Redox Properties and Stability Constants of Anion Complexes. An Electrochemical Study of the Complexation of Metal Hexacyanide Anions by Polyammonium Macrocyclic Receptor Molecules

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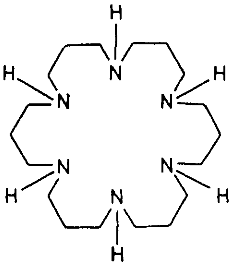
Summary Electrochemical studies on macrocyclic complexes of $M(CN)_6^{4-}$ (M = Fe, Ru) anions indicate a 1 : 1 stoicheiometry and monoelectronic, reversible, oxidation for these complexes, and illustrate the control of redox potential of anions by complexation with appropriate receptor molecules.

The modifications of the properties of metal *cations* brought about by complexation have been the subject of numerous studies and form a major chapter in cation co-ordination chemistry and in catalysis. Recent work on the co-ordination chemistry of *anions* has led to the development of several types of organic receptor molecules capable of binding various anionic species (see ref. 1a and references therein).

Among these receptors, novel polyaza-macrocycles have been synthesized recently, and it has been shown that their protonated forms yield stable and selective complexes with a variety of organic and inorganic anions.[1a] They bind particularly strongly anions like $Fe(CN)_6^{4-}$ and $Co(CN)_6^{3-}$, as well as anions of biological interest like citrate, AMP^{2-}, ADP^{3-}, and ATP^{4-}. One may expect that, as is the case for cations, complexation of anions will affect their physicochemical properties and their chemical reactivity.



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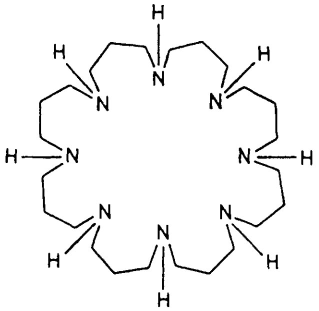

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We now describe some results of an electrochemical study of the stoicheiometry, the stability constants, and the redox properties of the four complexes formed by the macrocyclic ligands (**1**)–6H$^+$ and (**2**)–8H$^+$ with the complex anions $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$. The iron hexacyanide anion was chosen because of the widely studied redox properties of the corresponding Fe^{III}/Fe^{II} couple and the high stability of the complexes of $Fe(CN)_6^{4-}$ with (**1**)–6H$^+$ and (**2**)–8H$^+$.[1a] On the other hand, the choice of $Ru(CN)_6^{4-}$ was made in order to investigate its complexation by (**1**)–6H$^+$ and (**2**)–8H$^+$ and its redox properties in the complexes. Furthermore, both anions display interesting photochemical reactions which may be affected by complexation.[2]

Table. Electrochemical results (E and ΔE in mV) for the anion complexes formed by the macrocyclic polyammonium cations (**1**)–6H$^+$ and (**2**)–8H$^+$ with the substrate anions $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$.[a,b]

Species: ligand/$M(CN)^{4-}$	R[c]	E_{ap}[d]	E_{cp}[d]	ΔE_{ac}[d]	$E_{1/2}^{ox}$[e]	$\Delta E_{complex}$[e]
$Fe(CN)_6^{4-}$	0	220	160	60	190	0
(**1**)–6H$^+$/Fe	1·2	350	285	65	320	130
(**1**)–6H$^+$/Fe	15	365	310	55	330	140
(**1**)–6H$^+$/Fe	55	375	320	55	350	160
$Ru(CN)_6^{4-}$ [c]	0	745	685	60	705	0
(**1**)–6H$^+$/Ru	1·2	880	815	65	835[f]	130
(**2**)–8H$^+$/Fe	1·2	385	320	65	355	165
(**2**)–8H$^+$/Ru	1·2	—	~840	—	865	165[f]

[a] All measurements in aqueous solution containing $4{\cdot}5 \times 10^{-4}$ M of $K_4Fe(CN)_6$ or $K_4Ru(CN)_6$ and 0·1 M KCl at pH 5·5 adjusted with HCl. All potentials (E) refer to saturated calomel electrode (S.C.E.). [b] Ligands: the hydrochlorides (**1**)–6HCl and (**2**)–8HCl. [c] Concentration ratio R = [ligand]/[$M(CN)_6{}^{4-}$]. [d] Cyclic voltammetry at 50 mV/s: E_{ap} = anodic peak, E_{cp} = cathodic peak. [e] Rotating disc electrode (R.D.E.) voltammetry at 2000 rev./min. $\Delta E_{complex}^{ox} = E_{1/2}^{ox}\ (R = 1) - E_{1/2}^{ox}\ (R = 0)$. [f] Differential pulse (10 mV) voltammetry on R.D.E. (2000 rev./min).

