclic voltammogram for I in acetonitrile exhibits an oxidation that is at least quasi-reversible at $E_{1/2}$ 0.62 V (Fig. 4); scanning to higher potentials shows a second, irreversible, oxidation process at 1.1 V. The most probable assignment for these oxidation processes, is ligand-centred oxidation to give phenoxyl radicals, as is observed in the free

Fig. 1 Projections of the cation of 2b (a) down and (b) quasi-normal to the cone axis. 50% Displacement ellipsoids are shown for the non-hydrogen atoms.

Fig. 2 Cyclic voltammograms of (a) 2a, and (b) I in CH$_3$CN (0.10 mol dm$^{-3}$ Bu$_4$NBF$_4$), reported vs. Fc$/^\circ$/Fc. Scan rate 200 mV s$^{-1}$.
electrochemical oxidation of aryl ether units has also been related iron(II) complexes under the conditions explored; the former was structurally characterised as the FeCl$_2$NBF$_4$ salt. The electrochemical behaviour of the trisamide calix[4]arene iron complex 2a, and the previously described bisamide calix[4]arene iron complex 1, was studied. Reduction of the complexes gave the related iron(II) species, with complex 2a being more readily reduced than 1. Oxidation of the complexes was also observed, this process being assigned to oxidation of the phenoxy moieties.

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References