

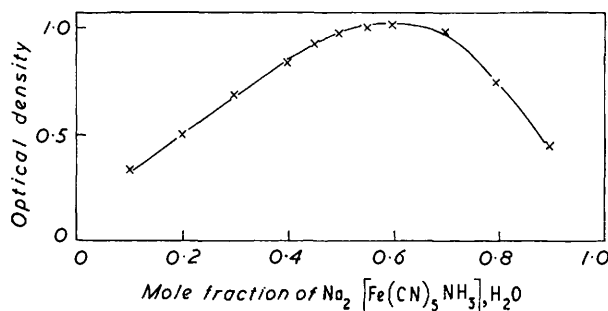
943. *Reactions of Disodium Pentacyanoamminoferrate with Aromatic Amines. Part II.*¹ *The Preparation and Properties of Compounds containing the Pentacyano-(p-anilinoanilino)ferrate Ion.*

By E. F. G. HERINGTON.

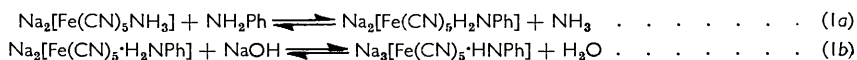
The reaction of the salt $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$ with aniline in alkaline solution is shown to give rise to the compound $\text{Na}_3[\text{Fe}(\text{CN})_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NHPh}]$, identical with the complex produced by the reaction of the same salt with *p*-aminodiphenylamine. Reduction of the complex ion prepared from aniline yields *p*-aminodiphenylamine, and reaction of the complex with nitrous acid gives the diazo-compound derived from *p*-aminodiphenylamine. The deep blue-green aqueous solution of the complex exhibits an absorption maximum at 660 $\text{m}\mu$ ($\log_{10} \epsilon$ 4.1). Some of the heavy-metal salts of the pentacyano-*p*-anilinoanilino-ferrate ion are precipitated from dilute acid solution as intensely coloured solids. Paper electrophoresis of aqueous solutions of the complex which had been stored for several months indicated that it decomposed slowly.

DISODIUM PENTACYANOAMMINOFERRATE,^{1,2} $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$, with aniline in alkaline solution gives blue-green solutions but the reaction is more complicated than that between the same reagent and *p*-aminophenol.¹ The salts $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$ and $\text{Na}_2[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]$

FIG. 1. "Continuous variation" experiment to determine the ratio in which the materials react.



yield the same products with aniline, showing that the ammonia molecule is not involved in the reaction. Paper electrophoresis of the material obtained by the reaction of aniline and disodium pentacyanoamminoferrate indicated the presence of four components. The material in the main band formed a blue-green zinc salt, which, after purification, was shown to have a composition $\text{Zn}_3[\text{Fe}(\text{CN})_5\text{C}_{12}\text{H}_{11}\text{N}_2]_2\cdot 8\text{H}_2\text{O}$. The molecular ratio in which the reagents were used in the reaction was found by the method of "continuous variation" (Job³) employing solutions buffered with borax; it was 3:2 for the ratio $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3] : \text{NH}_2\text{Ph}$ (see Fig. 1). The fall in the pH of the solution when the reactants are mixed is ascribed to the following reactions:



The small initial rise in the pH (see Experimental section) is the result of reaction (1a), but reaction (1b) quickly produces a fall. Equations (1a and b) do not, however, explain the stoichiometry of the reaction, nor do they account for the simultaneous formation of the salt $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$, so that these reactions must be followed by others.

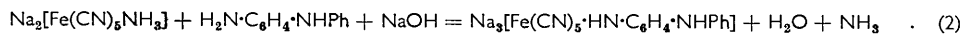
Reduction of the blue-green ion with sodium dithionite yielded *p*-aminodiphenylamine.

¹ Part I, Herington, *J.*, 1956, 2747.

