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Chloranilate Complexes of Iron(III) and Nickel(II)

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Nickel(II) and iron(III) have been found to complex with chloranilic acid in 1 : 1 and 1 : 2 ratios, respectively. The complexes were studied spectrophotometrically by the method of continuous variations in aqueous solutions at an ionic strength of 0.15 and at different values of pH and temperature. Formation constants and other thermodynamic properties have been determined. It is proposed that these complexes are chelates.

Chloranilic acid forms a red-purple solution with absorption bands in the visible (500—600 mμ) region. The interaction of metal ions with this acid in solution is detected by a color change. Many spectrophotometric analytical procedures for the determination of cations are based on this observation. It is usually assumed that there are no side reactions in the analytical processes. However, the chloranilate ion is by no means specific in its reactions and as a result, many interfering ions have been reported.[1]

It was the purpose of this research to study the complexes formed with iron and nickel in dilute solutions and to determine the empirical formulas as well as the formation constants. Since these complexes are highly colored a spectrophotometric method was used.

Experimental

Instrumentation. Preliminary experiments, to determine the wavelengths of maximum absorption and changes in spectra of the systems studied, were made on a Beckman DK 1 recording spectrophotometer. Absorbance measurements of the complexes were made on a Beckman DU spectrophotometer, the cell compartment of which was thermostated. For low temperatures, a dry box was provided around the cell compartment to prevent condensation of water vapor on the cell windows. All measurements were made with matched silica cells with a 10.00—0.01 mm light path. The instrument was operated at a constant slit width of 0.02 mm and maximum sensitivity.

A Beckman model GS pH meter, equipped with Beckman glass electrode (No. 40495, low sodium error), was used for all pH measurements. The instrument was operated on the expanded scale for maximum sensitivity.

Infrared spectra were run on a Perkin-Elmer model 337 and 137 double-beam spectrophotometer.

Materials. All solutions were prepared with distilled water which had been run through a mixed-bed deionization column containing Amberlite C-211 cation and Amberlite A-244 anion exchange resins. The chemicals were used without further purification except for chloranilic acid. The solutions were made by weighing the solid chemical or pipeting a stock solution into a volumetric flask and diluting at 25°C. Nickel chloride and nickel perchlorate solutions were analyzed gravimetrically by the dimethylglyoxime method.[2] A stock solution of ferric perchlorate was analyzed volumetrically with mercurous nitrate.[3]

Clark and Lubs' buffer systems were used as guides to prepare a series of standard buffer solutions.[4] From these, a series of samples at different pH values but at constant ionic strength could be made by mixing appropriate components and diluting to a given volume. The pH and ionic strength of each continuous variation sample was maintained constant within ± 0.05 units by the use of a proper buffer and by adding an amount of hydrochloric or perchloric acid such that the total formality of all acid added remained constant.

Chloranilic acid was purified by recrystallizing Fisher reagent grade material according to the method described by Thamer and Voigt.[5] The melting point of chloranilic acid is reported to be 283—284°C[6] but it was found that it sublimes at atmospheric pressures at 230°C. The sublimed and recrystallized products had the same absorption spectrum, molar extinction coefficient and hydrogen and chloride equivalent weights.

As the absorbance of a chloranilic acid solution gradually decreases with time and exposure to light, the stock solution was stored in a darkened container maintained at 1—5°C. Periodic checks revealed that the solution could be preserved in this way for a long period of time.

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[1] J. T. Baker Informational Aid, "Chloranilic Acid and its Metal Salts as Analytical Reagents." An English-language version of: *Bunseki Kagaku (Japan Analyst)*, **9**, 257 (1960).

[2] L. C. Howick and J. Jones, *Talanta,* **10**, 189 (1963).

[3] I. M. Kolthoff, "Volumetric Analysis," Vol. III, Interscience Publishers, New York (1957), p. 623.

[4] W. M. Clark, "The Determination of Hydrogen Ions," 3rd Ed., The Williams and Wilkins Company, Baltimore (1928).

