

Substituent Effects on Iron Diimine Complexes. I. Correlations with Thermodynamic and Spectral Properties in Aqueous Sulfuric Acid

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Substituent effects on iron complexes FeL_3^{2+} , of aliphatic diimine ligands, $H_3C-N=C(R)-C(R')=N-CH_3$ ($R, R' = H, H; H, CH_3; CH_3, CH_3; CH_3, C_2H_5; -CH_2CH_2CH_2CH_2-$; $-CH_2CH(CH_3)CH_2CH_2-$) or mixed diimine ligands, $C_5H_4N-C(R_1)=N(R_2)$, ($R_1, R_2 = H, CH_3; H, C_2H_5; H, n-C_3H_7; CH_3, CH_3; CH_3, C_2H_5; CH_3, n-C_3H_7; C_6H_5, CH_3$) are reported. Formal electrode potentials were obtained in 4.0 M H_2SO_4 and shown to correlate with $\Sigma\sigma^$ Taft polar parameters, except for substituents presenting large steric effects. Except for the *n*-propyl derivatives, it was possible to correlate all other compounds by considering that steric effects, E_s , were also additive. The failure to include the *n*-propyl data shows that steric effects within the iron diimine grouping are larger than could be accounted for by the simple steric parameters used. Good linear free-energy relationships are also obtained for $\log \epsilon$ (ϵ , molar absorptivity) at the maximum wavelength of the inverse charge transfer bands of the ferrous complexes and $\Sigma\sigma^*$, or $\log \epsilon$ of the charge transfer bands for the ferric complexes and $\Sigma\sigma^*$, in the aliphatic series. In the mixed series such correlations were not obtained as a result of a more important role of steric effects. Based on these correlations, estimates of $\Sigma\sigma^*$ and E_s for the cyclohexanedione derivatives were also obtained.*

Introduction

Iron diimine complexes of aromatic ligands, e.g., 1,10-phenanthroline and 2,2'-bipyridine, and its derivatives, have been used in the past 40 years as redox indicators,^{1,2} due to the reversibility of the chemical oxidation to the ferric forms, accompanied by profound color changes.

The analogous complexes with the aliphatic diimine structure ($H_3C-N=C(R)-C(R')=N-CH_3$)₃Fe(II) were prepared by Krumholz³ in 1953. Later on, Busch and Bailar⁴ synthesized the compounds that established a structural link between the purely aromatic diimine and the simple aliphatic diimine that will be called mixed diimine ligands

It has been shown that the oxidation of the complex is of purely aliphatic⁵⁻⁷ or mixed diimine⁸ ligands to

the corresponding ferric complexes can only be obtained at very high acid concentration, e.g., $> 10M H_2SO_4$. At lower acid concentration the consumption of equivalents of the oxidant increases, to produce new ligand-oxidized complexes.⁵⁻⁸

Linear free-energy correlations have been reviewed recently.⁹⁻¹¹ While it is very frequent to obtain good correlations between electrode potentials and substituent parameters, not very often good correlations with visible or UV absorption spectra are obtained.⁹ Few examples can be found in the literature.¹²⁻¹⁵

In the present report we show a systematic study of substituent effects on iron diimine complexes, by relating thermodynamic and spectral properties with substituent parameters. Inductive and steric effects were considered by means of its Taft parameters.

Experimental

The compounds were prepared and purified according to procedures described elsewhere.^{7,16,17}

For the aliphatic diimine series, electrode potentials were obtained by oxidizing with cerium(IV) sulfate (Merck, p.a.) an appropriate amount of the ferrous complex in 10 M H_2SO_4 (Merck, p.a.), and injecting 1 ml of this solution at 0°C into 30 ml of a solution of the ferrous complex at 25.0°C of adequate acid concentration under vigorous stirring so that the final acid concentration was 4.0 M. The electrode potential was obtained by extrapolating the measured potentials to zero time. The precision of this procedure is ± 0.01 to ± 0.02 V vs. sce, due to the fast disproportionation reaction of the ferric forms occurring at low acid concentration,^{7,18} yielding stable ligand-oxidized complexes. For the derivatives CH_3 , CH_3 and CH_3, C_2H_5 the disproportionation reaction occurred more slowly, so that it was possible to determine electrode potentials at lower acid concentrations. The cell and equipment used are described elsewhere.⁷

