1H-NMR and Electrochemical Studies on Ligated Iron(III)perchlorates in Acetonitrile-d₃**

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Summary. Half-wave potentials, \( E_{1/2} \), of \( \text{Fe(ligand)}_6^{3+/2+} \), as \( \text{ClO}_4^- \) salt, \([\text{ligand} = \text{N,N-dimethylformamide (dmf)}, \text{acetamide (aa)}, \text{N,N-dimethylacetamide (dma)}, \text{trimethylphosphate (tmp)}, \text{dimethylsulfoxide (dmso)}, \text{and acetonitrile (MeCN)}]\) are given. A linear correlation between \( E_{1/2} \) and Gutmann’s donor numbers of the ligands, a parameter which expresses quantitatively the Lewis donor properties towards hard acceptors, was found. Ligand replacement on \( \text{Fe(ligand)}_6^{3+} \) in acetonitrile-d₃ was studied by means of ¹H-NMR spectroscopy at 20°C. An average number of ligands coordinated to \( \text{Fe}^{3+} \), \( n_{\text{coord}} \), is given. \( n_{\text{coord}} \) increases with the ligand’s donor strength; i.e. \( \text{tmp} < \text{dmf} < \text{dmso} \).

Keywords. Half-wave potentials; Iron(III) complexes; Ligand exchange.

Introduction

Kinetic and mechanistic investigations of chemical reactions in non-aqueous solutions have become an important field of research in the last decade. The simplest fundamental processes (at least in a theoretical sense) such as solvent exchange reactions [1], electron selfexchange reactions [2, 3] and electron transfer reactions between substitution inert complexes [4, 5] have been dealt with.

However, in the case of electron transfer reactions one eventually has to extend such studies to substitution of labile systems since many practical redox agents are

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labile solvated metal ions, and such studies might prove to be interesting by themselves. A study in this regard is given in [6].

In the present paper we report on electrochemical and $^1$H-NMR studies on ligated iron(III) perchlorates, Fe(ligand)$_6^{3+}$ in acetonitrile solutions as part of our ongoing effort to study redox systems utilizing labile solvated metal ions as oxidants for substitution of inert complexes [7–9]. Strong donor solvents such as trimethylphosphate (tmp), N,N-dimethylformamide (dmf), dimethyl sulfoxide (dmso), acetamide (aa), and N,N-dimethylacetamide (dma) are used as ligands. As a competitor for possible ligand replacement, acetonitrile (MeCN), a solvent with relative poor solvating power towards Fe$^{3+}$, has been chosen.

Further, the study of solvated metal ions in solvents other than those used as ligands might be an informative and interesting approach to mixed solvents to achieve a better understanding of the relative solvating power of solvents.

**Experimental Part**

**Materials**

[Fe(ligand)$_6$](ClO$_4$)$_3$ (ligand = tmp, dmf, dmso, dma) was made according to standard procedures [10]. Fe(MeCN)$_6$(ClO$_4$)$_2$ was prepared by dissolving [Fe(OH)$_2$](ClO$_4$)$_2$ in acetonitrile and evaporating the solvent in the presence of 3 Å molecular sieve (activated at 300°C under vacuum). This procedure was repeated four times. The residue was recrystallized from MeCN, washed with anhydrous diethyl ether, and dried in vacuum at 50°C. [Fe(aa)$_6$](ClO$_4$)$_3$ was synthesized as described in [11]. The complex was precipitated from the reaction mixture upon the addition of anhydrous diethyl ether. The crude complex was recrystallized twice from MeCN, washed with anhydrous diethyl ether and dried in vacuum at room temperature for 24 h. Anal. calc. for C$_{18}$H$_{24}$P$_6$O$_{18}$Cl$_3$Fe (tmp): C 18.10, H 4.56; found: C 17.79, H 4.37. Anal. calc. for C$_{18}$H$_{24}$N$_6$O$_{18}$Cl$_3$Fe (dmf): C 27.27, H 5.34, N 10.60, Fe 7.04; found: C 27.26, H 5.27, N 10.48, Fe 7.04. Anal. calc. for C$_{18}$H$_{24}$S$_6$O$_{18}$Cl$_3$Fe (dmso): C 17.52, H 4.41; Fe 6.80; found: C 17.35, H 4.19, Fe 6.81. Anal. calc. for C$_{30}$H$_{42}$N$_6$O$_{18}$Cl$_3$Fe (dma): C 32.87, H 6.21, N 9.58, Cl 12.13, Fe 6.36; found: C 32.94, H 6.28, N 9.39, Cl 11.99, Fe 5.42. Anal. calc. for C$_{12}$H$_{36}$N$_6$O$_{18}$Cl$_3$Fe (aa): C 20.34, H 4.27, N 11.86; found: C 20.07, H 4.10, N 11.69. Anal. calc. for C$_{12}$H$_{36}$N$_6$O$_{18}$Cl$_3$Fe (MeCN): C 28.58, H 3.57, N 16.67; found: C 26.16, H 3.58, N 15.18. Microanalyses of the tmp and aa solvates were done by Galbraith Laboratories, Knoxville, TN. All other compounds were analyzed by the Microanalytical Laboratory of the University of Vienna. All solvents used for the synthesis of the iron complexes were purified according to a literature method [12]. Acetamide was purchased from Alpha Chemical Co., recrystallized twice from methanol and dried at 25°C under vacuum. Acetonitrile-d$_3$ (99.7% D) was obtained from MSD Isotopes Merck, dried over activated 4 Å molecular sieves, degassed by three consecutive freeze-pump-thaw cycles, and stored in an evacuated bulb in the dark until used.

$^1$H-NMR Measurements

Details of sample preparation are given in [2, 3]. Proton NMR spectra were collected on a Nicolet NT 200 WB and IBM NR 300 instruments operating at 200 and 300 MHz, respectively. The acquisition parameters on the Nicolet instrument were a 4.5 µs pulse width, a 500 ms post acquisition delay, a 10 000 to 20 000 Hz sweep width, a 32 K block size and 256 to 2 048 pulses. On the IBM instrument the acquisition parameters were a 2.0 µs pulse width, a 10 000 Hz sweep width, a 32 K block size, and 130 to 4 000 pulses. All measurements were carried out at 20±1°C. The temperature readings were calibrated against the temperature dependence of the proton chemical shifts of acidified (0.5% HCl) methanol [13]. Chemical shifts are given relative to tetramethylsilane (TMS) or to the signal of the residual protons of CD$_3$CN (1.939 ppm vs. TMS).