Synthesis of a novel macrocyclic dinuclear iron(III) complex and its electrochemical behaviour on an ultramicrodisc platinum electrode

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Summary

A new macrocyclic dinuclear iron(III) complex, prepared by condensing 2,6-diformylpyridine *N*-oxide with 1,3-diaminopropane in the presence of $FeCl_2 \cdot 4H_2O$, and formulated as $Fe_2LCl_6C_2H_5OH \cdot 6H_2O$, was characterized by its elemental analyses, by i.r., Mössbauer and e.p.r. spectra, and was investigated electrochemically. The results show that two iron ions are situated in the same chemical environment in the compound and that the electrode reaction can be considered as a double electron-transfer process. The diffusion coefficient is 2.16×10^{-6} cm^2 s^{-1} and $E^{o\prime}$ −0.169 V (*versus* s.c.e.) and $\alpha = 0.37$. The average electron transfer rate constant $k^{o\prime}$ is 2.8×10^{-3} cm s^{-1}.

Introduction

Microelectrodes as a detecting tool for electrochemical measurement have made considerable headway and have been widely used in low conductivity[1], fast-scan techniques[2] and microsystems[2] because of their unusual properties, such as very small size, high mass transport and short response time. At lower scan rates, the curve of a single linear sweep is of sigmoid shape, which is simply the steady-state character. Therefore, microelectrodes, especially the microdisc electrode, can be used to determine the diffusion coefficient and the standard formal potential from the *i–E* curve[4]. By the fast-scan technique, it can also be conveniently used to measure the fast electron-transfer rate constant and to study the kinetics of electron reaction without the influence of the charging current of the double layer capacitance and *iR* drop[5,6].

Macrocyclic transition metal complexes have been widely investigated for many purposes since the 1960s[7–9]. Among them is the macrocyclic Schiff base and its metal complexes, which were first introduced by Robson[10] *et al.* These workers synthesized a series of binuclear complexes from the cyclocondensation of methylisophthalaldehyde with 1,3-diaminopropane *via* a template procedure. In this paper, we describe the synthesis and properties of a new macrocyclic iron(III) complex from 2,6-diformylpyridine *N*-oxide with 1,3-diaminopropane by using the iron(II) ion as the template. We also have investigated its electrochemical behaviour on an ultramicrodisc platinum electrode.

Experimental

Materials

All reagents were analytical grade and were used as received. 2,6-Diformylpyridine *N*-oxide was prepared according to the literature method[11].

$Fe_2LCl_6 \cdot C_2H_2OH \cdot 6H_2O$

To an EtOH solution (30 cm^3) of $FeCl_2 \cdot 4H_2O$ (0.40 g, 2 mmol), an equimolar quantity of 2,6-diformylpyridine *N*-oxide (0.30 g) was added. The solution was stirred for 1 h, then 1,3-diaminopropane (0.15 g, 2 mmol) in EtOH (20 cm^3) was added dropwise. The mixture was maintained at the reflux temperature for 4 h. During the reaction, some deep-red–brown crystals deposited from the hot solution. The solids were collected, washed with cold EtOH and dried in air. Yield, 64%. (Found: C, 30.5; H, 4.5; N, 9.9; Fe, 13.2. $C_{22}H_{40}N_6O_9Fe_2Cl_6$ calcd.: C, 30.5; H, 4.8; N, 9.8; Fe, 13.0%.)

Measurements

Elemental C,H and N analyses were determined on a Perkin-Elmer 240C elementary analysis instrument (USA) and Fe by EDTA titration. I.r. spectra of the complex were obtained as KBr pellets in the 4000–400 and 600–100 cm^{-1} ranges, respectively, on a Nicolet-5DX FT-IR spectrometer. The e.s.r spectrum was recorded on a Bruker ER 200-D-SRC instrument. The Mössbauer spectrum was measured at 293 K using a conventional transmission spectrometer. As the source we used ^{57}Co(Pd) and the isomer shift data are given relative to α-Fe at room temperature. The data were analysed by a least-square fit routine assuming Lorenzian line shapes.

Water, used in electrochemical experiments, was twice distilled. A three-electrode system with a platinum wire counter electrode, a saturated calomel reference electrode (s.c.e.) and a microdisc platinum working electrode with a 10 μm diameter was employed. Prior to using the microdisc, the working electrode was polished with fine emery paper and then with alumina slurry (0.05 μm), rinsed with water. Electrochemical experiments were performed on a model BAS-100B electrochemical analyser with a PA-1 preamplifer (BAS, USA) in order to amplify current and filter out noise and a FPG-310 colour plotter (Fujitsu company, Japan) to record the voltammogram. The experimental temperature was maintained at 20 ± 0.1 °C. After the solution was deaerated with pure N_2 for 10 min, the electrochemical measurements were carried out under a N_2 atmosphere.

