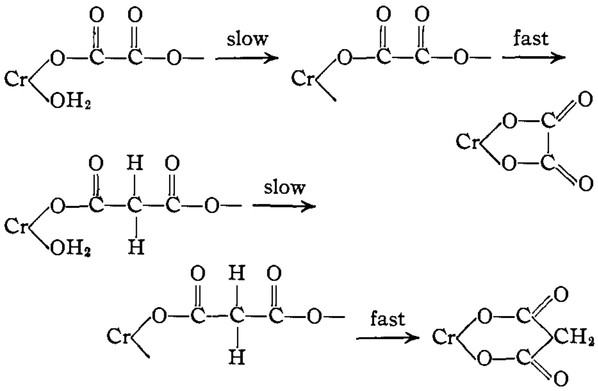
The various reactions reported in this investigation were studied over a range of temperatures from 10 to 40°. The values of K used for calculation ranged from 0.6×10^{-6} at 10° to 3.0×10^{-6} at 40°, as a result of determinations of the pH dependence at these temperatures. The results were plotted according to the theory of absolute reaction rates, and the heats of activation and entropies of activation shown in Table III were calculated.

TABLE III

	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, cal./deg. mole
$Cr(H_2O)_6^{+++} + Mal^{=}$	22.4	3.3
$Cr(Mal)(H_2O)_4^{+} + Mal^{=}$	23.1	4.4
$Cr(Mal)_2(H_2O)_2^{-} + Mal^{=}$	26.0	−5.1
$Cr(Ox)_2(H_2O)_2^{-} + Ox^{=}$	22.6	4.2

The heats of activation and entropies of activation for the first two chelation steps shown in Table III are not experimentally different from those previously obtained on similar reactions using oxalate. This may indicate that the actual slow step is identical and independent of the chelating agent. This would be the situation if the slow step being measured with the dissociation of a water molecule followed by a relatively rapid step which would be the formation of the ring.

By this mechanism the slow step would be nearly identical since the number of atoms in the final chelate ring would have little or no effect on the slow step. Plane and Taube[8] obtained 24 ± 2 kcal./mole for the heat of activation for water exchange. Our measurements are in agreement, and indicate dissociation as a possible mechanism of water exchange



The values obtained for the third step of chelation were sufficiently different that considerable difference in the nature of the third step was indicated when malonate was reacting. This may have been caused by the steric difficulty in forming the third six-membered ring around the central chromium.

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[8] R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

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Studies of Iron(III) Thiocyanate in Dioxane[1]

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The electric and magnetic dipole moments of iron(III) thiocyanate determined in dioxane solutions are 8.2 ± 1 D and 5.6 ± 0.2 B.M., respectively. In order to account for the high electric moment, the formation of a dioxane complex is suggested. The absorption spectra of iron(III) thiocyanate in various solvents give support to this view.

It is well established that the red color of iron(III) thiocyanate in aqueous solution is due to the existence of a complex cation $Fe(SCN)^{++}$, the stability constants of which and other Fe(III)-thiocyanate complexes have been determined at various ionic strengths by a number of investigators.[2] Iron(III) thiocyanate is soluble in a variety of organic solvents such as acetone, alcohol, dioxane, ether, etc., yielding violet solutions. Uri[3] concluded from conductometric measurements that only one compound between iron(III) ion and thiocyanate with a ratio of 1 to 3 exists in alcohol solution and that the cationic complexes $Fe(SCN)^{++}$ and $Fe(SCN)_2^{+}$ do not occur in this medium. Schlesinger and Van Valkenburgh[4] showed by cryoscopic and ebulliometric methods that iron(III) thiocyanate is dimeric both in benzene and in ether and that the absorption spectra in these solvents are the same as in aqueous solutions. A bridge structure, analogous to the generally accepted structure of iron(III) chloride Fe_2Cl_6, was proposed for the dimer by Schlesinger.[5] However, Mitchell and Macdonald[6] redetermined the molecular weight of iron(III) thiocyanate in organic solvents and found, in contradiction to the results of Schlesinger and Van Valkenburgh, that only the monomer is present in ether and alcohol solutions. They also observed that iron(III) thiocyanate cannot be extracted from aqueous solution by benzene and concluded that it is insoluble in benzene. In view of the uncertainty of the nature of this compound in solvents of low dielectric constant, we have determined the electric and magnetic dipole moments of iron(III) thiocyanate in dioxane solution, and its absorption spectra in benzene, dioxane, ether, ethylene chloride and tetrahydrofuran solutions in the hope of obtaining a probable structure for this compound.

