

### 541. Reactions of Disodium Pentacyanoamminoferrate with Aromatic Amines. Part I. The Preparation and Properties of Compounds containing the Pentacyano-*p*-hydroxyanilino-ferrate Ion.

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The reaction of the salt  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$  with *p*-aminophenol in alkaline solution is shown to give rise to the compound  $\text{Na}_3[\text{Fe}(\text{CN})_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}]$ . The deep blue aqueous solution of this salt exhibits an absorption maximum at 695  $\mu$  with  $\log_{10} \epsilon$  4.29. As many heavy-metal salts containing this anion can be precipitated from dilute acid solution as intensely coloured solids, trisodium pentacyano-*p*-hydroxyanilino-ferrate may find use as a spray reagent in paper chromatography.

THIS series of papers is concerned with the structure and properties of the compounds obtained by treating aromatic amines with disodium pentacyanoamminoferrate  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$ . Many primary and secondary aromatic amines give blue or green solutions with this reagent but the present paper relates only to the product obtained from *p*-aminophenol. This base was chosen for detailed study because experiment had shown that the resulting complex ion is of a simpler type than the complex ions obtained by the reaction of many aromatic amines with disodium pentacyanoamminoferrate.

There is little previous work on this topic. Anger<sup>1</sup> described a colour reaction which he claimed was specific for the detection of primary aromatic amines based on a reagent prepared by oxidising a 2% solution of trisodium pentacyanoamminoferrate  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$  with bromine-water: the violet colour obtained was "compensated" by addition of a further quantity of the salt solution and 2% of sodium carbonate was then added to the resulting yellow solution. This reagent was reported to give a green-blue colour with *p*-aminophenol. The constitutions of the products were not established.

Ohkuma<sup>2</sup> prepared a reagent for the same purpose made by adding hydrogen peroxide to an alkaline solution of trisodium pentacyanoamminoferrate. Experiments have now shown that the reagent solution used by Anger<sup>1</sup> and by Ohkuma<sup>2</sup> contained the salts  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$  and  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$ . Hence the coloured products they observed were often mixtures; for example, *p*-aminophenol reacts with the trisodium salt to give a green, and with the disodium salt to give a blue product, so accounting for the colour observed by Anger.

Since the nature of the above blue product was unknown it was necessary to establish whether it was or was not entirely organic. That the colour was associated with an anion was clearly shown by adding a suitable heavy-metal salt (*e.g.*, zinc or copper nitrate) to the solution, whereupon a heavy blue precipitate was obtained which was insoluble in dilute acetic acid. A magnetizable brown solid was produced by ignition in air of the paramagnetic blue precipitate obtained by adding zinc nitrate and was shown to contain iron by the ammonium thiocyanate test.

Paper-electrophoresis provided confirmation that the coloured complex carries a negative charge and showed that the colour was due to one anionic species. The molecular ratio in which the reagents combine was found by means of the method of "continuous variation" (see Job<sup>3</sup>) using solutions buffered with borax: it was 1:1.

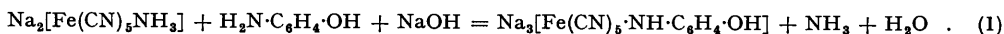
This ratio suggested that the reaction might be a simple replacement of ammonia by *p*-aminophenol to yield the ion  $[\text{Fe}^{\text{III}}(\text{CN})_5\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}]^{2-}$ . Indeed ammonia is liberated during the reaction; and the same complex is produced by aerial oxidation of an alkaline solution of the salt  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]$  in the presence of *p*-aminophenol as by reaction of the salt  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$  with the amine, thus establishing that there is no ammonia present in the coloured ion. On mixing of solutions of *p*-aminophenol and the disodium

<sup>1</sup> Anger, *Mikrochim. Acta*, 1937, 2, 3.

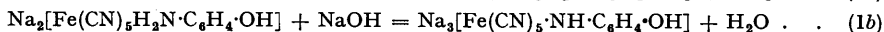
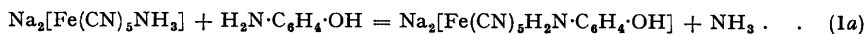
<sup>2</sup> Ohkuma, *J. Pharm. Soc. Japan*, 1952, 72, 1101.

