DALTON

Electron transfer between $Fe(CN)_6^{3-}$ and iodide promoted by supercomplexation with a polyammonium macrocycle

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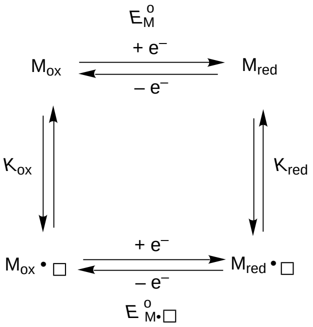
Some new properties promoted by the formation of a supercomplex between iron hexacyanometallates and the polyazamacrocycle [32]aneN_8 (1,5,9,13,17,21,25,29-octaazacyclodotriacontane) are described. In the presence of the polyazamacrocycle, thermal and photoinduced electron transfer from iodide to $Fe(CN)_6^{3-}$ were observed in moderately acidic media. The thermal reaction is slow ($k_{obs} = 8.9 \times 10^{-4}\ s^{-1}$, at 25 °C) and proceeds to an equilibrium ($K = 7\ \mathrm{M}^{-2}$, at 25 °C). The reaction is almost isoergonic, with favorable enthalpy and unfavorable entropy changes ($\Delta G° = -4.8$ kJ mol^{-1}, $\Delta H° = -160$ kJ mol^{-1}, $\Delta S° = -0.54$ kJ mol^{-1} K^{-1}). A photoinduced electron-transfer process, leading to additional iodide oxidation, was observed upon flash irradiation of equilibrated solutions. Following the photoinduced process, the system reverts to the thermal equilibrium in the dark. The promoting role of the macrocycle is thermodynamic for the thermal process (anodic shift in the $Fe^{II/III}$ potential upon supercomplex formation) and kinetic for the photoinduced process [formation of ion-paired species between hexacyanoferrate(III) and iodide upon supercomplex formation]. The thermal reaction is reversible in basic media (where the macrocycle deprotonates and supercomplex formation is prevented), providing an example of on/off switching by pH changes of an electron-transfer reaction.

The thermal and photochemical reactivity, as well as the redox, spectroscopic and photophysical properties of co-ordination compounds can be greatly modified by their inclusion into supramolecular structures (supercomplexes) involving appropriate macrocyclic receptors.[1–12] In these structures the macrocyclic receptor is bound by non-covalent interactions to the transition-metal complex, and thus can be viewed as a second-sphere co-ordination ligand.[3] Several examples of this chemistry have been described for the class of supercomplexes formed between metal cyanides and polyazamacrocycles of general type [*n*]ane$N_mH_m^{m+}$ (fully protonated form). For example, for the large macrocycle [32]ane$N_8H_8^{8+}$ ([32]aneN_8 = 1,5,9,13,17,21,25,29-octaazacyclodotriacontane), supercomplexes with metal cyanides of type $M(CN)_6^{3-}$ (M = Co^{III},[4] Cr^{III}[5] or Fe^{III}[6]) and $M(CN)_6^{4-}$ (M = Fe^{II}[6] or Ru^{II}[6]), $M(CN)_5(H_2O)^{2-}$ and $M(CN)_5Br^{3-}$ (M = Co^{III}[4]) and $M(bipy)(CN_4)^{2-}$ (M = Ru^{II}, bipy = 2,2′-bipyridine)[7] have been studied. In all cases, the main driving force for the formation of the supramolecular structure is the coloumbic attraction between the negatively charged co-ordination compound and the positively charged macrocycle. However, the supercomplex is not a simple ion-pair because hydrogen bonds between the protonated nitrogens of the macrocycle and the nitrogens of the cyanide ligands seem to play an important structural role.[7] As usual in supramolecular chemistry, the physical chemical characteristics of the supercomplexes are not the simple addition of the properties of each component, and the study of the new properties is one of the interesting aims in the investigation of supercomplex formation.

Among the new properties induced by supercomplex formation, of particular interest is the change in redox potential of the metal-based redox couple (Scheme 1). The shift in reduction potential upon supercomplex formation is always in the anodic direction (in Scheme 1, $K_{red} > K_{ox}$)[6,8] and the effect can be quite substantial.[6,7] On this basis, one can think of using the macrocycle as a 'switch' for redox reactions involving metal cyanides. For instance, by choosing a reaction partner S such that $E°_M < E°_S < E°_{M\cdot\square}$, switching between S_{ox} and S_{red} could be obtained, in principle, by addition or removal of the macrocycle [equation (1)]. An indirect, but easier way to achieve reversible switching would be to operate in the presence of macrocycle and switch on or off its supercomplexing ability by changes in pH [equation (2)].