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[1] Taken in part from the M.S. thesis of C. T. Fujii, Duquesne University, 1954.

[2] See, for instance, R. H. Betts and F. S. Dainton, THIS JOURNAL, **75**, 5721 (1953), where a thorough literature review is given.

[3] N. Uri, *J. Chem. Soc.*, 336 (1947).

[4] H. I. Schlesinger and H. B. Van Valkenburgh, THIS JOURNAL, **53**, 1212 (1931).

[5] H. I. Schlesinger, *ibid.*, **63**, 1765 (1941).

[6] K. M. Mitchell and J. Y. Macdonald, *J. Chem. Soc.*, 1310 (1951).

Dioxane was found to be the only non-polar solvent in which iron(III) thiocyanate is soluble to a moderate extent.

Experimental Procedures and Results

Materials.—Iron(III) thiocyanate was prepared by extracting an aqueous solution containing iron(III) sulfate and excess potassium thiocyanate, both of Mallinckrodt A.R. grade, with ether. The ether extract was dried over Drierite, filtered and evaporated under reduced pressure; the residue was dried thoroughly under high vacuum for several days. Iron(III) thiocyanate probably undergoes some internal oxidation-reduction during the evaporation, so that ordinary methods of purification would not be effective. However, the analysis of the dioxane extract of this preparation showed that thiocyanate and iron are in a mole ratio of 3.02 to 1 and the dioxane extract was used for the electric and magnetic dipole moment measurements. The analysis was carried out in the following manner. About 5 g. of the compound was shaken with 500 ml. of anhydrous dioxane overnight in a dark bottle and the solution filtered in a dry-box to remove the insoluble residue. Iron was determined by treating 100 ml. of the dioxane solution with excess bromine water to oxidize the thiocyanate, followed by precipitation of iron(III) hydroxide and ignition. Thiocyanate was determined by titrating a 25-ml. aliquot (diluted with water and acidified with nitric acid) with 0.1000 *N* silver nitrate solution using a 5-ml. microburet; iron(III) alum indicator was added near the end-point.

The solvents were purified according to standard procedures. Dioxane was refluxed with sodium and fractionally distilled, b.p. 101–101.5°. For spectral measurements, it was further dried over sodium–potassium alloy. Tetrahydrofuran was fractionated in a 30- by 2-cm. column of glass helices, b.p. 65–66°, and dried over sodium–potassium alloy. Mallinckrodt A.R. grade benzene and ether were dried over sodium–potassium alloy. Ethylene chloride was dried successively over phosphorus(V) oxide and anhydrous potassium carbonate and distilled, b.p. 84°.

Determination of Electric Dipole Moment.—The electric moment of iron(III) thiocyanate was obtained from measurements of the dielectric constant of a series of dioxane solutions at 30.0°. A stock solution was prepared and analyzed as described above; other solutions were made up by weighing out the stock solution and diluting with varying weighed amounts of dioxane. The dielectric constant measurements were made by determining the capacity difference between rotor positions of a variable cell by means of a heterodyne beat apparatus. It consisted of two oscillators, "The Jackson Model 106" manufactured by the Jackson Electrical Instrument Co. of Dayton, Ohio, and a model 201 A Signal Tracer manufactured by Precision Electronics of Chicago; a precision condenser, type 722-D, made by General Radio Co.; and a dielectric cell. Purified benzene, the dielectric constant of which was assumed to be 2.262 at 30°, was used in calibrating the dielectric cell.

The experimental results which include the weight fraction of iron(III) thiocyanate in solution, w_2, the dielectric constant of the solutions, ϵ, and their densities, d, determined by the usual pycnometer method at 30.0°, are summarized in Table I.

