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# Highly branched ferrocene-functionalised polyazacycloalkanes as electroactive receptors for transition-metal ions

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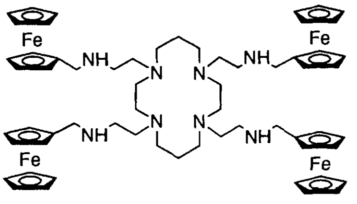
Reaction of *N,N′,N″,N‴*-tetrakis (2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec) with ferrocenecarbaldehyde and further reduction with $LiAlH_4$ resulted in the synthesis of the redox-active receptor *N,N′,N″,N‴*-tetrakis(4-ferrocenyl-3-azabutyl)-1,4,8,11-tetraazacyclotetradecane (tfabc). The protonation behaviour of tfabc and its complex formation with $Cu^{II}$, $Zn^{II}$ and $Cd^{II}$ have been studied in tetrahydrofuran–water (70:30 v/v) (0.1 mol $dm^{-3}$ $NBu^t{}_4ClO_4$, 25 °C). The potentiometric and electrochemical data indicate the formation of 1:1 and 1:2 (tfabc:$M^{2+}$) stoichiometries. The $E_{\frac{1}{2}}$ values for tfabc shift as a function of the pH from 389 (pH 10) to 482 mV (pH 2.5) and $E_{\frac{1}{2}}$ *vs.* pH curves for the tfabc–$H^+$–$M^{2+}$ systems (M = Cu, Zn or Cd) show that tfabc electrochemically recognises the presence of copper(II) selectively at pH < 5. The shift of $E_{\frac{1}{2}}$ appears to be caused by electrostatic forces and the $E_{\frac{1}{2}}$ *vs.* pH curves can be predicted in terms of the distribution diagrams of the tfabc–$H^+$–$M^{2+}$ systems.

There is considerable interest in the design and synthesis of novel electrochemically active ligands containing redox-active groups in close proximity to binding sites.[1–4] These molecules bearing electroactive moieties are important, among other fields, as new potential receptors which can electrochemically recognise the presence of substrates. Over the last decade co-ordination of Group I and II metal ions, transition-metal ions or anions have been reported to shift the redox potential of the redox groups in these electroactive species.[2,3] Redox-active groups such as ferrocene, cobaltocenium, nitrobenzyl, *etc.* have been attached to a large variety of cleverly designed molecules.[2,3] For instance it has recently been reported that ferrocenyl units covalently anchored to polyamines are good candidates electrochemically to recognise the presence of transition-metal ions and anions in aqueous media.[3] On the other hand we have recently reported that the functionalisation of polyamines with ferrocenyl groups leads to pH-responsive, redox-active molecules where the electrochemical recognition of transition-metal ions is tuned by the pH.[4] However, to our knowledge, no effort has been devoted to the functionalisation of large polyaza molecules with redox-active groups. Owing to the large number of co-ordination sites in polyazacycloalkanes they can form polynuclear metal complexes and form several metal–ligand stoichiometries in solution. Additionally these systems are expected to act as polybases leading to highly charged species at neutral pH and be candidates for electrochemical anion-co-ordination recognition (including biologically significant anions such as ATP, ADP and polyphosphates) and models for nucleic acid complexation.[5,6]

Following our interest in the synthesis of electroactive ligands[7] and molecular recognition we report here the functionalisation with redox-active groups of the highly branched polyazacycloalkane *N,N′,N″,N‴*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec) to give the redox-active molecule *N,N′,N″,N‴*-tetrakis(4-ferrocenyl-3-azabutyl)-1,4,8,11-tetraazacyclotetradecane (tfabc) and have studied its interaction with transition-metal ions.



tfabc

## Experimental

### Solvents and reagents

Ferrocenecarbaldehyde, lithium aluminium hydride, copper(II), cadmium(II) and zinc(II) nitrates were reagent quality and used without further purification. *N,N′,N″,N‴*-Tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec) was synthesised following literature procedures.[8] Tetrahydrofuran (thf) used was freshly distilled from sodium–benzophenone. From this solvent, thf–water (70:30 v/v) was easily prepared and used as solvent in the potentiometric and electrochemical studies. Carbonate-free potassium hydroxide and hydrochloric acid solutions were used in the potentiometric and electrochemical experiments. Tetra-*tert*-butylammonium perchlorate (0.1 mol $dm^{-3}$) was used as supporting electrolyte in this solvent mixture.

