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Substituent Effects on Iron Diimine Complexes. 3. Correlations with Thermodynamic and Spectral Properties in a 25 °C Molten Salt

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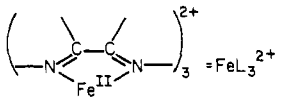
The study of thermodynamic and spectral properties of the iron diimine complexes is extended to a solvent system based on molten aluminum chloride and ethylpyridinium bromide in a 2:1 molar ratio. This solvent system presents an important advantage over acetonitrile being a totally anhydrous medium, in which ligand-oxidation processes of these complexes, found to occur in aqueous sulfuric acid and to a smaller extent in acetonitrile, do not take place. The effect of the substituents on the iron diimine chromophore on the half-wave potentials, $E_{1/2}$, of the FeL_3^{3+}/FeL_3^{2+} couples and on the frequencies of the inverse charge-transfer band is compared to that exhibited in other media. In this molten salt the thermodynamic stability of the ferric forms is greater than that of the ferrous forms, whereas the opposite trend exists in aqueous solutions. Correlations between $E_{1/2}$'s and Taft's polar and steric parameters of the substituents and frequencies of the inverse charge-transfer bands are presented and compared to those encountered in other solvents.

Introduction

Parts 1[1] and 2[2] of this series reported the effect of substituents on the iron diimine chromophore[3]



in aqueous sulfuric acid[1] and in acetonitrile[2] solutions, respectively. The complexes investigated included aliphatic[4] diimine complexes (L = $H_3CN{=}CR{-}CR'{=}NCH_3$) and mixed[5] diimine ligands (L = $C_5H_4N{-}CR_1{=}NR_2$), which establish a structural link between the aliphatic derivatives and the well-known aromatic diimine complexes derived from 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen). The latter compounds have been employed extensively as redox indicators due to the profound color changes associated with the reversible oxidation of the ferrous to ferric complexes,[6] which is independent of the acid concentration. The aliphatic, mixed, and aromatic diimine complexes of iron(II) have similar absorption spectral characteristics,[7] a very strong red-violet color, associated with the inverse charge transfer from occupied t_2 levels to the empty π^* orbitals, and similar types of kinetics of dissociation.[7,8] The similarity of the redox properties depends on the acid concentration of the medium.[9,10] A reversible chemical[9,10] or electrochemical[11] oxidation can be found only if the acid concentration is higher than 10 M H_2SO_4 (aliphatic) or 4 M H_2SO_4 (mixed).[12] At lower acid concentration ligand-oxidation reactions take place with the formation of new complexes, which contain oxidized ligands.[9,10,12] Ligand reactivity is a function of the structure of the aliphatic and mixed diimine ligands and is related to their formal electrode potential.[13,14] In acetonitrile[2] ligand-oxidation reactions are slowed down appreciably but not avoided due to the presence of minor amounts of water.

In 1975, some of us[15] reported the electrochemical oxidation behavior of two aliphatic diimine complexes (R, R′ = H, H and CH_3, CH_3) in a room-temperature molten salt composed of aluminum chloride and ethylpyridinium bromide in a 2:1 mole ratio.[16] In this Lewis acid medium, ethylpyridinium dialuminum heptahalide,[17,18] reversible one-electron electrochemical oxidations were found to occur. No solvation of the complexes was detected in this medium.[15]

In the present paper the electrochemical oxidations of 14 iron(II) complexes of aliphatic, mixed, and aromatic diimine ligands and their visible absorption spectral properties are presented and compared with the observed electrochemical and spectral behavior in sulfuric acid and acetonitrile solutions. Substituent effects are analyzed in terms of inductive and steric parameters,[19] which can be considered additive, as has been previously shown, for other media.[1,2] The effect of the dilution of the melt with benzene on the half-wave potentials is also examined.