TABLE I

DIELECTRIC POLARIZATION DATA OF IRON(III) THIOCYANATE IN DIOXANE SOLUTIONS AT 30.0°

w_2	ϵ	d
0.000000	2.216	1.02195
.000224	2.229	1.02199
.000614	2.244	1.02202
.000730	2.250	1.02204
.000959	2.258	1.02207
.001106	2.262	1.02209

The molar polarization for iron(III) thiocyanate at infinite solution, obtained by direct extrapolation of the dielectric constant and the density plots as previously described,[7] was calculated to be 1420. The molar refraction of iron(III) thiocyanate, taken to be that of iron(III) chloride[8] plus three times the difference between the refractivities of C–Cl and C–SCN bonds, was 55; the refractivity of the C–SCN bond was calculated from the data given for methyl and ethyl thiocyanates.[9] The permanent electric dipole moment of iron(III) thiocyanate was calculated according to the Debye equation to be 8.2 *D*. From a consideration of the experimental errors and neglecting atomic polarization, we believe this result is accurate within 1 Debye unit.

Determination of Magnetic Moment.—The magnetic susceptibility of a dioxane solution of iron(III) thiocyanate was measured at room temperature, 25°, using a Gouy balance. The apparatus and its calibrations have already been described.[10] The calibrated sample tube was filled with dioxane and the change in weight of the sample on application of the magnetic field was determined. A similar measurement was made for the tube filled with a dioxane solution of iron(III) thiocyanate. The molar susceptibility of iron(III) thiocyanate was calculated from the net difference in the two measurements according to Wiedemann's additivity law. The small diamagnetic contribution of iron(III) thiocyanate was estimated from the Pascal's constants and subtracted from the molar susceptibility. The effective magnetic moment of iron(III) thiocyanate calculated in the usual manner was 5.6 ± 0.2 B.M.

Measurement of Absorption Spectra.—The solutions used for the light absorption measurements were prepared under vacuum. A 1-cm. Pyrex cell and a dumper equipped with a fritted glass disc were mounted on a tapered joint attached to the vacuum line in such a manner that the contents of the dumper could be transferred into the absorption cell. A small amount of solid iron(III) thiocyanate was introduced into the dumper and the system thoroughly evacuated. Pre-dried solvent was distilled into the dumper to make up a solution of proper concentration; the solution was filtered through the fritted glass disc into the absorption cell and the latter sealed off while under vacuum. Iron(III) thiocyanate dissolved readily in dioxane, ether and tetrahydrofuran, but only to a very slight extent in benzene and ethylene chloride even after prolonged shaking. The absorption spectra of iron(III) thiocyanate in various solvents were measured on a Beckman Spectrophotometer. In order to estimate the molar extinction coefficient of iron(III) thiocyanate, the approximate concentration of the solutions was determined in the following manner. A known volume of the solution was evaporated to dryness and dissolved in the same volume of 0.5 *N* perchloric acid containing sodium thiocyanate. This solution was compared immediately on a Beckman spectrophotometer with a standard iron(III) solution containing the same concentrations of perchloric acid and sodium thiocyanate. The absorption spectra results are plotted in Fig. 1.

Discussion

In a non-polar solvent such as benzene or dioxane, iron(III) thiocyanate is essentially covalent. The neutral iron atom has the electron configuration KL$(3s)^2(3p)^6(3d)^6(4s)^2$ and several arrangements of the three bonds are possible. For instance, the iron atom may form three equivalent bonds by using three d orbitals, an electron in each d orbital pairing with the unpaired electron in the thiocyanate group to give a planar triangular configuration. Thus, a zero or low electric moment and a spin magnetic moment corresponding to one unpaired electron, 1.73 B.M., would be expected for iron(III) thiocyanate. However such a structure is unlikely since the electric and magnetic dipole moments of iron(III) thiocyanate determined in dioxane solutions are 8.2 D and 5.6 B.M., respectively. The trigonal bonds may also be formed by sp^2 hybrids leaving the five 3d electrons unpaired, but a molecule with this configuration would have

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(7) N. C. Li and T. L. Chu, THIS JOURNAL, **69**, 558 (1947).

