Spectrochemical Studies on the Anomalous Color Reactions of Some Iron(II) Chelate Compounds

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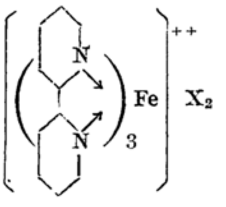
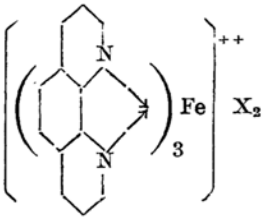
Introduction

The colors of simple salts containing ferrous ion are generally light green and the absorption spectra of their aqueous solutions have a weak, split band in the infra-red region at *ca.* 1,000 mμ and also a weak, continuous absorption in the ultraviolet region.⁽¹⁾ It was found by Yamasaki and his collaborators,⁽²⁾ however, that the ferrous complex salts containing 2, 2′-dipyridyl and 1, 10-phenanthroline ((I) and (II))



I



II

show very strong absorption bands in the visible and near ultraviolet regions which differ substantially from the absorption bands due to the ferrous ion or to the organic ligand molecules of these complexes. The position of visible bands of dipyridyl- and phenanthroline ferrous complexes are 520, 510 mμ respectively (*cf.* Fig. 1). Complex salts of other metals, such as Cu, Zn, Co and Ni, containing these ligand molecules have no such bands; therefore, the appearance of these new, strong bands seems to be characteristic of the ferrous complexes themselves.⁽³⁾

The present study deals with the absorption spectra of the peculiar color reactions shown by ferrous ions with a number of organic substances. The following organic compounds are

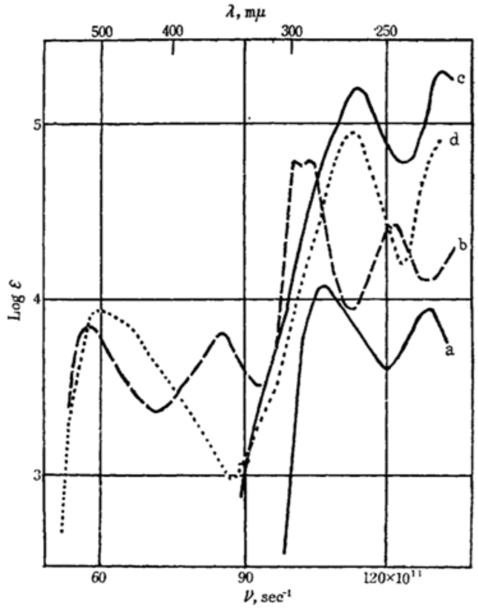


Fig. 1.—(a), 2, 2′-dipyridyl in H_2O; (b), $[Fe(dip)_3]Cl_2$ in H_2O; (c), 1, 10-phenanthroline in H_2O; (d), $[Fe(phen)_3]Cl_2$ in H_2O.

already known to show anomalous color reactions with a ferrous ion⁽⁴⁾:

(A) 2, 2′-Dipyridyl, 1, 10-phenanthroline and their derivatives: red.
(B) Dimethylglyoxime and dioximes with similar structures: red.
(C) Compounds containing the group —C(:NOH)—CO—: blue or green.
(D) α-Carboxylic acids of pyridine, quinoline and their derivatives: brown, violet, etc.
(E) 8-Hydroxyquinoline: red.⁽⁵⁾
(F) Pyrocatechol and related polyphenols: violet.⁽⁶⁾

Of these six groups, (A) was already studied in our laboratory; also (D) was studied earlier by Ley and his collaborators⁽⁷⁾ who showed

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(1) Th. Dreisch, *Z. Phys.*, **40**, 714 (1927); Th. Dreisch and O. Kallscheuer, *Z. phys. Chem*, **B59**, 19 (1939); R. H. Potteril, O. J. Walker and J. Weiss, *Proc. Roy. Soc.*, **A156**, 561 (1936).

(2) K. Yamasaki, This Bulletin, **15**, 461 (1940); K. Yamasaki, H. Yokoi and K. Sone, *J. Chem. Soc. Japan*, **69**, 137 (1948); *Chem. Abst.*, **44**, 9295 (1950).

