Macrocyclic Effect on Anion Binding. A Potentiometric and Electrochemical Study of the Interaction of 21- and 24-Membered Polyazaalkanes with $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$

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The interactions of the cyclic polyazaalkanes 1,4,7,10,13,16,19-heptaazacyclohenicosane, 1,4,7,10,13,16,19,22-octaazacyclotetracosane and of the open-chain counterparts 1,17-bis(methylamino)-3,6,9,12,15-pentaazaheptadecane and 1,20-bis(methylamino)-3,6,9,12,15,18-hexaazaicosane with the complex anions hexacyanoferrate(II) and hexacyanocobaltate(III) have been studied at 298.15 K in 0.15 mol dm^{-3} NaClO$_4$ by using potentiometric and electrochemical techniques. Both types of polyamines, cyclic and linear, form stable complexes with 1:1 anion:receptor stoichiometry. This result has been obtained either by treatment of electromotive force data with the computer program SUPERQUAD or by analysing the variations of $[Fe(CN)_6]^{3-}$–$[Fe(CN)_6]^{4-}$ voltammograms with the ratio $[Fe(CN)_6]^{4-}$:polyamine. A macrocyclic effect for anion binding is observed, namely the stability of the 'super-complexes' of the cyclic ligands is higher than those formed by their open-chain counterparts. Both types of ligands interact more strongly with $[Fe(CN)_6]^{4-}$ than with $[Co(CN)_6]^{3-}$. From the electrochemical measurements it has been estimated that the affinity of $[Fe(CN)_6]^{3-}$ for these polyammonium receptors is similar to that presented by the equally charged complex anion $[Co(CN)_6]^{3-}$.

'Super-complexes' are usually defined as compounds resulting from the second-sphere interaction between molecular receptors and complexed, neutral or charged species.[1] They display chemical and physico-chemical features as well defined as those of the molecules themselves. The molecular receptors most widely studied have been polyazamacrocycles in their protonated forms.[2–4] These cations are suitable as anionic receptors because of the highly charged species they form in aqueous solution even at neutral pH and their ability to form multisite hydrogen-bond networks. In previous papers we have reported on the interactions of the anions $[PdCl_4]^{2-}$, $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$ with the series of aza-crowns of general formula [3*k*]aneN$_k$ (k = 7–12).[3,4] In the present paper we update these data by analysing the 'super-complex' formation of the anions $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$ with the macrocycles 1,4,7,10,13,16,19-heptaazacyclohenicosane ([21]aneN$_7$) and 1,4,7,10,13,16,19,22-octaazacyclotetracosane ([24]aneN$_8$), and the open-chain polyamines 1,17-bis(methylamino)-3,6,9,12,15-pentaazaheptadecane (bmaph) and 1,20-bis(methylamino)-3,6,9,12,15,18-hexaazaicosane (bmahi) which can be considered their open-chain counterparts. Recently we have reported on the protonation and metal co-ordination behaviour of the last two ligands, observing, despite their non-cyclic topology, great similarities with the chemistry of the ligands [21]aneN$_7$ and [24]aneN$_8$.[5,6] The mono- and bi-nuclear copper(II) complexes of both types of ligand presented similar stabilities and a macrocyclic effect was not observed.[5] Therefore, it seemed interesting to extrapolate these considerations to the anion co-ordination chemistry and to investigate whether the cyclic topology of the receptor is a key point in super-complex formation.

Experimental

Materials.—The ligands [21]aneN$_7$, [24]aneN$_8$, bmaph and bmahi were synthesised as previously reported.[5,7,8] Their hydrochloride salts were used in both potentiometric and electrochemical measurements. The complex $K_3[Co(CN)_6]$ (Aldrich reagent grade) was recrystallized twice from ethanol–water before use. All the other products were Merck analytical reagents.

