

Electrochemical Behaviour of a Series of Fe(III) Complexes with Tetradentate Schiff Base Ligands

A. Kotočová* and J. Šima

Department of Inorganic Chemistry, Slovak Technical University, 81237 Bratislava, Slovakia

Summary. The electrochemical reduction of the Fe(III) complexes with a series of substituted N,N'-Ethylenebisacetonimines was investigated by cyclic voltammetry in acetonitrile solution at a platinum electrode. The substituent does not significantly influence the redox properties of the studied complexes. The symmetry of the redox orbital is responsible for the observed behaviour of the complexes.

Keywords. Electrochemistry; Iron; Symmetry of redox orbital; Tetradentate Schiff base ligands.

Elektrochemisches Verhalten einer Reihe von Fe(III)-Komplexen mit vierzähligen Schiffischen Basen als Liganden

Zusammenfassung. Die elektrochemische Reduktion der Fe(III)-Komplexe einer Reihe von substituierten N,N'-Ethylenbisacetonimininen wurde mittels cyclischer Voltammetrie in Acetonitril an einer Platinelektrode untersucht. Der Substituent beeinflusst die Redox Eigenschaften der untersuchten Komplexe nicht signifikant. Das beobachtete Verhalten der Komplexe wird von der Symmetrie des Redoxorbitals bestimmt.

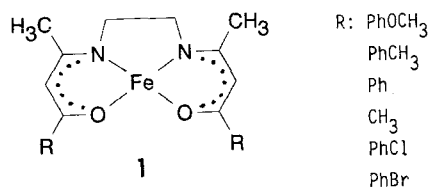
Introduction

In the preceding articles [1–6] we have discussed the redox properties of Co(II), Cu(II), and Ni(II) complexes with tetradentate Schiff base ligands. These compounds were found to form monomeric complexes [7], essentially keeping their square-planar geometry. A large amount of attention has been paid to changes in the redox properties of the complexes caused by axial and equatorial modifications of the inner coordination sphere with ligands or substituents of various electronic properties.

In all above complexes the redox orbital with the unpaired electron acting in the electrode oxidation (the electron is extracted) is localized in the complex plane (the d_{xy} orbital for the Cu(II) [1–4] and Ni(II) [5] complexes) or out of the complex plane (the d_{yz} orbital for the Co(II) [2–4] complexes).

The symmetry of the redox orbitals showed to be very important for the observed changes in the redox properties caused with the equatorial or axial modifications of the complexes.

In this paper, we describe recent results concerning the electrochemical reduction of some iron(III) tetradentate Schiff base complexes (**1**) (further denoted as $\text{FeN}_2\text{O}_2\text{R}_2^+$). On the basis of previous observations, this process corresponds to the addition of the electron to an energetically suitable redox orbital.



Experimental Part

The ligands were prepared according to a literature method [8].

The complexes $\text{FeN}_2\text{O}_2\text{R}_2^+$ were prepared by the reaction of Fe(III) chloride with the corresponding ligand directly in an electrolyzed cell at room temperature. Upon reaction, the color of the solution changed from light brown to a dark red. Tetrabutylammonium perchlorate (TBAP) was synthesized from perchloric acid and tetrabutylammonium hydroxide. Acetonitrile was obtained from Avondale Laboratories and used without further purification.

Cyclic voltammetric measurements were performed in a one-compartment three-electrode cell with a platinum-wire working electrode, a platinum-foil auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE). The SCE was separated from the test solution by a bridge filled with the solvent and the supporting electrolyte. A PA 3 polarographic analyzer (Laboratory Instruments, Prague) was employed for the experiments.

All experiments were carried out under an argon atmosphere at ambient temperature in acetonitrile solutions (0.05 mol dm^{-3} TBAP, $1.6 \times 10^{-3} \text{ mol dm}^{-3}$ complex) with scan rates 20, 50, 100, 200, and 500 mV s^{-1} . At the end of experiments, ferrocene was added to the test solution as an internal standard [9, 10].

