erably, and for this reason the quantity $\alpha$ goes through periodic variations. That is, $\alpha$ for two runs in which the deuterium run followed the hydrogen run is larger than for the inverted case, as one would expect if the catalyst is losing activity. The average value for $\alpha$ at 0° is 1.94. The data at 20° are insufficient to be conclusive, but the 2.1 value of $\alpha$ at 20° must be compared with 2.07 at 0°. Within the experimental error, then, the temperature coefficients (in the range 0–20°) for the hydrogen and deuterium reactions are the same. However, it is to be noted that a difference sufficient to take account of all the difference between the rates of the two reactions in terms of unequal activation energies would have escaped detection.

The observed ratio of two between the rates of the hydrogen and deuterium reactions might be due to any of a number of causes. Collision rates of hydrogen and deuterium with the surface would introduce a factor of 1.4; rates of adsorption may differ by as much as 3.3;[11] different rates of surface reaction may result in rates differing by a factor of 4.4, if the difference in zero-point energies of the Cu–H and Cu–D complexes be taken as 800 cal.[6] It is fairly obvious that we are dealing with something more than a collision frequency. However, extended discussion seems hardly profitable at this time.

Analysis showed no exchange between deuterium and ethylene on the copper catalyst at 0°.

## Summary

It has been found that the rate of reaction of hydrogen with ethylene is greater than that of deuterium by a factor of 2.5 in the homogeneous reaction at ~ 500°; and by a factor of 2 in the catalytic reaction over copper at 0°. Exchange reactions are unimportant.

[11] Soller, Goldwasser and Beebe, THIS JOURNAL, **58**, 1703 (1936).

PRINCETON, N. J. RECEIVED MAY 6, 1936

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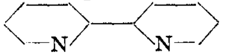
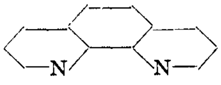
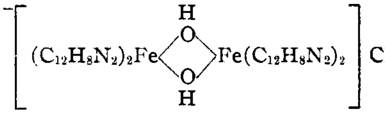
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

# The Structure and Properties of Mononuclear and Polynuclear Phenanthroline-Ferric Complexes[1]

BY ALLISON GAINES, JR., LOUIS P. HAMMETT AND GEORGE H. WALDEN, JR.

The beautifully complete papers in which Blau[2] reported the discovery of the unusually stable complexes which the bases dipyridyl  and *o*-phenanthroline  form with metallic ions propounded, nevertheless, a puzzling problem for valence theory in the existence of two different ferric complexes. One of these, blue in color, is obtained only by oxidation of the ferrous complex. Analysis of the chloroplatinate showed that its formula is $[Fe(C_{12}H_8N_2)_3]^{+++}$ and it would indeed be difficult to reconcile any other composition with the fact that it forms a mobile oxidant–reductant system with the ferrous complex, whose formulation as $[Fe(C_{12}H_8N_2)_3]^{++}$ is well established. By contrast direct reaction of phenanthroline and ferric salts leads to the formation of brown solutions from which Blau isolated no solid compounds. He noted, however, color reactions which suggested the existence of a brown complex with the same ratio, 3:1, of phenanthroline to ferric ion as that which obtains in the blue complex.

We have, however, obtained from these brown solutions a crystalline salt of definite composition whose properties correspond to the formula



$$\left[(C_{12}H_8N_2)_2Fe\overset{\overset{H}{O}}{\underset{\underset{H}{O}}{\diamond}}Fe(C_{12}H_8N_2)_2\right]Cl_4 \qquad (A)$$

of a tetraphenanthroline-diol-diferric chloride. The polynuclear complex ion contained in this salt appears to be the major constituent of the brown solutions. In spite of the fact that the phenanthroline–iron ratio in this complex is 2:1, there is no contradiction between our result and Blau's, which we have indeed confirmed, because in the formation of the bridge hydroxyl or "ol" groups, one hydrogen ion is set free from a water molecule for each ferric ion reacting. The combination of this hydrogen ion with phenanthroline raises to a value considerably above two

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[1] Dissertation submitted by Allison Gaines, Jr., in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the faculty of Pure Science, Columbia University.

[2] Blau, *Monatsh.*, **19**, 647 (1898).

the proportion of phenanthroline which may become combined as a consequence of the reaction of one ferric ion.

