Journal of Organometallic Chemistry, 243 (1983) 339–350
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SUBSTITUENT EFFECT OF CHELATED COBALT.

VI *. pK_a's OF THE CONJUGATE ACIDS OF *m*- AND *p*-*N*,*N*-DIMETHYLAMINOPHENYL(LIGAND)COBALOXIMES

KENNETH L. BROWN * and MICHAEL NGAMELUE

Department of Chemistry, The University of Texas at Arlington, Box 19065, Arlington, Texas 76019 (U.S.A.)

(Received July 30th, 1982)

Summary

The *meta* and *para* isomers of *N*,*N*-dimethylaminophenyl(aquo)cobaloximes have been prepared and the pK_a's of their conjugate acids have been determined for the complexes with six different axial ligands ($L = OH_2$, SCN^-, NCS^-, *S*-methyl-2-mercaptoethanol, CN^-, and N_3^-). These pK_a values have been correlated with those of 13 other *N*,*N*-dimethylanilinium ions with non-cobalt substituents via a dual substituent parameter equation which allows separation of inductive and resonance substituent effects. The results show that resonance interactions (of the anilium type) between the cobaloxime chelated cobalt centers and covalently bond *N*,*N*-dimethylaminophenyl groups are negligible for all complexes studied. In comparison with earlier work on ^{19}F NMR chemical shifts of fluorophenylcobaloximes in which substantial resonance effects were found, the current results imply that although the cobalt *d*-orbitals are most likely involved in resonance interactions between cobaloxime chelated cobalt centers and covalently bound aryl groups, negative charge cannot be stabilized on the cobalt atom by acceptance of an electron pair into an unoccupied cobalt *d*-orbital.

Introduction

In recent reports [1–5] we have studied the reactivity and other chemical properties of functional groups on the organic ligands of organocobaloximes in order to attempt to understand first the electronic influence of such chelated cobalt centers on covalently bound organic ligands and, eventually, the nature of the carbon–cobalt bond. Much of this work [1,2,4] has involved substituted phenylcobaloximes and has utilized the formalism of the Taft dual substituent parameter

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* For part V see Ref. 5.

0022-328X/83/0000-0000/$03.00

equation [6] (eq. 1) in which p^i is some correlatable property of a substituted benzene

$$p^i = \sigma_I \rho^i_I + \sigma_R \rho^i_R \tag{1}$$

derivative (ratio of rate or equilibrium constants for substituted and unsubstituted compounds or NMR chemical shifts of substituted relative to unsubstituted compounds), σ_I and σ_R are the inductive and resonance substituent parameters, respectively, ρ_I and ρ_R are the susceptibilities of the correlatable parameter to inductive and resonance effects, respectively, and the superscript i refers to the substitution position (*m*- or *p*-). Ehrenson et al. [6] have shown that a wide variety of aromatic reactivities and spectral properties can be correlated successfully via eq. 1 using four different σ_R scales indicative of the differences in resonance interaction of some substituents with different types of reaction (or detection) centers. Hence, $\sigma_{R(BA)}$ parameters are used for correlations of substituted benzoic acid acidities, alkylbenzoate hydrolyses, etc., $\sigma^-_{R(A)}$ parameters are used for substituted anilinium ion and benzene thiol acidities, σ°_R for substituted phenylacetic acids and substituted fluorobenzene ^{19}F chemical shifts, and σ^+_R parameters are used for certain reactions including ionization of substituted pyridinium ions and the decomposition of aryl diazonium salts.

Our initial studies along these lines involved determinations of σ_I and $\sigma_{R(BA)}$ values for cobaloxime chelated cobalt centers from measurements of the saponification rates of *m*- and *p*-carbomethoxyphenyl(ligand)cobaloximes [1,2] and showed that substantial resonance interactions could occur at least for cobaloximes with some *trans* axial ligands. However, inconsistencies between these data and NMR properties of similar complexes as well as subsequent determinations of σ_I values for some of the same cobalt centers by correlation of carboxyethyl(ligand)cobaloxime pK_a's with those of other substituted propionic acids [3] which failed to confirm the measured σ_I values have called these results into question. Apparently, the saponification mechanism for methylbenzoates with strongly electron donating cobalt substituents is not the same as that for the basis set compounds used to determine the ρ values for eq. 1.

In order to avoid such mechanistic complications and to extend our knowledge of the resonance interactions of chelated cobalt centers with covalently bound aryl groups, we consequently undertook a study of the acidities of the conjugate acids of *m*- and *p*-*N*,*N*-dimethylaminophenyl(ligand)cobaloximes which is the subject of this report.

Experimental

Materials. Dimethylglyoxime, cobaltous chloride, sodium and potassium hydroxide, hydrochloric acid, organic solvents, buffer components and inorganic salts were obtained in the highest purity commercially available and used without further purification. Glass distilled deionized water was used throughout.

