

## Effect of Pressure on Proton-Coupled Electron Transfer Reactions of Seven-Coordinate Iron Complexes in Aqueous Solutions

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For the first time, the effect of pressure on proton-coupled electron-transfer reactions of two selected seven-coordinate  $\text{Fe}^{\text{III}}(\text{H}_2\text{L})(\text{H}_2\text{O})_2$  systems [where  $\text{H}_2\text{L} = 2,6$ -diacetylpyridine-bis(semicarbazone) and 2,6-diacetylpyridine-bis(semioxamazine), respectively] was examined. The acid–base equilibria of the different  $\text{Fe}^{\text{III}}$  systems were investigated by spectrophotometric, potentiometric, and electrochemical titrations. On the basis of the obtained species distributions, the pH intervals in which the different protonated forms of the two studied systems exist were defined. In different pH ranges, a different number of protons (from 0 to 3 protons per electron) can be transferred during the redox process, which affects the change in the overall charge on the complexes. For all the different protonation forms of the studied complexes, the change in the redox potentials with pressure was measured and the redox reaction volume was obtained by high-pressure cyclic voltammetry. The results show that in the case of proton-coupled electron transfer, the reaction volume for the neutralization of protons contributes to the overall reaction volume. A linear correlation between  $\Delta z^2$  (change in the square of the charge) and the overall reaction volume of the complexes upon reduction,  $\Delta V_{\text{complex}}^0$ , was found. The average value of the intrinsic volume change for the selected seven-coordinate iron complexes was estimated from the intercept of the plot of  $\Delta V_{\text{complex}}^0$  versus  $\Delta z^2$  to be  $9.2 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$ . For the combined redox and protonation processes, the data are discussed in terms of linear correlations between  $\Delta z^2$  and the redox and neutralization reaction volumes reported in the literature.

### Introduction

Investigations on proton-coupled electron transfer (PCET) processes and the understanding of the fundamental aspects involved are of current interest since PCET reactions play an important role in many biological redox processes.<sup>1</sup> An interesting example of biologically relevant PCET reactions is the disproportionation of superoxide to hydrogen peroxide and dioxygen by Fe- and Mn-superoxide dismutases (SODs).<sup>2</sup> Disproportionation of  $\text{O}_2^{\cdot-}$  requires the uptake of two protons, in which the second proton assists product ( $\text{H}_2\text{O}_2$ )

dissociation from the metal center. This one-electron–two-proton transfer process seems to be a particularly desirable feature of the redox-active center for it to be an efficient SOD catalyst.

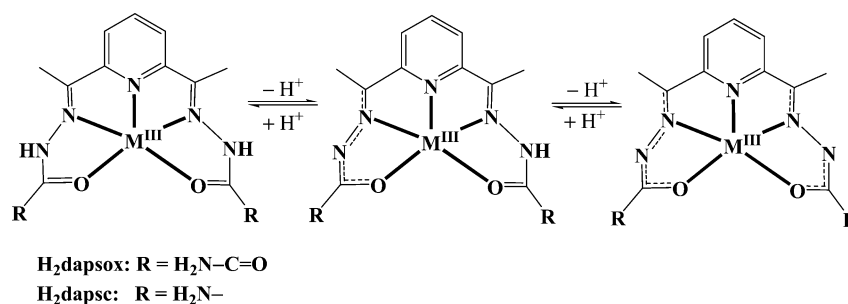
Riley et al.<sup>3</sup> have shown that seven-coordinate Fe(III) diaqua complexes with pentaaza macrocyclic ligands possess SOD activity and could be used as SOD functional mimics. In these systems, the aqua-hydroxo form of the complex is responsible for the high catalytic activity. However, at physiological pH, the catalytically inactive dihydroxo form of the pentaaza complex is also present in solution ( $\text{p}K_{\text{a}1} = 3.5\text{--}5.1$ ,  $\text{p}K_{\text{a}2} = 7.3\text{--}7.7$ ).<sup>3</sup> Thus, it would be desirable to have seven-coordinate Fe(III) complexes with higher  $\text{p}K_{\text{a}}$  values for the coordinated water molecules to yield higher catalytic activity under physiological conditions. At the same

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Scheme 1



time, because the assignment of species involved in a proton transfer that assists superoxide disproportionation is extremely difficult in the case of enzymatic systems, investigations on adequate model complexes could be of importance.

Modulation of the iron redox potential by deprotonation of the potentially heptadentate N-tripodal ligands has been examined.<sup>4</sup> It has also been reported that, in these systems, the protonation state controls the spin state of the iron center.<sup>4a</sup> However, all these studies involve complexes with a six-coordinate octahedral structure that does not change upon ligand deprotonation. We have studied the influence of the ligand protonation state on the geometry, coordination number, and electronic and magnetic properties of seven-coordinate pentagonal-bipyramidal complexes of planar pentadentate ligands.<sup>5</sup> Since seven-coordinate pentagonal-bipyramidal iron complexes with planar pentadentate ligands are interesting as potential SOD mimetics, the study of multiple proton-transfer processes coupled to redox reactions in such systems is of significant importance. In the seven-coordinate SOD mimetics studied so far, the possibility for a proton-transfer process in which the pentadentate ligand is involved does not exist.

As shown below, the seven-coordinate Fe(III) complexes of 2,6-diacetylpyridine-bis(acylhydrazone) chelates used in the present study enable such investigations of PCET processes in aqueous solution. These ligands can coordinate to the Fe(III) center in the neutral, mono-, and dianionic forms without changing their coordination mode (Scheme 1), and their acidity can be varied by changing the  $-\text{R}$  groups. The presence of additional carbonyl groups in  $\text{H}_2\text{-dapsox}$  enables the isolation of the Fe(III) complex from aqueous solution in the  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  form with a doubly deprotonated chelate,<sup>6</sup> whereas in the case of  $\text{H}_2\text{dapsc}$ , the isolated  $[\text{Fe}(\text{H}_2\text{dapsc})\text{Cl}_2]^+$  complex has the neutral pentadentate in the equatorial plane.<sup>7</sup> Because of the presence of the dianionic pentadentate in the  $[\text{Fe}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  complex, the  $\text{pK}_a$  values of the coordinated water molecules

are higher ( $\text{pK}_{a1} = 5.78$ ,  $\text{pK}_{a2} = 9.45$ )<sup>8</sup> than in the case of the above-mentioned Fe(III) SOD mimetics with pentaaza macrocyclic ligands. Therefore, the highly reactive aqua-hydroxo form is the major species in solution at physiological pH.

The two structurally similar pentagonal-bipyramidal  $\text{Fe}^{\text{III/II}}$  redox systems studied here have been shown to be good models to elucidate PCET processes. This is because the number of protons exchanged during the redox reaction varies along the studied pH range. Both complexes exhibit four acid–base equilibria in the pH range 1–12, and the corresponding equilibrium constants have been estimated independently by spectrophotometric, potentiometric, and electrochemical titration methods. The number of protons exchanged during the electrode reactions was evaluated from the slopes of appropriate  $E_{1/2}$ –pH plots ( $E_{1/2}$  = half-wave potential).

