115. *The Absorption Spectra of Cobalt Halide Solutions.*

By Roy J. MacWalter and Sidney Barratt.

The change in colour of solutions of cobalt chloride from red to blue under the action of heat and various agents is well known, and analogous changes take place in other cobalt halides. The phenomenon, first observed by von Babo (*Jahresber.*, 1857, 72), was attributed by him to dehydration, and this view was accepted in modified forms by Gladstone (*Phil. Mag.*, 1857, **14**, 418; J., 1858, **10**, 79), Hartley (*Proc. Roy. Soc.*, 1874, **22**, *A*, 241; *Trans. Roy. Soc. Dublin*, 1901, **7**, 253), and Russell (*Proc. Roy. Soc.*, 1880, **31**, *A*, 51, 81) in spectroscopic investigations. Measurements on the solubility of cobalt chloride in hydrochloric acid led Engel (*Bull. Soc. chim.*, 1892, **6**, 239) and Sabatier (*Compt. rend.*, 1888, **107**, 42) to postulate a complex compound as the blue chromophore.

More recently, Donnan and Bassett (J., 1902, **81**, 939) examined the problem electrochemically and observed that the red colour moved towards the cathode, and the blue towards the anode. They concluded that while the red substance was characteristic of simple cobalt ions, the blue consisted of a complex anion of the form $CoCl_3'$ or $CoCl_4''$. The blue solutions in organic solvents were brought into line with this theory, and the experiments were supported by conductivity experiments (Bein, *Z. physikal. Chem.*, 1898, **27**, 1; Denham, *ibid.*, 1909, **65**, 641) and ebullioscopic and cryoscopic determinations. Moore (*ibid.*, 1906, **55**, 641), from a spectroscopic study, adopted the complex-ion theory, while Jones and his collaborators (*Carnegie Inst. Publ.*, Nos. 60, 130, 260; *Amer. Chem. J.*, 1907, **37**, 126) put forward the view that these solutions formed a continuous series of loose hydrates, the lower members of which were blue. Lewis (*Z. Physik*, 1905, **57**, 224) gave a somewhat similar explanation, though he incorporated the theory of Donnan and Bassett. Houston (*Proc. Roy. Soc. Edin.*, 1911, **31**, 512; 1912, **32**, 56; 1913, **33**, 137) made the first quantitative attempt on the spectroscopic side of the problem, but his deductions were shown by Jones to be unsound. Hantzsch and Shibata (*Z. anorg. Chem.*, 1911, **73**, 309) postulated that cobalt in an unsaturated co-ordination state was blue, but in the saturated state it was red.

Within the last few years renewed interest has been taken in the problem. Hill and Howell (*Phil. Mag.*, 1924, **48**, 833; see also Howell, J., 1927, 158, 2039, 2843; 1929, 162) compared the spectra of cobalt halide solutions with those of cobalt pigments, and concluded that the system was blue or red accordingly as the cobalt atom was surrounded by 4 or 6 groups. This theory may be applied to aqueous solutions by assuming that the surrounding groups are water molecules. Gròh and Schmidt (*Z. anorg. Chem.*, 1925, **146**, 305; 1927, **162**, 321) determined the increase of the absorption maximum of acetone solutions of cobalt chloride on the addition of lithium chloride and explained their results in terms of the complex-ion theory of Donnan and Bassett. If the reaction $2CoCl_2 = CoCl_4'' + Co^{\cdot\cdot}$ has attained completion in acetone, the intensity of the blue colour should be doubled on the addition of 2 mols. of lithium chloride per atom of cobalt. This has been confirmed experimentally. Hantzsch (*Z. anorg. Chem.*, 1927, **159**, 273) has contended, however, that pyridine solutions of cobalt chloride have a poor conductivity, while on Gròh's arguments the salt should be completely ionised; he postulated the existence of pseudo-salts of the type Py_2CoCl_4. Rohde and Vogt (*Z. physikal. Chem.*, 1932, *B*, **15**, 353) from an examination of the spectrum of pyridine solutions of cobalt chloride at various temperatures agree with Hantzsch. Brode (*Proc. Roy. Soc.*, 1928, **118**, *A*, 286; Brode and Morton, *ibid.*, 1928, **120**, *A*, 21; *J. Amer. Chem. Soc.*, 1931, **53**, 2547) dealt analytically with the red absorption bands of solutions of cobalt halides in their corresponding acids, and showed that in each case the band may be resolved into six components whose frequencies and fundamentals are dependent on the nature of the anion. His study included organic solvents and he suggested that the alcoholic solutions are an intermediate stage between those in pyridine and quinoline and those in halogen acids. Bassett (J., 1930, 1784), from a phase-rule study of cobalt halide solutions, suggested that the red solutions contain a number of differently hydrated cations, and the blue solutions hydrated anions.