The study of this compound has led to conclusions about the acidity of ol-compounds, about the magnetic properties of polynuclear complexes and about the solubility method of studying complexes which have considerable general interest for problems of complex chemistry.

### The Crystalline Brown Chloride, Substance A

**Preparation.**—This new substance is conveniently prepared by the following method: 50 ml. of a 0.300 molar solution of ferric chloride (0.0150 mole of $Fe^{+++}$) is added to a well-stirred suspension of 5.400 g. of *o*-phenanthroline hydrate (0.0300 mole of phenanthroline) in 50 ml. of water. The phenanthroline dissolves, and after about an hour a brown crystalline precipitate begins to form. After standing overnight, this is filtered off, washed several times with small quantities of water and dried over sulfuric acid at 2–4 mm. absolute pressure. The yield is from 50 to 60% of the theoretical amount.

We have prepared six different samples from solutions of various compositions as follows.

TABLE I

| Sample | Mole ratio phenanthroline/iron | Concn. HCl |
|---|---|---|
| a | 3 | 0.00 |
| b, d | 3 | .04 |
| c, f | 2 | .00 |
| e | 2 | .04 |

**Analysis.**—Iron was determined by heating the sample in 1 *M* hydrochloric acid to decompose the complex, followed by reduction in the silver reductor[3] and titration with ceric sulfate. The accuracy of this procedure was checked by analyzing aliquots of a ferric chloride solution in the presence and in the absence of two moles of phenanthroline per mole of iron. Three portions in the absence of phenanthroline required an average of 17.42 ml. of ceric sulfate solution with an average deviation of 0.75 part per thousand. Three portions in the presence of phenanthroline required an average of 17.46 ml. with an average deviation of 1.1 parts per thousand.

Phenanthroline was determined by dissolving the sample in about 15 ml. of 6 *M* hydrochloric acid, heating to decompose the complex, and adding saturated mercuric chloride solution slowly from a buret, while the solution was stirred, until the total volume was 192 ml. After standing overnight the precipitate was transferred to a tared crucible with a porous porcelain bottom, washed free from chloride, dried at 110° and weighed. This procedure was verified on amounts of phenanthroline ranging from 0.0500 to 0.3000 g. both in the absence and presence of an equimolar amount of ferric chloride. The average value for the ratio weight phenanthroline/weight precipitate was 0.4001 with an average deviation of 4 parts per thousand in eight determinations. The precipitate is probably $(C_{12}H_8N_2)$-$HgCl_2$[4] for which the above factor is 0.3983. Morgan and Burstall[5] have used the entirely analogous iodide for the quantitative determination of $\alpha,\alpha'$-dipyridyl.

Chloride was determined by two methods. Method A was a modification of the standard precipitation of silver chloride in which the $[H^+]$ was increased to decompose the complex and the filtration was carried out at 80–90°, to avoid contamination with the silver phenanthroline complex which precipitates from the cold solution. An empirically determined correction was applied for the solubility of silver chloride under the standardized conditions. Method B was the thoroughly tested chromyl chloride distillation method of Robertson.[6] The special all-glass apparatus of Hammett and Lowenheim[7] was used for the analyses.

**Results of Analyses.**—Samples (a), (b) and (c) were analyzed without intensive drying. They showed the following values of the ratio moles phenanthroline/moles iron, (a) 2.10, (b) 2.078, (c) 2.081, and for moles chloride/moles iron (a) 2.06, (b) 2.013, (c) 1.987. Samples (d), (e) and (f) were analyzed after long-continued drying over 98% sulfuric acid and fresh calcium chloride at 2–4 mm. absolute pressure with the following results.

TABLE II

| Sample, found | Iron, % | Phenanthroline, % | Chloride, % |
|---|---|---|---|
| d | 11.00 | 72.24 | 14.17 |
| e | 11.00 | 72.40 | 14.31 |
| f | 11.07 | 72.30 | 14.23 |
| | 11.05 | 72.40 | 14.16 |
| Calcd. formula (A) | 11.06 | 71.50 | 14.05 |

**Hydration.**—The dried compound is very hygroscopic. Two samples were exposed to the atmosphere until constant weight was reached. One gained 7.47% and the other 7.06%. Assuming formula (A) a tetrahydrate would require 7.16%.

