# *Magnetic and Spectrophotometric Studies on Decoloration of Thiocyanato Iron(III) Complexes in Solutions. I*

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The reaction between iron(III) and thiocyanate ions has been studied in detail by many authors for more than 30 years. Despite the vast experimental data thus accumulated, no decisive conclusion seems to have been drawn as to the nature of the species which exist in the solutions. In 1953, reviewing all the reports ever published, S. Z. Lewin et al.[1] have shown the following series of equilibria as the basis upon which all of the experimental evidences can be correlated.

$$Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+} \tag{1}$$

$$FeSCN^{2+} + SCN^- \rightleftharpoons Fe(SCN)_2^+ \tag{2}$$

$$Fe(SCN)_2^+ + SCN^- \rightleftharpoons Fe(SCN)_3 \text{ or } [1/2Fe_2(SCN)_6] \tag{3}$$

$$Fe(SCN)_3 + SCN^- \rightleftharpoons Fe(SCN)_4^- \tag{4}$$

and probably also:

$$Fe(SCN)_4^- + SCN^- \rightleftharpoons Fe(SCN)_5^{2-} \tag{5}$$

$$Fe(SCN)_5^{2-} + SCN^- \rightleftharpoons Fe(SCN)_6^{3-} \tag{6}$$

On the other hand, in the field of chemical analysis the color reaction between iron(III) and thiocyanate ions has long been used as a proof of the existence of iron(III) ions, as well as being used as the procedure of its quantitative determination. However, in the abovementioned solutions there exists a gradual color change with time, which makes the quantitative measurements somewhat difficult. And indeed the explanation of this change itself is still in question. In 1952, Hiraki et al.[2] from the spectrophotometric measurements with a Dubosk spectrophotometer, reported that the fading of color is caused by the reduction of iron(III) to iron(II) by thiocyanate ions. If this reaction did exist, there should be a change of magnetic susceptibility of the solutions as the fading of color proceeds. Thus, the decoloration mechanism of the solutions is one of the most interesting subjects to be clarified in the field of magnetochemistry. In this paper were summarized the measurements of the magnetic susceptibility and the visible absorption spectra during the decoloration.

## Experimental

**Materials.**—Iron solution: A given amount of Mohr's salt was dissolved in distilled water containing several drops of conc. sulfuric acid. Adding a small amount of hydrogen peroxide (30%) in order to oxidize iron(II) to iron(III), the solution was heated on a water bath to expel the excess of hydrogen peroxide. After cooling, the solution was diluted to exactly 0.05 M with distilled water.

Potassium thiocyanate: The reagent of analytical grade was dissolved and diluted to 0.5 M with distilled water. The solution obtained was completely colorless and its test by $\alpha \cdot \alpha'$-dipyridyl was also negative. Therefore, neither iron(III) nor iron(II) ions can exist in our prepared solution.

Hydrochloric acid: The hydrochloric acid was purified by distillation until it gave a negative test for iron.

Sample solution: The solution to be measured was prepared by adding a given amount of hydrochloric acid and potassium thiocyanate to the iron stock solution and then was diluted to the desired concentrations.

**Measurements.** — The magnetic susceptibility of the solutions was measured from time to time during the decoloration by the torsion magnetometer with fused silica[3].

Absorption spectra were determined by a Beckman Model DU Spectrophotometer. Matched 10 mm. silica cells with quartz 9.5 mm. thick were used; this gave an effective optical path of 0.5 mm.

## Experimental Results

**Magnetic Data.**—The magnetic moments in Bohr magnetons for total iron in the solutions of thiocyanato iron(III) and thiocyanato iron(II) complexes are shown in Table I. The magnetic moment is calculated from the formula $\mu = 2.84\sqrt{\chi \times T}$ where $\chi$ is the susceptibility per gram atom of total iron in the solutions and $T$ the absolute temperature[4]. Here, any magnetic interaction is neglected, since all of the solutions are magnetically dilute. Fig. 1 shows

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[1] S. Z. Lewin and R. S. Wagner, *J. Chem. Educ.*, No. 9, 445 (1953).

[2] Y. Hiraki, K. Tamura and M. Katumi, *Sci. Repts. Saikyo Univ.*, 1, 19 (1952).

[3] H. Takaki, N. Kawai, C. Miyake and T. Morita, *J. Phys. Soc. Japan*, 13, 629 (1958).