Electromotive Force Measurements.—The potentiometric titrations were carried out in 0.15 mol dm^{-3} NaClO$_4$ at 298.15 K, using equipment described previously.[9] The reference electrode was an Ag–AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen-concentration probe by titrating known amounts of HCl with CO$_2$-free NaOH solutions and determining the equivalence point by Gran's method,[10] which yields the standard potential E° and the ionic product of water. The computer program SUPERQUAD[11] was used to calculate the stability constants. The ligand protonation constants employed in the calculations have already been reported.[5,12] Protonation of $[Fe(CN)_6]^{4-}$ occurs at pH < 4, therefore the protonation constants of this anion have also been taken into account.[13] The titration curves for each system were treated either as a single set or as separate entities without significant variations in the values of the stability constants. In the case of the $[Fe(CN)_6]^{4-}$–[24]aneN$_8$, –[21]aneN$_7$ and –bmahi systems, precipitation of the adducts formed was observed at pH < 4. For this reason all potentiometric measurements concerning these systems were performed at pH $\geqslant$ 4.

Electrochemical Measurements.—Cyclic voltammograms were obtained with a potentiostat (QR101), a signal generator (Newtronics 200P) and an *x-y* recorder (Riken-Denshi F-35). A standard three-electrode arrangement was used with a saturated calomel reference electrode (SCE), platinum-wire auxiliary electrode and platinum, gold and glassy carbon disk

Table 1 Logarithms of the equilibrium constants for super-complex formation between the ligands (L) [21]aneN_7, [24]aneN_8, bmaph, bmahi and the anions (A) $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$ determined at 298.15 K in 0.15 mol dm^{-3} $NaClO_4$*

	[21]aneN_7		[24]aneN_8		bmaph		bmahi	
Reaction	$[Fe(CN)_6]^{4-}$	$[Co(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-}$	$[Co(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-}$	$[Co(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-}$	$[Co(CN)_6]^{3-}$
A + L + 3H	31.03(4)	30.39(4)				31.15(2)		
A + L + 4H	39.15(4)	37.58(4)	39.73(3)	38.56(2)	40.40(1)	39.79(1)	40.71(2)	40.01(8)
A + L + 5H	44.39(4)	41.51(5)	46.06(4)	43.66(3)	46.45(2)	44.91(1)	48.66(1)	47.27(3)
A + L + 6H		44.14(5)	51.07(4)	47.45(3)	50.92(2)	48.57(1)	54.38(1)	52.19(3)
A + L + 7H		46.7(1)		50.41(3)	54.30(2)	51.06(2)	58.84(1)	55.80(2)
A + H_3L	3.4	2.7				2.4		
A + H_4L	5.1	3.5	4.1	2.9	3.6	3.0	2.7	2.0
A + H_5L	6.6	3.7	5.5	3.5	4.9	3.3	3.9	2.5
A + H_6L		4.2	7.1	3.9	6.0	3.6	5.2	3.0
A + H_7L		4.8		4.1	6.9	3.7	6.4	3.3

* Values in parentheses are standard deviations in the last significant figure. Charges have been omitted.

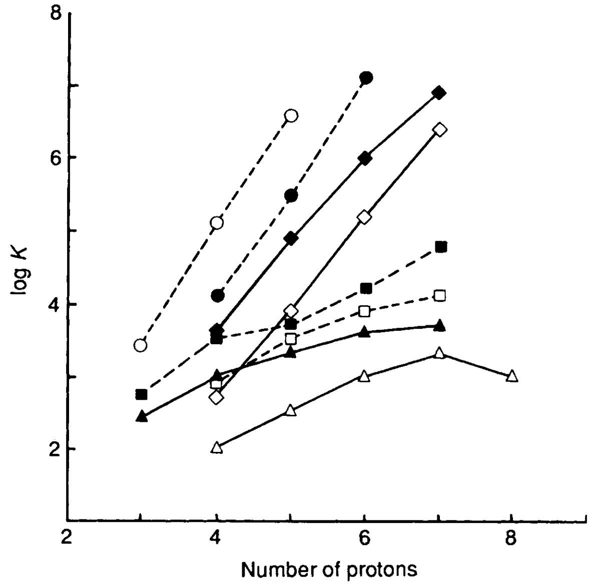

Fig. 1 Plot of log *K* values for the formation of super-complex species *vs.* the number of protons in the super-complexes. Systems: $[Fe(CN)_6]^{4-}$ + [21]aneN_7 (○), [24]aneN_8 (●), bmaph (◆), bmahi (◇); $[Co(CN)_6]^{3-}$ + [21]aneN_7 (■), [24]aneN_8 (□), bmaph (▲), bmahi (△)

working electrodes. All experiments were carried out under an argon atmosphere in a cell thermostatted at 298.15 K.

