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Proton Affinities of Some Cyanide and Aromatic Diimine Complexes of Iron, Ruthenium and Osmium

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Preparation of the neutral dicyano-bis-(2,2'-bipyridine)-ruthenium(II) and the corresponding osmium(II) complex is described. Proton affinities of these and related or similar iron(II) and iron(III) complexes are reported and discussed. Results of various studies reveal the following: (1) the cyano complexes possess measurable proton affinities, (2) the nitrogen atom of the cyanide group is the most likely site of protonation, (3) the nature of the central metal ion of the mixed complexes has a significant influence in determining their basicities, and (4) the tris-1,10-phenanthroline and tris-2,2'-bipyridine complexes of iron, ruthenium and osmium do not exhibit any readily measurable or detectable proton affinity.

Introduction

Several questions are to be dealt with in the present work, all concerning the proton affinities of complexes derived from 1,10-phenanthroline or 2,2'-bipyridine, cyanide, and the iron group metal ions.

It was reported earlier that the neutral dicyano-bis-(1,10-phenanthroline)-iron(II) and the analogous 2,2'-bipyridine complex display dibasic, reversible reactions with strong acid.^{1b} One question, which has yet to be answered satisfactorily, is where protonation takes place in these uncharged complexes. On the basis of studies first carried out in this laboratory, it was suggested that the central metal ion might be protonated.¹ Hamer and Orgel have since reported evidence which strongly suggests that protonation occurs at the cyanide groups to give rise to the isocyanide $[\text{Fe}(\text{phen})_2(\text{C}\equiv\text{NH})_2]^+$.² They found that the uncharged complex, on treatment with methyl sulfate, is converted to the methyl isocyanide derivative $[\text{Fe}(\text{phen})_2(\text{C}\equiv\text{NCH}_3)_2]^+$, with absorption spectrum characteristics that are essentially unalterable by treatment with sulfuric acid and which closely resemble those of the diprotonated species present in 12 M H_2SO_4 .² Wilkinson, who could find no clear evidence for hydrogen to metal bonding by high-resolution n.m.r. or infrared techniques, also has suggested that protonation probably involves the bound cyanide groups rather than the central metal atom.³ In the present study, the proton affinities of a number of related complexes are examined with the expectation that additional or more conclusive evidence regarding protonation sites can be found.

A second question concerns the validity of the alleged evidence for stable protonated species of tris-(1,10-phenanthroline)-iron(II) and tris-(2,2'-bipyridine)-iron(II) in concentrated solutions of strong acid, reported by Murmann and Healy.^{4,5} It is of interest to test their conclusions and, if confirmed, to relate these to results obtained for the cyanide, mixed ligand complexes. Clearly, this and the first mentioned question, also to be explored, are intimately related.

The third phase of inquiry concerns the influence of various structural features on proton affinity. The effective charge and size of the metal ion and the nature and number of ligands are factors to be considered.

Experimental

Materials.—The mixed ligand complexes of iron(II) and iron(III) were available from previous work; details concerning

their preparation, purification, and analyses have been reported earlier.⁶ Tris-(1,10-phenanthroline)-iron(III) perchlorate monohydrate and the 2,2'-bipyridine analog were prepared following literature procedures.^{7,8} Commercial grade ruthenium dioxide and osmium tetroxide were used to prepare the complex halide salts employed for the synthesis of the neutral dicyano complexes. The glacial acetic acid, thiourea, *o*-chloroaniline, and perchloric acid solutions used were described previously.^{1b} Standard solutions of sulfuric acid were prepared by mixing calculated amounts of 95% H_2SO_4 and acetic acid together with amounts of acetic anhydride equivalent to the water present from the sulfuric acid. After standing for several hours, the solutions were diluted to their appropriate volumes with acetic acid. The accuracy to which each concentration was thus known was completely adequate for the intended use.

Preparation of Dicyano-bis-(2,2'-bipyridine)-ruthenium(II) Trihydrate.—Potassium aquapentachlororuthenate(III) ("ruthenium red") was prepared as described by Charonnat,⁹ starting with ruthenium dioxide. A mixture of 2.0 g. of $\text{K}_2[\text{RuCl}_5\text{H}_2\text{O}]$, 2.0 g. of 2,2'-bipyridine, and 50 ml. of water was heated near its boiling temperature for ten minutes; 3.0 g. of NaCN was added to the hot solution (color changed from dark to lighter shade of green), and heating was continued for 15 more minutes; 0.30 g. of sodium hydrosulfite was then added (reduction and accompanying color change to dark orange-red occurred rapidly), and the hot solution was set aside to cool at room temperature. An orange-red precipitate was isolated, and the filtrate was retained to recover the large amount of $[\text{Ru}(\text{bipy})_3]^{++}$ present. The precipitate was washed first with a small amount of water and then generously with benzene to remove excess bipyridine. After two successive recrystallizations from hot water, taking care to filter out small amounts of insoluble matter which formed during heating, a yield of 0.5 g. of the desired product (air dried) was obtained.