Experimental Section

The iron(II) diimine complexes were prepared as perchlorates and purified by recrystallization according to ref 20 and 21. The melt preparation and purification are described in ref 22. The procedure for the electrochemical experiments is given in ref 23. A PARC Model

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Table I. Half-Wave Potentials on a Glassy-Carbon Electrode for the FeL_3^{3+}/FeL_3^{2+} Couples in the 2:1 $AlCl_3$-Ethylpyridinium Bromide (EtpyBr) Molten Salt and Its Benzene Solutions at 25 °C (All Potentials vs. Al Reference Electrode in 2:1 $AlCl_3$-EtpyBr Melt)[a]

no.	L = aliphatic diimine $H_3CN{=}CR{-}CR'{=}NCH_3$ R	R'	$E_{1/2}$, V (±0.01 V) 100% melt[c]	70% melt	50% melt
1	H	H	1.59		
2	H	CH_3	1.35	1.39	1.44
3	CH_3	CH_3	1.12	1.15	1.20
4	$CH_2CH_2CH_2CH_2$		1.11	1.14	1.18
5	$CH_2CH(CH_3)CH_2CH_2$		1.13		
6	H	C_6H_5	1.28	1.31	1.35

no.	L = mixed diimine[b] $C_5H_4N{-}CR_1{=}NR_2$ R_1	R_2	$E_{1/2}$, V (±0.01 V) 100% melt	70% melt	50% melt
7	H	CH_3	1.22	1.26	1.31
8	CH_3	CH_3	1.00	1.04	1.08
9	CH_3	C_2H_5	1.04		
10	CH_3	n-C_3H_7	1.07		
11	C_6H_5	CH_3	1.16	1.20	1.27
12	C_6H_5	C_6H_5	1.27		

no.	L = aromatic diimine[b]	$E_{1/2}$, V (±0.01 V) 100% melt	70% melt	50% melt
13	bpy	1.05	1.09	1.13
14	phen	1.06	1.10	1.15

[a] For the Fc^+/Fc couple $E_{1/2} = 0.25$ V for 100, 70, and 50% melt. [b] For these compounds adsorption of FeL_3^{2+} at the glass-carbon electrode was detected. [c] v/v.

170 was also employed in these investigations. Visible and UV spectra were recorded on a Cary Model 17 spectrometer.

Results and Discussion

Electrode Processes. The iron diimine complexes studied are shown in Table I. The electrochemical oxidations of all of the diimine complexes are reversible one-electron processes previously shown[15] by cyclic voltammetric or pulse voltammetric techniques for compounds **1** and **3**. Half-wave potentials, $E_{1/2}$, obtained by cyclic voltammetry, pulse voltammetry, and differential pulse voltammetry agree within 10 mV. Table I also lists the $E_{1/2}$ of the FeL_3^{3+}/FeL_3^{2+} couples in the 2:1 aluminum chloride–ethylpyridinium bromide $[EtP_4^+Al_2X_7^-]$ at 25 °C. The $E_{1/2}$ for the electrochemical oxidations of these compounds in solutions of melt and benzene are shown for some compounds in Table I.

As pointed out previously[15] for the aliphatic diimine compounds **1** and **3**, in this molten salt medium no solvation can be detected since the solvodynamic mean radii and the structural mean radii[11] are identical within the experimental error. A larger solvodynamic than structural radius has been found for these complexes in water,[24] sulfuric acid solutions,[11] and acetonitrile.[25]