To provide an insight into the fundamental aspects of PCET reactions, the effect of pressure on the thermodynamics of the electrode reactions was investigated in detail. The effect of pressure  $P$  on a thermodynamic equilibrium constant  $K^0$  is related to the overall reaction volume,  $\Delta V^0$ , which can be expressed in terms of the pressure dependence of the potential of the half-cell reaction (conventionally written as a reduction process) relative to a particular reference half-cell:

$$\Delta V^0 = -nF(\partial \Delta E^0 / \partial P)_T \quad (1)$$

where  $n$  is the number of moles of electrons transferred and  $F$  is the Faraday constant.<sup>9</sup> The measurement of  $E^0$  (identical with  $E_{1/2}$  as a first approximation) with electrochemical methods such as cyclic voltammetry (CV) or differential pulse voltammetry as a function of pressure leads to a  $\Delta V^0$  value for the reaction under the selected experimental conditions. The volume change associated with the reduction of the metal complex,  $\Delta V_{\text{complex}}^0$ , consists of the following contributions: (a) intrinsic volume changes  $\Delta V_{\text{intr}}^0$ , reflecting bond length and conformational changes in the structure of the complex and (b) electrostrictive volume changes  $\Delta V_{\text{elec}}^0$ , reflecting the contraction or expansion of the surrounding solvent in response to the change in charge on the complex.<sup>10</sup>

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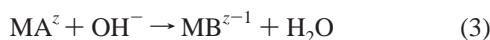
Electrostriction plays an important role in the electron-transfer process. According to the Drude–Nernst expressions,<sup>11</sup> the electrostrictive reaction volume should depend on  $\Delta z^2/r$  ( $\Delta z^2$  = is the change in the square of the charge,  $r$  is the effective complex ion radius<sup>12</sup>). However, it has been observed for a number of studied systems that  $\Delta V_{\text{elec}}^0$  depends linearly on  $\Delta z^2$  rather than on  $\Delta z^2/r$ .<sup>12–14</sup> This is a consequence of the fact that the difference in complex radii between different complexes is less important than the change in  $\Delta z^2$ .

Tregloan et al.<sup>13</sup> studied the reduction of differently charged Fe(III) complexes, which do not show any pH-dependent behavior in aqueous solution. They found a very good correlation between the reaction volume and the difference between the squares of the charges on the oxidized and reduced forms of the complexes, namely,

$$\Delta V_{\text{elec}}^0 = 4.3\Delta z^2 \quad (2)$$

where  $\Delta z^2 = z_{\text{oxidized}}^2 - z_{\text{reduced}}^2$ . Some recent studies on binuclear Ru(III)–Fe(II)<sup>14</sup> and Co(III)–Fe(II)<sup>15</sup> complexes showed that this correlation is very useful in the case of pure electron-transfer reactions.

A similar dependence on  $\Delta z^2$  was reported for the neutralization reaction volume for a series of differently charged complexes in aqueous solution.<sup>16</sup> A linear relationship between  $\Delta V^0$  and  $\Delta z^2$  for 19 neutralization reactions of the type



[M = Co(III), Rh(III), Fe(III), or Pt(IV); A = H<sub>2</sub>O, NH<sub>3</sub>, and C<sub>2</sub>O<sub>4</sub>H; and B = OH, NH<sub>2</sub>, and C<sub>2</sub>O<sub>4</sub>] was found to be

$$\Delta V^0 = (14.5 \pm 0.8) - (2.5 \pm 0.2)\Delta z^2 \quad (4)$$

where  $\Delta z^2 = (z - 1)^2 - z^2$ .

The goal of our study was to find a correlation between the reaction volume  $\Delta V^0$  and the change in overall charge  $\Delta z^2$  for the reduction of seven-coordinate Fe(III) complexes that is coupled to the transfer of different numbers of protons. This report presents, for the first time, results from the study of pressure effects on electron-transfer reactions of metal complexes that are coupled to proton-transfer processes. It will be shown that the measured reaction volume can also be expressed as a linear function of the change in the square of the overall charge on the metal complexes during PCET processes.

## Experimental Section

**Chemicals.** All reagents and solvents were commercially available (Sigma, Acros Organics, and Fluka) and used without further purification. Deionized Millipore water was used for all types of measurements. Freshly distilled solvents were used for all syntheses described below.

**[Fe<sup>II</sup>(H<sub>2</sub>dapsox)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.** 2,6-diacetylpyridine (0.163 g, 1 mmol) and semioxamazid (0.218 g, 2.1 mmol) were heated in a 2:1 mixture of methanol/acetonitrile (60 mL) up to 65 °C and refluxed for 2 h under an argon atmosphere. After this period, Fe-(ClO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (0.35 g, 1 mmol) was carefully added to the resulting white suspension under an argon atmosphere. The color of the suspension changed to gray, and the white precipitate dissolved slowly with time. After 5 h of refluxing, a part of the solvent mixture was removed under reduced pressure. The dark gray solution was filtered and placed in the refrigerator. A dark gray powder was collected after 2 days. Anal. Calcd for C<sub>13</sub>H<sub>19</sub>Cl<sub>2</sub>-FeN<sub>7</sub>O<sub>10</sub>: C, 27.88; H, 3.42; N, 17.51. Found: C, 27.56; H, 3.39; N, 17.62%.

A solution of the iron(III) counterpart {[Fe<sup>III</sup>(dapsox)(H<sub>2</sub>O)<sub>2</sub>]-ClO<sub>4</sub>} adjusted to pH = 2 was reduced by potentiostatically controlled electrolysis, and the spectrum of the product was identical with that of a solution of the synthesized [Fe<sup>II</sup>(H<sub>2</sub>dapsox)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> recorded at pH = 2 (Figure S1, Supporting Information).

**[Fe<sup>III</sup>(dapsox)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub>.** The complex was prepared and characterized as described previously.<sup>6</sup>

**[Fe<sup>III</sup>(H<sub>2</sub>dapsc)Cl<sub>2</sub>]Cl·2H<sub>2</sub>O and [Fe<sup>II</sup>(H<sub>2</sub>dapsc)(H<sub>2</sub>O)Cl]Cl.** The complexes were prepared following the procedure of Palenik et al.<sup>7a</sup>

**Spectrophotometric and Potentiometric pH Titrations.** The pH of the solutions was measured with a Mettler Delta 350 pH meter using a combined glass electrode. The latter was calibrated applying standard buffer solutions (pH = 4, 7, and 10) and 0.1 M HCl (pH = 1). The pH electrode was filled with NaCl instead of KCl to prevent precipitation of KClO<sub>4</sub>. The pH-dependent spectrophotometric titrations of [Fe(H<sub>2</sub>dapsox)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, [Fe(H<sub>2</sub>dapsc)Cl<sub>2</sub>]Cl, and [Fe(H<sub>2</sub>dapsc)(H<sub>2</sub>O)Cl]Cl were carried out with a Hewlett-Packard 8452A spectrophotometer. The complex solutions were prepared using 0.1 M Britton–Robinson<sup>17</sup> buffer solutions (pH = 2–12). In the range below pH = 2, no buffer solutions were used. The pH of the solutions was changed by the addition of HClO<sub>4</sub> or NaOH. The complex concentrations during these experiments were 5 × 10<sup>-5</sup> M, and the ionic strength was kept constant at I = 0.1 M (NaClO<sub>4</sub>). Measurements were performed under a nitrogen atmosphere. The calculation of the equilibrium constants (pK<sub>a</sub> values) and the resulting pH-dependent speciation was performed with the software package Specfit/32 global analysis.

Potentiometric titrations of [Fe(dapsox)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub>, [Fe(H<sub>2</sub>-dapsox)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, [Fe(H<sub>2</sub>dapsc)Cl<sub>2</sub>]Cl, and [Fe(H<sub>2</sub>dapsc)(H<sub>2</sub>O)Cl]Cl were performed on a METROHM 702 SM Titrimo in a jacketed, airtight glass titration cell equipped with a combined pH glass electrode (METROHM), a N<sub>2</sub> inlet and outlet, and a graduated 20 mL microburet (METROHM). The electrode was calibrated with a strong acid and a strong base so that a direct reading in hydrogen ion concentration would be made using four different commercially available standard buffer solutions of pH = 2, 4, 7, and 10. The ion product of water, that is, pK<sub>w</sub> = -log [H<sup>+</sup>][OH<sup>-</sup>] = 13.75, was determined experimentally. Carbonate-free 0.05 M sodium hydroxide or perchloric acid solutions were prepared with boiled, distilled, and nitrogen-saturated water and