Anal. Calcd. for $[\text{Ru}(\text{bipy})_2(\text{CN})_2]\cdot 3\text{H}_2\text{O}$: C, 50.7; H, 4.26; N, 16.2; H_2O , 10.4. Found: C, 50.2; H, 4.09; N, 16.0; H_2O , 10.1.

Preparation of Tris-(2,2'-bipyridine)-ruthenium(II) Cyanide Hexahydrate.—Sodium cyanide (10 g.) was added to the filtrate retained from preparation of the neutral dicyano complex. The precipitate which formed was isolated by suction filtration and recrystallized from hot water. The glistening, orange-red crystals were dried in air at room temperature; yield 1.2 g.

Anal. Calcd. for $[\text{Ru}(\text{bipy})_3](\text{CN})_2\cdot 6\text{H}_2\text{O}$: C, 52.6; H, 4.94; N, 15.35. Found: C, 52.8; H, 4.59; N, 15.13.

Preparation of Dicyano-bis-(2,2'-bipyridine)-osmium(II) Dihydrate.—A solid mixture of 1.3 g. of $(\text{NH}_4)_2[\text{OsCl}_6]$ (prepared from OsO_4 as described by Gilchrist¹⁰) and 4.0 g. of 2,2'-bipyridine was heated for one hour between 210° and 240° with frequent stirring. The cooled mass was extracted several times with benzene to remove unreacted bipyridine; 5.0 g. of NaCN and 200 ml. of water were added; and the mixture was heated at reflux for 90 minutes, during which time the color changed from red-brown to green and a small amount of black insoluble matter formed. After removing insoluble matter, the solution was evaporated to a volume of 100 ml. and set aside to cool at room temperature. Fine, glistening black needles were isolated from the dark green supernatant (the latter was retained for recovery of its $[\text{Os}(\text{bipy})_3]^{++}$ content). A yield of 0.8 g. was obtained following recrystallization from hot water and drying in air at room temperature.

Anal. Calcd. for $[\text{Os}(\text{bipy})_2(\text{CN})_2]\cdot 2\text{H}_2\text{O}$: C, 44.7; H, 3.40; N, 14.24. Found: C, 46.0; H, 3.38; N, 13.91.

(1) (a) Department of Chemistry, Northern Illinois University, DeKalb, Illinois. (b) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 5779 (1960).

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

(3) G. Wilkinson, in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 56.

(4) E. A. Healy and R. K. Murmann, *J. Am. Chem. Soc.*, **79**, 5827 (1957).

(5) R. K. Murmann and E. A. Healy, *ibid.*, **83**, 2092 (1961).

(6) A. A. Schilt, *ibid.*, **82**, 3000 (1960).

(7) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

(8) A. A. Schilt and R. C. Taylor, *J. Inorg. Nuclear Chem.*, **9**, 211 (1959).

(9) R. Charonnat, *Ann. chim. phys.*, [10] **16**, 5 (1931).

(10) R. Gilchrist, *Bur. Stand. J. Res.*, **9**, 282 (1932).

Preparation of Tris-(2,2'-bipyridine)-osmium(II) Iodine Trihydrate.—On adding an excess of potassium iodide to the filtrate which was retained from preparation of the neutral dicyano complex, a black crystalline precipitate formed. It was isolated by suction filtration, recrystallized from hot water containing a small amount of KI, and dried in air. The identity of the product was confirmed by its absorption spectrum in the visible region, which closely matched the spectrum reported by Burstall, Dwyer and Gyrfas¹¹ for the compound in question.