(3) It may be noted that the ferric complexes of these compounds also show similar bands⁽²⁾, and that W. W. Brandt and G. F. Smith (*Anal. Chem.*, **21**, 1313 (1949)) reported that the dipyridyl complex of ruthenium also shows an analogous band.

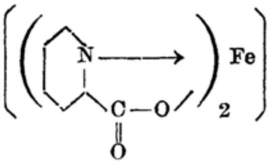
(4) F. Feigl, "Chemistry of the Specific, Selective and Sensitive Reactions," 1949.

(5) R. Berg, "Die analytische Verwendung von o-Oxychinolin "Oxin" und seiner Derivate," 1938.

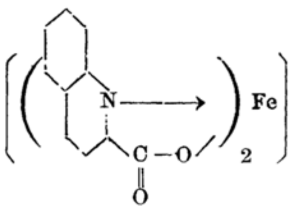
(6) Snell, "Colorimetric Methods of Analysis", Vol. II, 1937.

(7) H. Ley and C. Schwarte, O. Münnich, *Ber.*, **57B**, 349 (1924).

that the absorption spectra of such color reactions present great similarities with those of (A). Also in this case, a strong visible band appeared by chelate formation (III) (IV) which is completely different from the ligand absorption. Therefore, compounds belonging to the remaining three (B), (C) and (E), such as dimethylglyoxime, 8-hydroxyquinoline, α-nitroso-β-naphthol and nitroso-R salt which are the most common analytical reagents, were studied spectrophotometrically in regard to their anomalous coloration with a ferrous ion.



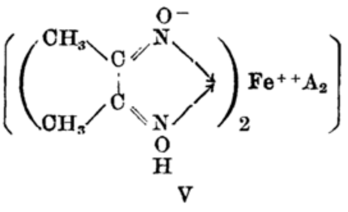
III



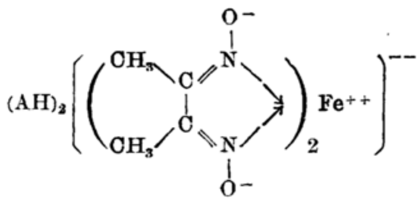
IV

Color Reaction with Dimethylglyoxime

Tschugaeff(4) discovered that a ferrous ion shows strong red coloration in the solutions containing dimethylglyoxime or dioximes having similar structures, and bases containing nitrogen such as NH_3, amines or pyridine. This coloration is, however, rather unstable, and readily fades away in contact with air, owing to the rapid oxidation of the ferrous to ferric state which is ineffective for color production; therefore small amounts of reducing agents must be added to the solution to obtain stable coloration. As the cause of the color, Tschugaeff assumed the formation of hexacoördinated complexes such as $[Fe(DH)_2A_2]$ ($DH_2 =$ dimethylglyoxime, $A = NH_3$ or amines) (V), although Cambi(8) prepared pyridine-containing complex salts of somewhat different composition, and Feigl(4) considered the possibility of ionic formula, such as $(AH)_2^+ [FeD_2]^{-2}$ (VI).



V



VI

By using hydrazine which is a reducing agent as the basic component, or by adding small amounts of sodium hydrosulfite crystals to the sample solutions, the present author has succeeded in preparing colored solutions containing a large exess of dimethylglyoxime and bases which were stable for about half an hour at least, and measured their absorption spectra in visible and near ultraviolet regions (Fig. 2). Dimethylglyoxime itself shows only a continuous absorption in the ultraviolet region which shifts in alkaline solutions to longer wave-lengths, a broad band appearing at *ca.* 260 mμ. However, the colored solution containing a ferrous ion and base shows a very strong, completely new absorption band in the visible region at *ca.* 510∼550 mμ, which is quite similar to those bands of the dipyridyl, phenanthroline and α-pyridinecarboxylic acid complexes already mentioned above, and such close similarity makes it highly probable that