### Synthesis of *N,N′,N″,N‴*-tetrakis(4-ferrocenyl-3-azabutyl)-1,4,8,11-tetraazacyclotetradecane (tfabc)

The free base *N,N′,N″,N‴*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (372 mg, 1 mmol) was refluxed in benzene with ferrocenecarbaldehyde (856 mg, 4 mmol). After 3 h the reaction mixture was evaporated to dryness. To the resulting orange-red oil were added freshly distilled thf and $LiAlH_4$. The mixture was heated to reflux for 1 h under a nitrogen atmosphere. Upon cooling, water (3 $cm^3$) was added, the mixture filtered and evaporated to dryness. Basic water and dichloromethane produced organic yellow phases which were dried with anhydrous magnesium sulfate. To the resulting dichloromethane solution acetonitrile was added and the mixture heated to remove the dichloromethane resulting in the precipitation of a crystalline solid which was filtered off, washed with acetonitrile and dried under vacuum (540 mg, 47%) (Found: C, 63.65; H, 7.20; N, 9.80. $C_{64}H_{84}Fe_4N_8$ requires C, 63.95; H, 7.20; N, 9.65%). NMR ($CDCl_3$): $^1H$, taec framework, δ 1.48 (q, 1 H), 2.34 (t, 2 H), 2.41 (s, 2 H), 2.45 (t, 2 H) and 2.57 (t, 2 H); ferrocenylmethyl framework, 3.46 (s, 2 H, $CH_2$), 4.06 (s, 2 H, $C_5H_4$), 4.09 (s, 5 H, $C_5H_5$) and 4.14 (s, 2 H, $C_5H_4$); $^{13}C$-{$^1H$}, taec framework, δ 23.37, 46.71, 50.74, 51.49 and 54.75; ferrocenylmethyl framework, δ 48.93 ($CH_2$), 67.67 ($C_5H_4$), 68.30 ($C_5H_5$) and 68.50 ($C_5H_4$).

### Physical measurements

The NMR spectra were measured on a Bruker AC-200 FT spectrometer operating at 300 K. Chemical shifts for $^1H$ and $^{13}C$-{$^1H$} are referenced to $SiMe_4$ and $CDCl_3$, respectively. Infrared spectra were taken on a Perkin-Elmer 1750 spectrophotometer as KBr pellets. Cyclic voltammograms were obtained with a Tacusel IMT-1 programmable function generator, connected to a PJT 120-1 potentiostat. The working electrode was platinum with a saturated calomel reference electrode (SCE) separated from the sample solution by a salt bridge containing the solvent–supporting electrolyte. The auxiliary electrode was a platinum wire. Potentiometric titrations were carried out in thf–water (70:30 v/v) using a reaction vessel water-thermostatted at 25.0 ± 0.1 °C under nitrogen. The titrant was added by a Crison microburette 2031. The potentiometric measurements were made using a Crison 2002 pH-meter and a combined glass electrode. The titration system was automatically controlled by a personal computer using a program to monitor the electromotive force values and the volume of titrant added. The electrode was dipped in thf–water (70:30 v/v) for 0.5 h before use. It was calibrated as a hydrogen concentration probe by titration of well known amounts of HCl with $CO_2$-free KOH solution and determining the equivalence point by Gran's method[9] which gives the standard potential $E'^{\circ}$ and the ionic product of water ($K'_w$ = $[H^+][OH^-]$). The logarithm of $K'_w$ for the solvent used was found to be −16.2 ± 0.2 (25 °C, 0.1 mol $dm^{-3}$ $NBu^t_4ClO_4$). The concentrations of the copper(II), zinc(II) and cadmium(II) solutions were determined using standard methods. The computer program SUPERQUAD[10] was used to calculate the protonation and stability constants. The titration curves for each system were treated either as a single set or as separated entities without significant variations in the values of the stability constants. Finally the sets of data were merged and treated simultaneously to give the stability constants: tfabc–$H^+$, three titration curves, 259 experimental points, pH 3–10; tfabc–$H^+$–$Cu^{2+}$, three titration curves, 230 experimental points, pH 3–9.2; tfabc–$H^+$–$Zn^{2+}$, three titration curves, 246 experimental points, pH 3–9.0; tfabc–$H^+$–$Cd^{2+}$, three titration curves, 225 experimental points, pH 3–9.1. The concentration of the tfabc was *ca.* 2 × $10^{-3}$ mol $dm^{-3}$ while that of the metal was in the range 4 × $10^{-3}$–1 × $10^{-3}$ mol $dm^{-3}$ depending on the formation of mono- and di-nuclear species.

