Electroreduction of Dioxygen Catalyzed by Ferric Carboxymethylene–Cyclam Complex

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Electrochemical analysis of a Fe^{3+} macrocyclic complex, involving N-carboxymethylene-1,4,8,11-tetraazacyclotetradecane, {Fe^{3+}[14]aneN$_4$Ac}$_2^+$, under aerobic conditions, shows a similar behaviour to that previously observed for the catalysts of O$_2$ electroreduction to H$_2$O. In aqueous 0.1 N KCl, {Fe^{3+}[14]aneN$_4$Ac}$_2^+$ undergoes a reversible Fe$^{3+}$/Fe$^{2+}$ reduction at $E_{1/2} = 0.12$ V vs SHE ($D_v = 6.5 \times 10^{-6}$ cm$^2$/sec) producing the Fe$^{2+}$ derivative, which reacts rapidly with dissolved O$_2$. Thus, the overpotential of the O$_2$ reduction is positively shifted by around 0.45 V, if either {Fe$^{3+}[14]aneN_4$Ac}$_2^+$ is present in solution or has been immobilized on a glassy carbon electrode by an Eastman AQ55D cation-exchange polymer. Because the reduction of O$_2$ by {Fe$^{3+}[14]aneN_4$Ac}$_2^+$ is thermodynamically unfavourable by 43.4 kJ/mol, generation of a highly reactive intermediate is postulated. Accordingly, electron spin resonance (ESR) spectroscopic studies of {Fe$^0$[14]aneN$_4$Ac}$^{2+}$ on reacting with KO$_2$ in DMSO exhibit the resonance transition ascribable to a low-spin Fe$^{3+}$ peroxide complex at 77 K, whereas {Fe$^{3+}[14]aneN_4$Ac}$_2^+$ on reacting with H$_2$O$_2$ in 0.1 N methanolic KOH shows ESR lines due to superoxide radicals (O$_2^-$) indicating a Haber-Weiss like reaction. On the basis of the electrochemical and spectroscopic data, mechanistic studies on the subject complex reactivity towards O$_2$ are reported.

**Key words**: iron macrocyclic complex, electroreduction, catalysis, dioxygen, superoxide

Reactions of Fe$^{2+}$/Fe$^{3+}$ macrocyclic complexes with dioxygen/superoxide continue to attract much attention [1–7] as for their relevance to enzymatic reactions [5] and electrocatalysis [2,4]. Recent studies have shown potential applications of the transition metal macrocyclic complexes for fuel cells [6] and biosensors [2b]. The electroreduction of O$_2$ to H$_2$O (O$_2$/H$_2$O) catalyzed by a Fe$^{3+}$L complex, exhibiting reversible electroreduction at around 0.0 V vs SHE, can be summarized in the following reaction scheme [2–4]:

Fe$^{3+}$L + e$^-$ $\rightarrow$ Fe$^{2+}$L

2Fe$^{2+}$L + O$_2$ + 2H$^+$ $\rightarrow$ 2Fe$^{3+}$L + H$_2$O$_2$

2Fe$^{3+}$L + H$_2$O$_2$ + 2H$^+$ $\rightarrow$ 2Fe$^{2+}$L + 2H$_2$O

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Because the catalytic $\text{O}_2/\text{H}_2\text{O}$ electroreduction requires the reduced form of the $\text{Fe}^{3+}$ catalyst, this process as a whole is driven by the $\text{Fe}^{3+}/\text{Fe}^{2+}$ electroreduction. Thus, the net dioxygen reduction occurs at a potential close to that of $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple [2,4]. Because the reduction of $\text{O}_2$ by $\text{Fe}^{2+}\text{L}$ is thermodynamically unfavourable, $E(\text{O}_2/\text{O}_2^-) = -0.33$ V at $\text{pH} = 7$ [8], the production of a highly reactive intermediate, such as a superoxy adduct, $[\text{Fe}^{3+}(\text{O}_2^-)\text{L}]^{2+}$, and a per oxy dimer, $[\text{LFe}^{3+}\text{O-}\text{OFe}^{3+}\text{L}]^{4+}$, is postulated [3,7]. For example, for $\text{Co}^{3+}$ cyclam ([(14)aneN₄]) complexes, the superoxy adduct, $[\text{Co}^{3+}(\text{O}_2^-)\text{L}]^{2+}$, is quickly formed by second-order kinetics, $k = 3 \times 10^6$ M⁻¹ s⁻¹, which subsequently transforms to its peroxy dimer on a reaction with another molecule of $\text{Co}^{3+}$ cyclam, $k = 5 \times 10^5$ M⁻¹ s⁻¹ [7]. Unfortunately, the $[\text{LCo}^{3+}\text{O-}\text{OCo}^{3+}\text{L}]^{4+}$ is relatively stable at room temperature (the rate of its thermal decomposition in water, $k = 3 \times 10^{-4}$ s⁻¹) [7b], therefore, the Co complex cannot act as a catalyst for $\text{O}_2$ electroreduction.

The search for metal complexes, that function as catalysts for the $\text{O}_2/\text{H}_2\text{O}$ electroreduction, directed us to the synthesis and electrochemical examination of the $\text{Fe}^{3+}$ macrocyclic complex involving N-carboxymethylene-1,4,8,11-tetraazacyclotetradecane, $\{\text{Fe}^{3+}[(14)\text{aneN}_4\text{Ac}^-]\}^{2+}$ [9]. For the schematic representation of the macrocyclic complex see Figure 1. It is assumed that the open coordination site on the $\text{Fe}^{3+}$ ion significantly accelerates the reaction with small nucleophilic agents such as $\text{O}_2$, superoxide (O₂⁻), and $\text{H}_2\text{O}_2$. In order to receive more structural information about intermediates of the $\{\text{Fe}^{2+}[(14)\text{aneN}_4\text{Ac}^-]\}^{+}/\text{O}_2$ reaction, ESR testing of an isoelectronic reaction system (i.e. $\{\text{Fe}^{3+}[(14)\text{aneN}_4\text{Ac}^-]\}^{2+}/\text{O}_2$⁻) has been performed. Recently, it has been demonstrated that ESR spectroscopy provides a convenient tool for structural and electronic studies of metal-$\text{O}_2$ adducts, obtained during the reaction of porphyrin and non-porphyrin iron complexes with $\text{H}_2\text{O}_2/\text{O}_2$⁻ [10–12]. The information on bonding geometry in Fe-o xo adducts can be obtained from relatively small g factor anisotropy in the higher magnetic field. For example, for $\text{Fe}^{3+}$ peroxide complexes derived from porphyrin, Cl$\text{Fe}^{3+}$TPP [10a], and non-porphyrin systems, $\text{Fe}^{3+}$DPC [11], the ESR transition occurs at $g = 1.96, 2.15, 2.30$ [10a], and $g = 2.017, 2.196, 2.278$ [11], respectively.