The electrochemical results (Table) indicate that the $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$ anions are appreciably more difficult to oxidize in the presence than in the absence of the macrocycles (**1**)–6H$^+$ or (**2**)–8H$^+$. The shifts in anodic oxidation potential $\Delta E_{1/2}^{ox}$ are similar for both $M(CN)_6^{4-}$ species [+130 mV with (**1**)–6H$^+$ and +165 mV with (**2**)–8H$^+$] and may be attributed to complexation of the anions by the polyammonium macrocycles, as previously shown for $Fe(CN)_6^{4-}$.[1a] All four complexes studied [$M(CN)_6^{4-} \subset L_{prot}$] [M = Fe or Ru; L_{prot} = (**1**)–6H$^+$ or (**2**)–8H$^+$] also exhibit similar behaviour in cyclic voltammetry (Figure). In the presence of (**1**)–6H$^+$ or (**2**)–8H$^+$ a new set of reduction peaks appears, in addition to the pair of peaks corresponding to the uncomplexed anions. The less anodic pair of peaks, which arises from the uncomplexed couple $M(CN)_6^{4-}/M(CN)_6^{3-}$, is observable in the range $0 < R < 1$, where R is the ratio of concentrations $L_{prot}/M(CN)_6^{4-}$. The more anodic pair of peaks corresponds to the complexed anions; they appear on introduction of ligand into the solution, and remain without other peaks when $R > 1$. Thus the complexes studied have 1 : 1 stoicheiometry. Further addition of protonated ligand ($1 < R < 55$) had no significant effect on the reversibility of the redox process and on the reduction potential (Table). The small additional potential shifts, observed (Table) in the presence of a large excess of ligand, may be explained by competing complexation of $Fe(CN)_6^{4-}$ and Cl^-.

Linear-sweep and cyclic voltammograms for the two Fe^{II} species, $Fe(CN)_6^{4-}$ and [$Fe(CN)_6^{4-} \subset$ (**1**)–6H$^+$], as well as for both oxidized forms $Fe(CN)_6^{3-}$ and [$Fe(CN)_6^{3-} \subset$ (**1**)–6H$^+$], show that the oxidation product of the complex is the corresponding Fe^{III} form, which reverts to the initial complex on scanning the potential back to less positive values. Therefore, the monoelectronic Fe^{II}/Fe^{III} interconversion occurs *without dissociation* of the complex; furthermore, it is reversible since $\Delta E_{ac} = E_{ap} - E_{cp}$ (Table) is close to 60 mV. Similar results have been obtained for [$Fe(CN)_6^{4-} \subset$ (**2**)–8H$^+$] and for the complexes of $Ru(CN)_6^{4-}$ with (**1**)–6H$^+$ and (**2**)–8H$^+$ (Table). The half-wave potential $E_{1/2}^{ox}$ measured on stationary waves is thus expected to be very close to the standard redox potential, $E°$, for all complexes.

The magnitude of the redox potential shifts produced by complexation depends more on the macrocyclic ligand than on the nature of the complexed anion. Indeed, the data for the four complexes of $M(CN)_6^{4-}$ (M = Fe or Ru) with (**1**)–6H$^+$ or (**2**)–8H$^+$ indicate that, for the same ratio R = 1·2, the shifts are identical irrespective of the complexed anion, but increase on changing the ligand from (**1**)–6H$^+$ to (**2**)–8H$^+$ (Table). This may be ascribed to the predominance of electrostatic interactions between the charges of the protonated ligand and of the complexed anion in determining the magnitude of the shifts, as they also dominate the stability of the complexes.[1a] It implies that, for a given anion redox couple and within a set of ligands of similar structure, the shifts are expected to be largest for the ligands of highest charge. Of course, structural effects will play an important role for ligands of significantly different shape and/or size.

The stability constants of the $Fe(CN)_6^{4-}$ complexes were determined by pH measurements.[1a] This method could not be used for $Fe(CN)_6^{3-}$, owing to the instability of the solution on the time-scale of such determinations. In contrast, the time-scale of electrochemical measurements is quite short, so that relative stabilities of oxidized and reduced complexes may be calculated from the measured $\Delta E_{complex}^{ox}$ values (Table).[3,4] Thus, from the known stabilities of reduced iron complexes,[1b] the stability constants of the oxidized anion [$Fe(CN)_6^{3-} \subset L_{prot}$] are 4·2 for L_{prot} = (**1**)–6H$^+$ and 5·0 for L_{prot} = (**2**)–8H$^+$. The lower stability of the complexes of the oxidized anion is consistent with the decrease in coulombic interactions between the anion and the protonated ligand.

