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Synthesis, Isolation and Characterization of Some Iron(II) Complexes with Mixed *α,α'*-Diimine Ligands[1]

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Syntheses are described for mixed ligand complexes of the type $[Fe(phen)_nL_{3-n}]X_2$ and $[Fe(terpy)(TPTZ)]X_2$ (where n = 1 or 2, phen = 1,10-phenanthroline, L = methyl, phenyl, nitro, or chloro substituted 1,10-phenanthroline, terpy = 2,2',2"-terpyridine, TPTZ = tris (2'-pyridyl)-1,3,5-triazine and X = ClO_4^- and I^-) and $[Fe(phen)_nL'_{3-n}]$ (where n = 2 and L' = 4,7-dihydroxy-1,10-phenanthrolinato, 4,7-diphenyl-1,10-phenanthroline-disulfonato or dimethylglyoximato; also where n = 1 and L' = 4,7-dihydroxy-1,10-phenanthrolinato, 1,10-phenanthrolinato, 1,10-phenanthroline-5-sulfonato or phenyl-2-pyridyl ketoximato). The formal oxidation-reduction potentials and visible absorption spectra of these mixed ligand complexes show certain regularities in comparisons with related unmixed complexes that are of theoretical interest and practical significance. These are discussed.

Introduction

Ligands containing the α,α'-diimine functionality, $-N=\overset{|}{C}-\overset{|}{C}=N-$, form particularly stable and intensely colored complexes with ions such as iron(II) and copper(I).[3] Some representative compounds which contain this functionality are 1,10-phenanthroline (phen), tris(2-pyridyl)-1,3,5-triazine (TPTZ), phenyl-2-pyridylketoxime, dimethylglyoxime ($DMGH_2$) and 2,2'-bipyridine (bipy).

Mixed ligand complexes may possess properties which are uniquely different from their parent trischelates. In theory they should be more stable than the individual binary species.[4,5] Pronounced spectral changes may accompany the mixing of the ligands. For example, $[Fe(phen)_2(CN)_2]$ is violet, $[Fe(phen)_3]^{2+}$ is orange-red, and $[Fe(CN_6]^{4-}$ is essentially colorless.

Low spin mixed ligand complexes of iron(II) of the type $[Fe(phen)_2X_2]$ where X = SCN^-[6] as well as high spin complexes where X = Cl^-, Br^-, N_3^-, NCO^-, or HCO_2^-[7,8,9] have been prepared. Their properties were reviewed by König.[10] Complexes of intermediate spin states where X = F^-, oxalate, or malonate have also been studied.[9,10,11] Diselenocyanato bis(2,2'-bipyridine)iron(II) has recently been prepared and seems to be best represented as $[Fe^{sp}(bipy)_2(NCSe)_2][Fe^{sf}(bipy)_2(NCSe)_2]$ bipy, where Fe^{sp} and Fe^{sf} denote iron(II) in the spin paired and spin free states, respectively.[12]

Dwyer and co-workers have synthesized and characterized numerous mixed ligand complexes of 1,10-phenanthroline and 2,2'-bipyridine with osmium and ruthenium. They synthesized mono-chelates of bivalent, tervalent and quadrivalent ruthenium of the type $[LH][RuLX_4]$ and $[RuLX_4]$, where X is Cl^-, H_2O, pyridine, 1/2 acetylacetonate or 1/3 terpyridine and L = phen or bipy.[13] They also synthesized bis-chelates of bivalent and tervalent ruthenium of the type $[RuL_2Y_2]$ where Y is Cl^-, Br^-, 1/2 acetylacetonate or pyridine.[14] A similar series of mono-chelated and bis-chelated complexes of osmium in the bivalent and tervalent oxidation states was prepared,[15,16] as well as a series of mixed ligand complexes of the type $[Os(terpy)Cl_3]$, $[Os(terpy)py_3]^{2+}$, $[Os(terpy)py_3]^{3+}$, $[Os(terpy)(bipy)X]^+$, $[Os(terpy)(bipy)X]^{2+}$, $[Os(terpy)py_2]^+$, and $[Os(terpy)py_2Cl]^{2+}$, where X is Cl^-, Br^-, I^-, NCS^-, NO_2^-, EtCN or MeCN, terpy is terpyridine and py is pyridine.[17] Broomhead and Dwyer prepared $[Ni(bipy)_2(phen)]^{2+}$ and $[Ni(bipy)(phen)_2]^{2+}$ as their chlorides and iodides and resolved them into their stereoisomers.[18] Mixed ligand complexes of chrómium, cobalt,[19,20,21] rhodium[22] and copper[23,24,25,26]

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of the type $[Cr(OX)_2L]^-$, $[Co(OX)L_2]^+$, $[RhLX_4]^-$, $[RhL_2X_2]^+$ and $[CuLL']$, (charges omitted) where OX is oxalate, L is bipy or phen, X is Cl^- or Br^- and L′ is a bidentate chelating agent, have been synthesized and characterized.

Mixed ligand complexes may have properties of special utility. Ferrocyphen, $[Fe(phen)_2(CN)_2]$, is useful as an acid base indicator in non-aqueous solvents, as an internal indicator for sodium nitrite titrations, and as a redox indicator,[3,27,28] while $K_2[Fe(phen)(CN)_4]$ has been employed as a precipitant in the amperometric determination of zinc.[29] In general, the extraction of a metal complex with an anion which is itself highly colored should result in increased sensitivity. Freiser *et al.* used this approach to devise a new and highly sensitive method for the determination of nickel by the formation and extraction of a complex of dithizone and nickel(II) phenanthroline (molar absorptivity of 4.91×10^4).[30] Dwyer and co-workers, among others, discovered that many of the substituted 1,10-phenanthrolines, either as free ligands or as complexes of Cu^{II}, Ru^{II}, Ru^{III}, Os^{II}, Os^{III}, and Fe^{II}, inhibit growth of various micro-organisms.[31,32,33,34,35] Also, many of the osmium and ruthenium mixed ligand complexes they prepared are useful as redox indicators.[36]