<sup>3</sup> Job, *Ann. Chim. (France)*, 1928, 9, 113; 1936, 6, 97.

salt adjusted to pH 11.0, the pH fell to 9.5. In view of similar observations on the reaction of aniline with this salt (unpublished work) the fall in pH was ascribed to reaction (1) :



However, this probably takes place in stages, *viz.* :



Some evidence for this is afforded by experiments in which concentrated ammonia solutions were employed. Very little change in colour was observed during 1 hr. when an ammonia solution was added to the blue solution obtained from the reaction of the salt  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$  with *p*-aminophenol. This indicated that the overall reaction (1) was not readily reversed when excess of ammonia was added. If, however, an alkaline solution of the salt  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$  containing ammonia was added to *p*-aminophenol then a brown colour resulted. The simplest explanation of these observations is that the large excess of ammonia forces reaction (1a) to the left and then the *p*-aminophenol is oxidized by the  $[\text{Fe}(\text{CN})_5\text{NH}_3]^{2-}$  ion in the same manner as this amine is oxidized by the ferricyanide ion. Thus the course of the reaction between *p*-aminophenol and the salt  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$  is changed by the addition of a large excess of ammonia.

The sodium salt of the complex prepared from *p*-aminophenol and disodium pentacyanoamminoferrate is a hygroscopic solid unsuited for analysis, so the zinc salt was made and shown by analysis to be  $\text{Zn}_3[\text{Fe}(\text{CN})_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}]_2\cdot 4\text{H}_2\text{O}$ . In one possible structure for the complex ion, the iron is bivalent and the nitrogen carries an odd electron, while in another the iron is trivalent and the group  $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  carries a negative charge.

The solubility of the lead salt of the new anion was compared with those of the lead salts containing the anions  $[\text{Fe}^{\text{III}}(\text{CN})_5\text{X}]$  and  $[\text{Fe}^{\text{II}}(\text{CN})_5\text{X}]$ . Adding a dilute acetic acid solution of lead acetate to solutions of the salt  $\text{K}_3[\text{Fe}^{\text{III}}(\text{CN})_6]$  or  $\text{Na}_2[\text{Fe}^{\text{III}}(\text{CN})_5\text{NH}_3]$  does not give a precipitate but if the same lead acetate solution is added to solutions of the salts  $\text{K}_4[\text{Fe}^{\text{II}}(\text{CN})_6]$  or  $\text{Na}_3[\text{Fe}^{\text{II}}(\text{CN})_5\text{NH}_3]$  precipitates are obtained. This lead acetate reagent with the new anion gave a blue precipitate, showing that the solubility of the lead salt of the pentacyano-*p*-hydroxyanilinoferrate ion resembles that of the complex cyanides containing bivalent iron.

The infrared spectra of these compounds were also measured. Emschwiler<sup>4</sup> has reported that the cyano-group gives rise to a more intense band in the ferrocyanides than in the ferricyanides and that these bands appear at 2040 and 2115  $\text{cm}^{-1}$  for potassium ferro- and ferri-cyanides respectively. Work at this laboratory<sup>5</sup> has shown that the position and intensity of the cyano-bands in the neighbourhood of 2000  $\text{cm}^{-1}$  for a number of sodium salts containing the group  $[\text{Fe}(\text{CN})_5\text{X}]$  are determined by the formal charge on the iron atom. These features of the spectra do not depend on the formal charge on the whole anion since similar cyano-bands were observed in  $[\text{Fe}^{\text{II}}(\text{CN})_5\text{NH}_3]^{3-}$  and  $[\text{Fe}^{\text{II}}(\text{CN})_5\text{H}_2\text{O}]^{3-}$  as in  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ , and in  $[\text{Fe}^{\text{III}}(\text{CN})_5\text{NH}_3]^{2-}$  and  $[\text{Fe}^{\text{III}}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  as in  $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ .

