Substituent Effects on Proton Affinities of Cyanide Ligands in Some Mixed Ligand Iron(II) Complexes

Alfred A. Schilt and Tom W. Leman[1]

ontribution from the Department of Chemistry, Northern Illinois University, eKalb, Illinois 60115. *Received December 12, 1966*

Abstract: A number of substituted 1,10-phenanthroline–iron(II) cyanide complexes of the type $[Fe(phen)_2(CN)_2]$ were prepared, and their relative basicities were determined by proton-exchange measurements in glacial acetic acid. A linear relationship was found between the ligand pK_a and the logarithm of the exchange constant. Infrared spectra show that the substituent groups have very little effect on cyanide stretching frequencies. These findings can be rationalized in terms of electronic theory.

In an earlier study of some mixed ligand complexes of iron(II) and iron(III) it was discovered that dicyanobis(1,10-phenanthroline)iron(II) and dicyanobis(2,2′-bipyridine)iron(II) form stable protonated species.[2] Further investigation revealed that these complexes react reversibly with strong acids and exhibit measurable dibasic character.[3] Subsequent work demonstrated that the cyanide ligands are responsible for the observed proton affinities.[4,5]

A later phase of inquiry concerns the role of various structural features on proton affinities. It is of interest to determine the effects of changes both in the central metal ion and in the aromatic diimine ligand. A study of the influence of the metal ion was reported previously.[5] The present study was undertaken to evaluate the effects of various substituent groups on the proton affinities of some iron(II) complexes of substituted 1,10-phenanthrolines and cyanide.

In addition to theoretical considerations, a practical impetus for studies of this type is the prospect of discovering new analytical reagents. Some tangible benefits have already been realized from studies of mixed ligand complexes.[6]

Experimental Section

Preparation of Complexes. Dicyanobis(1,10-phenanthroline)iron(II) dihydrate was available from a previous study;[2] the substituted derivatives were prepared similarly except for some slight but important procedural modifications. A solution of the tris chelate of iron(II) and the substituted phenanthroline, prepared by mixing 1.00 mmole of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, 3.00 mmoles of the phenanthroline, and 250 ml of water, was treated with potassium cyanide to obtain the desired complexes. Conditions and amounts of potassium cyanide suitable for preparation of the various complexes differed. To prepare the 5-nitro derivative, 2 mmoles of KCN was added to the solution of the tris chelate at room temperature; the purple precipitate that formed was washed generously with 1 *M* sulfuric acid, dilute ammonia, and finally water. The 5-phenyl derivative was obtained by adding 1 g of KCN to the tris chelate solution at the boiling temperature; after cooling to room temperature, the violet product was collected and washed generously with 2 *M* sulfuric acid, dilute ammonia, and finally water. All the other products were prepared by adding 4 g of KCN to boiling solutions of the tris chelates followed by continued heating near boiling for 10–15 min. The 5-chloro and 4,7-diphenyl derivatives were recrystallized from concentrated sulfuric acid by dilution with water and washed with dilute ammonia followed by generous amounts of water. The 5-methyl and 4,7-dimethyl derivatives were washed with water only, since the expected contaminates are known to be water-soluble. All products were dried *in vacuo* at room temperature. Results of analyses are given in Table I.

Spectrophotometric Titrations and Exchange Constants. Procedural details have been described earlier.[3] Measurements involving the 5-nitro derivative proved unreliable because of its low solubility in acetic acid. Also the complex apparently undergoes decomposition in the presence of perchloric acid, since absorbancy measurements decreased appreciably with time.

Reagents and Apparatus. Reagent grade chemicals were used. The thiourea was recystallized from ethanol and dried *in vacuo* prior to use. The *o*-chloroaniline was purified by repeated fractional crystallization followed by distillation. Perchloric acid solutions in acetic acid were prepared according to Fritz[7] and standardized against potassium acid phthalate.

Absorption spectra were recorded with a Cary Model 14 spectrophotometer. Infrared spectra of the solids in Nujol mulls were measured using a Beckman IR-8 instrument. A Beckman Model DU spectrophotometer was used to measure absorbancies at individual wavelengths of analytical interest.