For the cyclic voltammetry (CV)–pH titrations, alkaline solutions with a two-to-three-fold excess of ligand were prepared. In each experiment HCl solution was added stepwise to 25 cm^3 of the respective solution in order to vary the pH between 10 and 4. After each such addition both the cyclic voltammogram and the pH were measured.

To obtain the molar-ratio saturation curves a series of samples containing a constant amount of potassium hexacyanoferrate(II) and varying concentrations of ligand was prepared. The pH was adjusted to the required value by adding appropriate amounts of concentrated NaOH and/or HCl solutions. All samples were 0.15 mol dm^{-3} in $NaClO_4$ to maintain constant the ionic strength.

Results and Discussion

Stability Constants.—The equilibrium constants for super-complex formation between the polyamines [21]aneN_7, [24]aneN_8, bmaph and bmahi and the complex anions $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$ experimentally determined in this work are presented in Table 1. The great number of species present at equilibrium whose stability constants differ slightly means that it is advisable to use, when possible, alternative techniques in order to confirm the models derived from the analysis of the e.m.f. data. In the case of $[Fe(CN)_6]^{4-}$ independent electrochemical measurements, which will be discussed later, can be carried out and the results compared with those obtained by potentiometry. Unfortunately, owing to its electrochemical behaviour upon reduction,[14] such measurements cannot be performed in the case of $[Co(CN)_6]^{3-}$, and potentiometry is the only available method allowing for an accurate determination of stoichiometries and stability constants.

As shown in Table 1, in all the systems studied here only 1:1 receptor:anion species have been found. The minimum protonation degree of the ligands required for making the anion–receptor interaction appreciable is three for the ligands containing seven nitrogen donors ([21]aneN_7 and bmaph) and four for those with eight nitrogen donors ([24]aneN_8 and bmahi). As usually observed in this kind of system,[2,4,15] for a given polyammonium receptor (see Fig. 1), the stability of the super-complexed species increases with the protonation degree of the ligand. On the other hand, as can be seen in Table 2, super-complexes with lower charge are protonated more easily, and the extent of protonation decreases as the overall charge increases. For a given protonation degree of the ligand and a given anion, the super-complexes formed by the heptaaza ligands, [21]aneN_7 and bmaph, are more stable than those formed by [24]aneN_8 and bmahi respectively (see Fig. 1). Also, for a particular protonation degree, $[Fe(CN)_6]^{4-}$ complexes are more stable than those of $[Co(CN)_6]^{3-}$. Furthermore, the super-complexes formed by macrocyclic receptors are always more stable than those formed by their open-chain counterparts. All these considerations suggest, as already stated in previous reports,[2–4,14] that the major role in second-co-ordination-sphere interactions between charged species is played by coulombic forces, though other effects like hydrogen bonding and the topology of the receptor could also be of significance. The molecular structure of the crystalline compound $[H_4L][Co(CN)_6]I{\cdot}3H_2O$ (L = 1,1,4,4,7,7,10,10-octamethyl-1,4,7,10-tetraazacyclododecane), in which formation of hydrogen bonds is prevented by the quaternization of the amine groups, reveals that $[Co(CN)_6]^{3-}$ acts as a mere counter ion.[15] However, for the present systems the topological effect can be rationalized to some extent by means of coulombic forces, since for a given protonation degree a greater accumulation of charge density should be present in the cyclic molecules.