The sodium salt of the complex prepared from *p*-aminophenol is unsuited for examination by infrared spectroscopy. For the zinc and the lead salt the frequency of the cyano-band also depends on the nature of the metal outside the co-ordination shell, so samples of zinc ferricyanide, zinc ferrocyanide, and lead ferrocyanide were prepared for comparison. The results are summarized in Table I. Clearly the spectra of the zinc and lead salts of the complex resemble those with bivalent iron.

Nevertheless, a paramagnetic resonance line was not observed when a freshly prepared aqueous solution of the complex made from  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$  and *p*-aminophenol was examined with the specimen at room temperature or at the temperature of liquid nitrogen. If the structure had been entirely that of the ferrous ion a line should have been observable due to the unpaired electron associated with the organic group, but in fact no line was found.

<sup>4</sup> Emschwiler, *Compt. rend.*, 1954, **238**, 1414.

<sup>5</sup> Herington and Kynaston, *J.*, 1955, 3555.

TABLE I. *Infrared spectra of zinc and lead salts.*

Compound	Valency of Fe	Band (cm. <sup>-1</sup> )	Optical density of KCl disc (0.375" diam.) containing 1 mg. of complex salt
Zn ferricyanide .....	III	2177	0.73
Zn ferrocyanide .....	II	2100	1.39
Zn salt of <i>p</i> -aminophenol complex ...	—	2100	1.51
Pb ferrocyanide .....	II	2037	1.67
Pb salt of <i>p</i> -aminophenol complex ...	—	2040	1.64

This means either that the anion contains ferric ion, in spite of the chemical and infrared evidence to the contrary, or that the structure resonates between the two at a frequency greater than that of the 1.25 cm. wavelength used in the paramagnetic resonance spectrometer.

However, it is probably better to regard the two structures as canonical forms rather than different possible structures, and then the unpaired electron may be considered to lie in a  $\pi$ -type orbital covering the whole of the organic part of the anion, the iron atom and the cyano-group in *trans*-position to the organic ligand. Such a structure is compatible with many of the properties described.

The sodium salt of the *p*-aminophenol complex, dissolved in 0.2*N*-sodium hydroxide, has a single strong absorption band in the visible region (350—1000  $m\mu$ ) at 695  $m\mu$  with  $\log_{10} \epsilon$  4.29, and although this value is rather smaller than the corresponding figures for dyes such as malachite-green ( $\log_{10} \epsilon_{\max}$ , 4.5 at 600  $m\mu$ ) or crystal-violet<sup>6</sup> ( $\log_{10} \epsilon_{\max}$ , 5.0 at 583  $m\mu$ ) yet it is of comparable magnitude.

Strong reducing agents destroy the blue colour of the complex and regenerate *p*-aminophenol, as demonstrated by use of alkaline sodium dithionite and benzylation of the liberated base.

An attempt to prepare the free acid  $H_3[Fe(CN)_5 \cdot NH \cdot C_6H_4 \cdot OH]$  by adding concentrated hydrochloric acid to the aqueous solution of the trisodium salt gave a brilliant red colour which could not be extracted with ether. Filter paper impregnated with the blue salt  $Na_3[Fe(CN)_5 \cdot NH \cdot C_6H_4 \cdot OH]$  was allowed to dry in air and a spot of concentrated hydrochloric acid was placed on the paper which became red; cold methyl alcohol dissolved the red spot to give a red solution, but did not dissolve the blue salt; adding ether to the methyl alcohol solution gave a blue precipitate which yielded a blue aqueous solution but gave a red colour with concentrated hydrochloric acid. From these experiments it was concluded that the free acid is probably blue, but that it is red in the presence of concentrated hydrochloric acid. However, the blue colour of the ion is not immediately destroyed in phthalate buffer pH 4 or in 2*N*-acetic acid.