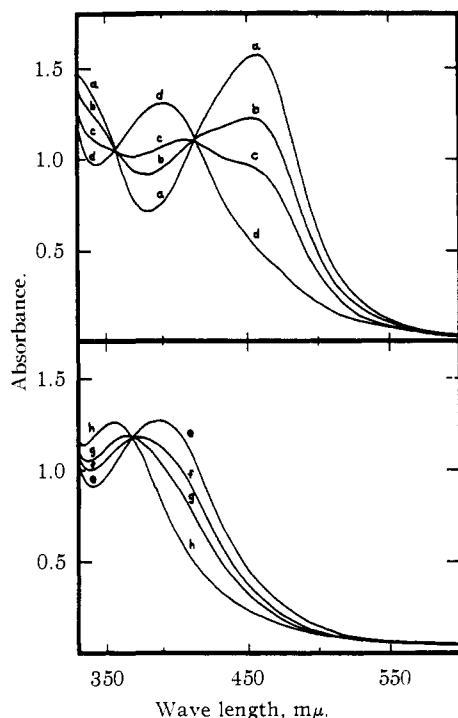


Fig. 1.—Absorption characteristics of dicyano-bis-(2,2'-bipyridine)-ruthenium(II) in glacial acetic acid as a function of moles of HClO_4 added per mole of neutral complex. Formal concentration of complex = $1.92 \times 10^{-4} M$; moles of HClO_4 per mole of complex: a, none; b, 0.46; c, 0.62; d, 1.00; e, 1.23; f, 1.93; g, 3.08; h, 19.2.

Attempted Preparation of Dicyano-bis-(1,10-phenanthroline)-ruthenium(II).—Only tarry products, believed to be polynuclear complexes involving hydroxy and/or cyanide bridging, were obtained on various attempts to synthesize the desired complex. When solutions of $[\text{Ru}(\text{phen})_2\text{Cl}_2]^+$ and sodium cyanide are refluxed, a dark green oil forms which gives an amorphous solid or tar on cooling. If $\text{Na}_2\text{S}_2\text{O}_5$ is added to the hot mixture, the dark green oily product is converted to a very dark violet colored tarry mass. Attempts to obtain crystalline products from the tarry ones proved unsuccessful. Similar results were observed when sodium hydroxide was used in place of sodium cyanide.

The very curious difference between the behaviors of $[\text{Ru}(\text{bipy})_2\text{Cl}_2]^+$ and $[\text{Ru}(\text{phen})_2\text{Cl}_2]^+$ on treatment with sodium hydroxide or cyanide appears to be due to differences in flexibilities rather than coordination strengths of the bidentate ligands.

Magnetic Measurements.—Magnetic susceptibilities were measured by the Gouy method at room temperature ($24\text{--}26^\circ$). The standards and diamagnetic corrections employed are given in reference 6, which also includes a brief discussion of the magnetic properties of the type of mixed ligand complexes in question. The relative precisions of the magnetic susceptibility measurements are estimated to range from 1 to 5%.

Identification of Protonated Species and Determination of Formation Constants in Acetic Acid.—For each complex, a large number of solutions were prepared in acetic acid, each having the same formal concentration of complex but a different concentration of perchloric or sulfuric acid (ranging from 0 to 6 M). The absorption characteristics of the solutions were examined over the spectral range 350–800 $m\mu$ using a Cary Model 11 recording spectrophotometer. Well defined isobestic points were displayed by the absorption curves which greatly simplified interpretation of the data. With increasing acid concentration, the successive formation of each new protonated species was marked by a new set of one or more isobestic points. Thus the

number of different protonated species formed by each complex could be determined. In certain cases it was possible to determine the stoichiometry of the reactions, and hence the identities of the species, by plotting the mole ratio of reactants vs. absorbance. For other cases, in which large concentrations of acid were necessary to produce the protonated species, identities are based on the assumption that only one proton adds at a time. Considering the results obtained thereby, together with the nature of the complexes, this assumption appears to be quite reasonable.

TABLE I
MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF SOLID COMPLEXES^a

Compound	$\chi_M \times 10^6$ (Compound)	μ_{eff} , B.M. (Metal ion)
$[\text{Fe}(\text{bipy})_2(\text{CN})_2] \cdot 3\text{H}_2\text{O}$	-110	0.61
$[\text{Ru}(\text{bipy})_2(\text{CN})_2] \cdot 3\text{H}_2\text{O}$	-155	.58
$[\text{Os}(\text{bipy})_2(\text{CN})_2] \cdot 2\text{H}_2\text{O}$	-181	.10

^a The data for the iron(II) complex are from ref. 6.

The formation constant, K_f , pertaining to the equilibrium between base (B), acid (HY) and salt (BHY) in acetic acid is defined as follows: $K_f = C_{\text{BHY}}/C_{\text{B}}C_{\text{HY}}$, where C represents analytical concentration of the substance noted by subscript. In the present study both ClO_4^- and HSO_4^- were employed and are represented by Y. Sulfuric acid was used when difficulty was experienced with high concentrations of perchloric acid in anhydrous acetic acid. Some of the complexes form insoluble perchlorate salts. Also, it is difficult to avoid oxidation (vigorous or otherwise) of solvent, etc., when perchloric acid is prepared much above 1 M in concentration in anhydrous acetic acid. The analytical concentrations of the three components are very simply determined by spectrophotometry, provided the total amounts and concentrations of base (metal complex) and acid taken are known.