Electrochemistry.—Anion–receptor, as well as metal–ligand, equilibria can be studied cyclovoltammetrically provided the

Table 2 Logarithms of the equilibrium constants for the stepwise protonation of super-complexes $[H_nL{\cdot}M(CN)_6]^{(n+m-6)} + H^+ \rightleftharpoons [H_{n+1}L{\cdot}M(CN)_6]^{(n+m-5)}$ where m = 2 for $[Fe(CN)_6]^{4-}$, 3 for $[Co(CN)_6]^{3-}$

	[21]aneN$_7$		[24]aneN$_8$		bmaph		bmahi	
n	$[Fe(CN)_6]^{4-}$	$[Co(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-}$	$[Co(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-}$	$[Co(CN)_6]^{3-}$	$[Fe(CN)_6]^{4-}$	$[Co(CN)_6]^{3-}$
3	8.1	7.2			9.9	8.6		
4	5.1	3.9	6.3	5.1	6.2	5.2	8.0	7.3
5		2.6	5.0	3.8	4.6	3.7	5.7	4.9
6		2.5		3.0	3.4	2.8	4.5	3.6

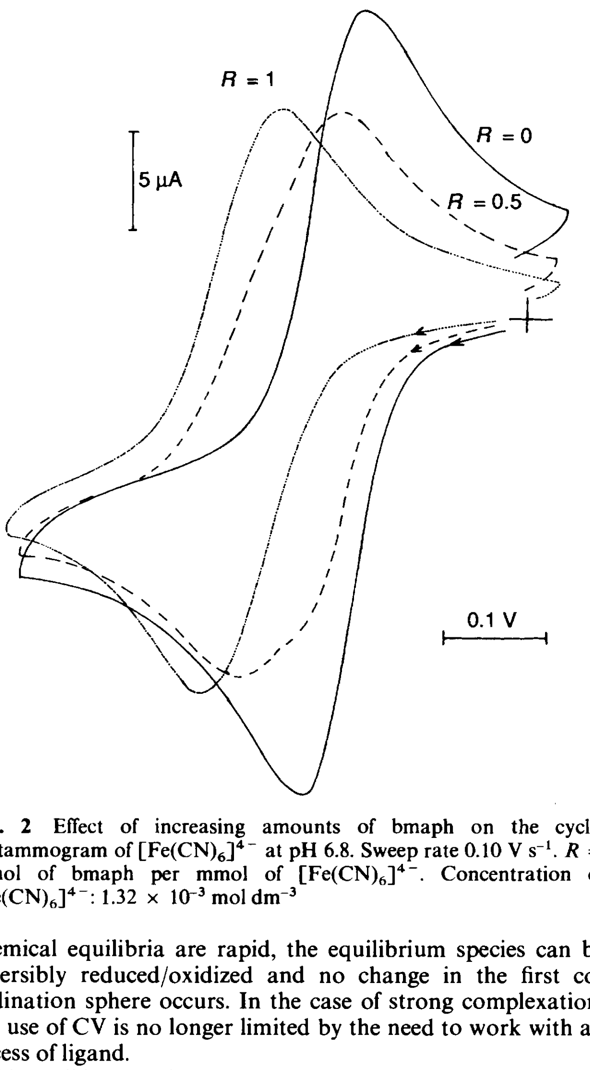

Fig. 2 Effect of increasing amounts of bmaph on the cyclic voltammogram of $[Fe(CN)_6]^{4-}$ at pH 6.8. Sweep rate 0.10 V s^{-1}. R = mmol of bmaph per mmol of $[Fe(CN)_6]^{4-}$. Concentration of $[Fe(CN)_6]^{4-}$: 1.32 × 10^{-3} mol dm^{-3}

chemical equilibria are rapid, the equilibrium species can be reversibly reduced/oxidized and no change in the first coordination sphere occurs. In the case of strong complexation, the use of CV is no longer limited by the need to work with an excess of ligand.

The well known electrochemical behaviour of the hexacyanoferrate(II) solutions involves a one-electron reversible couple. Addition of polyamine ligands results in significant alterations in this cyclovoltammetric response which depend on the ligand:$[Fe(CN)_6]^{4-}$ molar ratio, R, and the pH. The dependence of the cyclic voltammograms on R has been studied at given pH values. As shown in Fig. 2 for the ligand bmaph, increasing R leads to a decrease in cathodic and anodic peak currents and to a shift of the peaks toward more positive potentials. In acidic media, the cyclovoltammograms at R values close to 0.5 are rather broad and look like the overlap of two waves. In each case it was observed that for $R > 1$ the cyclic voltammogram remains almost unchanged and must correspond to the electrochemical processes involving the $[Fe(CN)_6]^{4-}$ super-complexes. These species display one-electron reversible oxidation at gold, glassy carbon and platinum electrodes, as indicated by the difference in potential between the anodic and cathodic peaks ($E_{p_c} - E_{p_a}$ = 60 mV).