Scheme 1 □ denotes the macrocycle centre

$$M_{ox} + S_{red} \xrightleftharpoons[-\square]{+\square} M_{red}\cdot\square + S_{ox} \qquad (1)$$

$$M_{ox} + S_{red} + \square \xrightleftharpoons[-H^+]{+H^+} M_{red}\cdot\square + S_{ox} \qquad (2)$$

In this article, we wish to present a study of the thermal redox reaction between $Fe(CN)_6^{3-}$ and I^-, promoted by [32]aneN_8-

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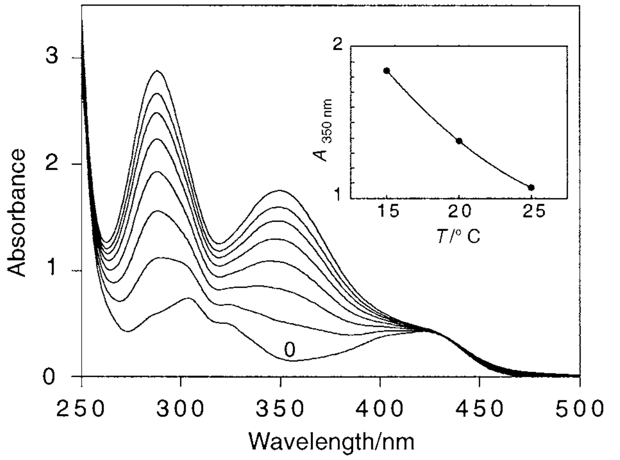

Fig. 1 Spectral changes induced by addition of 5 × 10^{-4} M [32]aneN$_8$H$_8$$^{8+}$ to a solution of 5 × 10^{-4} M Fe(CN)$_6$$^{3-}$ and 5 × 10^{-3} M iodide (pH = 4.4, acetate buffer, 25 °C, in the dark). In order of increasing UV optical densities, 0, 5, 10, 15, 20, 25, 30 and 40 ≡ 90 min. In the inset: temperature dependence of the 350 nm equilibrium absorbance

H$_8$$^{8+}$. The system, though not a perfect fit to the above-mentioned redox potential requirements, does indeed provide a simple example of the switching behaviour depicted in equation (1). In addition to the thermal process, an interesting photo-induced electron-transfer process is also observed in this system.

Results

Cyclic voltammetry experiments carried out on 4.5 × 10^{-3} M Fe(CN)$_6$$^{3-}$ aqueous solutions (0.04 M acetate buffer, pH = 4.4) showed that an anodic shift of 0.180 V takes place in the Fe(CN)$_6$$^{3-}$–Fe(CN)$_6$$^{4-}$ reduction potential upon addition of 4.8 × 10^{-3} or 6.9 × 10^{-3} M [32]aneN$_8$H$_8$$^{8+}$.‡

Solutions containing 5 × 10^{-4} M Fe(CN)$_6$$^{3-}$ and 5 × 10^{-3} M iodide in aqueous solution (pH 4.4, acetate buffer) were stable in the dark on the time-scale of the experiments. Upon addition of 5 × 10^{-4} M [32]aneN$_8$H$_8$$^{8+}$ a reaction takes place as indicated by pronounced UV spectral variations (Fig. 1). The reaction was completed in *ca.* 1 h. Inspection of the spectral variations indicate the formation of two new intense bands at 350 and 289 nm, characteristic of the species I$_3$$^-$.[13] The global reaction taking place can thus be written as in equation (3).

$$2\,\mathrm{Fe(CN)_6^{3-}\cdot[32]aneN_8H_8^{8+}} + 3\,\mathrm{I^-} \rightleftharpoons 2\,\mathrm{Fe(CN)_6^{4-}\cdot[32]aneN_8H_8^{8+}} + \mathrm{I_3^-} \qquad (3)$$

The kinetics of equation (3), under the experimental conditions used, was that of a first-order process, with the rate constant increasing with increasing temperature (Table 1). The final absorbance values reached at 25 °C correspond to an I$_3$$^-$ equilibrium concentration of 3.4 × 10^{-5} M (*i.e.*, to *ca.* 14% reduction of the Fe complex).§ The extent of conversion increased, as expected, with increasing iodide concentration and also increased markedly by decreasing the temperature (inset of Fig. 1). Equilibrium constants of reaction (3), calculated from such experiments, are reported in Table 1.

The reaction can be completely reversed, as shown by spectral variations leading back to the initial spectrum, by changing the pH to alkaline values.

Table 1 Equilibrium constants (K) for reaction (3), and pseudo-first-order rate constants of thermal equilibration in the forward and in the backward direction (k_{obs}, measured following addition of the macrocycle; k_{obs}, measured in the dark after flash excitation)

T/°C	K*/M^{-2}	10^4 k_{obs}*/s^{-1}	10^4 $k_{-\mathrm{obs}}$*/s^{-1}
15	65	3.1	3.9
20	20	6.1	6.7
25	7	8.9	11.7

* Estimated errors: ± 5%.

