[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

A Study of the Exchange of Nickel in Certain Complex Compounds Using Radioactive Nickel[1]

BY J. ENOCH JOHNSON[2] AND NORRIS F. HALL

In general, it has been found that exchange of the central atom in a complex ion or compound proceeds rapidly only when the bonds present approach ionic rather than covalent character. This has been assumed by many investigators (*e. g.*, Steigman[3]) to be the basis of the success of the Szilard–Chalmers method of concentrating radioactive isotopes. Certain exceptional cases have been discussed by Seaborg[4] and others[5] but in the majority of cases a satisfactory correlation has been demonstrated between exchange data and other types of evidence for covalent bonds. Magnetic susceptibility, interpreted in the light of quantum theory by Pauling,[6] gives evidence of bond type for complexes whose central atom can undergo a redistribution of electrons in changing from ionic or weak covalent bonds to strong covalent bonds. In certain 4-coördinated complexes,[7] X-ray data have definitely indicated covalent bonding by demonstrating a square planar arrangement of the coördinated groups.

Nickel forms a number of complex compounds and ions of the coördination type. Pauling pointed out that it is possible by pairing up all the electrons in the 3d shell of the nickel ion to obtain strong covalent (sp^{2}d) bonds resulting in a square planar structure, in contrast to the tetrahedral structure of weak covalent (sp^3) bonds. In the planar structure the nickel atom should be diamagnetic rather than paramagnetic as in the weak covalent tetrahedral structure and the simple nickel ion. A number of 4-coördinated nickel compounds have been found to be diamagnetic and X-ray examination has shown such diamagnetic nickel compounds to have a planar structure. Sugden[8] has prepared two diamagnetic geometrical isomers of nickel derivatives of several unsymmetrical glyoximes, which can be explained by assuming a planar structure.

Nickel also forms 6-coördinated complex ions such as (Ni dipyridyl$_3$)$^{++}$, some of which have been separated into optical isomers. Where optical resolution of coördination complexes has been demonstrated, strong covalent bonding is generally assumed.[9] According to the Pauling theory, the magnetic susceptibility of the nickel atom in 6-coördinated nickel complexes can give no evidence of covalency, because in either case there would be two unpaired electrons.

Due to these considerations, it was expected that exchange studies would show no exchange of simple nickel ions with 4-coördinated nickel compounds for which strong covalent bonds are indicated by magnetic susceptibility, X-ray examination and demonstration of geometrical isomers. Also 6-coördinated complex nickel ions for which strong covalent bonds are indicated by resolution of optical isomers should not show exchange with simple nickel ions. Nickel complexes having predominantly ionic or weak covalent bonds were expected to exhibit interchange of the nickel atoms.

Experimental

Preparation of Compounds.—The nickel complex compounds were prepared by procedures described in the literature references cited in footnotes to Table I. These compounds were analyzed for nickel by the gravimetric dimethylglyoxime method. The analytical results are given in Table I.

Radioactive Nickel.—The radioactive nickel (Ni^{65}, 2.6 hour half-life) used in this investigation was obtained by neutron bombardment of metallic zinc, nickel or an aqueous suspension of nickel dimethylglyoxime containing a little nickel chloride. The neutrons were produced by the bombardment of lithium or beryllium by deuterons accelerated by the voltage gradient supplied by an electrostatic generator in the University of Wisconsin physics department. Best results were obtained by bombarding metallic zinc with (Li + D) neutrons.

The irradiated metallic zinc was dissolved in hydrochloric acid and filtered. The residue was dissolved in perchloric acid and a little cupric chloride and nickel chloride added to the combined solutions. The nickel was precipitated by the addition of dimethylglyoxime and sodium acetate. The precipitate was dissolved in nitric acid–hydrochloric acid mixture (1:4) and evaporated to dryness to obtain the nickel chloride. This was taken up in water, neutralized with aqueous ammonia and diluted to give the desired concentration of nickel chloride. Alternatively, the metallic zinc was dissolved in nitric acid and the nitric acid removed by evaporating with hydrochloric acid before precipitating the nickel with dimethyl glyoxime.

Acetone, methyl cellosolve and ethyl cellosolve solutions of radioactive nickel perchlorate were prepared similarly except that the last precipitate of dimethylglyoxime was dissolved in dilute (30%) perchloric acid solution and evaporated nearly to dryness to decompose the organic part of the molecule. The residue was taken up in water, neutralized with aqueous ammonia, nickel perchlorate added to approximate the desired amount and the solution evaporated nearly to dryness. The residue was taken up in the appropriate solvent and diluted to give the concentration desired for the experiment.