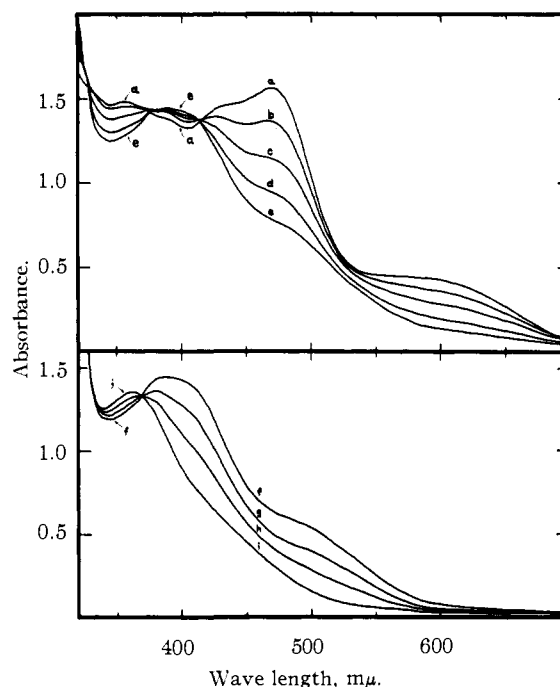


Fig. 2.—Absorption characteristics of dicyano-bis-(2,2'-bipyridine)-osmium(II) in glacial acetic acid as a function of moles of HClO_4 added per mole of neutral complex. Formal concentration of complex = $1.96 \times 10^{-4} M$; moles of HClO_4 per mole of complex: a, none; b, 0.37; c, 0.56; d, 0.75; e, 0.93; f, 1.12; g, 1.49; h, 1.86; i, 3.72.

Exchange Constants.—Thiourea and *o*-chloroaniline were selected as reference bases for the acid exchange measurements, since they had been used in the previous work on the analogous iron(II) complexes. Procedural details have been described earlier.^{1b} The molar absorptivity data used in the calculation of concentrations are listed in Table II.

(11) F. H. Burstall, F. P. Dwyer and E. C. Gyrfas, *J. Chem. Soc.*, 553 (1950).

TABLE II

MOLAR ABSORPTIVITIES IN ACETIC ACID		
A. Dicyano-bis-(2,2'-bipyridine)-ruthenium(II)		
Species	455 m μ	413 m μ
Ru(bipy) ₂ (CN) ₂	8020	5700
Ru(bipy) ₂ (CN) ₂ ·HClO ₄	2700	5700
Ru(bipy) ₂ (CN) ₂ ·2HClO ₄	760	1780
B. Dicyano-bis-(2,2'-bipyridine)-osmium(II)		
	600 m μ	413 m μ
Os(bipy) ₂ (CN) ₂	2170	7000
Os(bipy) ₂ (CN) ₂ ·HClO ₄	256	7000
Os(bipy) ₂ (CN) ₂ ·2HClO ₄	92	3500

Infrared Spectra.—Solid samples were measured, both as Nujol mulls and in pressed KBr disks, using a Perkin-Elmer Model 21 spectrophotometer and both rock-salt and potassium bromide optics. Hydrated and hydrochloride species of the neutral mixed ligand complexes of iron(II), ruthenium(II) and osmium(II) were examined. Solid hydrochlorides were obtained by placing anhydrous solids in a stream of dry hydrogen chloride; approximately two moles of gas were absorbed per mole of complex, as evidenced by the measured gain in weight. The hydrochlorides are yellow to orange in color.

Results

A. Chemical Evidence for Identification of Protonation Sites in Mixed Complexes. 1. **Undetectable Proton Affinities of Tris-1,10-phenanthroline and Tris-2,2'-bipyridine Complexes.**—Perchlorate salts of the tris 2,2'-bipyridine complexes of iron(II), ruthenium(II) and osmium(II), dissolved in glacial acetic acid, gave no evidence of reaction with perchloric acid when examined spectrophotometrically and potentiometrically. Dissolution of the same salts in concentrated, aqueous solutions of various acids produced changes in color in certain cases but not in others (see below). Wherever observed, the change in color could be shown to be a result of oxidation rather than protonation of the complex. Thus no evidence was found to indicate that either the central metal ion or the aromatic ligand could be protonated.

