# MIXED LIGAND COMPLEXES OF IRON(II) AS NONAQUEOUS ACID–BASE AND AQUEOUS OXIDATION–REDUCTION INDICATORS

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Studies conducted on the preparation and properties of the complexes of iron(II) and (III) with cyanide and aromatic diimine mixed ligands[1-3] indicate that they may be useful in a variety of ways in chemical analysis. Thus far analytical use has been made only of the neutral dicyano-bis-(1,10-phenanthroline)–iron(II) complex and of its 4,7-diphenyl-1,10-phenanthroline homolog. A highly selective, sensitive colorimetric method for the determination of cyanide based on formation and extraction of the former has been described[4]. The homologous phenyl-substituted complex was shown to be a suitable form in which trace amounts of iron can be quantitatively separated from copper and measured spectrophotometrically[5]. In the present study it is found that dicyano-bis-(1,10-phenanthroline)–iron(II) and dicyano-bis-(2,2'-bipyridine)–iron(II) are useful as acid–base and oxidation–reduction indicators. Future studies are anticipated which may lead to the use of the charged species in this series of mixed ligand complexes as precipitation reagents. The tetracyano-mono-(1,10-phenanthroline)–ferrate(II) anion, for example, which forms insoluble salts with a number of the heavy metal ions, may prove to be a practical and selective precipitation reagent. The tetracyano complex and its salts are highly colored; thus small amounts could be measured colorimetrically.

For simplicity and convenience, the trivial names ferrocyphen and ferrocypyr are proposed for dicyano-bis-(1,10-phenanthroline)–iron(II) and dicyano-bis-(2,2'-bipyridine)–iron(II), respectively; the cationic iron(III) species, obtained on oxidation of these neutral complexes, may then be referred to respectively as ferricyphen and ferricypyr.

It is believed that this marks the first time a metal complex of any kind has been found to be effective as an acid–base indicator. In any case, the use of a metal complex for such a purpose is sufficiently novel to prompt some elaboration as to its conception. During a recent investigation[3] it was found that ferrocyphen and ferrocypyr react rapidly and reversibly with strong acids to give stable mono-and diprotonated species. Acid exchange measurements, carried out in glacial acetic acid, indicated that ferrocyphen and ferrocypyr are similar to *o*-chloroaniline in basicity. In acetic acid solvent, the monoprotonated species proved to be very much weaker than *o*-chloroaniline, somewhat weaker than thiourea, yet considerably stronger than the solvent in competition for perchloric acid. Since the visible absorption characteristics, as well as the basicities, of the protonated and neutral species differ markedly, the neutral complexes should be able to function as acid–base indicators. This

contention is confirmed by the results of the present study. It is shown that the complexes are applicable as indicators for titrating certain bases in various nonaqueous solvents. Their possible applications in spectrophotometric titrations and in aqueous systems have yet to be investigated.

Formal redox potentials for ferrocyphen and ferrocypyr were measured in various concentrations of sulfuric acid. Confirming the fact that only the iron(II) species exhibit measurable basicities, the formal potentials are found to increase with increasing acid concentration. Interestingly, just the opposite trend is observed for the formal potentials of the ferroin complexes tris-(1,10-phenanthroline)–iron(II), tris-(5-nitro-1,10-phenanthroline)–iron(II), etc.[6].

The results of this investigation show the neutral mixed ligand complexes of iron(II) to be suitable for use as redox indicators. Several practical titrations are described. The suitability of ferrocyphen as an indicator for the titration of aromatic amines with sodium nitrite is especially notable.

Previous work has been reported concerning the properties of the tetracyano species. GEORGE, HANANIA AND IRVINE[7] found a value of 0.541 V for the standard reduction potential of the following couple (where bipy represents 2,2'-bipyridine):

$$[Fe\ bipy\ (CN)_4]^- + e = [Fe\ bipy\ (CN)_4]^{-2}$$
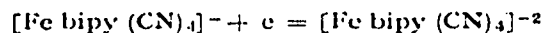
In 0.2 $M$ HCl a formal potential of 0.619 V was found. More positive potentials arise in acid because the iron(II) complex forms stable acid species whereas the iron(III) complex does not. The visible absorption characteristics of the iron(II) and iron(III) tetracyano species are not greatly different[2]; hence they are not believed to be suitable redox indicators. They could find application in spectrophotometric titrations, but this possibility has yet to be explored.