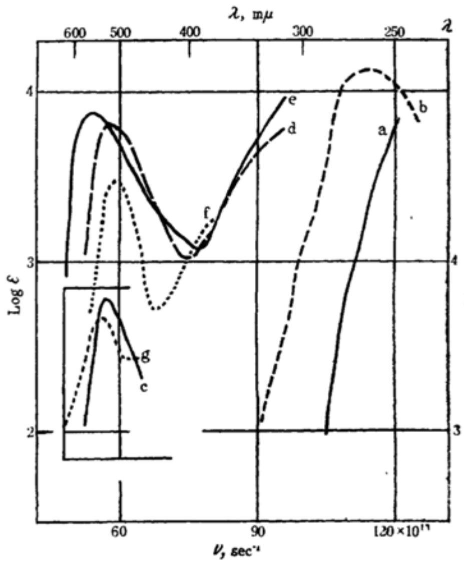


Fig. 2.—(a)∼(b), dimethylglyoxime, (a) in alcohol and (b) in 0.05 *N* KOH; (c)∼(f) Fe^{++} (0.00025 *M*) + DH_2 (0.0025 *M*), (c) $+NH_3$ (0.015 *M*), (d) $+N_2H_4$ (0.05 *M*), (e) +en (0.015 *M*) and (f) +pyridine (0.015 *M*); (g), $Ni(DH)_2$ colloidal solution (Juza).

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(8) Cambi, *Gazz. chim. ital.*, **63**, 767 (1393).

all of such bands are of similar origin in their electronic systems.

As is well known, the color of the nickel dimethylglyoxime complex is red unlike many nickel complex salts. Absorption spectra of this complex have never been reported, probably owing to its small solubility in ordinary solvents; however, the absorption curve of its colloidal solution reported by Juza⁽⁹⁾ shows a band at *ca.* 530 mμ, which is analogous to that of ferrous complexes. This phenomenon may be connected with the fact that both the nickel atom in planar configuration and the ferrous iron atom in octahedral configuration postulated by Tschugaeff contain the same number of electrons, and they are both diamagnetic,⁽⁸⁾ suggesting that their electronic states are much alike. Dimethylglyoxime complexes of other metals, such as Co^{III} and Cu, were known to show no similar bands.⁽¹⁰⁾

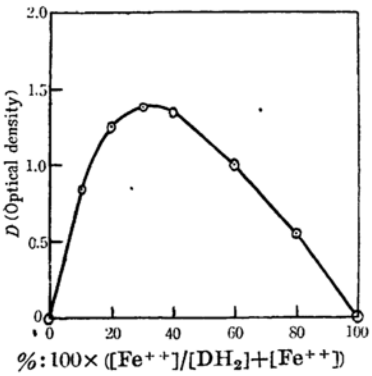
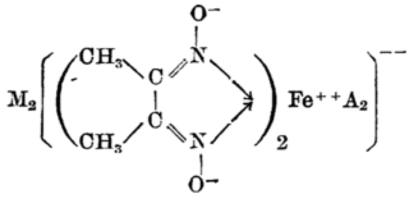


Fig. 3.—Composition curve for dimethylglyoxime-hydrazine complex; Pulfrich photometer, filter S47, $d=1$ cm., $[DH_2]+[Fe^{++}]=0.0025\,M$ in $0.05\,M$ N_2H_4.

In addition to these spectral measurements, the author tried to test the validity of Tschugaeff's formula (V) or other possible structures for these complexes. The combining ratio Fe:DH determined by Job's method⁽¹¹⁾ was 1:2 (Fig. 3). However, additions of nitrogen-bearing bases are necessery for coloration, and the position of a visible band depends definitely on the nature of the base. These facts suggest the coördination of the base to the central iron atom; as the coördination number of ferrous iron is usually six, the number of base molecules coördinated to an iron atom can be supposed to be two. Therefore, Tschugaeff's formula (V) seems to be in accord with these spectrochemical observations; however, the recent observation of Mathews and Diehl⁽¹²⁾ that the analogous complex with 1, 2-cyclohexanedionedioxime has a negative charge in its solution is incompatible with this structure and it supports Feigl's formula. The author's opinion is that the complex has some intermediate structure, such as (VII),

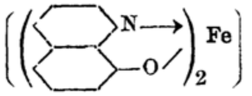


VII (M=H or cations)

which can explain all of these experimental evidences. The recent data of Mellon and Griffing⁽¹³⁾ on the spectra of these complexes are in general agreement with ours.