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were standardized by titrations with a 0.05 M potassium hydrogen phthalate solution. Gran's method<sup>18</sup> was used to confirm the absence of carbonate in the sodium hydroxide standard solution (carbonate content 0.13%). All solutions were adjusted to an ionic strength of 0.1 M with NaClO<sub>4</sub>. The temperature was maintained at 25.0 ± 0.1 °C by circulating thermostated water through the outer jacket of the cell. All measurements were carried out under a constant atmosphere of nitrogen above the solution and were repeated at least four times. The concentration of the complexes was 1 × 10<sup>-3</sup> M, and the ionic strength was kept constant at 0.1 M by NaClO<sub>4</sub>. The pK<sub>a</sub> values and species distribution of the complexes were calculated using the program TITFIT.<sup>19</sup>

**Electrochemical Measurements.** Cyclic voltammetric measurements were carried out with an Autolab PGSTAT 30 device (Eco Chemie). A conventional three-electrode arrangement was employed consisting of a gold disk working electrode (geometric area: 0.07 cm<sup>2</sup>) (Metrohm), a platinum wire auxiliary electrode (Metrohm), and a Ag/AgCl, NaCl (3 M) (Metrohm) reference electrode. The measurements in aqueous solutions were done in 0.1 M NaClO<sub>4</sub> supporting electrolyte. All solutions were initially thoroughly degassed with prepurified nitrogen (15 min), and a stream of N<sub>2</sub> gas was passed over the sample solutions during the measurements. The solutions were thermostated at 25 °C. The proton stoichiometry of the individual Fe<sup>III/II</sup>-L electrode reactions was evaluated from the slopes of E<sub>1/2</sub>-pH diagrams according to the Nernst equation.<sup>20</sup> The redox potentials reported in the text refer to an Ag/AgCl/3 M NaCl reference electrode (+0.214 V vs NHE, 25 °C). A modified 0.1 M Britton-Robinson buffer [mixture of acetic acid/acetate, PIPES = piperazine-N,N'-bis(2-ethanesulfonic acid), and boric acid/borate] had to be used to reach optimal buffering in the pH range 3.5–12. This buffer was applied to evaluate the pH dependence of the cyclic voltammetrically measured E<sub>1/2</sub> values. No buffer was used for the evaluation of the pH-dependent E<sub>1/2</sub> at pH < 3.5. The pK<sub>a</sub> values were calculated using the program EFIT.<sup>21</sup>

Electrochemical measurements under elevated pressure were performed in a homemade cell. A three-electrode system was employed. It consisted of a gold working disk electrode (geometric area: 0.02 cm<sup>2</sup>) (BAS), a platinum wire (Sigma-Aldrich) as an auxiliary electrode, and an Ag/AgCl reference electrode. The reference electrode was prepared as follows: the Ag wire covered with AgCl was placed in a shrink tube (BAS) filled with a 4 M NaCl solution and closed carefully with porous Vycor (BAS). The set of electrodes was placed into the Teflon cup, which was screwed into the electrochemical cell body. The cell was filled with a solution made up of 0.1 M NaClO<sub>4</sub> electrolyte and 1 mM complex. Nitrogen was bubbled through the solution for at least 25 min to ensure that oxygen had been removed. Then, the Teflon cup was closed with a Teflon plug and a screw. The assembled pressure vessel containing the cell was placed in a thermostated water jacket, and a period of 45 min was given to reach thermal equilibrium (25.0 ± 0.1 °C) of the cell after assembly and after each change in pressure. The pH values of solutions were controlled using perchloric acid, NaOH, and different buffer systems (MES, Collidine, CAPS). The buffer systems were selected in such a way that the effect of pressure on

**Table 1.** Fe(dapsox): Species in Aqueous Solution before and after Electrochemical Reduction, Number of Protons Transferred upon Reduction, the Difference in the Square of the Charge, pH Values at which Measurements were done, Measured Reaction Volumes, and  $\Delta V_{\text{complex}}^0 = \Delta V_{\text{cell}}^0 - \Delta V_{\text{Ag/AgCl}}^0 + nV_{\text{H}^+}^0$

Species	number of protons, n	$\Delta z_{\text{overall}}^2$	pH	$\Delta V_{\text{cell}}^0$ , cm <sup>3</sup> mol <sup>-1</sup>	$\Delta V_{\text{complex}}^0$ , cm <sup>3</sup> mol <sup>-1</sup>
	2	-3	2.9	+7.7 ± 0.2	+1 ± 2
	1	0	5.1	+4.7 ± 0.1	+6 ± 2
	1	0	8.0	+7.6 ± 0.2	+9 ± 2
	2	1	11.0	+23.8 ± 0.3	+17 ± 2

**Table 2.** Fe(dapsc): Species in Aqueous Solution before and after Electrochemical Reduction, Number of Protons Transferred upon Reduction, the Difference in the Square of the Charge, pH Values at which Measurements were done, Measured Reaction Volumes, and  $\Delta V_{\text{complex}}^0 = \Delta V_{\text{cell}}^0 - \Delta V_{\text{Ag/AgCl}}^0 + nV_{\text{H}^+}^0$

Species	number of protons, n	$\Delta z_{\text{overall}}^2$	pH	$\Delta V_{\text{cell}}^0$ , cm <sup>3</sup> mol <sup>-1</sup>	$\Delta V_{\text{complex}}^0$ , cm <sup>3</sup> mol <sup>-1</sup>
	0	5	2.0	+10.9 ± 0.2	+20 ± 2
	1	0	5.1	+8.6 ± 0.3	+10 ± 2
	2	-3	6.6	+7.7 ± 0.2	+1 ± 2
	3	-4	8.5	+11.7 ± 0.3	-2 ± 2
	2	-1	10.4	+11.9 ± 0.2	+6 ± 2
	3	0	12.0	+28.0 ± 1.0	+14 ± 3

the pK<sub>a</sub> values are known to be very small.<sup>22</sup> In the case of the [Fe<sup>III</sup>(dapsox)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup>/[Fe<sup>II</sup>(Hdapsox)(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> and [Fe<sup>III</sup>(H<sub>2</sub>dapsc)-(H<sub>2</sub>O)(OH)]<sup>2+</sup>/[Fe<sup>II</sup>(H<sub>2</sub>dapsc)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> redox couples (see Tables 1 and 2), measurements were performed at pH 5.1 in a MES buffer to prevent the use of acetate/acetic acid buffers, which show a significant pressure dependence of their pK<sub>a</sub> value.

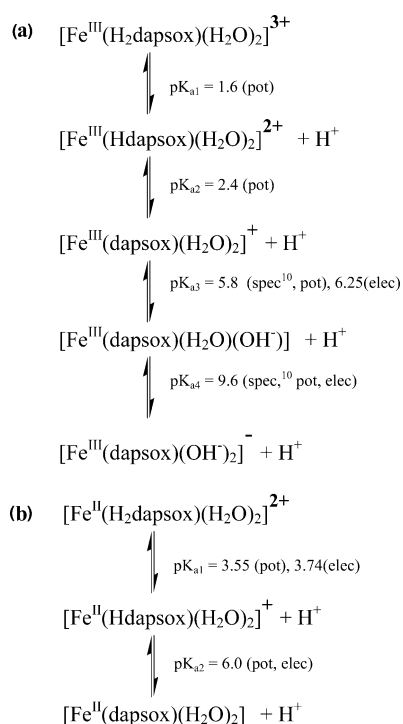
Scan rates were optimized for each system so as to obtain reversible (quasi-reversible) behavior with a peak separation  $\Delta E$  (difference between anodic and cathodic peaks) of around 60–80 mV. The peak separations as well as the half-wave potentials (E<sub>1/2</sub>) were determined from the original CV current peak positions and compared with those simulated by GPES software.<sup>23</sup> An excellent agreement between these values was found. The pressure runs were carried out in an ascending and descending pressure cycle, and each measurement was repeated at least three times.

To prove the validity of our data, high-pressure test measurements on the [Co(en)<sub>3</sub>]Cl<sub>3</sub> complex were performed, and the value of  $\Delta V^0$  was compared with reported data in the literature.<sup>24</sup> The dependence

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 (23) GPES: *General Purpose Electrochemical System for Windows*, Version 4.9; Eco Chemie B. V.: Utrecht, The Netherlands, 2001.