For the aliphatic series at 10 M H_2SO_4 ¹⁹ or the mixed diimine ligands, electrode potentials are identical to half-wave potentials determined by means of cyclic voltammetry. The agreement between electrode poten-

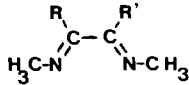
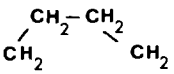
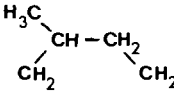
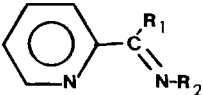
tials measured this way or through potentiometric titration is ± 0.01 V vs sce. A PARTM model 170 was used for the cyclic voltammetric measurements, and the cell used is described in the literature.¹⁹ All measurements were performed at $25.0 \pm 0.1^\circ$ C.

The visible absorption spectra of the ferrous and ferric complexes of mixed diimine ligands were obtained in $10M$ H_2SO_4 . It was necessary to extrapolate to zero time for the spectrophotometric measurements of the ferrous complexes, because of slow decomposition, so that the results are less accurate. A Zeiss-DMR-10 spectrophotometer was employed in these measurements.

Results and Discussion

The formal electrode potentials, $E^{o'}$, for the aliphatic series in $4.0M$ H_2SO_4 are assembled in Table I. The table also presents data for $E^{o'}$ at $10.5M$ H_2SO_4

TABLE I. Formal Electrode Potentials for Iron Complexes of Aliphatic and Mixed Diimine Ligands Couples, FeL_3^{3+}/FeL_3^{2+} , at 25.0° C.

	$E^{o'}$, V vs. sce	$E^{o'}$, V vs. sce
R,R'	$4.0M$ H_2SO_4	$10.5M$ H_2SO_4
H,H	1.01	0.81 ^a
H,CH ₃	0.81	0.62 ^a
CH ₃ ,CH ₃	0.64	0.45 ^a
CH ₃ ,C ₂ H ₅	0.66	0.48
	0.60	0.42
	0.63	0.44
C ₆ H ₅ , H	—	0.51
C ₆ H ₅ , CH ₃	—	0.44
	$E^{o'}$, V vs. sce ^b	
R ₁ , R ₂	$4.0M$ H_2SO_4	
H, CH ₃	0.80	
H, C ₂ H ₅	0.77	
H, <i>n</i> -C ₃ H ₇	0.68	
CH ₃ , CH ₃	0.63	
CH ₃ , C ₂ H ₅	0.65	
CH ₃ , <i>n</i> -C ₃ H ₇	0.67	
C ₆ H ₅ , CH ₃	0.79	

^aFrom reference 19. ^b ± 0.01 .

from cyclic voltammetric measurements partly reported elsewhere.¹⁹

The formal electrode potentials decrease by *ca.* 0.18 V per methyl group replacing hydrogen at the methine carbon. Increased loading of the ligand, as in the 1,2-cyclohexanedione derivative causes a further decrease of $E^{o'}$.

The formal electrode potentials for the complexes of mixed diimine ligands were also obtained from cyclic voltammetric measurements. All curves fit diagnostic criteria for a one electron reversible process, just as those previously reported in the literature.¹⁹ Figure 1 shows an experimental anodic current vs. potential curve and the calculated curve assuming a one electron reversible oxidation¹⁹ for a complex of mixed diimine ligand. The agreement between experimental and calculated results leads us to conclude that the electrochemical processes can be considered as reversible processes under diffusion control. The formal electrode potentials for the iron complexes of mixed diimine ligands are also assembled in Table I.

For the complexes of the mixed diimine ligands, on replacing on the methine carbon a hydrogen by a methyl group, the same decrease of $E^{o'}$ observed in the aliphatic series is shown.

It is interesting to note that within the experimental error, if R,R' = R₁, R₂, the observed $E^{o'}$ for the corresponding compounds are identical.