Color Reaction with 8-Hydroxyquinoline

Most of the complex salts formed by 8-hydroxyquinoline with bivalent metals are yellow, orange or yellowish green in color, showing strong absorption bands in the region of 370∼430 mμ with molecular extinction coefficients of several thousands; however, bands of comparable strengths are only rarely seen in the visible region.⁽¹⁴⁾ From the fact that the ferrous complex is red in color,⁽⁵⁾ it can be expected that some sort of special absorption band appears in the visible region also in this case. The author found that the ferrous complex precipitated from a weakly alkaline solution is reddish violet in color; however, this complex is very easily oxidized in air, like the dimethylglyoxime complexes, and changes into dirty black when brought in contact with air. It remains unchanged only in the mother solution containing strong reducing agents, *e. g.* hydrosulfite. Therefore the confirmation of its structure is extremely difficult, although it seems to be very probable that it has the structure (VIII) analogous



VIII

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(9) Juza, R. Langheim, "Physikalische Methoden im Chemischen Laboratotium", 1937, p. 250; *Angew. Chem.* **50**, 255 (1937).

(10) H. S. French and H. E. Acly, *J. Amer. Chem. Soc.*, **48**, 847 (1927) (Cu complex); R. Tsuchida *et al.*, This Bulletin, **12**, 83, 350 (1937) (Co complexes).

(11) P. Job, *Ann. chim.*, (10) **9**, 113 (1928).

(12) J. Mathews and Jr., H. Diehl, *Iowa State Coll. J. Sci.*, **23**, 279 (1949).

(13) M. Griffing and M. G. Mellon. *Anal. Chem.*, **19**, 1017 (1947).

(14) K. Sone, unpublished results.

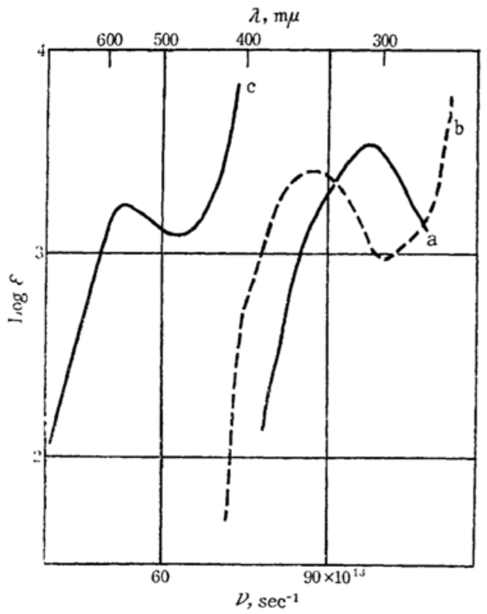
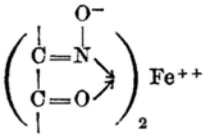


Fig. 4.—(a)∼(b), 8-hydroxyquinoline, (a) in alcohol and (b) in 0.2 *N* KOH; (c), Fe^{++} (0.0003 *M*) +8-hydroxyquinoline (0.005 *M*) + KOH (0.2 *N*).

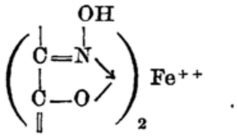
to the other metallic 8-hydroxyquinolinates precipitated under the same condition. The measurement of its absorption spectra is also difficult, and Fig. 4 (c) is that of a metastable solution of this complex produced by mixing dilute solutions of ferrous sulfate and 8-hydroxyquinoline with a large exess of the latter, which is stable for several hours in the presence of a small amount of hydrosulfite. Compared with the absorption curves of 8-hydroxyquinoline in neutral and alkaline solutions and the curves of metallic 8-hydroxyquinolinates mentioned above, it is clear that a new kind of absorption band appears at 560 mμ by the formation of this ferrous complex, the strong end absorption of its curve being due to the 8-hydroxyquinoline molecules present in excess.

Color Reaction with α-Nitroso-β-naphthol and Nitroso-R Salt

Organic compounds containing the group —C(NOH)—CO—, or the tautomeric group —C(NO):C(OH)— are known to produce blue coloration with the alkaline solutions containing ferrous ion, and complexes such as (IXa) or (IXb) are supposed to be responsible for these colors.



