Reactions of Coordinated Ligands. VII. The Structure and Reactivity of Iron(II) Benzyl Isonitrile Complexes[1]

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Dicyanotetrakis-(benzyl isonitrile)-iron(II) (I), cyanopentakis-(benzyl isonitrile)-iron(II) hydrogen sulfate (II), and hexakis-(benzyl isonitrile)-iron(II) sulfate (III) are all nitrated preferentially in the *para* position contrary to expectations based on the electronegativity of the uncoordinated methylene isonitrile group. No change in the distribution of isomers in nitration of III is achieved by replacing one or two benzyl isonitrile ligands (*i.e.*, I, II) in III by cyanide ligands. Replacement of benzyl isonitrile ligands in III by cyanide groups does alter the reactivity of the first aromatic ring nitrated in I and II, the reactivity of II toward NO_2^+ being the greatest. This increased nucleophilicity in one of the aromatic rings in II is attributed to a *trans* effect. Powerful electron-withdrawing groups in the *para* position of the benzyl isonitrile ligand facilitate the cyanide exchange in II and decrease the nucleophilicity of the cyanide group(s) toward further alkylation in a partially alkylated complex.

Introduction

The reactions and reactivities of a ligand may well be changed when coordinated to a metal. Further modifications may be introduced by the other ligands present in the complex.

We have found previously that benzyl isonitrile iron-(II) complexes are very stable toward concentrated acid and bases.[2] Our prior work showed further that the reactivity of cyanopentakis-(benzyl isonitrile)-iron(II) hydrogen sulfate toward the nitronium ion (NO_2^+) is greater than the reactivity anticipated for benzyl isonitrile.[3] We have also found[3] that contrary to expectations an electrophile is introduced predominantly into the *para* position of the aromatic ring(s) of the above complex. Hence it was of interest to determine precisely the extent of the *o*, *m*, *p* isomer distribution in a typical electrophilic reaction with cyanopentakis-(benzyl isonitrile)-iron(II) hydrogen sulfate and how the isomer distribution would vary with the introduction of each subsequent substituent.
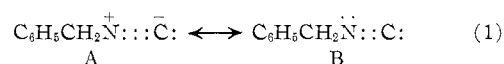
Theoretically the reactions and reactivity of one ligand could be further influenced by the other ligands in the complex. Therefore, the nitration of the aromatic rings in dicyanotetrakis-(benzyl isonitrile)-iron(II) (I), cyanopentakis-(benzyl isonitrile)-iron-(II) hydrogen sulfate (II), and hexakis-(benzyl isonitrile)-iron(II) sulfate (III) was investigated as a model electrophilic reaction system with the results reported in the present communication.
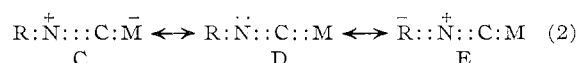
Results

A. Spectroscopic Studies.—The infrared spectra of several benzyl isonitrile iron(II) complexes are summarized in Table I. Two bands appear in the triple bond stretching frequency region. One at *ca.* 2200 cm.$^{-1}$ was assigned to the isonitrile stretching frequency and the other at 2092 cm.$^{-1}$ was assigned to the cyanide

stretching frequency, since this band is absent in isonitrile complexes which do not contain cyanide groups.

Two resonance structures may be written for benzyl isonitrile

$$C_6H_5CH_2\overset{+}{N}:::\overset{-}{C}: \longleftrightarrow C_6H_5CH_2\overset{..}{N}::C: \qquad (1)$$
$$A \phantom{:::\overset{-}{C}: \longleftrightarrow C_6H_5CH_2}B$$

The abundant physical evidence on the molecular structure of isonitriles, namely, infrared and Raman spectra,[4] nuclear magnetic resonance,[5] electron diffraction studies,[6] and dipole moment measurements,[7] indicate that the isonitrile group is best represented by the polar structure A. When coordinated to a metal, the isonitrile ligand can act both as a donor (C) as well as an acceptor of electrons (D)

$$\overset{+}{R}:\overset{..}{N}:::C:\overset{-}{M} \longleftrightarrow R:\overset{..}{N}::C::M \longleftrightarrow \overset{-}{R}::\overset{+}{N}::C:M \qquad (2)$$
$$C D E$$

As the charge on the central metal atom M increases the polar structure C is further favored and hence should be the predominant resonance form in the benzyl isonitrile iron(II) complexes investigated.[8] As the number of isonitrile groups increases from four to six (see Table I) the isonitrile band is further shifted toward higher wave numbers. This indicates that the contribution of resonance form D is greatest in hexakis-(benzyl isonitrile)-iron(II) bromide and that the isonitrile group is a better electron acceptor than the cyanide group. *para* Substituents, except for the strongly electron withdrawing carbomethoxy group, have relatively little influence on the isonitrile stretching frequency (Table I). The carbomethoxy group does split the isonitrile group into two bands, one intense band at 2207 cm.$^{-1}$ and one shoulder at 2168 cm.$^{-1}$. The

(1) Presented in part at the symposium on "Reactions of Coordinated Ligands and Homogeneous Catalysis," reprinted in Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p. 99. Part VI of this series: W. Z. Heldt. *J. Org. Chem.*, **27**, 2608 (1962).

(2) W. Z. Heldt, *J. Inorg. Nucl. Chem.*, **22**, 305 (1961).

(3) W. Z. Heldt, *J. Org. Chem.*, **27**, 2604 (1962).

(4) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, "Infrared and Raman Spectra of Polyatomic Molecules," D. van Nostrand Co., Inc., Princeton, N. J., 1959, pp. 332–334.

(5) (a) I. D. Kuntz, Jr., P. von R. Schleyer, and A. Allerhand, *J. Chem. Phys.*, **35**, 1533 (1961); (b) L. L. Ferstandig, *J. Am. Chem. Soc.*, **84**, 1323 (1962); (c) L. L. Ferstandig, *ibid.*, **84**, 3553 (1962).

(6) W. Gordy and L. Pauling, *ibid.*, **64**, 2952 (1942).

(7) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp. 249, 283, 317, and 321.

(8) (a) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961); (b) W. P. Griffith, *Quart. Rev.* (London), **16**, 108 (1962).

