Anion Coordination Chemistry. Hexacyanoferrate(II) Anion Complexed by a Large Polycharged Azacycloalkane. Potentiometric and Electrochemical Studies

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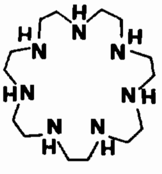
In the last few years much attention has been devoted to the coordination of anions [1, 2] and this type of interaction has recognized importance in many biological processes [3, 4]. This interest has led to the development of many ligands capable of binding various anionic species. Typical examples are cryptands which are able to incapsulate anions into their cavities [5]. Among the anionic species investigated there are also metal complexes like $[M^{n+}(CN)_6]^{(6-n)-}$ (M = Fe(II), Fe(III), Co(III), Ru(III) *etc.*). The binding of these metal complexes by highly positively-charged ligands has led to the coinage of the word: 'super complexes'. Here we report on the interactions between hexacyanoferrate(II) anion and the polyprotonated species of the large azamacrocycle 1,4,7,10,13,16,19-Heptaazacycloheneicosane (L).



(L)

Experimental

The synthesis of the macrocycle (L), its basicity constants and coordination capabilities have been reported elsewhere [6]. All materials KCl, $K_4[Fe(CN)_6]$ (C. Erba RPE ACS), standardized CO_2-free NaOH solutions, were either already of appropriate purity or purified for potentiometric and electrochemical uses. All potentiometric measurements were carried out in aqueous solution containing 1×10^{-3} mol dm^{-3} of ligand (L) and 1×10^{-3} mol dm^{-3} of the anion; the potentiometric apparatus has been previously described [7]. The computer program SUPERQUAD [8] was used to process potentiometric data and calculate the equilibrium constants. A classical three-electrode cell was used for electrochemical analysis by cyclic voltammetry [9]. The working electrode was a platinum microsphere, the auxiliary electrode was a platinum disc and the reference electrode was a calomel electrode (SCE).

Results and Discussion

In Table I the stability constants of the species which are present in the pH range investigated have been reported. To avoid protonation of the hexacyanoferrate(II) anion only experimental points above pH = 4 were used in the calculation of the equilibrium constants. In any case the first two protonation constants ($nH^+ + [Fe(CN)_6]^{4-} \rightleftarrows H_n[Fe(CN)_6]^{(4-n)-}$ n = 1, 2) of hexacyanoferrate(II), reported in ref. 10, have been taken into account in the calculation. As shown by the high values of the equilibrium constants, there is a strong interaction between $[Fe(CN)_6]^{4-}$ and protonated species of (L). No other important species have been found in the pH range investigated. The distribution of these 'super complexes' as function of pH is reported in Fig. 1 by using a DISPOL [11] computer program.

TABLE I. Stability Constants of Complexes between the Protonated Forms of (L) and $[Fe(CN)_6]^{4-}$ in Aqueous Solution, at 25 °C in 0.1 mol dm^{-3} KCl (standard state = 1 mol dm^{-3}).

Reaction	Log *K*
$H_4L^{4+} + [Fe(CN)_6]^{4-} \rightleftarrows H_4L[Fe(CN)_6]$	4.27(5)[a]
$H_5L^{5+} + [Fe(CN)_6]^{4-} \rightleftarrows H_5L[Fe(CN)_6]^+$	5.42(5)

[a] Values in parentheses are the standard deviations on the last significant figure.

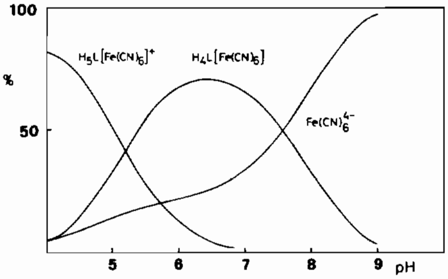


Fig. 1. Distribution diagram of the species: $H_5L[Fe(CN)_6]^+$, $H_4L[Fe(CN)_6]$ and $[Fe(CN)_6]^{4-}$ in the pH range 4–9.

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It is interesting to note that in the neutral pH range 5.5–7.5 the predominant species is the uncharged one $H_4L[Fe(CN)_6]$. At lower pH, as the degree of protonation of the ligand (L) increases, the most important species becomes $H_5L[Fe(CN)_6]^+$ (see Fig. 1). The last species is also the most stable (see Table I); the increasing stability of the 'super complex' as (L) becomes more charged (protonated) is indicative of the nature of the interaction between the two ions which is mainly electrostatic. Following the above trend one would expect that the strongest interaction would be between $[Fe(CN)_6]^{4-}$ and the more protonated species H_6L^{6+} and H_7L^{7+}. The nature of the macrocycle and its basicity constants allow the existence of the above species only at pH much below 4 where protonation of $[Fe(CN)_6]^{4-}$ occurs. Dietrich *et al.* reported in ref. 8 stability constants between $[Fe(CN)_6]^{4-}$ and the fully protonated species of macrocycles containing 6 and 8 nitrogen atoms separated by a propylenic chains. The logarithms of the stability constants reported by these authors are 6.9 and 8.9.