The above results have allowed the determination of the 1 : 1 stoicheiometry of the '*super complexes*' (complexes of complexes) formed by $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$ with both ligands (**1**)–6H$^+$ and (**2**)–8H$^+$, as well as the stability constants of the complexes formed by $Fe(CN)_6^{3-}$.

Also the results clearly demonstrate that the redox potential of *anionic* species may be shifted and controlled over a significant potential range by an appropriate selection of the macrocyclic or macropolycyclic receptor molecule. Conversely, they also show that electrochemical measurements represent an important tool for the study of anion complexes.

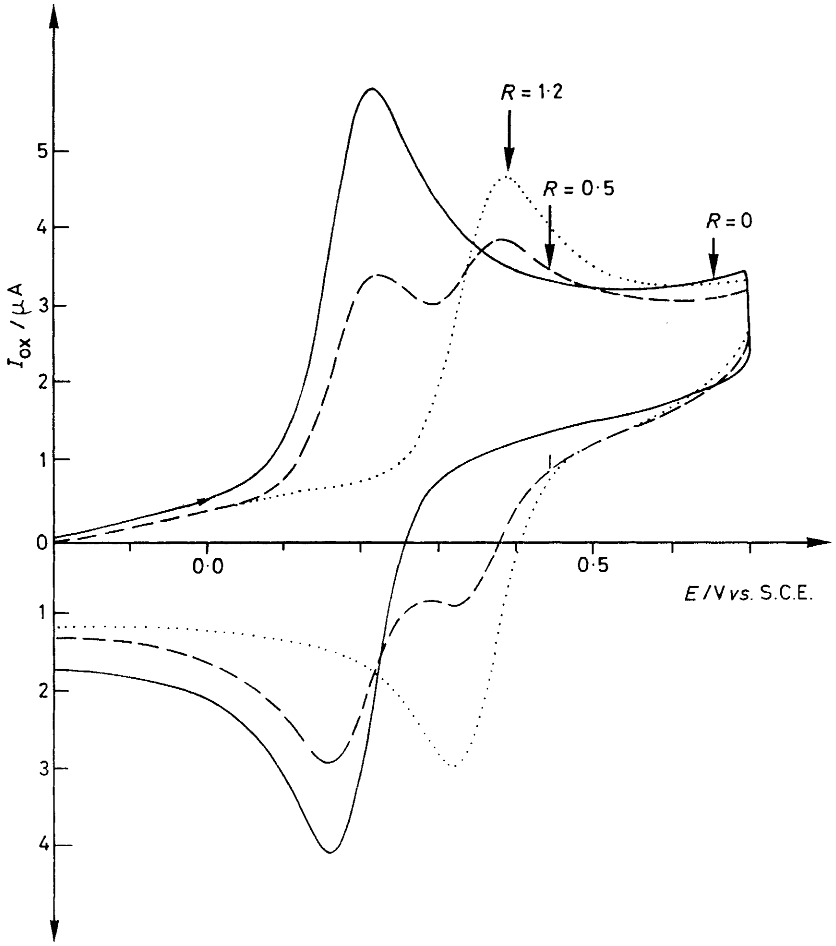

Figure. Cyclic voltammetry (50 mV/s) on Pt disc, in 0·1 M KCl; pH 5·5; $R = [(\mathbf{2})\text{–}8H^+]/[Fe(CN)_6^{4-}]$.

Similar effects may be expected for anion cryptates of the types already described (ref. 1a and references therein). They are of particular interest with respect to the redox reactivity of anions in inorganic and analytical chemistry as well as of anions of biological importance. For instance, it may be possible to extend these studies to carboxylate anions, such as citrate or oxalate, and to set up an electrochemical method for determining the relative stability of anion complexes of redox inactive anions (in the potential range covered) by competitive displacement of a redox active anion from its complex with a given ligand.

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[1] (a) B. Dietrich, M. W. Hosseini, J. M. Lehn, and R. B. Sessions, *J. Am. Chem. Soc.*, 1981, **103**, 1282; (b) in H_2O + 0.1M KCl, log K_s for complexes of $Fe(CN)_6^{4-}$ are 6.4 with (**1**)–6H$^+$ and 7.8 with (**2**)–8H$^+$, M. W. Hosseini and J. M. Lehn, unpublished results.

[2] V. Balzani and V. Carassiti, 'Photochemistry of Coordination Compounds,' Academic Press, New York, 1970.

[3] J. J. Lingane, *Chem. Rev.*, 1941, **29**, 1.

[4] C. G. Butler and R. C. Kaye, *J. Electroanal. Chem. Interfacial Electrochem.*, 1964, **8**, 463.