## Scheme 2



of the half-wave potential on pressure is shown in Figure S2 of the Supporting Information. The value of the reaction volume was found to be  $\Delta V^0 = 26.2 \pm 1.6 \text{ cm}^3 \text{ mol}^{-1}$ , which is in excellent agreement with  $\Delta V^0 = 26.7 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$  reported by Fu and Swaddle.<sup>24</sup>

## Results and Discussion

Determination of the  $\text{p}K_{\text{a}}$  Values of the Fe Complexes.

The seven-coordinate iron complexes investigated in this study have the pentadentate 2,6-diacetylpyridine-bis(acyl-hydrazone) ligands coordinated to the metal center in the equatorial plane and two water molecules in the apical positions.<sup>6,7</sup> Since these ligands can be coordinated to the iron center in neutral, mono-, or dianionic forms (Scheme 1) and the two coordinated water molecules can also be deprotonated, a total of four protons can be neutralized upon titration in the pH range 1–12.

In the case of the  $\text{Fe}^{\text{III}}(\text{dapsox})$  system, the  $\text{p}K_{\text{a}}$  values of the two coordinated water molecules were spectrophotometrically determined to be  $\text{p}K_{\text{a}1}^{\text{water}} = 5.78$  and  $\text{p}K_{\text{a}2}^{\text{water}} = 9.45$ .<sup>8</sup> Identical  $\text{p}K_{\text{a}}^{\text{water}}$  values were also found by potentiometric titrations, carried out in the present study in both directions (by adding an acid or base). Potentiometric titrations allowed us to determine two additional  $\text{p}K_{\text{a}}$  values,  $\text{p}K_{\text{a}1}^{\text{ligand}} = 1.6$  and  $\text{p}K_{\text{a}2}^{\text{ligand}} = 2.4$ , which correspond to the first and second deprotonations of the pentadentate ligand, respectively. The potentiometric titration curve for  $\text{Fe}^{\text{III}}(\text{dapsox})$  is shown in Figure S3 of the Supporting Information. The potentiometric and spectrophotometric results are summarized in Scheme 2, showing all deprotonation steps and corresponding  $\text{p}K_{\text{a}}$  values. These values were used to generate a species distribution plot (Figure 1). The speciation diagram for  $\text{Fe}^{\text{III}}(\text{dapsox})$  clearly shows three

predominant species in different pH ranges:  $[\text{Fe}^{\text{III}}(\text{dapsox})(\text{H}_2\text{O})_2]^+$  at pH = 4,  $[\text{Fe}^{\text{III}}(\text{dapsox})(\text{H}_2\text{O})(\text{OH})]$  at pH = 7.5, and  $[\text{Fe}^{\text{III}}(\text{dapsox})(\text{OH})_2]^-$  at pH = 11. The  $\text{p}K_{\text{a}}$  assignment is in good agreement with the previously studied kinetic behavior of  $\text{Fe}^{\text{III}}(\text{dapsox})$ .<sup>8</sup> It is important that, even in the low pH range, there is no free  $\text{Fe}^{3+}$  in the solution (no CV waves for  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+/2+}$  could be observed), which demonstrates a rather high stability of the complex species in both oxidation states.

Analysis of the potentiometric titration curve for  $\text{Fe}^{\text{II}}(\text{dapsox})$  allowed us to determine two  $\text{p}K_{\text{a}}$  values for the pentadentate ligand deprotonation:  $\text{p}K_{\text{a}1}^{\text{ligand}} = 3.55$  and  $\text{p}K_{\text{a}2}^{\text{ligand}} = 6.15$ . Since the deprotonation of coordinated water molecules occurs at pH > 12, we were not able to detect the corresponding  $\text{p}K_{\text{a}}^{\text{water}}$  value. The calculated species distribution for this complex is reported in Figure 2, and all the deprotonation steps with corresponding  $\text{p}K_{\text{a}}$  values are summarized in Scheme 2b.

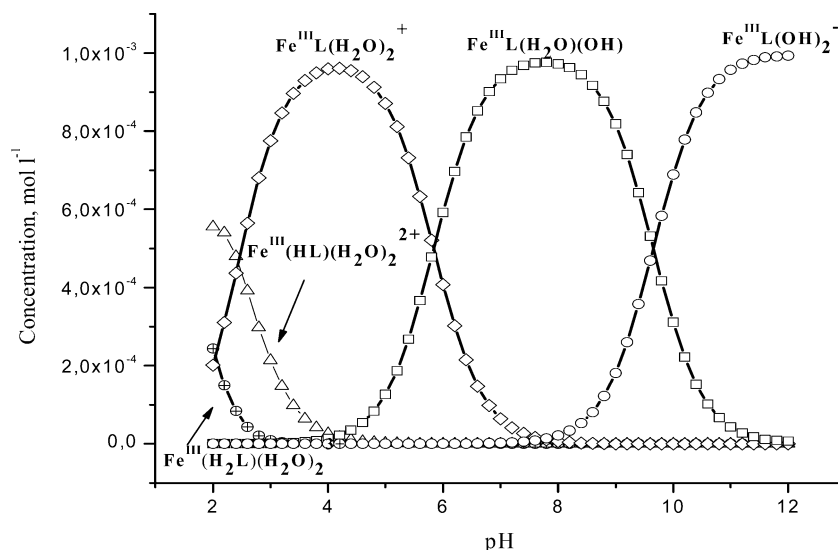
The  $\text{Fe}(\text{dapsc})$  complexes,<sup>7</sup> however, show different acid–base properties. In the case of the  $\text{H}_2\text{dapsc}$  pentadentate, the  $\text{Fe}(\text{III})$  complex crystallizes with two coordinated  $\text{Cl}^-$  anions in apical positions, whereas the  $\text{Fe}(\text{II})$  complex crystallizes with one  $\text{Cl}^-$  and one water molecule coordinated to the metal center. However, in aqueous solutions, both complexes are present in the diaqua form. Solutions of the complexes were treated with silver triflate and filtered to remove the  $\text{AgCl}$  precipitate. After this treatment, solutions were investigated spectrophotometrically. The determined  $\text{p}K_{\text{a}}$  values were compared with those obtained from a titration of the initial complex solutions, and the values were found to be identical.

Spectra recorded on changing the pH from 1 to 13 are shown in Figure S4 of the Supporting Information, whereas spectra of five different species present in aqueous solutions of  $\text{Fe}^{\text{III}}(\text{dapsc})$  (calculated using Specfit/32 global analysis software) are summarized in Figure 3. From the analysis of the pH-dependent UV–vis spectra, four  $\text{p}K_{\text{a}}$  values were found. The  $\text{p}K_{\text{a}}$  values determined from potentiometric titrations are in a good agreement with the spectrophotometric data, and the results are summarized in Scheme 3a, showing all deprotonation steps and corresponding  $\text{p}K_{\text{a}}$  values. Only the spectrophotometrically determined  $\text{p}K_{\text{a}4}$  value deviates significantly from the other values because of relatively small spectral changes that accompany the last deprotonation step. The corresponding species distribution diagram is shown in Figure 4.