The solvodynamic mean radii were obtained by means of the Stokes–Einstein equation, $r_{\text{solv}} = kT/(6\pi\eta D)$ (η = viscosity, k = Boltzmann constant, D = diffusion coefficient), with D obtained from the electrochemical measurements. For all the aliphatic diimine complexes of iron(II) the solvodynamic and structural mean radii were identical within the experimental error. For the mixed and aromatic diimine complexes the observed $r_{\text{solv}} < r_{\text{st}}$. In fact, the currents observed in the cyclic voltammograms, for instance, were about twice as large as expected on the basis of the calculated diffusion coefficients derived from structural mean radii. Since the coulometric $n = 1$, one would not expect that the current increase be due to catalytic currents. Adsorption of these iron(II) complexes at the surface of the glassy-carbon electrodes would increase the observed anodic and cathodic current peaks, because the electron transfer involves both the adsorbed material and the diffusing electroactive species from the bulk of solution.[26,27] The adsorbed material is oxidized.[26,27] This adsorption of the reagent implies an increase of the current function relative to that of the diffusion-controlled electrochemical process. The reversibility characteristics remain unchanged. Similar adsorption of the iron(II) diimine complexes has been found in acetonitrile solutions in the 0 to −1.5 V Ag/AgCl potential range on bright platinum electrodes.[28]

Of the half-wave potentials listed in Table I only those referring to the aliphatic diimine complexes are identical with the standard electrode potentials ($E_{1/2} = E° + (RT/nF) \ln (D_R/D_0)^{1/2}$). However, since the extent of the adsorption in the mixed series is essentially constant, the comparison of $E_{1/2}$ within this class of complexes reflects the trend of $E°$.

Thermodynamic Stability. The standard electrode potentials of the complex couples FeL_3^{3+}/FeL_3^{2+} compared to that of the Fe^{3+}/Fe^{2+} couple in the medium provide a measure of the relative thermodynamic stabilities of the ferric and ferrous complexes in the medium:[7]

$$FE°_{FeL_3^{3+}/FeL_3^{2+}} - FE°_{Fe^{3+}/Fe^{2+}} = \Delta G_{FeL_3^{3+}} - \Delta G_{FeL_3^{2+}} \qquad (1)$$

where the ΔG's are the free energies of formation of these complexes.

The 2:1 $AlCl_3$–EtpyBr has an anodic window of 1.8 V vs. Al reference electrode, limited by oxidation of bromide ions.[22] The couple Fe^{3+}/Fe^{2+} cannot be studied in this melt because Fe^{3+} ions oxidize bromide ions to bromine. Therefore $E°_{Fe^{3+}/Fe^{2+}} > 1.8$ V vs. Al in this medium. A better estimate can be made on the basis of data obtained in similar total chloride melts, e.g., 2:1 $AlCl_3$–n-butylpyridinium chloride[18,29] for which the anodic window is extended to 2.1 V vs. Al. From potentiometric results for the Fe^{3+}/Fe^{2+} couple in this total chloride melt by Hussey et al.,[30] $E°_{Fe^{3+}/Fe^{2+}} = 2.0$ V vs. Al (25 °C). If one compares the $E°$ of the aliphatic diimine complexes of iron with that for the Fe^{3+}/Fe^{2+} couple, one observes that $F(E°_{FeL_3^{3+}/FeL_3^{2+}} - E°_{Fe^{3+}/Fe^{2+}}) < 0$. These results indicate that in this medium the ferric forms are stabilized to a much larger extent than the ferrous forms.

In aqueous media the reverse stabilization order is encountered. For instance, let us compare the standard electrode potentials for the couples FeL_3^{3+}/FeL_3^{2+} with L = $H_3CN{=}C(CH_3)C(CH_3){=}NCH_3$, $E° = 1.00$ V,[1] and L = phen, $E° = 1.14$ V, with that of the Fe^{3+}/Fe^{2+} couple, 0.77 V in water.[7] In this case, $F(E°_{FeL_3^{3+}/FeL_3^{2+}} - E°_{Fe^{3+}/Fe^{2+}}) > 0$, indicating that upon complex formation in this medium the spin-paired ferrous forms are stabilized to a much greater extent than the ferric forms.