Recently Manfrin *et al.* [12] demonstrated by photochemical studies the enclosure of $[Co(CN)_6]^{3-}$ into these polyammonium receptors. Unfortunately, no direct comparison between our stability constants for (L) and those reported by Dietrich *et al.* [8] can be made because of the different basicity behaviour of the macrocycles investigated. Due to the long hydrocarbon chains bridging the adjacent nitrogen atoms in the macrocycles studied by Dietrich *et al.* these ligands are much more basic in the last protonation steps than is (L). As a consequence the complete protonation of the above macrocycles occurs at pH > 4, allowing the interaction between $[Fe(CN)_6]^{4-}$ and the fully protonated macrocycle to be studied.

The interactions between (L) and $[Fe(CN)_6]^{4-}$ anion were followed by cyclic voltammetry. In Fig. 2 the cyclic voltammograms of $[Fe(CN)_6]^{4-}$ at pH 4 without and with different amounts of (L) added are reported. At this pH only small amounts of uncomplexed $[Fe(CN)_6]^{4-}$ and $H_4L[Fe(CN)_6]$ are present, $H_5L[Fe(CN)_6]^+$ being the most important species. The concentration of $[Fe(CN)_6]^{4-}$ is 1×10^{-3} mol dm^{-3}, the amount of (L) added is expressed as a ratio (R) between the concentrations of (L) and $[Fe(CN)_6]^{4-}$ present in solution. The effect of adding the macrocycle (L) to the solution containing $[Fe(CN)_6]^{4-}$ is the appearance of a second oxidation-reduction signal shifted toward more anodic potential if compared with the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ couple in absence of (L) and which increases in relative intensity as R goes from 0 to 1. For R > 1 the voltammogram becomes independent from the concentration of (L). We attribute this voltammogram to the reversible complexed couple $H_5L[Fe(CN)_6]^+/H_5L[Fe(CN)_6]^{2+}$. A similar behaviour was observed by Peter *et al.* [13] for the previously cited azamacrocycles. In Fig. 3 we report the $E_{1/2}$ of the couple $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ as a function of pH in the presence and in absence of (L). Because the interaction between $[Fe(CN)_6]^{4-}$ and protonated species of (L) are strongly pH-dependent, the electrochemical behaviour of the 'complexed' $[Fe(CN)_6]^{4-}$ should also be pH-dependent. The curve reported in Fig. 3 can also be discussed taking into account the species distribution curves reported in Fig. 1. Above pH 9 the amount of $[Fe(CN)_6]^{4-}$ 'complexed' is negligible (see Fig. 1) and the redox behaviour is that one typical of the free $[Fe(CN)_6]^{4-}$. Between pH 7.5 and pH 9 there is a sharp rising of $E_{1/2}$ parallel to the increase of the concentration of the $H_4L[Fe(CN)_6]$. In the pH range 5.5–7.0 the $E_{1/2}$ is essentially constant, in this region the most important species is the neutral one $H_4L[Fe(CN)_6]$. In the pH range 4–5.5 the $E_{1/2}$ rises again as the con-

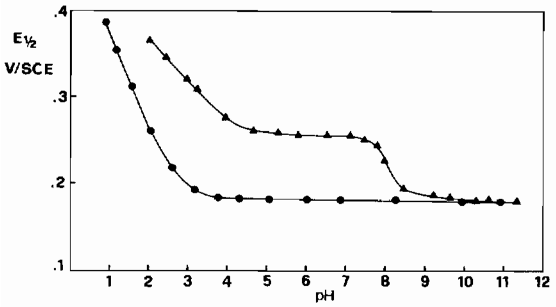

Fig. 2. $E_{1/2}$ in cyclic voltammetry (scan rate 50 mV s^{-1}, 0.1 mol dm^{-3} KCl) *vs.* pH. (●) In the absence of macrocyclic ligand, (▲) in the presence of macrocyclic ligand (L).

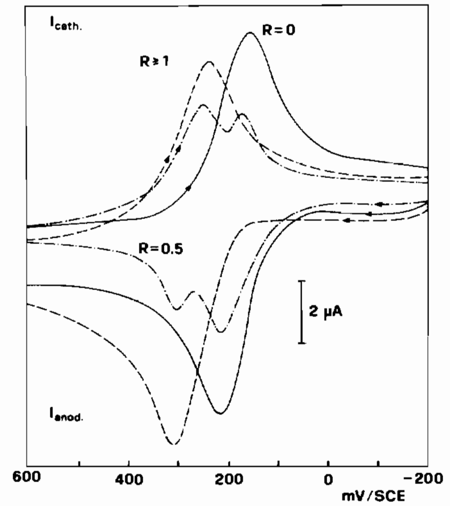

Fig. 3. Effect of increasing amounts of (L) on the cyclic voltammograms of $[Fe(CN)_6]^{4-}$. pH = 4, scan rate 50 mV s^{-1}, R = mmol of (L)/mmol of $[Fe(CN)_6]^{4-}$. Concentration of $[Fe(CN)_6]^{4-}$ 1×10^{-3} mol dm^{-3}.

centration of $H_5L[Fe(CN)_6]^+$ increases. Below pH 4 effects of the protonation of $[Fe(CN)_6]^{n-}$ (n = 3, 4) start to be predominant.

Acknowledgements

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