**Conductivity.**—The specific conductivity of a solution whose concentration, based upon formula (A), was 0.0005023 mole per liter, was found to be $2.5152 \times 10^{-4}$ mho. The specific conductivity of the water used in preparing the solution was $6.160 \times 10^{-6}$ mho. The molar conductivity is therefore 488.5 mho, which is an entirely reasonable figure for a salt of this type, provided all of the chloride is ionogen. A consideration of the acidic properties of the compound does not change this conclusion.

**Acid–Base Properties.**—Twenty-five ml. of a 0.00491 *M* solution of substance (A) (preparation (f)) was titrated with 0.02013 *M* sodium hydroxide using a glass electrode.[8] The titration curve is shown in Fig. 1 in which the points are experimental and the solid curve is calculated for a dibasic acid whose *pK* values are 4.30 and 6.40. The agreement is satisfactory except toward the end of the titration where some other reaction, leading to precipita-

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[3] Walden, Hammett and Edmonds, THIS JOURNAL, **56**, 57 (1934).

[4] Hieber and Mühlbauer, *Ber.*, **61**, 2149 (1928).

[5] Morgan and Burstall, *J. Chem. Soc.*, 2594 (1930).

[6] Robertson, *ibid.*, **107**, 902 (1915).

[7] Hammett and Lowenheim, THIS JOURNAL, **56**, 2620 (1934).

[8] We are indebted to Mr. M. F. Moose for these measurements, which were made on the apparatus described by Kiehl and Ellis, THIS JOURNAL, **57**, 2139 (1935); *Rev. Sci. Inst.*, **4**, 131 (1933).

TABLE III

| Substance | Moles Fe per liter | Magnetic pull on soln., $F_1$, g. | Density of soln., (27°) | Specific susceptibility of anhydrous solute × $10^6$ | Atomic susceptibility $\chi_{Fe} \times 10^6$ | Precision measure, % |
|---|---|---|---|---|---|---|
| $K_3Fe(CN)_6$ | 0.0400 | −0.0258<br>− .0260 | 1.0053 | 6.76 | 2350 | −3.11 |
| Substance A preparation (f) | .03995 | − .0283<br>− .0283 | 1.0035 | 1.10 | 823 | −6.71 |
| $[Fe(C_{12}H_8N_2)_3]_2(SO_4)_3$ | .03876 | − .025 | 1.0442 | 3.34 | 2860 | ... |

tion at the point marked by the arrow, overlaps the simple neutralization process.

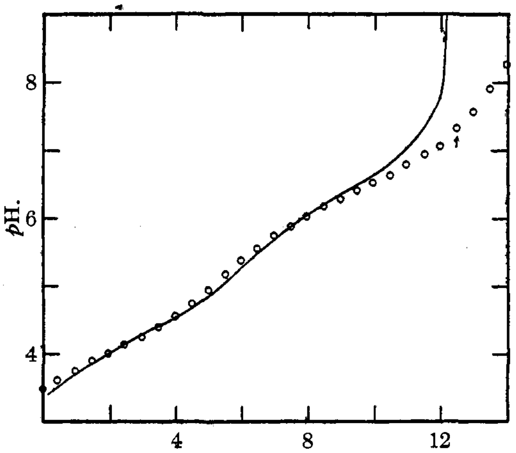

Fig. 1.—Titration of tetraphenanthroline-diol-diferric chloride solution with sodium hydroxide.

**Magnetic Properties.**—The magnetic susceptibilities of solutions of several ferric phenanthroline and other iron complexes were determined by the Gouy method.[9] Essentially, a definite volume of a solution of the substance to be investigated was placed in a glass tube which was suspended from one arm of an analytical balance so that the plane bottom of the tube was symmetrically placed in the magnetic field between the poles of a powerful electromagnet (*ca.* 20,000 gausses). The force exerted on the tube and contents was determined by weighing. Deducting the force exerted on the empty tube by the standardized field gives the force exerted on the solution. The equation relating the force on the solution with its susceptibility is $F = {}^1/_2A(\kappa_1 - \kappa_2)(H_1^2 - H_0^2)$ where

$A$ = cross-sectional area of the column
$\kappa_1$ = volume susceptibility of the solution
$\kappa_2$ = volume susceptibility of air
$H_1$ = field at plane bottom of the tube
$H_0$ = field at upper level of liquid