Commercially available, solid, substituted *N*,*N*-dimethylanilines (*m*-NO_2, *p*-CN, *p*-Br and *p*-NO_2) were recrystallized from 95% ethanol, air dried, and had the expected melting points [7–10] and ^{1}H NMR spectra. Commercially available, liquid, substituted *N*,*N*-dimethylanilines (H, *m*-CH_3 and *p*-CH_3) were treated with acetic anhydride to remove suspected *N*-methylaniline and aniline contaminants [11], redistilled at atmospheric pressure, and had satisfactory boiling points [7–10] and ^{1}H NMR spectra. Commercially unavailable, substituted *N*,*N*-dimethylanilines (*p*-F, *p*-CH_3O, *m*-CH_3O, *m*-F, *m*-CF_3 and *m*-Br) were synthesized by methylation of the substituted anilines with trimethylphosphate [11], purified by recrystallization or distillation, as appropriate, and gave satisfactory melting or boiling points and ^1H NMR spectra. The only previously unreported compound was *N,N*-dimethyl-*m*-trifluoromethylaniline: b.p. 48–49.5° C (3.0 mmHg), NMR (neat) δ (Me_4Si) 2.65 (s, 6.19H), 6.42–7.32 (m, 4.00H), Found: C, 57.40; H, 5.25; N, 7.17; F, 30.18. $C_9H_{10}NF_3$ calcd.: C, 57.14; H, 5.33; N, 7.40; F, 30.13%.

p-*N,N*-Dimethylaminophenyl(aquo)cobaloxime (*p*-$(CH_3)_2NC_6H_4Co(D_2H_2)OH_2$) was prepared [4] by addition of a seven-fold excess of *p*-*N,N*-dimethylaminophenylmagnesium bromide in THF to a slurry of chloroaquocobaloxime(III) [12] in THF under continuous argon purge. After one hour's reflux the reaction mixture was hydrolyzed, acidified to pH 7, and the solids (containing large amounts of 4,4'-*N,N*-dimethylaminobiphenyl) were separated by filtration. The desired product was purified by overnight Soxhlet extraction with methylene chloride followed by silica gel chromatography (acetone) of the methylene chloride extract. The yield was less than 1%. NMR (DMSO-d_6) δ (Me_4Si) 2.04 (s, 12.0H), 2.63 (s, 6.3H), 6.45–6.89 (m, 3.9H). Found: C, 45.13; H, 6.13; N, 15.97. $C_{16}H_{26}N_5O_5Co$ calcd.: C, 44.97; H, 6.13; N, 16.39%.

m-$(CH_3)_2NC_6H_4Co(D_2H_2)OH_2$ was synthesized analogously from *m*-*N,N*-dimethylaminophenylmagnesium bromide except that the Soxhlet extraction was performed with chloroform. Yield 29.4%. NMR (DMSO-d_6/$CDCl_3$) δ (Me_4Si) 2.07 (s, 12.0H), 2.68 (s, 6.25H), 6.50–6.83 (m, 4.0H). Found: C, 44.91; H, 6.19; N, 16.24. $C_{16}H_{26}N_5O_5Co$ calcd.: C, 44.97; H, 6.13; N, 16.39%.

Methods

UV and visible spectra and single wavelength absorbance measurements were made on a Cary 14 or Cary 219 recording spectrophotometer with the cell block thermostatted to 25.0 ± 0.1°C. pH measurements were made with a Radiometer PHM 64 pH meter with samples, standards and electrodes thermostatted to 25.0 ± 0.1°C. ^1H NMR spectra were recorded on a Varian T-60 or Nicolet NT-200 NMR spectrometer operating at 60 or 200 MHz, respectively. All work with organocobaloximes was performed in dim light and solutions were covered with aluminum foil whenever necessary. Ionic strength was maintained at 1.0 *M* with KCl throughout.

pK_a's of the conjugate acids of the *N,N*-dimethylanilines and the aquo- and cyano- (in excess KCN) complexes of *m*- and *p*-*N,N*-dimethylaminophenylcobaloxides (eqs. 2 and 3) were determined by spectrophotometric titration at the wavelength of maximal spectral change. In the case of the cyano complexes of the cobaloximes it was shown that no dissociation of coordination cyanide occurred at any pH in 0.075 *M* KCN. Absorbance data were fit to eq. 4, where A_x is the