The decrease of $E^{o'}$ with replacement of hydrogen atoms by methyl groups in the diimine chromophore²⁰ reflects a higher stabilization of the ferric forms of the complexes as compared to the stabilization of the ferrous forms, since the $E^{o'}$ reflects the difference of free energy of formation of the ferric and ferrous forms as follows:

$$FE_{FeL_3^{3+}/FeL_3^{2+}}^{o'} - FE_{Fe^{3+}_{aq}/Fe^{2+}_{aq}}^{o'} = \Delta G_{FeL_3} - \Delta G_{FeL_3^{2+}}$$

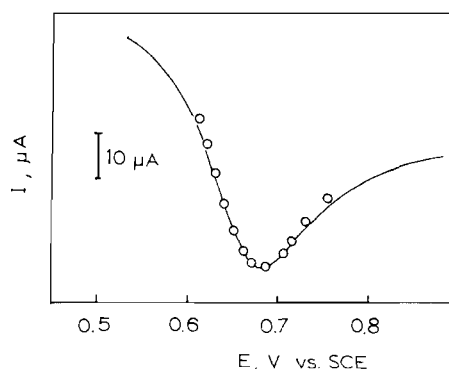


Figure 1. (○) Calculated anodic i vs. E curve assuming a one electron reversible process for the oxidation of the mixed ligand derivative R₁, R₂ = CH₃, C₂H₅, $2.5 \times 10^{-3}M$, in $4.0M$ H_2SO_4 . (—) Experimental i vs. E data. Scan rate = 100 mV/s.

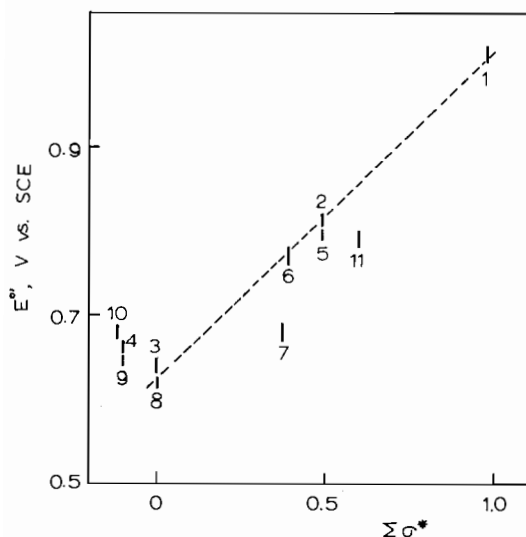


Figure 2. Polar Taft plot for substituent effects on iron diimine complexes: $(\text{CH}_3\text{-N}=\text{C}(\text{R})\text{-C}(\text{R}')=\text{NCH}_3)_3\text{Fe}$, R, R' : (1) H, H; (2) H, CH_3 ; (3) CH_3, CH_3 ; (4) $\text{CH}_3, \text{C}_2\text{H}_5$; $[\text{C}_5\text{H}_4\text{N}-\text{C}(\text{R}_1)=\text{N}-\text{R}_2]_3\text{Fe}$, R_1, R_2 : (5) H, CH_3 ; (6) H, C_2H_5 ; (7) H, $n\text{-C}_3\text{H}_7$; (8) CH_3, CH_3 ; (9) $\text{CH}_3, \text{C}_2\text{H}_5$; (10) $\text{CH}_3, n\text{-C}_3\text{H}_7$; (11) = $\text{C}_6\text{H}_5, \text{CH}_3$.

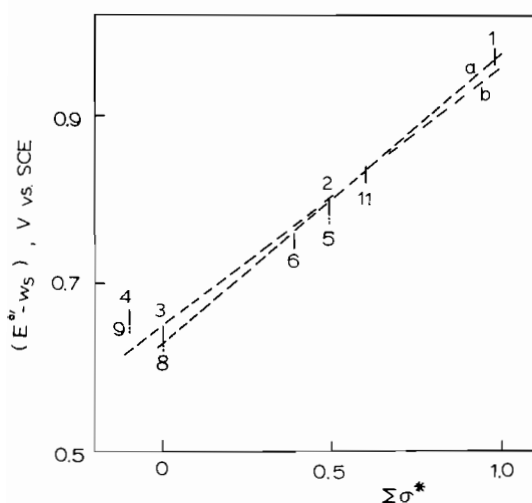


Figure 3. Taft plot for substituent effects on iron diimine complexes including polar and steric effects. The compounds identical to these in Figure 2. (a) Including $\text{CH}_3, \text{C}_2\text{H}_5$ compounds; (b) not including $\text{CH}_3, \text{C}_2\text{H}_5$ compounds.