Correlations between $E_{1/2}$ and Substituent Parameters. In the aliphatic diimine series the $E_{1/2}$'s decrease by ca. 0.24 V per methyl group replacing hydrogen at the methine carbon

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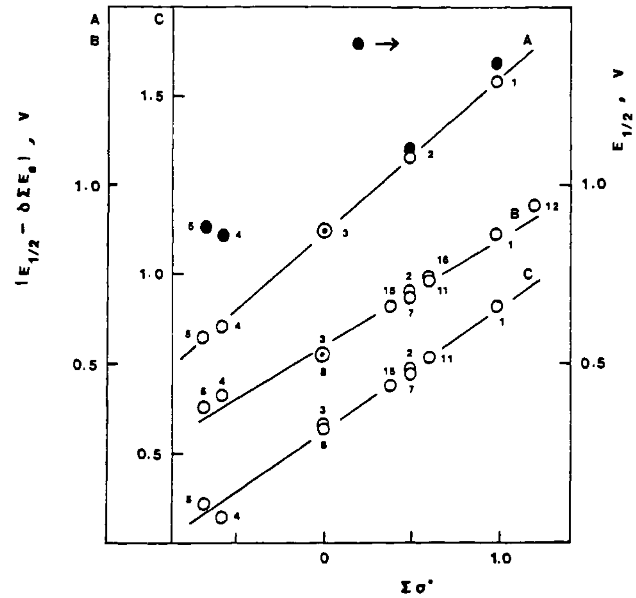

Figure 1. Half-wave potentials of the FeL_3^{3+}/FeL_3^{2+} couples as a function of the sum of the Taft polar parameters of the substituents in the iron diimine chromophore in the 2:1 $AlCl_3$:EtpyBr molten salt (right-hand-side scale). A, B, and C are the half-wave potentials, $E_{1/2}$, minus the steric contribution ($\delta\sum E_s$) (see eq 2) as a function of the sum Taft polar parameters ($\sum\sigma^*$) for the iron diimine complexes in the following: A, 2:1 $AlCl_3$:EtpyBr molten salt; B, acetonitrile with 0.2 M tetraethylammonium perchlorate; C, 4 M H_2SO_4 (left-hand scales). All $E_{1/2}$'s are relative to that of the ferrocenium/ferrocene couple at 25 °C in the corresponding medium. The numbers correspond to the compounds listed on Table I plus $Fe(C_5H_4N\text{-}CR_1{=}NR_2)_3^{2+}$ (R_1, R_2 = H, C_2H_5 (**15**); CH_3, C_6H_5 (**16**)).

(cf. Table I). From eq 1 it is clearly seen that the replacement of hydrogens by electron-donating methyl groups implies a greater stabilization of the ferric forms compared to that of the ferrous forms, due to the increasing σ-bonding ability of the ligands. A similar trend has been observed in sulfuric acid[1] and acetonitrile[2] solutions. As the substituents become bulkier as in the cyclohexanedione derivatives, the interplay of steric and inductive effects determines the observed potentials. For R, R′ = H, C_6H_5, the phenyl group can interact mesomerically with the diimine chromophore, as was also observed in other media.[1,2]

As shown in the previous papers of this series[1,2] the effect of the substituents on the $E_{1/2}$ of the FeL_3^{3+}/FeL_3^{2+} couple can be represented by

$$E_{1/2} = E^\circ_{1/2} + \rho^*\sum\sigma^* + \delta\sum E_s \tag{2}$$

where the σ^*'s and E_s's are the Taft polar[19] (excludes mesomeric effects and therefore compound **6**, R, R′ = H, C_6H_5 of the correlations) and steric parameters, respectively, of the substituents, which are considered additive. For the steric effects this approximation is poorer than for the polar effects.[1] By combining correlations of spectral and thermodynamic data,[1,2] it has been possible to estimate $\sum\sigma^*$ and $\sum E_s$ for the cyclohexanedione derivatives as $\sum\sigma^* = -0.58 \pm 0.06$ and $\sum E_s = 13 \pm 5$ for $CH_2CH_2CH_2CH_2$ and $\sum\sigma^* = -0.67 \pm 0.07$ and $\sum E_s = 15 \pm 5$ for $CH_2CH(CH_3)CH_2CH_2$.