Mention has been made above of the insolubility of the lead salt of the *p*-aminophenol complex; in general, the solubilities of the heavy-metal salts of the pentacyano-*p*-hydroxyanilino-ferrate ion resemble those of the ferrocyanides. The metal salts were investigated by placing a drop of the heavy-metal nitrate or chloride solution on paper which was then sprayed with the solution of  $Na_3[Fe(CN)_5 \cdot NH \cdot C_6H_4 \cdot OH]$  and washed with 2*N*-acetic acid. The papers were then examined for colour. The result depends both on the insolubility of the resulting compound in 2*N*-acetic acid and on the colour of the salt. The pentacyano-*p*-hydroxyanilino-ferrates of alkali and alkali-earth metals are soluble in water and in dilute acetic acid, but many other salts have a low solubility in water and dilute acid. However, these salts are not all equally coloured and the results of the spraying experiments may be considered in relation to the position of the metal in the Periodic Table. The cupric salt is an intense blue but the silver salt is a dirty blue when first formed and soon becomes brown in light and air. The zinc and the cadmium salt are violet-blue and blue respectively. The mercuric salt is paler than the zinc salt. No coloured stain was obtained with aluminium salts. The zirconium salt is insoluble and blue. Stannic chloride produces only a faint brown stain but stannous chloride gives a grey-blue spot. The lead salt is blue but is partly soluble and appears to be somewhat unstable, so that the paper when washed with 2*N*-acetic acid carries only a grey-blue stain. The thorium ( $Th^{4+}$ ) salt resembles the lead salt but is more stable, so that the paper carries a fairly strong blue stain. The paper

<sup>6</sup> Landolt-Bornstein's "Tabellen," 6th edn., Vol. I, Part 3, p. 287.

impregnated with antimony trichloride is not stained but that impregnated with bismuth ( $\text{Bi}^{3+}$ ) shows a diffuse blue patch.

The papers which had been spotted with rare-earth solution (1 ml. of Ce, Pr, Gd, and Ho solutions containing 10  $\mu\text{g.}$ -atom of rare earth) show a slight blue colour but these salts clearly have a high solubility. Chromium nitrate, ammonium molybdate, and sodium tungstate do not produce coloured stains. Uranyl nitrate produces a blue stain which, however, rapidly fades to grey-brown : this colour is not as intense as that formed by an equal amount of uranyl nitrate and potassium ferrocyanide. Manganese ( $\text{Mn}^{2+}$ ) gives a bright blue spot approximately half as intense as the zinc spot. Iron ( $\text{Fe}^{3+}$ ), cobalt ( $\text{Co}^{2+}$ ), and nickel ( $\text{Ni}^{2+}$ ) all give strongly coloured blue spots which differ somewhat in hue.

#### EXPERIMENTAL

*Preparation of Disodium Pentacyanoamminoferrate.*—Trisodium pentacyanoamminoferrate<sup>7</sup> was oxidized to disodium pentacyanoamminoferrate by nitrous acid.<sup>8</sup> The product was dried in a vacuum-desiccator ( $\text{P}_2\text{O}_5$ ) {Found : C, 21.4; N, 30.2; Fe, 21.5. Calc. for  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot\text{H}_2\text{O}$  : C, 22.4; N, 31.5; Fe, 20.9%}.

*Preparation of Trisodium Pentacyanoaquoferrate.*—This salt was prepared from sodium nitroprusside by reduction with hydroxylamine.<sup>8</sup>

*Purification of p-Aminophenol.*—Commercial *p*-aminophenol was purified by chromatography on alumina with a 1 : 4 (v/v) mixture of absolute alcohol and "AnalaR" benzene as eluant. A brown impurity remained on the column and removal of the solvent from the faintly yellow solution gave a slightly brown sample of *p*-aminophenol, m. p. 183° (decomp.).

*Preparation of Aqueous Solution of  $\text{Na}_3[\text{Fe}(\text{CN})_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}]$ .*—This blue salt is prepared by the reaction of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$  with *p*-aminophenol in the presence of a small quantity of sodium hydroxide, but as *p*-aminophenol is itself oxidized in air in alkaline solution the order of the addition of the reagents is important. The following conditions yielded the cleanest product : to 0.45 g. of *p*-aminophenol was added a solution prepared by dissolving 1.05 g. of the salt  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot\text{H}_2\text{O}$  in 40 ml. of 0.025N-sodium hydroxide. The mixture was at once shaken. It immediately became blue and reaction was almost complete in 1 hr. Small amounts of a brown by-product and of the salt  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]$  were formed and were removed by passing the blue solution down a short column of activated alumina. This solution can be kept at room temperature for several days with little deterioration but is best stored for long periods (e.g., 6 months) in a refrigerator at  $-10^\circ$ .