The irradiated metallic nickel was dissolved in boiling hydrochloric acid solution, precipitated by dimethyl glyoxime and treated as above. The irradiated nickel dimethylglyoxime was filtered from the suspension and the active nickel chloride solution was treated as above. It was found that the specific activity of the nickel ions was ten to fifteen times the specific activity of the nickel

---

(1) This paper is based on a thesis presented by J. Enoch Johnson in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Wisconsin, February, 1942.

(2) Present address: Chemistry Division, Naval Research Laboratory, Washington 20, D. C.

(3) Steigman, *Phys. Rev.*, **59**, 498 (1941).

(4) Seaborg, *Chem. Rev.*, **27**, 199 (1940).

(5) Ruben, *et al.*, THIS JOURNAL, **64**, 2297 (1942).

(6) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

(7) Mellor, *Chem. Rev.*, **33**, 137 (1943).

(8) Sugden, *J. Chem. Soc.*, 246 (1932).

(9) Johnson, *Trans. Faraday Soc.*, **28**, 845 (1932).

TABLE I

EXCHANGE OF NICKEL[a] IN COMPLEX COMPOUNDS

Complex compound	Analyses, % Ni Calcd.	Found	Solvent	Time of interaction, minutes	Specific activity Complex	Ni^{++} ion	Ratio [j] of spec. act.
bis-Methylbenzylglyoxime nickel[b]	13.31	13.44	Acetone	5	0.0	10.9	0.00
				60	0.0	10.7	.00
bis-Methyl-*n*-butylglyoxime nickel[c]	15.74	15.34	Me Cellosolve	5	1.3	39.4	.03
				5	0.8	39.5	.02
				60	1.3	40.0	.03
				60	1.3	38.6	.03
bis-N,N-Di-*n*-propyldithiocarbamate nickel[c]	14.27	14.15	Acetone	5	0.2	17.7	.01
				60	0.2	17.6	.01
				5	11.0	8.2	1.34[k]
				60	9.6	9.2	1.04[k]
				30	23.3	17.0	1.37[k]
				30	0.9	31.0	0.03
bis-N,N-Di-isoamyldithiocarbamate nickel[c]	11.22	11.13	Acetone	5	0.1	32.6	0.00
				60	0.2	35.8	0.01
				30	21.8	19.3	1.13[k]
				30	0.5	35.5	0.01
bis-Salicylaldoxime nickel[d]	17.75	17.65	Me Cellosolve	5	5.0	4.4	1.14
				60	4.3	4.7	0.91
				5	18.3	16.8	1.09
				60	17.3	18.1	0.96
bis-Salicylaldehyde nickel dihydrate[e]	17.42	17.16	Me Cellosolve	5	11.1	9.4	1.18
				5	10.0	11.5	0.87
				60	11.1	10.5	1.06
				60	11.1	11.3	0.98
bis-Salicylaldimine nickel[f]	19.63	19.32	Me Cellosolve	5	28.8	31.0	0.93
				60	32.3	30.3	1.06
				5	9.0	9.8	0.92
				60	8.5	8.8	0.97
bis-Salicylaldehyde-ethylenediamine nickel[g]	18.07	17.85	Et Cellosolve	5	0.2	21.7	0.01
				5	0.0	22.6	0.00
				60	0.0	21.6	0.00
				60	0.0	21.2	0.00
tris-Ethylenediamine nickelous chloride dihydrate[h]	16.97	16.58	Water	5	14.0	14.7	0.95
				60	14.2	13.9	1.02
				5	8.2	8.1	1.01
				60	8.0	7.7	1.04
tris-α,α'-Dipyridyl nickelous chloride heptahydrate[i]	8.16	7.80	Water	5	5.5	22.1	0.25
				60	9.9	13.3	0.75
				5	12.3	35.2	0.35
				40	19.4	23.5	0.83
				90	20.9	21.6	0.97