Figure 1 shows the $E_{1/2}$'s of the aliphatic diimine series as a function of $\sum\sigma^*$ in the molten salt. Clearly the bulky cyclohexanedione derivatives do not fit a correlation that does not take into consideration steric effects. When steric effects are included, a very good correlation (line A in the figure)

$$E_{1/2} - 0.02\sum E_s = 0.86 + 0.44\sum\sigma^* \tag{3}$$

with a correlation coefficient CC = 0.999 is obtained. All the potentials plotted in this figure are referred to that of the ferrocenium/ferrocene couple in the respective medium.[31,32] For acetonitrile (line B) one obtains

$$E_{1/2} - 0.01\sum E_s = 0.55 + 0.29\sum\sigma^* \tag{4}$$

with a CC = 0.98, and for 4 M H_2SO_4 (line C)

$$E_{1/2} - 0.02\sum E_s = 0.56 + 0.35\sum\sigma^* \tag{5}$$

with a CC = 0.990. From the slopes of these correlations (eq 3–5) one can conclude that as a result of the increased σ-bonding ability of the ligand the greater stabilization of the ferric forms as compared to that of the ferrous forms increases in the order

acetonitrile < 4 M H_2SO_4 < 2:1 $AlCl_3$–EtpyBr

By comparing the absolute potentials relative to that of the ferrocenium/ferrocene couple in these solvents, one can conclude that the molten salt medium better stabilizes the ferrous forms. The thermodynamic stability of the ferrous forms increases as

acetonitrile ≈ 4 M H_2SO_4 < 2:1 $AlCl_3$–EtpyBr

The plots of Figure 1 for acetonitrile (B) and 4 M H_2SO_4 (C) also include iron complexes of mixed diimine ligands, and it is clearly seen that the effect of the pyridine moiety in the mixed series on the $E_{1/2}$'s is identical with that of two $=NCH_3$ groups (cf. the following compounds: **3**, **8**; **2**, **7**; **11**, **16**) within the experimental error. Since in the molten salt medium there is weak adsorption of FeL_3^{2+} complexes when L is a mixed or aromatic diimine ligand, the comparison of potentials in the aliphatic and mixed series cannot be made. However, inspection of the data in Table I shows a similar trend of $E_{1/2}$'s with increased σ-bonding ability of the ligand (cf. compounds **7** and **8**) and that an interplay of steric and inductive effects inverts the trend of the $E_{1/2}$'s (cf. compounds **8**, **9**, and **10**). Compounds **11** and **12** do not exhibit mesomeric interactions with the diimine chromophore due to the presence of the pyridine moiety.[33] However, steric effects for these compounds, as well as for **9** and **10**, are important. A linear correlation can be also obtained in this series if one corrects for the steric effects; $E_{1/2} - 0.04\sum E_s = 0.74 + 0.41\sum\sigma^*$. The correlation is displaced ca. 100 mV toward more negative potentials with respect to that of the aliphatic series. It is very likely that the E°'s in the mixed series are ca. 100 mV more anodic than the measured $E_{1/2}$'s.

Effect of Melt Dilution with Benzene on the $E_{1/2}$'s. Inspection of Table I shows that as the Lewis acidity of the melt is decreased by dilution with benzene from $C_{Al_2X_7^-} = 3.30$ M (pure melt) to 2.31 M (50% v/v) the $E_{1/2}$'s of all FeL_3^{3+}/FeL_3^{2+} couples increase by 70–110 mV. It is important to emphasize that under the same experimental conditions the $E_{1/2}$ ferrocenium/ferrocene does not change (see Table I), implying that liquid-junction potentials must be under 10 mV.