The purpose of this paper is to report the preparation and characterization of a representative variety of iron(II) chelates with mixed ligands of the ferroin type, which includes 1,10-phenanthroline, substituted 1,10-phenanthrolines, phenyl-2-pyridyl ketoxime, 2,2′-2″-terpyridine, tris(2′-pyridyl)-1,3,5-triazine, and dimethylglyoxime. Their formal redox potentials and visible absorption characteristics were measured to determine to what extent small changes in ligand field symmetries would perturb these properties. It was also of interest to learn if any additive relationships could be found that would enable one to predict an appropriate combination of mixed ligands to produce a given desired property. Earlier, related studies have demonstrated additivity of substituent effects in substituted 1,10-phenanthrolines[3] and for certain properties of their metal chelates, for example stability constants and formal redox potentials of iron(II) chelates[37] and wavelengths of maximum absorbance of copper(I) and iron(II) chelates.[38,39] This study differs from previous ones in that the substituent effect for each individual ligand in a complex can be examined to discover if it contributes additively with those of the other ligands to produce the overall effect observed for the complex.

Experimental Section

Materials and Apparatus. All of the complexing agents were obtained from the G. Frederick Smith Chemical Company (Columbus, Ohio) and used as received, except for 5-nitro-1,10-phenanthroline which was recrystallized from distilled water. All other chemicals were reagent grade. A Cary Model 14 recording spectrophotometer and 1.00 cm silica cells were used to measure absorption spectra. A Corning Model 7 pH meter equipped with glass and saturated calomel electrodes was used to make all pH measurements. A Beckman Model G pH meter equipped with platinum and saturated calomel electrodes was used for potentiometric measurements.

Analysis. Carbon, hydrogen, and nitrogen analyses were performed using a Perkin-Elmer 240 elemental analyzer. Formula weights were determined by potentiometric titrations of weighed samples in 1 *M* sulfuric acid with standard ceric sulfate solution.

Preparation of Iodide Salts of Mixed Ligand Complexes. All of the iodide salts were prepared by the same general procedure. The preparation of bis(1,10-phenanthroline)-4,7-dimethyl-1,10-phenanthroline iron(II) iodide dihydrate is described as a representative example. To a solution of 0.4360 g (2.200 mmol) of 1,10-phenanthroline monohydrate and 0.2489 g (1.100 mmol) of 4,7-dimethyl-1,10-phenanthroline monohydrate in 20 ml of hot (ca. 50°C) ethyl alcohol, a solution of 0.3058 g (1.100 mmol) of iron(II) sulfate heptahydrate in 20 ml of distilled water was added, dropwise, with stirring. The resulting deep-red solution was evaporated to 15 ml by passing a stream of filtered air over the hot, stirred solution. The solution was filtered, cooled to room temperature and 0.7 g of sodium iodide, dissolved in 10 ml of distilled water, was added, dropwise, while stirring. After cooling in an ice bath, the red-brown precipitate which formed was collected by suction filtration. The precipitate was dissolved in a minimum amount of boiling distilled water. The solution was filtered, cooled rapidly in an ice bath, and the precipitate collected by suction filtration, washed twice with 5 ml portions of ice water, twice with 5 ml portions of diethyl ether, and dried in air (yield 0.80 g, 80%).

For ligands of low solubility in ethyl alcohol (5-phenyl-1,10-phenanthroline, TPTZ and terpy) methyl alcohol was used as the reaction medium. The mixed ligand complexes $[Fe(phen)_2(5\text{–}\Phi\text{–}phen)]I_2 \cdot 2H_2O$, $[Fe(phen)_2(4,7\text{–}di\Phi\text{–}phen)]I_2 \cdot 2H_2O$, $[Fe(phen)(4,7\text{–}di\Phi\text{–}phen)_2]I_2 \cdot 2H_2O$, and $[Fe(phen)(4,7\text{–}diMe\text{–}phen)_2]I_2 \cdot 2H_2O$, because of their greater insolubility in aqueous solution, were recrystallized from ethyl alcohol. $[Fe(phen)(5\text{–}Cl\text{–}phen)_2]I_2 \cdot 2H_2O$ and $[Fe(phen)(5\text{–}Me\text{–}phen)_2]I_2 \cdot 2H_2O$ were recrystallized from methyl alcohol.

Preparation of Perchlorate Salts of Mixed Ligand Complexes. Solutions of the complexes, prepared as described above, were treated with stoichiometric

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amounts of $NaClO_4$ to quantitatively precipitate the perchlorate salts. The mixed ligand complexes were recrystallized from distilled water, except $[Fe(phen)_2(5-\Phi-phen)](ClO_4)_2 . H_2O$ and $[Fe(phen)_2(4,7-di\Phi-phen)](ClO_4)_2 . 2H_2O$ were recrystallized from ethyl alcohol and $[Fe(phen)(4,7-di\Phi-phen)_2](ClO_4)_2 . H_2O$ was recrystallized from methyl alcohol.

Preparation of bis(5-sulfonato-1,10-phenanthroline)-1,10-phenanthroline iron(II) trihydrate; $[Fe(5-SO_3-phen)_2(phen)] . 3H_2O$. To a boiling solution of 0.1982 g (1.000 mmol) of 1,10-phenanthroline monohydrate and 0.5584 g (2.000 mmol) of 1,10-phenanthroline-5-sulfonic acid in 50 ml of distilled water, neutralized with sodium hydroxide, was added, dropwise, a solution of 0.2780 g (1.000 mmol) iron(II) sulfate heptahydrate in 20 ml of distilled water. The resulting deep-red solution was heated for 5 minutes at 90-100°C, cooled in an ice bath, and passed slowly (2 drops per second) through a small (20 cm long, 1.4 cm i.d.) column containing a mixed bed resin of equal quantities of Dowex 1-X10 ion exchange resin (50-100 mesh, in the hydroxide form) and Dowex 50W-X4 ion exchange resin (50-100 mesh, in the hydrogen form). The product was obtained on evaporating the effluent to dryness by passing a stream of filtered air over the heated (ca. 40°C) solution (yield 0.58 g 72%).