$$XC_6H_4N(CH_3)_2H^+ \rightleftarrows XC_6H_4N(CH_3)_2 + H^+ \quad (2)$$

$$K_a = [XC_6H_4N(CH_3)_2][H^+]/[XC_6H_4N(CH_3)_2H^+] \quad (3)$$

$$pH_x = pK_a + \log(|A_x - A_{AH}|/|A_{A^-} - A_x|) \quad (4)$$

absorbance of a substituted *N,N*-dimethylaniline at pH_x, and A_{AH} and A_{A^-} are the titration end points, i.e. the absorbance at pH < $pK_a - 2$ and pH > $pK_a + 2$, respectively. Data for *p*-nitro-*N,N*-dimethylaniline whose pK_a value is too low for direct determination of A_{AH} were fit instead to eq. 5 where $P = |A_{\mathrm{AH}} - A_{\mathrm{A^-}}|$, and A_x, $A_{\mathrm{A^-}}$

$$|A_x - A_{\mathrm{A^-}}| = P - K_a|A_x - A_{\mathrm{A^-}}|/[\mathrm{H^+}] \qquad (5)$$

and A_{AH} are defined as above.

Potassium azide was titrated potentiometrically at 0.01 *M* with HCl and the pK_a of its conjugate acid determined as described previously [3,13].

Binding constants, K_f^B (eqs. 6 and 7 and Scheme 1) and K_f^A (eqs. 8 and 9 and Scheme 1) for the ligands thiocyanate, *S*-methyl-2-mercaptoethanol, and azide to *m*-

$$(\mathrm{CH_3})_2\mathrm{NC_6H_4Co(D_2H_2)OH_2} + \mathrm{L} \rightleftarrows (\mathrm{CH_3})_2\mathrm{NC_6H_4Co(D_2H_2)L} \qquad (6)$$

$$K_f^B = [(\mathrm{CH_3})_2\mathrm{NC_6H_4Co(D_2H_2)L}]/[(\mathrm{CH_3})_2\mathrm{NC_6H_4Co(D_2H_2)OH_2}][\mathrm{L}] \qquad (7)$$

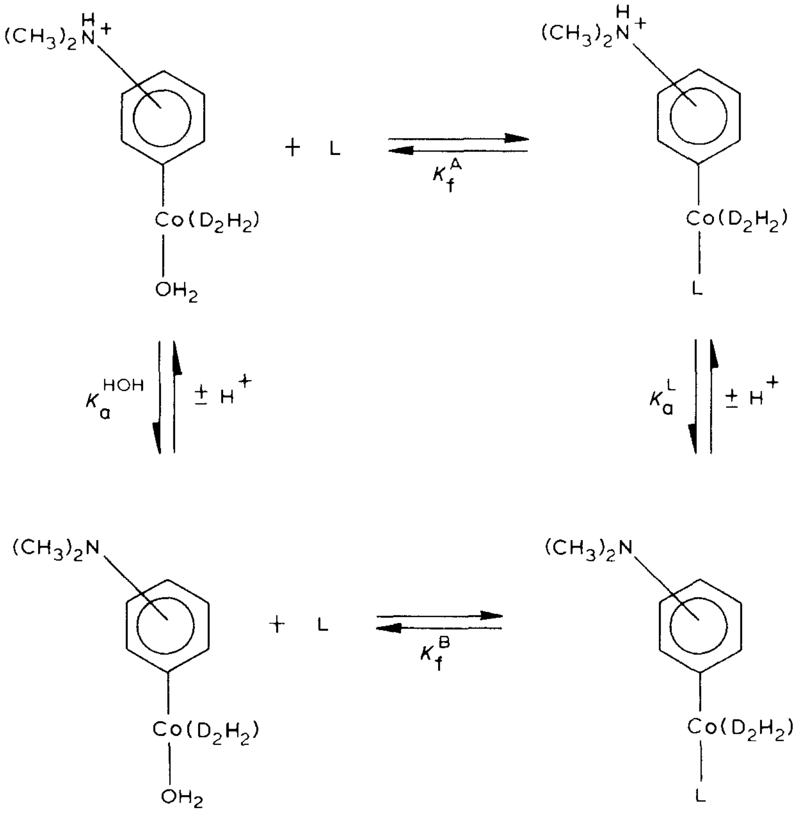
$$\mathrm{H(CH_3)_2NC_6H_4Co(D_2H_2)OH_2}^+ + \mathrm{L} \rightleftarrows \mathrm{H(CH_3)_2NC_6H_4Co(D_2H_2)L}^+ \qquad (8)$$

$$K_f^A = [\mathrm{H(CH_3)_2NC_6H_4Co(D_2H_2)L}^+]/[\mathrm{H(CH_3)_2NC_6H_4Co(D_2H_2)OH_2}^+][\mathrm{L}] \qquad (9)$$

and *p*-$(\mathrm{CH_3})_2\mathrm{NC_6H_4Co(D_2H_2)OH_2}$ and their conjugate acids, respectively, were determined spectrophotometrically at pH > 8.05 and pH < 3.93, respectively, by the method previously described [14]. When necessary, apparent binding constants, K_f^{app}, were corrected for ligand protonation by eq. 10, where α_L is the fraction of

$$K_f = K_f^{\mathrm{app}}/\alpha_L \qquad (10)$$

SCHEME 1



ligand as the unprotonated species calculated from eq. 11, where K_L is the K_a value

$$\alpha_L = K_L/(K_L + [H^+]) \tag{11}$$

of the conjugate acid of the ligand (eqs. 12 and 13).