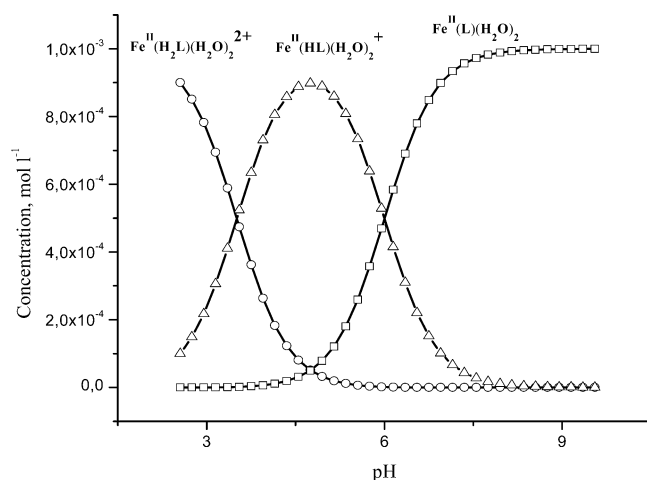
The coordinated  $\text{H}_2\text{dapsc}$  pentadentate is less acidic than  $\text{H}_2\text{dapsox}$ , which has two adjacent carbonyl groups. Thus, the first  $\text{p}K_{\text{a}1}$  of  $\text{Fe}^{\text{III}}(\text{dapsc})$  is assigned to the deprotonation of one water ligand. The  $\text{p}K_{\text{a}1}$  of  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  is 2.2,<sup>25</sup> and taking into consideration the effect of three nitrogen and two oxygen donors coordinated to the  $\text{Fe}^{3+}$  center, a somewhat higher  $\text{p}K_{\text{a}}$  value for the deprotonation of a coordinated water molecule is expected (Scheme 3a). As reported later, the formation of a  $\mu$ -oxo dimer can be observed during the

(24) Fu, Y.; Swaddle, T. W. *J. Am. Chem. Soc.* **1997**, *119*, 7137–7144.

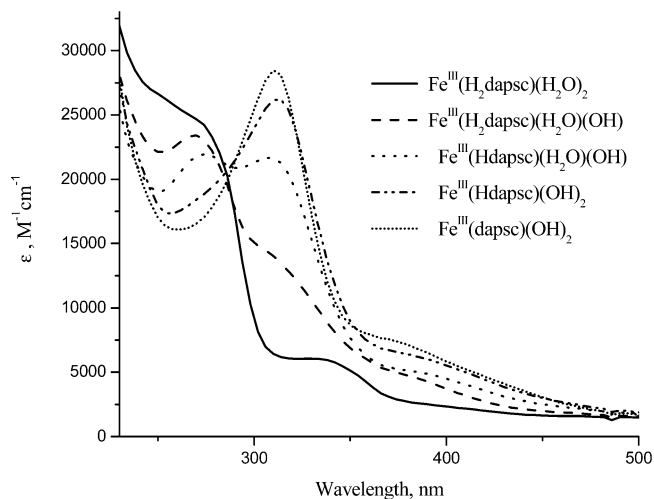
(25) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper and Row: New York, 1983; Chapter 7.



**Figure 1.** Calculated species distribution for Fe<sup>III</sup>(dapsox). Conditions: [Fe<sup>III</sup>(dapsox)] = 1 mM, *T* = 298 K, *I* = 0.1 M NaClO<sub>4</sub>.



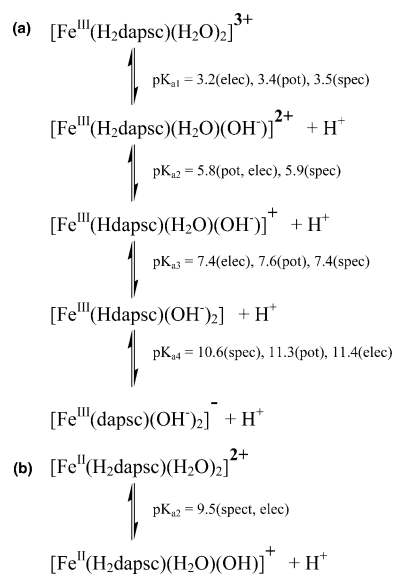
**Figure 2.** Calculated species distribution for Fe<sup>II</sup>(dapsox). Conditions: [Fe<sup>II</sup>(dapsox)] = 1 × 10<sup>-3</sup> M, *T* = 298 K, *I* = 0.1 M (NaClO<sub>4</sub>).



**Figure 3.** Spectra of different species of Fe<sup>III</sup>(dapsc) as a function of pH from 1.1 to 13. Conditions: [Fe<sup>III</sup>(dapsc)] = 5 × 10<sup>-5</sup> M, *T* = 298 K, *I* = 0.1 M NaClO<sub>4</sub>.

electrochemical titration between pH 3 and 5. This supports the deprotonation of the coordinated water molecule in this pH range.

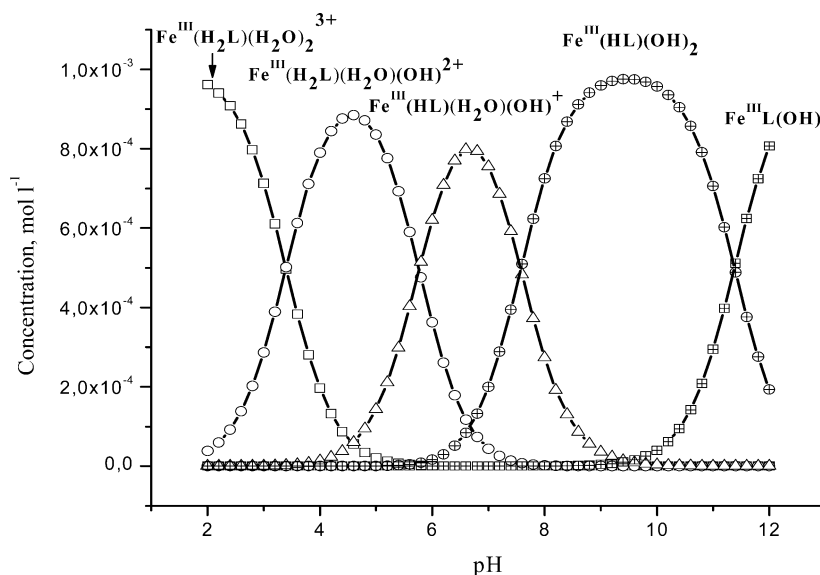
### Scheme 3



The second p*K*<sub>a2</sub> for Fe<sup>III</sup>(dapsc) can be assigned to the first deprotonation step of the chelate. It is known that the analogous Cr(III) complex with pentadentate dapsc can be isolated with a singly deprotonated form of the ligand at pH > 3.<sup>7b</sup> Taking into account that the [Fe<sup>III</sup>(H<sub>2</sub>dapsc)(H<sub>2</sub>O)(OH)]<sup>2+</sup> species has a lower charge than [Cr<sup>III</sup>(H<sub>2</sub>dapsc)(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup>, it is reasonable to expect a higher p*K*<sub>a</sub> value for the first deprotonation step of the chelate in the case of the Fe(III) complex (Scheme 3a).

The next p*K*<sub>a3</sub>, calculated to be 7.6, represents the deprotonation of the second coordinated water molecule, and since [Fe<sup>III</sup>(Hdapsc)(H<sub>2</sub>O)(OH)]<sup>+</sup> has a positive charge, this p*K*<sub>a</sub> value is lower than the corresponding p*K*<sub>a2</sub><sup>water</sup> of the neutral [Fe<sup>III</sup>(dapsox)(H<sub>2</sub>O)(OH)] species. Thus, the p*K*<sub>a4</sub> = 11.3 is assigned to the second deprotonation step of the chelate.

