Magnetic and Spectrophotometric Studies on the Decoloration of Thiocyanatoiron(III) Complexes in Solutions. III. Structure of Thiocyanatoiron(III) Complex in Organic Solvents

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The present writer has reported the nature of the reaction between iron(III) ion and thiocyanate ions in aqueous solution in detail[1,2]. The experimental data obtained so far are rather consistently explained when we consider hypothetically the formation of a dimer containing iron(II) and iron(III) coupled by hydroxo bridges during the course of chemical reaction. However, there still remains a question whether the magnetic time change we observed is attributable to the above-mentioned dimer, or to the higher complexes, such as $Fe(NCS)_2{}^+$, $Fe(NCS)_3$, $Fe(NCS)_4{}^-$,…, which are formed by the prolonged replacement of the coordinated H_2O, Cl^- ion etc. of the preexisting complexes with thiocyanate ions whose binding is of the so-called inner orbital type. In order to elucidate this, it is necessary at least to extract a definite species of complex having a known chemical formula by using an organic solvent and then to measure its magnetic property, because in the aqueous solution there are so many species of complexes, as shown in the previous paper[1], that it is difficult to consider which species is responsible for the measured magnetism and absorption. This paper deals with the results of measurements and the inferred structure of thiocyanatoiron(III) complex extracted by organic solvent.

Experimental

Materials. — Ferric perchlorate was prepared by dissolving an appropriate amount of electrolytic iron in perchloric acid (about 4 N), oxidizing with hydrogen peroxide (30%), and evaporating the solution until crystals appeared. After perchloric acid was added to dissolve the deposit, the solution was evaporated again. The procedure was repeated until the solution gave a negative test for chloride and iron(II) ions. Violet crystals separated on cooling were filtered off with a sintered glass filter and recrystallized twice from distilled water. The stock solution of iron was prepared by dissolving the crystal of ferric perchlorate in water to the concentration of 1000 p. p. m.

The peroxides were removed from ether by shaking with a solution of ferrous sulfate acidified with sulfuric acid, until the organic phase no longer gave the test for peroxides and then the ether was purified by distillation.

Ethyl acetate used was of analytical grade.

Extraction of thiocyanatoiron(III) complex was carried out by adding the proper amount of potassium thiocyanate and shaking the iron solution with a given volume of organic solvent. After standing the whole solutions for fifteen minutes, the organic phase was separated from the aqueous solution.

Measurements.—Magnetic and spectrophotometric measurements were made as described previously[1].

Results and Discussion

The magnetic moment for total iron in the ether solution of thiocyanatoiron(III) complex was found to be 6.0 Bohr magnetons. This value indicates that thiocyanatoiron(III) complex in the organic phase possesses a magnetic moment corresponding to five unpaired electrons, showing the outer orbital type of binding. Fig. 1 shows the spectral curve of the complex in organic solvents, such as ether or ethyl acetate. The absorption maximum found at 511 mμ is slightly longer in wavelength as compared to the already reported value of the complexes having one or two thiocyanate ions in term.

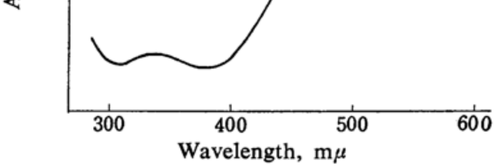

Fig. 1. Absorption spectrum of thiocyanato-iron(III) complex in ethyl acetate.

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1) C. Miyake, This Bulletin, 33, 867 (1960).

2) C. Miyake, ibid., 34, 471 (1961).

As to the constitution of extracted thiocyanatoiron(III) complex, no definite conclusion can be drawn as yet relating to the ratio of thiocyanate ions to iron in the complex. Babko[3] has reported the existence of $HFe\cdot(NCS)_4$ in an ether phase analogously to $HFeCl_4$ [4]. Other authors have postulated a complex having the chemical formula of $Fe(NCS)_3$ [5-8]. In our attempt to determine the ratio by gravimetric analysis of iron and sulfur as ferric oxide and barium sulfate, respectively, the values obtained are ranged over 3 to 4, the mean value being 3.6. On the other hand, repeated attempts were made to prepare crystalline thiocyanatoiron(III) complex by the evaporation of organic solutions. In no case was a pure product obtained, as the product always contained an insoluble residue whose magnetic moment was slightly smaller than that expected for a complex having five unpaired electrons. These problems are going to be studied in our laboratory and will be reported in the future. But, at least it is clearly concluded that what was extracted by the organic solvent was a higher complex possessing three or four thiocyanate ions in it. The fact that the absorption maximum in the ether phase shifts to longer region than that in the aqueous solution, that is, about 470 mμ to 511 mμ, supports the existence of the higher complex in the organic phase, when we take into account the bathochromic effect due to the increase of thiocyanate ions in the complexes.

Thus, the remarkable time change of the magnetic moment of thiocyanatoiron(III) complexes which we confronted in the aqueous solution and reported previously can be attributed to the dimer possessing hydroxo bridges and the inner orbital type of binding with the smaller magnetic moment.

Summary

Thiocyanatoiron(III) complex was extracted by organic solvents. The magnetic moment of the complex was found to be 6.0 Bohr magnetons which is characteristic of the iron(III) complexes possessing the outer orbital type of binding. The absorption spectrum in the visible region of the complex shows the maximum of absorbance at 511 mμ.

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3) A. K. Babko, *Chem. Abstr.*, **51**, 4121 *b* (1957).

4) R. J. Myers, D. E. Metzler and E. H. Swift, *J. Am. Chem. Soc.*, **72**, 3767 (1950).

5) J. Y. McDonald, K. M. Mitchell and A. T. S. Mitchell, *J. Chem. Soc.*, **1951**, 1574.

6) K. M. Mitchell and J. Y. McDonald, ibid., **1951**, 1310.

7) L. Melnik, H. Fraser and H. F. Beeghly, *Anal. Chem.*, **25**, 867 (1953).

8) A. Okáč and M. Hniličková, *Collection Czechoslov. Chem. Communs.*, **25**, 68 (1960).