$$LH \rightleftarrows L^- + H^+ \tag{12}$$

$$K_L = [L^-][H^+]/[LH] \tag{13}$$

Values for the pK_a's of the $H(CH_3)_2NC_6H_4Co(D_2H_2)L$'s (p$K_a^L$ in Scheme 1) which were not determined by direct spectrophotometric titration were calculated from eq. 14 based on the cyclic nature of the equilibria in Scheme 1.

$$K_a^L = K_a^{HOH} \times K_f^B/K_f^A \tag{14}$$

Results and discussion

Values for the pK_a's of the conjugate acids of the *N*,*N*-dimethylanilines with non-cobalt substituents (i.e. the basis set data) are given in Table 1. These values were fit to the *m*- and *p*- forms of eq. 1 (where $p^i = \log(K_a^i/K_a^o)$ and K_a^o is the K_a of *N*,*N*-dimethylaniline) by the method of least squares to provide the following values for the susceptibility parameters: $\rho_I^p = 3.919$, $\rho_R^p = 4.038$, $N = 7$, $f = 0.051$; $\rho_I^m = 3.320$, $\rho_R^m = 0.910$, $N = 7$, $f = 0.035$. As anticipated from considerations of simple resonance theory, these results show that delocalization makes a substantially smaller contribution to the substituent effect in the *m*- than in the *p*-position. These correlations may be visualized using the two-dimensional graphical procedure of Wells et al. [15] in which eq. 1 is recast as eq. 15.

$$\log(K_a/K_a^o) = \bar{\sigma}\bar{\rho} \tag{15}$$

where

$$\bar{\rho} = \rho_I + \rho_R \tag{16}$$

TABLE 1

pK_a's OF THE CONJUGATE ACIDS OF SUBSTITUTED *N*,*N*-DIMETHYLANILINES[a,b]

Substituent	pK_a	
	para	*meta*
H	5.48 ± 0.01	
CN	2.09 ± 0.01	–
Br	4.59 ± 0.01	4.12 ± 0.02
CH_3	5.92 ± 0.01	5.67 ± 0.01
NO_2	0.91 ± 0.01 [c]	2.93 ± 0.02
F	5.38 ± 0.01	4.21 ± 0.01
CH_3O	6.14 ± 0.01	5.08 ± 0.01
CF_3	–	3.83 ± 0.01

[a] 25.0 ± 0.1°C, ionic strength 1.0 *M*. [b] From spectrophotometric titration using eq. 4, except as noted. [c] From spectrophotometric titration using eq. 5.

$$\bar{\sigma} = \sigma_I + \lambda\sigma_R/(1 + |\lambda|) \tag{17}$$

and

$$\lambda = \rho_R/\rho_I \tag{18}$$

Plots of $\log(K_a/K_a^o)$ vs. $\bar{\sigma}$ for the *m*- and *p*-correlations are shown in Fig. 1.

Binding constants for thiocyanate ion, *S*-methyl-2-mercaptoethanol, and azide ion to *m*- and *p*-$(CH_3)_2NC_6H_4Co(D_2H_2)OH_2$ (K_f^B, Scheme 1) and their conjugate acids (K_f^A, Scheme 1) are given in Table 2. As cobaloximes are well known to form both *N*- and *S*-liganded isomers with thiocyanate ion [4,17–20] we anticipated a similar effect for the thiocyanate complexes of the *N,N*-dimethylaminophenylcobaloximes. Observation of the 200 MHz ^1H NMR spectra of 0.01 *M* solutions of these cobaloximes in saturating (i.e. 1.0 *M*) SCN^- (in D_2O made 5% (v/v) in methanol-d_4 as internal reference) proved this assumption to be correct as both the equatorial methyl resonance and the *N,N*-dimethyl resonance were observed to be doubled due to equilibrium formation of the *N*- and *S*-liganded species with interconversion apparently slow on the NMR time scale. For example, the thiocyanate complex of *m*-$(CH_3)_2NC_6H_4Co(D_2H_2)OH_2$ at pH 8.70 showed two resonances for the *N,N*-dimethylamino group at 2.713 and at 2.732 ppm in a ratio of about 1/10 and two resonances for the equatorial methyls at 2.108 and at 2.124 ppm, also in a ratio of nearly 1/10. Following Marzilli [19] and Burmeister et al. [20] we assigned the upfield resonances of each pair to the *N*-liganded isomer and the downfield resonances to the *S*-liganded isomer. Hence, by careful integration of the individual resonances we calculated the equilibrium constant, K_{S-N}^B, (eqs. 19 and 20, Scheme 2)