[a] The radioactive nickel salt used was nickel perchlorate, except for the runs using water as the solvent, in which cases nickel chloride was used. [b] Sugden, *J. Chem. Soc.*, 246 (1932). [c] Cavell and Sugden, *ibid.*, 621 (1935). [d] Cox, *et al.*, *ibid.*, 459 (1935). [e] Tyson and Adams, THIS JOURNAL, **62**, 1228 (1940). [f] Pfeiffer and Buchholz, *J. prakt. Chem.*, **129**, 163 (1931). [g] Dubsky and Sokol, *Coll. Czech. Chem. Comm.*, **3**, 548 (1931). [h] Werner, *Z. anorg. Chem.*, **21**, 201 (1899). [i] Pfeiffer and Tappermann, *Z. anorg. allgem. Chem.*, **215**, 273 (1933). [j] This ratio is obtained by dividing the specific activity of the complex by the specific activity of the simple nickel ion. [k] In these experiments, concentrated aqueous ammonia was added immediately before precipitation of the complex by dilution with water.

in the nickel dimethylglyoxime, demonstrating the application of the Szilard–Chalmers principle, and giving strong indication that there is no exchange between the two forms of nickel involved.

Exchange Procedure.—The general method of determining the exchange of nickel between the 4-coördinated nickel compounds and simple nickel ions was to mix at room temperature (about 25°) a solution (in acetone, methyl cellosolve or ethyl cellosolve) of the complex compound with a solution of radioactive nickel perchlorate in the same solvent. After an appropriate time interval, the complex compound was separated from the solution by dilution with several volumes of water. In the case of bis-methylbenzylglyoxime nickel and bis-salicylaldimine nickel, sodium chloride was added to salt out the complex compound.

The activity of the complex compound was measured on the solid precipitate or on a solution of the compound in dilute hydrochloric acid or, in the case of the dithiocarbamate compounds, in acetone. The activity of the nickel ions in the filtrate was determined by precipitation by the usual method with dimethylglyoxime, dissolving this precipitate in dilute hydrochloric acid solution and diluting to the desired volume. The activity measurements were made on the solution or on the dimethyl glyoxime precipitate.

The determination of exchange of nickel between 6-coördinated complex nickel ions and radioactive nickel chloride was made by mixing the aqueous solutions. The tris-ethylenediamine nickel ion was separated by precipitation with chloroplatinic acid or sodium thiosulfate solution. The precipitate was redissolved in 60% perchloric acid to determine its activity. In the case of the tris-dipyridyl nickel ion, the nickel ion was separated from the solution by precipitating with dimethylglyoxime, leaving the dipyridyl nickel ion in solution. The filtrate was evaporated to a small volume, filtered again and diluted with water to the desired volume.

Analysis for Nickel.—All the analyses for nickel were made by the gravimetric method using dimethylglyoxime. The weight of nickel was obtained by using the value of 20.3% as the percentage of nickel in the dimethylglyoxime precipitate. In case the solution to be analyzed contained nickel combined with an organic substance besides dimethylglyoxime, the solution was evaporated with 60% perchloric acid until it fumed strongly. The solution was cooled, diluted with water and handled in the usual manner. If the solution contained an organic solvent such as acetone, this was evaporated off before treatment with perchloric acid. It was found necessary to fume strongly with sulfuric acid in analysis of solutions containing dipyridyl to decompose it prior to nickel analysis.

Measurements and Calculations.—The activity of the nickel samples was determined by the use of a Geiger-Mueller counter. For counting dry samples the counter tube was contained in a felt-padded brass jacket fitted into a lead box built in two parts. The sample contained on a small watch glass was placed on a brass holder and slipped into a slot below the counter tube. Solution samples were run into an annular glass jacket which was slipped over the counter tube. Solutions whose activity was to be measured were usually made up to 25 ml. in a volumetric flask. Since the volume of the annular jacket was approximately 15 ml., it was completely filled each time so that all measurements were made under the same conditions.

The observed activity (counts/min.) was corrected for background count (12–15 counts/min.), for counting losses and for the decay of the radioactive nickel. The specific activity (counts per minute per milligram of nickel) was calculated by dividing the corrected counts per minute by the number of milligrams in the sample. The samples contained approximately 10–20 mg. of nickel. The corrected activity for active samples was usually 100–400 counts per minute.

The results of the exchange experiments are given in Table I. The values given under the heading "Ratio of Specific Activities" is the ratio of the specific activity of the nickel in the complex compound to the specific activity of the simple nickel ion. The value of this ratio should be 1.00 when complete exchange has occurred.