Preparation of 4,7-diphenyl-1,10-phenanthroline-disulfonato bis(1,10-phenanthroline)iron(II) tetrahydrate; $[Fe\ 4,7-di(\Phi SO_3)-phen](phen)_2] . 4H_2O$. To a boiling solution of 0.6437 g (1.200 mmol) of 4,7-diphenyl-1,10-phenanthroline-disulfonic acid disodium salt and 0.4757 g (2.400 mmol) of 1,10-phenanthroline monohydrate in 20 ml of hot distilled water was added, dropwise, with stirring, a solution of 0.3336 g (1.200 mmol) of iron(II) sulfate heptahydrate in 20 ml of distilled water. The deep-red solution that formed was heated at 90-100°C for 5 minutes and cooled in an ice bath. The dark red precipitate that formed was collected by suction filtration, washed twice with 5 ml portions of ice water and dried in air (yield 0.99 g, 84%).

Preparation of bis(4,7-dihydroxy-1,10-phenanthrolinato)-1,10-phenanthroline iron(II) trihydrate; $[Fe[4,7-(OH)(O)-phen]_2(phen)] . 3H_2O$. To a hot (70-80°C), freshly prepared solution of 0.5471 g (2.200 mmol) of 4,7-dihydroxy-1,10-phenanthroline hydrochloride, 0.2180 g (1.100 mmol) of 1,10-phenanthroline monohydrate and 0.5 g of sodium dithionite dihydrate in 50 ml of 2 *M* ammonium hydroxide contained in a 125 ml glass-stoppered Erlenmeyer flask was added, dropwise, with stirring, a solution of 0.3058 g (1.100 mmol) of iron(II) sulfate heptahydrate in 20 ml of distilled water. The resulting green-brown solution was heated at 70-80°C for 4 minutes in the stoppered flask and cooled in an ice bath. Glacial acetic acid was added, dropwise, to the solution until precipitation of the product was complete (ca. 6 ml). The black precipitate was collected by suction filtration and dissolved in 100 ml of 1 *M* ammonium hydroxide solution containing 0.5 g of sodium dithionite dihydrate. The green-brown solution was filtered, and glacial acetic acid (ca. 6 ml) was again added dropwise to precipitate the desired product. The black precipitate was collected by suction filtration, washed with 3 ml of ice water and dried in air (yield 0.78 g, 100%).

Preparation of 4,7-dihydroxy-1,10-phenanthrolinatobis(1,10-phenanthroline) iron(II) trihydrate; $[Fe(4,7-diO-phen)(phen)_2] . 3H_2O$. To a hot (70-80°C), freshly prepared solution of 0.5946 g (3.000 mmol) of 1,10-phenanthroline monohydrate, 0.3731 g (1.500 mmol) of 4,7-dihydroxy-1,10-phenanthroline hydrochloride and 0.7 g of sodium dithionite dihydrate in 75 ml of concentrated ammonium hydroxide contained in a 125 ml glass-stoppered Erlenmeyer flask was added, dropwise, with stirring, a solution of 0.4170 g (1.500 mmol) of iron(II) sulfate heptahydrate in 20 ml of distilled water. The deep purple solution was heated at 70-80°C for 5 minutes in the stoppered flask and cooled in an ice bath. The black precipitate was collected by suction filtration, washed with 5 ml of 1 *M* ammonium hydroxide and dissolved in 50 ml of 0.1 *M* acetic acid. After filtration, the solution was treated with 50 ml of a 5% solution of sodium dithionite dihydrate in concentrated ammonium hydroxide to precipitate the product. The precipitate was collected by suction filtration, washed with 5 ml of 1 *M* ammonium hydroxide, and dissolved in 300 ml of 95% ethyl alcohol. A small amount of a dark brown-black material was removed by filtration and discarded. The deep-blue filtrate was evaporated to dryness by passing a stream of filtered air over the hot (ca. 50°C), stirred solution to obtain the final product (yield 0.34 g, 33%).

Preparation of bis(phenyl-2-pyridyl ketoximato)-1,10-phenanthroline iron(II) monohydrate; $[Fe(C_{12}H_9N_2O)_2(phen)] . H_2O$. A solution of 0.3336 g (1.200 mmol) of iron(II) sulfate heptahydrate in 20 ml of distilled water was added, dropwise, with stirring, to a hot (70-80°C) solution of 0.4757 g (2.400 mmol) of phenyl-2-pyridyl ketoxime, 0.2378 g (1.200 mmol) of 1,10-phenanthroline monohydrate and 0.5 g sodium dithionite dihydrate in 100 ml of concentrated ammonium hydroxide contained in a 250 ml, glass-stoppered Erlenmeyer flask. The deep-purple solution was heated at incipient boiling for 5 minutes in the stoppered flask and cooled to room temperature. After removing a deep-purple precipitate by suction filtration, 175 ml of 5 *M* sodium hydroxide solution was added to the filtrate, which was still highly colored, and a second crop of precipitate was collected by suction filtration. The filtrate, which was now only weakly purple-red in color, was extracted three times with 25 ml portions of chloroform. The precipitates were dissolved in chloroform and combined with the chloroform extract. The solution was filtered, washed with 50 ml of distilled water, and evaporated to dryness by passing a stream of filtered air over the hot (ca. 50°C), stirred solution. The deep-purple product was washed twice with 10 ml portions of diethyl ether and dried in air (yield 0.56 g, 72%).