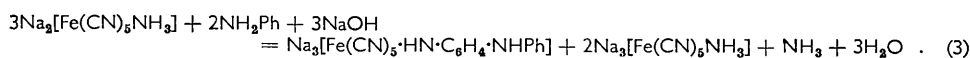
² Herington, *Nature*, 1955, 176, 80.

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

The complex was also destroyed by reaction with nitrous acid, and the resulting organic compound was coupled with β -naphthol to yield an azo-dye identical (as established by infrared spectroscopy) with that prepared by the diazotisation of *p*-aminodiphenylamine and coupling of the resulting diazo-compound with β -naphthol. Measurement of colour intensities of the respective azo-dyes indicated that the conversion of aniline into *p*-aminodiphenylamine by $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$ was almost quantitative. These observations demonstrate that the blue-green ion has the formula $[\text{Fe}(\text{CN})_5 \cdot \text{HN} \cdot \text{C}_6\text{H}_4 \cdot \text{NHPH}]^{3-}$. The structure was confirmed by infrared spectrometry and by paper electrophoresis which showed that the ion obtained by reaction of aniline with disodium pentacyanoamminoferrate was identical with that obtained by reaction of *p*-aminodiphenylamine with the same salt, *i.e.*, by the reaction:

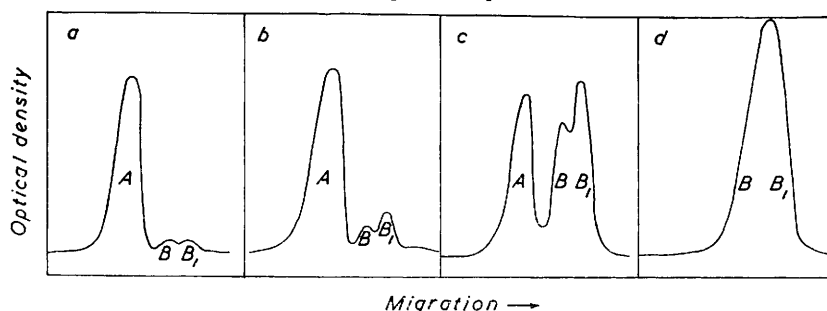


Therefore the reaction between aniline and disodium pentacyanoamminoferrate can be represented by equation (3):



in agreement with the observed stoichiometry, the pH change, the simultaneous formation of the salt $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$, the analysis of the zinc salt, with the material produced by reduction and with the compound formed by the reaction with nitrous acid.

FIG. 2. Paper electrophoresis.



a) 1 day, (b) 3 days, (c) 15 days, (d) 71 days after mixing aniline and $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$ solutions. A is a blue-green band, B and B_1 are violet-blue bands.

Some of the properties of the complex ion can be explained readily in terms of a canonical form in which the iron is bivalent and the nitrogen carries an odd electron. Thus, for example, the frequency and intensity of the cyano-bands in the infrared spectrum resemble those of zinc ferrocyanide. However the lead salt, unlike lead ferrocyanide, is soluble in dilute acetic acid.

Clearly the reactions of *p*-aminophenol and of aniline with $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$ differ in that the hydroxyl group in *p*-aminophenol stabilises the ion $[\text{Fe}(\text{CN})_5 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}]^{3-}$ (see Part I), whereas the absence of such a hydroxyl group in aniline causes the anilino-group first produced within the complex to be unstable so that further reactions take place until the relatively stable ion $[\text{Fe}(\text{CN})_5 \cdot \text{HN} \cdot \text{C}_6\text{H}_4 \cdot \text{NHPH}]^{3-}$ is formed. This can, however, slowly undergo a change as revealed by paper electrophoresis (see Figs. 2a—d).

