Inorganica Chimica Acta, 214 (1993) 193–196

Note

Appending two non-equivalent ferrocene fragments to a metallocyclam core

Giancarlo De Santis, Luigi Fabbrizzi*,
Maurizio Licchelli, Carlo Mangano
and Piersandro Pallavicini

Dipartimento di Chimica Generale, Università di Pavia, via Taramelli 12, 27100 Pavia (Italy)

(Received June 4, 1993; revised July 12, 1993)

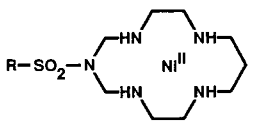
Abstract

A three-component system in which two non-equivalent ferrocene fragments are appended to a metallocyclam subunit has been prepared through an Ni^{II} template synthesis. The system undergoes two distinct and consecutive reversible one-electron oxidation processes centred on the two ferrocene fragments, but decomposes on oxidation of the Ni^{II} centre.

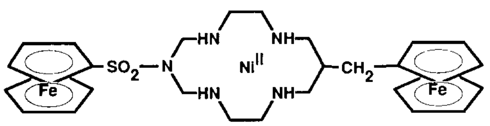
Introduction

The tendency of ferrocene (Fc) to undergo a reversible one-electron oxidation process to the stable ferrocenium cation (Fc^+) has been recognised since its first appearance on the chemical stage [1]. Since then the ferrocene fragment has been appended to molecules of different kind to control or modify their properties and reactivity through the Fc/Fc^+ redox change. For instance, the coordinating tendencies of a given ligand (e.g. a crown ether or a cryptand) are drastically reduced on oxidation of the appended ferrocene moiety [2]. Moreover, linking of ferrocene to another fragment, active through a reversible one-electron change, may generate a two-electron redox system. In particular, covalent linking of a ferrocene moiety to a nickel(II) cyclam subunit (active through the Ni^{II}/Ni^{III} couple) has given the two-component system **1**, able to release two electrons at distinctly different potentials, E_1 and E_2 [3]. As the two redox centres do not communicate, E_1 and E_2 values are close to those observed for the two individual components. Such an approach is quite general and can be extended to build up multi-component systems, containing n fragments and capable of exchanging n electrons. If the fragments are different from each other, the n electrons should be released at n different potentials.

In order to test such an approach, we have prepared the three-component system $[\mathbf{3}]^{2+}$ consisting of one metallocyclam subunit and two non-equivalent ferrocene fragments.



R = Fc **1**, C_6H_5 **2**



3

Experimental

(Ferrocenyl)methyl-diethyl malonate (**4**) and ferrocenesulfonamide were prepared as described in the literature [4, 5].

UV–Vis spectra were measured on a Hewlett-Packard 8452A diode array spectrophotometer.

Electrochemical studies

MeCN was distilled over CaH_2 and stored under nitrogen over molecular sieves. $[Bu_4N]ClO_4$ (Fluka, polarographic grade) was used without further purification. Electrochemical measurements (cyclic voltammetry, CV, and differential pulse voltammetry, DPV) were performed in a conventional three-electrode cell, using a P.A.R. 273 potentiostat/galvanostat, controlled by an IBM AT personal computer. The working electrode was a platinum microsphere and the counter-electrode was a platinum foil. A silver wire was used as a pseudo-reference electrode and was calibrated using cobaltocene as an internal standard. In a separate experiment, the potential associated to cobaltocene/cobaltocenium redox change was measured versus the ferrocene/ferrocenium couple ($E_{1/2} = 1.33$ V). Thus, all the potentials reported in this work have been referred to the classical Fc^+/Fc standard couple. Controlled-potential coulometry experiments were performed on MeCN solutions (5×10^{-4} mol dm^{-3}) employing a platinum gauze as a working electrode.

---

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

Syntheses

6-(Ferrocenyl)methyl-1,4,8,11-tetraazaundecane-5,7-dione (5)

(Ferrocenyl)methyl-diethyl malonate (8.0 g, 22.2 mmol) was added in several portions to an excess of ice-cooled anhydrous 1,2-diaminoethane (50 cm^3), under a nitrogen atmosphere. After allowing the resulting solution to return to room temperature, magnetic stirring was continued for 6 days. The orange–brown solution was concentrated on a rotary evaporator to 5 cm^3 and the resulting slurry filtered under nitrogen. The solid residue was repeatedly washed with diethyl ether and dried in a nitrogen stream. 6.5 g of orange–brown product were recovered. Yield 76%. *Anal.* Found: C, 55.84; H, 6.71; N, 14.42. Calc. for: $C_{18}H_{26}FeN_4O_2$: C, 56.00; H, 6.73; N, 14.41%.