Results and Discussion

With the exception of the 5-nitro derivative, all of the mixed ligand complexes could be titrated spectrophotometrically in glacial acetic acid with standard perchloric acid. The titration data provided several bits of useful information about each complex: number of protonated species formed and their identities, formula weight of the complex, and spectral characteristics of the various species. Titration of the dicyanobis(1,10-phenanthroline)iron(II), although previously described,[3] was repeated for purpose of confirmation. The spectrophotometric results, with well-defined isosbestic points appearing in all cases, conclusively demonstrated that three equilibria species are involved for each complex: the non-, mono-, and diprotonated forms. In each case the first equivalence point was distinct and precisely determinable; the second was just discernible. Formula weights were calculated on the basis of the first end point. Further use of the titration data was made in evaluating molar absorptivities of the various species at analytically significant wavelengths. Values for the monoprotonated complexes were deduced from the first equivalence point in the spectrophotometric titration curves by the usual extrapolation procedure. Spectral constants for the neutral and for the diprotonated complexes (in the presence of a 500-fold excess of $HClO_4$) were measured directly. The

---

(1) National Science Foundation Summer Research Participant.

(2) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).

(3) A. A. Schilt, *ibid.*, **82**, 5779 (1960).

(4) N. K. Hamer and L. E. Orgel, *Nature*, **190**, 439 (1961).

(5) A. A. Schilt, *J. Am. Chem. Soc.*, **85**, 904 (1963).

(6) (a) A. A. Schilt, *Anal. Chem.*, **30**, 1409 (1958); (b) *Anal. Chim. Acta*, **26**, 134 (1962); (c) *Anal. Chem.*, **35**, 1599 (1963); (d) A. A. Schilt and A. V. Nowak, *ibid.*, **36**, 845 (1964); (e) A. A. Schilt and J. W. Sutherland, *ibid.*, **36**, 1805 (1964); (f) A. A. Schilt and A. M. Cresswell, *Talanta*, **13**, 911 (1966).

(7) J. S. Fritz, "Acid Base Titrations in Nonaqueous Solvents," G. Frederick Smith Chemical Co., Columbus, Ohio, 1952.

Table I. Analysis of Complexes

Formula of complex	Calculated: Formula wt	%C	%H	%N	Found: Formula wt	%C	%H	%N
[Fe(5-Me-phen)$_2$(CN)$_2$]·3H$_2$O	550	61.1	4.76	15.3	545	61.8	4.93	15.2
[Fe(5-Ph-phen)$_2$(CN)$_2$]·3H$_2$O	675	67.7	4.48	12.5	692	69.9	4.58	12.6
[Fe(5-Cl-phen)$_2$(CN)$_2$]·2H$_2$O	573	54.5	3.17	14.7	577	56.1	3.24	14.2
[Fe(5-NO$_2$-phen)$_2$(CN)$_2$]·2H$_2$O	594	52.5	3.05	18.9	...	51.6	3.04	18.8
[Fe(4,7-Me$_2$-phen)$_2$(CN)$_2$]·4H$_2$O	596	60.4	5.41	14.1	590	61.0	5.44	14.4
[Fe(4,7-Ph$_2$-phen)$_2$(CN)$_2$]·3H$_2$O	827	72.6	4.63	10.2	831	73.1	4.64	10.2

Table II. Absorption Characteristics in Acetic Acid

Complex [Fe(P)$_2$(CN)$_2$] where P represents	Wave-length, mμ	Molar absorptivities of species[a]: X	X·HClO$_4$	X·2HClO$_4$
1,10-Phenanthroline	545	7720	1660	138
	463	6080	6080	1140
	363	674	2300	5260
5-Methyl-1,10-phenanthroline	545	7680	1190	365
	463	6230	6230	1370
	363	739	2640	5160
5-Phenyl-1,10-phenanthroline	545	8260	1055	380
	470	6790	6790	1830
	363	1240	2510	5430
5-Chloro-1,10-phenanthroline	550	7730	854	237
	475	5690	5690	1710
	363	1090	1610	4460
4,7-Dimethyl-1,10-phenanthroline	530	9100	942	179
	463	7040	7040	1300
	363	1120	2180	6760
4,7-Diphenyl-1,10-phenanthroline	559	11980	1650	278
	484	9720	9720	1910
	363	2270	3130	10730

[a] Where X, X·HClO$_4$, and X·2HClO$_4$ represent the non-, mono-, and diprotonated complexes, respectively.