An interesting trend is apparent in the formal redox potentials of the complexes: a decrease in potential of approximately 0.2 V results each time an aromatic diimine ligand is displaced from coordination with iron by two cyanide ligands. To illustrate, complexes in the iron–cyanide-2,2'-bipyridine system and their approximate formal potentials in strong acid solutions are [Fe bipy$_3$]$^{+3}$/[Fe bipy$_3$]$^{+2}$, 1.0 V; [Fe bipy$_2$ (CN)$_2$]$^+$/[Fe bipy$_2$(CN)$_2$], 0.8 V; [Fe bipy(CN)$_4$]$^-$/[Fe bipy(CN)$_4$]$^{-2}$, 0.6 V; [Fe (CN)$_6$]$^{-3}$/[Fe (CN)$_6$]$^{-4}$, 0.4 V.

APPARATUS AND REAGENTS

A Beckman pH meter, Model G, was used for potentiometric titrations. For nonaqueous acid–base titrations a conventional glass electrode and silver–silver chloride reference electrode were used. When titrations were performed in acetic anhydride the silver–silver chloride electrode was immersed in a saturated acetic anhydride solution of silver and lithium chlorides which was in electrical contact with the solution titrated by means of a capillary-fibre junction[8]. For all other titrations the reference electrode was immersed directly in the solution titrated. A platinum electrode and saturated calomel reference electrode (fibre-capillary type) were employed for aqueous redox titrations.

Procedural details for the synthesis of dicyano-bis-(1,10-phenanthroline)–iron(II) dihydrate (ferrocyphen) and dicyano-bis-(2,2'-bipyridine)–iron(II) trihydrate (ferrocypyr) are given elsewhere[2]. Solutions of the solid complexes were prepared as indicators. For acid–base titrations, 25 mg of the solid complex was dissolved in 100 ml

of the solvent to be used for the titration and 1 ml of this indicator solution added to approximately every 25 ml of solution to be titrated. For aqueous redox titrations, 0.3 g of the solid complex was dissolved in 100 ml of concentrated acid, of the kind to be used in the titration, and 1 ml of this indicator solution was added to approximately every 100 ml of solution to be titrated. Limited solubilities preclude preparation of more concentrated indicator solutions in both cases.

The nonaqueous solvents used were of reagent quality; no basic impurities were detectable.

### Standard perchloric acid in acetic acid

A 0.1 M solution was prepared by the method of FRITZ[9] and standardized by potentiometric titration against potassium acid phthalate in acetic acid.

### Standard perchloric acid in acetic anhydride – acetic acid mixture

A 0.05 M solution was prepared as described by STREULI[8] and standardized with potassium acid phthalate by potentiometric titration in acetic acid.

### Standard ceric sulfate solution

A solution 0.05 M in cerium(IV) and approximately 0.9 M in $H_2SO_4$ was prepared using ceric hydroxide (G. Frederick Smith Chemical Co.) and the procedure described by DIEHL AND SMITH[10]. Arsenious oxide was employed for standardization.

### Standard potassium dichromate, 0.1 N

This was prepared by dissolving a weighed sample of dry, primary standard grade $K_2Cr_2O_7$ and diluting to a known volume with distilled water.

### Standard vanadium(V) solution, 0.02 M

A 2.4-g sample of ammonium vanadate was dissolved in 16 ml of concentrated sulfuric acid and diluted to 1 l with distilled water. The molarity of the final solution was determined by potentiometric titration versus a standardized solution of ferrous ammonium sulfate.

### Sodium nitrite solution, 0.1 M

Reagent grade $NaNO_2$ was dried at 110° for 2 h; a weighed sample was dissolved and diluted to exactly 1 l with distilled water; the molarity was calculated, assuming absolute purity.

### EXPERIMENTAL

### Acid–base titrations in nonaqueous solvents

Preliminary tests were carried out to determine which solvents of those commonly employed for nonaqueous titrations might prove suitable in conjunction with the use of the neutral complexes as indicators. Criteria for suitability were the following: (1) the solvent should dissolve a sufficient amount of the complex to be colored thereby, (2) the addition of 1–3 drops of the 0.1 M perchloric acid titrant to the solution should result in a pronounced and easily recognized color change, and (3) the color change should be reversible on adding a weak base. Acetone, dioxane, ethyl

acetate, and benzene failed to dissolve the complexes. Varying degrees of solubility were observed in isopropyl alcohol, ethylene glycol, and diethyl cellosolve; however excessive amounts of acid were necessary to produce significant color changes. Solvents which provided all of the sought-for characteristics are glacial acetic acid, acetic anhydride, chloroform, chlorobenzene, nitrobenzene, nitromethane, and acetonitrile.