For the tube used and the constant field which was maintained the force exerted when the tube was filled with water to the constant level which was also used for the solutions was −0.0296 g. Using Brant's[10] values obtained at 20° for the volume susceptibility of water, $-0.71798 \times 10^{-6}$, and for that of air, $+0.0288 \times 10^{-6}$, this gave a value for the quantity ${}^1/_2A(H_1^2 - H_0^2)$, by means of which, together with the measured force when the tube was filled with the solution, the volume susceptibility of the latter can be calculated. Division of this figure by the density, which was determined at 27°, the average temperature of the experiments, gives the mass susceptibility of the solution, $\chi_1$.

By Wiedeman's law of the additivity of susceptibilities the value for the solute may be calculated from the relation

$$m_1\chi_1 = m_s\chi_s + m_w\chi_w$$

in which $m$ is mass in grams, $\chi$ is specific susceptibility, and the subscripts 1, s and w refer to solution, solute, and water, respectively.

Multiplication of $\chi_s$ by the formula weight associated with one gram atom of iron in the compound, and subtraction from the resulting figures of the sum of the Pascal additive values for the susceptibilities of the various atoms of carbon, nitrogen, etc., present gives a quantity which should be a good approximation (in spite of the constitutive effects and other inaccuracies of the Pascal relationship) to the atomic susceptibility of the iron atoms present in the compound. It is so listed in column 6 of Table III, which gives the results on solutions of the brown chloride (preparation (f)), of potassium ferricyanide, and of the blue triphenanthroline ferric sulfate. The latter solution was prepared by oxidizing a solution of phenanthroline ferrous sulfate in 0.7 molar sulfuric acid with lead dioxide, and filtering through porous porcelain. The susceptibility was determined immediately. The value of the magnetic pull in the table was obtained by graphical extrapolation to the time when filtration was started of the following values: 20 min., −0.0217; 40 min., −0.0187; 75 min., −0.0143; 125 min., −0.0117 g. The volume susceptibility of the 0.7 molar sulfuric acid was found to be identical with that of water, and its density was 1.0451.

Our value for the atomic susceptibility of the iron in potassium ferricyanide is in approximate agreement with the value of Gray and Birse[11] obtained from measurements on solution, and with that of Ishiwara[12] from measurements on the solid salt. The value for the susceptibility of the iron in the blue complex is nearly the same as that which it has in ferricyanide, which emphasizes the probability that this value is typical for ferric iron in complexes which involve electron sharing. The values of magnetic moment in Bohr magnetons ($P_B$) calculated from these susceptibilities by the equation

$$P_B = \sqrt{3RT\chi_{Fe}}/5593$$

are 2.4 for ferricyanide, 2.6 for the blue triphenanthroline ferric ion. These are considerably higher than the

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[9] Stoner, "Magnetism and Atomic Structure," E. P. Dutton Co., New York, 1926, p. 40.

[10] Brant, *Phys. Rev.*, **17**, 678 (1921).

[11] Gray and Birse, *J. Chem. Soc.*, **105**, 2707 (1914).

[12] Ishiwara, *Science Reports of the Tôhoku Imperial University*, **3**, 310 (1914).

theoretical value of 1.73 of the spin moment of a single unshared electron, but this excess is also observed with other ions containing a single unshared electron, and is generally attributed to incomplete quenching of the orbital moment.[13]

The magnetic moment of the iron atom in the brown ferric complex is, however, only 1.4 Bohr magnetons. It is therefore much smaller than the moment of ferric ion in other stable ferric complexes. It is even considerably smaller than the theoretical minimum value of 1.73, which corresponds to the spin moment only. This result is extremely important in connection with the question of the molecular weight of the complex ion.

**Diffusibility.**—Measurements of diffusibility offer one of the most promising means of studying the molecular dimensions of ions in solution, although their quantitative interpretation is still open to considerable question.[14]

Qualitative diffusion experiments were made with collodion bags, gelatin test-tubes and a fritted glass membrane. A solution initially 0.02 *M* in tri-*o*-phenanthroline ferrous chloride required some four hours to reach equilibrium by diffusion through a collodion membrane, while a comparable set-up for the brown phenanthroline ferric complex salt did not reach equilibrium on standing overnight.