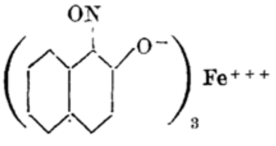
IXa



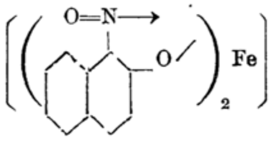
IXb

Preliminary observations on isonitrosoacetone and isonitrosoacetacetic ester, the simplest compounds containing this group, revealed that the ferrous complexes of these substances possess a new strong absorption band at *ca.* 600 mμ, which is also quite different from the ligand absorption.

The same kind of reactions are observed also by aromatic compounds, and *o*-nitrosophenol and α-nitroso-β-naphthol are known to give green complexes. The latter substance and its sulfonate derivatives were studied earlier by Hoffman and Ilinsky and more recently by Sarver, Griffith and Ségal⁽¹⁵⁾. Although Hoffman considered the origin of color to be a ferric salt of the type (Xa), other authors preferred the formula (Xb) which, according to their experimental evidences, contains ferrous ion.



Xa



Xb

The present author studied the ferrous complex of α-nitroso-β-naphthol in ethyl acetate solution⁽¹⁶⁾, and found that it has a strong visible band which is again quite different from the ligand absorption. The curve Fig. 5 (a) and (b) shows respectively the absorption spectra of α-nitroso-β-naphthol in alcoholic and alkaline solutions. In addition to the strong band at 370∼385 mμ, a weak band appears in the latter curve at *ca.* 570 mμ. However, when the green precipitate formed

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(15) O. Hoffmann, *Ber.*, **24**, 3741 (1891); M. Ilinsky and G. v. Knorre, *ibid.*, **18**, 2728 (1885); Sarvar, *Ind. Eng. Chem., Anal. Ed.*, **10**, 378 (1938); M. Griffing, M. G. Mellon, *Anal. Chem.* **19**, 1014 (1947); J. Ségal *Compt. rend.*, **227**, 1266 (1948).

(16) *Cf.* R. Vanossi *Anales soc. cient. argentina*, **131**, 226 (1941).

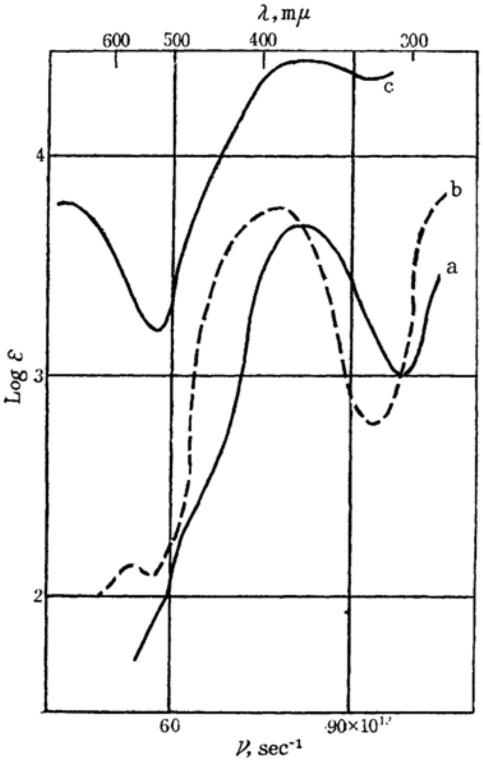
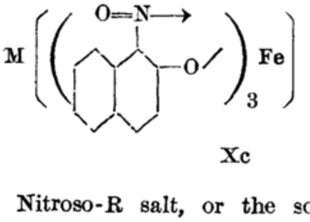


Fig. 5.—(a) ∼ (b), α-nitroso-β-naphthol, (a) in alcohol and (b) in 0.2 *N* KOH; (c), ethyl acetate extract of ferrous complex, containing 0.000055 *M* of Fe^{++}, the initial mixing ratio of Fe^{++} to reagent being 1:6.

by the action of excess amounts of α-nitroso-β-naphthol with ferrous sulfate in weakly alkaline solution was extracted by ethyl acetate and the absorption spectra of the extracted solution was measured, a very strong band was found to appear in the neighborhood of 700 mμ, and although this complex is gradually oxidized in air changing into a black substance, It was found by rapid measurements that this new band attains its maximum absorption when about 3 moles of α-nitroso-β-naphthol are mixed with one mole of ferrous ion. Therefore the structure of this substance seems to be of hexacoördinated type, such as (Xc), instead of the conventinal formula (Xb) used by previous investigators.