**Figure 1.** Schematic representation of $\{\text{Fe}^{3+}[(14)\text{aneN}_4\text{Ac}^-]\}^{2+}$. 
EXPERIMENTAL

**Materials:** The synthesis of the chloride salt of Fe$^{3+}$ N-carboxymethylene-1,4,8,11-tetraazacyclotetradecane, $\{\text{Fe}^{3+}(\text{Cl}^-)[\text{14} \text{aneN}_4\text{Ac}^-]\}\text{Cl}$, and its PF$_6^{-}$ derivative was carried out as described in [9]. In aqueous 0.1 M KCl the chloride salt exhibits absorption at $\lambda_{\text{max}} = 344$ nm ($\varepsilon = 2.2 \times 10^4$ M$^{-1}$ cm$^{-1}$) and 234 nm ($\varepsilon = 19.5 \times 10^3$ M$^{-1}$ cm$^{-1}$). A solution of Eastman-AQ 55D polymer (28% dispersion in water) was purchased from Eastman Kodak Co. A saturated solution of potassium superoxide (KO$_2$) in DMSO (2 mM) was prepared as described in [13]. Solvents and reagents were of the highest purity available from Aldrich Chemical Co.

**Physical techniques:** UV-Visible spectra were measured on a Hewlett-Packard 8452 diode array spectrophotometer. ESR spectra were run with a computer-controlled Varian E-112 spectrometer operating in the X-band. Instrumental settings were: modulation frequency, 100 kHz; time constant, 0.1 second; sweep width, 120 or 4000 Gauss; microwave frequency, 9.16 GHz. Before measuring, samples were frozen (77 K) in a round quartz tube ($\phi = 2$ mm). For experiments with superoxide, the reaction was initiated by mixing an equal volume (1 ml) of an aerobic DMSO solution containing 2 mM of $\{\text{Fe}^{3+}(\text{Cl}^-)[\text{14} \text{aneN}_4\text{Ac}^-]\}\text{PF}_6$ with saturated solution of KO$_2$ in DMSO (~2 mM) at room temperature. The final concentration of these compounds, therefore, became half of their starting concentration. After mixing samples were put immediately to an ESR Dewar flask filled out with liquid nitrogen (this operation took less than 15 seconds). Then an ESR spectrum was acquired. For the experiments with hydrogen peroxide, typically 0.1 ml of 0.1 M aqueous H$_2$O$_2$ was added to a 1 ml of 0.1 N methanolic KOH containing 2 mM of $\{\text{Fe}^{3+}(\text{Cl}^-)[\text{14} \text{aneN}_4\text{Ac}^-]\}\text{Cl}$, under aerobic conditions. After mixing in an ESR tube, and then freezing with liquid nitrogen, ESR spectra were acquired following the procedure described above for the reaction with KO$_2$.

Electrochemical experiments were carried out with a computer-controlled Versa-State potentiostat from EG&G Princeton Applied Research. The M270 software for the data acquisition and data processing was provided by EG&G Princeton Applied Research. The electrolysis was performed with a three-compartment cell. The working electrode was a glassy carbon plate (0.3 cm$^2$) or a 1 mm diameter glass carbon (GC) minielectrode in Kel-F (Bioanalytical Systems), or a 5-µm diameter disk microelectrode in 2-mm glass tube (Cypress System, Inc.). The auxiliary electrode was a platinum wire separated by a glass frit from working electrode compartment and the reference electrode was Ag/AgCl (E$^\circ$ = 0.198 V versus SHE) wire immersed in 4 M KCl and separated from the main compartment by a capillary formed by sealing platinum wire in Pyrex. Prior to experiments the GC electrodes were polished with 0.05 micron gamma alumina (Buehler). Residual polished material was removed from the surface by sonication in a DI (deionized) water bath. Aqueous solution typically contained 0.1 M KCl as supporting electrolyte. For electroanalysis with acidity over the pH range between 2 and 10, the acidity of aqueous 0.1 N KCl adjusted by 0.1 N Hepes buffer, 0.1 N HCl and 0.1 N NaOH. In non-aqueous solvents, the supporting electrolyte was tetrabutylammonium tetrafluoroborate (TBAB).

In order to prepare a $\{\text{Fe}^{3+}[\text{14} \text{aneN}_4\text{Ac}^-]\}^{2+}$ covered electrode, the GC minielectrode was immersed in a (0.26 mM) solution obtained from 0.5 mg of the chloride salt of this Fe$^{3+}$ complex dissolved in 5 ml of the commercially available Eastman-AQ 55D polymer (before that the polymer was 4-times diluted in DI water to get 7% hydrosol). The electrode was then dried under air for 24 hours and washed with DI water. After this, an adhering film was obtained. The surface concentration of $\{\text{Fe}^{3+}[\text{14} \text{aneN}_4\text{Ac}^-]\}^{2+}$ on the covered GC electrode (5.1 $\times$ 10$^{-12}$ mol/cm$^2$) was calculated from voltammetric measurements based on the method presented elsewhere [4].