TABLE I

INFRARED SPECTRA OF ISONITRILE COMPLEXES[a]

| Compound | CNR str. freq., cm.$^{-1}$ (± 5 cm.$^{-1}$) | | $\Delta\nu$ (complexed − free) $C_6H_5CH_2NC$ | | CN str. freq., cm.$^{-1}$ (± 5 cm.$^{-1}$) | |
	In CHCl$_3$	In KBr wafer	In CHCl$_3$	In KBr wafer	In CHCl$_3$	In KBr wafer
$C_6H_5CH_2NC$	2146	...	...	...	...	...
$(C_6H_5CH_2NC)_4Fe(CN)_2$	2180	2165	(+)34	(+)19	2092	2130
$(C_6H_5CH_2NC)_5FeCNBr$	2200	2200	(+)54	(+)54	2092	2130
$(C_6H_5CH_2NC)_6FeBr_2$	2223	2220	(+)77	(+)74		
$(o\text{-}CH_3C_6H_4NC)_5FeCNBr$	2190				2120	
$(m\text{-}CH_3C_6H_4NC)_5FeCNBr$	2190				2125	
$(p\text{-}CH_3C_6H_4CH_2NC)_5FeCNBr$	2190				2115	
$(p\text{-}ClC_6H_4CH_2NC)_5FeCNBr$	2189				2125	
$(p\text{-}CH_3O_2CC_6H_4CH_2NC)_5FeCNBr$	2207, 2168				2087	

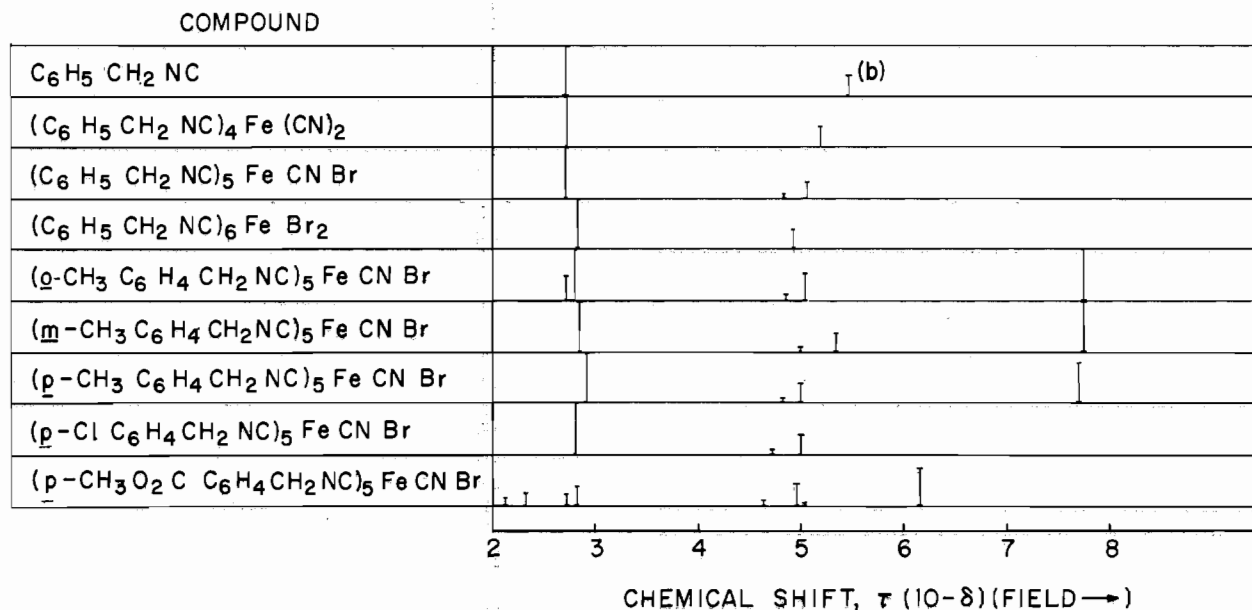[a] Perkin-Elmer Model 21 instrument, double-beam, NaCl prisms.

Fig. 1.—Proton nuclear magnetic resonance spectra of iron(II) benzyl isonitrile complexes: (a) Instrument, A-60 n.m.r. spectrometer, manufactured by Varian Associates, Palo Alto, Calif. Spectra were taken in CDCl$_3$ internally referenced *vs.* (CH$_3$)$_4$Si. The height of the lines represents relative intensities of bonds in one complex. (b) Triplet centered at $\tau = 5.43$, $J_{NH} = 2$ c.p.s.

latter band may indeed indicate that one isonitrile group is best represented by resonance structures such as D and E.

The proton nuclear magnetic resonance spectra are summarized in Fig. 1. All lines are singlets unless otherwise indicated. The relative intensities of the absorption bands check well with the assigned structures. The relative intensities of the bands of I (Fig. 1) were 5 ($\tau = 2.73$) and 2 ($\tau = 5.20$), representing the aromatic hydrogen and methylene hydrogen, respectively. In II (Fig. 1) the intensities were 25 ($\tau = 2.72$), 2 ($\tau = 4.82$), and 8 ($\tau = 5.08$), indicating 25 aromatic hydrogens and 5 methylene groups of which one is different from the other four. Since this shift of one methylene group occurs only in the pentakis-(benzyl isonitrile) complexes (Fig. 1), it must be the methylene group *trans* to the cyanide which is shifted downfield from (CH$_3$)$_4$Si to 4.82 τ.

According to Dailey and Shoolery in a system such as XCH$_2$X' there is a close relationship between the deshielding of neighboring protons by substituent X and

its electronegativity.[9] As the number of isonitriles in a complex is increased from four to six, a progressive deshielding of the methylene groups is, in fact, observed. This observation checks with the conclusions derived from infrared data; namely, that, with progressive increase in the number of isonitrile groups in the complex the resonance form best representing the coordinated isonitrile group is C. A plot of the CNR stretching frequency of the ligands *vs.* the chemical shift, τ, of the methylene group of the ligands yields a linear relationship (Fig. 2). Quantitatively the Dailey–Shoolery scale may be expressed by

$$\tau\text{-alkyl} = 9.767 - \sum_i \sigma i_{\text{eff}} \qquad (3)$$

where τ-alkyl is the proton frequency in the system XCH$_2$X', 9.767 is the τ value for methane, and σi_{eff} is the effective shielding constant of X'. Assuming the value of τ-alkyl to be[9] 7.92, then the shielding constant

(9) (a) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955); (b) C. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N.Y., 1959, p. 59.
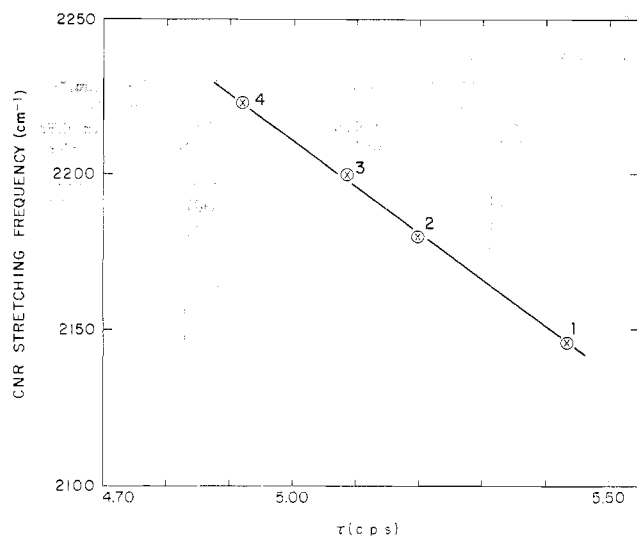
Fig. 2.—A linear relationship between the CNR stretching frequency and the proton chemical shift (τ) for $-CH_2-$ in benzyl isonitrile complexes: 1, benzyl isonitrile; 2, $(C_6H_5CH_2NC)_4$-$Fe(CN)_2$; 3, methylene groups *cis* to cyanide in $(C_6H_5CH_2NC)_5$-$FeCNBr$; 4, $(C_6H_5CH_2NC)_6FeBr_2$.

for the isonitrile group can be calculated in various environments; for example, in benzyl isonitrile it is 2.49; in complex I it is 2.72; in II it is 2.84; and in III, 3.00.