The same solutions poured on gelatin gels in test-tubes showed about a 3:2 penetration ratio in an overnight test with the ferrous complex having the higher diffusion rate.

The technique of McBain and Liu,[15] using a 0.2-cm. membrane of G-4 fritted glass, was applied to the two solutions. The *KD* value obtained for the ferric complex salt was 0.0035 and for the ferrous complex salt 0.0042. Flushing the cell with distilled water effectively removed all coloration due to the ferric salt prior to the diffusion of the ferrous salt, but the ferrous complex stained the membrane so that a treatment with chromic acid mixture was required to clean it. A subsequent pair of diffusion runs gave a *KD* value of 0.0048 for the ferric salt and of 0.0055 for ferrous. The changed values, showing an increased membrane porosity, are nevertheless in the same direction, and support the conclusion that the ferric complex has a higher average molecular weight than has the ferrous complex, whereas the empirical formulas have the reverse relation.

We were unable to make diffusion measurements in the presence of a large concentration of another electrolyte, as is necessary if the diffusibility of the complex ion alone is to be obtained,[16] because the brown salt is so easily salted out by other electrolytes.

**Particle Size.**—An unfiltered solution of sample (f) showed a bright field in the ultramicroscope. However, a freshly prepared solution and the filtrate from the above solution were optically void. The substance must polymerize on standing in solution, a fact corroborated by visible precipitates formed in 0.01 *M* solutions after standing for a week, but the freshly prepared solution is probably a true solution, rather than a colloidal one. Because of this aging of the solutions all measurements reported in this article were made not more than three hours after the preparation of the solution.

**Composition and Structure.**—The substance is unquestionably a definite compound. It forms crystals of visible dimensions; its composition is independent of the composition of the solution from which it is prepared within a considerable range of variation of acidity and phenanthroline concentration (see Table I); and the analysis agrees closely with the simple proportion of 1 Fe to 2 Cl to 2 phenanthroline.

The composition is necessarily that represented by the formula $Fe(C_{12}H_8N_2)_2(OH)Cl_2$, because some negatively charged constituent other than the two chloride ions must be present to balance the three positive charges of the ferric ion, and hydroxyl ion is the only possibility. As Table II shows, the actual proportions of iron, chlorine and phenanthroline in the dried compound agree excellently with this composition.

While the interpretation of the conductivity results is complicated by the hydrolysis reaction, they demonstrate beyond question that the chlorine atoms are free chloride ions, and not nonionogen chlorine in the complex.

Here as always with polynuclear complex ions, the molecular weight is difficult to establish. That we have to do with a polynuclear complex seems beyond doubt. The low diffusibility by comparison with the similar but mononuclear phenanthroline ferrous ion is practically conclusive evidence; moreover, the magnetic properties and the nature of the acid–base titration curve strongly support the conclusion. There is no physical picture to account for the existence in a mononuclear ferric complex of a magnetic moment less than the 1.73 Bohr magnetons which correspond to the spin moment of a single unpaired electron, and no moment less than this has in fact been observed in a substance containing an odd number of electrons. It is therefore extremely probable on this basis alone that we have to do with a polynuclear complex in which two or more ferric ions are rigidly bound together in such a way that their individual magnetic moments partially neutralize each other. The existence of such a phenomenon as this has been several times suggested, but it has not previously been observed with certainty.

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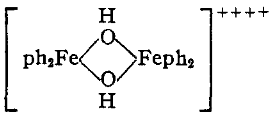
[13] This question has been discussed by Noyes, Pitzer and Dunn, THIS JOURNAL, **57**, 1234 (1935), in connection with the susceptibility of argentic ion.

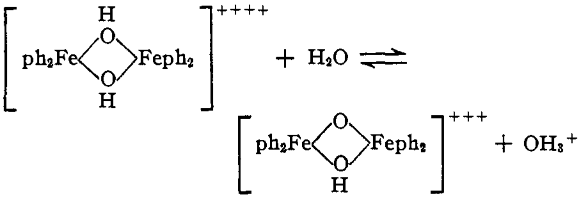
[14] (a) Jander and Jahr, *Kolloid Beihefte*, **41**, 1, 297 (1935); (b) Brintzinger, *et al.*, *Z. anorg. Chem.*, **220**, 201 (1934), and others.