Fe<sup>II</sup>(H<sub>2</sub>dapsc) was titrated spectrophotometrically in the range 5 ≤ pH ≤ 12. At pH < 5, no spectral changes could be detected (see Figure S5, Supporting Information). Analysis of the spectra allowed us to determine only one p*K*<sub>a</sub> value,



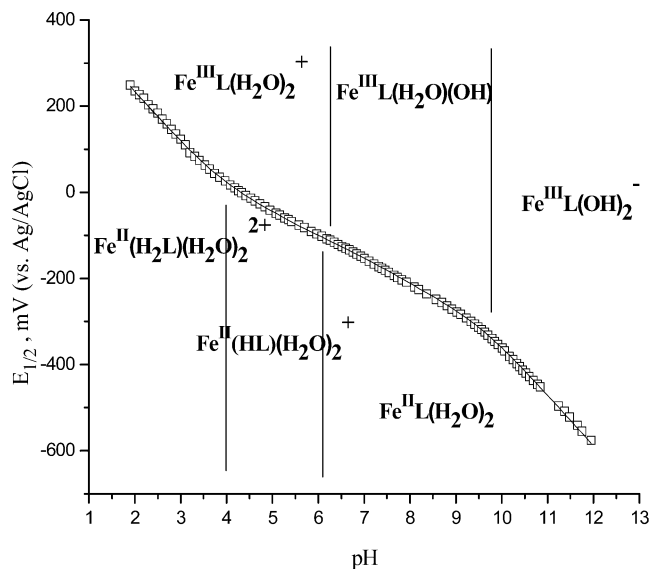
**Figure 4.** Calculated species distribution for Fe<sup>III</sup>(dapsc). Conditions: [Fe<sup>III</sup>(dapsc)] = 1 mM,  $T = 298$  K,  $I = 0.1$  M NaClO<sub>4</sub>.

assigned to the deprotonation of a water molecule coordinated to the Fe(II) center ( $pK_a^{\text{II}} = 9.5$ ). The change in absorbance upon titration at 304 nm, where the largest change in absorbance was observed, is shown in Figure S6 of the Supporting Information. The obtained  $pK_a$  value is identical to  $pK_a^{\text{II}}$  for Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>.<sup>25</sup> This suggests that the electronic nature of the Fe(II) center remains unchanged upon coordination of the neutral H<sub>2</sub>dapsc pentadentate chelate and that the axially coordinated water molecules are not affected by the (N)<sub>3</sub>(O)<sub>2</sub> donor set in the equatorial plane.

**Electrochemical Behavior and pH Dependence.** The Fe<sup>III/II</sup>(dapsox) couple shows reversible electrochemical behavior (Figure S7, Supporting Information) with  $E_{1/2} = 0.216$  V versus NHE and  $\Delta E_p = 60$  mV at pH 4.4. Fe<sup>III/II</sup>(dapsc) exhibits analogous reversible behavior.

To determine the number of protons involved in PCET, a detailed study of the pH-dependent redox potentials was performed. The  $E_{1/2}$  values of both Fe complexes strongly depend on pH, showing a gradual negative shift in the reduction potential for the Fe(III)/Fe(II) couple with increasing pH. When the pH is higher than 10, the voltammograms become quasi-reversible with  $\Delta E > 90$  mV. By fitting the pH-dependent redox potential curve using the software EFIT, the  $pK_a$  values of both oxidation states of Fe(dapsox) and Fe(dapsc) were determined. Furthermore, from the slopes of the titration curves, the number of protons, which are taken upon one-electron reduction in the different pH ranges, can be calculated from the Nernst equation.<sup>20</sup>

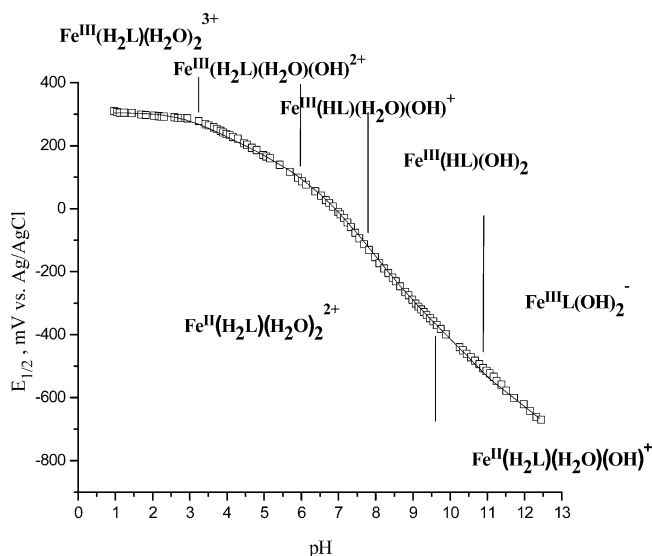
The  $pK_a$  values for Fe<sup>III</sup>(dapsox) and Fe<sup>II</sup>(dapsox), which were estimated from the electrochemical measurements, are in a good agreement with those calculated from potentiometric and spectrophotometric titration data. The assignment of the Fe(III) and Fe(II) species (Scheme 2) is also in agreement with the number of protons transferred upon reduction in the particular pH range (Figure 5). At pH < 4 and pH > 10, a “two-proton–one-electron transfer” occurs, whereas between pH 4 and 10, a “one-proton–one-electron transfer” occurs.



**Figure 5.** pH-dependent redox potential diagram for the Fe(dapsox) system. Conditions: [Fe<sup>III</sup>(dapsox)] =  $1 \times 10^{-3}$  M, Au working electrode, scan rate = 50 mV/s,  $T = 298$  K, and  $I = 0.1$  M NaClO<sub>4</sub>. The solid line represents fit data (EFIT).

In the case of the Fe<sup>III</sup>(dapsc) complex, at low pH, the redox potential is independent of [H<sup>+</sup>]; that is, the complex reduction proceeds without proton transfer. On going to higher pH, dimer formation was observed in the cyclic voltammogram between pH 3 and 5, with two characteristic reductions at  $E_{\text{red1}} = +0.25$  V and  $E_{\text{red2}} = 0$  V (vs Ag/AgCl at pH = 3.5). At pH > 5, the second reduction peak disappears. This fact proves our assumption that the first  $pK_{a1}^{\text{III}} = 3.4$  refers to the deprotonation of a coordinated water molecule. The  $pK_a$  values of Fe<sup>III</sup>(dapsc) and Fe<sup>II</sup>(dapsc), which result from the pH-dependent cyclic voltammetric measurements ( $pK_{a1}^{\text{III}} = 3.2$ ,  $pK_{a2}^{\text{III}} = 5.8$ ,  $pK_{a3}^{\text{III}} = 7.4$ ,  $pK_{a4}^{\text{III}} = 11.4$ ,  $pK_{a1}^{\text{II}} = 9.5$ ; Figure 6), are similar to those obtained from other titrations. The corresponding acid–base equilibria of Fe<sup>III</sup>(dapsc) and Fe<sup>II</sup>(dapsc) (Scheme 3) account for the number of protons transferred upon reduction in different pH ranges (Figure 5). One should note that within



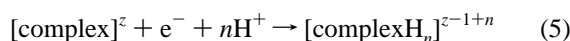


**Figure 6.** pH-dependent redox potential diagram for the Fe(dapsc) system. Conditions:  $[\text{Fe}^{\text{III}}(\text{dapsc})] = 1 \times 10^{-3} \text{ M}$ , Au working electrode, scan rate = 50 mV/s,  $T = 298 \text{ K}$ , and  $I = 0.1 \text{ M NaClO}_4$ . The solid line represents fit data (EFIT).

the pH range 7.5–9.5, three protons are taken upon reduction, which was not observed in the case of the Fe(dapsox) system.

**Effect of Pressure on PCET.** On the basis of the spectrophotometric, potentiometric, and electrochemical studies, and the generated species distribution curves, pH values for the high-pressure cyclic voltammetric measurements were selected in a way that the different protonated forms of the Fe(dapsox) and Fe(dapsc) systems are present in solution as the predominant species. The shifts in the half-wave potentials ( $E_{1/2}$ ) with pressure were followed for all the different protonated forms of Fe(dapsox) and Fe(dapsc). The values of  $E_{1/2}$  and the peak separations  $\Delta E$  for all systems as a function of pressure are reported in the Supporting Information (Table S1). The pressure dependence of the half-wave potentials is illustrated for the  $[\text{Fe}^{\text{III}}(\text{dapsox})(\text{H}_2\text{O})_2]^+ / [\text{Fe}^{\text{II}}(\text{Hdapsox})(\text{H}_2\text{O})_2]^+$  and  $[\text{Fe}^{\text{III}}(\text{dapsc})(\text{OH})_2]^- / [\text{Fe}^{\text{II}}(\text{Hdapsc})(\text{H}_2\text{O})(\text{OH})]^+$  couples, which show the largest and lowest values of the corresponding  $\Delta V_{\text{cell}}^0$ , respectively, in Figure 7.