B. Assignment of Stereoconfiguration to Dicyano-tetrakis-(benzyl isonitrile)-iron (II).—Only one dicyano-tetrakis-(benzyl isonitrile)-iron(II) complex, m.p. 229–230° (I), was obtained by various routes in our work. Assuming that the complex is octahedral,[10] the stereoconfiguration of this complex could hence be *cis* or *trans*. The *trans* configuration was assigned to this complex on the basis of proton n.m.r. studies and Raman spectra.

As was pointed out above, a cyanide group located in the *trans* position to a benzyl isonitrile group displaced the proton frequency of the methylene group downfield as compared to the proton frequency of the benzyl isonitrile ligand *trans* to another benzyl isonitrile ligand. Since all methylene groups in the dicyanotetrakis-(benzyl isonitrile)-iron(II) complex are equivalent (Fig. 1), the *trans* structure is suggested by this evidence.

Additional support for this *trans* assignment may be derived from a comparison of the infrared and Raman spectra of this complex in chloroform as the solvent. The symmetry group of the *trans* isomer of I should be D_{4h} and of the *cis* isomer C_{2v}.[11,12] Hence, the infrared spectrum of the D_{4h} group should contain one active CN line and one active RNC line not coincident with one active polarized CN Raman line and two active (one polarized and the other depolarized) RNC Raman lines. The C_{2v} symmetry group requires that the in-

frared and Raman vibrations for CN and RNC, including the polarized Raman lines, be coincident.

After several recrystallizations from acetic anhydride, the yellowish tint of compound I almost disappeared and its Raman spectrum could be determined in chloroform using the blue mercury line excitation. The Raman spectrum of I in chloroform was rather poorly resolved but it showed four lines: a band centered at 2180 cm.$^{-1}$ consisting apparently of two lines at 2170 and 2190 cm.$^{-1}$, a sharp line at 2225 cm.$^{-1}$, and one broad band at 3065 cm.$^{-1}$. The infrared spectrum of the same compound in chloroform showed two sharp lines in the triple bond stretching region: 2180 cm.$^{-1}$ assigned to the RNC groups and 2092 cm.$^{-1}$ assigned to the CN groups (see Table I). The noncoincidence of the infrared and Raman active lines lends support to the D_{4h} assignment and hence to the *trans* assignment for compound I.[13]

C. Polarographic Studies.—Diffusion current *vs.* concentration studies were made on compounds I, II, and III. The half-wave potentials ($E_{1/2}$) measured *vs.* a saturated calomel electrode in absolute methanol are summarized in Table II. The reduction current of I

TABLE II
POLAROGRAPHIC STUDIES[a]

Compound	$E_{1/2}$, v.[b]	i_d μa.	Approx. no. of electrons transferred
$(C_6H_5CH_2NC)_4Fe(CN)_2$	−1.6	[c]	
$(C_6H_5CH_2NC)_5FeCNHSO_4$	−1.2	2.4	1.6
	−1.45	2.6	1.7
	−1.62	5.9	3.9
$(C_6H_5CH_2NC)_6FeSO_4$	−1.3	9.3	6.2
	−1.78	[c]	

[a] The reductions were carried out in absolute methanol solution (dropping mercury *vs.* saturated calomel electrode) at 25°. Concentration of isonitrile complexes = 1.0×10^{-3} M, supporting electrolyte, $LiClO_4$ (0.1 M). (The limiting potential range in this system was (+)0.5 to (−)1.9 v.) [b] Values for each compound correspond to first, second, and third waves. [c] Merges with cut-off and could not be accurately measured.

increased quite sharply from −1.6 v. but merged with the cut-off blank at −1.9 v. before any plateau was noted. Compound II gave three well defined reduction waves at −1.2, −1.45, and −1.62 v. Compound III yielded two reduction waves, the first ill-defined and the second merging with the cut-off blank having an $E_{1/2}$ of approximately −1.30 and −1.78 v.

By application of the Ilkovič equation to the overall reduction employing 6×10^{-6} cm.^{2}/sec. as an approximate diffusion coefficient for I, II, and III (a value frequently found for diffusion coefficients of many ions and organic molecules),[14] the number of electrons involved with each reduction wave can be

(10) H. M. Powell and G. W. R. Bartindale, *J. Chem. Soc.*, 799 (1945).

(11) (a) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. van Nostrand Co., Inc., Princeton, N. J., 1945, pp. 11, 105, and 134; (b) H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1944, p. 376.

(12) The author wishes to thank Dr. J. R. Downing for the assignments of infrared and Raman lines.

(13) This conclusion is correct if the assignment of I to the D_{4h} and C_{2v} classes is not altered substantially by the slight out-of-plane bending of the CH_2$^-$ bond.[10]

(14) L. Meites, "Polarographic Techniques," Interscience Publishers, Inc., New York, N. Y., 1950, p. 73.

TABLE III

RELATIVE ISOMER DISTRIBUTION IN THE NITRATION OF BENZYL ISONITRILE COMPLEXES

Complex	Reaction med. H_2SO_4 in vol., %	Moles of NO_2 introduced into 1 mole of complex Calcd.	Moles of NO_2 introduced into 1 mole of complex Found[a]	Methyl nitrobenzoates expressed in % o	Methyl nitrobenzoates expressed in % m	Methyl nitrobenzoates expressed in % p
$(C_6H_5CH_2NC)_4Fe(CN)_2$ (I)	100	1		14.9	29.7	55.2
	82	1	1.0	15.4	28.1	58.5
	82	2	1.8	16.2	23.6	60.2
	82	3	2.7	15.7	23.2	62.0
	82	4	3.7	15.8	25.7	59.0
$(C_6H_5CH_2NC)_5FeCNHSO_4$ (II)	100	1		10.2	45.5	44.3
	82	1	1.0	18.0	23.7	60.5
	82	2		16.5	22.0	61.5
	82	3		16.8	23.2	60.0
	82	4		15.2	26.0	59.0
$(C_6H_5CH_2NC)_6FeSO_4$ (III)	100	1		0.4	36.2	63.0
	82	1	1.0	14.6	23.7	61.8
	82	2		12.6	25.5	62.0
	82	3		13.8	25.9	59.8
	82	4		14.0	27.6	58.2
	82	6		12.3	27.5	60.5

[a] Determined by ultimate analysis for mononitrated complexes, reduction of nitro groups by Ti(III) (ref. 15), and an infrared spectroscopic method (ref. 3) for polynitrated complexes of I.

estimated. These values are summarized in Table II. These values for the number of electrons transferred are necessarily tentative until further data become available, which should then allow us to ascertain whether the currents measured are due to kinetic effects in the vicinity of the dropping mercury electrode.