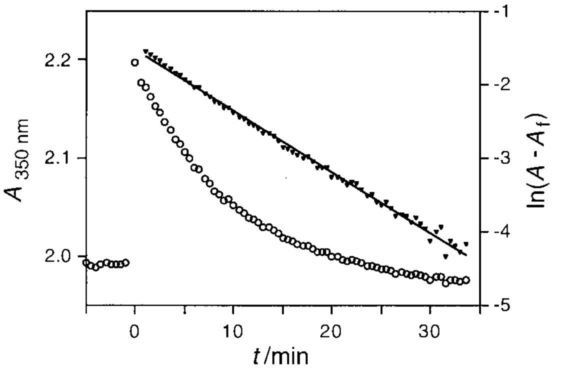

Fig. 2 Variation in the 350 nm absorbance of equilibrated solutions (same conditions as Fig. 1) following flash irradiation (○); first-order plot of the decay kinetics (▼)

The influence of light on the system was also investigated, by irradiating a thermally equilibrated aqueous solution {5 × 10^{-4} M Fe(CN)$_6$$^{3-}$, 5 × 10^{-3} M iodide, 5 × 10^{-4} M [32]aneN$_8$H$_8$$^{8+}$, pH 4.4} with a flash of visible light ($\lambda > 400$ nm, flash duration ≈ 20 ms). Flash irradiation gives rise to an instantaneous increase in the I$_3$$^-$ absorption bands, followed by a slow decrease in the dark leading back to the initial absorption spectrum (Fig. 2).¶ The kinetics of the thermal back reaction was appreciably first order (Fig. 2) with the rate constant increasing with temperature (Table 1).

The thermal and photochemical results described above are independent of the presence of molecular oxygen, as checked by comparison between air-equilibrated and nitrogen-purged solutions.

Discussion

The formation of supramolecular adducts between Fe(CN)$_6$$^{n-}$ (n = 3 or 4) and [32]aneN$_8$H$_8$$^{8+}$ was previously characterized.[6] Under the experimental conditions used in this work (pH 4.4), both forms of the co-ordination compound can be considered to be completely associated with the macrocycle, with a plausible supramolecular structure as presented in Fig. 3. In the absence of the macrocycle, the standard reduction potential of Fe(CN)$_6$$^{3-}$ is $E° = 0.358$ V,[15] and oxidation of iodide ($E° = 0.536$ V)[15] is thermodynamically unfavorable. In the presence of [32]aneN$_8$H$_8$$^{8+}$, the redox potential of the co-ordination compound is increased by 0.180 V, and thus reaction (3) becomes essentially isoergonic ($\Delta G° = +0.002$ eV, 1 eV ≈ 96.488 kJ mol^{-1}) allowing the formation of measurable amounts of products. The equilibrium constant measured by UV/VIS absorption spectrophotometry (Table 1) is not far from unity at 25 °C, in reasonable agreement with these expectations. When the pH

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‡ Under slightly different experimental conditions, an increase of 0.165 V was obtained in previous work.[6]

§ Upon standing for long periods (*e.g.*, 12 h) in the dark, some degradation is observed (slight but measurable decrease of absorbance at 350 nm). The process is more pronounced at high temperature. All the measurements were performed on freshly prepared solutions and at temperatures not higher than 25 °C, where degradation is completely negligible.

¶ In these experiments, the final spectrum after the dark back reaction is actually lower by a very small amount (less than 1%) than the initial one. This suggests that an additional irreversible photochemical reaction takes place, albeit in relatively small yields. Such a process, most probably associated with the intrinsic photoreactivity[14] of Fe(CN)$_6$$^{3-}$, can be clearly seen in continuous irradiation experiments and is enhanced by the use of UV light.

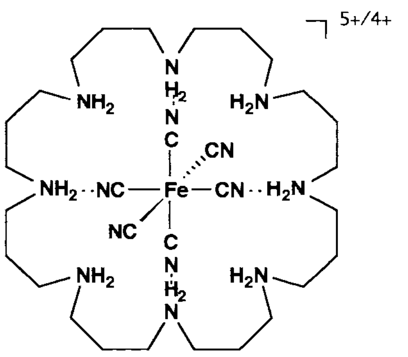

Fig. 3 Schematic structure of the supercomplex between $Fe(CN)_6^{n-}$ ($n = 3$ or 4) and $[32]aneN_8H_8^{8+}$