Preparation of dimethylglyoximatobis(1,10-phenanthroline)iron(II) dihydrate; $[Fe(C_4H_6N_2O_2)(phen)_2] . 2H_2O$. To a hot (90-100°C), stirred solution of 1.1892 g (6.000 mmol) of 1,10-phenanthroline monohydrate, 0.3480 (3.000 mmol) of dimethylglyoxime, 0.8 g sodium hydroxide and 1 g of sodium dithionite dihydrate in 200 ml of distilled water was added dropwise 0.8341 g (3.000 mmol) of iron(II) sulfate heptahydrate dissolved in 20 ml of distilled water. The resulting deep-blue solution was heated in the stoppered flask at incipient boiling for 5 minutes, filtered, cooled to room temperature and to it was added 0.3 g of sodium dithionite dihydrate and 28 g of sodium hydroxide. The deep-blue precipitate that formed was collected by suction filtration, washed three times with 5 ml portions of diethyl ether and dissolved in 300 ml of 1 *M* ammonium hydroxide containing 0.5 g of sodium dithionite dihydrate. The deep-blue solution was filtered and sodium hydroxide was added until precipitation of the product ensued (ca. 20 g). Protected from the atmosphere in a glove bag filled with nitrogen, the product was collected by suction filtration, washed three times with 5 ml portions of concentrated ammonium hydroxide, three times with 5 ml portions of diethyl ether and sucked dry. The deep-blue solid was dried *in vacuo* (Yield 1.18 g, 70%). Analysis of the product by flame photometry indicated less than 0.1% sodium content. Measurement of the magnetic susceptibility of the solid by the Gouy method indicated a magnetic moment for iron of 1.02 ± 0.06 B.M.

Formal Redox Potentials. Formal redox potentials were determined by potentiometric titration of weighed samples dissolved in 1 *M* sulfuric acid with standard ceric sulfate solution. Solutions of the cationic mixed ligand complexes were prepared from their iodide salts. To prevent interference from iodide, the solutions were treated with a 10% excess of silver sulfate solution. Neither excess silver nitrate nor precipitated silver iodide were found to interfere. Filtration was unnecessary. The formal potential was taken as the potential at 50% titration. The complexes $[Fe(TPTZ)(terpy)]^{2+}$, $[Fe(5{-}SO_3{-}phen)_2(phen)]$, and $[Fe(phen)(5{-}NO_2{-}phen)_2]^{2+}$ decompose at an appreciable rate in acidic solution. Formal redox potentials were obtained for these by following the potential *vs.* time after adding all at once enough standard ceric sulfate solution to oxidize 50% of the sample. The potential obtained by extrapolation to zero time was taken as the formal potential.

Mole Ratio Studies. Some special solution conditions and procedures were necessary to determine the identities of the complexes by the well known mole ratio technique.

To identify the mixed 1,10-phenanthroline, dimethylglyoxime complex, solutions were prepared as follows. Into 25 ml volumetric flasks were pipeted 5 ml of 1 *M* ammonium hydroxide, 2 ml of freshly prepared 10% sodium dithionite, 5.00 ml of 3.00×10^{-4} *M* tris(1,10-phenanthroline)iron(II) sulfate, and from 0 to 12 ml of 5.00×10^{-4} *M* dimethylglyoxime in ethanol. After dilution to volume with distilled water and a reaction time of 24 hours, the absorption spectra of the solutions were recorded.

The mixed complexes of 1,10-phenanthroline and 4,7-dihydroxy-1,10-phenanthroline were identified by spectral examination of solutions prepared as follows. Into 50 ml beakers were pipeted 5.00 ml of 2.25×10^{-4} *M* tris(1,10-phenanthroline)iron(II) sulfate, 5 ml of freshly prepared 5% solution of sodium dithionite in concentrated ammonium hydroxide, 10 ml of ethanol, and 0 to 5.00 ml of 7.50×10^{-4} *M* solution of 4,7-dihydroxy-1,10-phenanthroline in 0.01 *M* sodium hydroxide. After heating for 5 minutes at 70-80°C, the solutions were cooled to room temperature, transferred to 25 ml volumetric flasks, and diluted to volume with distilled water.

Solutions to identify the mixed complex of TPTZ and terpy were prepared as follows. Into 50 ml beakers were pipeted 5.00 ml of 1.50×10^{-4} *M* solution of $[Fe(TPTZ)_2]SO_4$ in 40% ethanol, 5 ml of pH 4.5 buffer (1 *M* sodium acetate and acetic acid), 2 ml of 10% hydroxylamine hydrochloride, and 0 to 8.00 ml of 3.00×10^{-4} *M* solution of terpy in 4% ethanol. After heating 2 to 3 minutes at about 70°C, the solutions were cooled to room temperature, transferred to 25 ml volumetric flasks, and diluted to volume with distilled water.

Identities of the mixed complexes of 1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline were established by spectral examination of solutions prepared as follows. Into 100 ml volumetric flasks were pipeted 30 X ml of 2.50×10^{-3} *M* solution of 4,7-diphenyl-1,10-phenanthroline in ethanol, X ml of 2.50×10^{-3} *M* solution of 1,10-phenanthroline in 25% ethanol, 5 ml of pH 7 buffer (1 *M* ammonium acetate) and 2 ml of 10% hydroxylamine hydrochloride. To the contest of each flask, 10.00 ml of 2.53×10^{-4} *M* iron(II) sulfate was added slowly with stirring. Sufficient ethanol to make a final concentration of 50% was added, and the solutions were diluted to final volume with distilled water.

Visible Absorption Spectra. Solutions of the mixed ligand complexes were prepared for spectral determination by dissolving weighed samples of the solids in measured volumes of aqueous ethanol. To discourage dissociation of the complexes, the solutions were prepared to contain excesses of the free ligands (ca. 10^{-5} *M* in each) in the same mole ratio as in the complexes. Because 4,7-dihydroxy-1,10-phenanthroline is insoluble in aqueous ethanol, solution of complexes with this ligand were prepared without either free ligand present. Solutions of $[Fe(TPTZ)(terpy)]I_2 \cdot 2H_2O$ were prepared to contain only excess TPTZ, after it was discovered that excess terpyridine displaces TPTZ from the mixed ligand complex.