## Results and Discussion

### Synthesis and characterisation

Reaction of the free base *N*,*N*′,*N*″,*N*‴-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec) with ferrocene-carbaldehyde results in a red oil. Although we have not fully characterised this complex it should be the Schiff-base derivative *N*,*N*′,*N*″,*N*‴-tetrakis(4-ferrocenyl-3-azabut-3-enyl)-1,4,8,11-tetraazacyclotetradecane, as suggested by the fact that its reduction with lithium aluminium hydride results in the octaaza derivative *N*,*N*′,*N*″,*N*‴-tetrakis(4-ferrocenyl-3-azabutyl)-1,4,8,11-tetraazacyclotetradecane (tfabc) which can be isolated as a yellow solid. A high-purity material for potentiometric purposes can be obtained from hot acetonitrile as thin yellow plate crystals. The $^1H$ NMR spectrum shows tfabc as a highly symmetric molecule on the NMR time-scale and only five resonances were observed. Three of them between δ 4.06 and 4.15 are assignable to the ferrocenyl moieties. A singlet at δ 3.46 is attributed to the $CH_2$ group attached to the ferrocenyl moiety and a singlet, three triplets and a quintuplet between δ 3.48 and 2.57 are assigned to the $CH_2$ groups from the taec framework. The $^{13}C$ NMR spectrum, IR and analytical data are also consistent with the proposed formulation.

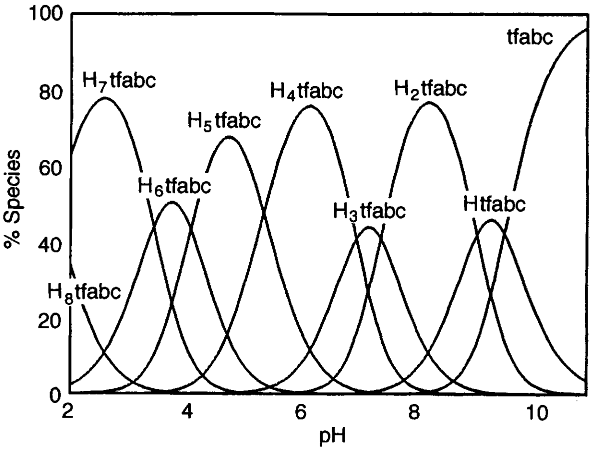


**Fig. 1** Distribution diagram for the tfabc–$H^+$ system

**Table 1** Stepwise protonation constants of tfabc determined at 298.1 K in 0.1 mol $dm^{-3}$ $NBu^t_4ClO_4$ in thf–water (70:30 v/v)

| Reaction[a] | log *K*[b] | Δlog *K* |
|---|---|---|
| tfabc + H $\rightleftharpoons$ Htfabc | 9.57(1) | |
| Htfabc + H $\rightleftharpoons$ $H_2$tfabc | 9.09(1) | 0.48 |
| $H_2$tfabc + H $\rightleftharpoons$ $H_3$tfabc | 7.40(3) | 1.69 |
| $H_3$tfabc + H $\rightleftharpoons$ $H_4$tfabc | 6.98(5) | 0.42 |
| $H_4$tfabc + H $\rightleftharpoons$ $H_5$tfabc | 5.36(6) | 1.62 |
| $H_5$tfabc + H $\rightleftharpoons$ $H_6$tfabc | 4.09(8) | 1.27 |
| $H_6$tfabc + H $\rightleftharpoons$ $H_7$tfabc | 3.44(9) | 0.65 |
| $H_7$tfabc + H $\rightleftharpoons$ $H_8$tfabc | 1.7(1) | 1.7 |

[a] Charges have been omitted for clarity. [b] Values in parentheses are standard deviations on the last significant figure.