6-(Ferrocenyl)methyl-1,4,8,11-tetraazaundecane (6)

A solution of BH_3 1 mol dm^{-3} in THF (100 cm^3) was added to a solution of **5** (1.5 g, 3.89 mmol) in anhydrous THF (100 cm^3), under a nitrogen atmosphere. After refluxing for 3 days, a clear orange solution was obtained which was cooled to room temperature, treated with 50 cm^3 of MeOH and concentrated to 10 cm^3. The resulting deep orange oily solution was purged with nitrogen and added to a purged mixture of MeOH, water and 37% aqueous HCl (85 cm^3, 5:2:1.5 ratio). The resulting solution was refluxed for 1 h, then cooled to room temperature, made basic with 5 mol dm^{-3} NaOH and extracted with CH_2Cl_2 The organic extracts were dried over Na_2SO_4 and, after evaporation of the solvent, 0.8 g of crude product was recovered as a thick oil. Yield 57%. The product was characterised as the hydrochloride, **5**·4HCl. *Anal.* Found: C, 43.05; H, 6.80; N, 10.98. Calc. for: $C_{18}H_{34}Cl_4FeN_4$: C, 42.91; H, 6.75; N, 11.11%.

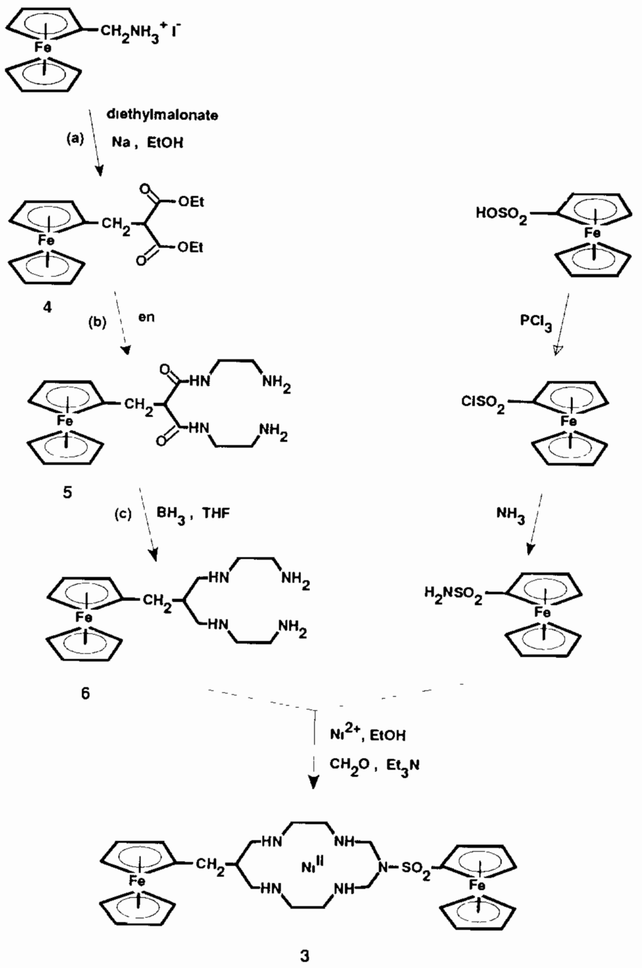
[1-Ferrocenesulfonyl-8-(ferrocenyl)methyl-1,3,5,10,13-pentaazacyclotetradecane]nickel(II) perchlorate ($3(ClO_4)_2$)

0.504 g of **5**·4HCl (1 mmol) were dissolved in hot EtOH (100 cm^3) and treated with 4 mmol of triethylamine. The resulting solution was dropped into a round-bottomed flask containing $NiCl_2$ (0.237 g, 1 mmol) in EtOH (30 cm^3). Then ferrocenesulfonamide (0.265 g, 1 mmol) in EtOH, triethylamine (0.15 cm^3) and 40% aqueous formaldehyde (1 cm^3) were added. The solution was warmed at 60 °C under magnetic stirring for 7 days, then concentrated on a rotary evaporator. A brown precipitate was obtained after addition of water; it was filtered off, washed with water and dried *in vacuo*. Yield 27%. *Anal.* Found: C, 46.89; H, 5.49; N, 8.85. Calc. for: $C_{30}H_{41}Cl_2Fe_2N_5NiO_2S$: C, 46.37; H, 5.31; N, 9.01%. Mass spectrum (FAB): 705.1 (required MW for complex cation: 705).