D. Nitration Studies.—We have found previously that the aromatic rings in II can be easily nitrated, brominated, sulfonated, and alkylated.[3] In this prior work the nitrated products were chromatographed prior to analysis, and the nitrated isonitrile complexes were oxidized with alkaline potassium permanganate, yielding 60–72% of nitrated benzoic acids. After esterification with diazomethane the relative concentrations of the isomeric methyl nitrobenzoates were determined by an infrared spectroscopic method. The *para* isomer was the predominant or only isomer isolated by this procedure.

To obtain results on a quantitative basis we now employed 82% (by volume) sulfuric acid as the reaction medium in the nitration reaction to avoid adventitious sulfonation of the isonitrile complexes. Furthermore, the reaction products were not purified prior to oxidation in order to determine the precise isomer distribution as accurately as possible. When complexes I, II, and III were nitrated in this fashion with 1 mole of nitric acid per mole of complex, the resultant mixtures analyzed remarkably well for the monosubstituted products (see Experimental part). In 100% sulfuric acid, mononitration was accompanied by sulfonation; for example, when III was nitrated in 100% sulfuric acid, a complex containing precisely one –SO_3H group and one –NO_2 group per mole of III was isolated. The crude nitrated products in the foregoing experiments were oxidized with aqueous permanganate, yielding benzoic acids in 85–92% conversions. The resulting benzoic acids were esterified

(15) C. K. Ingold and M. S. Smith, *J. Chem. Soc.*, 907 (1938).

with an excess of an ethereal diazomethane solution as described previously and were analyzed by a gas–liquid chromatographic method. This method was more sensitive than the previously employed infrared method; nitrated methyl benzoates could be determined in one part/1000 parts of methyl benzoate (to ±5%) and in 1 part/100 parts of methyl benzoate (to ±1.0%) when dissolved in chloroform. The data obtained in such a fashion, most of which were double checked, are summarized in Table III.

Nitration of I, II, and III with 1–4 moles of nitric acid per mole of isonitrile complex yielded the corresponding isonitrile complexes with 1–4 nitro groups/mole of complex (Table III). Polynitrated complexes of II were adhesive oils which separated out after the nitrating mixture was diluted with water. Polynitrated complexes of III, which were obtained after dilution of the reaction mixture, were insoluble in the common organic solvents. Neutral, boiling permanganate solution converted these complexes to benzoic acids. The reproducibility of the relative isomer ratios resulting from repeated nitration of the isonitrile complexes with the same molar ratio of nitric acid to complex but giving varying conversions (80–92%) to benzoic acids leads us to the belief that the incomplete conversion to benzoic acids is mainly due to handling losses.

Discussion

The infrared spectra of the isonitrile complexes I, II, and III indicated (see above) that the ionic form $RN^+:::C:M^-$ (C) of the isonitrile group is the most pronounced form in all three complexes, being most predominant in III, less in II, and least in I. This contention is supported by the progressive deshielding of the methylene group hydrogens adjacent to the isonitrile group (see Fig. 1 and 2). Form C, which

resembles an immonium ion,[16] should exert a strong electronegative effect on the benzene ring and hence should be *meta* directing. As pointed out earlier,[3] nitration of trimethyl benzyl ammonium chloride yields 88% of the *meta* isomer and only 12% of the *ortho* and *para* isomers.[17]

Unfortunately, the preferred reaction site of electrophiles with free benzyl isonitrile ligand is the isonitrile group itself and hence no meaningful isomer distribution studies could be made on this compound for comparative purposes.[3] In all three complexes the substituent entered the ring preferentially in the *para* position (Table III). Two extreme explanations can be suggested for this behavior:
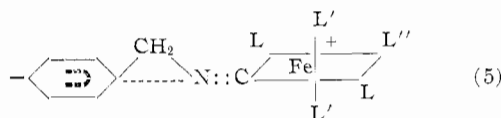
(1) The isomer distribution summarized in Table III for complexes I, II, and III is the same as might possibly be observed in the noncomplexed ligand.

(2) Cotton and Zingales have shown that the ionic structure (C) is enhanced the higher the valency of the central metal atom.[8a] Hence, one should expect in the benzyl isonitrile complexes even a greater preponderance of the *meta* isomer as compared to the free ligand. However, back donation of electrons from iron to the isonitrile group facilitates formation of resonance hybrids such as F in the transition state, thereby *changing* the isomer distribution and increasing the reactivity of the aromatic ring toward electrophiles.[18]

$$R::\ddot{N}::C::M \ (D) \tag{4}$$
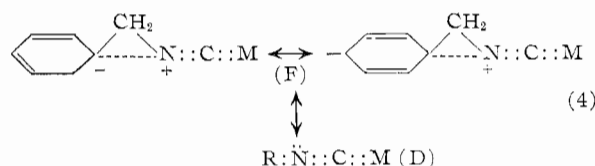
Indeed the reactivity of the first aromatic ring in complex II toward the nitronium ion approximates to that of benzene (Table IV), whereas even a partial charge located on an isonitrile nitrogen should decrease the reactivity of the aromatic ring when compared with benzene[19] (Table III).

This interesting behavior led us to investigate the electron donor capabilities of the isonitrile ligand as influenced by the other ligands in the complex during electrophilic reactions. Complexes I, II, and III may be represented by the structure

where L = $C_6H_5CH_2NC$ and L′, L′′ = CN or C_6H_5-CH_2NC. The relative reactivities of I, II, and III, as measured by competition for nitronium ion (NO_2^+) in sulfuric acid, are summarized in Table IV.[20] The laborious separation procedures gave results reproducible only to *ca.* ±30%. Nevertheless, the differences between the complexes are sufficiently large to establish a reactivity sequence for the nitronium ion, NO_2^+, this sequence being II > I > III, and corresponding to 19:2:1. From spectral data one could expect the following reactivity sequence: I > II > III. Two possibilities for the reversal of the reactivities of II > I may be considered:

(1) The cyanide groups (structure 5, L′′ = C_6H_5-CH_2NC, L′ = CN) in I deactivate the aromatic ring(s) by a negative inductive effect.

(2) In the *trans* effect, the limiting form of the transition state in (5) can form more easily if the Fe–C bond in the isonitrile is strengthened by π-bonding, *i.e.*, donation of the Fe electrons into the unoccupied p-orbitals of the isonitrile carbon. Flow of electrons away from the iron will place a positive charge on Fe; the *trans* cyanide group in II (structure 5, L′ = $C_6H_5CH_2NC$, L′′ = CN) competes for the same set of orbitals and since it is a strong electron donor toward iron, but a weaker electron acceptor from iron than the RNC group, it minimizes the positive charge and enhances structure 5.