**RESULTS AND DISCUSSION**

**Electrochemistry:** As shown in Figure 2 (solid line), the cyclic voltammogram of the chloride salt of $\{\text{Fe}^{3+}[\text{14} \text{aneN}_4\text{Ac}^-]\}^{2+}$, dissolved in aqueous KCl (degassed with argon), exhibits a single set of redox peaks with a formal redox potential at $E_{1/2} = -0.08$ V vs. Ag/AgCl. Furthermore, in the more positive potential range, an irrevers-
ible electrooxidation at \( E_p = 0.94 \) V vs. Ag/AgCl ascribable to the ligand oxidation is recorded. Based on calculations performed using the Malachesky expression [14] and voltammograms acquired with different scan rates (from 49 to 250 mV/sec), there has been confirmed \( n = 1 \), and the diffusion coefficient for the Fe\(^{3+}\) complex, \( D_0 = 6.5 \times 10^{-6} \) cm\(^2/\)sec.

As expected from the molecular structure of \{Fe\(^3+\)[14]aneN\(_4\)Ac\(^–\}\(^2+\), the potential of the Fe\(^{3+}/Fe^{2+}\) redox couple exhibits pH dependence (\( E_{1/2} \) negatively shifts with pH value). For example, for the 0.1 N KCl solution with pH = 10.6 adjusted with 0.1 N NaOH, the electroreduction occurs at \( E_{1/2} = −0.44 \) V vs. Ag/AgCl. However, for the \{Fe\(^3+\)[14]aneN\(_4\)Ac\(^–\}\(^2+\)/KCl solution with pH = 8.6 adjusted with 0.1 M Hepes buffer, two step electroreduction at \( E_{1/2} = −0.08 \) and \( −0.44 \) V vs. Ag/AgCl is monitored. This indicates that the redox couple monitored at \( E_{1/2} = −0.44 \) V comes from the Fe\(^{3+}/Fe^{2+}\) electroreduction of a hydroxy derivative of the macrocyclic complex, \{Fe\(^3+\)(OH\(^–\))[14]aneN\(_4\)Ac\(^–\)\(^+\). Probably, at the higher range of pH, the open coordination site on the Fe\(^{3+}\) ion is mainly occupied by an OH\(^–\) ion. However, in neutral (0.1 N KCl) or acidic solutions (0.1 N HCl), the axial position is substituted by an aqua molecule (for octahedral complexes, aqua molecules are more powerful nucleophiles than chlorine anions) [15]. The negative shift of \( E_{1/2} \) demonstrates that the nucleophilic OH\(^–\) ions stabilize the Fe\(^{3+}\) redox form by around 0.36 V. Furthermore, corresponding to Kaden’s work on transition metal complexes involving [14]aneN\(_4\)Ac\(^–\) with Cu\(^{2+}\) and Ni\(^{2+}\) [9b], the protonation constant for the pendant carboxylate group is around \( pK_H = 3.01 \). This points that for \{Fe\(^3+\)[14]aneN\(_4\)Ac\(^–\)\(^2+\) at pH > 3, one of the axial site of the central cation is always occupied by –CH\(_2\)COO\(^–\) moiety. On the other hand, UV-Visible spectra of \{Fe\(^3+\)[14]aneN\(_4\)Ac\(^–\)\(^2+\) acquired in 0.1 N HCl and 0.1 M KCl exhibit the same MLCT absorption band at \( \lambda_{max} = 344 \) nm. This indicates that –CH\(_2\)COO\(^–\) in \{Fe\(^3+\)[14]aneN\(_4\)Ac\(^–\)\(^2+\) has been bound to the central Fe\(^{3+}\), and has not hydrolyzed under pH range used in the study.

Figure 2. Cyclic voltammograms of \{Fe\(^3+\)[14]aneN\(_4\)Ac\(^–\)\(^2+\) (3.1 mM) acquired at the GC minielectrode in aqueous 0.1 M KCl degassed by argon, solid line, and saturated by air (0.24 mM, O\(_2\)) [16], broken line; 0.1 V/sec, 25°C.
CV measurements performed for \( \{\text{Fe}^{3+}[14\text{aneN}_4\text{Ac}^-]\}^{2+} \) under aerobic conditions lead to a similar behaviour to that previously observed for the catalysts of \( \text{O}_2/\text{H}_2\text{O} \) electroreduction [1–4]. Accordingly, in aqueous 0.1 N HCl containing \( \{\text{Fe}^{3+}[14\text{aneN}_4\text{Ac}^-]\}^{2+} \), the potential of dioxygen reduction depends on the complex concentration, and is shifted to more positive potentials, as shown in Figure 3 (b). In comparison, the \( \text{O}_2 \) analogue is irreversibly reduced at around \( E = –0.50 \text{ V vs. Ag/AgCl} \) at the GC electrode, as shown in Figure 3(a). When the complex concentration is 3–4 times higher than that of \( \text{[O}_2 \text{]} \), the cathodic wave of \( \{\text{Fe}^{3+}[14\text{aneN}_4\text{Ac}^-]\}^{2+} \) and \( \text{O}_2 \) overlap at \( E_p = –0.08 \text{ V} \). Moreover, the area under this CV peak is approximately four times higher than that of the macrocyclic complex alone, indicating that 4 electrons are involved, and \( \text{O}_2 \) may be reduced to \( \text{H}_2\text{O} \), in the acidic environment.

**Figure 3.** Cyclic voltammograms of aqueous 0.1 N HCl saturated by air, 0.24 mM, \( \text{O}_2 \) [16], (a); cyclic voltammograms of 0.1 N HCl saturated with air and containing 0.80, 0.57, 0.44, 0.36, 0.31, 0.27, and 0.18 mM of \( \{\text{Fe}^{3+}[14\text{aneN}_4\text{Ac}^-]\}^{2+} \), respectively, (b); cyclic voltammogram of 0.80 mM \( \{\text{Fe}^{3+}[14\text{aneN}_4\text{Ac}^-]\}^{2+} \) in 0.1 N HCl saturated with air, solid line, and degassed by argon, broken line, (c); 0.1 V/sec, 25°C.