Results and discussion

Sulfonamides were proved to be effective locking fragments in the template synthesis of azacyclam ligands [6]. In particular, ferrocenesulfonamide has been recently used to build up a ferrocene–cyclam conjugate system [3]. The same approach, in which ferrocenesulfonamide behaves as a molecular padlock in the closure of the macrocycle ring, has been employed to prepare the bis-ferrocene–metallocyclam system, **3**. The synthetic route to **3** is outlined in Scheme 1.

First, a ferrocenemethyl fragment was appended to the α-carbon of diethylmalonate (step a); then, (ferrocenyl)methylmalonate (**4**) underwent room temperature aminolysis in ethylenediamine to give the tetramine diketone **5** (step b), which was reduced to the tetramine **6** by prolonged reflux with BH_3 in THF (step c). Finally, after *in situ* complexation in ethanol with a stoichiometric amount of nickel(II) chloride, **6** underwent a template cyclisation process in the presence of excess formaldehyde and of stoichiometric ferrocenesulfonamide. The chloride complex salt [**3**]Cl_2 was ob-



Scheme 1

tained as a microcrystalline yellow–brown product which gave satisfactory elemental analysis. It was further characterised through the high resolution mass spectrum (FAB), which showed a molecular peak at 705.1 (calculated molecular weight for $[\mathbf{3}]^{2+}$: 705) and a peak at 704.2 (corresponding to the $\{[\mathbf{3}]^{2+}-\mathrm{H}^+\}$ species). The two more abundant fragmentation peaks at 442.2 and 427.2 have been assigned to the $\{[\mathbf{3}]^{2+}-\mathrm{FcSO_2N}<\}$ and $\{[\mathbf{3}]^{2+}-\mathrm{H}^+-\mathrm{FcSO_2NCH_2}<\}$ species, respectively. The perchlorate salt $[\mathbf{3}](\mathrm{ClO_4})_2$ was obtained by redissolution of the chloride in the minimum amount of methanol and dropwise addition of a saturated $\mathrm{NaClO_4}$ methanolic solution.

The redox behaviour of $[\mathbf{3}]^{2+}$ in acetonitrile (MeCN) has been investigated by voltammetric techniques. The cyclic voltammetry profile (potential scan rate 200 mV s^{-1}, solid line in Fig. 1) displays two quasi-reversible one-electron waves (at 0 and 0.31 V) and an irreversible ill-defined peak around 800 mV. For comparative purposes, an analogous voltammetric investigation was carried out on an MeCN solution 0.1 mol dm^{-3} in $\mathrm{Bu_4NClO_4}$ which was equimolar in the three components of **3**, i.e. (i) plain ferrocene, (ii) ferrocenesulfonamide and (iii) the $\mathrm{Ni^{II}}$ complex $\mathbf{2}(\mathrm{ClO_4})_2$ in which an arylsulfonamido group has been incorporated into the cyclam framework (dotted line in Fig. 1). The three observed reversible waves in the dotted profile correspond to the oxidation of the three individual fragments (in order of increasing potential): ferrocene < ferrocenesulfonamide (the oxidation of this latter molecule takes place at a distinctly more positive potential, i.e. it is more difficult, than for plain ferrocene, due to the electron withdrawing effect exerted by the appended $-\mathrm{SO_2}-$ group) < $\mathrm{Ni^{II}}$ macrocyclic complex. Comparison of the two cyclic voltammetry profiles indicates that in the three-component system $[\mathbf{3}]^{2+}$ the oxidation processes involving the two appended ferrocene moieties take place regularly, at the potentials E_1 and E_2, which are nearly coincident with those observed for the separated fragments. However, in the potential range expected for the $\mathrm{Ni^{II}/Ni^{III}}$ oxidation of the aza-macrocyclic subunit, only a poorly defined and completely irreversible peak has been observed. Moreover, controlled potential electrolysis at a potential 120 mV more positive than E_1 indicated the consumption of one electron and made the solution take the typical blue–green colour of the ferrocenium chromophore. On the other hand, the coulometry experiment at a potential 120 mV more positive than E_2 showed a continuous increase of the integrated current profile, indicating a multi-electron irreversible oxidation process and decomposition. Decomposition was also indicated by the colour change of the solution from blue to brownish. Multi-electron consumption and decomposition was observed also on electrolysing a fresh solution of **3** at a potential value corresponding to that of the third irreversible peak (900–950 mV).