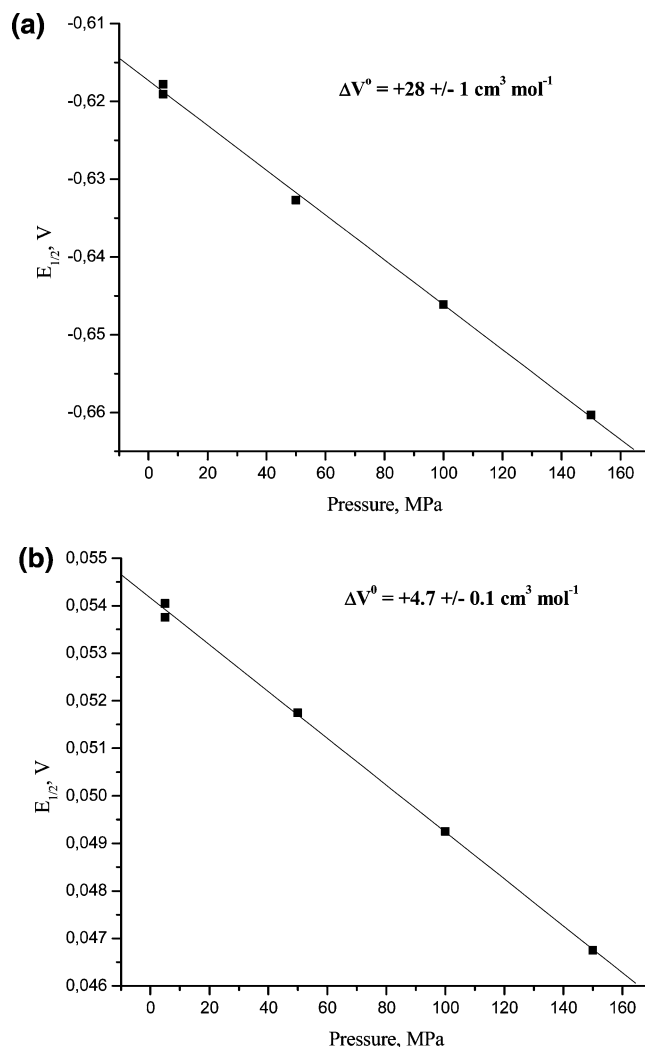
The investigated reactions are all of the type



and the values of  $\Delta V_{\text{cell}}^0$ , calculated according to eq 1, can be considered to consist of

$$\Delta V_{\text{cell}}^0 = \Delta V_{\text{ref}}^0 + \Delta V_{\text{PCET}}^0 = \Delta V_{\text{ref}}^0 + \Delta V_{\text{complex}}^0 - nV_{\text{H}^+}^0 = \Delta V_{\text{ref}}^0 + (\Delta V_{\text{elec}}^0 + \Delta V_{\text{intr}}^0)_{\text{complex}} - nV_{\text{H}^+}^0 \quad (6)$$

where  $\Delta V_{\text{ref}}^0$  is the half-cell contribution for a Ag/AgCl reference electrode,  $\Delta V_{\text{elec}}^0$  is the electrostrictive volume change on the complex,  $\Delta V_{\text{intr}}^0$  is the intrinsic volume change on the complex,  $V_{\text{H}^+}^0$  is the partial molar volume of the proton as a reactant, and  $n$  is the number of protons transferred. The half-cell reaction volume for the Ag/AgCl



**Figure 7.** (a) Pressure dependence of the half-wave potential for  $[\text{Fe}^{\text{III}}(\text{dapsc})(\text{OH})_2]^- / [\text{Fe}^{\text{II}}(\text{H}_2\text{dapsc})(\text{H}_2\text{O})(\text{OH})]^+$  at pH 12. Scan rate = 0.05  $\text{V s}^{-1}$ ,  $T = 298 \text{ K}$ ,  $I = 0.1 \text{ M NaClO}_4$ . (b) Pressure dependence of the half-wave potential for  $[\text{Fe}^{\text{III}}(\text{dapsox})(\text{H}_2\text{O})_2]^+ / [\text{Fe}^{\text{II}}(\text{Hdapsox})(\text{H}_2\text{O})_2]^+$  at pH 5.1 (MES buffer). Scan rate = 0.05  $\text{V s}^{-1}$ ,  $T = 298 \text{ K}$ ,  $I = 0.1 \text{ M NaClO}_4$ .

reference electrode was determined by Sun et al.<sup>26</sup> and reported to be  $\Delta V_{\text{ref}}^0 = -9.0 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$ . As mentioned above,  $\Delta V_{\text{intr}}^0$  arises from changes in bond lengths and angles upon reduction, whereas  $\Delta V_{\text{elec}}^0$  depends strongly on changes in charge. With the application of eq 2, eq 6 can be expressed as

$$\Delta V_{\text{complex}}^0 = \Delta V_{\text{cell}}^0 - \Delta V_{\text{ref}}^0 + nV_{\text{H}^+}^0 = \Delta V_{\text{intr}}^0 + k\Delta z_{\text{overall}}^2 \quad (7)$$

where  $k$  is an empirical parameter. In the present case,  $\Delta z_{\text{overall}}^2$  for reaction 5 results not only from the change in the oxidation state of the metal center but also from changes in the overall charge as a result of the different number of protons involved in the reduction process.

The partial molar volume of the proton,  $V_{\text{H}^+}^0$ , was estimated by various methods in the past (in water at 25 °C),

(26) Sun, J.; Wishart, J. F.; van Eldik, R.; Shalders, R. D.; Swaddle, T. W. *J. Am. Chem. Soc.* **1995**, *117*, 2600.



as reported by Millero.<sup>27</sup> The average values for  $V_{H^+}^0$  were found to be  $-4.2 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$  and  $-4.7 \pm 1.1 \text{ cm}^3 \text{ mol}^{-1}$ .<sup>27</sup> In another study,<sup>16</sup> the reaction volumes for 19 different neutralization reactions (eq 3) were determined. On combining eq 3 with the dissociation of a water molecule, for which the reaction volume is  $-22.2 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$ ,<sup>22,28</sup> it can be converted to a protonation reaction, namely,



The combination of eq 4 with the given volume for the dissociation of water results in the following expression for eq 8.

$$\Delta V^0 = \Delta V_{\text{elec}}^0 - V_{H^+}^0 = (2.5 \pm 0.2)\Delta z^2 + (7.7 \pm 0.8) \quad (9)$$

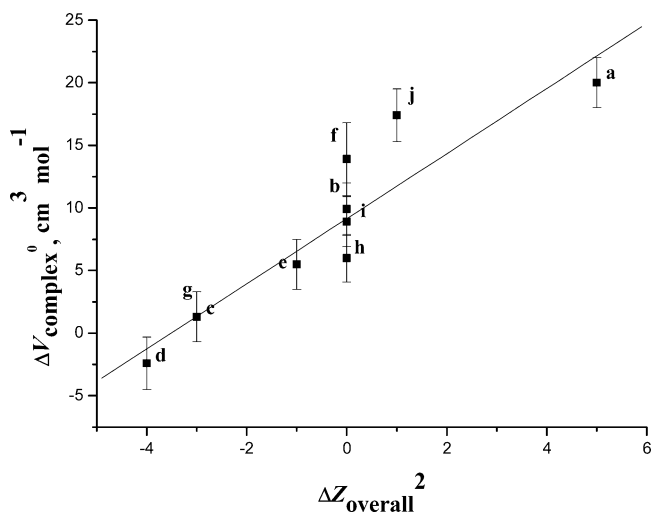
Thus, the experimental value for  $V_{H^+}^0$  that results from the 19 studied neutralization reactions is  $-7.7 \pm 0.8 \text{ cm}^3 \text{ mol}^{-1}$ , which is in an agreement with the value reported by Stokes and Robinson.<sup>29</sup>

In the present study on the redox reactions of seven-coordinate Fe(III) complexes coupled to the transfer of different numbers of protons (eq 5), the experimental value of  $V_{H^+}^0 = -7.7 \pm 0.8 \text{ cm}^3 \text{ mol}^{-1}$  was adopted since it is based on data obtained for deprotonation reactions of metal complexes and, as such, is closely related to the proton transfer processes studied here. In Tables 1 and 2, the studied reactions are summarized along with the experimentally obtained values of  $\Delta V_{\text{cell}}^0$  and the calculated values of  $\Delta V_{\text{complex}}^0$ , corrected for the reference electrode contribution and the effect of the different number of protons transferred upon reduction as formulated in eq 7. The error limits for  $\Delta V_{\text{complex}}^0$  were calculated from the error limits for the various contributing terms in eq 7.