[4] J. H. Van Vleck. "The Theory of Electric and Magnetic Susceptibilities", Oxford University Press, Oxford (1932), p. 282.

TABLE I. MAGNETIC MOMENTS OF IRON IN BOTH THIOCYANATO IRON(III) AND THIOCYANATO IRON(II) COMPLEXES N HYDROCHLORIC ACID SOLUTIONS*,**

| Magnetic moment(Bohr magneton) | |
|---|---|
| Iron(III) | Iron(II) |
| 5.92 | 5.45 |
| 5.91 | 5.46 |
| 5.91 | 5.44 |

* 0.05 M thiocyanato iron(III) complex, 0.12 N hydrochloric acid solution.

** All of the measurements were made fifteen minutes after the solutions were prepared.

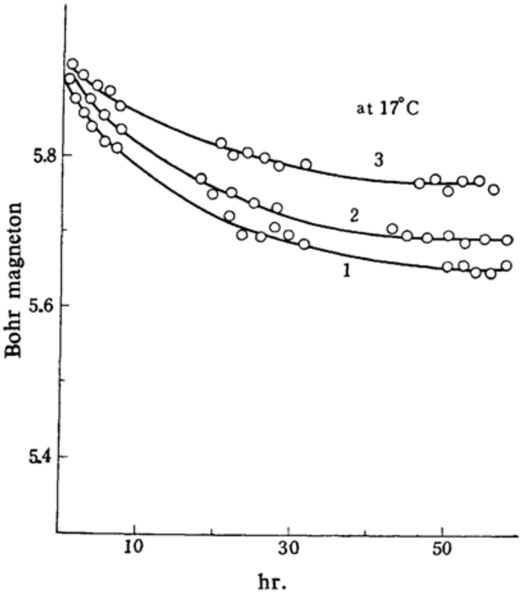

Fig. 1. Dependency of decrease in magnetic moment of iron upon concentration of hydrochloric acid. (0.005 M iron(III), 0.05 M thiocyanate ion solutions).
1 : 0.012 N HCl 2 : 0.12 N HCl
3 : 1.2 N HCl

the decrease in magnetic moment of the solutions with varying concentrations of hydrochloric acid, when the amount of thiocyanate ions in the solutions are held constant. Fig. 2 represents the similar decrease with varying concentrations of thiocyanate ions.

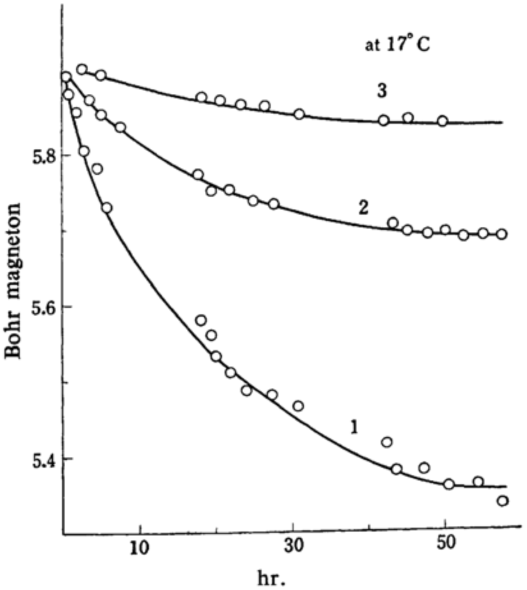

Fig. 2. Dependency of decrease in magnetic moment of iron upon concentration of thiocyanate ions. (0.005 M iron(III), 0.12 N hydrochloric acid solutions).
1 : $[Fe(III)]/[NCS^-]=1:100$
2 : 〃 $=1:10$
3 : 〃 $=1:0.14$

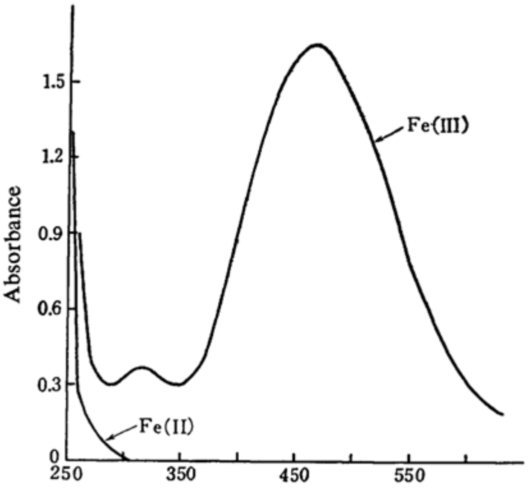

Fig. 3. Absorption spectra of thiocyanate iron(III) and thiocyanato iron(II) complexes in hydrochloric acid solutions.