A variety of titrations were performed to evaluate the applicability and effectiveness of ferrocyphen and ferrocypyr as acid–bases indicators. Four different solvents and a number of selected weak bases were employed. The general procedure was the same in every case. Table I gives the pertinent data and results.

TABLE I

TITRATIONS IN NONAQUEOUS SOLVENTS

| Solvent | Substance titrated | g per aliquot | Method | E (mV) or color vs. extent neutralization | | | | Purity found (%) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 0% | 50% | 99% | 101% | | |
| Acetic acid | NaC₂H₃O₂ | 0.2885 | pot | 185 | 230 | 363 | 511 | 99.6 | |
| | | | phen | R | R | O | Y | 99.5 | 99.6 |
| | | | pyr | P | P | O | Y | 99.4 | |
| Acetic acid | Pyridine | 0.2750 | pot | 180 | 215 | 350 | 550 | 99.1 | |
| | | | phen | R | R | R | Y | 99.1 | |
| | | | pyr | P | P | P | Y | 99.0 | 99.1 |
| Acetic acid | 1-Naphthylamine | 0.4273 | pot | 190 | 218 | 346 | 492 | 99.5 | |
| | | | phen | R | R | O | Y | 99.5 | 99.7 |
| | | | pyr | P | P | O | Y | 99.7 | |
| Acetic acid | p-Bromoaniline | 0.5045 | pot | 192 | 219 | 352 | 483 | 99.0 | |
| | | | phen | R | R | O | Y | 98.8 | 98.1 |
| | | | pyr | P | P | pale R | Y | 98.3 | 98.7 |
| Acetic acid | o-Chloroaniline | 0.3544 | pot | 280 | 324 | 446 | 495 | 99.3 | |
| | | | phen | R | O | OY | Y | 99.6 | |
| | | | pyr | P | R | OY | Y | 100.1 | 98.7 |
| Acetic acid | 2,4-Dichloro-aniline | 0.4756 | pot | 337 | 389 | 472 | 489 | 98.1 | |
| | | | phen | R | O | OY | Y | 96 | |
| | | | pyr | P | O | OY | Y | 99 | |
| Acetic anhydride | LiCl | 0.0118 | potᵈ | 426 | 516 | 715 | 910 | 79.5 | |
| | | | phen | P | P | O | Y | 80.1 | |
| | | | pyr | V | V | OY | Y | 78.1 | |
| Acetic anhydride | KBr | 0.0174 | potᵈ | 410 | 683 | 880 | 966 | 99 | |
| | | | phen | P | O | Y | Y | — | |
| | | | pyr | V | O | Y | Y | — | |
| Acetic anhydride | NaC₂H₃O₂ | 0.0257 | potᵈ | 299 | 390 | 619 | 960 | 99.9 | |
| | | | phen | P | P | R | Y | 100.1 | 99.9 |
| | | | pyr | V | V | pale R | Y | 100.3 | |
| Acetic anhydride | Pyridine | 0.0204 | potᵈ | 330 | 484 | 679 | 935 | 99.0 | |
| | | | phen | P | P | O | Y | 98.7 | 98.9 |
| | | | pyr | V | V | OY | Y | 98.5 | |

TABLE I (Cont.)