The effects of changes in solvent and pH were studied for those complexes that possess ligands with ionizable hydrogens.

Results and Discussion

Direct combination of reactants rather than a displacement type reaction was employed in preparing the mixed ligand complexes. Formation of the desired complex was favored by mixing exactly stoichiometric amounts of reactants in the proper order, *i.e.*— the iron(II) sulfate solution was added slowly to the solution of the free ligands, to assure that the free ligands concentrations were always in the desired molar ratio and in excess of the iron concentration.

Table I. Elemental Analyses and Formula Weights of Mixed Ligand Complexes. Iodide Salts and Neutral Complexes.

Complex[a]	Calculated %C	Calculated %H	Calculated %N	Calculated F.W.	Found[b] %C	Found[b] %H	Found[b] %N	Found[b] F.W.
$[\mathrm{Fe(phen)_2(5{-}NO_2{-}phen)}]\mathrm{I_2} \cdot 2\mathrm{H_2O}$	46.43	2.92	10.53	927	46.60	2.78	10.14	930
$[\mathrm{Fe(phen)_2(5{-}\Phi{-}phen)}]\mathrm{I_2} \cdot 2\mathrm{H_2O}$	52.41	3.35	8.73	962	51.62	3.31	8.92	1150[c]
$[\mathrm{Fe(phen)_2(4,7{-}di\Phi{-}phen)}]\mathrm{I_2} \cdot 2\mathrm{H_2O}$	55.29	3.49	8.09	1039	55.43	3.64	7.43	*d*
$[\mathrm{Fe(phen)_2(4,7{-}diMe{-}phen)}]\mathrm{I_2} \cdot 2\mathrm{H_2O}$	49.91	3.53	9.19	914	50.30	3.21	9.01	910
$[\mathrm{Fe(phen)_2(5{-}Cl{-}phen)}]\mathrm{I_2} \cdot 2\mathrm{H_2O}$	46.96	2.96	9.13	921	47.75	3.33	9.37	920
$[\mathrm{Fe(phen)_2(5{-}Me{-}phen)}]\mathrm{I_2} \cdot 2\mathrm{H_2O}$	49.36	3.36	9.33	900	49.92	3.26	9.45	890
$[\mathrm{Fe(phen)(5{-}NO_2{-}phen)_2}]\mathrm{I_2} \cdot 2\mathrm{H_2O}$	44.29	2.69	11.48	976	42.07	2.57	11.27	*e*
$[\mathrm{Fe(phen)(4,7{-}di\Phi{-}phen)_2}]\mathrm{I_2} \cdot 2\mathrm{H_2O}$	60.52	3.72	7.06	1191	60.42	3.75	6.44	*d*
$[\mathrm{Fe(phen)(4,7{-}diMe{-}phen)_2}]\mathrm{I_2} \cdot 2\mathrm{H_2O}$	50.98	3.83	8.92	942	50.29	3.87	8.93	940
$[\mathrm{Fe(phen)(5{-}Cl{-}phen)_2}]\mathrm{I_2} \cdot 2\mathrm{H_2O}$	46.14	2.58	8.97	937	45.19	2.25	8.77	940
$[\mathrm{Fe(phen)(5{-}Me{-}phen)_2}]\mathrm{I_2} \cdot 2\mathrm{H_2O}$	49.91	3.53	9.19	914	50.39	3.38	8.94	910
$[\mathrm{Fe(phen)(5{-}Cl{-}phen){-}(5,6{-}diMe{-}phen)}]\mathrm{I_2} \cdot 2\mathrm{H_2O}$	48.11	3.29	8.86	949	47.51	3.26	8.78	960
$[\mathrm{Fe(terpy)(TPTZ)}]\mathrm{I_2} \cdot 2\mathrm{H_2O}$	42.74	3.37	13.59	927	42.91	2.97	13.47	920
$\{\mathrm{Fe(phen)[4,7{-}(OH){-}(O){-}phen]_2}\} \cdot 3\mathrm{H_2O}$	60.68	3.96	11.79	713	60.62	3.78	11.99	*d*
$[\mathrm{Fe(phen)_2(4,7{-}diO{-}phen)}] \cdot 3\mathrm{T_2O}$	63.54	4.15	12.35	681	63.52	3.88	12.46	*d*
$[\mathrm{Fe(phen)(5{-}SO_3{-}phen)_2}] \cdot 3\mathrm{H_2O}$	53.47	3.49	10.39	809	53.92	3.65	10.55	830
$\{\mathrm{Fe(phen)_2[4,7{-}di(\Phi SO_3)phen]}\} \cdot 4\mathrm{H_2O}$	58.90	3.91	8.59	979	57.75	3.83	8.75	990
$[\mathrm{Fe(phen)(ketoximato)_2}] \cdot 2\mathrm{H_2O}$	66.67	4.35	12.96	649	66.62	4.19	12.02	*e*
$[\mathrm{Fe(phen)_2(DMG)}] \cdot 2\mathrm{H_2O}$	59.39	4.63	14.84	566	58.73	4.25	14.83	*e*

[a] Abbreviations of the ligands are: phen = 1,10-phenanthroline; terpy = 2,2′,2″-terpyridine; TPTZ = tris(2′-pyridyl)-1,3,5-triazine; 4,7-diO-phen = the dinegative anion of 4,7-dihydroxy-1,10-phenanthroline; 4,7-(OH) (O)-phen = the mononegative anion of 4,7-dihydroxy-1,10-phenanthroline; 4,7-di(ΦSO₃)-phen = the dinegative anion of 4,7-diphenyl-1,10-phenanthroline-disulfonate; ketoximato = the mononegative anion of phenyl-2-pyridyl ketoxime; and DMG = the dinegative anion of dimethylglyoxime. [b] Each value of elemental analysis is the average of at least two determination. [c] Slow electrode response resulting in overtitration and a larger formula weight. [d] Complex too insoluble in 1 *M* H_2SO_4 for titration. [e] Complex dissociates too rapidly in acidic solution for titration.