As hydrogen atoms are replaced by the electron donating methyl groups, a higher σ bonding ability of the ligands should be observed, and consequently the decrease of E° . An interplay of steric effects could account for changes in the direction of E° with the increase of σ bonding ability of the ligand. Thus, for the complexes with mixed diimine ligands, $\text{R}_1, \text{R}_2 =$

H, CH_3 ; H, C_2H_5 ; H, $n\text{-C}_3\text{H}_7$, as the σ bonding ability of the ligands increases the E° decreases, as one should expect (see Table I). On the other hand, for the compounds $\text{R}_1, \text{R}_2 = \text{CH}_3, \text{CH}_3$; $\text{CH}_3, \text{C}_2\text{H}_5$; $\text{CH}_3, n\text{-C}_3\text{H}_7$, the reverse direction is observed, possibly indicating a more important contribution of steric effects.

In the mixed derivative $\text{R}_1, \text{R}_2 = \text{C}_6\text{H}_5, \text{CH}_3$, the phenyl group has a very large twisting angle, as shown by the theoretical calculations by Favini and Simionetta²¹ on analogous compounds. It is likely that in this compound the phenyl group does not present mesomeric effects.

The results can be best explained in terms of correlations of E° with Taft parameters. As was observed for several substituted aromatic diimine complexes²² it is likely that polar effects are also additive. A plot of E° vs $\Sigma\sigma^*$ ^{9,10} for the iron complexes of aliphatic and mixed diimine complexes is shown in Figure 2. A fairly good correlation is observed for all compounds studied except for those containing phenyl or n -propyl groups, that certainly present large steric effects.

In an attempt to obtain a better correlation with these data, steric effects, E_s , were introduced and assumed to be additive. The more general equation

$$E^\circ = E^\circ_0 + \rho^*\Sigma\sigma^* + \delta\Sigma E_s$$

was applied.^{9,11} The n -propyl derivatives were excluded from the correlation, since it is not likely that a steric factor for an isolated n -propyl group will hold for an n -propyl group close to pyridine rings and the R_1 group in the mixed diimine ligands.

The equation: $E^\circ = 0.65 + 0.29\Sigma\sigma^* + 0.017\Sigma E_s - 0.017\Sigma E_s$ was obtained. A new plot (Figure 3) of $(E^\circ - 0.017\Sigma E_s)$ vs. $\Sigma\sigma^*$ was obtained and is linear within the experimental errors (C.C. = 0.98). The important fact in this new correlation is that now the $\text{C}_6\text{H}_5, \text{CH}_3$ derivative falls perfectly on line, thus indicating that mesomeric effects are not of importance in this case. These data corroborate the assumption that the phenyl group presents a very large twisting angle. If the derivatives $\text{R}_1, \text{R}_2 = \text{R}, \text{R}' = \text{CH}_3, \text{C}_2\text{H}_5$, are not considered, a much better correlation is obtained (C.C. = 0.997), thus showing that effectively the steric effects for these two complexes are larger than the sum of individual steric effects.

As the acid concentration decreases, the E° increases, in spite of the large liquid junction potentials. This trend had also been observed in the aromatic diimine complexes.^{1,2,23} Table II shows data for the $\text{R}, \text{R}' = \text{CH}_3, \text{CH}_3$ at several acid concentrations. Within the experimental error, there seems to exist a linear correlation between these E° and the Hammett acidity function.²⁴

In the aliphatic series, the phenyl groups may present mesomeric and steric effects. These effects are more evident if we also compare absorption spectral data^{16,25} for the inverse charge transfer bands, $t_2 \rightarrow \pi^*$, on the

TABLE II. Formal Electrode Potentials as a Function of Hammett Acidity Function for the R, R' = CH₃, CH₃ Derivative at 25.0°C.

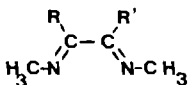
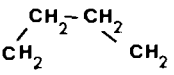
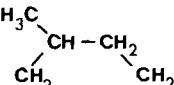
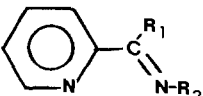
E ^o , V vs. sce	-H ₀
0.73	0.08
0.70	0.28
0.685	0.74
0.665	1.37
0.64	1.84
0.45	5.16

iron(II) complexes and the charge transfer bands, $\pi \rightarrow t_2$, on the iron(III) complexes.