*Preparation of Solid  $\text{Na}_3[\text{Fe}(\text{CN})_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}]$ .*—The sodium salt was precipitated from aqueous solution by alcohol-ether. The solid, which was of such a dark blue colour as to appear almost black, was filtered off on paper. However, this solid was so hygroscopic that it stuck fast to the paper and was not investigated further.

*Paper Electrophoresis.*—An "EEL" paper-electrophoresis apparatus was employed. The paper strips were saturated with 0.1N-sodium hydroxide, and a current of 4 mA was passed through two strips in parallel. This current corresponded to a voltage drop of 3.5 v/cm. on each paper. One volume of a solution of the salt  $\text{Na}_3[\text{Fe}(\text{CN})_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}]$ , prepared as above, was diluted with 4 vol. of 0.1N-sodium hydroxide, and 0.025 ml. of the resulting solution was put on the paper strip. A single blue band was formed which moved at the rate of 0.89 cm. hr.<sup>-1</sup> v<sup>-1</sup>. A sample of the complex which had been purified by passage down an alumina column gave only a single blue band, but the crude product of the reaction of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$  with *p*-aminophenol showed in addition one or two faintly coloured bands which moved slowly under the influence of the applied potential, and a very pale yellow band (due to the ion  $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ , detected by spraying with ferric chloride solution) which moved more rapidly than the main band.

*"Continuous Variation"*.—The following solutions were prepared. Solution A contained 19.07 g. of borax per l. Solution B contained 0.0228 g. of the salt  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot\text{H}_2\text{O}$  in 200 ml. of distilled water. Solution C contained 0.0138 g. of *p*-aminophenol in 200 ml. of distilled water. A series of solutions of total volume 12 ml. containing 6 ml. of solution A and varying amounts of solutions B and C and water were made, in such a manner that the overall molarity of the salt  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot\text{H}_2\text{O}$  plus *p*-aminophenol was constant. For example, the solution containing this salt and *p*-aminophenol in the ratio 1 : 1 was prepared by mixing 6.00 ml.

<sup>7</sup> Herington, *Analyst*, 1953, **78**, 174.

<sup>8</sup> Hofmann, *Annalen*, 1900, **312**, 1.

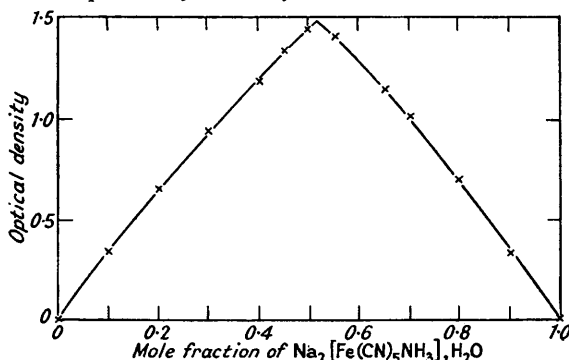
of solution A, 0.98 ml. of water, 3.00 ml. of solution B, and 2.02 ml. of solution C. Similarly a solution with a salt to *p*-aminophenol ratio of 1 : 9 was prepared by mixing 6.00, 1.76, 0.60, and 3.64 ml. respectively. The appropriate volume of solution C was added to each as the last step.

The absorption of each solution was measured with a Spekker absorptiometer, 1 cm. cells, a tungsten lamp, and filter No. 608 being used. The readings obtained for the solutions 4 hr. after mixing are presented in the Figure. The curve has its maximum at a ratio of 0.51 : 0.49, showing that the coloured complex is formed by the reaction of 1 mole each of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot\text{H}_2\text{O}$  and *p*-aminophenol.

*Aerial Oxidation of Solution of  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]$  in the Presence of *p*-Aminophenol.*—The salt  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]$  (0.1 g.) was dissolved in 0.025*N*-sodium hydroxide (5 ml.), and the solution poured on to *p*-aminophenol (0.1 g.). The solution, which was stirred in contact with air, immediately became green but after 3 hr. had a deep blue colour. This solution was shown by the following tests to contain the same ion as that resulting from the reaction of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$  with *p*-aminophenol. A mixture of the products made from  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]$  and  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$  was examined by paper electrophoresis and yielded only a single blue band. The corresponding zinc salts were prepared by precipitation from dilute acetic acid, and the infrared spectra were shown to be identical.