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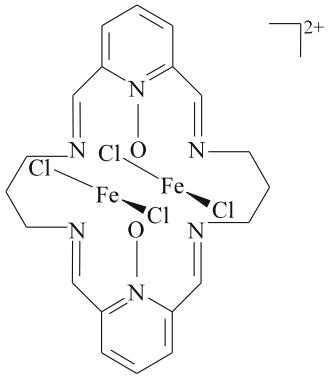
Results and discussion

Synthesis and characterization

The cyclocondensation of 2,6-diformylpyridine *N*-oxide and 1,3-diaminopropane was achieved *via* the conventional template method, and the macrocycle was obtained as its iron(III) complex. Reaction in the absence of metal salt led to gums, indicative of oligomer formation. Direct evidence for the generation of the Schiff base arises from the i.r. spectrum, which shows a strong band at 1640 cm^{-1}, ascribed to ν(C=N). Absorptions at 1700 and 3100–3300 cm^{-1} were not observed. These would be present if residual carbonyl or primary amine groups were present[12]. The far-i.r. spectrum exhibits a medium intensity band at 246 cm^{-1} attributed to the ν(Fe—Cl) stretching vibrations, which proves the coordination of chlorine atoms[13]. The structure of the compound is shown in structure *(1)*.



(1)

The resulting macrocyclic dinuclear iron(III) complex has been obtained, though iron(II) was utilized as the template ion. The oxidation of iron(II) to iron(III) is apparently due to the presence of O_2 while the reaction system was exposed to air. The elementary analyses agree well with those of theory. This complex is very soluble in water and moderately soluble in polar organic solvents.

Mössbauer spectroscopy

Mössbauer spectroscopy can be used to identify the variation in iron valence and electron densities around the nucleus. Figure 1 shows the presence of only two peaks, which are absolutely symmetric. This fact suggests that the two iron ions in Fe_2L are situated in the same chemical environment. The isomer shift and quadruple splitting found for the complex at 293 K (see Table 1) confirm the Fe^{3+} state. Meanwhile the e.s.r. paramagnetism signature of the complex was detected at room temperature. However, no e.s.r. for Fe^{2+} has been observed, demonstrating the complete oxidation of iron(II) to iron(III). Thus we conclude that both iron ions of this complex exist in the Fe^{3+} state, rather than in the Fe^{2+} state, although Fe^{2+} was used in synthesis. In the preparation of the iron(III) complex, a fast reaction between iron(II) and the ligand forms the iron(II) complex, which is then rapidly oxidized to the corresponding iron(III) complex.

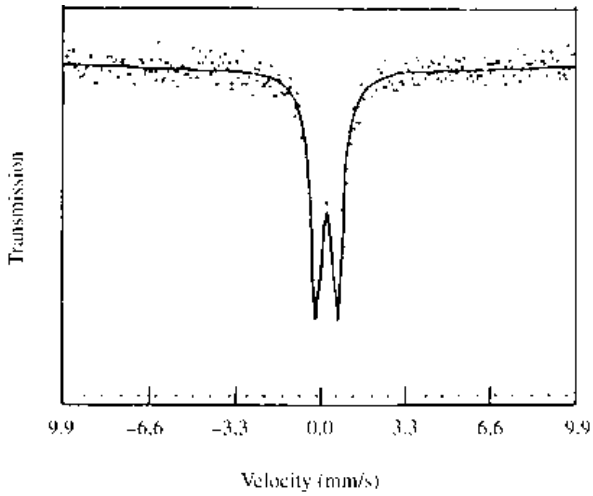


Figure 1. Mössbauer spectra of the complex at 293 K

Table 1. Mössbauer parameters of the complex

Isomer shift (mm/s)	Quadruple splitting (mm/s)
0.470	0.836

Electrochemical study

Cyclic voltammetry carried out in a 7.4×10^{-4} mol/dm^3 aqueous solution of Fe_2L complex using 0.1 mol/dm^3 KNO_3 as a supporting electrolyte is shown in Figure 2. Because cyclic voltammetry exhibits only one reduction wave, it indicates that two iron ions exist in the same chemical environment and this electrode reaction can be thought as a double electron-transfer reaction (n = 2). This sort of complex can be used to prevent single electron-transfer from forming an intermediate product[14].

At a lower scan rate, the steady-state voltammetric curve on microdisc electrode can be expressed as:

$$i_{(E)} = 4nFC^*Dr/[1 + \exp(-\xi_{(E)})]$$

where $\xi_{(E)} = nF/\{RT[E_t - E^{o'}]\}$, r is the radius of electrode and other parameters have their usual meanings. The limiting current is $i_d = 4nFC^*Dr$. Based on i_d and the *E versus* Ln$[(i_d - i)/i]$ curve, the diffusion coefficient and standard formal potential can be obtained. Both