[5] B. J. Thamer and A. F. Voigt, *J. Phys. Chem.*, **56**, 225 (1952).

[6] C. D. Hodgman, Ed., "Handbook of Chemistry and Physics," 42nd Ed., The Chemical Rubber Publishing Co., Cleveland, Ohio (1960), p. 918.

Theoretical

Empirical Formulas. The color change which occurs when iron(III) or nickel(II) is mixed with chloranilic acid was attributed to complex formation rather than an oxidation reduction reaction. This conclusion was based upon the result of a comparison of electrode reactions and the kinetic stability of the absorption spectra.

Empirical formulas for the complexes in the two systems were determined by the method of continuous variations.[7] For this a series of solutions was prepared in which the ratio of the concentration of the metal ions and the chloranilate ions was varied but the total concentration was kept constant. The ionic strength and the pH of all solutions were maintained the same by the use of appropriate buffers. The absorbances of these solutions were measured with water as reference. From these the absorbances of chloranilic acid at the same pH and ionic strength as the complex were substracted and the differences plotted against the concentration of the acid divided by the sum of the concentrations of the acid and metal.

Formation Constant. The method of matching absorbance[8] is applicable to systems in which the complex species absorbs at wavelength different from that of the reactants. In the nickelous chloranilate and ferric chloranilate systems, the complexes absorb at the same wavelength as the chloranilic acid, however, the absorbance of the complex in each is different from that of the acid. The general equation for the reaction is given by:

$$M^{+m} + iH_nCh^{n-2} \rightleftarrows MCh_i^{m-2i} + inH^+ \quad (1)$$

where M is the metal ion of charge m; n, the number of hydrogen ions associated with the chloranilate ion (Ch^{-2}) and i the number (one or two) of ligands in the complex molecule.

Later in the paper a more complete discussion will be given justifying the assumption that at relatively high pH values the complex is in the form of a chelate and therefore does not evolve hydrogen ion. Making this assumption, Eq. (1) can be transformed to read:

$$M^{+m} + iCh^{-2} \rightleftarrows MCh_i^{(m-2i)} \quad (2)$$

The formation constant corresponding to Eq. (2) is:

$$K_{fi} = \frac{[MCh_i^{(m-2i)}]}{[M^{+m}][Ch^{-2}]^i} \quad (3)$$

Expressing the ligand concentration in terms of the dissociation constants of chloranilic acid k_1 and k_2 and hydrogen ion concentration gives:

$$\begin{aligned}[H_nCh^{(n-2)}] &= [H_2Ch] + [HCh^{-1}] + [Ch^{-2}] \\ &= [Ch^{-2}]\left(\frac{[H_2Ch]}{[Ch^{-2}]} + \frac{[HCh^{-1}]}{[Ch^{-2}]} + 1\right) \\ &= [Ch^{-2}]\left(\frac{[H^+]^2 + [H^+]k_1 + k_1k_2}{k_1k_2}\right) \\ &= [H_nCh^{(n-2)}]_0 - i[MCh_i^{(m-2i)}] \end{aligned} \quad (4)$$

Solving for the twice ionized acid ion gives:

$$[Ch^{-2}] = \frac{\{[H_nCh^{(n-2)}]_0 - i[MCh_i^{(m-2i)}]\}(k_1k_2)}{([H^+]^2 + [H^+]k_1 + k_1k_2)}$$

since $k_1 = \frac{[H^+][HCh^{-1}]}{[H_2Ch]}$ and $k_2 = \frac{[H^+][Ch^{-2}]}{[HCh^{-1}]}$.

The extinction coefficient of the complex (a_i) can be evaluated by calculating the limiting apparent extinction coefficient of the complex as a function of increasing or decreasing metal ion concentration.

The limiting extinction coefficient of the complex ML, where M represents the metal and L the ligand, was obtained by holding M in constant concentration of the complex and its absorption varied with changing concentration of L, but at relatively low concentration of L, the concentration of complex became the same as the concentration of L. Hence the absorption of the complex was its absorption at the concentration of L. The same procedure was used holding L constant and in large excess. The same limiting extinction coefficient was found in each case.