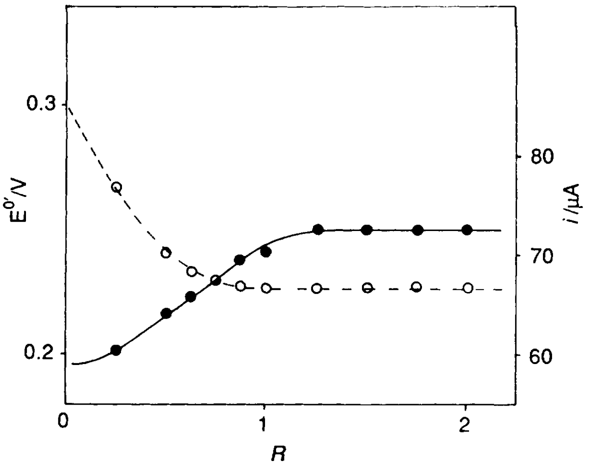

Fig. 3 Plots of the peak potential (continuous line) and the peak current (dashed line) *vs.* the ratio R = mmol of bmaph per mmol of $[Fe(CN)_6]^{4-}$ at pH 6.5. Concentration of $[Fe(CN)_6]^{4-}$: 2.64 × 10^{-3} mol dm^{-3}

In addition, the anodic peak current, i_{p_a}, varies linearly with the square root of the scan rate in the range 0.01–0.25 V s^{-1}, which indicates the electrochemical process is diffusion-controlled. Accordingly, well defined values of the formal potential of the couple, $E^{\circ\prime} = (E_{p_c} + E_{p_a})/2$, and the diffusion coefficient of the hexacyanoferrate(II) super-complex, D_c, can be calculated.[15] For all the systems studied, plots of the peak potential and the peak current against the ligand:$[Fe(CN)_6]^{4-}$ molar ratio, R, exhibit a sharp break close to R = 1, indicating[16,17] the formation of strong complexes with 1:1 $[Fe(CN)_6]^{4-}$:ligand stoichiometry. For example, in Fig. 3 such plots are presented for the system $[Fe(CN)_6]^{4-}$–bmaph. Further, to confirm the stoichiometry of these super-complex species, theoretical voltammograms were calculated and compared with those experimentally obtained.

Simulation of CV has been reported as a useful method to study complexation equilibria,[18–21] since both the shapes and positions of the current *vs.* potential curves are influenced by R, pH and stability constants. Theoretical cyclovoltammograms were calculated by assuming that: (*i*) the $[Fe(CN)_6]^{4-}$ ion and the super-complex species are reversibly oxidized at the planar electrode; (*ii*) the chemical processes are sufficiently fast that equilibrium is always established; (*iii*) the pH of the solution does not change during the potential scan, not even near the electrode surface; (*iv*) the complex formed is strong enough to ensure its complete formation under the experimental conditions; (*v*) the intensities of the superimposed electrode currents are additive. From this last supposition, the current at a given applied potential, E, can be calculated by adding the currents due to both super-complex and free $[Fe(CN)_6]^{4-}$ oxidation processes, *i.e.* as in equation (1) where c_M and c_C are the

$$i = nFAa^{\frac{1}{2}}[D_M^{\frac{1}{2}}c_M\pi^{\frac{1}{2}}\chi(at) + D_C^{\frac{1}{2}}c_C\pi^{\frac{1}{2}}\chi(at)] \quad (1)$$