Table III. Equilibrium (Proton-Exchange) Constants[a] in Acetic Acid

Complex [Fe(P)$_2$(CN)$_2$] where P represents	Reference base: o-Chloroaniline K_1	o-Chloroaniline K_2	Thiourea K_1	Thiourea K_2
1,10-Phenanthroline	1.1 ± 0.1	0.04 ± 0.01	52 ± 5	0.15 ± 0.05
5-Methyl-1,10-phenanthroline	1.3 ± 0.2	0.06 ± 0.02	61 ± 6	0.18 ± 0.05
5-Phenyl-1,10-phenanthroline	0.91 ± 0.05	0.09 ± 0.05	43 ± 6	0.12 ± 0.02
5-Chloro-1,10-phenanthroline	0.40 ± 0.05	0.04 ± 0.01	19 ± 1	0.08 ± 0.02
4,7-Dimethyl-1,10-phenanthroline	1.7 ± 0.3	0.15 ± 0.04	95 ± 2	0.28 ± 0.04
4,7-Diphenyl-1,10-phenanthroline	0.80 ± 0.05	0.03 ± 0.01	49 ± 2	0.11 ± 0.01

[a] The constants K_1 and K_2 refer, respectively, to the following equilibria in acetic acid: (1) complex + B·HClO$_4$ = B + complex·HClO$_4$; (2) complex·HClO$_4$ + B·HClO$_4$ = B + complex·2HClO$_4$. The reference base is represented as B. Each value in the table is the mean of four or more independent measurements; all measurements fall within the stated limits.

results are compiled in Table II and were employed in exchange constant measurements. The three different wavelengths selected for analysis in each case (see Table II) were the following: (1) the wavelength of maximum absorbance of the nonprotonated complex (530–559 mμ), (2) the isosbestic point of the non- and monoprotonated species (463–484 mμ), and (3) 363 mμ, a wavelength where all of the diprotonated complexes absorb strongly (not necessarily at maximum absorbance but a convenient, reproducible wavelength setting).

Results of the proton-exchange-constant measurements are given in Table III. Values obtained for the unsubstituted derivative, dicyanobis(1,10-phenanthroline)iron(II), compare favorably with those found previously.[3] Measurements on this complex were repeated for the present study to provide a set of internally consistent data. All of the constants in Table III are based upon measurements made using the same solvent batch, spectrophotometer, titrant solution, and samples of reference bases. Hence the relative proton affinities of the complexes should be reliably indicated by the constants. The nature of the measurements is such that optimum accuracy and precision are obtained when the reference base and mixed ligand complex have identical proton affinities. For this reason, the values of K_1 with *o*-chloroaniline and of K_2 with thiourea could be more reliably determined than the others.

Figure 1 shows that the logarithm of the exchange constant is linearly related to the pK_a of the phenanthroline ligand. The four series of plots are essentially linear and have approximately the same slopes. Additivity of free-energy relationships is indicated. This is convincing evidence that the major influences of the substituent groups are due to electronic factors. Electron donor substituents that increase the basicity of the phenanthroline (increase pK_a) also increase the basicities of the cyanide ligands. Conversely, electron-withdrawing substituents decrease the basicity of both.

The ligand pK_a values, employed in constructing Figure 1, are literature values or averages in cases where two or more have been reported. Values are 4.91 for unsubstituted,[8–10] 5.26 for 5-methyl-,[9,11,12] 4.76 for 5-phenyl-,[8,9] 4.26 for 5-chloro-[9], 5.94 for 4,7-dimethyl-,[11,13] and 4.84 for 4,7-diphenyl-1,10-phenanthroline.[8]

The fact that the basicities of the cyanide ligand are

---

(8) A. A. Schilt and G. F. Smith, *J. Phys. Chem.*, **60**, 1546 (1956)

(9) W. W. Brandt and D. K. Gullstrom, *J. Am. Chem. Soc.*, **74**, 3532 (1952).

(10) K. Yamasaki and M. Yasuda, *ibid.*, **78**, 1324 (1956).

(11) M. Yasuda, K. Sone, and K. Yamasaki, *J. Phys. Chem.*, **60**, 1667 (1956).

(12) W. A. E. McBryde, D. A. Brisbin, and H. Irving, *J. Chem. Soc.*, 5245 (1962).

(13) D. A. Brisbin and W. A. E. McBryde, *Can. J. Chem.*, **41**, 1135 (1963).