**Spectrophotometric Data.**—Fig. 3 shows the spectral curve of thiocyanato iron(III) complexes and that of thiocyanato iron(II) complexes in hydrochloric acid solutions. Of all the present absorption measurements, some representative curves of thiocyanato iron(III) complexes with varying concentrations of thiocyanate ions are shown in Fig. 4. The maxima of the absorbance at about 470 mμ due to thiocyanato iron(III) complexes shift to the region of longer wave length. This bathochromic effect may be attributed to the increase in ratio of the number of coordinated thiocyanate ions to that of coordinated chloride ions. At the same time, the absorbances at the maxima increase with increasing concentrations of thiocyanate ions. The other absorption maxima at about 320 mμ are probably due to chloro iron(III) complexes as shown

TABLE II. EFFECTS OF CONCENTRATIONS OF BOTH HYDROCHLORIC ACID AND THIOCYANATE IONS TO ABSORBANCES AT ABOUT 470 mμ AND 320 mμ

| | Increase of $[\mathrm{NCS}^-]$ | Increase of [HCl] |
|---|---|---|
| | Absorbance at about 470 mμ | |
| Wavelength of max. absorbance | bathochromic | constant* |
| absorbance | increase | decrease* |
| Rate of decrease in absorbance | increase | decrease |
| | Absorbance at about 320 mμ | |
| Wavelength of max. absorbance | bathochromic* | bathochromic |
| absorbance | decrease* | increase |
| Rate of decrease in absorbance | constant* | decrease |

* The absence of notable effect.

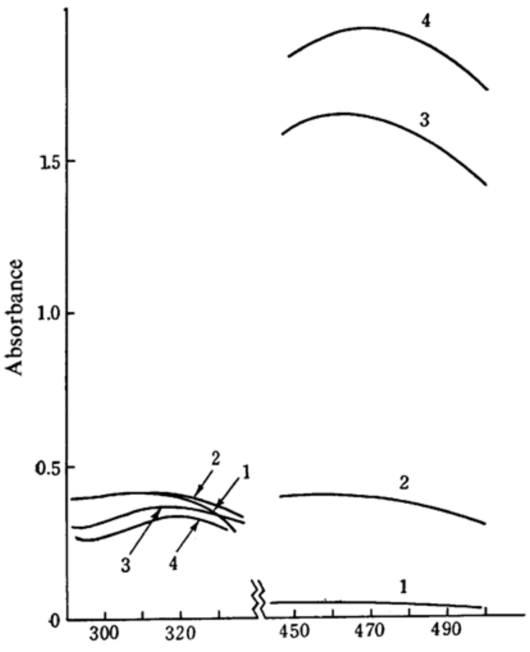

Fig. 4. Absorption spectra of thiocyanato iron(III) complex solutions with varying concentration of thiocyanate ions. (0.005 M iron(III), 0.12 N hydrochloric acid solutions).
1 : 0.0005 M, 2 : 0.005 M, 3 : 0.05 M, 4 : 0.7 M

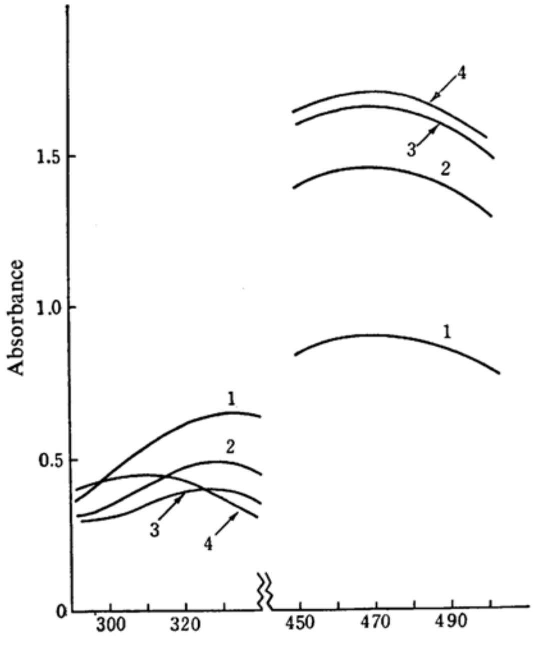

Fig. 5. Absorption spectra of thiocyanato iron(III) complex solutions with varying concentration of hydrochloric acid. (0.005 M iron(III), 0.05 M thiocyanate ion solutions).
1 : 3.6 N, 2 : 1.2 N, 3 : 0.6 N, 4 : 0.12 N