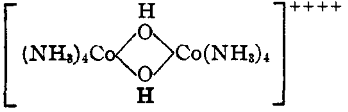
[15] McBain and Liu, THIS JOURNAL, **53**, 59 (1931).

[16] Jander and Winkel, *Z. physik. Chem.*, **149A**, 102 (1930).

The binuclear structure  which we have proposed is consistent with the general principles of complex chemistry developed by Werner. The coördination number of the iron atoms is six, as it is in other stable ferric complexes (each phenanthroline molecule with its two nitrogen atoms counts of course two in reckoning this value). The ease of formation and stability of the double ol bridge are well established with cobaltic and chromic ammines and are basic features of those important theories of colloidal oxides which Stiasny[17] and Thomas[18] have developed.

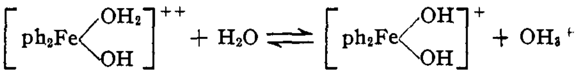
The acidic properties of the substance (the *p*H of 0.00491 *M* aqueous solution is 3.5) might seem inconsistent with this structure but they are not so in reality. The only way in which a substance with the structure suggested can react acid is by loss of hydrogen ions from an ol bridge, forming an oxo bridge



and it is true that this process does not occur to a significant extent with the cobalt derivatives, which are the most thoroughly studied examples of substances containing these bridges. Such substances as  are reported as giving neutral aqueous solutions. There is, however, every reason to expect that the hydrogen ions should be much less firmly bound in the iron compound than in the cobaltic compound.

Both the ol compounds and the simple aquo compounds are derivatives of oxonium ion, $OH_3^+$, in which one hydrogen ion in the case of an aquo compound (such as $[Co(NH_3)_5OH_2]^{+++}$), and two hydrogen ions in the case of ol compounds, have been replaced by a metallic ion. This substitution decreases the acidity cumulatively; in the cobalt case $[Co(NH_3)_5OH_2]^{+++}$ has an acidity constant of $2 \times 10^{-6}$, while the ol compounds are so weakly acid that their aqueous solutions are neutral. The work of Uémura and Suéda[19] shows, however, that aquo chromic ions are considerably more acid than are analogous aquo cobaltic ions, while the work of Brönsted and Volqvartz[20] shows that aquo ferric ions are more acid than are analogous chromic ions. That is to say, the introduction of one ferric ion into oxonium ion decreases the acidity much less than the introduction of one cobaltic ion; the second ferric ion likewise should have a smaller effect than the second cobaltic ion. It is therefore extremely probable that ol-ferric compounds will be more acidic and have less firmly bound hydrogen ions than do ol-cobaltic compounds.

On titration with alkali the behavior of the substance agrees with that to be expected of a dibasic acid, except when nearly two moles of hydroxyl ion have been added (for two iron atoms) when some other process which leads to a precipitation is superimposed. This is shown in Fig. 1 in which the points are experimental and the solid curve is calculated for a dibasic acid. The behavior is consistent with the proposed formula, which contains two dissociable hydrogen ions, one on each of the ol bridges. It does not serve to eliminate the possibility of a more highly polymerized ion, because the experimental curve also agrees with predicted ones for acids of higher basicity than two, but it does furnish another proof of the impossibility of a mononuclear formula. The only possible structure of the latter type is that of an aquohydroxo ion which must titrate as a monobasic acid



It is completely impossible to fit our experimental results to such a process.

## On Solutions Containing Ferric Salts and Phenanthroline

The high yields obtained in the preparation of the crystalline brown chloride (A) suggest strongly that it is a major constituent of the solutions obtained by mixing ferric chloride and phenanthroline. It is not the sole constituent, as several kinds of evidence demonstrate.

**The Magnetic Titration of Ferric Chloride with Phenanthroline.**—We have determined the magnetic susceptibilities of a series of solutions con-

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[17] Stiasny *et al.*, *Colegium*, **752**, 902 (1932), and others.

[18] Thomas *et al.*, THIS JOURNAL, **56**, 794 (1934), and others.

[19] Uémura and Suéda, *Bull. Chem. Soc. Japan*, **10**, 50, 267 (1935); *Bull. faculté arts métiers Tokyo*, **4**, 29 (1935).