*pH Measurements.*—The measurements were made with an "Alki" glass electrode and a pH-meter (Cambridge Instrument Co.). The electrode was calibrated by the use of a borax buffer at pH 9.18 (19.071 g. of "AnalaR" borax made up to 1 l. with boiled distilled water).

Composition by method of "continuous variation."



*p*-Aminophenol (0.0184 g.) was dissolved in distilled water (10 ml.), and the pH measured by the glass electrode was adjusted to 11.0 by the addition of 0.02*N*-sodium hydroxide; the salt  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot\text{H}_2\text{O}$  (0.053 g.) was dissolved in water (15 ml.) and the pH adjusted to 11.0 as above. The latter solution was stirred by means of a magnetic stirrer, the *p*-aminophenol solution was poured in, and pH readings were taken. The pH fell to 9.4 within the first 0.25 min., then rose and became sensibly constant after 3 min. The blue colour had been then nearly fully developed. The pH after 30 min. was 10.02 and after 67 min. was 10.06. However, recalibration of the glass electrode at the end of the experiment gave a pH value of 9.66 instead of 9.18, *i.e.*, the reading was 0.48 too high and therefore the final pH was 9.58 instead of 10.06. A similar result was obtained in another experiment, when the salt solution was poured into a *p*-aminophenol solution. Other glass electrodes were tried, including an ordinary glass electrode. In an experiment with such an electrode and slightly more concentrated solutions the pH fell from 11.00 to 9.00 and then rose to 9.76. These values correspond to an overall change from 11.00 to 9.22 when the glass electrode had been recalibrated at the end of the experiment. The reaction thus appears to interfere with the performance of the glass electrode but the results of all the experiments agree in showing that the pH falls finally by about 1.5 units when solutions of the concentrations given above are mixed.

*Preparation and Analysis of Zinc Pentacyano-*p*-hydroxyamminoferrate.*—To a solution of zinc nitrate (3 g.) in dilute acetic acid (20 ml. of glacial acetic acid and 100 ml. of water) was added 40 ml. of an aqueous solution of the purified sodium salt prepared as described above. The gelatinous blue precipitate was filtered off (Whatman No. 1 paper) and washed with distilled water until the filtrate was neutral. The zinc salt was dried [ $\text{NaOH}$ , then  $\text{Mg}(\text{ClO}_4)_2$  in a vacuum] {Found: C, 30.5, 30.2; H, 2.0, 2.0; N, 19.7, 19.8; Zn, 21.7, 23.4, 23.3; Fe, 13.1, 13.0.  $\text{Zn}_3[\text{Fe}(\text{CN})_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}]_2\cdot 4\text{H}_2\text{O}$  requires C, 30.8; H, 2.3; N, 19.6; Zn, 22.9; Fe, 13.0%}.

*Infrared Measurements.* The zinc and the lead salt were prepared by precipitation from solution, under the following conditions.

(a) *Zinc ferrocyanide.* Potassium ferrocyanide (0.4 g.) was dissolved in water (10 ml.) and glacial acetic acid (5 ml.) was added, followed by 0.1M-zinc nitrate (30 ml.). The gelatinous white precipitate was filtered off, washed with 2N-acetic acid, and dried in a desiccator.

(b) *Zinc ferricyanide.* Potassium ferricyanide (0.39 g.) was dissolved in water (10 ml.) and glacial acetic acid (5 ml.), and 0.1M-zinc nitrate (30 ml.) added. The resulting yellow precipitate was removed on a Whatman No. 44 paper, washed with 2N-acetic acid, and dried in a desiccator.

(c) *Zinc pentacyano-p-hydroxyanilino-ferrate.* The solid prepared as described above was used for the spectroscopic measurements.