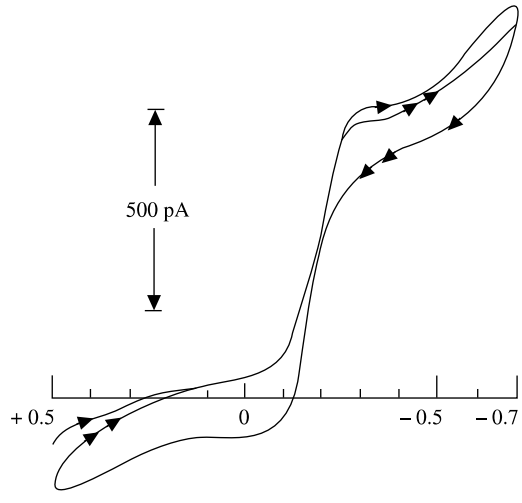


Figure 2. Cyclic voltammograms of 0.74 mM Fe_2L at a Pt microdisc electrode of r = 5.0 μm at 100 mV/s

the cathodic and anodic curves are sigmoid shapes as illustrated in Figure 2. The diffusion coefficient of 2.16×10^{-6} cm^2/s (if $n = 2$) can also be obtained from the limiting current, which approximates favourably to a value of 2.3×10^{-6} cm^2/s for the reported macrocyclic complex FeTPPCl[15].

The *E versus* Ln$[(i_d - i)/i]$ curve is shown in Figure 3. From its intercept and slope $E^{o\prime} = -0.169$ V (*versus* s.c.e.) and $\alpha n = 0.74$, if $n = 2$, $\alpha = 0.37$. The value of $E^{o\prime}$ is more negative than that of $Fe(CN)_6^{3-}$ (0.12 V *versus* s.c.e) and close to those in a porphyrin ring, and iron(III) EDTA complex (−0.12 V). The standard formal potentials of porphyrin are usually between 0.0 and −0.3 V[16]. These results indicate that the stability of the iron(III) complex synthesized in this work is better than that of $Fe(CN)_6^{3-}$ and is equivalent to the stability of

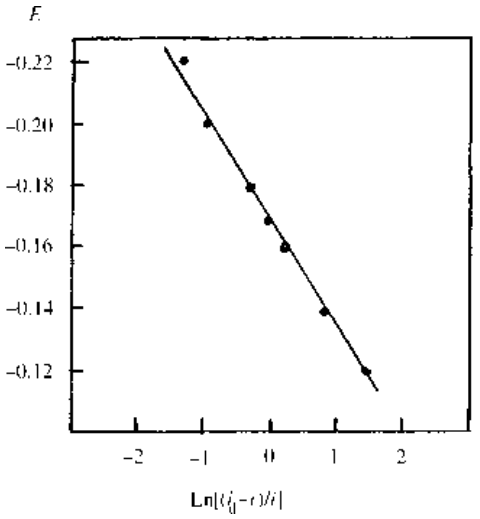


Figure 3. The *E versus* Ln$[(i_d - i)/i]$ curve from the cathodic data in Figure 2

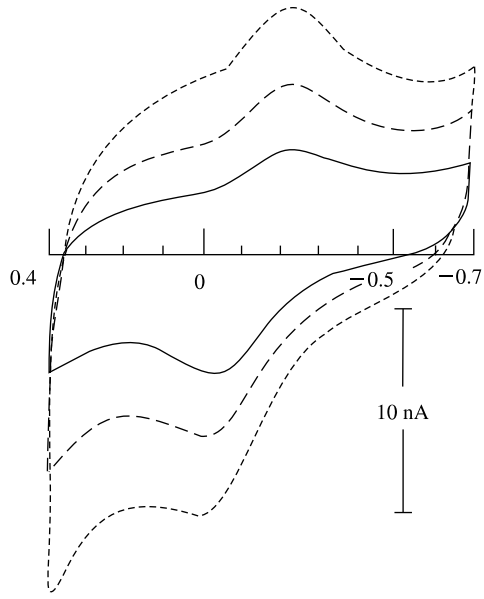


Figure 4. Fast sweep cyclic voltammograms of 0.74 mM Fe_2L at a Pt microdisc electrode with a radius of 5.0 μm at (—) 10, (- - -) 20, (· · · ·) 30 V/s

other iron chelate complexes, especially those with porphyrin ligands.

Figure 4 shows the cyclic voltammograms of iron(III) complex at faster scan rates. The voltammograms show that the peak current linearly increases with the increasing square root of the scan rate; ΔE_p also increases as the scan rate increases. These results demonstrate that the electrode process is controlled by diffusion and by the electron transfer rate. Using Nicholson's[17] equation ($0.3 < \alpha < 0.7$), the electron transfer rate constant, $k^{o\prime}$, of 2.6, 2.4, 2.9 and 3.2×10^{-3} can be obtained at 10, 20, 30 and 40 V/s, respectively, with an average value of 2.8×10^{-3} cm s^{-1}. This value is an order of magnitude lower than that of $Fe(CN)_6^{3-}$ (*ca.* 10^{-2} cm/s)[18], but at the same level as the cytochrome c, which has an electron transfer rate constant between 1×10 cm/s[19] and 6.6×10^{-3} cm/s[20] at various modified electrodes. However, the biomolecule does not directly exchange electrons at a bare electrode. Thus, it is of interest to note that a double electron-transfer of the prepared Fe_2L complex can be carried out on a bare electrode.

Acknowledgements

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