At least two papers in the literature report the existence of stable protonated species of tris-(1,10-phenanthroline)-iron(II) and of the analogous 2,2'-bipyridine complex in concentrated acid solutions.^{4,5} Therefore the experimental results obtained in the present investigation will be presented below in some detail.

The behaviors of [Fe(phen)₃](ClO₄)₂, [Fe(bipy)₃](ClO₄)₂ and [Os(bipy)₃](ClO₄)₂ on dissolution in various concentrated acids were found to be similar, except for differences in reaction rates. Concentrated sulfuric, perchloric and nitric acid each produced the same change in color in a given complex but at grossly different rates. The new color in each case corresponded to that of the metal(III) complex. No change in color was observed when concentrated hydrochloric or phosphoric acid was used. When dissolved in concentrated sulfuric acid at temperatures well below 0°, the colors of the metal(II) complexes remained unchanged for several hours.

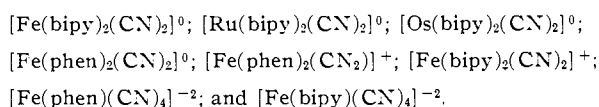
Absorption spectra of concentrated sulfuric acid solutions of [Fe(phen)₃](ClO₄)₂ and [Fe(phen)₃](ClO₄)₃ are identical with respect to wave lengths of their maxima. Addition of such commonly used reductants as hypophosphorous acid, zinc amalgam, arsenic(III) or ferrocyanide to portions of either solution was without noticeable effect. Clearly, reduction of the Fe(III)

species is not kinetically favorable in these cases. On dilution with water to approximately 10 M sulfuric acid, both solutions changed from blue to orange-red in color. Once again the spectra were identical, indicating that the iron(III) species oxidize water and are reduced to iron(II) species on dilution. Completely analogous results were obtained when [Fe(bipy)₃](ClO₄)₂ and [Fe(bipy)₃](ClO₄)₃ were compared in experiments similar to the above.

All of the above changes in color produced by strong acids are accompanied by pronounced changes in magnetic susceptibilities. As reported by Murmann and Healey,^{4,5} the diamagnetic complexes are gradually converted to paramagnetic species, at essentially the same rate as the change in color. It should be noted that only those acids which are known to have strong oxidizing character when concentrated would give rise to these effects.

The formal oxidation-reduction potentials for the [Ru(bipy)₃]⁺³-[Ru(bipy)₃]⁺² couple are considerably higher than the corresponding potentials for the analogous iron and osmium couples.¹² It was not especially surprising therefore to observe that the orange [Ru(bipy)₃]⁺² complex, unlike the others, was unchanged by dissolution and long standing in concentrated sulfuric acid. Addition of sodium perchlorate to the solution brought about a slow, gradual change in color to green, indicative of oxidation to the Ru(III) complex.

2. **Relationship between Number of Protonated Species Formed by and Number of Cyanide Ligands Present in the Complex.**—The complexes listed were found to form the same number of protonated species as the number of cyanide ligands possessed



In the case of two of the iron(III) complexes, [Fe(phen)(CN)₄]⁻ and [Fe(bipy)(CN)₄]⁻, formation of three different protonated species in anhydrous acetic acid-sulfuric acid solutions could be recognized for each. Results obtained using concentrated sulfuric acid alone as the solvent strongly suggest that a fourth proton can be added by each of these iron(III) complexes. These results are described below.

A bright yellow solution is obtained on dissolving H[Fe(phen)(CN)₄] in concentrated sulfuric acid. If the solution is progressively diluted by adding small portions of water, each addition causes a change in color. A broad spectrum of colors can be observed: first yellows, then greens, blues, purple, and finally red. The color changes are instantaneous and reversible. When followed spectrophotometrically, no isosbestic points were found and the wave length of maximum absorption of the single visible absorption band moved continuously from somewhere above 800 in 18 M to about 525 m μ in 4 M sulfuric acid. Since the highest protonated species found in acetic acid has a blue color and maximum absorption at 592 m μ , it seems very probable that there is at least one additional (a fourth) proton per complex ion added in concentrated sulfuric acid.

When examined in identical fashion, H[Fe(bipy)(CN)₄] gave completely analogous results. The succession of colors observed on dilution with water was orange, yellows, greens, purple to rose-red. The wave length of maximum absorbance of the visible absorp-

(12) W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Rev.*, **54**, 959 (1954).