(8) T. J. Lane, P. A. McCusker and B. C. Curran, *ibid.*, **64**, 2076 (1942).

(9) E. C. E. Hunter and J. R Partington, *J. Chem. Soc.*, 2826 (1932).

(10) T. L. Chu and S. C. Yu, THIS JOURNAL, **76**, 3367 (1954).

no electric moment. Other types of trigonal hybrids all lead to configurations which cannot account for either the observed electric or magnetic moment.

In the bridge structure proposed for the dimer by Schlesinger,[5] the iron atom probably would be hybridized in the sp^3 state and form the fourth bond by attaching itself to the nitrogen atom of the thiocyanate group of another iron(III) thiocyanate molecule. The molecular weight determination on iron(III) thiocyanate in dioxane was attempted during this investigation; the results, however, were erratic because of its limited solubility. It seems very unlikely, however, that the double molecules exist in dioxane solution, as the dimer would have a relatively low electric moment.

The high electric moment of iron(III) thiocyanate observed in dioxane solution is probably due to the formation of a tetrahedral dioxane complex in which the iron atom forms its fourth bond with the oxygen of a dioxane molecule. The resulting complex would have a spin magnetic moment corresponding to five unpaired electrons and this is in agreement with the observed magnetic moment of 5.6 B.M. Moreover, the absorption spectra of iron(III) thiocyanate in various solvents seem to support this view. The benzene, ether and ethylene chloride solutions of iron(III) thiocyanate exhibit a common absorption band at 5120 Å. while the dioxane and tetrahydrofuran solutions show an absorption band at 5460 Å., indicating that the light absorbing species in dioxane is different from that in benzene or ether. Since little if any complexing is expected to take place in ethylene chloride, the absorption band at 5120 Å. is probably characteristic of the simple uncomplexed iron(III) thiocyanate (assuming the molecular weight determination by Mitchell and Macdonald is correct) which exists in benzene and ether solutions. The shift of absorption band in dioxane or tetrahydrofuran solution is probably due to the formation of the complex mentioned above. It is probably this complex formation which renders iron(III) thiocyanate much more soluble in dioxane than in benzene. The lack of complex formation in ether solution may be attributed to the hindrance of the bulky ethyl groups.

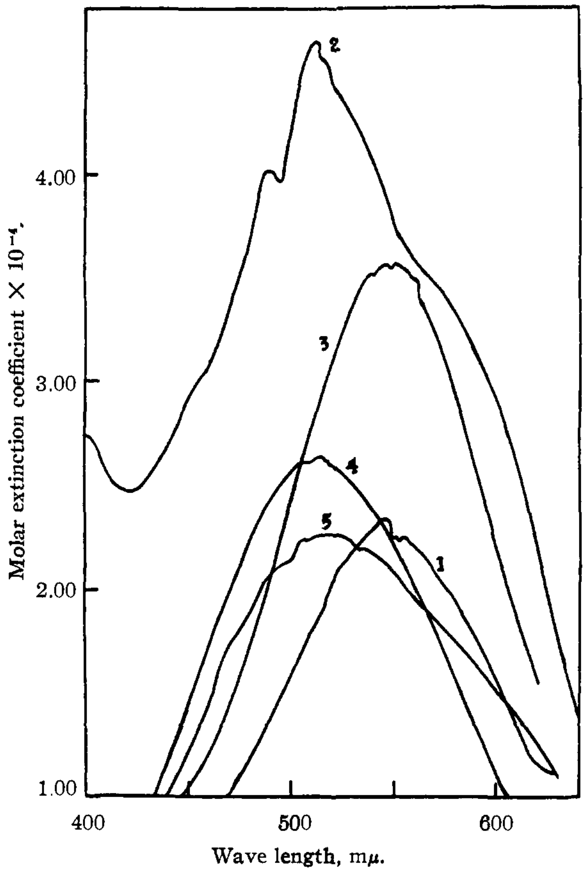

Fig. 1.—Absorption spectra of $Fe(SCN)_3$ in: 1, dioxane; 2, ethylene chloride; 3, tetrahydrofuran; 4, ether; 5, benzene.

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