Table II. Elemental Analyses of Mixed Ligand Complexes. Perchlorate Salts.

Complex[a]	Calculated %C	Calculated %H	Calculated %N	Found[b] %C	Found[b] %H	Found[b] %N
$[\mathrm{Fe(phen)_2(5{-}NO_2{-}phen)}]\mathrm{(ClO_4)_2} \cdot \mathrm{H_2O}$	50.37	2.93	11.43	49.91	2.84	11.92
$[\mathrm{Fe(phen)_2(5{-}\Phi{-}phen)}]\mathrm{(ClO_4)_2} \cdot \mathrm{H_2O}$	56.71	3.40	9.45	57.93	3.45	9.32
$[\mathrm{Fe(phen)_2(4,7{-}di\Phi{-}phen)}]\mathrm{(ClO_4)_2} \cdot 2\mathrm{H_2O}$	58.61	3.69	8.54	58.56	3.82	8.56
$[\mathrm{Fe(phen)_2(4,7{-}diMe{-}phen)}]\mathrm{(ClO_4)_2} \cdot \mathrm{H_2O}$	54.24	3.59	9.99	53.88	3.36	9.98
$[\mathrm{Fe(phen)_2(5{-}Cl{-}phen)}]\mathrm{(ClO_4)_2} \cdot \mathrm{H_2O}$	51.00	2.97	9.91	51.09	3.02	10.14
$[\mathrm{Fe(phen)_2(5{-}Me{-}phen)}]\mathrm{(ClO_4)_2} \cdot \mathrm{H_2O}$	53.71	3.41	10.16	54.14	3.63	10.50
$[\mathrm{Fe(phen)(5{-}NO_2{-}phen)_2}]\mathrm{(ClO_4)_2} \cdot \mathrm{H_2O}$	47.86	2.68	12.40	47.09	2.67	12.64
$[\mathrm{Fe(phen)(4,7{-}di\Phi{-}phen)_2}]\mathrm{(ClO_4)_2} \cdot \mathrm{H_2O}$	64.50	3.79	7.52	65.64	4.20	7.49
$[\mathrm{Fe(phen)(4,7{-}diMe{-}phen)_2}]\mathrm{(ClO_4)_2} \cdot \mathrm{H_2O}$	55.25	3.94	9.66	55.30	4.25	9.55
$[\mathrm{Fe(phen)(5{-}Cl{-}phen)_2}]\mathrm{(ClO_4)_2} \cdot \mathrm{H_2O}$	49.01	2.74	9.53	49.09	2.70	9.66
$[\mathrm{Fe(phen)(5{-}Me{-}phen)_2{-}(ClO_4)_2}] \cdot \mathrm{H_2O}$	54.24	3.59	9.99	54.52	3.78	10.17
$[\mathrm{Fe(phen)(5{-}Cl{-}phen){-}(5,6{-}diMe{-}phen)}]\mathrm{(ClO_4)_2} \cdot \mathrm{H_2O}$	52.10	3.34	9.59	52.55	3.42	9.61
$[\mathrm{Fe(terpy)(TPTZ)}]\mathrm{(ClO_4)_2} \cdot 2\mathrm{H_2O}$	47.39	3.25	15.07	47.23	3.03	15.35

[a] See Table I for abbreviations. [b] Each value represents the average of at least two determinations.

Table III. Formal Oxidation-Reduction Potentials of Mixed Ligand Complexes in 1 *M* H_2SO_4 at 25°C.

Complex	Formal Potential, Volt Found	Formal Potential, Volt Predicted[a]
$[\mathrm{Fe(phen)_2(4,7{-}diMe{-}phen)}]^{2+}$	0.99	1.00
$[\mathrm{Fe(phen)(4,7{-}diMe{-}phen)_2}]^{2+}$	0.93	0.93
$[\mathrm{Fe(phen)_2(5{-}Cl{-}phen)}]^{2+}$	1.10	1.09
$[\mathrm{Fe(phen)(5{-}Cl{-}phen)_2}]^{2+}$	1.13	1.13
$[\mathrm{Fe(phen)_2(5{-}Me{-}phen)}]^{2+}$	1.04	1.04
$[\mathrm{Fe(phen)(5{-}Me{-}phen)_2}]^{2+}$	1.02	1.02
$[\mathrm{Fe(phen)_2(5{-}\Phi{-}phen)}]^{2+}$	1.07	1.07
$[\mathrm{Fe(phen)_2(5{-}NO_2{-}phen)}]^{2+}$	1.09	1.13
$[\mathrm{Fe(phen)(5{-}NO_2{-}phen)_2}]^{2+}$	1.24	1.21
$[\mathrm{Fe(phen)(5{-}SO_3{-}phen)_2}]$	1.16	1.17
$\{\mathrm{Fe(phen)_2[4,7{-}di(\Phi SO_3){-}phen]}\}$	1.07	1.07
$[\mathrm{Fe(phen)(5{-}Cl{-}phen)(5,6{-}diMe{-}phen)}]^{2+}$	1.05	1.06
$[\mathrm{Fe(TPTZ)(terpy)}]^{2+}$	1.02	1.0

[a] Based on the additivity of substituent effects per ligand and the following formal reduction potentials in 1 *M* H_2SO_4 of the substituted 1,10-phenanthroline tris-chelates of iron(II) (numbers in parentheses are reference numbers): unsubstituted, 1.06 (3); 4,7-diphenyl, 1.12 (3); 4,7-dimethyl, 0.87 (3); 5-sulfonic acid, 1.23 (3); 4,7-diphenyl-disulfonate, 1.09 (3); 5-phenyl, 1.08 (37); 5-chloro, 1.16 (This Work); 5-methyl, 1.01 (This Work); 5-nitro, 1.28 (This Work); 5,6-dimethyl, 0.97 (39); $\mathrm{Fe(terpy)_2}^{2+}$, 1.20 (3); $\mathrm{Fe(TPTZ)_2}^{2+}$, 0.8±0.1 (This Work).