Behavior with Dimethylglyoxime.—In preliminary experiments to find satisfactory means of separating the complex nickel compounds from the nickel perchlorate and nickel chloride, the behavior of these compounds of nickel in the presence of dimethylglyoxime was studied. These observations seemed noteworthy because of the striking correlation with the exchange data for these compounds. Nickel tris-dipyridyl chloride in aqueous solution gave no precipitate with dimethylglyoxime whereas the nickel tris-ethylenediamine ion gave an immediate precipitate of nickel dimethylglyoxime. The addition of 1% alcoholic dimethylglyoxime to the acetone solutions of the nickel complexes with the two glyoximes, the two dithiocarbamates and disalicylaldehyde–ethylenediamine did not give a precipitate even after an hour. An immediate precipitate of nickel dimethylglyoxime was formed when the dimethylglyoxime solution was added to the methyl cellosolve solution of bis-salicylaldoxime nickel and bis-salicylaldehyde nickel. bis-Salicylaldimine nickel in acetone solution did not give an immediate precipitate, but after dilution with water a precipitate of nickel dimethylglyoxime formed after a short time.

Results and Discussion

bis-Methylbenzylglyoxime Nickel.—Sugden[8] found this compound to be diamagnetic and he succeeded in separating two geometrical isomers which he called the α-form, m. p. 168°, and the β-form, m. p. 75–77°. Sugden concluded that this isomerism is made possible by the planar configuration of the four Ni–N bonds. The α-isomeride (m. p. 167–168°) was used in these exchange experiments. As was expected, the data in Table I show that no exchange occurred between the nickel atoms in bis-methylbenzylglyoxime nickel and nickel perchlorate within sixty minutes under the conditions of the experiment.

bis-Methyl-*n*-butylglyoxime Nickel.—Cavell and Sugden[10] reported that this compound is diamagnetic and that it occurs in two steroisomeric forms. Because of this proof of a planar configuration of the bonds, no exchange was expected to occur between the nickel atoms of the compound and nickel ions in homogeneous solution. The results of the activity measurements are interpreted to mean that no exchange had occurred. The slight activity of the nickel complex is attributed to the fact that the precipitate of the nickel glyoxime was not wet appreciably by the wash water, which could allow radioactive nickel ions to remain adsorbed on the precipitate.

***bis*-N,N-Di-*n*-propyldithiocarbamate Nickel.**—Malatesta[11] and Cavell and Sugden[10] found this compound to be diamagnetic. Malatesta stated further that the dithiocarbamates of nickel in general maintain the diamagnetic state in solution as well as in the fused condition. Cavell and Sugden were unable to isolate stereoisomers of this compound and concluded that this was probably due to a symmetrical structure of the molecule. Peyronel,[12] on the basis of X-ray measurements, found this compound to be planar. The sum of this information made it seem likely that no exchange of nickel atoms would be found with this compound. The exchange data show that no exchange had occurred when separation of the complex compound from the nickel perchlorate was made by simply diluting with water. In the experiments where concentrated aqueous ammonia was added to facilitate the precipitation of the complex, complete exchange was obtained within five minutes. Because this did not agree with the results obtained when the ammonia treatment was omitted, this phenomenon was further investigated with the di-isoamyl dithiocarbamate complex of nickel.

bis-N,N-Di-iso-amyldithiocarbamate Nickel.—Although no structural data were available

---

(10) Cavell and Sugden, *J. Chem. Soc.*, 621 (1935).

(11) Malatesta, *Gazz. chim. ital.*, **67**, 738 (1937).

(12) Peyronel, *Z. Krist.*, **103**, 157 (1941).

for this compound, there was no reason to believe that it should behave differently from the di-*n*-propyl derivative. The exchange experiments were performed in essentially the same way as with the propyl compound. The data show that no appreciable exchange had occurred when the separation of the complex from the nickel perchlorate was made by merely diluting with water. However, when concentrated aqueous ammonia was added to the acetone solution before dilution with water, complete exchange occurred. The time elapsing between the addition of ammonia and the complete separation of the precipitated complex compound by filtration was less than two minutes. It was concluded that the presence of ammonia has a profound effect upon the stability of the nickel dithiocarbamate structures. Ammonia apparently weakens the bonds of the complex units to the nickel so much that thermal exchange may occur in a short time at room temperature.