The proton n.m.r. spectrum of II indicated that one methylene group in II was shifted downfield by 0.25 τ (Fig. 1), as compared with the four other methylene groups in the complex. If the methylene group *trans* to the cyanide group is bent sufficiently out of the plane of the isonitrile group, a diamagnetic anisotropic deshielding of the protons may occur. The decreased angle between the nitrogen and the methylene group indicates a potentially greater proximity between the nitrogen atom and the aromatic ring and hence a more facile electron transmission from iron to the aromatic ring. Partial out-of-plane bending of the $=N-CH_2-$ bond was deduced previously by Powell and Bartindale from the X-ray analysis of dicyanotetrakis-(methyl isonitrile)-iron(II) and hexakis-(methyl isonitrile)-iron(II) hydrogen sulfate.[10] These data seem to indicate that the *trans* effect is the more important effect in our case.[21]

Further evidence for a resonance hybrid approximating structure 5 comes from the polarographic half-wave potentials ($E_{1/2}$) (Table II). The sulfate ion is not reduced on the dropping mercury electrode.[22] Therefore, the relative sequence of $E_{1/2}$, which is the most negative for I > III > II, must mean that a de-

(16) The bond length data for methyl cyanide suggest that resonance form A contributes 74% to the hybrid (L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 3rd Ed., 1960, p. 270). The CNR vibration in the triple bond region is displaced for I by (+)34 cm.⁻¹, for II by (+)54 cm.⁻¹, and for III by (+)77 cm.⁻¹ toward *higher* wave length, indicating even a greater contribution for form C to the resonance hybrid in the complexes as compared with the free ligand.

(17) F. R. Goss, C. K. Ingold, and I. S. Wilson, *J. Chem. Soc.*, 2440 (1926); F. R. Goss, W. Hankard, and C. K. Ingold, *ibid.*, 250 (1927); C. K. Ingold and I. S. Wilson, *ibid.*, 810 (1927).

(18) Resonance hybrid "F" is related to the resonance hybrids which occur in numerous "neighboring group participations." For a review see: E. S. Gould, "Mechanism and Structure of Organic Chemistry," Henry Holt and Co., New York, N. Y., 1960, Chapter 14, and A. Streitwieser, *Chem. Rev.*, **56**, 675 (1956).

(19) The previously reported relative reactivities of complex II with benzene in sulfuric acid as the solvent are incorrect (ref. 3), for the reaction mixture has since been found to be heterogenous under the competitive reaction conditions employed.

(20) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 245.

(21) A similar *trans* effect was observed first by Wojcicki and Basolo in the carbon monoxide exchange in Mn(CO)₅X (where X = Cl, Br, I): A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

(22) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1952, p. 558.

TABLE IV^a

RELATIVE REACTIVITIES OF BENZYL ISONITRILE IRON(II) COMPLEXES WITH THE
NITRONIUM ION IN SULFURIC ACID AND ACETIC ANHYDRIDE

Competing species	Reaction medium	Added HNO$_3$ (in moles)	Separating procedures[b]	Material accounting[c] of complexes, %	Reactivity ratio	Average
II (C$_6$H$_5$CH$_2$NC)$_5$FeCNHSO$_4$ (1 mole) with C$_6$H$_6$ (1 mole)	Ac$_2$O	1	Determine C$_6$H$_5$NO$_2$ by l.–g.c.; oxidize complex to benzoic acids, esterify; determine methylnitro benzoates by l.–g.c.	...	1.4	
III (C$_6$H$_5$CH$_2$NC)$_6$FeSO$_4$ (1 mole) with C$_6$H$_6$ (1 mole)	Ac$_2$O	1	Determine C$_6$H$_5$NO$_2$ by l.–g.c.; oxidize complex to benzoic acids, esterify; determine methylnitro benzoates by l.–g.c.	...	0.11	
II (C$_6$H$_5$CH$_2$NC)$_5$FeCNHSO$_4$ (1 mole) with I (C$_6$H$_5$CH$_2$NC)$_4$Fe(CN)$_2$ (1 mole) Concentrations of Σ complexes 0.05–0.15 M	82% H$_2$SO$_4$	1	(a) chromatography on alumina (Woelm) neutral activity grade 1. Elute with chloroform → acetone → methanol	85	2.1^d	2
			(b) Fractional extraction of complexes of type II with methyl ethyl ketone	82–98	1.4^d	
II (C$_6$H$_5$CH$_2$NC)$_5$FeCNHSO$_4$ (1 mole) with III (C$_6$H$_5$CH$_2$NC)$_6$FeSO$_4$ (1 mole) Concentrations of Σ complexes 0.15 M	82% H$_2$SO$_4$	1	(a) Fractional extraction of complexes of type III with boiling water	75–92	23	19
			(b) Fractional extraction of complexes of type II with methyl ethyl ketone		16	
I (C$_6$H$_5$CH$_2$NC)$_4$Fe(CN)$_2$ (1 mole) with III (C$_6$H$_5$CH$_2$NC)$_6$FeSO$_4$ (1 mole) Concentration of Σ complexes 0.05–0.15 M	82% H$_2$SO$_4$	1	(a) Fractional extraction of complexes of type III with water	80–98	8.8	8
			(b) Fractional extraction of complexes of type I with chloroform	85	6.8	

^a The solubility of complex I in acetic anhydride at 25° is only *ca.* 1 g./300 ml.; because of the large resulting volume after the reaction mixture was drowned in ether, a large amount of nitrobenzene was lost in the concentration of organic filtrates and the determination of the reactivity ratio was irreproducible.   ^b See experimental part for details.   ^c Total accounting of nitrated and unnitrated complexes.   ^d Reactivity ratio is the ratio of the total *isolated* nitrated species of II in mmoles divided by the total isolated nitrated species of I in mmoles.

localization of electrons takes place in the cyanide and/or isonitrile ligands in the complexes. The greater the delocalization of electrons within the complex, the greater the ease of formation of hybrids such as (5) and the less negative should be the half-wave potential. This means that in complex II the greatest delocalization of electrons takes place in accord with the evidence cited above.[23]

It is also of interest to note that the half-wave potential of complex I is greater than that of III; generally there is an inverse linear correlation between the half-wave potential $E_{1/2}$ and the cation localization energy L_{r+}[24] in an aromatic system. Hence, one should expect the reactivity of III toward NO$_2^+$ to be greater than the reactivity of I. The actual reversal of reactivities may mean that in the nitration of the neutral species I the cyanide groups exhibit a negative inductive effect on the aromatic rings within the complex.

(23) A. A. Vlček, *Discussions Faraday Soc.*, **29**, 114 (1960); A. A. Vlček, "Advances in the Chemistry of Coordination Compounds," Proceedings of the 6th International Conference on Coordination Chemistry, S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 598.

(24) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, New York, N. Y., 1962, p. 178 (Table 7.1), p. 336 (Table 11.4), and discussion in Chapters 7 and 11.

The relative amounts of the *ortho, meta,* and *para* isomers in the nitration of I, II, and III in 82% sulfuric acid remain remarkably constant (Table III). Even when subsequent nitro groups are introduced into the already nitrated complexes the isomer ratios show no substantial change. Hence, we must conclude that no *substantial* change in isomer distribution can be effected by replacing the benzyl isonitrile ligands in III by cyanide groups. This replacement merely affects the reactivity (rate) of the aromatic groups in the complex. The absence of any change in the isomer distribution is the more remarkable since complex I is presumably neutral, II a monopositive cation, and III a dipositive cation in 82% sulfuric acid.