Fortunately, this simple approach proved effective; alternative synthetic routes would have involved more complications and greater risk of contamination from unreacted starting materials or from displaced ligands. A disadvantage of this procedure, however, is that the reactants are mixed in the same proportion as the expected stoichiometry of their reaction; consequently, elemental analysis of the precipitated product does not suffice to establish its identity. In the present sudy it was thus also necessary to determine if the product was a single substance. The determination was relatively simple and conclusive in each case, because of distinctive differences in properties of the possible products. Results of elemental analyses and formula weight determinations are compiled in Tables I and II. Additional evidence and further details are presented below.

All of the complexes that could be successfully titrated potentiometrically with standard cerium(IV) (see Table III) yielded titration curves with only one detectable equivalence point. If the isolated products had consisted of mixtures of simple complexes with sufficiently different formal potentials, two end points would have been observable. This was demonstrated by titrating an equimolar mixture of $[Fe(phen)_3]SO_4$ and $[Fe(4,7\text{-}dimethyl\text{-}phen)_3]SO_4$. Two well defined breaks in the titration curve and formal potentials of 1.06 and 0.87 volt, respectively, were found.

Potentiometric titrations of $[Fe(phen)_2(DMG)]$, $[Fe(phen)_2(4,7\text{-}diO\text{-}phen)]$ and $[Fe(phen)(4,7\text{-}(OH)(O)\text{-}phen)_2]$ were impractical because of their instabilities in acid solutions. Confirmation of their identities was therefore established by mole ratio studies. Well defined isosbestic points were exhibited by the spectra (see Table IV), and plots of mole ratios versus absorbances at appropriate wavelengths showed distinct maxima corresponding to the formulas of the complexes as written. It is interesting that no evidence for the formation of a bis(dimethylglyoximato)-1,10-phenanthroline iron(II) species could be found, accounting for our repeated failures to isolate such a product.

Table IV. Isosbestic Points for Interconvertible Species.

Complexes	Isosbestic Points, nm
$[Fe(phen)_3]^{2+}$, $[Fe(phen)_2(DMG)]$	530
$[Fe(phen)_3]^{2+}$, $[Fe(phen)_2(4,7\text{-}diO\text{-}phen)]$	425, 529
$[Fe(phen)_2(4,7\text{-}diO\text{-}phen)]$ $[Fe(phen)(4,7\text{-}(OH)(O)\text{-}phen)_2]$	478, 600
$[Fe(TPTZ)_2]^{2+}$, $[Fe(TPTZ)(terpy)]^{2+}$	367, 450, 660
$[Fe(terpy)_2]^{2+}$, $[Fe(TPTZ)(terpy)^{2+}$	415, 500

Limited solubility in acid precluded potentiometric titration of the mixed ligand complexes of 4,7-diphenyl-1,10-phenanthroline. Their absorption spectra proved to be very similar to those expected for mixtures of the *tris*-chelates $[Fe(phen)_3]^{2+}$ and $[Fe(4,7\text{-}diphenyl\text{-}phen)_3]^{2+}$. Although no isosbestic points were evident, plots of absorbances at 512 and at 533 nm as a function of mole fraction of 4,7-diphenyl-1,10-phenanthroline displayed detectable changes in slope at mole fractions of 0.33 and 0.66, corresponding to the formation of the two possible mixed ligand species. Additional evidence of mixed ligand complexation was obtained by extraction tests. Since $[Fe(4,7\text{-}diphenyl\text{-}phen)_3]SO_4$ is quantitatively extractable into isoamyl alcohol and $[Fe(phen)_3]SO_4$ is not extractable, an aqueous mixture of the two can be resolved by extraction to give an isoamyl alcohol layer with an absorption maximum at 533 nm and an aqueous layer with maximum absorbance at 510 nm. On the basis of such a test it was possible to demonstrate that the 4,7-diphenyl-1,10-phenanthroline products prepared in this study were indeed mixed ligand complexes, not mixtures of equivalent amounts of unmixed *tris*-chelates. Various salts of the $[Fe(phen)(4,7\text{-}diphenyl\text{-}phen)_2]^{2+}$ cation were readily extractable from aqueous solutions into isoamyl alcohol; both phases exhibited maximum absorbance at 527 nm. Similar behavior was observed for salts of the $[Fe(phen)_2(4,7\text{-}diphenyl\text{-}phen)]^{2+}$ cation; although extractability was lower, both phases showed maximum absorbance at 518 nm.

Formal oxidation-reduction potentials of the mixed ligand complexes are listed in Table III together with predicted values, calculated on the basis that substituent effects per ligand are additive. An example will illustrate the calculation. The formal potentials of $[Fe(phen)_3]^{2+}$ and $[Fe(5\text{-}Cl\text{-}phen)_3]^{2+}$ are 1.06 and 1.16 volts, respectively. Assuming that the 0.10 volt difference is the additive effects of three 5-chloro substituents, each contributing an increase of 0.033 volt, the mixed complex $[Fe(phen)_2(5\text{-}Cl\text{-}phen)]^{2+}$ should have a formal potential of $1.06 + 0.033$ or 1.09 volts. Close agreement between experimental and predicted values are observed for all cases, except for the 5-nitro-1,10-phenanthroline derivatives. If the effects per ligand are indeed additive, we are unable to account for the latter disparities. Certainly the good agreement between observed and calculated values, especially for the $[Fe(phen)(5\text{-}Cl\text{-}phen)(5,6\text{-}diMe\text{-}phen)]^{2+}$ complex, demonstrates that practical estimates can be predicted for the formal potentials of mixed phenanthroline complexes. Such predictions can serve to select appropriate ligand combinations for a given desired potential. A special case is represented by the mixed complex $[Fe(TPTZ)(terpy)]^{2+}$. Here the two ligands are not as closely related as are mixed phenanthrolines, so addivity of ligand effects is less probable. The close agreement between observed and predicted formal potentials in this case may simply be fortuitous. Further study of other examples would be interesting. Unfortunately, the two other complexes of this type in the present study $[Fe(phen)(ketoximato)_2]$, dissociate so rapidly in sulfuric acid that reliable measurements of formal potentials were impractical.