TABLE III
SPECTRAL DATA AND FORMATION CONSTANTS OF PROTONATED COMPLEXES IN ACETIC ACID

Base (B)	Equilibria	—Base—		—Conjugate acid—		Isosbestic points, m μ		K _f
		λ_0 , m μ	a_0	λ_0 , m μ	a_0			
[Fe(phen) ₂ (CN) ₂]NO ₃	B + H ₂ SO ₄ = (HB)(HSO ₄)	522	530	550	530	537		2
	(HB)(HSO ₄) + H ₂ SO ₄ = (H ₂ B)(HSO ₄) ₂			~570	530	560		0.2
[Fe(bipy) ₂ (CN) ₂]NO ₃	B + H ₂ SO ₄ = (HB)(HSO ₄)	525	180	540	190	530		3
	(HB)(HSO ₄) + H ₂ SO ₄ = (H ₂ B)(HSO ₄) ₂			~575	~180	573		0.2
H[Fe(phen)(CN) ₄]	B + HClO ₄ = (HB)(ClO ₄)	524	290	560	280	713	553	~1
	B + H ₂ SO ₄ = (HB)(HSO ₄)			560	280	713	553	0.5
H[Fe(bipy)(CN) ₄]	(HB)(HSO ₄) + H ₂ SO ₄ = (H ₂ B)(HSO ₄) ₂			592	283	575		.20
	B + H ₂ SO ₄ = (HB)(HSO ₄)	506	110	567	107	559		.33
[Fe(phen)(CN) ₄] ⁻	(HB)(HSO ₄) + H ₂ SO ₄ = (H ₂ B)(HSO ₄) ₂			~597	~107	582		.17
	K ₂ B + HClO ₄ = KHB + KClO ₄	428	3200	397	3200	415		>>10 ³
	KHB + HClO ₄ = H ₂ B + KClO ₄			362	3200	372		~10 ³
	H ₂ B + H ₂ SO ₄ = (H ₃ B)(HSO ₄)			337	3400	348		30
[Fe(bipy)(CN) ₄] ⁻	(H ₃ B)(HSO ₄) + H ₂ SO ₄ = (H ₄ B)(HSO ₄) ₂			325	3800	338		0.6
	K ₂ B + H ₂ SO ₄ = KHB + KHSO ₄	425	2340	414	2430	430	374	>>10 ³
	KHB + H ₂ SO ₄ = H ₂ B + KHSO ₄			376	2520	389	348	~10 ³
	H ₂ B + H ₂ SO ₄ = (H ₃ B)(HSO ₄)			362	2490	367		20
	(H ₃ B)(HSO ₄) + H ₂ SO ₄ = (H ₄ B)(HSO ₄) ₂			352	2510	358		1.2

tion band lies above 800 m μ , in the near-infrared, for the complex in concentrated sulfuric acid. Here also, it is very likely that at least four protonated species are formed.

B. Evidence from Infrared Spectra.—The results of the infrared studies do not afford any definitive evidence regarding protonation sites. However, failure to detect the presence of certain predictable absorption bands appears to preclude certain possibilities.

In light of studies by Chatt and Hayter on some hydrido-complexes of Fe(II), Ru(II) and Os(II),¹³ one might expect to observe strong bands due to ν_{M-H} in the range 1700–2000 cm.⁻¹ and possibly weak, broad bands due to δ_{M-H} in the range 600–800 cm.⁻¹ if the central metal ion is protonated. No such bands were detected.

Bands assignable to N–H stretching or bending frequencies were not found. Conceivably, they might have been present but highly broadened. Hydrogen bonded species frequently exhibit extremely broad N–H bands where ionic character is low.¹⁴

Only two significant differences were apparent between spectra of the hydrates and hydrochlorides of [Fe(bipy)₂(CN)₂], [Ru(bipy)₂(CN)₂] and [Os(bipy)₂(CN)₂]. The absorption band due to the cyanide group, near 2100 cm.⁻¹, is broader and lower in absorptivity for the hydrochlorides than for the hydrates. In the case of the osmium complex, this same band is split into two bands (2000 and 2080 cm.⁻¹), each of lower intensity, on formation of the hydrochloride. A second difference is observed in the KBr region where a band of weak to medium intensity near 520 cm.⁻¹ for the hydrates appears to be split into two similar bands, symmetrically displaced about the position of the former, on formation of the hydrochlorides. The bands in question may arise from metal–carbon vibrations. For the hydrates of the iron(II), ruthenium(II) and osmium(II) complexes, the bands are found at 528, 517 and 522 cm.⁻¹, respectively. In the same order, the pairs of bands for the hydrochlorides are at 500 and 535, 500 and 535 and 500 and 545 cm.⁻¹.