Many of the salts of the pentacyano-(*p*-anilinoanilino)ferrate ion are highly coloured; the sodium salt exhibits maximum absorption at $660 \text{ m}\mu$ ($\log_{10} \epsilon 4.1$). The lead and the uranyl salt are soluble in 0.2N-acetic acid, but several of the heavy metals give insoluble precipitates. The metal salts were investigated by placing a drop of the heavy-metal nitrate or chloride solution on paper which was then sprayed with a solution of sodium pentacyano-(*p*-anilinoanilino)ferrate purified by electrophoresis. The paper was washed

with 0.2*N*-acetic acid to remove excess of reagent, and the paper was then examined for colour. The result depends both on the insolubility of the salt in 0.2*N*-acetic acid and on the colour of the salt. The pentacyano-(*p*-anilinoanilino)ferrates of alkali and alkaline-earth metals are soluble in dilute acid. However, the following salts are insoluble: cupric, blue; silver, blue-green; zinc, blue-green; cadmium, blue; mercuric, violet-blue (soon decolorised in air); mercurous, blue; zirconium, green. The aluminium salt is not precipitated. Stannic chloride gives no colour but the stannous salt gives a pale green precipitate which rapidly loses its colour in air. The lead and the thorium salt give no colours. Antimony trichloride does not give a stain but bismuth (Bi^{3+}) gives a green precipitate. Solutions of the rare earths (1 mg. of the oxides of Ce, Pr, Gd, Nd, and Eu, severally, in 1 ml. of solution) did not give stains on the paper. Chromium nitrate produced a faint blue stain but ammonium molybdate, sodium tungstate, and uranyl nitrate did not. Manganese (Mn^{2+}) gave a brown spot; iron (Fe^{3+}), cobalt (Co^{2+}), and nickel (Ni^{2+}) gave coloured precipitates which were blue, green, and green respectively.

EXPERIMENTAL

A method for the preparation of disodium pentacyanoamminoferrate has been described.¹ Freshly distilled aniline was used.

p-Aminodiphenylamine.—*N*-Nitrosodiphenylamine⁴ was isomerised to *p*-nitrosodiphenylamine (Fischer and Hepp⁵). This was reduced to *p*-aminodiphenylamine by tin and hydrochloric acid, as recommended by Ikuta,⁶ except that instead of the tin salt being treated with hydrogen sulphide, the base was extracted with ether after the complex had been decomposed with excess of sodium hydroxide. Removal of the ether left the amine, m. p. 64° (from benzene); acetyl compound, m. p. 154°.

Diazotisation and Coupling of p-Aminodiphenylamine.—*p*-Aminodiphenylamine (0.25 g.) in acetic acid (5 ml.) and water (60 ml.) at 0° was treated with sodium nitrite (0.5 g.) in cold water (25 ml.). After 5 min. the diazo-compound was extracted with ethyl methyl ketone (100, 25, and 25 ml.); the extract was washed with water and was then added to β -naphthol (0.7 g.) in water (100 ml.) containing sodium hydroxide (5 g.). The resulting azo-dye was extracted with two further quantities of ethyl methyl ketone so that the overall weight of the wet ketonic solution finally obtained was 84 g. A portion of solution was used to measure the amount of *p*-aminodiphenylamine formed from aniline (see below) and another portion was evaporated and the infrared spectra of the resulting purplish-black solid were recorded.

Paper Electrophoresis.—This was carried out as previously described.¹ A solution containing the complex was prepared by shaking aniline (0.18 g.) with $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot\text{H}_2\text{O}$ (0.7 g.) in 0.025*N*-sodium hydroxide (20 ml.) for 12 hr. The resulting solution was stored at room temperature and samples were withdrawn at appropriate intervals. Electrophoreses of portions of the blue-green solution of the complex (0.025 ml.) were carried out on paper saturated with 0.1*N*-sodium hydroxide. The current was passed for 3.5 hr. (3.5 v/cm.), then the paper was treated with *m*-zinc nitrate solution, washed with 2*N*-acetic acid, and air-dried. The paper was clarified by means of liquid paraffin and the light adsorption was measured by the aid of an E.E.L. scanner fitted with a Chance Green-Glass Filter.