| Solvent | Substance titrated | g per aliquot | Method[a] | E (mV) or color[b] vs. extent neutralization | | | | Purity found (%) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 0% | 50% | 99% | 101% | | |
| Chloroform | Pyridine | 0.3089 | pot | —342 | 223 | 343 | 565 | 99.0 | |
| | | | phen | V | P | R | Y | 99.0 | 99.0 |
| | | | pyr | B | B | P | Y | 99.1 | 99.0 |
| Chloroform | 1,10-Phenanthroline[c] | 0.0628 | pot | —148 | 320 | 370 | 531 | 100.0 | |
| | | | phen | V | P | R | Y | 100.0 | 100.6 |
| | | | pyr | B | P | R | OY | 100.3 | 100.9 |
| Chloroform | o-Chloroaniline | 0.3506 | pot | —294 | 360 | 469 | 520 | 99.9 | |
| | | | phen | V | O | Y | pale Y | 97.7 | 98.6 |
| | | | pyr | B | R | Y | pale Y | 99.3 | |
| Chloroform | 2,4-Dichloroaniline | 0.4771 | pot | —370 | 418 | 514 | 533 | 99.3 | |
| | | | phen | V | O | pale Y | pale Y | ~97 | |
| | | | pyr | B | O | pale Y | pale Y | ~97 | |
| Chlorobenzene | 1-Naphthylamine | 0.0470 | pot | —340 | 268 | 405 | 497 | 99.6 | |
| | | | phen | V | R | O | Y | 99.6 | 99.4 |
| | | | pyr | B | R | O | OY | 100.3 | |
| Chlorobenzene | 2,2'-Bipyridine[c] | 0.1726 | pot | —276 | 300 | 437 | 560 | 99.9 | |
| | | | phen | V | V | V | Y | 99.7 | |
| | | | pyr | B | P | P | Y | 99.9 | 99.7 |
| Chlorobenzene | o-Chloroaniline | 0.2045 | pot | —170 | 381 | 488 | 521 | 99.4 | |
| | | | phen | V | O | OY | Y | 100 | |
| | | | pyr | B | R | OY | Y | 101 | |

[a] Potentiometric titrations are designated by "pot"; unless otherwise noted, the glass and Ag–AgCl electrodes were immersed directly in the solution titrated. Visual titrations are indicated by the notation "phen" where ferrocyphen and by "pyr" where ferrocypyr was used as indicator.
[b] Colors: V(violet), B(blue), P(purple), R(red), O(orange), OY(golden), Y(yellow).
[c] Perchlorate salt precipitates during titration.
[d] Glass electrode vs. Ag–AgCl in acetic anhydride saturated with lithium chloride and silver chloride as the reference electrode.

*General procedure.* Weigh out a 0.01–0.02 mole sample of the base to be titrated, dissolve it in the solvent selected, and dilute to 250.0 ml in a volumetric flask. Pipet 50.0 ml of this solution into the titration vessel, add 50 ml more of the solvent and 4 ml of ferrocyphen or ferrocypyr indicator solution, and titrate with standard perchloric acid solution. For titrations in acetic anhydride use the 0.05 $N$ perchloric acid–acetic anhydride–acetic acid solution; for all others, use the standard 0.1 $N$ perchloric acid in acetic acid solution. Record both the potentiometric data and the solution color as a function of the titrant added. Then titrate successive aliquots visually using the appropriate color response of the indicator, ascertained from the first titration, to detect the equivalence point. Determine and correct for the amount of acid consumed by the indicator; calculate the percent purity of the sample.

*Determination of formal redox potentials*

Solutions of the complexes, prepared in sulfuric acid of known concentration, were titrated potentiometrically using platinum and saturated calomel electrodes,

standard ceric sulfate titrant, and a 5-ml buret. Since the solid complexes were very slow to dissolve in the more dilute acid solutions, the weighed samples were first dissolved in 0.5 ml of concentrated acid and then diluted with a known volume of sulfuric acid of the desired concentration. Some solutions were prepared by shaking an excess of the solid complex with the sulfuric acid for several min and then filtering off the undissolved solid. Although this did not permit use of weighed samples, it served to give crude estimates of solubilities and to check on the reliability of the other dissolution procedure. Limited solubility of the iron(II) complexes precluded potentiometric measurements both in neutral solutions and in acid solutions more dilute than those employed here.

Formal reduction potentials (versus the standard hydrogen electrode) for the Fe(III)/Fe(II) complex systems and the Ce(IV)/Ce(III) couple were determined from the 50% and 200% experimental titration points, respectively. Potentiometric measurements prior to the end-point could be taken almost immediately after the addition of each increment of titrant; beyond the end-point the electrode response was quite slow so that considerable time was required for the gradually increasing readings to attain reasonably constant values. The formal potentials found for the Ce(IV)/Ce(III) couple may be slightly low in some cases for this reason. However the main interest in these was to test the reliability of the potentiometric measurements; in most cases the agreement with previously determined values is satisfactory. As a further check of the procedure, the amount of complex found was compared with that taken for titration. The results are compiled in Table II.