### Acid–base behaviour

Table 1 gives the stepwise protonation constants of tfabc and Fig. 1 its distribution diagram determined at 298.1 K in thf–water (70:30 v/v) using 0.1 mol $dm^{-3}$ $NBu^t_4ClO_4$ as supporting electrolyte. Unlike the parent compound taec both in thf–water (70:30 v/v) and in aqueous solution,[11] it is possible for tfabc to determine the basicities of all eight protonations steps. The protonation constants of the first four protonation steps are organised into two groups, the first two being significantly higher than the third and fourth. While Δ(log *K*) between the values of the first two constants is 0.48, the difference between the protonation constants of the second and the third steps is 1.69 logarithmic units and that between the third and the fourth is 0.42 logarithmic units. Between the fourth and fifth steps again a reduction in basicity is observed and steady decreases occur for the remaining steps. For the parent taec, both in water and thf–water,[6,11] the protonation constants are basically

**Table 2** Stability constants for the complex formation of $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ with tfabc in thf–water (70:30 v/v) at 298.1 K in 0.1 mol $dm^{-3}$ $NBu^n_4ClO_4$

| Reaction[a] | $Cu^{2+}$ | $Zn^{2+}$ | $Cd^{2+}$ |
|---|---|---|---|
| $M + tfabc + 3H \rightleftharpoons M(H_3tfabc)$ | 37.08(2)[b] | 31.54(1) | 31.80(2) |
| $M + tfabc + 2H \rightleftharpoons M(H_2tfabc)$ | 33.37(3) | 25.87(2) | 26.57(1) |
| $M + tfabc + H \rightleftharpoons M(Htfabc)$ | 26.17(6) | 18.75(2) | 19.22(7) |
| $M + tfabc \rightleftharpoons M(tfabc)$ | 17.13(9) | 9.43(9) | |
| $2M + tfabc \rightleftharpoons M_2(tfabc)$ | 25.25(8) | 15.50(3) | 17.37(2) |
| $2M + tfabc + H_2O \rightleftharpoons M_2(tfabc)(OH) + H$ | | 8.20(8) | 9.89(3) |
| $2M + tfabc + 2H_2O \rightleftharpoons M_2(tfabc)(OH)_2 + 2H$ | | −0.14(3) | 0.80(5) |
| $M + M(tfabc) \rightleftharpoons M_2(tfabc)$ | 8.1 | 6.1 | |
| $H + M(tfabc) \rightleftharpoons M(Htfabc)$ | 9.0 | 9.3 | |
| $H + M(Htfabc) \rightleftharpoons M(H_2tfabc)$ | 7.2 | 7.1 | 7.3 |
| $H + M(H_2tfabc) \rightleftharpoons M(H_3tfabc)$ | 3.7 | 5.7 | 5.2 |
| $M_2(tfabc) + H_2O \rightleftharpoons M_2(tfabc)(OH) + H$ | | −6.1 | −7.5 |
| $M_2(tfabc)(OH) + H_2O \rightleftharpoons M_2(tfabc)(OH)_2 + H$ | | −8.3 | −9.1 |

[a] Charges have been omitted for clarity. [b] Values in parentheses are standard deviations on the last significant figure.

distributed in two groups, corresponding to strong base behaviour in the first four steps and a much weaker in the last four.* As evidenced by NMR spectroscopy, the reason for this grouping with taec is that protons are attached first to the primary amino groups of the arms. In tfabc there are important topological and electronic differences which might account for the different basicity sequence. First, it does not have primary nitrogen atoms in the arms but secondary ones. Secondly, the bulky ferrocene groups should reduce the mobility of the arms giving rise to a higher conformational rigidity which would affect the charge distribution in the molecule. The high charge achieved by tfabc in solution suggest that this compound could be a potential receptor for anions in aqueous solvents.

