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Mixed Ligand Complexes of Iron(II) and (III) with Cyanide and Aromatic Di-imines

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The mixed ligand complexes of iron(III) with cyanide and 2,2'-bipyridine and with 1,10-phenanthroline and cyanide have been prepared. Improved procedures were found for the preparation of the analogous iron(II) series. Protonated species of the neutral, mixed ligand complexes of iron(II) have been isolated. The spectral and magnetic properties of both series of complexes, as well as the protonated species, were examined. An interpretation of the visible absorption spectra in terms of previously rationalized views concerning the probable nature of the electronic transitions responsible for absorption in very similar complexes, suggests that protonation of the iron(II) complexes involves the central ferrous ion rather than the ligands. No such distinction could be inferred for the case of the iron(III) complexes.

Introduction

About 25 years ago, Barbieri succeeded in preparing some compounds intermediate between ferrocyanides and ferroamines.[1] His published work appears to have been overlooked by many present-day investigators and reviewers. The writer, unaware of Barbieri's contributions, recently reported a similar investigation[2] which in essence duplicated the earlier work but also revealed further information concerning these mixed ligand iron(II) complexes. The neutral dicyano-bis-(1,10-phenanthroline)-iron(II) complex was found to be especially interesting because of its unique properties, particularly the pronounced solvent dependence of its visible absorption characteristics.[2,3] The chemical and physical properties observed for this neutral complex led to its application in analysis; they provide the basis for a rapid, sensitive and highly selective method for the colorimetric determination of cyanide ions.[4]

The present investigation was undertaken to learn more about the nature of the iron(II) complexes of this series, to prepare and study the mixed ligand complexes of iron(III) and to provide additional background for the development, perhaps, of further analytical applications based upon the chemistry of these complexes.

Experimental

Procedures for the preparation and isolation of the mixed ligand complexes of iron(II) with cyanide and 1,10-phenanthroline or 2,2'-bipyridine have been described earlier by Barbieri.[1] These proved to be adequate in the present work; however it was observed that certain modifications effected decided improvements in yields, crystallinity of products and economy of time and reagents. Complete procedural details are therefore included here for preparation of the iron(II) complexes as well as for preparation of the newly synthesized iron(III) complexes.

Preparation of Dicyano-bis-(1,10-phenanthroline)-iron(II) Dihydrate.—The dark red solution obtained on dissolving 6.0 g. of 1,10-phenanthroline monohydrate (0.030 mole) together with 3.9 g. of ferrous ammonium sulfate hexahydrate (0.010 mole) in 400 ml. of distilled water was heated to just below the boiling point. A freshly prepared solution of 10 g. of KCN in 10 ml. of water was added all at once to the hot solution. After brief stirring the solution was left to cool at room temperature during which time well formed, small, crystalline platelets slowly developed. After a few hours aging the dark violet product was isolated by suction filtration, washed generously with distilled water and dried *in vacuo* at room temperature (yield 5.0 g., 99%). To the filtrate, which should contain approximately 2 g. of 1,10-phenanthroline resulting from its displacement from iron(II) by cyanide ions, was added 40 ml. of concentrated hydrochloric acid. After boiling this solution (in the hood) to effect complete removal of hydrogen cyanide, 1.3 g. of ferrous ammonium sulfate hexahydrate was added and then sufficient ammonium hydroxide to adjust the *p*H to between 9 and 11. The resulting deep red solution was heated to near boiling (if an excess of ferrous ion inadvertently has been added the hydrous ferric oxide which precipitates at this stage should be filtered out before proceeding), 7 g. of KCN in 10 ml. of water was added all at once, and the hot solution was left standing to cool at room temperature. The crystalline product was recovered as before (yield 1.6 g., 99%).

When used as starting material for the synthesis of other complexes the product obtained above was not further purified. For purposes of spectral and magnetic measurements a portion of the initial product was recrystallized from concentrated sulfuric acid. Other possible solvents are chloroform or nitrobenzene but large volumes or continuous extractions are necessary due to low solubilities. In a typical recrystallization from H_2SO_4, 2 g. of the complex is dissolved in 10 ml. H_2SO_4 (95%) to give a clear, bright yellow solution. Approximately 500 ml. of distilled water is then added very slowly with vigorous stirring. A coarsely crystalline yellow precipitate develops early which on further dilution of the supernatant undergoes several changes in hue passing through orange and red and finally turning a dark violet. Thorough washing with water to remove the last detectable trace of acid followed by drying *in vacuo* at room temperature provides a product indistinguishable from one recrystallized from chloroform. A yield in excess of 95% is obtained.

Anal. Calcd. for $[Fe\ phen_2(CN)_2]\cdot 2H_2O$: Fe, 11.1; N, 16.67; H_2O, 7.1. Found: Fe, 11.2; N, 16.64; H_2O, 6.8.