TABLE II

FORMAL REDOX POTENTIALS AT 25° IN SULFURIC ACID SOLUTIONS

| $H_2SO_4$ | | Weight of complex | | Formal potentials (V) | |
|---|---|---|---|---|---|
| M | Volume (ml) | Taken (g) | Found (g) | Ce(IV)/Ce(III) | Fe(III)/Fe(II) |
| | | A. Ferrocypyr | | | |
| 12 | 50 | 0.0512 | 0.0519 | 1.54 | 0.979 |
| 10 | 50 | 0.0537 | 0.0540 | 1.47 | 0.901 |
| 6 | 50 | 0.0321 | 0.0323 | 1.43 | 0.817 |
| | 100 | a | 0.0770 | 1.42 | 0.824 |
| 4 | 100 | 0.0220 | 0.0221 | 1.43 | 0.794 |
| | 100 | a | 0.0175 | 1.44 | 0.780 |
| 2 | 200 | 0.0200 | 0.0200 | 1.44 | 0.791 |
| | 200 | a | 0.0193 | 1.43 | 0.781 |
| | | B. Ferrocyphen | | | |
| 12 | 50 | 0.0501 | 0.0490 | 1.53 | 0.990 |
| 10 | 50 | 0.0390 | 0.0396 | 1.47 | 0.925 |
| 6 | 100 | 0.0209 | 0.0220 | 1.42 | 0.852 |
| | 100 | a | 0.0210 | 1.40 | 0.852 |
| 4 | 100 | 0.0058 | 0.0062 | 1.40 | 0.822 |
| | 100 | a | 0.0030 | 1.41 | 0.814 |
| 2 | 200 | 0.0050 | 0.0052 | 1.40 | 0.806 |
| | 200 | a | 0.0057 | 1.41 | 0.806 |

a Amount necessary to nearly saturate the solution with the complex; excess solid filtered off before titrating supernatant solution.

## Oxidation–reduction titrations

A brief survey of the more common oxidants and reductants was made to ascertain which would undergo sufficiently rapid reaction with the reduced and oxidized forms of the proposed indicators to be suitable in titrations. In strongly acidic solutions, ferrocyphen and ferrocypyr are oxidized reversibly and with great rapidity by Ce(IV), V(V), $Cr_2O_7^{-2}$, $BrO_3^-$, $IO_4^-$, or HONO. Oxidation under similar conditions occurs much more slowly and at various rates using $IO_3^-$, $H_2O_2$, $S_2O_8^{-2}$, or $HNO_3$. The oxidized indicators ferricyphen and ferricypyr are readily reduced in strong acid solutions by Fe(II), Sn(II), Cu(I), Sb(III), I⁻, and hydroquinone. Reduction by As(III), $SO_2$, hydroxylamine, or hydrazine is extremely slow except in very dilute acid or neutral solutions.

All of the titrations were performed using ferrocyphen as the indicator. Since ferrocyphen and ferrocypyr have nearly identical formal reduction potentials and exhibit similar color changes on oxidation, it is assumed that they can be used interchangeably.

*Titration of iron(II).* Preliminary titrations, performed potentiometrically in the presence of added ferrocyphen, demonstrated the need for adding phosphoric acid to lower the formal potential of iron(II) (and thus the equivalence point potential) so that the indicator response would coincide with potentiometric end-points. Subsequent titrations were performed according to the following directions: pipet 10.00 ml of the iron solution (in this case a solution containing 39.216 g Mohr's salt per l), add 5 ml of concentrated phosphoric acid followed by sufficient concentrated sulfuric or