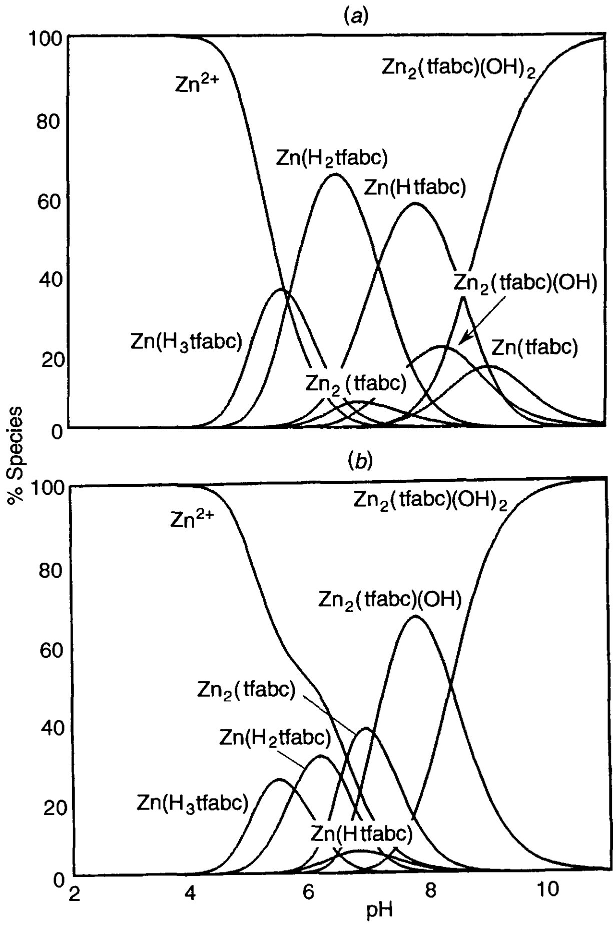


**Fig. 2** Distribution diagram for the tfabc–$H^+$–$Zn^{2+}$ system: (*a*) tfabc:$Zn^{2+}$ = 1:1; (*b*) tfabc:$Zn^{2+}$ = 1:2

### Metal-ion co-ordination studies

Table 2 gives the stability constants for the complex formation of $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ with tfabc in the solvent thf–water (70:30 v/v). Mono- and bi-nuclear complexes are formed with all three metal ions. The number of protonated species displayed by the mononuclear species in conjunction with the high constants associated with the first and second protonations of the metal complexes $\{[M(tfabc)]^{2+} + H^+ \rightleftharpoons [M(Htfabc)]^{3+}$ and $[M(Htfabc)]^{3+} + H^+ \rightleftharpoons [M(H_2tfabc)]^{4+}\}$ strongly suggest that not all the nitrogen atoms are involved in the co-ordination. A similar feature was found for the parent taec in water.[11] The presence of free donor atoms in tfabc favours the formation of polynuclear complexes. For instance, Fig. 2 shows a plot of the distribution with the pH of the complex species existing in the system $Zn^{2+}$–tfabc for 1:1 and 2:1 molar ratios, and it can be seen that while at 1:1 ratio the main species in solution are mononuclear, at 2:1 ratio the binuclear species clearly predominate over a wide pH range. As expected, the stabilities of the copper(II) complexes are significantly higher than those of the zinc(II) and cadmium(II) complexes. The stability of the cadmium(II) complexes are, on the other hand, slightly higher than those of the zinc(II) ones. One of the most interesting features displayed by the zinc(II) complexes of taec was the remarkably high acidity of the water co-ordinated to the metal ion, $pK_a < 5.3$ from the species concentrations.[11] In water $[Zn_2(taec)(OH)]^{3+}$ formed directly from the triprotonated $[Zn_2(H_3taec)]^{7+}$ species without detection of intermediate mono- or bi-nuclear species. X-Ray diffraction studies on the solid compound $[Zn_2(taec)(OH)][ClO_4]_3$ and conductimetric measurements in solution proved that this acidity could be accounted for by the presence of a bridging hydroxo group. The situation for tfabc in the mixed solvent thf–water would be similar although the acidity is a little bit lower. The $pK_a$ value of 6.1 obtained in this solvent is still very low and strongly suggests that a similar structure could be present in the zinc(II) complexes of tfabc. The acidity observed for the analogous bimetallic complex of cadmium(II) is also very high although a little bit lower than that of the zinc(II) complexes which is surely due to the larger size of this metal ion. Also hydroxo binuclear species have been found for both metal ions. The acidity constants for these complexes $\{[M_2(tfabc)(OH)]^{3+} + H_2O \rightleftharpoons [M_2(tfabc)(OH)_2]^{2+} + H^+;$ $M^{2+} = Zn^{2+}$, $pK_a = -8.3$, $M^{2+} = Cd^{2+}$, $pK_a = -9.1\}$ are still

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* Stepwise protonation constants of taec determined in thf–water (70:30 v/v) at 298.1 K in 0.1 mol $dm^{-3}$ $NBu^n_4ClO_4$: log *K* 10.26(1), 9.88(2), 9.08(3), 8.63(5), 7.57(6), 4.27(9) and 3.02(9).