Molar absorptivities and wavenumbers of maximum absorbance of the mixed ligand complexes are compiled in Table V. Predicted values listed were calculated assuming that the individual ligand effects are additive, *i.e.*—the mixed chelate value is the weighted average of the two unmixed chelate values. Wavenumbers of maximum absorbance, in general, agree with predicted values. Exceptions are notable for $[Fe((TPTZ)(terpy)]^{2+}$, $[Fe(phen)_2(DMG)]$, [Fe(phen)-

Table V. Visible Absorption Data.

Complex[a]	Solution		Absorption Maxima			
	% EtOH		Predicted		Observed	
	(by vol.)	pH	$\bar{\nu}$, cm^{-1}	ε	$\bar{\nu}$, cm^{-1}	ε
[Fe(phen)(5–Me–phen)$_2$]I$_2$	10	7	19,480	11,800	19,493	11,700
[Fe(phen)$_2$(5–Me–phen)$_2$]I$_2$	10	7	19,544	11,500	19,607	11,600
[Fe(phen)$_2$(5–Φ–phen)]I$_2$	10	7	19,458	11,600	19,531	11,800
[Fe(phen)$_2$(4,7–diΦ–phen)]I$_2$	20	7	19,326	14,900	19,267	13,700
[Fe(phen)(4,7–diΦ–phen)]I$_2$	20	7	19,044	18,600	18,939	18,000
[Fe(phen)$_2$(4,7–diMe–phen)]I$_2$	10	7	19,582	12,100	19,569	11,700
[Fe(phen)(4,7–diMe–phen)$_2$]I$_2$	10	7	19,556	13,000	19,531	12,200
[Fe(phen)$_2$(5–NO$_2$–phen)]I$_2$	10	7	19,608	11,200	19,607	11,000
[Fe(phen)(5–NO$_2$–phen)$_2$]I$_2$	10	7	19,608	11,400	19,801	10,400
[Fe(phen)$_2$(5–Cl–phen)]I$_2$	10	7	19,586	11,300	19,607	11,300
[Fe(phen)(5–Cl–phen)$_2$]I$_2$	10	7	19,556	11,500	19,569	11,500
[Fe(phen)(5–Cl–phen)(5,6–diMe–phen)]I$_2$	10	7	19,456	11,800	19,493	11,400
[Fe(TPTZ)(terpy)]I$_2$	5	7	17,474	17,600	18,115	13,800
[Fe(phen)$_2$(4,7–di(ΦSO$_3$)–phen)]	10	7	19,302	14,800	19,305	14,200
[Fe(phen)$_2$(5–SO$_3$–phen)$_2$]	10	7	19,556	11,800	19,607	11,500
[Fe(phen)$_2$(4,7–diO–phen)]	20	1	—	—	20,833	8,900
	20	8	—	—	20,000	7,500
					17,391	7,100
[Fe(phen)(4,7–(OH)(O)–phen)$_2$]	40	4	—	—	20,833	7,900
	40	12	19,356	13,500	24,390	10,000
					17,857	6,900
[Fe(phen)$_2$(DMG)]	40	12	—	—	19,607	7,700
[Fe(phen)(ketoximato)$_2$]	20	13	18,656	14,100	19,047	11,200
	20	6	—	—	19,493	9,160
	95	—	—	—	19,047	10,800

[a] See Table I. for abbreviations. [b] Predicted assuming additivity of ligand effects and using the following molar absorptivities and wavelengths, respectively, for the binary unmixed chelates of iron(II) (numbers in parentheses are reference numbers): phen, 11,100 at 510 nm (3); 5-Me-phen, 12,200 at 515 nm (40); 5-Φ-phen, 12,700 at 522 nm (3); 4,7-diΦ-phen, 22,400 at 533 nm (3); 4,7-diMe-phen, 14,100 at 512 nm (3); 5-NO$_2$-phen, 11,500 at 510 nm (3); 5-Cl-phen, 11,700 at 512 nm (37); terpy, 12,500 at 552 nm (3); 4,7-di(ΦSO$_3$)-phen, 22,100 at 535 nm (41); 5-SO$_3$-phen, 12,200 at 512 nm (41); 4,7-dihydroxy-phen, 14,800 at 520 nm (3); and phenyl-2-pyridyl ketoxime, 15,600 at 550 nm (3).

(4,7–(OH)(O)–phen)$_2$] and [Fe(phen)(ketoximato)$_2$], where pH effects and gross dissimiliarities in ligand types preclude reliable predictions. Agreement between observed and predicted values of molar absorptivity is considerably worse. In 8 out of 17 cases the observed values are significantly less than predicted. Dissociation of the complexes in solution would cause low results, however precautions were taken to minimize this source of error. It is concluded that predictions based on additivity of ligand effects which ignore effects accompanying changes in symmetry, are unreliable with respect to molar absorptivities. The present study indicates that the loss in ligand field symmetry which results on mixing the ligands is in general accompanied by a loss in absorption intensity, since none of the mixed ligand complexes gave an observed absorptivity significantly greater than predicted.

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