Fig. 2*a* shows the curve obtained from a sample of the complex stored for 1 day. The paper strip exhibited a blue-green band *A*, and two small violet-blue bands *B* and *B*₁. The bands in Fig. 2*a* had moved from the left under the action of the applied potential. Fig. 2*b*, *c*, and *d*, obtained from samples stored for 3, 15, and 71 days respectively, showed an additional yellow band to the right of *B*₁ that was probably due to the ion $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$ since the yellow band gave coloured precipitates with acid solutions of the radicals Zn^{2+} , Fe^{3+} , Fe^{2+} , Pb^{2+} , Cu^{2+} , and UO_2^{2+} similar to those produced by the ion $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$ with the same radicals.

Figs. 2 show that in 71 days the material responsible for band *A* had disappeared and had been replaced by the materials in bands *B* and *B*₁.

⁴ Hickinbottom, "Reactions of Organic Compounds," Longmans, Green & Co., London, 1941, p. 286.

⁵ Fischer and Hepp, *Ber.*, 1886, **19**, 2991.

⁶ Ikuta, *Annalen*, 1888, **243**, 272.

Preparation and Analysis of Zinc Pentacyano-p-(anilinoanilino)ferrate.—On to aniline (0.16 g.) was poured a solution containing $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot\text{H}_2\text{O}$ (0.7 g.) in 0.1N-sodium hydroxide (5 ml.). The solution was shaken for 30 min., then 2 ml. portions of the solution were put on the upper ends of two Whatman's seed test papers. The papers were inserted into a preparative paper-electrophoresis apparatus of the type described by Cannon and Gilson⁷ but fitted with carbon-rod instead of platinum-wire electrodes. The papers were saturated with 0.1N-sodium hydroxide and an electric current was passed. After 3.5 hr. the papers were removed, the blue-green bands cut out, and the materials in them extracted at room temperature with 0.1N-sodium hydroxide. To the resulting coloured solution zinc nitrate (1 g.) in water (5 ml.) was added, and then glacial acetic acid (12 ml.). The blue-green precipitate was removed by means of a centrifuge, and the highly coloured gel was washed with water until the decanted liquid was neutral. The zinc salt was dried [NaOH , then $\text{Mg}(\text{ClO}_4)_2$ in a vacuum] {Found: C, 38.6; H, 3.6; N, 18.2; Zn, 17.9; Fe, 10.7. $\text{Zn}_3[\text{Fe}(\text{CN})_5\text{HN}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_5]_2\cdot 8\text{H}_2\text{O}$ requires C, 37.9; H, 3.6; N, 18.2; Zn, 18.2; Fe, 10.4%}.

"Continuous Variation."—This experiment was carried out as described previously.¹ The absorption of each solution was measured with a Spekker absorptiometer employing 1 cm. cells, a tungsten lamp, and filter No. 606. The readings obtained for the solutions 24 hr. after mixing are plotted in Fig. 1, which shows that the maximum colour occurs for a solution containing 0.6 mol. of inorganic salt. This curve has a very flat maximum, showing that the complex obtained from aniline is less stable than that from *p*-aminophenol (compare Fig. 1 of this paper with the Figure in ref. 1). Other curves which were obtained indicated that the colour had not fully developed 2.25 hr. after mixing and that the complex had started to decompose 120 hr. later.

pH Measurements.—The measurements were made with an "Alki" glass electrode and a pH-meter (Cambridge Instrument Co.).¹ Aniline (0.02 ml.) was dissolved in distilled water (10 ml.), and the pH was adjusted to 11.16 by addition of 0.02N-sodium hydroxide (0.93 ml.). The salt $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot\text{H}_2\text{O}$ (0.101 g.) was dissolved in water (20 ml.) and the pH similarly adjusted to 11.14. The aniline solution was poured into the salt solution and pH readings were taken. The pH rose to 11.20 after 1 min., fell to 10.85 after 4 min., and then very rapidly to 8.45 after 5 min.; 16 min. later the value was 8.4 and after 60 min. was 8.18. Recalibration of the electrode at the end of the experiment showed that a reading of 9.60 corresponded to a pH of 9.15, *i.e.*, the meter was reading 0.45 unit too high. The overall pH change was thus from 11.14 before the solutions were mixed to 7.73 after 1 hr.