The frequencies and logarithms of molar absorptivities for all compounds studied are presented in Table III. In the aliphatic series, as we replace hydrogen atoms for the more electron donating groups, the frequencies of both charge transfer bands decrease (see Table III). This trend parallels that observed for the E^o. However, if we replace a hydrogen by a phenyl group, a

larger decrease of both frequencies is observed (1.3 and 5.0 kK, respectively for the ferrous and ferric compounds). Correspondingly, the E^o in 10.5M H₂SO₄ decreases 0.30 V vs. sce, as compared to the 0.18 V decrease on methyl groups. If we now replace the remaining hydrogen by a methyl group, the frequency for the charge transfer and of the ferrous complex increase (0.3 kK) while that for the ferric decreases (0.5 kK). The E^o obtained is now only 0.07 V vs. sce smaller than that for the H₂C₆H₅ derivative. These data imply that in the derivative R, R' = H, C₆H₅, the phenyl group can interact with the diimine grouping directly through a resonance effect, that is partially perturbed by the replacement of the hydrogen by a methyl group, thus explaining the small decrease of E^o. The phenyl group exhibits in this compound a somewhat larger twisting angle. It is interesting to compare now the data for the mixed diimine ligands, R₁, R₂ = C₆H₅, CH₃ and H, CH₃. From Table I we can observe that the E^o for both compounds are identical within the experimental error (*cf.* the 0.30 V decrease in the other series). The frequencies of both

TABLE III. Frequencies and Logarithms of Molar Absorptions for Iron(II) and Iron(III) Complexes of Aliphatic^a and Mixed Diimine Complexes in 10.5M H₂SO₄.

	Fe(II) Complexes		Fe(III) Complexes ^b	
	ν , kK	$\log[\epsilon(M^{-1} \text{ cm}^{-1})]$	ν , kK	$\log[\epsilon(M^{-1} \text{ cm}^{-1})]$
R, R'				
H, H	18.0	3.93	26.9	3.34
H, CH ₃	17.8	3.98	26.8	3.43
CH ₃ , CH ₃	17.7	4.025	26.7	3.49
CH ₃ , C ₂ H ₅	17.5	4.03	26.5	3.50
	17.23	4.07	25.7	~3.5
	17.21	4.085	25.6	>3.3
C ₆ H ₅ , H	16.7	4.04 ₅	21.9	3.23
C ₆ H ₅ , CH ₃	17.0	4.02	21.4	3.04
	Fe(II) Complexes		Fe(III) Complexes	
	ν , kK	$\log[\epsilon(M^{-1} \text{ cm}^{-1})]$	ν , kK	$\log[\epsilon(M^{-1} \text{ cm}^{-1})]$
R ₁ , R ₂				
H, CH ₃	18.1	4.04	18.0	2.69
H, C ₂ H ₅	18.0	4.01	18.7	2.71
H, <i>n</i> -C ₃ H ₇	18.1	>4.0	18.8	>2.9
CH ₃ , CH ₃	17.9	4.07	18.7	2.91
CH ₃ , C ₂ H ₅	17.7	3.94	18.8	2.71
CH ₃ , <i>n</i> -C ₃ H ₇	17.6	~3.8	18.7	~2.7
C ₆ H ₅ , CH ₃	17.7	4.13	17.7	~3.1

^a Partly from references 16 and 22. ^b From reference 24.

charge transfer and inverse charge transfer bands for ferrous and ferric complexes decrease only by 0.4 and 0.3 kK respectively (as compared to 1.3 and 5.0 kK for the other series). In this compound, $R_1, R_2 = C_6H_5, CH_3$, the phenyl group thus presents the largest twisting angle and cannot interact with the diimine group-*ing via* mesomeric effects.

If we now compare the derivative $R, R' = R_1, R_2 = H, CH_3$ and CH_3, CH_3 , a decrease of 0.1 and 0.2 kK, respectively, for the aliphatic and mixed series is observed for ferrous complexes, and 0.1 and 0.3 kK for the ferric compounds. The similarity of these numbers and the identity of the $E^{0'}$ reveal that the effect of these groups on the diimine chromophore is not dependent on the presence of the pyridine ring. For the other mixed diimine ligands, the interplay of steric effects causes a non-systematic trend of the frequency shifts.