$$(CH_3)_2NC_6H_4Co(D_2H_2)SCN^- \rightleftarrows (CH_3)_2NC_6H_4Co(D_2H_2)NCS^- \tag{19}$$

$$K_{S-N}^B = [(CH_3)_2NC_6H_4Co(D_2H_2)NCS^-]/[(CH_3)_2NC_6H_4Co(D_2H_2)SCN^-] \tag{20}$$

for conversion of the *S*-liganded isomer to the *N*-liganded isomer to be 0.0890 ± 0.0141. This value, along with those similarly obtained for the *p*-isomer and the

TABLE 2

EQUILIBRIUM CONSTANTS FOR BINDING OF VARIOUS LIGANDS TO *p*- AND *m*-*N,N*-DIMETHYLAMINOPHENYLCOBALOMIXES[a]

L	pK_L	*para*			
		pH	α_L	K_F^{APP} (M^{-1})	K_F^A (M^{-1})
SCN^-	0.85[b]	3.76 ± 0.03	1.000	72.8 ± 2.4	72.8 ± 2.4
		8.17 ± 0.01	1.000	76.9 ± 2.4	
S-Methyl-	–	3.77 ± 0.03	–	13.3 ± 0.3	13.3 ± 0.3
-2-mercaptoethanol		8.18 ± 0.03	–	16.0 ± 0.6	
N_3^-	4.41 ± 0.01[c]	3.82 ± 0.02	0.205 ± 0.008	45.5 ± 1.8	217 ± 12
		8.13 ± 0.03	1.000	301 ± 7	

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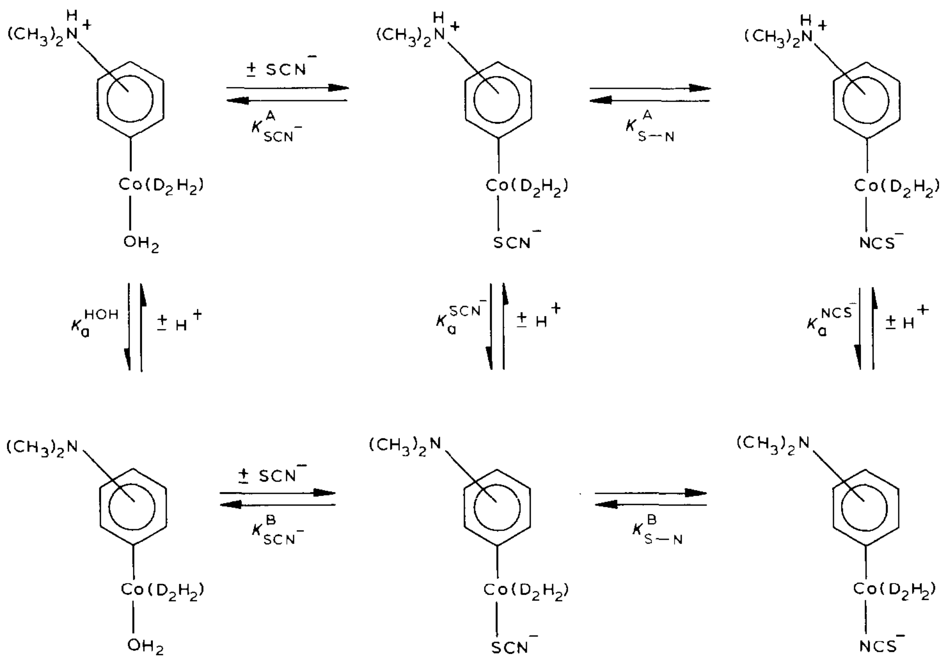
[a] 25.0 ± 0.1°C, ionic strength 1.0 *M*. The equilibrium constants are defined in Scheme 1. [b] Ref. 16. [c] This work. [d] Average of three values calculated from eq. 10.