Similar dependence had been found in acid solutions. For instance, for the $Fe(phen)_3^{3+}/Fe(phen)_3^{2+}$ couple the values of $E^{\circ\prime}$ as a function of H_2SO_4 concentration, in parentheses, are 1.14 (0), 1.06 (1 M), 0.96 (4 M), and 0.76 (8 M) V.[34] For the FeL_3^{3+}/FeL_3^{2+} couple with L = $H_3CN{=}C(CH_3){-}C(C$-

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Table II. Wavenumbers at the Absorbance Maxima of the Inverse Charge-Transfer Bands for the FeL_3^{2+} Complexes in the 2:1 $AlCl_3$–Ethylpyridinium Bromide Molten Salt and Acetonitrile, Water, and H_2SO_4 Solution

	L = $H_3CN{=}CR{-}CR'{=}NCH_3$		ν, 10^3 cm^{-1}			
no.	R	R′	molten salt	acetonitrile[2]	H_2O[4,36,38]	11 M H_2SO_4
1	H	H	18.02	18.05	18.05	18.02
2	H	CH_3	17.8	17.76	. . .	17.8
3	CH_3	CH_3	17.6	17.6	17.6	17.7
4	$CH_2CH_2CH_2CH_2$		17.1	17.18	17.18	17.25
6	H	C_6H_5	16.6	16.55	16.6	16.7

	L = $C_5H_4N{-}CR_1{=}NR_2$		ν, 10^3 cm^{-1}			
no.	R_1	R_2	molten salt	acetonitrile	4 M H_2SO_4	11 M H_2SO_4
7	H	CH_3	18.1	18.2	18.15	18.08
8	CH_3	CH_3	17.9	17.95	17.9	17.9
11	C_6H_5	CH_3	17.7	17.7	17.6	17.7
12	C_6H_5	C_6H_5	17.3	17.25	17.3	. . .

		ν, 10^3 cm^{-1}	
no.	L = aromatic diimine	molten salt	4 M H_2SO_4
13	bpy	19.2	19.15
14	phen	19.6	19.6

H_3)=NCH_3, the values of $E^{\circ\prime}$ as a function of H_2SO_4 are 1.00 (0) 0.94 (1 M), 0.88 (4 M), and 0.69 (10.5 M).[1] The formal electrode potentials decrease strongly with increasing acid concentration.[34] While activity and ion pairing effects were invoked as important factors, the total decrease of $E^{\circ\prime}$'s cannot be accounted for on the basis of these parameters. The effect as a whole is not clearly understood.[7]

A parallel between the behavior of $E^{\circ\prime}$'s in proton and Lewis acid solutions exists for these complexes. The magnitude of the effect is larger in the molten salt system than in aqueous acid solutions.

Visible Absorption Spectra. The iron(II) diimine complexes display an intense ($\epsilon_{max} \approx 10^4$ M^{-1} cm^{-1}) band with a maximum at 500–600 nm and a characteristic shoulder toward smaller wavelengths.[1,7] A second broad-band system appears between 400 and 330 nm in the spectra of the aromatic and mixed diimine complexes. The band at 500–600 nm has been assigned to an inverse charge transfer $t_2 \rightarrow \pi^*$.[35] The shoulder toward larger wavenumbers represents the first member of a vibrational progression as suggested by Krumholz[36] in 1964 and further confirmed by resonance Raman studies by Nakamoto et al.[37] In the case of R, R′ = H, C_6H_5 and CH_3, C_6H_5 there is a second system of bands with structure in the 500–600-nm regions, assigned to metal to ligand charge transfer due to the lowering of the symmetry of the complex.[20]

Table II compares the maxima wavenumbers of the inverse charge-transfer bands in the molten salt medium, acetonitrile, water, and 11 M H_2SO_4. The maxima in all four media are very similar within 4 nm, indicating that the molten salt does not interact with the complexes in solution.

Correlations between the frequencies of the inverse charge-transfer band and the $E_{1/2}$'s are very similar to those observed in acid[1] or acetonitrile[2] solutions.