Reduction of the Complex Ion formed by the Reaction of Aniline with $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$.—Reducing agents, such as hydrazine hydrate, sodium dithionite, sodium hydrogen sulphite, hydrogen sulphide, and a hydrochloric acid solution of stannous chloride destroyed the colour and decomposed the complex. Zinc in hydrochloric acid and hydroxylamine hydrate did not.

The following experiment showed that *p*-aminodiphenylamine was liberated when the complex was reduced. The salt $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot\text{H}_2\text{O}$ (2.5 g.), dissolved in 0.02N-sodium hydroxide (10 ml.), was poured on aniline (0.25 ml.). After the mixture had been stirred for 2 hr. a 5% w/w solution of sodium hydroxide (10 ml.) was added and the complex was reduced by the addition of solid sodium dithionite. The solution which changed to a pale-greenish colour and contained a suspended solid was extracted with ether. A brown oil which slowly solidified was obtained after removal of the ether. A portion of this material was chromatographed in benzene on alumina with 0.5% v/v of ethanol in benzene as eluant. A single band moved down but a small amount of dirty brown residue was left at the top of the column, showing that the product recovered from the ether was essentially one component. The infrared spectrum of the material was identical with that of authentic *p*-aminodiphenylamine, and the material yielded an acetyl derivative, m. p. 158°, mixed m. p. 154° with *p*-acetamidodiphenylamine.

Reaction of Nitrous Acid with the Product formed by the Action of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]$ on Aniline.—The salt $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot\text{H}_2\text{O}$ (2.5 g.), dissolved in 0.02N-sodium hydroxide (70 ml.), was poured on aniline (0.25 g.). The solution was stirred for 1 hr. and then cooled in ice after acetic acid (5 ml.) had been added. Sodium nitrite (1 g.) in ice-cold water (50 ml.) was added, and after 5 min. the solution was extracted with ethyl methyl ketone (100, 25, and 25 ml.). The extract was washed with water and shaken with an aqueous solution (120 ml.) of β -naphthol (0.7 g.) and sodium hydroxide (5 g.). The resulting red azo-compound was extracted into ethyl methyl ketone (wt. of final extract 101 g.). A portion of this solution was evaporated to dryness

⁷ Cannon and Gilson, *Chem. and Ind.*, 1954, **32**, 120.

and the purplish-black solid was shown by means of its infrared spectrum to be the same compound as obtained from the coupling of diazotised *p*-aminodiphenylamine and β -naphthol (see above). By diluting a further portion of the ketonic solution (0.2 ml.) with ethyl methyl ketone (9.8 ml.) and measuring the light absorption in a 1 cm. cell with filter No. 603 in a Spekker absorptiometer it was shown that approximately 100% of the aniline had been converted into *p*-aminodiphenylamine; the azo-compound prepared from authentic *p*-aminodiphenylamine was used as a standard for the measurements.

Reactions of p-Aminodiphenylamine with Na₂[Fe(CN)₅NH₃].—*p*-Aminodiphenylamine (0.36 g.) was shaken for 17 hr. with Na₂[Fe(CN)₅NH₃], H₂O (0.7 g.) in 0.025N-sodium hydroxide (20 ml.). The blue-green solution was filtered and examined by paper electrophoresis. The appearance of the paper was similar to that produced by a freshly prepared sample of the aniline complex (see Fig. 2a) except that band B was slightly weaker. Paper electrophoresis with a 1 : 1 mixture by volume of the aniline product and of the *p*-aminodiphenylamine product showed that the corresponding coloured bands had the same mobility. Moreover, paper electrophoresis of a sample of the *p*-aminodiphenylamine product which had been kept for 14 days showed that this material decomposed in the same way as the complex prepared from aniline. The complex freshly prepared from *p*-aminodiphenylamine and the salt Na₂[Fe(CN)₅NH₃] was reduced with sodium dithionite and the liberated base extracted with benzene. The material recovered was shown to be *p*-aminodiphenylamine by its m. p. and mixed m. p. 64°.