Preparation of Dicyano-bis-(2,2'-bipyridine)-iron(II) Trihydrate.—A procedure completely analogous to that used above for the corresponding 1,10-phenanthroline-containing complex was employed. The initial product was obtained in the form of large, well-formed, dark violet needles and in high yield. The portion used for subsequent measurements was recrystallized from concentrated sulfuric acid as described above, washed generously with distilled water, and dried *in vacuo* at room temperature. Recrystallization provided a finely divided product for which these analytical results were obtained.

Anal. Calcd. for $[Fe\ bipy_2(CN)_2]\cdot 3H_2O$: Fe, 11.8; N, 17.8; H_2O, 11.4. Found: Fe, 12.0; N, 17.6; H_2O, 11.6.

Preparation of Potassium Tetracyano-mono-(1,10-phenanthroline)-ferrate(II) Tetrahydrate.—A mixture of 1.0 g. of dicyano-bis-(1,10-phenanthroline)-iron(II) dihydrate and 400 ml. of an aqueous solution containing 40 g. of KCN was heated in a steam-bath for a period of five days. After cooling and filtration to remove the small amount of unreacted solid, the filtrate was extracted with portions of chloroform until no further violet coloration was produced in the $CHCl_3$ layer. Evaporation of the dark orange, aqueous phase to a volume of approximately 100 ml. with subsequent cooling gave a dark orange-red crystalline product which was collected by suction filtration. When this was dissolved in a small amount of water, it was found to contain a small amount of a grey, amorphous, insoluble material. The contaminate was removed by filtration and found to contain silica (from the reaction vessel) and traces of iron. Almost complete evaporation of the filtrate was required before recrystallization of the orange product could be achieved from

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[1] G. A. Barbieri, *Atti accad. Lincei*, **20**, 273 (1934).

[2] A. A. Schilt, THIS JOURNAL, **79**, 5421 (1957).

[3] J. Bjerrum, A. W. Adamson and O. Bostrup, *Acta Chem. Scand.*, **10**, 329 (1956).

[4] A. A. Schilt, *Anal. Chem.*, **30**, 1409 (1958).

water; recovery from the original reaction mixture therefore appears to be favored by the high concentration of electrolyte and its effect on the solubility of the desired product. The final product was dried in air at room temperature; yield 0.88 g. (90%).

Anal. Calcd. for $\mathrm{K_2[Fe\ phen(CN)_4]\cdot 4H_2O}$: Fe, 11.4; N, 17.1. Found: Fe, 11.6; N, 16.8.

Preparation of Potassium Tetracyano-mono-(2,2'-bipyridine)-ferrate(II) Trihydrate.—This compound was obtained in good yield (95%) by a procedure analogous to that described above for its 1,10-phenanthroline analog. A period of 24 hr. in a steam-bath is sufficient for essentially complete reaction. The dark orange-brown crystalline product after recrystallization from a small quantity of water was dried in air at room temperature.

Anal. Calcd. for $\mathrm{K_2[Fe\ bipy(CN)_4]\cdot 3H_2O}$: Fe, 12.5; N, 18.8; $\mathrm{H_2O}$, 12.1. Found: Fe, 12.3; N, 18.1; $\mathrm{H_2O}$, 11.7.

Preparation of Hydrogen Tetracyano-mono-(2,2'-bipyridine)-ferrate(II) Trihydrate.—This substance was obtained in good yield by adding a slight excess of 6 *M* hydrochloric acid to an ice cold solution of the potassium salt. After washing with cold, dilute hydrochloric acid the yellow crystalline product was dried *in vacuo* at room temperature.

Anal. Calcd. for $\mathrm{H_2[Fe\ bipy(CN)_4]\cdot 3H_2O}$: Fe, 15.0; N, 22.6. Found: Fe, 15.2; N, 23.0.

Preparation of Dicyano-bis-(1,10-phenanthroline)-iron-(III) Nitrate Tetrahydrate.—To 2.6 g. of dicyano-bis-(1,10-phenanthroline)-iron(II) dihydrate was added 10 ml. of concentrated nitric acid (70%). Reaction ensued at once accompanied by evolution of nitrogen dioxide to give a deep purple colored solution. The mixture was warmed slightly to effect complete dissolution and reaction; it was then diluted with 300 ml. of distilled water to give a finely divided, purple precipitate. After heating this mixture to obtain a clear purple solution, it was set aside to cool at room temperature. While standing overnight, slow recrystallization gave rise to long, well-formed, dark purple, glistening needles which were isolated by suction filtration, washed with water and dried in air; yield 2.2 g. (71%).

Anal. Calcd. for $\mathrm{[Fe\ phen_2(CN)_2]NO_3\cdot 4H_2O}$: Fe, 9.27; C, 51.8; H, 4.02; N, 16.3; $\mathrm{H_2O}$, 12.0. Found: Fe, 9.28; C, 52.0; H, 3.96; N, 15.9; $\mathrm{H_2O}$, 11.3.