When the sulfuric acid concentration is increased, I, II, and III should be protonated at the isonitrile nitrogen atom or the cyanide nitrogen atom. This could lead to a change in the isomer distribution in the nitration of these complexes. As can be seen from Table III, this prediction is borne out; in all cases the *meta* isomer ratio increases. The greatest increase of the *meta* isomer occurs in complex II, which seems to indicate a protonation of the cyanide group. This de-

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Table V

Reactions of Labeled Potassium Cyanide with $(p\text{-}XC_6H_4CH_2NC)_5FeCNBr$ in 90% Methanol–10% Water

Number	Complex (mmoles)	KC^{14}N, (mmoles)	mg. of complex isolated (%)	μcuries	% exchange[a]	σ
1	$(m\text{-}CH_3C_6H_4CH_2NC)_5FeCNBr$ (0.5)	1.0	265 (74.0)	0.81	30.0	−0.069
2	$(p\text{-}CH_3C_6H_4CH_2NC)_5FeCNBr$ (0.5)	1.0	313 (62.5)	0.87	32.2	−0.170
3	$(C_6H_5CH_2NC)_5FeCNBr$ (0.5)	1.0	201 (53.9)	1.39	51.4	0.000
4	$(p\text{-}ClC_6H_4CH_2NC)_5FeCNBr$ (0.5)	1.0	281 (61.2)	1.67	62.0	+0.227
5	$(p\text{-}CH_3O_2CC_6H_4CH_2NC)_5FeCNBr$ (0.5)	1.0	250 (48.1)	1.85	68.5	+0.619

[a] For discussion see W. Z. Heldt, *J. Inorg. Nucl. Chem.*, **24**, 73 (1962).

activation of II toward electrophilic agents by complex formation of the isonitrile and/or cyanide nitrogen with a strong Lewis acid (AlCl₃) was observed earlier[3] and is supported by the recent findings of Shriver, who isolated several BF₃· complex cyanide complexes.[25]

If structure 5 is indeed an important resonance structure in II, then the effective charge on the iron atom should decrease as the electron-withdrawing power of the *para* substituent increases. Hence the proportion of the *meta* isomer introduced into unsubstituted rings should, and in fact does, increase with each nitro group introduced into the rest of the system (Table III). Furthermore, preliminary data indicate[26] that the reactivity of the unsubstituted aromatic rings in II decreases relative to benzene the more nitro groups there are present in the remainder of the complex.

Electron-withdrawing groups in the *para* position of the aromatic rings in II facilitate the cyanide exchange with labeled potassium cyanide. This rate increase is roughly proportional to the electron-withdrawing power of the substituents as measured by Hammett's σ values[27] (see Table V).

$$X = CH_3O_2C > Cl > H > CH_3$$
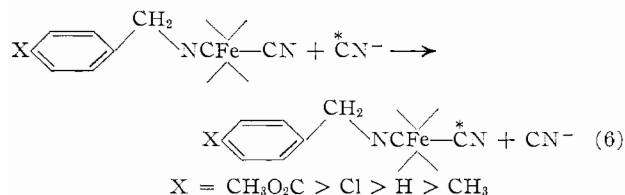
Electron-withdrawing groups will tend to place a positive charge on iron and this suggests a heptacoordinated transition state intermediate (S_N2).[28] It should be noted that such a postulate is contrary to the high crystal field activation energy ($\Delta E_a = 8.5$ kcal.) which an S_N2 mechanism requires.[29] Electron-withdrawing groups also facilitate the exchange of the cyanide in the transalkylation reaction of isonitrile complexes of type II where compounds such as $(p\text{-}O_2NC_6H_4CH_2NC)_5FeBr_2$ and $(C_6H_5COCH_2NC)_5FeBr_2$ were isolated.[30]

(25) D. F. Shriver, *J. Am. Chem. Soc.*, **84**, 4611 (1962).
(26) W. Z. Heldt, unpublished results.
(27) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).
(28) A. W. Adamson, J. P. Welker, and W. B. Wright, *J. Am. Chem. Soc.*, **73**, 4786 (1951); A. G. MacDiarmid and N. F. Hall, *ibid.*, **76**, 4222 (1954).
(29) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 109.
(30) W. Z. Heldt, *J. Inorg. Nucl. Chem.*, **24**, 265 (1962).

If the cyanide group donates electrons to the iron atom, electron-withdrawing groups in the *para* position of the benzyl ligand should further decrease the basicity of the cyanide nitrogen. Indeed, the ease of alkylation of the partially alkylated ferrocyanide complexes $K_3[RCH_2NCFe(CN)_5]$, $K_2[(RCH_2NC)_2Fe(CN)_4]$, etc., is decreased as the electron-withdrawing power of the *para* substituent group is increased, *i.e.*, the rate of alkylation decreases in the sequence[2]: $p\text{-}CH_3C_6H_4CH_2Br \cong o\text{-}CH_3C_6H_4CH_2Br > C_6H_5CH_2Br > p\text{-}ClC_6H_4CH_2Br > p\text{-}CH_3O_2CC_6H_4CH_2Br >> p\text{-}O_2NH_6H_4CH_2Br$. It should be remembered that the differences in the rate of alkylation of the partially alkylated ferrocyanide complexes represent a composite rate which is due to the nucleophilicity of the nitrogen *and* the dissociation of the alkyl halides.

The various results cited seem to be in good agreement with resonance structure 5 for the cyanopentakis-(benzyl isonitrile)-iron(II) cation and support the presence of a *trans* effect of the cyanide on the reactivity of the aromatic ring contained in the *trans* benzyl isonitrile group.

Experimental

Materials.—$(C_6H_5CH_2NC)_6FeBr_2$ was prepared from 272 g. (0.74 mole) of dry potassium ferrocyanide and 812 g. (4.5 moles) of benzyl bromide by heating the reaction mixture for 48 hr. on a steam bath with rapid stirring in a vessel closed by a calcium chloride tube and subsequently allowing the reaction mixture to stand for 10 days at room temperature. The excess benzyl bromide was removed with petroleum ether and the reaction mixture was extracted three times with 1 l. of boiling chloroform. Upon slow evaporation 458 g. of yellow crystals was obtained. The crude product was extracted three times with 500 ml. of methyl ethyl ketone, which extracted the $(C_6H_5CH_2NC)_5FeCNBr$ component from the reaction mixture, leaving 200 g. of $(C_6H_5CH_2NC)_6FeBr_2$, m.p. 132–133°. After one more recrystallization from methyl ethyl ketone, the product melted at 134–135°. No depression of the melting point of this specimen was observed on admixture with $(C_6H_5CH_2NC)_6FeBr_2$ prepared by a different route,[2] and the two infrared spectra were superimposable.

$[(C_6H_5CH_2NC)_6Fe]_2SO_4$ was prepared by heating 86 g. (0.1 mole) of $(C_6H_5CH_2NC)_6FeBr_2$ in 250 ml. of 80% sulfuric acid for 1 hr. while bubbling nitrogen through the stirred solution at a rapid rate. The reaction mixture was poured on ice and the cold water-insoluble reaction products were recrystallized several times from methyl ethyl ketone, yielding 70 g. of white crystals which melt after drying at 70° (0.1 mm.) at 198–199°.