Results and Discussion

In acetonitrile solution, all Fe(III) complexes studied undergo a one-electron cathodic process at a platinum electrode between 1.58 and -0.20 V (*vs.* SCE) which gives voltammetric responses consisting of a reduction peak on the forward scan and a corresponding oxidation peak on the backward scan (Fig. 1). The number of electrons (n) involved in the redox process was determined using the Malachuk equation [11] and was found to be 0.97 ± 0.04 . The separation of reduction and oxidation potential, E_{pc} and E_{pa} , respectively, was in the range of 125–140 mV for the scan rate of 50 mV s^{-1} .

The data show lack of reversibility (*quasi-reversible* behaviour) for the studied complexes indicating that iron(II) complexes formed upon reduction are structurally not very similar to the initial iron(III) complexes. At our experimental conditions, the reversible couple ferrocenium/ferrocene (Fc^+/Fc , $E_f = 0.36 \text{ V vs. SCE}$) has a ΔE_p value of 80 mV, which was used as the criterion for electrochemical reversibility. The formal potentials (E_f) were calculated as the average of the cathodic (E_{pc}) and anodic (E_{pa}) peak potentials. The values E_f of the complexes covered the range from -0.29 to $-0.25 \text{ vs. } E_f$ of the redox system Fc^+/Fc .

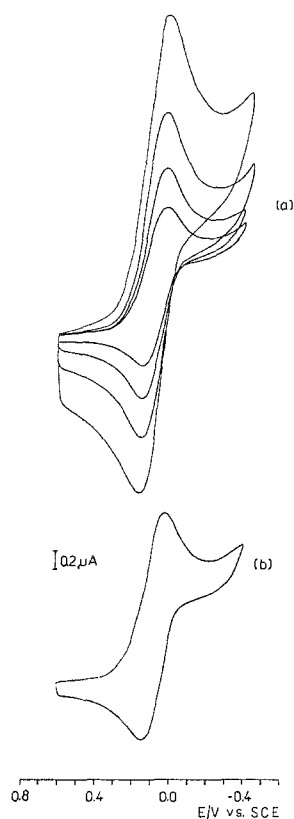


Fig. 1. Cyclic voltammograms in acetonitrile containing 0.05 M TBAP at a platinum electrode: (a) of $\text{FeN}_2\text{O}_2\text{Ph}_2$ at scan rates of 50, 100, 200, and 500 mV s^{-1} ; (b) of FeCl_3 at a scan rate of 100 mV s^{-1} ($E_f = -0.28 \text{ V vs. } E_f(\text{F}^+/\text{F})$)

The peak-current-ratio ($i_{\text{pa}}/i_{\text{pc}}$), ranging from 0.80 to 0.88 at $v = 50 \text{ mV s}^{-1}$, indicates that the iron(II) complexes are unstable in acetonitrile solution, undergoing probably subsequent chemical reactions. In addition, plots of peak current versus $v^{1/2}$ between 50 and 500 mV s^{-1} were linear indicating a diffusion-controlled process.

The E_f values, the peak potential separations, ΔE_p , and the peak-current ratios $i_{\text{pa}}/i_{\text{pc}}$ obtained from the cyclic voltammograms at 50 mV s^{-1} are summarized in Table 1.

In order to examine these processes in more detail, cyclic voltammograms were evaluated according to the theory of Nicholson and Shain [12]. Analysis of

Table 1. Electrochemical Properties of the $\text{FeN}_2\text{O}_2\text{R}_2^+$ Complexes

R	E_f (V)	ΔE_p (mV)	$i_{\text{pa}}/i_{\text{pc}}$	σ_m^a
CH_3	-0.29 ₀	125	0.84	-0.07
PhOCH_3	-0.28 ₅	120	0.88	0.05
PhCH_3	-0.27 ₃	130	0.80	0.06
Ph	-0.27 ₄	140	0.84	0.06
PhCl	-0.27 ₃	125	0.84	0.15
PhBr	-0.25 ₄	120	0.86	0.15

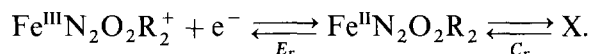
^a Hemmett substituent constant [14]