For the ML and ML_2 types of complexes, a similar procedure yielded the limiting extinction coefficient for the ML complex when the metal was in excess, and the limiting extinction coefficient for the ML_2 complex when L was in excess.

The extinction coefficient of the chloranilic acid can be obtained by absorption measurements on a series of solutions of different concentrations of the acid at the same pH and ionic strength.

The absorbance of any solution is given by:

$$A = 1(a_0[H_nCh^{(n-2)}] + a_i[MCh_i^{(m-2i)}]) \quad (5)$$

Expressing the equilibrium concentration of chloranilic acid in terms of the initial acid concentration and complex concentration yields:

$$\begin{aligned} A = 1(&a_0[H_nCh^{(n-2)}]_0 \\ &+ [MCh_i^{(m-2i)}](a_i - {}_ia_0)) \end{aligned} \quad (6)$$

The concentration of the complex can be expressed as:

$$[MCh_i^{(m-2i)}] = \frac{A - la_0[H_nCh^{(n-2)}]_0}{l(a_i - {}_ia_0)} \quad (7)$$

where a_0 and a_i are the extinction coefficients of chloranilic acid and the complex respectively; l is the length of the light path; A, the absorbance of the solution and $[H_nCh^{(n-2)}]_0$ the initial concentration of chloranilic acid.

By substituting the concentrations of the complex, the metal and the ligand into Eq. (3), the following expression for the formation constant is obtained:

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7) P. Job, *Ann chim. Paris*, **9**, 113 (1928).

8) R. T. Foley and R. C. Anderson, *J. Am. Chem. Soc.*, **71**, 909 (1949).

$$K_{fi}=\frac{\Delta A(\Delta a)^i[(\mathrm{H}^+)^2+(\mathrm{H}^+)k_1+k_1k_2]^i}{[[\mathrm{M}^{+m}]_0\Delta a-\Delta A]\,[[\mathrm{H}_n\mathrm{Ch}^{(n-2)}]_0\Delta a-{}_i\Delta A]^i(k_1k_2)^i} \tag{8}$$

where

$$\Delta A = A - la_0[\mathrm{H}_n\mathrm{Ch}^{(m-2)}]_0$$
$$\Delta a = l(a_i - {}_ia_0)$$

Results

The empirical formulas of nickel and ferric chloranilate complexes were found to be 1 : 1 and 1 : 2 respectively by the method of continuous variations. The curves shown in Fig. 1 are obtained by making the correction for the absorbance of the chloranilic acid remaining in solution at equilibrium.

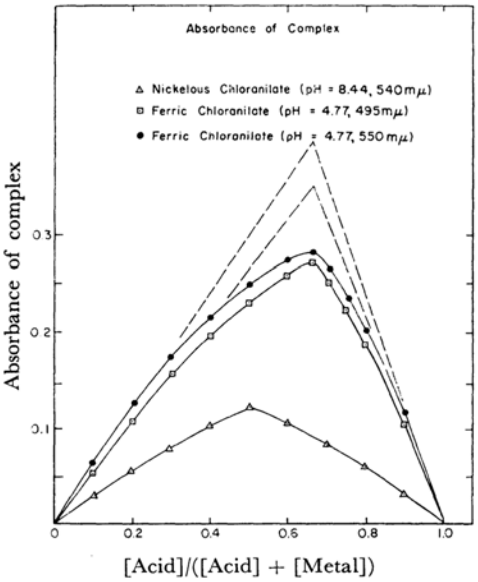

Fig. 1. Typical continuous variation calculated curve.

The formation constants of the complexes were determined using Eq. (8). The dissociation constants of the acid k_1 and k_2 determined by other workers⁵⁾ are not at the desired ionic strength. These were therefore, determined by a spectrophotometric⁵⁾ method.