Anal. Calcd. for [(C₆H₅CH₂NC)₆Fe]₂SO₄: C, 60.38; H, 4.43; N, 8.80; Fe, 5.85; S, 3.86. Found: C, 60.87; H, 4.69; N, 9.05; Fe, 6.04; S, 3.36.

Nitration.—(O₂NC₆H₄CH₂NC)Fe(C₆H₅CH₂NC)₃(CN)₂ was prepared by addition of 1.692 g. (3 mmoles) of (C₆H₅CH₂NC)₄Fe-(CN)₂ to 100 ml. of 82% sulfuric acid containing 3.3 mmoles of nitric acid and stirring the reaction mixture for 15 min. at room temperature. The reaction mixture was then poured on ice, yielding 1.9 g. of white crystals, which were crystallized from a methyl ethyl ketone–methanol mixture and melted at 180–185° after drying at 70° (0.1 mm.).

Anal. Calcd. for (O₂NC₆H₄CH₂NC)Fe(C₆H₅CH₂NC)₃(CN)₂·H₂O: C, 62.10; H, 4.75; N, 14.92; Fe, 8.49. Found: C, 61.63; H, 4.60; N, 14.55; Fe, 8.55.

(O₂NC₆H₄CH₂NC)Fe(C₆H₅CH₂NC)₄(CNHSO₄) was prepared from 1.328 g. (2 mmoles) of II and 2.0 mmoles of HNO₃ in 15 ml. of 82% sulfuric acid as described above. The product mixture was crystallized from hot methyl ethyl ketone and melted after drying at 70° (0.1 mm.) at 143–147°.

Anal. Calcd. for (O₂NC₆H₄CH₂NC)Fe(C₆H₅CH₂NC)₄(CN-HSO₄): C, 60.81; H, 4.35; N, 12.11; Fe, 6.89; S, 3.96. Found, C, 61.56; H, 4.60; N, 11.45; Fe, 7.24; S, 4.05. The infrared spectrum exhibits strong bands at 1528 cm.⁻¹ (NO₂) and 1235 cm.⁻¹ (HSO₄).

(O₂NC₆H₄CH₂NC)Fe(C₆H₅CH₂NC)₅SO₄ was prepared from 2.418 g. (3 mmoles) of (C₆H₅CH₂NC)₆FeSO₄ and 30 ml. of 82% sulfuric acid containing 3.3 mmoles of nitric acid as described above. The product, 2.6 g., was crystallized from methyl ethyl ketone. After drying at 70° (0.1 mm.), the material melted at 189–192°.

Anal. Calcd. for (O₂NC₆H₄CH₂NC)Fe(C₆H₅CH₂NC)₅SO₄·3-H₂O: C, 60.43; H, 4.96; N, 10.28; Fe, 5.85. Found: C, 60.13; H, 5.23; N, 8.67; Fe, 6.29. The infrared spectrum shows strong bands at 1525 cm.⁻¹ (NO₂) and 1230 cm.⁻¹ (SO₄).

When (C₆H₅CH₂NC)₆FeSO₄ (2.418 g., 3 mmoles) was nitrated with nitric acid (3.3 mmoles) in 10 ml. of 100% sulfuric acid at 0°, a partially sulfonated compound was isolated by pouring the reaction mixture on ice and recrystallizing the product from a methyl ethyl ketone–methanol mixture. After drying at 70° (0.1 mm.), the material melted at 174–175°.

Anal. Calcd. for (HO₃SC₆H₄CH₂NC)(O₂NC₆H₄CH₂NC)Fe-(C₆H₅CH₂NC)₄SO₄: C, 57.19; H, 4.10; N, 12.50; Fe, 5.54; S, 6.36. Found: C, 56.77; H, 4.48; N, 12.50; Fe, 5.44; S, 6.35. Infrared analysis (in KBr) shows strong bands at 1525 cm.⁻¹ (NO₂) and 1224 cm.⁻¹ (SO₃H).

Oxidation.—The total nitrated product mixture was then oxidized with permanganate.[3] The conversion to benzoic acid and substituted benzoic acids was 85–93% (mole) when a neutral solution of permanganate was used instead of a 10% sodium hydroxide solution employed previously.[3] The acids were converted quantitatively into their methyl esters by esterification with a slight excess of diazomethane.[3]

Gas–Liquid Chromatographic Analysis.—The chloroform solutions of the methyl esters were analyzed by gas–liquid chromatography using a F.M. model 500[31] vapor fractometer. An 8 ft., 0.25 in. diameter, copper column was packed with 20% (weight) silicon rubber (SE-52)[32] on 60–80 Chromo super support,[33] and helium (40 cc./min.) was employed as the carrier gas. The temperature of the column was 200°, of the detector cell, 280°, and of the injection port, 280°.

The relative response data of the materials investigated were obtained by analyzing synthetic mixtures of the isomeric methyl nitrobenzoates in known proportions. An error of less than ±1.5 relative per cent was found for most constituents. In mixtures of *para*- and *meta*-nitrobenzoates the error became larger (> ±5%) if less than 10% of one of the components was present in the synthetic mixture. The relative amount of a component in a mixture was calculated from the integrated

areas for each component. The retention times observed for the products investigated are given in Table VI.

TABLE VI

Compound	Column temp., °C.	Retention time, min.
Acetic anhydride	150	1.0
Nitrobenzene	150	6.0
Methyl benzoate	200	4.1
Methyl *o*-nitrobenzoate	200	11.2
Methyl *p*-nitrobenzoate	200	12.2
Methyl *m*-nitrobenzoate	200	13.2

Competition Experiments (Table IV).   A.   In Sulfuric Acid.—Two mmoles of I and 2 mmoles of II were dissolved in 50 ml. of 82% sulfuric acid at 26 ± 0.2° and, immediately after the solids dissolved, 7 ml. of a 3.3 *M* nitric acid solution (2.3 mmoles) in 82% sulfuric acid was added. The solution was stirred at 26° for 10 min. and was then poured on *ca.* 300 g. of ice. The complexes were separated by two methods (Table IV). The first method consisted of chromatography of the reaction mixture on 300 g. of Woelm[34] neutral alumina, activity grade 1, suspended in chloroform. The products were eluted from the column with 50% chloroform–acetone, FI = 1090 mg. (the tetrakis-(benzyl isonitrile) complexes) and with 100% acetone, FII = 1402 mg. (the pentakis-(benzyl isonitrile) complexes). Infrared analysis of the nitro group in FI and FII in chloroform as the solvent at 1525 cm.⁻¹ indicated that FI contained 0.09 mmole of NO₂ groups and FII 1.85 mmoles. The identity of FI with the nitrated tetrakis-(benzyl isonitrile) complexes was established by crystallization from a methyl ethyl ketone–methanol mixture; the melting point of this specimen was 180–185°. The infrared spectrum of FII was identical with that of the mononitrated compound of cyanopentakis-(benzyl isonitrile)-iron(II) hydrogen sulfate prepared above. In the second method the same reaction mixture was separated by fractional extraction of the pentakis-(benzyl isonitrile) complexes with boiling methyl ethyl ketone (see below).