### TABLE III
STANDARDIZATION OF 0.1 N FeSO₄ USING FERROCYPHEN INDICATOR

| Titrant | Solution | End-point recognition | Normality |
|---------|----------|----------------------|-----------|
| K₂Cr₂O₇ | 1 M H₂SO₄ | Potentiometric | 0.1001 |
|  | 1 M H₂SO₄ | Orange → yellow green | 0.0999 |
|  | 2 M H₂SO₄ | Orange → yellow green | 0.1000 |
|  | 4 M H₂SO₄ | Yellow green → green | 0.1002 |
|  | 6 M H₂SO₄ | Green → blue green | 0.1004 |
|  | 1 M HCl | Indistinct color change | — |
|  | 2 M HCl | Yellow → green | 0.0999 |
|  | 4 M HCl | Yellow → green | 0.1001 |
|  | 5 M HCl | Indistinct color change | — |
| HVO₃ | 4 M H₂SO₄ | Potentiometric | 0.1002 |
|  | 1 M H₂SO₄ | Yellow → pale blue | 0.0999 |
|  | 2 M H₂SO₄ | Yellow → pale blue | 0.1004 |
|  | 4 M H₂SO₄ | Yellow → pale blue | 0.1003 |
|  | 6 M H₂SO₄ | Yellow → pale blue | 0.1003 |
|  | 1 M HCl | Orange → pale blue | 0.1002 |
|  | 2 M HCl | Yellow → pale green | 0.1003 |
|  | 4 M HCl | Indistinct color change | — |
| Ce(SO₄)₂ | 6 M H₂SO₄ | Potentiometric | 0.1001 |
|  | 1 M H₂SO₄ | Orange → pale blue | 0.0999 |
|  | 6 M H₂SO₄ | Yellow → pale blue | 0.1002 |
|  | 1 M HCl | Orange → pale blue | 0.1001 |
|  | 2 M HCl | Yellow → pale yellow | 0.0997 |
|  | 4 M HCl | Indistinct color change | — |

hydrochloric acid and water to give 100 ml of the desired acid concentration, add 1 ml of indicator solution (0.3 g ferrocyphen in 100 ml of concentrated phosphoric acid, and titrate with standard oxidant to the first distinct, sharp change in color (see Table III for specific details). Blank titrations were made to correct for the amount of titrant necessary for oxidation of the indicator.

Tests performed on the solutions retained after titration showed the indicator reaction to be reversible. Prolonged storage in an excess of either oxidant or reductant produced no deleterious effect on indicator behavior.

*Titration of hydroquinone.* Potentiometric titration of hydroquinone in the presence of added ferrocyphen with the vanadium(V) titrant demonstrated that the visual and potentiometric end-points coincide almost exactly, even as the acid concentration is varied. Using cerium(IV) as the titrant, visual end-points were observed to occur slightly before the potentiometric inflection points. The differences were in the range of 1000–2000 p.p.m. and hence are within the expected limits of experimental error.

Visual titrations were performed according to the directions: weigh a 0.03–0.04-g sample, dissolve in 100 ml of acid (either hydrochloric or sulfuric, 1–6 M), add 1 ml of indicator (0.3 g ferrocyphen in 100 ml of concentrated sulfuric acid), and titrate with the standard oxidant to the first distinct, sharp change in color. Blank titrations are necessary to correct for the amount of titrant consumed by the indicator. The results are given in Table IV.

TABLE IV

TITRIMETRIC ASSAY OF HYDROQUINONE USING FERROCYPHEN INDICATOR

| Titrant | Solution | End-point recognition | % Purity |
|---|---|---|---|
| $Ce(SO_4)_2$ | 1 M $H_2SO_4$ | Orange → colorless | 99.4 |
| | 6 M $H_2SO_4$ | Yellow → very pale yellow | 101.3 |
| | 1 M HCl | Orange → colorless | 99.9 |
| | 1 M $H_2SO_4$ | Potentiometric | 99.7 |
| $HVO_3$ | 1 M HCl | Orange → pale green | 99.7 |
| | 2 M HCl | Yellow → pale green | 99.6 |
| | 0.5 M $H_2SO_4$ | Orange → pale green | 99.6 |
| | 4 M $H_2SO_4$ | Yellow → pale green | 99.5 |
| | 1 M HCl | Potentiometric | 99.6 |

Tests performed on the solutions retained after titration demonstrated that the indicator reaction behaves reversibly. Storage for several hours of the solutions to which an excess of either hydroquinone or titrant had been added was without noticeable effect on the indicator or its response.

*Titration of primary aromatic amines.* Samples of various amines were titrated using the following procedure: weigh out a 2–3- mmol sample of the amine, dissolve in 100 ml of 6 M hydrochloric acid, add 1 ml of indicator solution (0.3 g ferrocyphen in 100 ml of concentrated hydrochloric acid), and titrate with standard sodium nitrite to a violet colored end-point that will persist for at least 3 min. A titration blank was measured to correct for the amount of titrant consumed by the indicator. Results are given in Table V.