Table 2. Dependence of $i_{pa}(i_{pc})^{-1}$, E_{pc} , $i_{pc}v^{-1/2}$ vs. v for $\text{FeN}_2\text{O}_2\text{Ph}_2$.

v (mVs^{-1}) ^a	E_{pc} (V) ^a	E_{pa} (V) ^a	$i_{pa}(i_{pc})^{-1}$
50	0.03	0.15	0.87
100	0.03	0.15	0.87
200	0.03	0.15	0.84
500	0.02	0.17	0.82

^a vs. SCE

voltammograms shows that the studied complexes present a “kinetic case”, *i.e.* a homogeneous chemical reaction is coupled to the electrode process. By using appropriate diagnostic criteria ($i_p v^{-1/2}$ vs. v ; $i_{pa}(i_{pc})^{-1}$ vs. v ; E_{pc} , E_{pa} vs. v ; Table 2) it was qualitatively found that the one-electron reduction of the studied complexes was followed by a reversible chemical reaction belonging to $E_r C_r$ mechanism. The identity of the species X was not investigated.



The fact that the reduction process is not significantly influenced by the substituent R in the equatorial plane (a modification of the complex equatorial plane) can be connected with the symmetry of the redox orbital to which the electron was added.

The formal potential of the one-electron reduction for the iron complexes shifts slightly upon changing electronic properties of the substituent R (cf. Table 1). The Hammett correlation [13] of E_f vs. $\Sigma\sigma$ was $\rho = 0.062$ V ($r^2 = 0.67$ for the linearly regressed line).

The studied ferric complexes belong to the family of the high-spin d^5 -compounds, possessing both the in-plane (d_{xy} , $d_{x^2-y^2}$) and out-of-plane (d_{zx} , d_{yz} , d_{z^2}) orbitals suitable for the electron addition. The insignificant substituent effect on the E_f values may be explained by the fact that the electron is added to the d_{zx} or d_{yz} orbitals which are influenced only slightly by the substituent R in the equatorial plane of the complex.

Electrochemical studies reveal a near-reversible, diffusion-controlled $\text{FeN}_2\text{O}_2\text{R}_2^+/\text{FeN}_2\text{O}_2\text{R}_2$ couple at potentials that are not significantly different from the uncomplexed $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple in acetonitrile. In addition, the potential of this redox couple cannot be tuned by a modification of the equatorial plane of the complex.

References

- [1] Kotočová A., Šíma J. (1980) *Inorg. Chim. Acta* **40**: 115
- [2] Kotočová A., Šíma J. (1981) *Chem. Zvesti.* **35**: 793
- [3] Kotočová A. D., Valigura D., Fodran P., Šíma J. (1984) *Inorg. Chim. Acta* **88**: 135
- [4] Kotočová A., Valigura D., Fodran P., Šíma J. (1984) *Chem. Zvesti.* **38**: 67
- [5] Kotočová A., Šíma J., Valigura D., Fodran P. (1987) *Inorg. Chim. Acta* **128**: 11
- [6] Kotočová A., Valigura D., Šíma J. (1991) *J. Coord. Chem.* **24**: 363

- [7] Wei R. M. C., Cummings S. C. (1973) *Inorg. Nucl. Chem. Letters* **9**: 43
- [8] Valigura D., Holubiková V., Kalužik J., Fodran P., Šima J., Golier I. (1982) Abstract of Papers, Vol. II, XXII ICCO, (Kozponti Kémiai Kutató Intézet, Budapest), p. 837
- [9] Gritzner G., Rechberger P., Gutmann V. (1976) *Mh. Chem.* **107**: 809
- [10] Duschek O., Rechberger P., Gutmann V. (1974) *Mh. Chem.* **105**: 62
- [11] Malachuk P. A. (1969) *Anal. Chem.* **41**: 1493
- [12] Nicholson R. S., Shain I. (1964) *Anal. Chem.* **36**: 706
- [13] Zuman P. (1970) *Substituent Effects in Organic Polarography*. Alfa, Bratislava
- [14] Hansch C., Leo A., Taft R. W. (1991) *Chem. Rev.* **91**: 165

Received May 11, 1993. Accepted (revised) July 8, 1993