Lee, Shastri, and Amis⁹⁾ be measuring absorbance as a function of pH found k_1 for chloranilic acid to be infinite. The absorbance *versus* pH of these authors lead to these conclusions, but the data was in error for some unknown reason. Their value, determined by the above method, of pK_a, which corresponds to pK_2 in the present work, was 2.75 compared to 2.72—0.05 reported here. The dissociation constants determined from spectrophotometric methods are given in Table 1.

TABLE 1. DISSOCIATION CONSTANTS OF CHLORANILIC ACID AT 25°C

	pk_1	pk_2	Ionic strength
Spectro-photometric	0.812±0.01	2.72±0.05	0.15

Tables 2 and 3 summarize the formation constants and thermodynamic properties of the complexes at different values of pH and temperature.

For the nickelous chloranilate system the values are given for chloride as well as perchlorate media.

For the ferric chloranilate system, the values are given at two wavelengths and for the first and second formation constants. The first and second formation constants are calculated from data taken at 490—495 mμ.

The absorption spectrum of the ferric chloranilate complex is shown at different pH values in Fig. 2. The absorption decreases on increasing pH with the greatest effect occurring in the region of 550—580 mμ. The absorption of the nickelous chloranilate complex decreases and shifts to longer wavelengths on increasing pH.

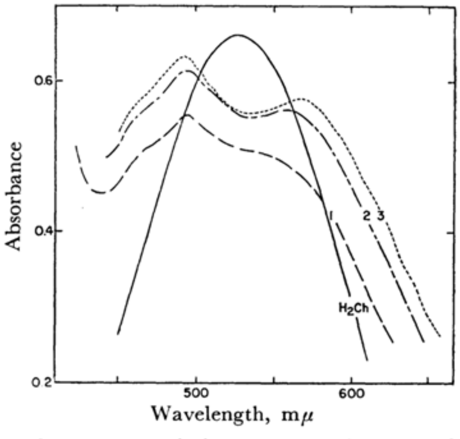

Fig. 2. Spectra of ferric chloranilate complex.
Complex concentration, 3×10⁻⁵ M
Chloranilic acid concentration, 3.2×10⁻⁴ M

Curve number	pH
1	4.77
2	3.74
3	2.89
H_2Ch	0.70

Discussion

The complexes in the two systems are almost certainly chelates, since a single metal to oxygen

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9) W. F. Lee, N. K. Shastri and E. S. Amis, *Talanta*, **11**, 685 (1964).

TABLE 2. CONSTANTS FOR THE NICKELOUS CHLORANILATE

pH ± 0.5	log K_{f_1} 25°C	pH ±0.05	log K_{f_1} 15°C	log K_{f_1} 25°C	log K_{f_1} 35°C	$-\Delta F^\circ$ kcal/mol	$-\Delta H^\circ$ kcal/mol	$+\Delta S^\circ$ cal/deg/mol
3.71	4.398							
4.86	4.322	2.67		4.634		6.31		
5.82	4.301	3.75		4.204		5.73		
6.87	4.279	5.74		4.000		5.45		
7.71	4.255	7.56	4.079	4.041	4.000	5.51	1.66	−12.9
		8.44	4.079	4.000	3.903	5.45	1.66	−12.7

The formation constants were calculated using 0.155 for k_1 and 0.0019 for k_2.

TABLE 3A. K_{f_1} CONSTANTS FOR THE FERRIC CHLORANILATE SYSTEM

pH ±0.05	log K_{f_1} 15°C	log K_{f_1} 25°C	log K_{f_1} 35°C	$-\Delta F^\circ$ kcal/mol	$-\Delta H^\circ$ kcal/mol	$+\Delta S^\circ$ cal/deg/mol
Wavelength 490—495 mμ						
2.89		5.929		8.08		
3.74		5.732		7.82		
4.77	5.911	5.813	5.748	7.94	3.36	−15.4
Wavelength 550—580 mμ						
2.89		6.193		8.45		
3.74		5.724		7.81		
4.77	5.821	5.513	5.155	7.51	14.7	+24.4

The formation constants were calculated using 0.155 for k_1 and 0.0019 for k_2.