Interesting electrochemical results have been obtained in an aqueous KCl solution saturated with air, 0.24 mM of \( \text{O}_2 \) [16], containing 10-times more concentrated \( \{\text{Fe}^{3+}[14\text{aneN}_4\text{Ac}^-]\}^{2+} \), see Figure 2 (dotted line). Under these conditions, two redox couples at –0.08 and –0.44 V have been observed. Moreover, the latter couple is less developed, and the anodic wave of the redox couple at –0.08 V is partially diminished in size. This observation indicates that a part of the \( \text{Fe}^{2+} \) complex generated at \( E_{1/2} = –0.08 \text{ V} \) is consumed on reacting with \( \text{O}_2 \) producing a species that undergoes the reversible electroreduction at –0.44 V. Because this potential is close to that of \( \{\text{Fe}^{3+}[14\text{aneN}_4\text{Ac}^-]\}^{2+} \) in basic solutions, a generation of this complex hydroxy de-
rivative, \(\{\text{Fe}^{3+}(\text{OH}^-)_{14}\text{aneN}_4\text{Ac}^-\}^+\), is postulated under these conditions. This is consistent with the fact that the \(\text{O}_2/\text{H}_2\text{O}\) electroreduction is accompanied with \(\text{H}^+\) cations consumption and \(\text{OH}^-\) ions accumulation.

In order to verify, whether \(\{\text{Fe}^{3+}[\text{14}]{\text{aneN}_4}\text{Ac}^-\}^{2+}\) molecules occupying the solution layer adjacent to the electrode are being transformed to their hydroxy derivative during the experiments of \(\text{O}_2/\text{H}_2\text{O}\) electroreduction, a GC electrode covered with the macrocyclic complex has been prepared. This “modified electrode” has been subsequently applied for the next experiments on \(\text{O}_2\) electrolysis. For this purpose, the cation-exchangeable Eastman-AQ 55D polymer has been used as an immobilization agent (for the modification procedure, see the Experimental). This choice has been dictated by the availability of the polymer as 28% hydrosol, which readily dissolves the chloride salt of \(\{\text{Fe}^{3+}[\text{14}]{\text{aneN}_4}\text{Ac}^-\}^{2+}\). Recently, the Eastman-AQ polymer has been used for GC electrodes modification with cationic compounds, such as \(\text{Ru(bpy)}_3^{2+}\) and \(\text{MV}^{2+}\) [17,18].

It has been assumed that the polymer anionic chain efficiently retards the diffusion of \(\{\text{Fe}^{3+}[\text{14}]{\text{aneN}_4}\text{Ac}^-\}^{2+}\) ions by electrostatic attractions. Accordingly, a multiple CV cycling with the “\(\{\text{Fe}^{3+}[\text{14}]{\text{aneN}_4}\text{Ac}^-\}^{2+}\) modified electrode” has to show an electrochemical response of the polymer bonded complex, as well as products of its chemical side reactions. As illustrated in Figure 4 with broken line, the single CV acquired for 0.1 M KCl at the “\(\{\text{Fe}^{3+}[\text{14}]{\text{aneN}_4}\text{Ac}^-\}^{2+}\) modified electrode” is similar to that recorded for the diluted \(\{\text{Fe}^{3+}[\text{14}]{\text{aneN}_4}\text{Ac}^-\}^{2+}\) at the uncovered GC (used directly after cleaning), if only a single potential scan is applied. However, this behaviour dramatically changes when a multiple CV cycling is being applied, as shown in Figure 4 with solid lines. In aqueous 0.1 N KCl saturated by \(\text{O}_2\) (1.22 mM) [16], the repetitive CV cycling between 0.3 and –0.8 V causes a gradual decay of the redox cou-

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**Figure 4.** Multiple cyclic voltammograms of 0.1 M KCl saturated by \(\text{O}_2\) (1.22 mM) [16] at the GC minielectrode covered by the Eastman-AQ 55D polymer incorporating \(\{\text{Fe}^{3+}[\text{14}]{\text{aneN}_4}\text{Ac}^-\}^{2+}\), 0.1 V/sec, 25°C. The broken lines represents the first CV scan in the solution degassed by argon.
ple at $-0.04$ V, associated with a regular developing of a new redox couple at $-0.36$ V ascribable to the hydroxy derivative, \( \text{Fe}^{3+} (\text{OH}^-)[14\text{aneN}_4\text{Ac}^-]^{2+} \). Of course, this can be explained by a pH change in the polymer matrix following the CV cycling (i.e. accumulation of \( \text{OH}^- \) ions, which are subsequently bonded to this complex open coordination site). In other words, the pH of the solution layer adjacent to the electrode surface increases to a value sufficient for hydrolysis of the incorporated Fe\(^{3+}\) complex. Therefore, the final CV pattern well matches that one assigned already to the hydroxy derivative, \( \text{Fe}^{3+} (\text{OH}^-)[14\text{aneN}_4\text{Ac}^-]^+ \).

It has been well established that Fe\(^{3+}\)-oxo complexes are generally more stable in non-aqueous environments than in water (in \( \text{H}_2\text{O} \), they undergo thermal or water induced dissociation) \([19a]\). To explore the transient species (intermediates), generated during the \( \text{O}_2/\text{H}_2\text{O} \) electroreduction in the presence of \( \text{Fe}^{3+}[14\text{aneN}_4\text{Ac}^-]^{2+} \), CV measurements in dry DMSO have been performed. As shown in Figure 5, \( \text{Fe}^{3+}[14\text{aneN}_4\text{Ac}^-]^{2+} \) undergoes an one-electron electroreduction at \( E_{1/2} = -0.19 \) V \([9a]\), in dry and argon degassed DMSO. However, under aerobic conditions (DMSO, \([\text{O}_2] \sim 2 \) mM \([16]\)), both the electroreduction of \( \text{Fe}^{3+}[14\text{aneN}_4\text{Ac}^-]^{2+} \) and the electroreduction of \( \text{O}_2 \) are irreversible and overlap at \( E_p = -0.34 \) V. Contrary, \( \text{O}_2 \) alone is reversibly reduced in DMSO at \( E_{1/2} = -0.64 \) V, as reported before \([19a, c]\). This electrochemical response indicates that the Fe\(^{2+}\) redox form, produced at the electrode