SCHEME 2



conjugate acids of both isomers are given in Table 3. These values for isomerization equilibrium constants were then used in conjunction with the spectrophotometrically determined apparent binding constants for thiocyanate ion to each complex (Table 2) to calculate the true thermodynamic formation constants for the *S*- and *N*-liganded species via eqs. 21 and 22, and eqs. 23 and 24, respectively, which are readily derived

$$K^{A}_{SCN} = K^{A}_{f}/\left(1 + K^{A}_{S-N}\right) \tag{21}$$

	meta				
K_f^B (M^{-1})	pH	α_L	K_f^{app} (M^{-1})	K_f^A (M^{-1})	K_f^B (M^{-1})
	3.71 ± 0.03	1.000	78.7 ± 3.0	78.7 ± 3.0	
76.9 ± 2.4	8.14 ± 0.01	1.000	60.7 ± 2.7		60.7 ± 2.7
	3.80 ± 0.02	–	13.2 ± 0.4	13.2 ± 0.4	
16.0 ± 0.6	8.19 ± 0.02	–	16.5 ± 0.6		16.5 ± 0.6
	3.49 ± 0.02	0.107 ± 0.005	27.0 ± 0.6	263 ± 7[d]	
301 ± 7	3.74 ± 0.01	0.178 ± 0.005	46.3 ± 1.1		
	3.79 ± 0.01	0.194 ± 0.006	53.7 ± 1.5		
	8.07 ± 0.02	1.000	256 ± 12		256 ± 12

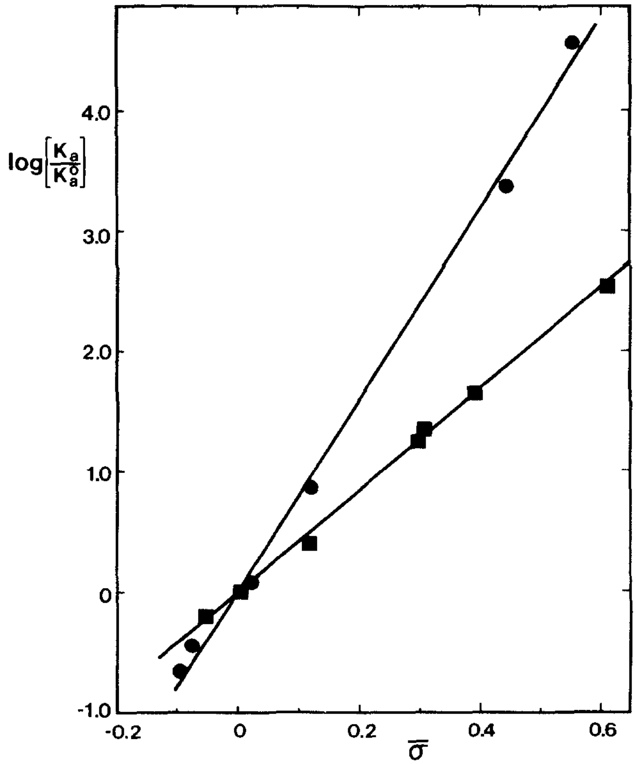


Fig. 1. Derived two-dimensional plots of the dual substituent parameter analysis of the pK_a's of the conjugate acids of substituted N,N-dimethylanilines using eqs. 15–18. (■), m-$XC_6H_4N(CH_3)_2$, $\bar{\rho} = 4.229$, $\lambda = 0.274$; (●), p-$XC_6H_4N(CH_3)_2$, $\bar{\rho} = 7.957$, $\lambda = 1.030$.

TABLE 3

EQUILIBRIUM CONSTANTS FOR FORMATION AND INTERCONVERSION OF NCS⁻ AND SCN⁻ LIGANDED *m*- and *p*-*N*,*N*-DIMETHYLAMINOPHENYLCOBALOXIMES[a]

Complex formed	Isomer	pH	K^{a}_{S-N}	K^{B}_{S-N}	K_f^A (M^{-1})	K_f^B (M^{-1})
Co-SCN⁻	*para*					72.6 ± 3.2
		8.04		0.0597 ± 0.0040		
Co-NCS⁻	*para*					4.33 ± 0.35
Co-SCN⁻	*para*				64.3 ± 3.0	
		2.09	0.132 ± 0.007			
Co-NSC⁻	*para*				8.49 ± 0.56	
Co-SCN⁻	*meta*					55.7 ± 3.0
		8.70		0.0890 ± 0.0140		
Co-NCS⁻	*meta*					4.96 ± 0.78
Co-SCN⁻	*meta*				64.2 ± 3.8	
		1.88	0.226 ± 0.030			
Co-NCS⁻	*meta*				14.5 ± 1.8	

[a] 25.0 ± 0.1°C, ionic strength 1.0 M. See Scheme 2 for definitions of the equilibrium constants and the text for the method of determination.

$$K_{\mathrm{SCN}}^{\mathrm{B}} = K_{\mathrm{f}}^{\mathrm{B}}/\left(1 + K_{\mathrm{S-N}}^{\mathrm{B}}\right) \tag{22}$$

$$K_{\mathrm{NCS}}^{\mathrm{A}} = K_{\mathrm{f}}^{\mathrm{A}}/\left(1 + 1/K_{\mathrm{S-N}}^{\mathrm{A}}\right) \tag{23}$$

$$K_{\mathrm{NCS}}^{\mathrm{B}} = K_{\mathrm{f}}^{\mathrm{B}}/\left(1 + 1/K_{\mathrm{S-N}}^{\mathrm{B}}\right) \tag{24}$$

from the equilibria described in Scheme 2 and the law of mass action. The values of the true formation constants for the *N*- and *S*-liganded species thus obtained are listed in Table 3.