concentrations of free $[Fe(CN)_6]^{4-}$ and of the complex, and D_M

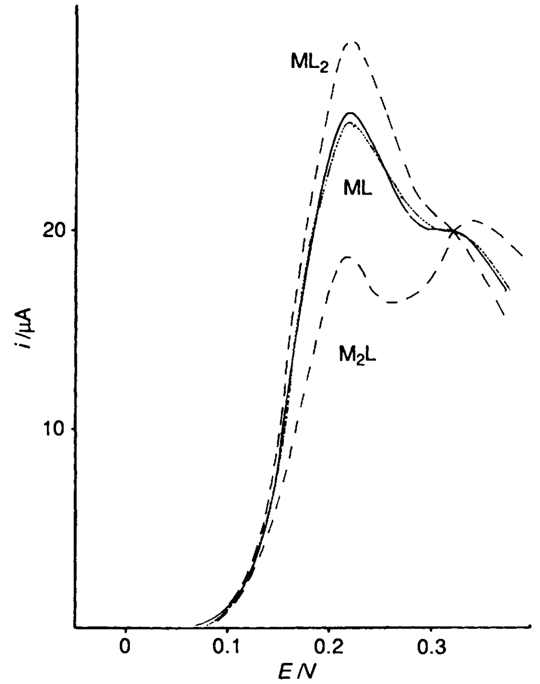

Fig. 4 Comparison between theoretical cyclic voltammograms (continuous and dashed lines) for 1:1, 1:2 and 2:1 $[Fe(CN)_6]^{4-}$: [24]aneN_8 stoichiometries and experimental cyclic voltammogram (dotted line). Concentrations of $[Fe(CN)_6]^{4-}$ and [24]aneN_8 are 10^{-3} and 2.5×10^{-4} mol dm^{-3}, respectively

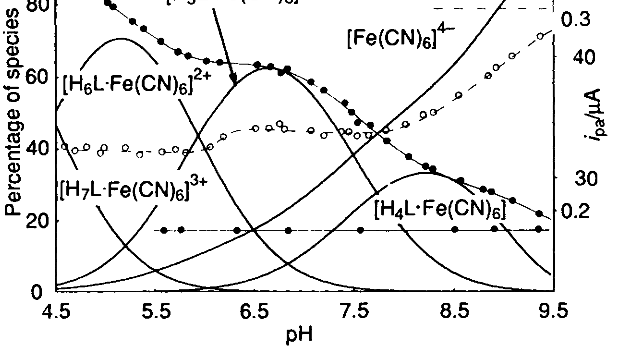

Fig. 5 Distribution diagram (——) of the species present in the system $[Fe(CN)_6]^{4-}$–bmahi and anodic peak currents (- -○- -) and formal potentials (—●—) of the couple $\{[Fe(CN)_6]^{4-}–[Fe(CN)_6]^{3-}\}_{Complexed}$ *vs.* pH. Concentrations of $[Fe(CN)_6]^{4-}$ and bmahi are 2.00×10^{-3} and 2.80×10^{-3} mol dm^{-3}, respectively. Horizontal lines correspond to anodic peak currents (- - -) and formal potentials (—●—) of the uncomplexed $[Fe(CN)_6]^{4-}–[Fe(CN)_6]^{3-}$ couple

Table 3 Logarithms of the equilibrium constants for super-complex formation of $[Fe(CN)_6]^{3-}$ (A) estimated from cyclovoltammetric data at 298.15 K in 0.15 mol dm^{-3} $NaClO_4$*

Reaction	[21]aneN_7	[24]aneN_8	bmaph	bmahi
A + L + 3H	30.4			
A + L + 4H	37.4	38.6	39.6	40.2
A + L + 5H	41.6	44.0	44.7	47.4
A + L + 6H		48.0	48.5	52.3
A + L + 7H			51.1	56.0
A + H_3L	2.8			
A + H_4L	3.4	2.9	2.8	2.0
A + H_5L	3.8	3.8	3.2	2.6
A + H_6L		4.4	3.6	3.1
A + H_7L			3.7	3.5

* Charges have been omitted.

and D_C their respective diffusion coefficients, $a = nFV/RT$, and the other symbols have their usual meaning. The values of the current function, $\pi^{\frac{1}{2}}(at)$, have been tabulated[22] as a function of the difference between the applied potential, *E*, and the half-wave potential of the electrode process. Accordingly, two different values of the current function, $\pi^{\frac{1}{2}}(at)$, must be computed for each value of the applied potential. Assuming complete formation of the complex for solutions with $R > 1$, as indicated by the constancy of the cyclovoltammetric parameters, the half-wave potential of the super-complex reduction can be directly determined from these cyclic voltammograms. In addition, the measured peak currents, i_p, allow the determination of an experimental value of D_C, which depends on the complex stoichiometry. Therefore, theoretical cyclic voltammograms can be obtained for different stoichiometries and compared with experimental data. For example, Fig. 4 shows the experimental cyclovoltammogram for a solution of $[Fe(CN)_6]^{4-}$ and bmahi at pH 6.50 with $R = 0.25$ conjointly with the theoretical curves calculated for several stoichiometries. As can be observed, a good agreement is obtained between the experimental cyclic voltammogram and those calculated for a 1:1 $[Fe(CN)_6]^{4-}$: ligand stoichiometry.