Preparation of Dicyano-bis-(2,2'-bipyridine)-iron(III) Nitrate.—This substance was obtained in the form of glistening red, cube-shaped crystals by a procedure analogous to that described above for its 1,10-phenanthroline analog; yield 68%.

Anal. Calcd. for $\mathrm{[Fe\ bipy_2(CN)_2]NO_3}$: Fe, 11.6; C, 54.8; H, 3.34; N, 20.3. Found: Fe, 11.5; C, 54.9; H, 3.34; N, 20.5.

Preparation of Dicyano-bis-(1,10-phenanthroline)-iron-(III) Perchlorate.—Since the perchlorate salt of this complex ion is considerably more insoluble than the nitrate, it may be obtained readily by adding a solution of sodium perchlorate to a solution of the nitrate salt. An alternate synthesis was developed, however, to substantiate that the iron(II) complex is merely oxidized by nitric acid and not otherwise modified, *e.g.*, to give a nitro species. Possible contamination by nitrate ions was a further consideration.

Chlorine gas was passed into a suspension of 1.0 g. of dicyano-bis-(1,10-phenanthroline)-iron(II) in 100 ml. of 1 *M* hydrochloric acid while heating below boiling and until, after a few minutes, a clear, purple solution was produced. To this was added 2 g. of $\mathrm{NaClO_4}$ dissolved in about 20 ml. of water. The purple crystalline precipitate which formed was aged in contact with the supernatant for several hours, collected by suction filtration, washed with water and dried at room temperature *in vacuo*. A yield of 1.1 g. was obtained.

Anal. Calcd. for $\mathrm{[Fe\ phen_2(CN)_2]ClO_4}$: Fe, 9.84; C, 55.0; H, 2.85; N, 14.8. Found: Fe, 9.80; C, 55.6; H, 3.00; N, 14.5.

Preparation of Dicyano-bis-(2,2'-bipyridine)-iron(III) Perchlorate.—A bright red crystalline product was obtained in excellent yield following a procedure analogous to that given above for the corresponding 1,10-phenanthroline-containing substance.

Anal. Calcd. for $\mathrm{[Fe\ bipy_2(CN)_2]ClO_4}$: Fe, 10.7; C, 50.8; H, 3.10; N, 16.2. Found: Fe, 10.7; C, 51.0; H, 3.06; N, 16.0.

Preparation of Hydrogen Tetracyano-mono-(1,10-phenanthroline)-ferrate(III) Dihydrate.—Chlorine gas was passed into a solution of 0.88 g. of potassium tetracyano-mono-(1,10-phenanthroline)-ferrate(II) tetrahydrate in 100 ml. of distilled water until the initial orange color was transformed to dark red. The resulting chlorine-saturated solution was placed in an ice-bath immediately after adding 5 ml. of concentrated hydrochloric acid. Small, thick, dark violet needles, which subsequently crystallized from the cold solution, were collected by suction filtration, washed well with cold and dilute hydrochloric acid (saturated with $\mathrm{Cl_2}$) and dried *in vacuo* at room temperature. A yield of 0.75 g. was obtained.

The product gives a red solution in water which turns orange-yellow on adding reductants, *e.g.*, hydroxylamine hydrochloride. When dried at 110° *in vacuo* both hydrogen cyanide and water of hydration are lost and the color of the solid is transformed to dark brown.

Anal. Calcd. for $\mathrm{H[Fe\ phen(CN)_4]\cdot 2H_2O}$: Fe, 14.8; C, 50.9; H, 3.48; N, 22.3. Found: Fe, 14.6; C, 50.6; H, 3.43; N, 21.8; loss *in vacuo* at 110°, 14.7.

Preparation of Hydrogen Tetracyano-mono-(2,2'-bipyridine)-ferrate(III) Dihydrate.—Long, iridescent, red needles were obtained by a procedure similar to that described above for the 1,10-phenanthroline analog; 95% yield.

Anal. Calcd. for $\mathrm{H[Fe\ bipy(CN)_4]\cdot 2H_2O}$: Fe, 15.8; C, 47.6; H, 3.71; N, 23.8. Found: Fe, 16.0; C, 47.6; H, 3.76; N, 24.4; loss *in vacuo* at 110°, 17.4.

Preparation of Dicyano-bis-(1,10-phenanthroline)-iron-(III) Tetracyano-mono-(1,10-phenanthroline)-ferrate(III) Hexahydrate.—A solution of 0.40 g. of $\mathrm{[Fe\ phen_2(CN)_2]NO_3\cdot 4H_2O}$ in 100 ml. of hot water was mixed with 100 ml. of a solution saturated with chlorine and containing 0.30 g. of dissolved $\mathrm{H[Fe\ phen(CN)_4]\cdot 2H_2O}$. On standing at room temperature a dark red-brown, crystalline precipitate formed; this was collected by suction filtration, washed with water and dried *in vacuo*. A yield of 0.56 g. was obtained.