A plot of $E^{0'}$ as a function of the frequency of the inverse charge transfer band for the ferrous complexes of aliphatic diimine ligands is shown in Figure 4. For the simplest aliphatic substituent, a linear correlation within the experimental error is observed. This type of correlation has been reviewed by Vlček.²⁶ In the $E^{0'}$ for reversible processes the free energy change and the properties of the redox orbitals are related.²⁶ In the charge transfer process mentioned above, electrons are transferred from essentially localized t_2 orbitals to delocalized π^* orbitals, this process being an intramolecular redox process. However, since the shifts of frequencies are very small, correlations between logarithms of the molar absorptivities for the intramolecular redox processes for iron(II) and iron(III)

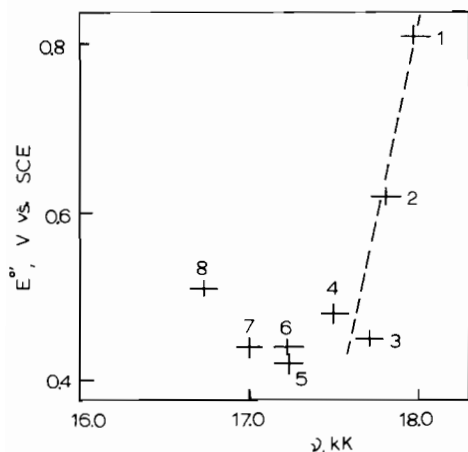


Figure 4. Plot of the formal electrode potentials for the couples FeL_3^{3+}/FeL_3^{2+} vs. the frequency of the inverse charge transfer bands for the ferrous compounds, in 10.5 M H_2SO_4 . L = $H_3CN=C(R)=C(R')=NCH_3$, R, R' = (1) H, H; (2) H, CH_3 ; (3) CH_3, CH_3 ; (4) CH_3, C_2H_5 ; (5) $CH_2-CH_2-CH_2-CH_2$; (6) $CH_2-CH(CH_3)-CH_2-CH_2$; (7) CH_3, C_6H_5 ; (8) H, C_6H_5 .

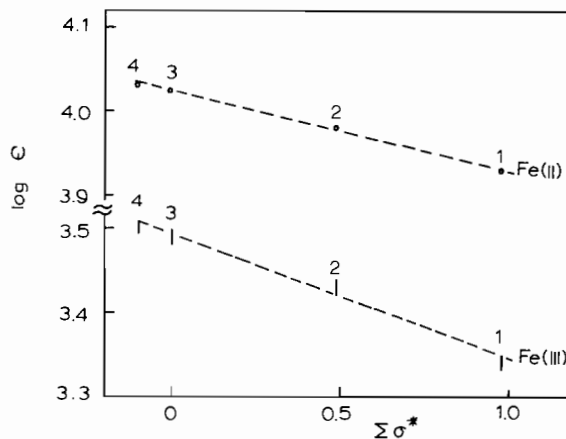


Figure 5. Plot of logarithms of molar absorptivities for the ferrous and ferric complexes of aliphatic diimine ligands vs. Taft polar parameters. Numbers refer to same compounds as in Figure 4.

complexes with the polar $\Sigma\sigma^*$ Taft parameters were tried. Figure 5 shows such correlations (C.C. >0.99).

Using the correlation presented in Figure 5, for ferrous complexes it is possible to estimate rough values for σ^* for the cyclohexanedione derivatives as -0.55 and -0.7 for $-CH_2CH_2CH_2CH_2-$ and $-CH_2CH(CH_2)CH_2CH_2-$, respectively. From the correlation presented in Figure 3 it is also possible to estimate steric parameters for those substituents in the complex as 6 and 11, respectively.

Conclusions

This paper presents for the first time correlations between thermodynamic and spectral properties with Taft's polar and steric parameters for iron diimine complexes of aliphatic diimine ligands and mixed (aliphatic-aromatic) diimine ligands. Correlations of thermodynamic properties with Hammett parameters are long known only for iron complexes of aromatic diimine ligands.

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