TABLE 3B. K_{f_2} CONSTANTS FOR THE FERRIC CHLORANILATE SYSTEM

±0.05 pH	log K_{f_2} 15°C	log K_{f_2} 25°C	log K_{f_2} 35°C	$-\Delta F^\circ$ kcal/mol	$-\Delta H^\circ$ kcal/mol	$+\Delta S^\circ$ cal/deg/mol
Wavelength 490—495 mμ						
2.89		9.693		13.2		
3.74		9.545		13.0		
4.77	9.952	9.843	9.827	13.4	2.60	−36.2
Wavelength 550—580 mμ						
2.89		9.805		13.4		
3.74		9.501		13.0		
4.77	9.735	9.467	9.238	12.6	10.35	−7.4

The formation constants were calculated using 0.155 for k_1 and 0.0019 for k_2.

bond is weak.10) The comparatively large formation constants of these complexes denote strong bonding. In general, the complexes are stable in the pH range studied, which is analogous to metal oxalate complexes.11) The values of the formation constants, in the pH ranges presented in Tables 2, 3A and 3B are practically independent of pH.

That the nickelous and ferric chloranilates are chelates has been experimentally established by infrared studies which indicate the carbonyl and carbon oxygen bands to split. The accompanying shift in the carbonyl is toward lower wave numbers and that of the carbon oxygen bond

TABLE 4. INFRARED ABSORPTION BANDS
(Wave Numbers)

Assignment	Chloranilic acid	Nickelous chloranilate	Ferric chloranilate
C=O	1620	1620	1620
C=O		1530	1560
C−O	1370	1390	1360
C=O		1310	1300
C−O	1250		
Ar-OH	1200		

Ar, the ring structure of the acid

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10) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, Oxford (1950), p. 1451.

11) K. Yatsimirskii and V. P. Vasilev, "Instability Constants of Complex Compounds" (Translated from the Russian), ed. by R. H. Prince, Pergamon Press, New York (1960), pp. 161—162.

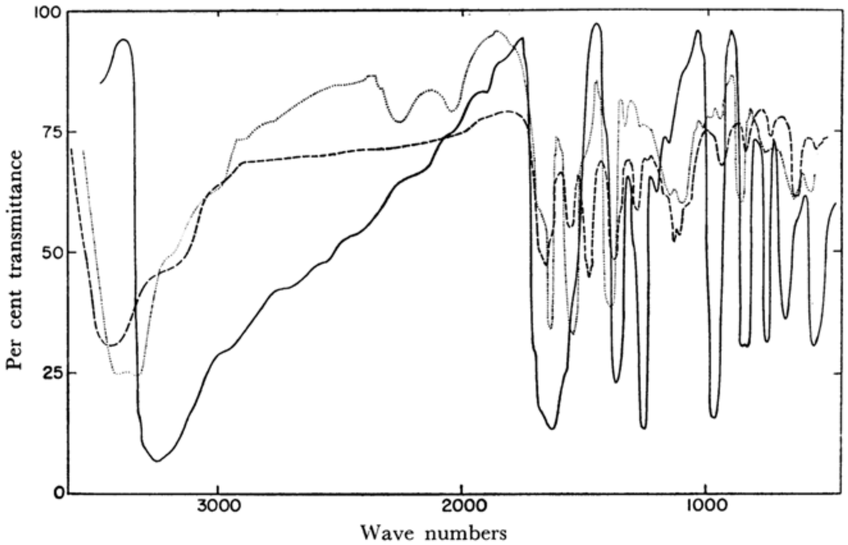

Fig. 3. —— Infrared spectrum of chloranilic acid
---- Infrared spectrum of ferric chloranilate
······ Infrared spectrum of nickelous chloranilate
(Concentration, about 1% in potassium bromide)