The hexakis-(benzyl isonitrile) complexes were conveniently separated from either the pentakis- or tetrakis-(benzyl isonitrile) complexes by fractional extraction of the former with boiling water in which the last compounds are virtually insoluble or by fractional extraction with boiling methyl ethyl ketone. The concentration of the nitrated complexes was determined by measuring the strong nitro band at 1525 cm.⁻¹ in their infrared spectrum.

The solubilities in boiling methyl ethyl ketone of the various isonitrile complexes are given in Table VII.

TABLE VII

Compound	Solubility, g./ml.
(C₆H₅CH₂NC)₄Fe(CN)₂	1/815
[O₂NC₆H₄CH₂NC / (C₆H₅CH₂NC)₃]Fe(CN)₂	1/2300
(C₆H₅CH₂NC)₅FeCNHSO₄	1/5.5
[O₂NC₆H₄CH₂NC / (C₆H₅CH₂NC)₄]FeCNHSO₄	1/14.5
(C₆H₅CH₂NC)₆FeSO₄	1/210
[O₂NC₆H₄CH₂NC / (C₆H₅CH₂NC)₅]FeSO₄	1/1250

B.   In Acetic Anhydride.—To a solution of 1.867 g. (2.5 mmoles) of (C₆H₅CH₂NC)₅FeCNHSO₄ in 100 ml. of acetic anhydride at 26° is added 5 ml. of 1 *M* benzene solution in acetic anhydride (5.0 mmoles) and, after 5 min. stirring with a magnetic stirrer, 1 ml. of a 2.5 *M* nitric acid solution in acetic anhydride

(31) F. M. Scientific Corp., Avondale, Pa.
(32) General Electric Co., Silicon Products Dept., Waterford, N. Y.
(33) West Engineering Laboratories, Hermose Head, Calif.

(34) M. Woelm-Eschwege, Chemical and Pharmaceutical Mfg., Germany. Prepared according to Brockmann and Schodder, *Ber.*, **74**, 73 (1941).

(prepared by addition of 90% nitric acid to acetic anhydride). After stirring for 15 min. at this temperature the reaction mixture is drowned in 2 l. of diethyl ether; the ether layer is decanted, the oily residue is washed twice with 100 ml. of ether, and the ether solution is concentrated to 10 ml. by distilling the ether through a column of *ca.* 20 plates. Gas–liquid chromatography indicates that the sample contains 0.09 mmole of nitrobenzene (read from a reference line prepared from standard solutions). The insoluble semisolid material, 1.630 g., is oxidized with potassium permanganate in water,[3] the acid mixture is esterified with diazomethane, and the resulting esters are dissolved in 10 ml. of chloroform and are analyzed for methyl nitrobenzoates by the liquid–gas chromatographic method described above, indicating the presence of 0.12 mmole of methyl nitrobenzoates.

Exchange Reactions of KC¹⁴N with (*p*-XC₆H₄CH₂NC)₅FeCNBr. —To 0.5 mmole of the isonitrile complex in 45 ml. of absolute methanol was added a solution of 1.0 mmole of KC¹⁴N in 5 ml. of water containing a total of 2.7 μcuries. The reaction mixture

was stoppered and was stirred with a magnetic stirrer at 23° for 58 hr. The reaction mixture was then poured into 50 ml. of 60% sulfuric acid solution, the methanol was evaporated under reduced pressure, and the remaining solution was heated on a steam bath for 30 min. Subsequently it was extracted three times with 50 ml. of chloroform; the chloroform extracts were dried with magnesium sulfate (anhydrous) and the chloroform removed by evaporation. The resultant complexes were crystallized from methyl ethyl ketone. After drying at 25° (0.1 mm.) the complexes were weighed and analyzed for C¹⁴ as a solution in methanol by the method of Hayes.[35] The results obtained are summarized in Table V.

Contribution from the Wm. A. Noyes Laboratory, Chemistry Department,
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Spectrochemical Studies of the Primary Alkylamine Complexes of Nickel(II) and an Evaluation of the Donor Properties of Amines

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The trends in the donor properties of ammonia and some alkylamines toward the Lewis acids iodine and phenol are qualitatively explained by consideration of the differences in the relative importance of polarization and electrostatic forces in the various adducts. An assignment for the trends in these properties is offered for a series of amines and applied to correlate the magnitude of the interaction in several adducts. Similar considerations can be used to qualitatively explain the positions ammonia and the primary alkylamine donors occupy in the spectrochemical series of the cation nickel(II). Even though the alkylamines are easily displaced from the coordination sphere by water, the amines occupy a higher position in the spectrochemical series than water. The greater stability of ammonia than amine complexes in water is due to several effects, a very important one being the higher heat of hydration of methylamine than ammonia. Water does not appear to form stronger bonds than methylamine with nickel(II).

Introduction

The basicity of amines has long attracted the interest of inorganic and organic chemists. If only the inductive factor were operative in the series NH₃, RNH₂, R₂NH, and R₃N (where R is alkyl), one would predict a regular increase in basicity with increased alkyl substitution. It was found that the pK_B values for a series of methylamines deviated from this order, producing the following sequence of increasing basicity

$$NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$$
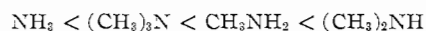
The existence of back strain in trimethylamine was proposed.[2] In an excellent analysis of this problem Pearson and Vogelsong[3,4] have discussed the energetics of this system and have shown clearly that pK_B data cannot be interpreted in terms of the magnitude of the

interaction between an acid and a base. It is necessary to consider contributions from solvation terms, ion-pair association, and entropy effects in explaining pK_B data.

The main concern of this article is with the magnitude of the interaction between acids and amines. The criteria employed are enthalpies of formation of adducts between aliphatic amines and iodine[5] measured in the weakly solvating medium carbon tetrachloride. These reported enthalpies are compared with enthalpies of formation of amine–phenol adducts in carbon tetrachloride. Toward phenol smaller differences in the enthalpies of formation of the adducts are observed for this series of amines than for the iodine adducts. A qualitative proposal is offered to account for the difference in donor properties manifested by these amines toward iodine and phenol.

It is generally accepted[6] that nickel(II) coordinates less readily with monodentate alkyl-substituted amines

(1) Abstracted in part from the Ph.D. theses of D. W. Meek and R. Longhi, University of Illinois, Urbana, Illinois, 1961 and 1962, respectively.
(2) H. C. Brown and M. D. Taylor, *J. Am. Chem. Soc.*, **69**, 1332 (1947).
(3) R. G. Pearson and D. C. Vogelsong, *ibid.*, **80**, 1038 (1958), and references contained therein.
(4) R. G. Pearson and D. C. Vogelsong, *ibid.*, **80**, 1048 (1958), and references contained therein.

(5) H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960).
(6) J. C. Bailar, Jr., and D. H. Busch, "The Chemistry of Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, p. 62.