(M = H or cations)

Xc

Nitroso-R salt, or the sodium salt of α-nitroso-β-naphthol-3,6-disulfonic acid, produces green soluble complex which is very stable even after standing for many hours. The characteristics of the absorption spectra of this complex are quite similar to those of α-nitroso-β-naphthol, the absorption of the new band becoming still stronger. Owing to the higher stability of the colored solution, the

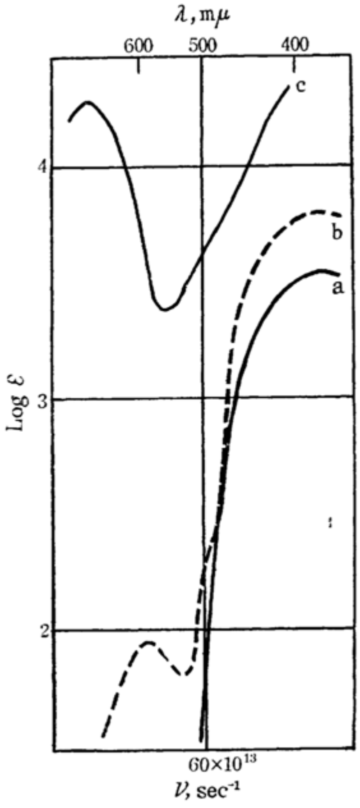


Fig. 6.—(a) ∼ (b), nitroso-R salt, (a) in H_2O and (b) in 0.2 *N* KOH; (c), Fe^{++} (0.0001*M*) +nitroso-R salt (0.0003 *M*) +NaOAc (0.05*M*).

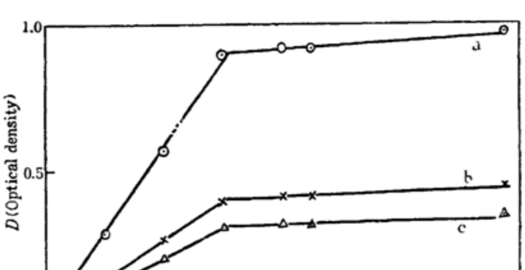
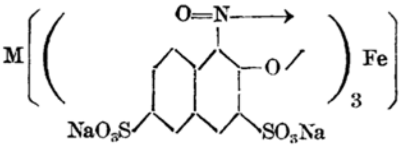


Fig. 7.—"Molar ratio" curve for nitroso-R salt complex; Pulfrich photometer, filter (a) S61, (b) S57, (c) S53, $d=1$ cm., Fe^{++} (0.00011 *M*) +nitroso-R· salt (variable amt.) in 0.05 *M* NaOAc.

exact determination of the composition of the colored complex becomes possible in this case, with the result that the molar ratio of ligand to iron is 3:1, as in the case of α-nitroso-β-naphthol, showing the validity of analogous hexacoördinated formula (XI) in this complex (Figs. 6 and 7). Recent data of Griffith *et al.* agree fairly well with the author's.



XI

Discussion

From the experimental results described above, it seems to be fairly clear that, although the structure of these complex salts are different, all of them show a strong absorption band in the visible region, with maximum wave-lengths ranging from 500 to 720 mμ and log $\mathcal{E}$ of 3∼4, which cannot be attributed to the ferrous ion or to the organic ligand molecules. They are only rarely observed in the complexes of other metals with these ligands and are therefore quite characteristic of these ferrous complexes studied (*cf.* Table 1).