C. Equilibrium Constants in Acetic Acid.—The various exchange constants and formation constants are included in Tables III and IV. In summary, the

results indicate that (1) the metal ion has an important influence on the proton affinity of the complex, (2) 1,10-phenanthroline appears to enhance the proton affinity, slightly more than does 2,2'-bipyridine in the mixed complexes, and (3) iron(III) complexes exhibit much weaker affinities than do the corresponding iron(II) complexes. The results are not sufficiently complete to enable further distinctions to be drawn concerning other structural features of the complexes.

TABLE IV

EQUILIBRIUM (EXCHANGE) CONSTANTS^a FOR: BHCIO₄ + X = XHCIO₄ + B IN ACETIC ACID

X	B		
	<i>o</i> -Chloroaniline	Thiourea	Solvent ^b
Fe(bipy) ₂ (CN) ₂	0.9 ± 0.1	35 ± 3	^c
Ru(bipy) ₂ (CN) ₂	2.8 ± .3	140 ± 40	^c
Os(bipy) ₂ (CN) ₂	1.34 ± .4	500 ± 300	^c
Fe(bipy) ₂ (CN) ₂ ·HClO ₄	0.005 ± 0.003	0.11 ± 0.01	3000
Ru(bipy) ₂ (CN) ₂ ·HClO ₄	.008 ± .006	0.36 ± .01	4000
Os(bipy) ₂ (CN) ₂ ·HClO ₄	.026 ± .002	1.6 ± .1	14000

^a Each value is the mean of four or more independent measurements; all measurements fall within the stated limits. Data for the iron(II) complex are taken in part from ref. 1. ^b The constants in this column actually refer to the equilibrium in acetic acid: HClO₄ + X = X·HClO₄; individual measurements fall within ±50% of the mean values reported. ^c Value of the constant is too large to estimate by technique employed.

It appears reasonable to predict that proton affinities should increase as the number of cyanide groups bound to the central metal atom is increased, simply as a consequence of the increased negative (or less positive) charge. Attempts to demonstrate this experimentally were only partially successful. Formation constants of acid species of hexacyanoferrate(II) and hexacyanoferrate(III) could not be measured satisfactorily in acetic acid solvent due to difficulties associated with their decomposition. However, measurements in aqueous systems have been successfully made by Jordan and Ewing on these same species.¹⁵ Also, acidity constants for H₂[Fe(bipy)(CN)₄] in aqueous solutions have been determined by George, Hanania and Irvine.¹⁶ These results indicate that in water

(13) J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 2605, 5507 (1961).

(14) R. C. Taylor, personal communication.

(15) J. Jordan and G. J. Ewing, *Inorg. Chem.*, **1**, 587 (1962).

(16) P. George, G. I. H. Hanania and D. H. Irvine, *J. Chem. Soc.*, 2548 (1959).

$[\text{Fe}(\text{CN})_6]^{-4}$ is approximately 300-fold stronger as a base than is $[\text{Fe}(\text{bipy})(\text{CN})_4]^{-2}$.

Discussion

The results clearly indicate that acid affinity arises from the cyanide ligand rather than the aromatic diimine ligand or central metal ion. Complexes bearing two cyanide ligands are found to give rise to two different acid species; with four cyanide groups, at least four unique acid species are formed. No measurable acid affinity is observed for similar complexes without cyanide ligands. Thus it appears that a proton can add to each and every cyanide group present in the complex. Presumably the site of protonation is at the nitrogen atom of the cyanide group. Certainly it seems unlikely that the carbon atom could bond effectively to both the metal ion and a proton.

Infrared results, although not conclusive, appear to substantiate the above. The major differences between spectra of protonated and non-protonated species are in absorption bands assignable to the cyanide groups. Failure to observe a characteristic N-H stretching frequency may be due to extreme broadness of the band. Were it not for the great difficulty of excluding traces of moisture which absorb strongly in the spectral region of interest, the problem might readily be resolved.

The previous rationale that the central metal ion might be protonated¹ is convincingly refuted by the present results. If protonation could occur at the metal ion, one would expect the tris aromatic diimine complexes to behave accordingly. Moreover, it is unreasonable to expect that as many as four protons, as found in the tetracyano species, could be bonded to the metal ion. Failure to find any infrared or n.m.r.³ evidence also tends to refute metal protonation.