[20] Brönsted and Volqvartz, *Z. physik. Chem.*, **134**, 97 (1928).

taining a constant concentration of ferric chloride and varying proportions of phenanthroline with the results shown in Table IV and Fig. 2. Except for the last point, each one represents the mean of two or more measurements with a maximum deviation of 0.0002 g. There are several points of interest about this "magnetic titration curve."

TABLE IV

| Ferric chloride (mole/liter) | *o*-Phenanthroline (mole/liter) | Magnetic pull on soln., $F_1$, g. | Density of soln. (27°) | Atomic susceptibility of ferric ion $\times 10^6$ | Precision measure, % |
|---|---|---|---|---|---|
| 0.03870 | 0.00 | −0.0084 | 0.9965 | 13,760 | .. |
| .03867 | .01935 | − .01700 | .9974 | 8,140 | 0.49 |
| .03865 | .03870 | − .02337 | .9997 | 4,020 | .99 |
| .03865 | .05800 | − .02630 | 1.0011 | 2,120 | 2.21 |
| .03865 | .07740 | − .02765 | 1.0028 | 1,270 | 3.81 |
| .03865 | .1160 | − .02715 | 1.0052 | 1,620 | 2.94 |
| .03872 | .1560 | − .02425 | 1.0087 | 3,550 | 1.31 |
| .03864 | .2320 | − .02340 | 1.0119 | 4,140 | 3.81 |

The gradual curvature shows that several overlapping equilibria are present. Because of the well-verified additivity of magnetic susceptibilities, the curve would consist of two intersecting straight lines if the solutions contained only mixtures of hydrated ferric ion and one phenanthroline complex.

The curve has a pronounced minimum in the neighborhood of the proportion of 2 phenanthroline to 1 iron, the ratio present in the crystalline salt. This is consistent with the hypothesis that the tetraphenanthroline diol diferric ion is a preponderant constituent of solutions containing this proportion of phenanthroline and iron. The rise on both sides, together with the curvature, demonstrates, however, that other compounds of phenanthroline and ferric iron of higher susceptibility are formed in which the ratio may be either greater or smaller than two.

The difference in susceptibility between solutions of the pure crystalline salt and solutions made by adding two moles of phenanthroline to one of ferric chloride is outside of the probable experimental error and indicates the presence in the latter solution of a certain amount of these complexes of higher susceptibility.

**Colorimetric Work.**—Tests were made in a colorimeter of the intensity of color developed by the addition of ferrous sulfate to solutions containing various proportions of phenanthroline and ferric chloride, the brown color of the ferric complex being compensated in the usual way. In all cases, the intensity of the color increased with time, the more rapidly the greater the proportion of phenanthroline. Extrapolation to zero time showed that solutions containing phenanthroline and ferric iron in the proportion of 1:1 or 2:1 contain no phenanthroline in a form which reacts immediately with ferrous iron, whereas solutions containing proportions of 3:1, of 4:1, and of 9.16:1 contain about two-thirds of the phenanthroline present above the ratio of 2:1 in a form which does not react immediately with ferrous ion. A part but certainly not all of this unreactive phenanthroline is in the form of phenanthrolinium ion. Further interpretation of these experiments must await a knowledge of the equilibrium and kinetics of the ferrous phenanthroline reaction which is now being sought in another research in this Laboratory.

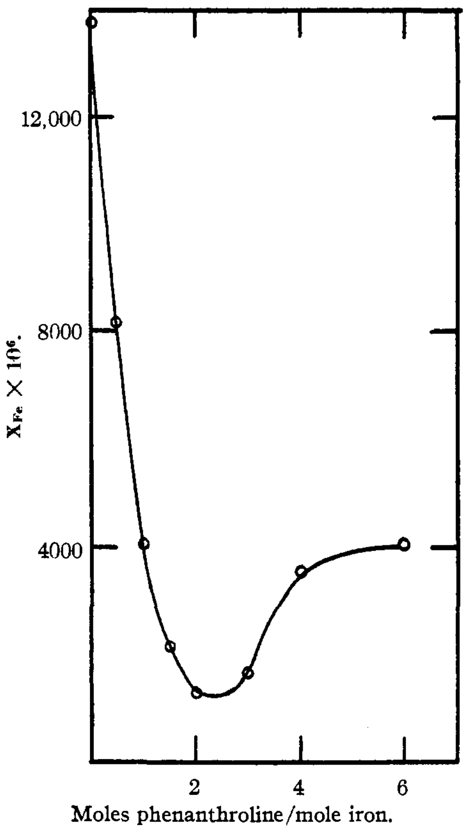

Fig. 2.—Magnetic titration curve.