Anal. Calcd. for $\mathrm{[Fe^{III}\ phen_2(CN)_2][Fe^{III}\ phen(CN)_4]\cdot 6H_2O}$: Fe, 12.2; C, 55.0; H, 3.96; N, 18.3. Found: Fe, 12.6; C, 56.9; H, 3.96; N, 18.5.

Preparation of Dicyano-bis-(2,2'-bipyridine)-iron(III) Tetracyano-mono-(2,2'-bipyridine)-ferrate(III) Octahydrate.—Long, slender, brown needles were obtained in approximately 80% yield by a procedure similar to that described above for the 1,10-phenanthroline analog.

Anal. Calcd. for $\mathrm{[Fe^{III}\ bipy_2(CN)_2][Fe^{III}\ bipy(CN)_4]\cdot 8H_2O}$: Fe, 12.7; C, 49.1; H, 4.58; N, 19.1. Found: Fe, 12.4; C, 49.4; H, 4.61; N, 19.2.

Addition Product of Dicyano-bis-(1,10-phenanthroline)-iron(II) with Sulfuric Acid.—A solution of the iron(II) complex in 95% $\mathrm{H_2SO_4}$ was cooled in an ice-bath and then distilled water was added slowly with stirring to dilute the acid. After about a five-fold dilution of the solution a yellow precipitate formed. This was isolated by suction filtration and washed with acetone until it turned bright orange. (In earlier attempts to isolate this product it was found that excessive washing with acetone will transform its color to red and eventually to violet.) The bright orange solid was stored *in vacuo* over Ascarite at 78° for several days; during this period the color turned golden yellow. Earlier attempts to remove any excess sulfuric acid at higher temperatures resulted in decomposition.

The golden yellow product was found to be diamagnetic. On washing a weighed sample with water it turned dark violet; the combined wash water was titrated with standard sodium hydroxide to determine the sulfuric acid content.

Anal. Found: C, 45.3; H, 3.53; N, 11.8; $\mathrm{H_2SO_4}$, 28.0. Calcd. for $\mathrm{[Fe\ phen_2(CN)_2]\cdot 3H_2O\cdot 2H_2SO_4}$: C, 43.5; H, 3.62; N, 11.7; $\mathrm{H_2SO_4}$, 27.3.

Addition Product of Dicyano-bis-(2,2'-bipyridine)-iron-(II) with Hydrochloric Acid.—Distilled water was added slowly with stirring to an ice cold solution of the iron(II) complex in 36% hydrochloric acid. After a several fold dilution a red-orange precipitate was produced. Following isolation by suction filtration the product was dried *in vacuo* at room temperature. The solid was found to be diamagnetic. When a portion was moistened with water it turned violet in color. For determination of HCl a weighed portion was added to water, and the highly colored mixture was titrated potentiometrically with standard sodium hydroxide.

Anal. Found: C, 52.4; H, 3.76; N, 17.0; HCl, 9.0. Calcd. for $[\mathrm{Fe\ bipy_2(CN)_2}]\cdot\mathrm{HCl}\cdot2\mathrm{H_2O}$: C, 53.6; H, 3.87; N, 17.1; HCl, 7.3.

Analyses.—For determination of iron, weighed samples were decomposed in dilute hydrochloric acid by prolonged heating to expel hydrogen cyanide completely. In the case of the iron(III) complexes it proved expedient to add sufficient sodium bisulfite to effect reduction, since in their higher oxidation state these complexes are considerably more resistant to attack by acid. An excess of either 1,10-phenanthroline or 2,2′-bipyridine, depending on the nature of the initial complex, then was added to aliquots of the solutions thus obtained. After addition of hydroxylamine hydrochloride and sufficient ammonium hydroxide to adjust the *p*H to between 4–9 the solutions were diluted to a known volume and their iron concentrations determined spectrophotometrically.

Water was determined as the loss in weight on heating *in vacuo* over phosphorus pentoxide.

Carbon, hydrogen and nitrogen analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Absorption Spectra.—Freshly prepared solutions of the solid complexes in known concentrations were examined spectrophotometrically using a Cary Recording Spectrophotometer (Model 11), matched silica cells of path length 1.000 ± 0.001 cm. and slit widths ranging from 0.01 to 0.02 mm. The wave length region 325–800 mμ was scanned.