in Fig. 5.5) In Table II, the results of spectrophotometric measurements are summarized. Here, it seems to be of importance for the following discussion to compare the time-change in magnetic moment (already shown in Figs. 1 and 2) and the similar change in absorbance at about 470 mμ (shown in Fig. 6).

## Discussion

Before going directly into the discussion, the following remarks seem to be necessary.

The magnetic measurement is quite useful and important for determining the electronic spatial configuration in the complex containing transition element. For example, if the complex be assumed to have the inner orbital type of binding, then the 3d-electrons of iron(III) ion are necessarily paired, leaving only one residual electron to be unpaired, giving 1.7 Bohr magnetons (theoretical) to the complex. But on the other hand, when the complex has a binding of the so-called outer orbital type, all of the 3d-electrons of iron(III)

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5) M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi and T. Kitagawa, This Bulletin, 30, 433 (1957).

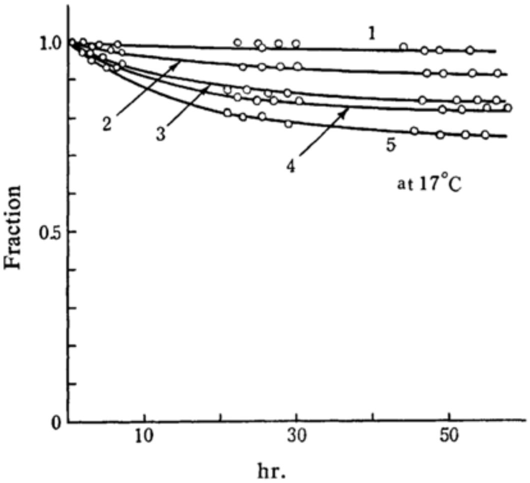


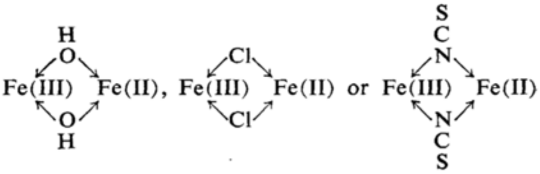
Fig. 6. Decrease of absorbances with time at about 470 m$\mu$ of ferric thiocyanate solutions.
1: corresponds to 3 in Fig. 2
2: 3 in Fig. 1
3: 2 in Figs. 1 and 2
4: 1 in Fig. 1
5: 1 in Fig. 2

ion are left unpaired, thus giving 5.9 Bohr magnetons (theoretical). In case of iron(II), the complex with the inner orbital type has no magnetic moment and that with the outer orbital type has 4.8 Bohr magnetons (theoretical), respectively. The number of unpaired electrons $n$ of complex can generally be calculated from the magnetic measurements by the formula $\mu=\sqrt{n\times(n+2)}$.

The present magnetic observations which are shown in the preceding section and tabulated in Table I, show that thiocyanato iron(III) complex has five unpaired electrons and thiocyanato iron(II) complex four unpaired electrons, both belonging to the outer orbital type of binding. If the decoloration depends upon the simple reduction of iron(III) to iron(II) by thiocyanate ions, it is required that the magnetic moment decreases by 0.47 Bohr magneton and completely reduced solutions become colorless. This is evident from Fig. 3 in which it is shown that the iron(II) has no absorption in the region of visible light.

Although the magnetic data in Figs. 1 and 2 seem to support the idea that the above-mentioned simple reduction had actually been taking place, the spectrophotometric data are not favourable, because the absorbances at 470 m$\mu$ are still greater even after the decrease of the magnetic moment. In order to harmonize the above-mentioned discrepancy there must be another scheme by which all of the obtained data can be consistent. If we assume that the iron(II) ion already reduced in the solutions and the iron(III) ion still remaining were combined through the bridges of hydroxo ions, chloride ions or thiocyanate ions, and also that they were formed in the so-called "binuclear complex" or "dimer", whose unpaired electron is single, the reduction of the magnetic moment in solution and the amount of the remaining color may be plausible, despite the fact that a question still remains whether or not the free iron(III) ion and that combined into the dimer have the same absorbance character in the region of visible light.