(d) *Lead ferrocyanide.* To a solution of lead acetate (1.2 g.) in water (10 ml.) and glacial acetic acid (2 ml.) was added aqueous potassium ferrocyanide (0.4 g. in 10 ml.). The white precipitate was removed on a Whatman No. 44 paper, washed with water until neutral, and dried in a vacuum desiccator.

(e) *Lead pentacyano-p-hydroxyanilino-ferrate.* To a solution of lead acetate (0.6 g.) in water (5 ml.) and acetic acid (2 ml.) was added sodium pentacyano-p-hydroxyanilino-ferrate solution (15 ml.) prepared as above. The blue precipitate was removed on a Whatman No. 44 paper but as the filtrate was blue the lead salt must be appreciably soluble. The precipitate was washed with a little water and dried.

Samples of the above salts and of *p*-aminophenol were finely ground and were incorporated in pressed potassium chloride discs.<sup>9</sup> The spectra of these discs were recorded on a double-beam spectrometer,<sup>10</sup> with the results shown in Table 2.

TABLE 2. *Infrared bands (cm.<sup>-1</sup>) of various salts and of p-aminophenol.*

Zn ferricyanide .....	3450 sb; 2177 s.
Zn ferrocyanide .....	3350 sb; 2110 s.
Zn salt of <i>p</i> -aminophenol complex .....	3450 sb; 3270 sh; 2100 s; 1960 w; 1642 s; 1622 w.sh; 1582 sh; 1515 m; 1460 w; 1416 m; 1370 w; 1316 w; 1286 w; 1230 w; 1167 m; 1097 w; 1078 sh; 1023 w; 997 w; 951 w; 886 w; 869 m; 783 w.
Pb ferrocyanide .....	3450 sb; 2037 s; 1643 w; 938 w.
Pb salt of <i>p</i> -aminophenol complex .....	3450 mb; 2040 s; 1628 m; 1583 w.sh; 1488 m; 1422 sh; 1368 w; 1287 w; 1232 w; 1164 m; 1096 w; 1020 w; 987 w; 868 m; 787 w.
<i>p</i> -Aminophenol .....	3310 m; 3230 sh; 3040 m; 2950 m; 2830 m; 2700 m; 2605 s; 2498 m; 2003 w; 1872 w; 1742 w; 1695 w; 1620 m; 1600 sh; 1516 s; 1480 s; 1390 s; 1345 sh; 1325 sh; 1260 s; 1240 s; 1217 sh; 1171 m; 1154 m; 1121 w; 1094 m; 1012 m; 970 s; 948 sh; 920 m; 847 m; 829 s; 819 sh; 751 s; 705 m.

b = broad, s = strong, w = weak, sh = shoulder.

The CN bands near 2000 cm.<sup>-1</sup> have already been discussed. The simple ferro- and ferricyanides exhibit very few bands, but the zinc and lead salts of the pentacyano-*p*-hydroxyanilino-ferrate ion show many bands arising from the organic part of the complex. However, the spectra of these salts exhibit less structure than the spectrum of *p*-aminophenol itself.

*Reduction of the Pentacyano-p-hydroxyanilino-ferrate Ion with Sodium Dithionite.*—The salt Na<sub>2</sub>[Fe(CN)<sub>5</sub>NH<sub>2</sub>].H<sub>2</sub>O (0.7 g.) was dissolved in 0.025N-sodium hydroxide (20 ml.), and the resulting solution was poured on *p*-aminophenol (0.22 g.). The solution was stirred for 1 hr. and then extracted with benzene (2 × 50 ml.). The aqueous solution was then decolorized by adding sodium dithionite (1 g.); 25% w/w sodium hydroxide solution (9 ml.) and benzoyl chloride (2 ml.) were added and the resulting solution was shaken for 5 hr. The solid (0.5 g.), separated and dried in a vacuum-desiccator, had m. p. 235° alone or mixed with *p*-benzamido-phenyl benzoate (m. p. 235°). The infrared spectra of the two materials were identical.

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<sup>9</sup> Hales and Kynaston, *Analyst*, 1954, **79**, 702.

<sup>10</sup> Hales, *J. Sci. Instr.*, 1953, **30**, 52.

<sup>11</sup> Herington, *Nature*, 1955, **176**, 80.