Magnetic Measurements.—The magnetic susceptibilities of the solid samples were determined by the Gouy method employing water and solid ferrous ammonium sulfate hexahydrate as calibration standards. Measurements were made at room temperature (29–31°) only. Values given in column 2 of Table I are the molar susceptibilities of the complex compounds; the results in column 3 have been corrected for the diamagnetisms of ligands and ions. These diamagnetic corrections were used: cyanide ion, -18×10^{-6}; perchlorate ion, -34×10^{-6}; water, -13×10^{-6}; nitrate ion, -20×10^{-6}; potassium ion, -13×10^{-6}; 2,2′-bipyridine, -95×10^{-6}; 1,10-phenanthroline, -119×10^{-6}.

TABLE I

MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF SOLID COMPLEXES[a]

Compound	$\chi_M \times 10^6$ (compound)[b]	$\mu_{\mathrm{eff.}}$ (B.M.) (iron ion)
$[\mathrm{Fe\ phen_2(CN)_2}]\cdot2\mathrm{H_2O}$	−107	0.68
$]\mathrm{Fe\ bipy_2(CN)_2}]\cdot3\mathrm{H_2O}$	−110	.61
$\mathrm{K_2}[\mathrm{Fe\ bipy(CN)_4}]\cdot3\mathrm{H_2O}$	−159	.42
$\mathrm{H_2}[\mathrm{Fe\ bipy(CN)_4}]\cdot3\mathrm{H_2O}$	− 22	.60
$[\mathrm{Fe\ phen_2(CN)_2}]\mathrm{NO_3}\cdot4\mathrm{H_2O}$	1926	2.34
$[\mathrm{Fe\ bipy_2(CN)_2}]\mathrm{NO_3}$	1946	2.31
$[\mathrm{Fe\ phen_2(CN)_2}]\mathrm{ClO_4}$	2021	2.38
$[\mathrm{Fe\ bipy_2(CN)_2}]\mathrm{ClO_4}$	1933	2.31
$\mathrm{H}[\mathrm{Fe\ phen(CN)_4}]\cdot2\mathrm{H_2O}$	2069	2.36
$\mathrm{H}[\mathrm{Fe\ bipy(CN)_4}]\cdot2\mathrm{H_2O}$	2129	2.37
$[\mathrm{Fe\ phen_2(CN)_2}][\mathrm{Fe\ phen(CN)_4}]\cdot6\mathrm{H_2O}$	4333	2.43
$[\mathrm{Fe\ bipy_2(CN)_2}][\mathrm{Fe\ bipy(CN)_4}]\cdot8\mathrm{H_2O}$	3666	2.25

[a] Barbieri (ref. 1) has reported these gram susceptibilities for the substances indicated: $[\mathrm{Fe\ bipy_2(CN)_2}]\cdot3\mathrm{H_2O}$, -0.244×10^{-6}; $\mathrm{K_2}[\mathrm{Fe\ bipy(CN)_4}]\cdot3\mathrm{H_2O}$, -0.352×10^{-6}; $[\mathrm{Fe\ phen_2(CN)_2}]\cdot3\mathrm{H_2O}$, -0.385×10^{-6}. Magnetic moments were given in Weiss magnetons; the moments of the complexes, in terms of Bohr magnetons and in the order cited, are 0.57, 0.36 and 0.47 B.M. [b] The relative precisions of the magnetic susceptibility measurements are estimated to range from 1 to 5%.

Results and Discussion

Observations Concerning Solubility and Proton Affinity of the Neutral Iron(II) Complexes.—The solubilities of dicyano-bis-(1,10-phenanthroline)-iron(II) and its 2,2′-bipyridine analog definitely appear to be related to the ability of the solvent to either associate through hydrogen bonding with the complexes or to produce charged species of the complexes by hydrogen ion donation. Observations which support this premise are described below.

Solvents which fail to dissolve any significant quantity of the neutral iron(II) complexes include diethyl ether, petroleum ether, carbon tetrachloride, ethyl acetate, ethylenediamine, *p*-dioxane, benzene and acetone. Although insolubility in basic solvents generally prevails, there are exceptions, *e.g.*, pyridine and N,N′-dimethylformamide both dissolve amounts sufficient to give deep violet colored solutions. It is observed that small amounts of water when added to either acetone or *p*-dioxane provide for solubility of the complexes, even though water by itself dissolves relatively little. The dielectric strength as well as the acidic character of the solvents are thereby increased. Obviously both are important solubility factors; however, in this instance it is difficult to conclude which factor is dominant.

Acidic solvents display varying dissolution strengths with respect to the neutral complexes. Moderate solubility is observed in weak to mildly strong acidic solvents such as ethanol, chloroform, nitrobenzene, formamide, β-naphthol and acetic acid. Strong and concentrated mineral acids dissolve large amounts of the complexes with appreciable effects on color but without decomposition.