The probable formula of the dimer is considered to be one of the following three types:



The study of the problem concerning the determination of the actual type existing in the present solutions must be continued. However, a series of reactions up to the above-mentioned formation of dimer, seems to be initiated in any way by the partial reduction of iron(III) to iron(II) as has already been stated. This argument is directly proved in Figs. 1, 2 and 6, which indicate that the solution with greater decrease in magnetic moment shows a greater decreases in absorbance. At the same time, we can say from the figures that both the decoloration and demagnetization with time proceed almost proportionally to the concentration of thiocyanate ions and inversely proportionally to the acidity of the solutions (hydrochloric acid). The acidity is generally considered to suppress the power of reduction of thiocyanate ions[6]. These tendencies are shown in Table II.

On the basis of the formation of the dimer which the present author has proposed, both the magnetic and spectrophotometric data are summarized in the following way. In the formation of the dimer which we supposed to have the inner orbital type of binding, five unpaired electrons of the original iron(III) ion and six electrons of iron(II) ion are paired with each other, leaving in the dimer only one unpaired electron. The number of the unpaired electrons thus reduced, hence the reduction of magnetic moment, is quite large. Therefore, we can say that the number of the originally unpaired electrons of 2×Fe(III),

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6) G. Charlot, "L'analyse qualitative et les réactions en solution", Masson et C$^{ie}$ (1957), p. 334.

ten, are reduced and finally only one unpaired electron is left in the dimer.

Supposing that $\alpha$-fractions of iron(III) in the original solutions are reduced to iron(II) and converted into the 1 : 1 dimer with iron(III), the final number of the unpaired electrons in the dimer is given by

$$5\times(1-2\alpha)+\alpha=5-9\alpha \tag{1}$$

and the corresponding theoretical magnetic moment by

$$\{5.92^2\times(1-2\alpha)+1.73^2\times\alpha\}^{1/2} \tag{2}$$

In the above relation only the spin contribution to the magnetic moment is taken into consideration and at the same time for simplicity's sake, the true equilibrium conditions in the formation of the dimer is ignored.

On the other hand, the spectrophotometric fractional absorbances of the solutions can be expressed by

$$\varepsilon\times(1-\alpha) \tag{3}$$

where $\varepsilon$ is the molar extinction coefficient. Here, the difference of the extinction coefficient between free iron(III) and iron(III) in the dimer are again neglected. The present results of measurements so far obtained seem to show a good agreement with the above relations (2) and (3).

Werbel et al.[7], in their results for the same substance using 0.06 M thiocyanato iron(III) complex in 1.9 M perchloric acid solution, have reported that the magnetic moment of 5.88 Bohr magnetons was obtained about one hour after its preparation and that about one percent of the total amount of iron(III) originally present was converted into iron(II). They have also pointed out that the magnetic moment of thiocyanato complex is too small to account for the reaction due to simple reduction from iron(III) to iron(II), because of the too small difference in magnetic moment between them. The result obtained by Werbel et al. seems, however, to be quite reasonably explained on the present consideration of the existence of dimer.

## Summary

The decoloration mechanism of thiocyanato iron(III) complex solutions was investigated by means of both the magnetic and spectrophotometric methods. The data for the magnetic measurements supported that the decoloration was caused by the simple reduction of iron(III) to iron(II) by thiocyanate ions. But such a simple model of the reduction was not favourable for the observed decoloration, because the decrease in the absorbance was too small, being only about twenty percent. In order to eliminate this discrepancy, another scheme was proposed, which ascribes the magnetic and spectral observations to the formation of a binuclear complex of iron(III) and iron(II), a so-called dimer, during the decoloring reaction. This dimer possesses only one unpaired electron and accordingly very small magnetic moment, but possesses the significant absorbance due to iron(III). On this model, the greater decrease in magnetic moment and the rather smaller decrease in absorbance which we obtained, were quite satisfactorily clarified.

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[7] B. Werbel, V. H. Debeler and W. C. Vosborgh, *J. Am. Chem. Soc.*, 65, 2329 (1943).