On the other hand, the pH-dependent stepwise formation of different super-complex species can be studied from the peak potential and peak current variations with pH obtained for $[Fe(CN)_6]^{4-}$ solutions in the presence of a constant excess of ligand. Fig. 5 shows the pH dependence of the formal potential and the anodic peak current for a solution 2.00×10^{-3} mol dm^{-3} in $[Fe(CN)_6]^{4-}$ and 2.80×10^{-3} mol dm^{-3} in bmahi; breaks in these curves indicate the presence of different species in solution. As can be seen, the cyclovoltammetric data are in good agreement with the distribution diagram deduced from the potentiometrically determined stability constants.

Accordingly, we can reasonably represent the electrode processes involving the complex species by equation (2) (charges have been omitted).

$$Fe^{II}(H_pL) \rightleftharpoons Fe^{III}(H_qL) + (p - q)H + e^- \qquad (2)$$

The effect of the respective stability constants on cyclic voltammograms obtained at different pH values for a given *R* can be studied by means of the shifts in the formal potential of the $\{[Fe(CN)_6]^{4-}–[Fe(CN)_6]^{3-}\}_{complexed}$ couple with respect to the formal potential of the $\{[Fe(CN)_6]^{4-}–[Fe(CN)_6]^{3-}\}_{free}$ couple. By adapting the classical polarographic[23–26] and cyclovoltammetric[27–29] methods and assuming complete complexation by cyanide ions, we can write equation (3), where $\beta_{Fe^{II}}$ and $\beta_{Fe^{III}}$ are the cumulative stability constants for the formation of hexacyanoferrate-(II) and -(III) super-complexes, respectively.

$$E^{\circ} = E^{\circ\prime}(M^{II}–M^{III}) + (RT/nF)\ln(\beta_{Fe^{II}}[L][H]^p/\beta_{Fe^{III}}[L][H]^q) \qquad (3)$$

In the case of a simple equilibrium system, $\beta_{Fe^{III}}$ can be obtained from the limiting value of the shift in the cyclovoltammetric formal potential, $\Delta E^{\circ\prime} = E^{\circ\prime}_C - E^{\circ\prime}_M$, if $\beta_{Fe^{II}}$ is known.[29] This approach can be used in the case of stepwise pH-dependent complex formation when a reasonable separation exists between the pH ranges in which the different species prevail. Thus, we can make an estimation of some of the $\beta_{Fe^{III}}$ values from the $\beta_{Fe^{II}}$ values (see Table 3), determined potentiometrically, and the formal potentials in the plateaux of the CV–pH titration curve as in equation (4).

$$\Delta E^{\circ\prime} = 0.059 \log(\beta_{Fe^{II}}/\beta_{Fe^{III}}) \text{ (V at 298 K)} \qquad (4)$$

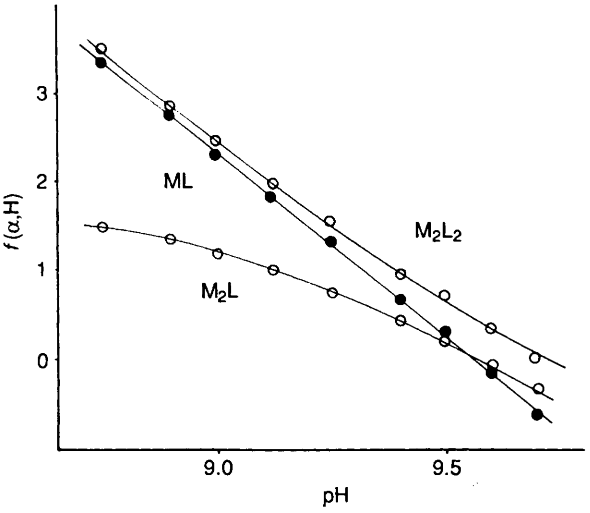

Fig. 6 Application of the Viossat method (ref. 31) to the system $[Fe(CN)_6]^{4-}$–bmahi. Plot of $f(\alpha, H)$ *vs.* pH for 1:1, 2:2 and 2:1 $[Fe(CN)_6]^{4-}$:[24]aneN_8 stoichiometries