More direct and convincing substantiation for the above premise is provided by the observation that solid complexes containing acid, bound in seemingly stoichiometric amounts, can be isolated. It is also found that either the anhydrous or hydrated form of these complexes will absorb dry hydrogen chloride gas rapidly and change in color thereby from dark violet to orange. This, in addition to the fact that no isosbestic point is observed for the spectra, rules out the possibility that the color changes are due to conversions between *cis* and *trans* isomers. Moreover, it confirms that the acid present in solids crystallized from strong acid solutions is not simply occluded during rapid growth and coagulation processes.

The basicity of the neutral complexes is further evidenced by the fact that these can be successfully titrated with perchloric acid in a glacial acetic acid system. Potentiometric titrations indicate that both behave as very weak monobasic substances in glacial acetic acid. This work, together with additional studies concerning application of these neutral complexes as acid-base indicators for non-aqueous titrations, will be reported elsewhere. It is pertinent, however, to emphasize here that the neutral complexes exhibit dibasic character in strong, concentrated, mineral acids. In such systems there would be three inter-convertible species; therefore an isosbestic point in absorption spectra should not be expected.

Magnetic Properties.—It is known that the hexacyanoferrate(II) ion, the tris-(1,10-phenanthroline)-iron(II) ion and the tris-(2,2′-bipyridine)-iron(II) ion are all diamagnetic. The corresponding iron(III) complexes have magnetic moments between 2.3 and 2.4 Bohr Magnetons, indicating

TABLE II

VISIBLE ABSORPTION CHARACTERISTICS OF THE MIXED LIGAND COMPLEXES IN VARIOUS SOLVENTS[a]

Compound	Solvent	Band	Absorption band characteristics			
			λ_0, mμ	ν_0, cm.$^{-1}$	a_0	δ, cm.$^{-1}$
$[Fe\ phen_2(CN)_2]$	$CHCl_3$	I	600	16700	9980	800
		II	∼525	19040	∼7200	∼2500
		III	371	26950	1500	300
	EtOH	I	561	17800	8840	950
		II	∼488	20500	∼6400	∼2400
		III	355	28200	900	500
	0.6 *M* H_2SO_4	I	∼509	19700	∼6000	∼1000
		II	∼450	22200	∼6000	∼3000
		III	∼325	30800	∼ 300	∼ 400
	12 *M* H_2SO_4	I	∼400	25000	∼5000	∼2000
		II	367	27200	∼6000	∼3000
		III	∼328	30500	∼ 70	∼ 200
$[Fe\ bipy_2(CN)_2]$	$CHCl_3$	I	608	16400	8160	700
		II	∼543	18400	∼4000	∼1000
		III	384	26040	8190	1700
	EtOH	I	570	17600	6930	1000
		II	∼506	19800	∼3000	∼1000
		III	373	26800	6790	2300
	0.6 *M* H_2SO_4	I	∼533	19000	∼1000	∼1000
		II	∼492	20300	∼4700	∼2000
		III	348	28700	5080	3000
	2 *M* H_2SO_4	I		Absent		
		II	467	21400	4240	2600
		III	∼340	29400	∼4000	
	6 *M* H_2SO_4	I		Absent		
		II	414	24150	4340	2300
		III		Absent		
	12 *M* H_2SO_4	I		Absent		
		II	402	24900	4410	1900
		III		Absent		
$K_2[Fe\ phen(CN)_4]$	95% EtOH		514	19450	4920	2050
	H_2O		462	21600	4420	2340
	0.1 *M* NaOH		462	21600	4410	2340
	0.1 *M* HCl		424	23600	3220	2900
$K_2[Fe\ bipy(CN)_4]$	95% EtOH	I	535	18700	2950	1600
		II	373	26800	4070	2300
	0.1 *M* NaOH	I	482	20750	2880	1800
		II	348	28700	3470	2600
	0.1 *M* HCl	I	438	22800	2230	2600
		II	∼325	30800	∼2800	∼2000
$[Fe\ phen_2(CN)_2]NO_3$	95% EtOH	I	525	19050	1150	2100
		II	359	27900	∼3600	∼1700
	H_2O	I	529	18900	597	2200
		II	355	28200	∼3600	∼1500
	0.2 *M* H_2SO_4	I	536	18700	434	2200
		II	356	28100	∼3600	∼1500
$[Fe\ bipy_2(CN)_2]NO_3$	H_2O	I	544	18400	200	1400
		II	∼394	25400	∼1200	∼1000
	0.6 *M* HNO_3	I	545	18350	210	1480
		II	∼394	25400	∼1300	∼1000
$H[Fe\ phen(CN)_4]$	95% EtOH	I	467	21400	289	2400
		II	383	26100	∼2300	
		III	360	27800	∼2400	
	0.1 *M* $NH_4C_2H_3O_2$ *p*H ∼7)	I	506	19700	298	2400
		II	∼375	26700	∼1620	
		III	355	28200	2060	
	0.1 *M* HCl	I	506	19700	286	2400
		II	∼371	27000	∼1600	
		III	355	28200	∼2100	
$H[Fe\ bipy(CN)_4]$	95% EtOH	I	∼430	23300	∼ 300	∼1000
		II	385	26000	2200	2000