Values of the pK_a's of the $H(CH_3)_2NC_6H_4Co(D_2H_2)L$'s (i.e. p$K_a^L$ in Schemes 1 and 2) for L = SCN^-, NCS^-, N_3^-, and *S*-methyl-2-mercaptoethanol were then calculated from eq. 14, based on the cyclic nature of the equilibria in Schemes 1 and 2 and are collected in Table 4 along with those for L = OH_2 and CN^- which were determined by direct spectrophotometric titration. These pK_a values were used in conjunction with eq. 1 and the susceptibility parameters determined from the basis set data (Table 1) to calculate the σ_I and $\sigma_{R(A)}^-$ substituent parameter values for the $Co(D_2H_2)L$ centers which are also given in Table 4. For comparison values of σ_I and σ_R^o for some of the same cobaloxime chelated cobalt centers previously determined in methanol from correlation of the ^{19}F NMR chemical shifts of *m*- and *p*-$FC_6H_4Co(D_2H_2)L$ via eq. 1 [4], and values of σ_I previously determined in aqueous solution (ionic strength 1.0 *M*) from correlation of $HOOCCH_2CH_2Co(D_2H_2)L$ acidities with those of other substituted propionic acids [3] are also listed in Table 4.

Comparison of the currently determined σ_I values with those previously determined in methanol (Table 4) shows rather poor agreement, the σ_I values in aqueous solution all being substantially less negative than those in methanol.

TABLE 4

pK_a's OF THE CONJUGATE ACIDS OF *N,N*-DIMETHYLAMINOPHENYL(LIGAND)COBALOXIMES AND SUBSTITUENT CONSTANTS FOR THE COBALOXIME CHELATED COBALT CENTERS[a]

L	Isomer	pK_a	σ_I [b]	$\sigma_{R(A)}^-$ [b]	σ_I [c]	σ_R^o [c]	σ_I [d]
OH_2	*para*	6.05 ± 0.01 [e]	−0.132	−0.013			−0.162
	meta	5.93 ± 0.01 [e]					
Co-SCN^-	*para*	6.00 ± 0.02 [f]	−0.161	+0.028	−0.284	−0.228	
	meta	5.99 ± 0.04 [f]					
Co-NCS^-	*para*	6.34 ± 0.04 [f]	−0.298	+0.076	−0.343	−0.217	
	meta	6.40 ± 0.05 [f]					
S-Methyl-2-mercapto ethanol	*para*	5.97 ± 0.02 [f]					
	meta	5.83 ± 0.02 [f]	−0.098	−0.026	−0.134	−0.253	−0.045
CN^-	*para*	6.45 ± 0.01 [e]	−0.239	−0.009	−0.452	−0.188	
	meta	6.28 ± 0.01 [e]					
N_3^-	*para*	5.91 ± 0.03	−0.149	+0.038			
	meta	5.94 ± 0.02					

[a] 25.0 ± 0.1°C, ionic strength 1.0 *M*. [b] This work. [c] Ref. 4, from ^{19}F NMR chemical shifts of *m*- and *p*-fluorophenyl(ligand)cobaloxime in MeOH. [d] Ref. 3, in aqueous solution, 25.0 ± 0.1°C, ionic strength 1.0 *M*. [e] From direct spectrophotometric titration. [f] Calculated from eq. 14.

However, this is not at all surprising considering our finding of substantial solvent effects on σ_I values of cobaloxime chelated cobalt centers in our study of $FC_6H_4Co(D_2H_2)L$ ^{19}F chemical shifts [4]. For instance, the value of σ_I for $Co(D_2H_2)L$, L = 4-carboxamidopyridine, was found to be -0.328 in DMSO but only -0.201 in methanol. The agreement between the currently determined σ_I values and those previously determined in aqueous solution [3] from carboxyethylcobaloxime pK_a's, despite the limited amount of data available for comparison, seems much better and gives some confidence that the current analysis has been carried out correctly and that the measurements are reasonably accurate.