bis-Salicylaldoxime Nickel.—Cox[13] and coworkers found that the nickel and palladium compounds of salicylaldoxime are isomorphous, which is significant since all quadricovalent palladium compounds are planar in structure. The nickel compound was found by them to be diamagnetic. However, Malatesta[14] reported that bis-salicylaldoxime nickel is paramagnetic to the extent of 2.70 magnetons. The results of the exchange experiments given in Table I show complete interchange of the nickel atoms within five minutes in methyl cellosolve solution. This might seem to substantiate Malatesta in regard to the magnetic susceptibility of this compound. However, Willis and Mellor[15] recently reported this compound to be diamagnetic in the solid state and in benzene solution, but to be paramagnetic to the extent of 1.1 and 3.1 Bohr magnetons in chloroform and pyridine, respectively. They postulated, in the case of pyridine, the formation of an octahedral complex containing pyridine in equilibrium with the planar molecules. But they felt that chloroform would be unlikely to form such a complex. They agreed that the difference of stability of square and tetrahedral complexes may in some cases be so small that the solvent may cause partial conversion to the tetrahedral structures as was earlier suggested by French, Magee and Sheffield[16] in the case of bis-formylcamphor-ethylenediamine nickel in methanol solution. The present authors feel that the exchange observed with bis-salicylaldoxime nickel in methyl cellosolve solution does indicate a change of bond type.

bis-Salicylaldehyde Nickel.—This compound is paramagnetic in the solid state and in pyridine solution and is therefore believed to have predominantly ionic or weak covalent bonds. As was expected from this information, complete exchange occurred with nickel ions in methyl cellosolve solution within five minutes.

bis-Salicylaldimine Nickel.—Tyson and Adams[17] found this compound to be diamagnetic in the solid state as did Willis and Mellor,[15] although the latter found it to be paramagnetic to the extent of 2.3 Bohr magnetons in pyridine solution. The results of the exchange experiments show complete exchange within five minutes in acetone solution. The addition of sodium chloride in the separation of the complex compound is not believed to have caused the exchange of nickel atoms because the addition of sodium chloride was used in the separation of bis-methylbenzylglyoxime nickel which showed no exchange. It is more probable that the covalent bonds of the diamagnetic solid compound are modified sufficiently by the solvent to allow thermal exchange.

bis-Salicylaldehyde-ethylenediamine Nickel.—Willis and Mellor[15] recently reported this compound to be diamagnetic both in the solid state and in pyridine solution. The exchange study of this compound was made in ethyl cellosolve solution and the results show definitely that there was no exchange of nickel atoms within an hour. The presence of another five-membered ring in this complex molecule apparently stabilizes the molecule which is otherwise similar in structure to bis-salicylaldimine nickel and bis-salicylaldoxime nickel.

tris-Ethylenediamine Nickelous Chloride Dihydrate.—Rosenbohm[18] and Cambi, Cagnasso and Tremolada[19] found this compound to have a magnetic susceptibility sufficient to show two unpaired electrons just as in the simple nickel ion. However, Pauling's explanation of the stability of 6-coördinated nickel complexes does not require pairing of all the valence electrons. Consequently, magnetic susceptibility measurements are of no value in predicting stability. Bucknall and Wardlaw[20] were able to resolve the tartrates and *d*-camphor sulfonates of this complex ion, but the optical activity was lost on conversion of these salts to the chloride. The results in Table I show that the nickel atoms in the ethylenediamine complex ion exchanged completely with nickel ion in water within five minutes. This was not unexpected due to the failure to resolve this complex ion into stable optical isomers.

tris-α,α'-Dipyridyl Nickelous Chloride Heptahydrate.—Morgan and Burstall[21] were able to resolve this complex nickel chloride into its optical isomers. This has been substantiated by others. These optically active salts racemize in aqueous solution. For example, it was reported that racemization is complete after 115 minutes at

---

(13) Cox, *et al.*, *J. Chem. Soc.*, 459 (1935).

(14) Malatesta, *Gazz. chim. ital.*, **68**, 319 (1938).

(15) Willis and Mellor, THIS JOURNAL, **69**, 1237 (1947).

(16) French, Magee and Sheffield, *ibid.*, **64**, 1924 (1942).

(17) Tyson and Adams, THIS JOURNAL, **62**, 1228 (1940).

(18) Rosenbohm, *Z. physik. Chem.*, **93**, 693 (1919).

(19) Cambi, Cagnasso and Tremolada, *Gazz. chim. ital.*, **64**, 758 (1934).

(20) Bucknall and Wardlaw, *J. Chem. Soc.*, 2739 (1928).

(21) Morgan and Burstall, *Nature*, **127**, 854 (1931); *J. Chem. Soc.*, 2213 (1931).