From the behavior of the indicator during the titrations it is evident that its reaction responds reversibly with respect to the titration reaction. Upon rapid addition of large increments of titrant, prior to the equivalence-point, ferrocyphen underwent complete and rapid oxidation followed more slowly by a gradual return to the reduced

TABLE V

TITRIMETRIC ASSAY OF PRIMARY AROMATIC AMINES
USING FERROCYPHEN INDICATOR

| Amine | HCl M | Replicate determinations % Purity[a] | | | |
|---|---|---|---|---|---|
| Aniline | 4 | 98.9 | (98.9) | | |
| Aniline | 6 | 99.3 | 99.5 | 99.4 | (99.2) |
| Aniline | 8 | 99.3 | (99.1) | | |
| Aniline | 9 | 99.2 | 99.9 | | |
| p-Bromoaniline | 6 | 100.1 | 99.7 | | |
| o-Chloroaniline | 6 | 99.9 | 100.1 | | |
| 1-Naphthylamine | 6 | b | | | |
| 2,4-Dichloroaniline | 6 | 100.2 | 100.1 | | |

[a] Values given in parentheses were obtained by potentiometric titration.
b Visual end-point detection was impossible because titration gives colored products.

condition. Such behavior could be produced many times throughout the course of any given titration, and apparently, without adversely affecting the ability of the indicator to function properly. Since reduction of ferricyphen cannot be effected by the aromatic amines in question, it appears that one of the diazotization products or reaction intermediates is responsible for the reversibility of the indicator in this case. No attempt was made to elucidate the indicator reaction mechanism.

Aniline was titrated potentiometrically in the presence of ferrocyphen to determine the color of the indicator in the immediate neighborhood of the electrometric end-point. The change in color of the indicator from light yellow to pale violet was observed to coincide almost exactly with the potentiometric end-point in each of three different hydrochloric acid concentrations employed: 4, 6 and 8 M. Considerable time, up to 1 h, was required to complete each potentiometric titration, because either or both chemical and electrode systems were slow to reach equilibrium and, of course, many equilibrium measurements were needed. No deleterious effect on the reversibility of the indicator after this time was noticeable.

A modest saving of time could be achieved by using 6 M hydrochloric acid as the solvent medium. Total elapsed time to complete the titration of aniline, for example, in 6 M HCl by visual end-point detection was approximately 10 min; in 4 M and 9 M acid the respective times averaged 15 and 10 min.

## SUMMARY

The neutral mixed ligand complexes dicyano-bis-(1,10-phenanthroline)–iron(II) and dicyano-bis-(2,2'-bipyridine)–iron(II) are suitable indicators for the titration of various weak bases in nonaqueous solvents. They also serve as practical indicators for certain redox titrations in aqueous solutions; their applicability in the determination of primary aromatic amines is especially noteworthy. Formal potentials of the complexes in different concentrations of sulfuric acid are reported; the results confirm earlier findings that the neutral iron(II) complexes form stable protonated species.

## RÉSUMÉ

Les complexes fer(II)–dicyano-bis-(1,10-phénanthroline) et fer(II)–dicyano-bis-(2,2'-dipyridine) conviennent très bien, comme indicateurs aux titrages de diverses bases faibles en milieu non-aqueux, de même qu'à certains titrages redox en solutions aqueuses et tout spécialement au dosage d'amines aromatiques primaires.

## ZUSAMMENFASSUNG

Die neutralen Mischkomplexe Dicyano-bis-(1,10-phenanthrolin)–eisen(II) und Dicyano-bis-(2,2'-bipyridin)–eisen(II) eignen sich als Indikatoren für die Titration schwacher Basen in nicht-wässrigen Lösungsmittel sowie für gewisse Redox Titrationen in wässriger Lösung. Auf ihre Anwendung bei der Bestimmung von aromatischen primären Aminen wird besonders hingewiesen.

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# REDUCTION OF AMMONIUM NITRATE WITH TITANIUM(III) CHLORIDE IN ACID MEDIA*

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Investigation of the determination of nitrate in acid media using an indirect titanous titration has led to the proposal of a new mechanism of nitrate reduction. It has been shown that the reduction of nitrate to ammonium ion as proposed by KNECHT AND HIBBARD[1] is not quantitative when only a moderate excess (50 to 100%) of the titanous salt is present.

TOMIČEK[2] reported that the direct potentiometric titration of nitrate solutions with titanous chloride is not possible because the reaction takes place very slowly. Therefore, to eliminate the time dependence when a small excess is present, a back-

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