Figure 5. Cyclic voltammograms of \( \text{Fe}^{3+}[14\text{aneN}_4\text{Ac}^-]^{2+} \) (1.8 mM) in DMSO containing 0.1 M \( \text{Bu}_4\text{NBF}_4 \) and degassed by argon, (a); 1.8 mM of \( \text{Fe}^{3+}[14\text{aneN}_4\text{Ac}^-]^{2+} \) in DMSO containing 0.1 M \( \text{Bu}_4\text{NBF}_4 \) saturated by \( \text{O}_2 \), 2.1 mM \([16]\), (b); 1.8 mM of \( \text{Fe}^{3+}[14\text{aneN}_4\text{Ac}^-]^{2+} \) in DMSO containing 0.1 M \( \text{Bu}_4\text{NBF}_4 \) saturated by \( \text{O}_2 \), 2.1 mM \([16]\), (c); at GC minielectrode, 0.1 V/sec, 25°C.
surface, is rapidly consumed on a follow up chemical reaction, obeying an EC mechanism (see Scheme 1). Obviously, the Fe$^{2+}$ complex reacts with O$_2$ present in the DMSO solution. Corresponding to the metalloporphyrin catalyzed O$_2$ electroreduction [1–4], initially generated Fe$^{3+}$-oxo intermediates undergo intramolecular electron transfer giving isoelectronic superoxy adducts, {Fe$^{3+}$\((O_2^-)(14\)anexAc$\}^+$. 

Scheme 1

\[
\begin{align*}
\text{[Fe}^{3+}\text{CAc}^-)^+ & \rightarrow \text{[Fe}^{2+}\text{CAc}^-)^+ + e^- \\
\text{O}_2 & \rightarrow \text{[Fe}^{2+}\text{(O}_2\text{)CAc}^-)^+ \\
\text{oxo adduct} & \rightarrow \text{[Fe}^{3+}\text{(O}_2\text{)CAc}^-)^+ \\
\text{superoxy adduct} & \rightarrow \text{[Fe}^{3+}\text{(O}_2\text{)CAc}^-)^+ + e^- \\
\text{ferryl} & \rightarrow \text{[Fe}^{2+}\text{CAc}^-)^+ \rightarrow \text{[Fe}^{3+}\text{CAc}^-)^+ \\
\text{μ-oxo-dimer} & \rightarrow \text{[Fe}_3\text{CAc}^-)^+ - 20H \rightarrow 2\text{H}_2\text{O} \\
\text{H}_2\text{O}_2 + 2\text{[Fe}^{3+}\text{CAc}^-)^+ & \rightarrow \text{[Fe}^{3+}\text{CAc}^-)^+ \rightarrow \text{[Fe}^{2+}\text{CAc}^-)^+ + \text{H}_2\text{O}_2 + 2\text{[Fe}^{3+}\text{CAc}^-)^+ \\
\text{Fenton reaction} & \rightarrow \text{[Fe}^{3+}\text{CAc}^-)^+ + \text{OH} + \text{OH}^- \\
\text{Haber-Weiss reaction} & \rightarrow \text{[Fe}^{3+}\text{CAc}^-)^+ + \text{[Fe}^{2+}\text{CAc}^-)^+ \\
\text{C }& = \text{[14]anexAc}
\end{align*}
\]

A proposed mechanism of O$_2$ electroreduction catalyzed by {Fe$^{3+}$\(14\)anexAc$\}^2+$. Indecisive reactions are indicated by question mark.

The latter reacts with another molecule of the electrochemically generated Fe$^{2+}$ complex giving a peroxo dimer, {O$_2$(Fe$^{3+}$\(14\)anexAc$\}$_2)$^2+$}. In the next step, in the cathodic peak at \(E = -0.86 \text{ V}\), this dimer is reduced to a mixed-valence Fe$^{3+/2+}$ peroxo dimer, [9a]. Alternatively, this peak is related to an electroreduction of {Fe$^{3+}$\(O_2^-\)(14\)anexAc$\}^+ to a peroxo species, {Fe$^{3+}$\(O_2\)\(2\)\(+\)\(14\)anexAc$\}^+$. Unfortunately, the electroreduction of superoxy adducts is expected at more negative potential than that of superoxide, corresponding to the dioxygen chemistry, (E(O$_2$\(2$/\text{O}_2$\(2$/\text{c}$45$) = $-2.2 \text{ V vs. SHE}$)[8,19a]. The mixed-valence peroxo dimer, or more likely products of
its decomposition to \( \{\text{Fe}^{3+}(\text{O}_2)\}_{14}\text{aneN}_4\text{Ac}^- \) and \( \{\text{Fe}^{2+}\}_{14}\text{aneN}_4\text{Ac}^- \)^+ are electro-oxidized at the broad anodic waves around 0.5–0.9 V and −0.6 V, respectively, corresponding to \( E(\text{O}_2^-/\text{H}_2\text{O}_2) = 0.89 \) V [19a] and the redox potential of \( \{\text{Fe}^{2+}\}_{14}\text{aneN}_4\text{Ac}^- \)^+.