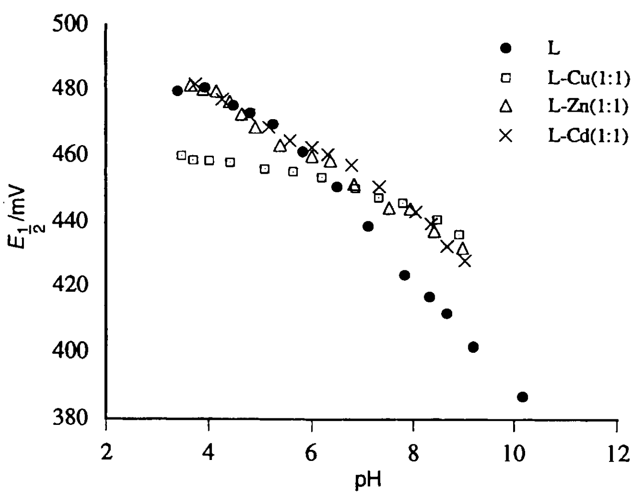

**Fig. 3** Half-wave potential ($E_{\frac{1}{2}}$) *versus* pH for the tfabc (L)–H$^+$ and tfabc–H$^+$–M$^{2+}$ systems (M$^{2+}$ = Cu$^{2+}$, Zn$^{2+}$ or Cd$^{2+}$)

high in comparison with those for complexes of related polyamines.[12]

### Electrochemical study

The electrochemical behaviour of the electroactive molecule tfabc has been studied using standard methods. Cyclic voltammetry and rotating disc electrode (rde) data were obtained under the same conditions used for the potentiometric measurements (thf–water 70:30 v/v, NBu$^t_4$ClO$_4$ as supporting electrolyte, platinum electrode). Cyclic voltammograms of the tfabc–H$^+$ and tfabc–H$^+$–M$^{2+}$ systems exhibit a well defined reversible four-electron wave over all the pH range studied corresponding to the oxidation of the four ferrocenyl groups. Different plots of peak potential against ligand-to-metal ratio show a break close to 2 indicating that complexes with 1:2 tfabc:metal stoichiometries are formed as confirmed by the potentiometric results.

The half-wave potential ($E_{\frac{1}{2}}$) of tfabc changes as a function of pH, ranging from 389 mV *versus* SCE at pH 10 to 482 mV at pH 2.5. At pH < 2.5 the diffusion intensity in r.d.e. experiments decreases and is not retrieved when the pH is increased, suggesting that some kind of decomposition occurs. Taking into account this behaviour, the electrochemical data were taken from pH 3 until precipitation was observed in the reaction vessel (pH ≈ 11 for free tfabc, pH ≈ 9.0 for the tfabc–M$^{2+}$ systems). Fig. 3 shows a plot of $E_{\frac{1}{2}}$ *versus* pH for the tfabc–H$^+$ and tfabc–H$^+$–M$^{2+}$ systems (M = Cu$^{2+}$, Zn$^{2+}$ or Cd$^{2+}$). At pH > 6 the $E_{\frac{1}{2}}$ values for tfabc and for a 1:1 molar ratio mixture of tfabc and Zn$^{2+}$ or Cd$^{2+}$ are nearly the same, whereas at pH < 6 the presence of these metal ions shifts $E_{\frac{1}{2}}$ to anodic potentials. Copper(II) shows a similar behaviour at pH > 6 but in the range pH 3–6 its presence shifts the $E_{\frac{1}{2}}$ value to cathodic potentials when compared with that of free tfabc. This is in agreement with the potentiometric results taking into account that at pH < 5 copper is the only metal ion able to react with tfabc. The presence of Cu$^{2+}$ at pH 4 for example is reflected in the shift of $E_{\frac{1}{2}}$ to more cathodic potentials or by the increase in the diffusion intensity if a constant potential is applied at for example 0.46 V. Under these conditions Cd$^{2+}$ and Zn$^{2+}$ do not produce any important change in the electrochemical properties of the solution.