It should, however, be pointed out that, in agreement with Taft's conclusions regarding solvent effects on σ_R parameters for electron donating substituents [21], we have found σ_R^o values for cobaloxime chelated cobalt centers to be remarkably insensitive to solvent effects [4]. Hence, the σ_R^o value for 4-carboxamidopyridine liganded cobaloxime centers was found to be -0.225 in DMSO and -0.252 in methanol [4], values which probably differ by less than the experimental error involved in their determination. Consequently, direct comparison of the currently determined $\sigma_{R(A)}^-$ values with our previous σ_R^o values should be possible. Inspection of the $\sigma_{R(A)}^-$ values in Table 4 shows that they are extremely small for all L and their signs are apparently randomly distributed. We can thus conclude that resonance interactions of the anilinium type (eq. 25) are negligible for cobaloxime chelated cobalt centers, the minor differences among the determined $\sigma_{R(A)}^-$ values probably falling within experimental error. This indicates the inability of the chelated cobalt centers to stabilize negative charge by acceptance of an electron pair into an unoccupied *d*-orbital. It should be pointed out that observations that $-\sigma_R^o > -\sigma_{R(A)}^-$ are quite common for substituents with relatively low-lying *d*-orbitals (such as SCH_3 and I) while substituents lacking such *d*-orbitals (such as CH_3, Cl and Br) have $-\sigma_R^o \equiv -\sigma_{R(A)}^-$ [6]. Hence the fact that $-\sigma_R^o > -\sigma_{R(A)}^-$ for cobaloxime chelated cobalt centers may be taken as evidence for involvement of the metal *d*-orbitals in the resonance interactions of these substituents.

(25)

We have also attempted to fit our data to the dual substituent parameter equation with non-linear resonance effects (DSP-NLR, eq. 26) of Bromilow et al. [22] in which a single set of resonance substituent constants, σ_R^o, is used for all correlations and variations in resonance interaction with different detecting groups are accounted for by ε, the resonance demand parameter, which is treated as a fit parameter. A comparison of the fit of our basis set data (Table 1) via eq. 1 (DSP with $\sigma_{R(A)}^-$ values) and via eq. 26 (DSP-NLR with σ_R^o values [6]) is shown in Table 5. Only in the case of the *meta-N,N*-dimethylanilinium pK_a's, in which resonance contributions are minor and the maximized value of the demand parameter, ε, is very close to zero, does the DSP-NLR give a comparable fit to the DSP. In the case of the *para*-data set the DSP-NLR fit is considerably worse than that provided by the DSP and does not meet Taft's criterion for a good fit (i.e. $f < 0.1$) [6]. In order to insure that this

$$P^i = \sigma_I \rho_I^i + \sigma_R^o \rho_R / (1 - \varepsilon \sigma_R^o) \qquad (26)$$

TABLE 5

FIT PARAMETERS FOR DSP AND DSP-NLR CORRELATIONS OF ANILINIUM AND *N*,*N*-DIMETHYLANILINIUM pK_a's

Data set	Subst. position	Ref.	DSP-$\sigma_{R(A)}^-$				DSP-NLR			
			N	ρ_I	ρ_R	*f*	ρ_I	ρ_R	ϵ	*f*
N,*N*-Dimethylanilinium	*para*	This work	7	3.919	4.038	0.051	2.950	7.529	3.7	0.107
N,*N*-Dimethylanilinium	*meta*	This work	7	3.320	0.910	0.035	3.550	1.261	−0.05	0.040
N,*N*-Dimethylanilinium	*para*	[23]	6	3.753	4.075	0.039	4.101	7.333	1.9	0.084
N,*N*-dimethylanilinium	*meta*	[23,24]	6	4.106	−0.517	0.046	4.225	−0.571	5.0	0.043
Anilinium	*para*	[23,24]	12	3.224	3.337	0.052	3.964	5.193	0.6	0.131
Anilinium	*meta*	[23,24]	10	2.968	0.598	0.053	3.189	0.702	−0.6	0.068

comparison is not biased by some non-random variation in our data sets (particularly the fact that our pK_a's have been determined at ionic strength 1.0 M) we have applied both the DSP and DSP-NLR treatments to data sets of thermodynamic pK_a values of *m*- and *p*-*N*,*N*-dimethylanilinium ions and anilinium ions taken from the literature (Table 5). Again, only for the *meta* data sets are the DSP-NLR and DSP correlations of comparable precision and while the DSP-NLR fit for the *para*-*N*,*N*-dimethylanilinium ions is "good" by Taft's criterion ($f = 0.084$) it is far less good than the DSP correlation ($f = 0.039$). Furthermore, the wide variation in the maximized value of the demand parameter, ε, required to give the best DSP-NLR fits for the *para* data sets fails to inspire great confidence in this method. We conclude that while the DSP-NLR clearly has many useful applications [22], it does not represent an improvement over the DSP for correlations of anilinium pK_a's.

Acknowledgement

This research was supported by the Robert A. Welch Foundation, Houston, Texas, Grant #Y-749.

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