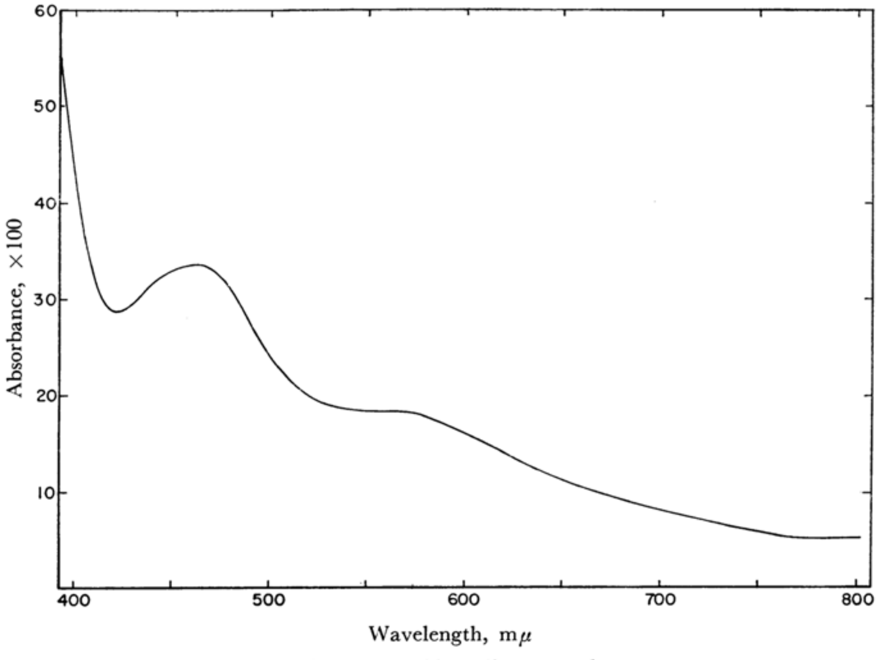

Fig. 4. Ferric chloranilate complex.
3×10^{-4} mol/l 95 vol% dioxane 25±2°C
2×10^{-1} mol/l, $HClO_4$ 5 vol% water

is toward higher, see Table 4. In this table it is also seen that the aromatic hydroxyl band of the chloranilic acid has completely dissappeared in the complexes. The infrared spectra of chloranilic acid, ferric chloranilate and nickel chloranilate are shown in Fig. 3.

The absorption spectra of chloranilic acid and its complexes with most of the transition metals are similar with the exception of iron. The wavelengths of maximum absorption are slightly shifted but the values of the extinction coefficient of the complex is 10^3—10^4 times larger than that of the metal, but only 5—10 times larger or smaller than chloranilic acid itself. This implies that the absorption of the complex is due to the electronic transitions of the ligand. The slight shift in the wavelength of maximum absorption can be explained by resonance.

The ferric chloranilate complex shows two absorption bands 490—495 and 550—580 mμ. Their maxima lie on either side of the peak for chloranilic acid which is 510—540 mμ. At both maxima, the complexing ratio is 1 : 2. A possible explanation is that the ferric chloranilate complex can exist in two different forms. One possibility is that in one complex the ligand rings are in the same plane (coplanar) and in the other the ligand rings are not in the same plane (nonplanar).

The calculated formation constants for the ferric complex are reduced to first order approximations as a result of the overlap of the absorption bands for the two species. In aqueous solution, the free energy difference between the two complexes is small, thus allowing their co-existence.

It was observed that in 95 volume per cent dioxane 5 volume per cent water, an absorbance peak at about 465 mμ was prominent, while an absorbance at about 575 mμ showed only a shoulder. The concentration of the complex was 3×10^{-4} molar, that of the perchloric acid was 0.2 molar, and the temperature was 25°C. Thus the intensity of absorption by the complex that absorbed at the shorter wavelength region was much less affected by the addition of dioxane to the solvent than was the intensity of absorption by the complex which absorbed at the longer wavelength region. Both regions of absorption were shifted to somewhat lower wavelengths. See Fig. 4.

On long standing or if the temperature is raised appreciably, the blackish complex becomes light yellow.

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