The plot of  $\Delta V_{\text{complex}}^0$  versus  $\Delta z^2$  according to eq 7, using the data in Tables 1 and 2, is presented in Figure 8. Although the results include the data for two different seven-coordinate Fe complexes that undergo PCET reactions that involve the transfer of a different number of protons, the plot shows a satisfactory fit and can be expressed as

$$\Delta V_{\text{complex}}^0 = (9.2 \pm 0.7) + (2.6 \pm 0.3)\Delta z_{\text{overall}}^2 \quad (10)$$

The intercept of the plot corresponds to the intrinsic volume change ( $\Delta V_{\text{intr}}^0$ ) associated with the electrochemical reduction of the pentagonal-bipyramidal Fe(III) complexes. Although it is not easy to predict the contribution from intrinsic volume changes for nonspherical complexes, the obtained value of  $+9.2 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$  is in good agreement with  $\Delta V_{\text{intr}}^0 = +9.6 \text{ cm}^3 \text{ mol}^{-1}$  determined for the reduction of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ .<sup>10</sup> From structural data, the increase in the Fe–H<sub>2</sub>O bond length upon reduction is  $0.131 \text{ \AA}$ .<sup>30</sup> On the basis of crystallographic data available for Fe<sup>III</sup>(dapsc) and



**Figure 8.** Plot of  $\Delta V_{\text{complex}}^0$  versus  $\Delta z_{\text{overall}}^2$ , where  $\Delta V_{\text{complex}}^0 = \Delta V_{\text{cell}}^0 - \Delta V_{\text{ref}}^0 + nV_{H^+}^0$  and  $\Delta z_{\text{overall}}^2 = z_{\text{oxid}}^2 - z_{\text{red}}^2$ . Fe(dapsc): pH = 2 (a), 5.1 (b), 6.6 (c), 8.5 (d), 10.4 (e), and 12 (f). Fe(dapsox): pH = 2.9 (g), 5.1 (h), 8.0 (i), and 11.0 (j).

Fe<sup>II</sup>(dapsc),<sup>7a,31</sup> the increase in the average equatorial bond length is approximately  $0.1 \text{ \AA}$  during reduction. However, as a result of the presence of a deprotonated pentadentate in the case of the Fe(III) complexes and a protonated form in the case of Fe(II) complexes, a somewhat larger change than  $0.1 \text{ \AA}/\text{bond}$  is expected. A similar contribution is expected from the apical bonds in the case of the reduction of Fe(III)–hydroxo to Fe(II)–aqua species, since Fe–OH bonds are known to be shorter than Fe–OH<sub>2</sub> bonds. Thus, in the light of these possible deviations, the average value of  $+9.2 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$  is quite acceptable for the intrinsic volume change upon reduction of the studied Fe(III) complexes. The deviation of some of the data points from the linear plot in Figure 8, especially around  $\Delta z^2 = 0$ , can possibly be accounted for in terms of deviations in the value of  $\Delta V_{\text{intr}}^0$  from the average value quoted above. In particular, in the case of Fe(dapsox) (h and j in Figure 8), the larger deviations from the linear plot can be explained by the fact that at pH 5.1, upon reduction, only a single protonation of the larger and more rigid pentadentate ligand takes place, which will cause a significantly smaller intrinsic volume change than the protonation of two coordinated OH<sup>−</sup> ligands at pH 11.0 that results in the elongation of the Fe–O bonds. In the case of Fe(dapsc) at pH 12.0 (f in Figure 8), a number of factors can play a role. As a result of the fact that the complex is triply protonated upon reduction, whereas at the same time there is no change in the absolute charge, a larger intrinsic volume change is also expected. In this case, the protonation of one coordinated OH<sup>−</sup> also occurs and results in the elongation of the Fe–O bond, which is even more pronounced because of the trans influence caused by the remaining nonprotonated OH<sup>−</sup> group.

The slope of the plot in Figure 8 is very close to that observed for the series of neutralization reactions studied

(27) Millero, F. J. In *Water and Aqueous Solutions; Structure, Thermodynamics and Transport Properties*; Horne, R. A., Ed.; Wiley-Interscience: New York, 1972; Chapter 13.

(28) Millero, F. J.; Hoff, E. V.; Cahn, L. J. *Sol. Chem.* **1972**, *1*, 309.

(29) Stokes, R. H.; Robinson, R. A. *Trans. Faraday Soc.* **1957**, *53*, 301–304.

(30) Li, J.; Fisher, C. L.; Chen, J. L.; Bashford, D.; Noodleman, L. *Inorg. Chem.* **1996**, *35*, 4694–4702.

(31) (a) Palenik, G. J.; Wester, D. W. *Inorg. Chem.* **1977**, *17*, 864–870. (b) Sommerer, S. O.; Baker, J. D.; Palenik, G. J. *Inorg. Chem.* **1992**, *31*, 563–567.

before<sup>16</sup> and is smaller than that observed for redox processes in which no coupled proton-transfer reactions occur.<sup>13</sup> The smaller slope suggests a weaker electrostriction dependence, and electrostriction effects for PCET reactions follow the trend observed for proton-transfer reactions. It should, however, also be kept in mind that the earlier studies on pure electron-transfer reactions<sup>10,12,13</sup> included only six-coordinate octahedral complexes, whereas the present work deals with seven-coordinate pentagonal-bipyramidal complexes, in which case the charge is spread out over a larger coordination sphere, on which basis somewhat diluted electrostriction effects are to be expected.

## Conclusions

For the first time, the acid–base equilibria of seven-coordinate Fe(III) and Fe(II) complexes with 2,6-diacetylpyridine-bis(acylhydrazone) chelates could be studied in detail, and the speciation over a wide pH range could be resolved. On the basis of these data, the effect of pressure on the redox processes in which a different number of protons are involved (from 0 to 3 protons per electron) was studied for all the different protonation forms of the two selected complexes. This is the first time that the effect of pressure on the redox potential of proton-coupled electron-transfer processes has been studied. Interestingly, previously reported linear correlations found between  $\Delta z^2$  and the redox reaction volumes<sup>12,13</sup> and the neutralization reaction volumes<sup>16</sup> for

different types of transition metal complexes were also observed in the present study in which the two processes were combined. Consequently, the change in overall charge is not only caused by the change in the oxidation state of the metal center but also by protonation/deprotonation of the pentadentate chelate or the coordinated water ligand. Thus, the approximately linear dependence of the reaction volume on  $\Delta z^2$  seems to have general application and was shown to be valid for proton-coupled electron transfer as well.

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**Supporting Information Available:** Table S1 summarizes all electrochemical measurements for the studied complexes as a function of pH and pressure and lists values of  $E_{1/2}$  and  $\Delta E$ ; Figure S1 reports the UV–vis spectrum of  $[\text{Fe}^{\text{II}}(\text{H}_2\text{dapsox})(\text{H}_2\text{O})_2]^{2+}$ ; Figure S2 reports the dependence of the half-wave potential on pressure for  $[\text{Co}(\text{en})_3]\text{Cl}_3$ ; Figures S3–S6 represent different potentiometric and spectrophotometric titration data; Figure S7 reports cyclic voltammograms of  $[\text{Fe}^{\text{III}}(\text{dapsox})(\text{H}_2\text{O})_2]$  at different scan rates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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