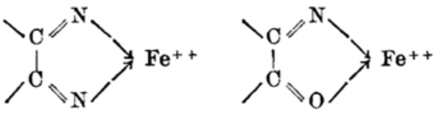
Table 1

Reagent	Probable structure of the complex	Absorption, maximum mμ	Absorption, maximum log ε*
2, 2′-dipyridyl	(I)	520, 352	3.8
1, 10-phenanthroline	(II)	510	3.9
α-pyridine carboxylic acid and derivs.	(III), (IV)	500∼560	2.5∼3**
dimethylglyoxime			
+NH_3		525	3.8
+N_2H_4	(V), (VI) or	520	3.8
+en	(VII)	550	3.9
+pyridine		510	3.5
8-hydroxyquinoline	(VIII)	560	3.2
isonitrosoacetone and derivs.	(IX)	ca. 600	
α-niroso-β-naphthol	(Xc)	ca. 700	3.8
nitroso-R salt	(XI)	720	4.3

* Molecular extinction coefficients of the complexes were calculated for one mole of ferrous ion.

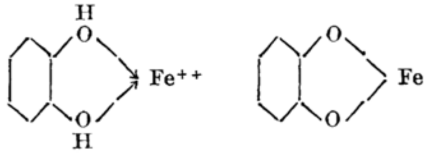
** Estimated values from the data of Ley *et al.*

From the examination of the probable structures of these complexes it becomes evident that some sort of unsaturated five-membered ring formation, such as (a) or (b), occurs in all of them in common.



a b

Of course, the positions of double bonds in these rings may be variable owing to the resonance effects. Therefore the existence of such an intramolecular ring can be assumed as a sort of chromophore which produces this kind of new absorption band. Thereby the unsaturated state of the whole ring, that is to say, the possibility of resonance of the π-electrons over all four non-metallic atoms composing the ring, seems to be essential for the color, because ethylenediamine does not form such a colored complex and 8-aminoquinoline, which has a similar structure with 8-hydroxyquinoline, only produces yellow ferrous complex⁽¹⁷⁾ which may be due to the fact that their NH_2 groups become saturated with the coördination to the iron and therefore they are impossible to participate in the resonating system. It may be added that the violet compounds produced by *o*-diphenols and analogous polyphenols (*cf.* Introduction) with ferrous ion may contain an intramolecular ring of similar structure (c-1) or (c-2).



c-1 c-2

Similar chromophore action of an intramolecular organometallic ring was formerly observed by Willis and Mellor⁽¹⁸⁾ in the case of diamagnetic nickel complexes, and the ferrous complexes reported in this study might be regarded as its second example. In the case of nickel complexes a close relation was found between the magnetic properties of the complexes and the appearance of a new absorption band; however, no definite relation can be found by ferrous complexes, as the band appears in both para- and diamagnetic complexes.⁽⁸⁾

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(17) G. J. Burrows and E. Ritchie, *J. Proc. Roy. Soc. New South Wales* **72**, 113 (1939).

(18) Willis and Mellor, *J. Amer. Chem. Soc.*, **69**, 1237 (1947).

Experimental

Reagents.—Mohr's salt of extra pure grade was used as the source of ferrous ions. All the organic reagents are analysis grade samples and, when necessary, were purified by repeated recrystallization.

Preparation of Samples.—In the preparation of sample solutions with dimethylglyoxime and 8-hydroxyquinoline, a minute amount of hydrosulfite crystalls was added to the solutions, except in the case of the hydrazine complex to prevent air oxidations. Sample solutions of α-nitroso-β-naphthol were prepared by mixing the alcoholic solution of the organic reagent and aqueous solution of Mohr's salt in a 10% solution of sodium acetate, and by rapidly extracting the formed precipitate with ethyl acetate.

Spectral Measurements.—Measurements of absorption spectra were made by a Spekker spectrophotometer combined with a medium quartz spectrograph. A Pulfrich photometer was also used in the visible region. The measurements on nitroso-R salt were made with the Beckman DU spectrophotometer which was put at our disposal in the later stage of this study.

Summary

Absorption spectra of colored complex salts formed by ferrous ion with dimethylglyoxime, 8-hydroxyquinoline, α-nitroso-β-naphthol and nitroso-R salt were studied. The origin of a strong absorption band in the visible region in all of these complexes was attributed to the formation of unsaturated intramolecular five-membered rings. Determination of the composition of the complexes was made spectrophotometrically in the case of dimethylglyoxime, α-nitroso-β-naphthol and nitroso-R salt.

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