**Solubility Effects.**—Attempts to investigate the nature of the phenanthroline complexes by the solubility method which has been so often applied to the investigation of complex compounds gave a most surprising result which led us to determine the solubility of phenanthroline in the various media shown in Table V. All measurements were made at 25° by rotating an excess of phenanthroline with the solution named in a thermostat until analyses made on two successive days showed no further change. Phenanthroline was determined by the mercuric chloride precipitation method previously described. Each figure shown in the table is the average of at least two determinations with a probable error of about 1%.

TABLE V

| Soln. | Concn. of soln., moles per liter | Concn. of *o*-phenanthroline, moles per liter | Concn. of *o*-phenanthroline less water soly. of *o*-phenanthroline, moles per liter | Moles of *o*-phenanthroline per mole of other component |
|---|---|---|---|---|
| Pure water | | 0.01627 | | |
| $FeCl_3$ | 0.003640 | .03834 | 0.02207 | 6.07 |
| $FeCl_3$ | .007240 | .06567 | .04450 | 6.04 |
| HCl | .009953 | .03824 | .02197 | 2.21 |
| NaCl | .002014 | .01604 | −.00023 | .. |
| $FeCl_2$ | .009390 | .06510 | .04883 | 5.20 |
| $NiCl_2$ | .005614 | .03937 | .02310 | 4.11 |
| $H_2SO_4$ | .004898 | .03762 | .02135 | 4.36 |

There will be noted in every case except that of sodium chloride a large increase in solubility over that in water. Even in the case of the acids, where one would expect one equivalent of acid to dissolve at the most one mole of base, we find an increase in solubility which is of the order of 2.2 moles of base per equivalent of acid. Ferrous ion and nickel ion form extremely stable complexes in which the proportion of phenanthroline to metallic ion is three. There is no evidence whatsoever from the composition of solid salts of the existence of complexes in which the proportion is greater than three. Yet one mole of ferrous chloride dissolves 5.2 moles more of the base than does water; one mole of nickel ion increases the solubility by 4.1 moles. Evidently, then, the presence in a solution of phenanthroline combined either with hydrogen ion or with a metallic ion leads to a considerably increased solubility of phenanthroline in the solution, presumably as a result of the formation of some secondary complex of low stability. The quantity of this excess dissolved phenanthroline bears no simple ratio either to the quantity of combined phenanthroline or to the ionic charge of the complex in which it is present. This peculiar phenomenon may be confined to phenanthroline and bases of similar structure or it may not; it obviously must be reckoned with in any future studies on complex ions by the solubility method.

Of the somewhat over six moles of phenanthroline dissolved by ferric chloride, two can be assigned to the formation of the complex of structure A, about two more to the hydrogen ion liberated in the formation of that compound. The remainder may be due to the loose kind of combination which produces the excess solubility in the case of the other metallic ions, but it is difficult to see how this kind of combination could account for the increase in magnetic susceptibility which we have observed when the proportion of phenanthroline to iron is greater than two.

We wish to acknowledge the kindness of Professors Samuel J. Kiehl, Victor K. La Mer and Arthur W. Thomas in lending special apparatus and of Henry A. Boorse, in making preliminary magnetic susceptibility measurements.

## Summary

A brown crystalline substance has been prepared by the direct reaction of phenanthroline and ferric chloride solution. The properties of this substance are consistent with the assumption that it is a tetraphenanthroline-diol-diferric chloride.

Evidence is presented showing the probable existence of other compounds in the mother liquor.

The acid–base properties of the polynuclear complex extend the knowledge of this characteristic of the ol bridge as established with cobaltic and chromic compounds.

The unusually low magnetic susceptibility of the new complex suggests the partial neutralization of the magnetic moments of the two iron atoms, and is additional evidence of a polynuclear structure.

The magnetic susceptibility of the blue triphenanthroline–ferric complex ion approximates that of the ferricyanide ion.

Evidence is presented showing that stable phenanthroline complexes whose composition has been established in the solid state may, in solution, add more phenanthroline, forming secondary complexes of lower stability.

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