Zinc Salt of the Complex prepared by Reaction of p-Aminodiphenylamine with Na₂[Fe(CN)₅NH₃].—The salt Na₂[Fe(CN)₅NH₃], H₂O (0.35 g.) in 0.025N-sodium hydroxide (10 ml.) was poured on *p*-aminodiphenylamine (0.18 g.) and was shaken for 20 hr. The solution was filtered and diluted to 200 ml., and acetic acid (20 ml.) was added, followed by 0.1M-zinc nitrate (35 ml.). The precipitate was filtered off, washed until neutral, and dried [NaOH and then Mg(ClO₄)₂ in a vacuum]. The infrared spectrum obtained from this material dispersed in a potassium chloride disc was identical with that from a purified sample of the zinc salt made from aniline and Na₂[Fe(CN)₅NH₃] (see below).

Infrared Spectrum of Zinc Pentacyano-(p-anilinoaniline)ferrate.—The spectrum of the zinc salt, prepared from aniline and Na₂[Fe(CN)₅NH₃] purified by paper electrophoresis (see above) was obtained by incorporating the solid in a pressed potassium chloride disc. The Table shows the spectrum of this material and of some related compounds.

The bands at 2093 cm.⁻¹ due to the CN group in zinc pentacyano-(*p*-anilinoanilino)ferrate resembled the band produced by CN groups in zinc ferrocyanide both in frequency and in width.

Infrared absorption bands (cm.⁻¹).

Zn ferricyanide.....	3450 sb; 2177 s.
Zn ferrocyanide	3350 sb; 2110 s.
Zn pentacyano-(<i>p</i> -anilino- anilino)ferrate	{ 3440 m; 3305 m; 2093 s; 1611 m; 1587 m.sh.; 1567 m.sh.; 1490 m; 1427 m; 1393 m; 1178 m; 1026 w; 1000 w; 867 w; 853 w; 798 w; 754 w; 695 w.
Aniline (liquid)	4950 w; 4460 w; 3990 w; 3330 s; 3210 sh; 3020 m; 2745 w; 2620 w; 2330 w; 2145 w; 2085 w; 1928 w; 1838 w; 1776 w; 1692 sh; 1620 s; 1602 s; 1502 s; 1470 sh; 1385 w; 1333 w; 1316 w; 1280 s; 1200 w; 1176 m; 1155 m; 1120 w; 1053 w; 1030 w; 998 w; 883 m; 828 m; 755 s; 693 s.
<i>p</i> -Aminodiphenylamine (solid as thin film)	3400 s; 3070 m; 2905 w; 1626 sh; 1600 s; 1518 s; 1502 sh; 1453 w; 1413 w; 1387 w; 1330 sh; 1305 s; 1266 s; 1244 sh; 1221 sh; 1175 m; 1152 w; 1114 w; 1078 w; 1026 w; 1011 w; 993 w; 875 m; 825 sh; 792 w; 747 s; 693 s.

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

Moreover, the optical density of the disc (0.375" diam.) containing 1 mg. of the complex salt was 1.58, similar to that for a disc containing zinc ferrocyanide rather than (0.73) for one containing zinc ferricyanide.^{2,8} The spectrum of zinc pentacyano-(*p*-anilinoanilino)ferrate does not resemble closely that of either aniline or *p*-aminodiphenylamine but has many bands attributable

⁸ Herington and Kynaston, *J.*, 1955, 3555.

to the organic part of the ion. The band at 754 cm^{-1} probably arises from the out-of-plane CH bending absorption in the aromatic ring.⁹

A preliminary note on this work has been published.² I thank Mr. W. Kynaston for the infrared measurements. The work described formed part of the research programme of the Chemical Research Laboratory and this paper is published by permission of the Director, National Chemical Laboratory, Teddington, Middlesex.

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TEDDINGTON, MIDDLESEX.

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⁹ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 65.