TABLE II (*continued*)

Compound	Solvent	Band	Absorption band characteristics			
			λ_0, mμ	ν_0, cm.$^{-1}$	a_0	δ, cm.$^{-1}$
		III	335	29800	~1500	
	0.1 *M* $NH_4C_2H_3O_2$ (*p*H ~7)	I	506	19800	109	1600
		II	416	24000	940	700
		III	375	26700	1490	1600
	0.1 *M* HCl	I	508	19700	107	1700
		II	417	24000	920	700
		III	376	26700	1450	1300

[a] The symbol (~) preceding certain of the above quantities indicates them to be only approximate. The bands in question appear as shoulders or partial bands for which the characteristics were estimated by assuming the bands to approximate Gaussian error curves (ref. 7). Wherever such approximations seemed too severe, the data are omitted.

the existence of one electron with unpaired spin. All these complexes are therefore considered to involve $3d^24s4p^3$ bond orbitals.[5,6] It is reasonable to expect that the mixed ligand complexes studied here should exhibit similar magnetic properties, as it seems quite unlikely that a new set of bonding orbitals would result on mixing the ligands. The data presented in Table I are found to be consistent with such an expectation.

The magnetic data are also of interest as confirmatory evidence that the substances isolated during this investigation are indeed iron(III) complexes rather than addition or decomposition products.

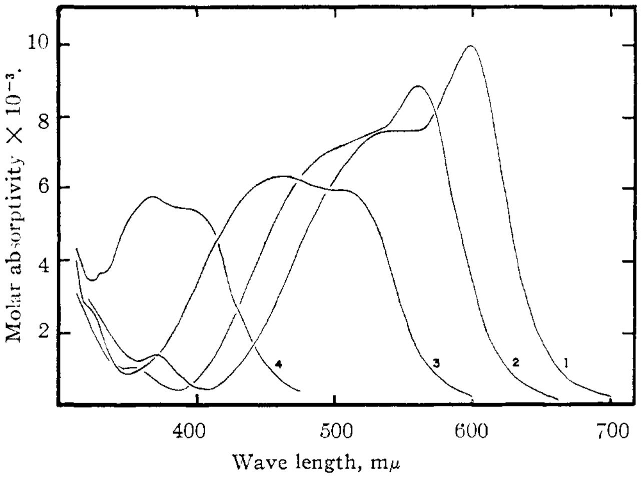

Fig. 1.—Molar absorptivity curves for dicyano-bis-(1,10-phenanthroline)-iron(II) in various solvents: (1) chloroform, (2) absolute ethanol, (3) 0.6 *M* sulfuric acid, (4) 12 *M* sulfuric acid.

It is rather frequent in practice to observe magnetic moments as large as 0.6 Bohr Magneton for diamagnetic substances. Factors such as temperature-independent paramagnetism, impurities and uncertainties in diamagnetic corrections could account for this. The magnetic moments of the iron(II) complexes given in Table I might for such reasons be considered essentially equal to zero. However, it is conceivable that more refined and extensive measurements might show that slight but significant magnetic changes accompany the changes in symmetry which presumably occur on mixing ligands as dissimilar as cyanide and the aromatic di-imine type.

Magnetic studies on the protonated species of the neutral iron(II) complexes indicate these to be decidedly diamagnetic. The observed magnetic susceptibilities after correction for the diamagnetism of the ligands suggest that the ferrous ion is appreciably diamagnetic. Here again, more extensive and refined measurement is necessary to ascertain whether the effect is real.

Absorption Spectra.—Characteristics of the absorption bands of the various complexes, examined in a variety of solvents and solutions, are compiled in Table II. The wave length (λ_0), wave number ($\bar{\nu}_0$) and molar absorptivity (a_0) all refer to absorption maxima, and δ is the half-width ($\delta = |\bar{\nu} - \nu_0|$ where $\bar{\nu}$ is the wave number where $a = a_0/2$ on the band). The effect of solvent on the spectra of the iron(II) complexes is illustrated for the 1,10-phenanthroline series in Figs. 1 and 2.

Perhaps the most interesting aspect of the spectrophotometric results is the pronounced dependence of the spectral characteristics of the iron(II) complexes on the nature of the solvent. The absorption spectra of the iron(III) complexes, on the other hand, are by comparison only slightly affected by changes in the solvent; however only a very limited number of solvents could be tried. The iron(III) complexes are too insoluble in most non-aqueous solvents and also they are susceptible to reduction when dissolved, *e.g.*, reduction of the tetracyano species occurs almost instantaneously in dilute ammonia or sodium hydroxide solutions. The spectral data given for the iron(III) complexes in 95% ethanol are subject to suspicion, even though freshly prepared solutions were measured, since reduction was observed to occur slowly. In the case of dicyano-bis-(2,2'-bipyridine)-iron(III) nitrate in 95% ethanol the rate of reduction was so appreciable that the spectral results are omitted.