In all these solvents there is a linear correlation between $E_{1/2}$ and the energy $h\nu$, where ν is the frequency of the inverse charge-transfer band (compare Tables I and II) for small substituents: e.g., R, R′ = H, H; H, CH_3; CH_3, CH_3. As the substituents become bulkier, the correlation departs from linearity. The inverse charge-transfer process upon irradiation corresponds to an intramolecular redox process, during which the interatomic distances remain constant, and the total number of electrons remains invariant.[39] The $E_{1/2}$ (identical to E°) reflects the charge of free energy (or free enthalpy) of the system, whereas $h\nu$ reflects the change of inner energy of the system.[39] When linear correlations between $E_{1/2}$ and ν are found, they reflect the following: (a) the interatomic distances in the reduced and oxidized form do not differ appreciably; (b) the donor part of the molecule does not change considerably throughout the series; (c) ΔH_{solv} and ΔS° are constant throughout the series.[39] The departure of the linearity observed in this series of complexes as the ligands become bulkier indicates considerable differences in ΔH_{solv}.[39]

Conclusion

In 2:1 aluminum chloride–ethylpyridinium bromide, a totally anhydrous solvent system of high Lewis acidity, all types of iron diimine complexes exhibit reversible one-electron oxidation to the corresponding very stable iron(III) compounds. No ligand reactivity has been observed in this solvent, even upon lowering the acid concentration by dilution with the cosolvent benzene[29] in contrast with other solvents in which ligand-oxidation processes assisted by nucleophilic attack of the solvent are found (aliphatic[10] and mixed[12] diimine ligands) except at very high concentration. In these processes, the ferric forms are reduced with concomitant solvent-assisted ligand oxidation.[10,12] In the molten salt system or their benzene solutions the thermodynamic stability of the ferric forms is greater than that of the ferrous forms, whereas in aqueous solutions the reverse relative order of stability exists. The stability of the ferric forms of aliphatic and mixed diimine ligands in this molten salt suggests that this medium and analogous room-temperature molten salts[17,18,29] offer a unique possibility for spectroscopic studies (NMR, EPR) of these compounds.

Correlations between the $E_{1/2}$'s of the FeL_3^{3+}/FeL_3^{2+} couples and the Taft polar and steric parameters were found in this medium. They indicate a faster increase in thermodynamic stability of the ferric forms as compared to those of the ferrous forms in this medium, as compared to 4 M H_2SO_4 or acetonitrile. Such correlations are very useful in tailoring new complexes with suitable thermodynamic and special properties.

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Registry No. **1** (Fe^{3+}), 43211-77-4; **1** (Fe^{2+}), 20498-13-9; **2** (Fe^{3+}), 57255-27-3; **2** (Fe^{2+}), 52572-91-5; **3** (Fe^{3+}), 57255-28-4; **3** (Fe^{2+}), 38681-99-1; **4** (Fe^{3+}), 57255-30-8; **4** (Fe^{2+}), 52572-94-8; **5** (Fe^{3+}), 57255-31-9; **5** (Fe^{2+}), 57255-21-7; **6** (Fe^{3+}), 57254-95-2; **6** (Fe^{2+}), 57255-23-9; **7** (Fe^{3+}), 61973-01-1; **7** (Fe^{2+}), 47558-80-5; **8** (Fe^{3+}), 61973-04-4; **8** (Fe^{2+}), 47664-80-2; **9** (Fe^{3+}), 61973-05-5; **9** (Fe^{2+}), 47735-58-0; **10** (Fe^{3+}), 61973-06-6; **10** (Fe^{2+}), 61973-09-9; **11** (Fe^{3+}), 61973-07-7; **11** (Fe^{2+}), 47860-49-1; **12** (Fe^{3+}), 73503-65-8; **12** (Fe^{2+}), 19428-66-1; **13** (Fe^{3+}), 18661-69-3; **13** (Fe^{2+}), 15025-74-8; **14** (Fe^{3+}), 13479-49-7; **14** (Fe^{2+}), 14708-99-7.

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