Although e.m.f. measurements carried out at different concentrations of the reactants could differentiate between 1:1 and more aggregated species (*n*:*n*), the low solubility of the adducts formed restricts the concentration range investigated. Thus, the pH dependence of the peak currents has been used to confirm the mononuclear character of the super-complex species as well as the number of protons involved in their stepwise formation equilibria.[30,31] If we consider the formation equilibrium in the form (5), in which *m* represents the degree of

$$M + nL + qH \rightleftharpoons \frac{1}{m} M_mL_{nm}H_{qm} \tag{5}$$

condensation of the complex, we can write expression (6). In this

$$\beta^{1/m} = \frac{\alpha^{1/m} c_M{}^{(1/m-1)}(1 + \Sigma\beta_j[H]^j)^n}{(1-\alpha)m^{1/m}(c_L - n\alpha c_M)^n[H]^q} \tag{6}$$

equation β_j represents the cumulative protonation constants of the ligand and c_L and c_M the analytical concentrations of the ligand and hexacyanoferrate(II) species, respectively. The molar fraction of complexed hexacyanoferrate(II), α, can be estimated from the height of the cyclovoltammetric waves assuming the peak current to be proportional to the concentration of electroactive species. This is valid for small differences between the formal potentials of the super-complex and free hexacyanoferrate(II) ions electrode processes. If each super-complex species prevails largely in a well defined interval of pH, equation (6) can be rewritten as (7). Providing the β_j values are known

$$\begin{aligned} f(\alpha, H) &= \log\left[\frac{\alpha^{1/m}}{(1-\alpha)(c_L - n\alpha c_M)^n}\right] + n\log(1 + \Sigma\beta_j[H]^j) \\ &= \text{constant} - q\text{pH} \end{aligned} \tag{7}$$

from potentiometric data, this equation implies a linear relationship between $f(\alpha, H)$ and pH only for the correct values of *q*. For instance, data in Fig. 5 have been used to perform calculations which allow the determination of these coefficients for the first step of complexation of hexacyanoferrate(II) by bmahi. At pH between 8.5 and 9.5, α can be calculated from the peak current, i_p, at a given pH, and the peak currents, $i_p{}^M$ and $i_p{}^C$, at the foot and the plateau of the curve $i_p = f(\text{pH})$, respectively, as in equation (8). As shown in Fig. 6, $f(\alpha, H)$ varies linearly with pH for a 1:1 hexacyanoferrate(II):bmahi stoichiometry; the slope of this linear representation is $q = 4$, in agreement with potentiometric results which indicate the involvement of four protons.

$$\alpha = (i_p - i_p{}^M)/(i_p{}^C - i_p{}^M) \tag{8}$$

Conclusion

Both e.m.f. and electrochemical measurements confirm the formation of highly stable 1:1 'super-complexed' species. A further development of the electrochemical study also allows us to establish unequivocally the monomeric nature of these super-complexes. As previously observed,[2,4] the strength of the interaction for a given ligand mainly depends on the charge of both the receptor and the anion. The stability constants electrochemically estimated for the anion $[Fe(CN)_6]^{3-}$ are quite similar to those potentiometrically obtained for the equally charged $[Co(CN)_6]^{3-}$. Coulombic forces are also reflected by the topology of the receptors. For a given protonation degree of the ligand, a greater density of charge accumulates on the cyclic ligand, producing more stable super-complexes (see Fig. 1). These results confirm the existence of a macrocyclic effect on anion binding for polyammonium receptors. However, the complementarity between the topological requirements of the receptor and substrate seems to be of great importance in establishing such an effect.

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