**ESR studies:** As outlined in the Introduction, the \( \text{O}_2/\text{H}_2\text{O} \) electroreduction catalyzed by transition metal complexes proceeds with production of paramagnetic intermediates, such as superoxy and peroxy adducts, as well as antiferromagnetic peroxy dimers of appropriate metal complexes [1–4]. In order to elucidate, whether those species participate in the \( \{\text{Fe}^{3+}\}_{14}\text{aneN}_4\text{Ac}^- \)^2+/\( \text{O}_2 \) electroreduction, ESR measurements at 77 K have been performed for a mixture of the \( \text{Fe}^{3+} \) macrocyclic complex with potassium superoxide. There has been assumed a mechanistic resemblance of the \( \{\text{Fe}^{3+}\}_{14}\text{aneN}_4\text{Ac}^- \)^2+ reactivity towards superoxide \( (\text{O}_2^-) \) to the isoelectronic reaction between the \( \text{Fe}^{2+} \) form of this complex, \( \{\text{Fe}^{2+}\}_{14}\text{aneN}_4\text{Ac}^- \)^+, and dioxygen. The latter is expected to take place during the \( \{\text{Fe}^{2+}\}_{14}\text{aneN}_4\text{Ac}^- \)^2+/\( \text{O}_2 \) electroreduction.

As shown in Figure 6 (a, b, d), the ESR spectrum of a dry DMSO solution containing 2 mM of \( \{\text{Fe}^{3+}\}_{14}\text{aneN}_4\text{Ac}^- \)^2+ acquired after rapid mixing with \( \text{KO}_2 \) in dry DMSO (~2 mM) is quite different from that recorded for \( \{\text{Fe}^{3+}\}_{14}\text{aneN}_4\text{Ac}^- \)^2+ analogue dissolved either in DMSO or in MeOH. Obviously, the spectral line broadening observed for \( \{\text{Fe}^{3+}\}_{14}\text{aneN}_4\text{Ac}^- \)^2+ in DMSO is attributable to the relatively low magnetic permeability of DMSO, as well as the high concentration of the applied macrocyclic complex. Following the addition of KO\(_2\)/DMSO to \( \{\text{Fe}^{3+}\}_{14}\text{aneN}_4\text{Ac}^- \)^2+/DMSO, a decay of the \( \text{O}_2^- \) radicals ESR lines at \( g_|| = 2.09 \) and \( g_\perp = 2.00 \) [19a,b], accompanied by a significant change in the ESR spectrum of this \( \text{Fe}^{3+} \) macrocyclic complex have been found. These changes relate to a disappearance of \( \{\text{Fe}^{3+}\}_{14}\text{aneN}_4\text{Ac}^- \)^2+ ESR lines at \( g = 2.51, 2.23 \) and 1.91, and development of a new resonance transition with apparently smaller \( g \) anisotropy at \( g = 2.32, 2.22 \) and 2.02. As reported before [9a], the \( \text{Fe}^{3+} \) macrocyclic complex exhibits the resonance transition typical of \( \text{Fe}^{3+} \) low-spin octahedral complexes with a large rhombic distortion. Thus, the apparent rhombicity decrease observed on the \( \{\text{Fe}^{3+}\}_{14}\text{aneN}_4\text{Ac}^- \)^2+/KO\(_2\) mixing can be explained in terms of this complex symmetry change, following a substitution of \( \text{O}_2^- \) for the open coordination site on the iron centre and a peroxy complex formation, \( \{\text{Fe}^{3+}(\text{O}_2)\}_{14}\text{aneN}_4\text{Ac}^- \}, \) (the ESR spectra of \( \text{Fe}^{3+} \) porphyrin [10a] and non-porphyrin peroxy complexes [10b, 11] are reported elsewhere). Most likely, the \( \text{O}_2^- \) substitution for the Cl− labile axial ligand in \( \{\text{Fe}^{3+}\}_{14}\text{aneN}_4\text{Ac}^- \)^2+, associated with a transient \( \text{Fe}^{2+}\text{-oxo} \) adduct formation, is followed by an outer-sphere electron transfer from another \( \text{O}_2^- \) radical. Then, after an intramolecular electron transfer, *i.e.* the \( \text{Fe}^{2+}\text{/Fe}^{3+} \) oxidation, \( \{\text{Fe}^{3+}(\text{O}_2)\}_{14}\text{aneN}_4\text{Ac}^- \} \) is formed that is observed in the ESR experiments, see Figure 6 (d).

\[
\text{Fe}^{3+}\text{L} + \text{O}_2^- \rightarrow \text{Fe}^{2+}(\text{O}_2)\text{L} + \text{O}_2^- \rightarrow \text{Fe}^{3+}(\text{O}_2^-)\text{L}
\]

However, this hypothetical reaction is thermodynamically unfavourable since \( E(\text{O}_2^-/\text{O}_2) > E(\text{O}_2^-/\text{O}_2^-) \).
In order to explore the reactivity of \( \text{Fe}^{3+} \mid \text{[14]aneN}_4\text{Ac}^- \) towards \( \text{H}_2\text{O}_2 \), which is initially produced on the \( \text{O}_2 \) electroreduction (probably, via hydrolysis of either \( \text{Fe}^{3+}(\text{O}_2^2-\text{c}_{45})\mid \text{[14]aneN}_4\text{Ac}^- \) or \( \text{O}_2(\text{Fe}^{3+} \mid \text{[14]aneN}_4\text{Ac}^-)_2^{2+} \)), control ESR experiments on the \( \text{Fe}^{3+} \) complex reaction with hydrogen peroxide have been performed. In the first approach, a methanolic solution of \( \text{Fe}^{3+} \mid \text{[14]aneN}_4\text{Ac}^- \) was mixed with 0.1 M aqueous \( \text{H}_2\text{O}_2 \), however, in the second experiment the hydrogen peroxide solution has been added to 0.1 N methanolic KOH containing \( \text{Fe}^{3+} \mid \text{[14]aneN}_4\text{Ac}^- \) \( 2^{2+} \), under the same concentration conditions. As expected, the ESR spectrum of \( \text{Fe}^{3+} \mid \text{[14]aneN}_4\text{Ac}^- \) does not change on mixing with hydrogen peroxide in methanol, indicating that \( \text{Fe}^{3+} \mid \text{[14]aneN}_4\text{Ac}^- \) \( 2^{2+} \) cannot be reduced by \( \text{H}_2\text{O}_2 \) under these conditions. However, on \( \text{Fe}^{3+} \mid \text{[14]aneN}_4\text{Ac}^- \) \( 2^{2+}/\text{H}_2\text{O}_2 \) mixing in methanolic KOH interesting ESR results have been received, as shown in Figure 6 (e) (for the experimental details see the Experimental). Generally, the ESR spectrum is dominated by the