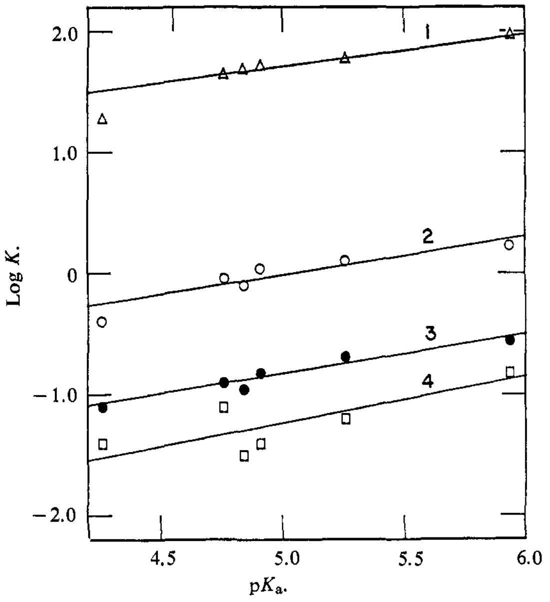

Figure 1. Plots of logarithm of exchange constant *vs.* ligand pK_a: (1) K_1 with thiourea; (2) K_1 with *o*-chloroaniline; (3) K_2 with thiourea; and (4) K_2 with *o*-chloroaniline.

affected by far-removed substituents in the phenanthroline ligands can be rationalized in the following manner. Electron donor groups tend to increase electron density between iron and the phenanthroline nitrogen atoms. Consequently the tendency for iron to back-donate electrons to cyanide is enhanced (increased π bonding); also the tendency for iron to withdraw electron density from the cyanide ligands is diminished (decreased σ bonding). Either or both effects would give rise to increased electron density about the cyanide nitrogens, thereby increasing their affinity for protons.

Infrared spectra of the complexes were examined to determine what effects substituent groups in phenanthroline have on the carbon–nitrogen force constant of the cyanide ligands. The C≡N stretching frequencies (given in Table IV) proved to be nearly the same for all. This was indeed surprising. If the substituent groups influence basicity of cyanide ligands by electronic effects, then the carbon–nitrogen force constant should seemingly also be affected. A rational explanation, consistent with the one given above for basicity, can be offered. According to Jones, an increase in π bonding between iron and cyanide is accompanied by a decrease in the carbon–nitrogen force constant, whereas a decrease in σ bonding increases the force constant.[14] Hence C≡N stretching frequencies would be essentially unaffected if an increase in π bonding were to be accompanied by a proportionate decrease in σ bonding and *vice versa.* This is apparently the case for the complexes studied here.

Table IV. Cyanide Stretching Frequencies of Solids as Nujol Mulls

	Absorption frequencies, cm^{-1}
$[Fe(phen)_2(CN)_2]\cdot 2H_2O$	2075, 2062
$[Fe(5\text{-}Me\text{-}phen)_2(CN)_2]\cdot 3H_2O$	2072
$[Fe(5\text{-}Ph\text{-}phen)_2(CN)_2]\cdot 3H_2O$	2079
$[Fe(5\text{-}Cl\text{-}phen)_2(CN)_2]\cdot 2H_2O$	2079
$[Fe(5\text{-}NO_2\text{-}phen)_2(CN)_2]\cdot 2H_2O$	2083
$[Fe(4,7\text{-}Me_2\text{-}phen)_2(CN)_2]\cdot 4H_2O$	2079
$[Fe(4,7\text{-}Ph_2\text{-}phen)_2(CN)_2]\cdot 3H_2O$	2083

On the basis of the spectral and basicity measurements, and the above considerations, it is concluded that substituent groups alter the proton affinities of cyanide ligands by electronic effects. Substituents that tend to withdraw electrons from phenanthroline nitrogen atoms tend to decrease π bonding and increase σ bonding between iron and cyanide, thereby decreasing the basicities of the cyanide nitrogens. Conversely, electron donation by substituents affects bonding and basicities in the opposite fashion.

The possibility that steric factors are operative and significant in determining relative basicities cannot be dismissed entirely. However, any gross steric effect should be manifested by a significant deviation in the plots of Figure 1. None are discernible. The substituent groups in the phenanthroline rings, for the complexes studied here, are quite distant and directed away from the chelate rings, so that they should not clash nor otherwise hinder activity at the cyanide ligands. Whether the complexes in solution have the *cis* or a *trans* configuration and what effect protonation might have on the configuration of the cyanide ligands are unknown factors. The presence of a single infrared absorption band in the C≡N stretch region suggests that the substituted complexes have the *trans* configuration in the solid state. The configuration and infrared spectra of the unsubstituted dicyanobis(1,10-phenanthroline)iron(II) and related compounds, including osmium and ruthenium, were discussed in an earlier study.[15]

(14) L. H. Jones, *Inorg. Chem.*, 2, 777 (1963).

(15) A. A. Schilt, *ibid.*, 3, 1323 (1964).