17°, or in about sixty minutes at 20°. The fact that this salt is resolvable indicates that its complex ion is quite stable. The results in Table I show that the nickel atom in the complex ion exchanges at a measurable rate with the simple nickel ion in water solution. No attempt was made to establish the rate of this exchange under varying conditions. The observed interchange indicates that racemization of the optical isomers may be due to partial dissociation of the complex ion. This exchange of the nickel atom in the dipyridyl complex is interesting because Ruben, *et al.*,[5] found a slow exchange of iron atoms between ferrous ion and ferrous α,α'-dipyridyl ion, although the latter is diamagnetic so that no exchange was predicted.

Acknowledgments.—The authors wish to thank Dr. Truman P. Kohman who made helpful suggestions, Dr. J. L. McKibben who built the counting apparatus and operated the electrostatic generator for the preparation of the radionickel and Mr. Dave Frisch who also operated the generator. This work was supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

Summary

1. The nickel exchange of ten nickel coördination compounds was studied using Ni^{63} as the tracer. In the main the results, which are discussed in detail, show a satisfactory correlation with predictions of bond type based on other criteria.

2. bis-Methylbenzylglyoxime nickel, bis-methyl-*n*-butylglyoxime nickel, bis-N,N-di-*n*-propyldithiocarbamate nickel, bis-N,N-di-iso-amyldithiocarbamate nickel and bis-salicylaldehyde-ethylenediamine nickel was found not to exchange under the experimental conditions used in accordance with expectation based on the magnetic and other structural evidence for strong covalent bonds. The two dithiocarbamate compounds of nickel did, however, show exchange with nickel perchlorate in the presence of ammonia.

3. bis-Salicylaldehyde nickel and tris-ethylenediamine nickel chloride were found to exchange as predicted.

4. bis-Salicylaldoxime nickel and bis-salicylaldimine nickel, although diamagnetic in the solid state, were found to exchange. This is believed to be evidence that these compounds exhibit a change of bond type when dissolved in methyl cellosolve.

5. Although tris-α,α'-dipyridyl nickel chloride heptahydrate has been resolved into its optical isomers and was not therefore expected to exchange, it did exchange at a measurable rate. This may be connected with the racemization observed for this compound.

MADISON, WISCONSIN RECEIVED FEBRUARY 3, 1948

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Reaction of Ferrous and Ferric Iron with 1,10-Phenanthroline. I. Dissociation Constants of Ferrous and Ferric Phenanthroline

BY T. S. LEE, I. M. KOLTHOFF AND D. L. LEUSSING

The intensely red colored complex of divalent iron and phenanthroline is used extensively for the colorimetric determination of iron and as an oxidation–reduction indicator. The dissociation constants of ferrous and ferric phenanthroline have hitherto not been determined, nor has a systematic study been made of the effect of acid on the dissociation of these complexes. Moreover, no study has been made of the kinetics of the formation and the dissociation of either complex. Such information is of general and especially of analytical interest.

The present paper is divided into three parts: (1) the basic strength of phenanthroline, (2) dissociation of "ferroin" (the ferrous phenanthroline complex) and (3) the dissociation of "ferriin" (the ferric phenanthroline complex).

In a subsequent paper the kinetics of formation and dissociation of ferroin and ferriin will be discussed.

Experimental

Materials Used.—1,10-Phenanthroline ("ortho-phenanthroline") monohydrate was obtained from the G. Frederick Smith Chemical Co. The phenanthroline content of several different samples of this compound was found by conductometric titration with acid to be 100 ± 1% of theoretical. Standard solutions of phenanthroline and phenanthrolium chloride were prepared by dissolving the calculated amount of phenanthroline in water or in standard hydrochloric acid.

Standard solutions of the following compounds were prepared from analytical reagent chemicals and standardized by accepted procedures: ferrous sulfate, sulfuric acid, hydrochloric acid, ceric sulfate and potassium chloride.

Potentiometric Titration of Phenanthroline with Hydrochloric Acid.—One-hundredth M phenanthroline solution in water was titrated at room temperature with 0.2 N hydrochloric acid. The *p*H was measured with a glass electrode (Leeds and Northrup *p*H Meter, Model No. 7661).

Determination of *p*H of Mixture of Phenanthrolium Chloride and Phenanthroline.—Solutions were prepared which were 0.0200 M in phenanthroline, 0.0100 M in hydrochloric acid, and 0.001, 0.010, 0.100, 0.500 or 1.00 M in potassium chloride. The *p*H of these solutions was measured at 25 ± 0.1° with the apparatus described above.

Conductometric Titration of Phenanthroline with Hydrochloric Acid.—One hundredth M phenanthroline solution in water was titrated with 0.2 N hydrochloric acid. The titration was carried out at room temperature in a titration conductance cell with freshly platinized elec-