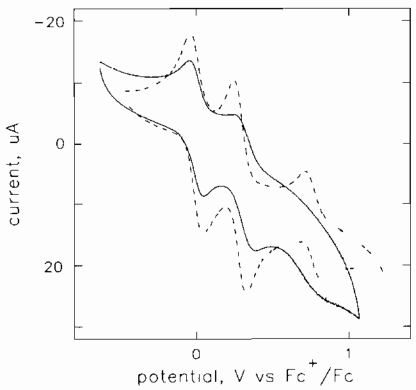


Fig 1. Cyclic voltammetry profiles for a solution 10^{-3} mol dm^{-3} in $\mathbf{3}(\mathrm{ClO_4})_2$ (solid line); a solution 10^{-3} mol dm^{-3} in ferrocene, 1-sulfonamideferrocene and $\mathbf{2}(\mathrm{ClO_4})_2$ (dotted line). MeCN solution 0.1 mol dm^{-3} in $\mathrm{Bu_4NClO_4}$, at 25 °C; platinum working electrode; potential scan rate 200 mV s^{-1}.

The electrochemical behaviour described above clearly indicates the poor stability of the fully oxidised form of the three-component system **3**. In particular, the strong intramolecular electrostatic repulsions in the $\mathrm{Fc^+{-}Ni^{III}{-}Fc^+}$ species cause decomposition and fragmentation, accounting for the irreversibility of the third oxidation step. Decomposition of the electroactive species even during the electrolysis at a potential value of E_2+120 mV depends upon the fact that at this potential the unstable fully oxidised species begins to form and induces multi-electron consumption and simultaneous fragmentation.

This work has further demonstrated the versatility of ferrocene residues as building blocks to multicomponent redox systems. In particular, assembling through a $\mathrm{Ni^{II}}$ template reaction the two non-equivalent $\mathrm{Fc{-}CH_2{-}}$ and $\mathrm{Fc{-}SO_2{-}}$ fragments generates a system able to release two electrons at two well separated potentials E_1 and E_2. However, using the ionic $\{\mathrm{Ni^{II}cyclam}\}^{2+}$ subunit as a third one-electron component and as a bridge generates on oxidation quite strong electrostatic repulsions that make the three-centre redox system decompose.

Acknowledgement

We are indebted to CNR – Progetto Finalizzato Chimica Fine II, for financial support.

References

1 G. Wilkinson, M. Rosenblum, M.C. Whiting and R.D. Woodward, *J Am Chem Soc.*, *74* (1952) 2125.

2 (a) P.D. Beer, O. Kocian, R J. Mortimer and P Spencer, *J. Chem Soc, Chem Commun*, (1992) 602, (b) P.D. Beer, E L. Tite and A. Ibbotson, *J. Chem Soc, Dalton Trans*, (1991) 1691, (c) P.D. Beer, J.E. Nation, S.L.W. McWhinnie, M.E. Harman, M.B. Hursthouse, M.I. Ogden and A.H White, *J Chem Soc., Dalton Trans.*, (1991) 2485; (d) P.D. Beer, H. Sikanyika, C Blackburn, J.F. Mc Aleer and M.G.B. Drew, *J. Chem Soc, Dalton Trans*, (1990) 3295; (e) P.D Beer, *Chem Soc. Rev*, *18* (1989) 409; (f) J.C Medina, C Li, S.G. Bott, J.L. Atwood and G.W. Gokel, *J. Am Chem Soc*, *113* (1991) 366.

3 A. De Blas, G. De Santis, L. Fabbrizzi, M. Licchelli, C Mangano and P. Pallavicini, *Inorg Chim Acta, 115* (1992) 202.

4 A. Dormond and J Decombe, *Bull Chem Soc Fr*, (1968) 3673.

5 G R. Knox and P.L. Pauson, *J Chem Soc.*, (1958) 692.

6 A De Blas, G. De Santis, L. Fabbrizzi, M. Licchelli, A.M. Manotti Lanfredi, P. Morosini, P. Pallavicini and F. Ugozzoli, *J Chem. Soc*, *Dalton Trans*, (1993) 141