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**Figure 6.** X-band ESR spectra acquired for \( \text{Fe}^{3+} \mid \text{[14]aneN}_4\text{Ac}^- \) \( 2^{2+} \) (2 mM) in methanol (a); in DMSO (b); in methanolic KOH, 0.1 M (c); on mixing with equal volume of DMSO saturated with \( \text{KO}_2 \), 2 mM [13], (d); on mixing with 0.1 ml of aqueous \( \text{H}_2\text{O}_2 \) (0.1 M) in methanolic KOH, 0.1 M, (e); at 77, under anaerobic conditions. The numbers inside relate to the g parameter values.
resonance transition that matches the ESR pattern of this Fe$^{3+}$ macrocycle in methanol [9a], however at $g = 2.00$ and 2.09 the RES lines due to O$_2^-$ radicals [19b] are monitored. Moreover, some ESR indications for a peroxy Fe$^{3+}$ complex can be also found at $g = 2.32$. The observation of superoxide radicals is particularly interesting in the context of the experiment with KO$_2$ presented above, where the ESR lines of O$_2^-$ have not been confirmed. Most likely, the superoxide production comes from this ferric complex catalyzed decomposition of H$_2$O$_2$, i.e. the long-known catalysis of H$_2$O$_2$ degradation by Fe$^{3+}$ ions proposed by Haber and Weiss [20], as shown below:

$$\text{Fe}^{3+}\text{L}^+ + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{LFe}^{2+}\text{O}_2 \text{H} \rightarrow \text{Fe}^{2+}\text{L}^+ + \text{HO}_2^-$$

Furthermore, the superoxide can be also produced on the following reaction of the Fe$^{2+}$ redox form with H$_2$O$_2$, i.e. on a Fenton like reaction of \{Fe$^{2+}$[14]aneN$_4$Ac$^-$\}. The classical Fenton reaction (H$_2$O$_2$/Fe$^{2+}$) [20b] involves the production of ‘OH radical intermediates. These radicals, as strong oxidants (E('OH/OH$^-$) = 2.31 V) [8], rapidly oxidize H$_2$O$_2$ (k = 1.2–4.5 × 10$^7$ M$^{-1}$ s$^{-1}$) giving O$_2^-$. [8,11]. Of course, the Haber-Weiss (Fenton) like reaction is pH dependent [20]. In the case of \{Fe$^{3+}$[14]aneN$_4$Ac$^-$\}$^{2+}$, the reaction is accelerated by the H$_2$O$_2$ hydrolysis to HO$_2^-$ ions, subsequently being substituted for the open coordination site on the Fe$^{3+}$ reagent. Therefore, the superoxide radicals have been mainly observed in methanolic KOH. Of course, the small amount of water introduced to the reaction mixture with H$_2$O$_2$ accelerates hydrolysis of peroxy intermediates. Thus, they are only partially, monitored in the ESR measurements.

In contrast to Fe$^{2+}$ cyclam (Fe$^{2+}$[14]aneN$_4$) [21], \{Fe$^{2+}$[14]aneN$_4$Ac$^+$\} exhibits a particularly high reactivity towards O$_2$. This can be explained in terms of these complexes redox behaviour, and the macrocycle structural effects. Comparing to Fe$^{2+}$[14]aneN$_4$, the redox potential of \{Fe$^{2+}$[14]aneN$_4$Ac$^-$\}$^{+}$ is negatively shifted by around 0.7 V stabilizing the Fe$^{3+}$ state. Furthermore, the vacancy in the coordination sphere of \{Fe$^{3+}$[14]aneN$_4$Ac$^-$\}$^{2+}$ readily accelerates the reaction with O$_2$, and its reduced forms. It is documented that the overpotential for the O$_2$ electroreduction in an aqueous solution of \{Fe$^{3+}$[14]aneN$_4$Ac$^-$\}$^{2+}$ is positively shifted by around 0.45 V. This indicates that the Fe$^{3+}$ macrocyclic complex can be applied as a catalyst for dioxygen electroreduction.

In the pioneering works on the Fe$^{3+}$ porphyrins catalyzed O$_2$/H$_2$O electroreduction, suitable superoxy adducts are considered as intermediates [2,4]. Presumably, similar transient species are produced during the O$_2$/H$_2$O electroreduction in the presence of \{Fe$^{3+}$[14]aneN$_4$Ac$^-$\}$^{2+}$ (as shown in Scheme 1) since analogous CV responses are recorded for the Fe$^{3+}$ macrocyclic complex and the metalloporphyrins. The high affinity of \{Fe$^{3+}$[14]aneN$_4$Ac$^-$\}$^{+}$ to O$_2$ is ascribable to the accessibility of the vacant coordination site on the Fe$^{2+}$ ion for labile ligands. It means that an O$_2$ molecule can be easily substituted for a ligating group occupying the vacancy, which exhibits smaller nucleophilicity, such as H$_2$O and Cl$^-$ [9,15]. Alternatively, the O$_2$ binding causes the paramagnetic iron centre to become diamagnetic due to coupling between two un-
paired electrons of \(^3\)O\(_2\), and Fe\(^{2+}\) central cation [19a]. Since OH\(^-\) ions are more nucleophilic agents than O\(_2\) molecules and O\(_2^-\) radicals, the hydroxy derivative, \(\{\text{Fe}^{3+}(\text{OH})[14]\text{aneN}_4\text{Ac}^-\}\)\(^{2+}\), retards the O\(_2\)/O\(_2^-\) binding. Therefore, no catalysis for dioxygen electroreduction with \(\{\text{Fe}^{3+}[14]\text{aneN}_4\text{Ac}^-\}\)\(^{2+}\) is observed, in basic environments.