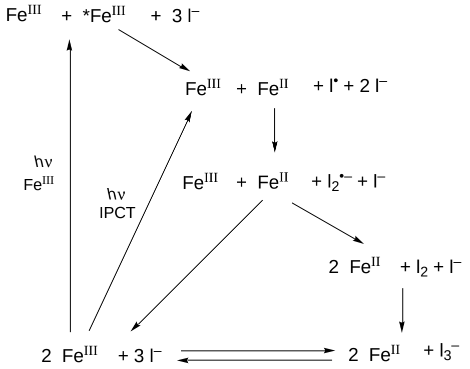

Fig. 4 Schematic energy level diagram for the photoinduced electron-transfer reaction; Fe^{III} and Fe^{II} refer to the supercomplexes with $32[ane]N_8H_8^{8+}$ which are, at least partially, ion-paired with I^-

is changed to alkaline values, the supercomplex dissociates and the reverse exergonic reaction takes place. This behaviour provides a simple example of a switchable redox system based on supercomplex formation. In the present case, the switching effect is only partial (from 0–14% conversion at 25 °C, from 0–26% at 15 °C) but systems with 100% on/off response can be easily designed, in principle, by a suitable choice of the redox potential of the reaction partner (see above).

The standard enthalpy change of reaction (3) can be calculated through a van't Hoff plot of the equilibrium data of Table 1, giving $\Delta H° = -160$ kJ mol^{-1}. Thus, the process is substantially exothermic and the very small driving force must arise from a large unfavourable entropic factor (with $K = 7$ M^{-2} at 25 °C, $\Delta G° = -4.8$ kJ mol^{-1} and $\Delta S° = -0.54$ kJ mol^{-1} K^{-1}).

As far as the photochemical reaction is concerned, the exceedingly short lifetime of the $Fe(CN)_6^{3-}$ excited states forbids any type of bimolecular process. On the other hand, several examples have been described[13,16–19] of unimolecular photoinduced electron transfer taking place in ion-pairs involving iodide and positively charged co-ordination compounds. A qualitative energy level diagram as shown in Fig. 4 can be useful to discuss the photoinduced reaction. Independently of whether the ion-pair charge transfer (IPCT) state is populated directly by light absorption or indirectly through upper molecular excited states, the first event that originates from the IPCT state, taking place on a time-scale much faster than the lifetime of the flash lamp, is the formation of the one-electron redox products, an Fe^{II} complex and atomic iodine.|| This high-energy species is probably stabilized by formation of the transient radical anion $I_2^{\bullet -}$, which can either give back electron transfer to reform the reactants or reduce, in a second one-electron transfer step, an additional Fe^{III} species. To the extent to which the secondary forward pathway takes place, the concentration of the final product, I_3^-, is suddenly altered upon flash excitation and subsequent relaxation to the thermal equilibrium can be observed as a dark process.

It may be noticed that, in this system, evolution towards the equilibrium can be monitored by two independent pathways: (*i*) in the forward direction, after switching on the process by addition of the macrocycle; (*ii*) in the opposite direction, after perturbing the equilibrium by flash excitation. Both relaxation processes experimentally follow first-order kinetics, and the two rate constants appreciably coincide (Table 1). Thus the system behaves as a typical first-order equilibrium, where the relaxation kinetics gives, independent of the direction in which it is observed, the sum of forward and back reaction rate constants. The reason for the forward reaction being (pseudo)first-order is obvious, as one of the reactants, I^-, is present in vast excess. For the back reaction no obvious explanation is available, although arguments based on ion pairing between I_3^- and Fe^{III} supercomplex products could be invoked to justify the observed first-order behaviour.

Conclusion

The results described in this work exemplify the ability of polyazamacrocycles to promote (otherwise impossible) reactions of metal cyanide complexes. In the case of the thermal oxidation of iodide by hexacyanoferrate(III) the role of the macrocycle is to provide extra stabilization to the product complex, making the reaction *thermodynamically* accessible. In the case of the photochemical process, the thermodynamic requirements are largely offset by the photon energy and the main role of the macrocycle is to make the process *kinetically* allowed: the switch of charge type of hexacyanoferrate(III) upon supercomplexation permits the formation of strong ion-pairs between iodide and the complex, in which optical or ultrafast photoinduced electron transfer can take place.

Experimental

The preparation of $[32]aneN_8{\cdot}8HClO_4$ was carried out as described previously.[7] The other reagents were commercially available and of analytical grade. All measurements were carried out in acetate buffer (pH 4.4) prepared from 0.4 M NaO_2CMe and $HClO_4$. Absorption measurements were carried out on a Perkin-Elmer lambda 6 spectrophotometer, and flash lamp experiments were conducted according to previous work.[20] Cyclic voltammetry experiments were run on a PAR 273 potentiostat connected to a conventional three-electrode cell assembly (Ag–AgCl, Pt wire, glassy carbon); solutions were Ar purged for 15 min.

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|| It is assumed that the IPCT state is dissociative, *i.e.*, the primary products originate from the lower vibrational level.

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