Contrary to reports in the literature,^{4,5} the tris-(1,10-phenanthroline)-iron(II) and analogous 2,2'-bipyridine complex are found not to possess any measurable affinity for acids. The color and magnetic changes effected in these complexes on dissolution in certain specific acids have been found to be a consequence of their oxidation rather than protonation. This fact is all the more convincingly demonstrated when the properties of the tris complexes are compared to those of the mixed ligand cyano complexes, for which there is no question concerning their ready protonation. A number of important distinctions are evident. The mixed complexes give immediate color changes on adding any strong acid; the simple complexes do not. In concentrated sulfuric acid, the mixed ligand complexes of iron(II) remain diamagnetic; the simple iron(II) complexes gradually give rise to paramagnetic species, accompanied by a change in color at essentially the same rate. The formal reduction potentials of the mixed ligand complexes of iron increase with increasing acid concentration¹⁷; the opposite is true for the simple complexes.¹² The $[\text{Ru}(\text{bipy})_3]^{+2}$ complex, having a much higher formal oxidation-reduction potential, does not behave at all like the corresponding iron(II) and osmium(II) complexes on treatment with strong acids; the $[\text{Fe}(\text{bipy})_2(\text{CN})_2]$ and corresponding Ru(II) and Os(II) complexes all exhibit similar behaviors in strong acids. All of the phenomena observed for the simple tris complexes of iron(II) and osmium(II) on treatment with certain strong acids can be satisfactorily explained in terms of oxidation but not protonation. In certain concentrated acids (nitric, sulfuric or perchloric), the tris complexes are gradually oxidized by the solvent and/or atmospheric oxygen. On dilution with water, the formal reduction potentials of the

complexes are increased to the point where water can be oxidized with the accompanying reduction of the complexes to the metal(II) state.

The exchange constants, compiled in Table IV, reveal an interesting trend: proton affinities of the uncharged complexes of type $[\text{M}^{\text{II}}(\text{bipy})_2(\text{CN})_2]$ increase in going from Fe(II) to Ru(II) to Os(II), with relative values in the approximate order as 1:3:14, respectively. Since estimated ionic radii for Fe^{+2} , Ru^{+2} and Os^{+2} are very nearly the same (0.83, 0.81 and 0.88 Å, respectively),¹⁸ it appears that the differences among the three complexes could be the result of either differences in effective ionic charges of the metal ions or differences in their tendencies to back-donate electrons (π -bond) to the ligands. The first mentioned possibility leads to the prediction that proton affinities should decrease as the central metal ion takes on increasingly greater effective positive charge. Such is indeed the case for the iron(II)-iron(III) systems. Only the latter of the two possibilities would account for the observed trend in basicities. Thus as the degree of π -bonding increases, as is believed to be the case on going from the iron(II) to the osmium(II) complex, the proton affinity would also increase. Conceivably, protonation of a nitrogen atom in a cyanide ligand could enhance the degree of π -bonding between metal ion and cyanide group, so that protonation and π -bonding would be essentially synergistic, *i.e.*, mutually enhancing, with respect to one another. It should prove interesting to test the validity of this hypothesis.

The fact that the iron(III) complexes exhibit weaker affinities for acids than do the corresponding iron(II) complexes is reasonable in terms of either valence bond or electrostatic theory. The Fe^{+3} with its greater charge and smaller size should polarize or decrease the electron density about the nitrogen atom in the cyanide groups more so than the Fe^{+2} , thus decreasing the basicity in comparison. From the valence bond approach, the lesser availability of electrons from Fe^{+3} , compared to Fe^{+2} , for π -bonding results in a lesser contribution of electron density from the metal ion to the ligand and thus the basicity of the complex is lower.

The spectral changes produced on addition of strong acids to solutions of the cyano complexes can be explained as a consequence of protonation at the cyanide nitrogen atoms. It is postulated that either a $n \rightarrow \pi$ or $\pi \rightarrow \pi$ transition is responsible for the intense visible absorption of the iron(II) complexes. In both cases, the positive charge introduced on protonation of the cyanide nitrogen atom would be expected to increase the requisite energy for excitation of electrons into participation with the π electron system of the aromatic ligands. A hypsochromic shift would thus accompany protonation. The weaker visible absorption bands of the iron(III) complexes probably arise from d-d type electronic transitions. Apparently, protonation at the cyanide ligands decreases the ligand field strength, degenerate energy levels are split to a lesser degree, and a spectral shift to the red results.

It would seem from the results of this study that any and all cyano complexes should exhibit some tendency to form protonated species. Further studies with this in mind are contemplated. Preliminary results indicate that mixed ligand complexes of copper, cobalt and nickel, analogous to the type studied here, also undergo color changes on absorbing dry hydrogen chloride or on treatment with strongly acidic solvents.

(17) A. A. Schilt, *Anal. Chim. Acta*, **26**, 131 (1962).

(18) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 66.