It has been postulated that the oxo-adduct, \(i.e\). \(\{\text{Fe}^{2+}(\text{O}2)[14]\text{aneN}_4\text{Ac}^-\}\)\(^+\), undergoes the intramolecular electron transfer to the isoelectronic superoxide adduct, \(\{\text{Fe}^{3+}(\text{O}_2^-)[14]\text{aneN}_4\text{Ac}^-\}\)\(^+\). This species can be reduced either by another molecule of the Fe\(^{2+}\) macrocyclic complex or by a superoxide, if present (see Scheme 1). However, which mechanism dominates remains unclear. Presumably, it depends which compound is in excess. For \([\{\text{Fe}^{3+}[14]\text{aneN}_4\text{Ac}^-\}\] \(> [O_2]\), the Fe\(^{3+}\) peroxy dimer, \(\{O_2(\text{Fe}^{3+}[14]\text{aneN}_4\text{Ac}^-\)\)\(^{2+}\) seems to be mainly produced, however, for the diluted samples (where \([\{\text{Fe}^{3+}[14]\text{aneN}_4\text{Ac}^-\}\] \(< [O_2]\) the direct Fe\(^{3+}\) peroxy adduct, \(\{\text{Fe}^{3+}(\text{O}_2^-)[14]\text{aneN}_4\text{Ac}^-\}\) formation by the electrochemically generated O\(_2^-\) radicals can also be involved. Both the peroxy adduct and the peroxy dimer easily hydrolyse to the mother Fe\(^{3+}\) complex and hydrogen peroxide, if the reaction is conducted in an aqueous solution. In the next step, the released peroxide is consumed upon the follow up Fenton like reaction of the electrochemically generated Fe\(^{2+}\) redox form [11]. The reduction of H\(_2\)O\(_2\) by \(\{\text{Fe}^{2+}[14]\text{aneN}_4\text{Ac}^-\}\)\(^+\) is thermodynamically favourable because \(E(\text{H}_2\text{O}_2/\text{OH}, \text{OH}^-) = 0.32\) V [8].

As shown in Scheme 1, the O\(_2\)/H\(_2\)O electroreduction in aqueous solutions of \(\{\text{Fe}^{3+}[14]\text{aneN}_4\text{Ac}^-\}\)\(^{2+}\) proceeds with production of several intermediates, such as superoxo and peroxy adducts, peroxy dimers, oxo-radicals, \textit{etc}. Comparing to Co\(^{3+}[14]\text{aneN}_4\text{O}_2\) system [3], this process as a whole is controlled by the generation of the peroxy dimer intermediate, \(\{O_2(\text{Fe}^{3+}[14]\text{aneN}_4\text{Ac}^-\)\)\(^{2+}\). It has been believed that this highly reactive dimer rapidly transforms to a high valent iron complex [22], in this work probably in the form of \(\{\text{Fe}^{4+}\text{O}[14]\text{aneN}_4\text{Ac}^-\}\)\(^-\). This highly oxidative reagent (commonly known as a ferryl species [8,19a]) could be readily reduced with \(\{\text{Fe}^{2+}[14]\text{aneN}_4\text{Ac}^-\}\)\(^+\) giving a \(\mu\)-oxo-dimer [22], \(\{O(\text{Fe}^{3+}[14]\text{aneN}_4\text{Ac}^-\)\)\(^{2+}\). Because \(\mu\)-oxo-dimers belong to the group of particularly inert (inactive) iron compounds [23], production of \(\{O(\text{Fe}^{3+}[14]\text{aneN}_4\text{Ac}^-\)\)\(^{2+}\) could be associated with a degradation of the macrocyclic complex. Fortunately, production of a \(\mu\)-oxo-dimer from \(\{\text{Fe}^{3+}[14]\text{aneN}_4\text{Ac}^-\}\)\(^{2+}\) on the O\(_2\) electroreduction has not been confirmed in this work. Probably, ferryl species are mainly produced in non-aqueous environment, thus a spontaneous hydrolysis of \(\{O_2(\text{Fe}^{3+}[14]\text{aneN}_4\text{Ac}^-\)\)\(^{2+}\) to \(\{\text{Fe}^{3+}[14]\text{aneN}_4\text{Ac}^-\}\)\(^{2+}\) and H\(_2\)O\(_2\) kinetically prevents the \(\mu\)-oxo-dimer formation. However, a kind of \(\{\text{Fe}^{3+}[14]\text{aneN}_4\text{Ac}^-\}\)\(^{2+}\) deactivation could be rather related to production of \(\{\text{Fe}^{3+}(\text{OH})[14]\text{aneN}_4\text{Ac}^-\}\)\(^+\) that follows the O\(_2\)/H\(_2\)O electroreduction. This hydrolysis results in the unfavourable (negative) shifting of this complex redox potential, as well as in the retardation of O\(_2\) substitution for the open coordination site on the iron centre.

In conclusion, \(\{\text{Fe}^{3+}[14]\text{aneN}_4\text{Ac}^-\}\)\(^{2+}\) behaves similarly to the catalysts of dioxygen electroreduction if the electrolysis is conducted in acidic environment.
However, in neutral and basic aqueous solutions this process inhibits the Fe$^{3+}$ complex hydrolysis to its OH$^{-}$ derivative. It is proposed that the O$_2$/H$_2$O electroreduction catalyzed by the Fe$^{3+}$ complex involves the following 4 chemical reactions: (1) the formation of Fe$^{3+}$ superoxy adduct, (2) the formation of Fe$^{3+}$ peroxy dimer, (3) the Fenton reaction of the Fe$^{2+}$ complex, and (4) the oxidation of the Fe$^{2+}$ complex by OH radicals. Accordingly, the reducible O$_2$ molecules pass through the following 3 transient states: O$_2$.–, H$_2$O$_2$ and OH radical. For this, 4 molecules of the Fe$^{2+}$ complex are involved to provide 4 electrons.

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