If the particular electronic transitions responsible for the absorption bands were unequivocally known, it would perhaps be possible to account for the solvent dependence of the spectra, since the spectral shifts appear to be intimately related to the acidic character of the solvent. In the absence of such knowledge it is at least of interest to interpret the results and observations of this investigation in terms of what has been previously rationalized

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

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

(7) C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1495 (1954).

about the nature of the spectra of very similar complexes.

Williams has examined the absorption spectra given in the literature for a number of complex ions of analytical importance; the regularities apparent in the spectra of the iron(II) and iron(III) complexes of 1,10-phenanthroline, 2,2'-bipyridine and their substitution derivatives were considered in some detail.[8] He suggests that the intense absorption bands in the visible region for the diamagnetic iron(II) complexes of these aromatic diimines arise from excitation of a 3d electron to a level which can participate or couple with the empty π levels of the ligand. If such a partial electron transfer does occur, it would account for the regularities in spectral shifts observed when various substituents are introduced in the aromatic rings, *i.e.*, substituents which are known to influence the electron acceptor character of the ligand in at least a qualitatively predictable fashion.[8] The diamagnetic iron(II) complexes studied in the present work apparently interact or associate rather intimately with protons or hydrogen bonding species. If such interaction involves the ligands only, then a bathochromic shift would be expected on the basis that the energy level of the excited state would be decreased by an amount proportional to the energy of interaction. The observed "shifts" with increasing acid concentration, however, are in the opposite direction, *i.e.*, toward the blue. It would appear, then, if the above hypotheses are valid, that the proton interacts directly with the central metal ion, presumably with one of the filled and perturbed 3d orbitals. In this event the energy level of the ground state should be lowered and the absorption bands would shift toward the blue region of the spectrum.

It is believed that the absorption characteristics of the paramagnetic complexes of iron(III) investigated in this work can be satisfactorily understood on the basis of 3d–3d transitions which are coupled with partial charge transfer to the cation from the ligand. Transitions of this type have been suggested for similar complexes by Williams.[8] It would be expected that the more positive ferric ion should interact to a lesser degree with protons and that less pronounced spectral shifts would accompany changes in the acidic character of the solvent. If on the other hand interactions of an acidic nature occur at the ligands, then partial charge transfer to the cation would be discouraged. Both views lead to equivocal conclusions concerning the direction and relative magnitude of anticipated spectral shifts.

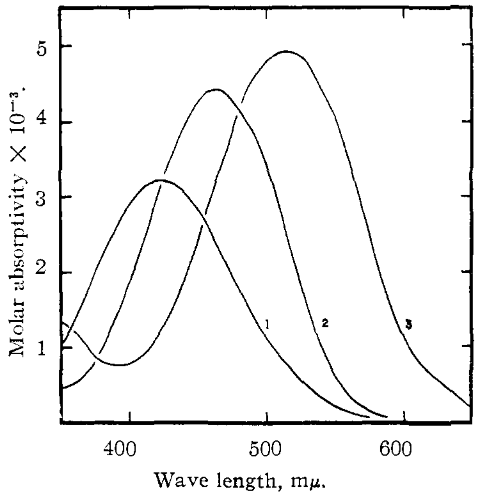

Fig. 2.—Molar absorptivity curves for potassium tetracyano-mono-(1,10-phenanthroline)-ferrate(II) in various solvents: (1) 0.1 *M* hydrochloric acid, (2) either pure water or 0.1 *M* sodium hydroxide (same curve), (3) aqueous ethanol (95% ethanol, by volume).

At this point in the discussion it is pertinent to note that the existence of stable protonated species of 1,10-phenanthroline and 2,2'-bipyridine metal chelates has been postulated previously by a number of other investigators to account for the observed acid dependence of dissociation rates.[9–11] The results of the present study, in particular the successful isolation of protonated iron(II) species, constitute another convincing argument in support of such an hypothesis.

A very recent communication[12] presents evidence of protonation of ferrocene by strong acids. Proton affinity of metal complexes involving various degrees of π bonding character may be a rather common phenomenon. It is anticipated that further studies with this possibility in mind will be forthcoming and should prove most interesting.

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(8) R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

(9) T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1948).

(10) D. W. Margerum, R. I. Bystroff and C. V. Banks, *ibid.*, **78**, 4211 (1956).

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

(12) M. Rosenblum and J. O. Santer, THIS JOURNAL, **81**, 5517 (1959).