It has been suggested that several factors can be responsible for the oxidation potential shift in electrochemically active molecules. In our case, owing to the absence in tfabc of any electron delocalisation between the redox-active groups and the binding sites through the organic group attached to them, the ferrocene–substrate interaction would be expected to be electrostatic, and therefore a linear relationship between the charge of the complexes and the oxidation potential should be observed. The $E_{\frac{1}{2}}$ data reflect the average value of the oxidation potentials of all the ferrocene-containing species in solution. In a similar manner we can define an average charge as $z_{av} = \Sigma x_i z_i$ where $z_i$ and $x_i$; are the charge and the molar fraction of the *i*th electroactive species in solution, respectively; $z_{av}$ can be calculated from the distribution diagram obtained from potentiometric measurements. Fig. 4 shows a plot of $E_{\frac{1}{2}}$ against $z_{av}$ which is linear from pH 10 to 4.5. At pH < 4.5 a saturation effect appears to occur and an increase in the complex charge does not produce any change in the ferrocenyl group oxidation potential. Fig. 5 shows a plot of $z_{av}$ *versus* pH for the systems tfabc–H$^+$ and tfabc–H$^+$–M$^{2+}$ (1:1 molar ratio; M = Cu, Zn or Cd) from potentiometric data. The similarity between Figs. 3 and 5 reveals that whereas the binding sites control the kind and strength of the different complexes in solution, the role of the ferrocene moieties is to transform the host–guest total charge into an electric signal in the electrochemical experiment.

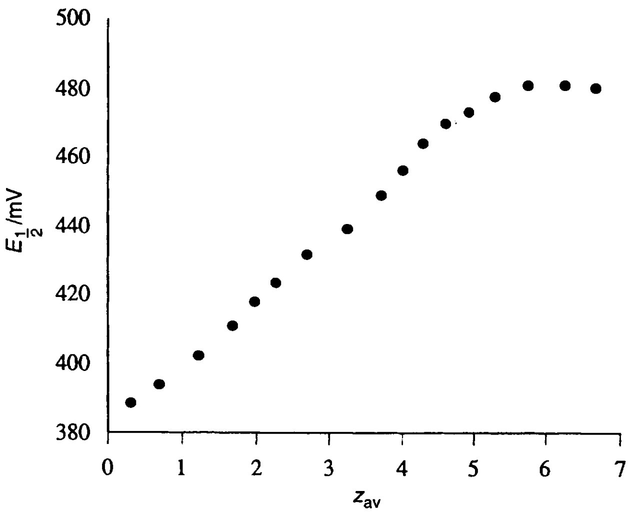

**Fig. 4** Half-wave potential ($E_{\frac{1}{2}}$) *versus* average charge ($z_{av}$) for the tfabc–H$^+$ system

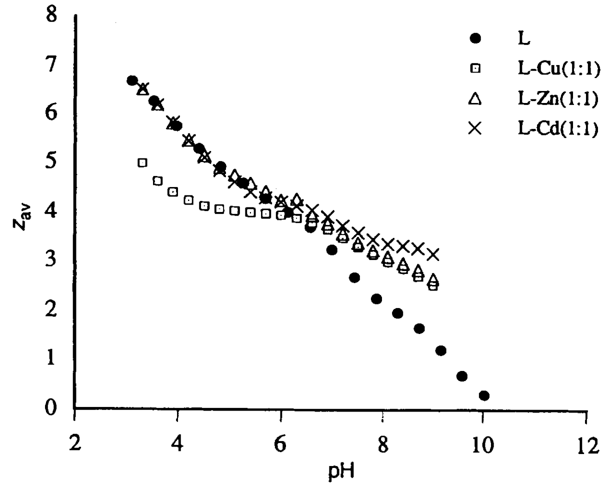

**Fig. 5** Average charge ($z_{av}$) *versus* pH for tfabc (L)–H$^+$ and tfabc–H$^+$–M$^{2+}$ systems (M$^{2+}$ = Cu$^{2+}$, Zn$^{2+}$ or Cd$^{2+}$)

## Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (proyecto PB91-0807-C02-02 and PB90-0700-CO2) for support.

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*Received* 22*nd January* 1996; *Paper* 6/00464D