The present work has been concerned with spectrophotometric measurements on cobalt halides with a view to establish the extent to which the conversion into the blue phase can proceed.

EXPERIMENTAL.

The Judd Lewis sector spectrophotometer was used in conjunction with a Hilger constant-deviation glass spectograph. The source of light was a 500 c.p. " Pointolite " lamp, which gave greater steadiness than a condensed spark. This source introduced a serious difficulty in measuring the resultant photograph, since points of equal density on continuous spectra are more difficult to match than with a line spectrum. However, two methods were devised for this purpose, of which one is now described briefly, full details being given elsewhere (*J. Sci. Instr.*, 1933, **10**, 312).

The introduction of an interferometer before the slit of the spectrophotometer caused the continuous spectrum to be crossed by a series of dark interference fringes, whose separation could be varied by adjusting the distance apart of the two half-silvered mirrors composing the interferometer. In this way, the reading of the match points was made comparable in ease with that of a line source, and possessed the advantage of both uniformity of intensity and distribution.

Special attention was paid to the photographic technique. The accuracy of the determination of match-points is largely determined by the contrast of the final negative. This was especially necessary in using the interference fringes since the edges of the fringe are normally not sharp. The photographic plate was chosen from the varieties giving the best contrast, and developed in a quinol–potassium hydroxide developer which gives great contrast. This factor is further increased by long development (5½ minutes), which also reduces the chance of unevenness in this process. The resulting plate, after being fixed and washed, was reduced in Farmer's reducer, the contrast being again enhanced. Subsequent intensification with a mercury–silver intensifier improved the accuracy still further. After this treatment the fringes were as clearly defined as spectral lines.

Hilger's new type of Baly tube, fitted with a micrometer adjustment, served as an absorption cell. For experiments at higher temperatures, it was placed in a double-walled jacket, and water maintained at the appropriate temperature was circulated through it by a rapid pump. All connexions to the jacket were made with flexible metal tubing, and the pump was mounted on a separate bench to avoid vibration of the photometer. For temperatures above 80° an electric furnace was used.

The cobalt chloride was free from nickel, and initial experiments showed that no recrystallisation was necessary. A saturated solution in laboratory distilled water was prepared, and stored in a large flask suspended in a thermostat at 21°. The solutions were made by diluting weighed samples of this stock solution to a known volume. The concentration of the stock solution was found to be constant during several months.

At higher temperatures than that of the room, each solution prepared by the above method was heated to the required temperature in a closed vessel for at least an hour before filling the cell. The maximum changes in density of these solutions over the whole range were found to be considerably less than the experimental error. For solutions more concentrated than the stock solutions, an appropriate amount of solid was added to the solution, heated to the required temperature, and the concentration of a sample measured.

The concentration of the salt was determined by electrolysis from ammoniacal solution on a rotating platinum cathode.

I. *Cobalt Chloride Solutions.*—(a) *Aqueous solutions.* From an examination of Hill and Howell's absorption curves of cobalt pigments (*loc. cit.*) it appeared that the absorption bands characteristic of the two entities (red and blue) overlap only over a small range of wave-lengths. In these circumstances it appeared practicable to observe the disappearance of the red substance on heating solutions of cobalt chloride by measurements on that part of the absorption band where absorption characteristic of the blue phase did not interfere, and thence to calculate equilibrium data for the reaction.

To this end, the absorption curves of red solutions of cobalt chloride were measured over a range of concentration from 0·220 to 3·41M (saturated solution) at 20° in order to determine the extent of deviation of the red form from Beer's law. In Table I the molecular extinction coefficients $(\log I_0/I)/lc$ are given for this range at three wave-lengths.

TABLE I.

Concn.	0·220	0·655	1·008	1·385	2·38	3·41
5000 Å.	5·35	5·35	5·80	5·80	7·30	8·50
4800 Å.	4·50	4·50	4·60	4·60	5·30	6·30
4600 Å.	3·30	3·30	3·80	3·40	4·10	4·23

In the most concentrated solutions examined, the blue form was entirely absent, as indicated by the absence of a band in the red region of the spectrum, but a definite increase in the deviation from Beer's law was noticeable above a concentration of 1·4M.

These measurements were repeated at 40°, 60° and 80°, the concentration range being increased to include the maximum concentration at each temperature. For solutions which did not show the band of the blue form, the molecular extinction coefficient increased with concentration in the same manner as at 20°. In each case the curve of molecular extinction coefficient–concentration showed a change of direction in the region of 1—1·4M, and it is possible that at this point there is a change in the hydration of the cobalt ion responsible for the absorption band.

At the higher temperatures, in cases where the blue form had been produced, the molecular extinction coefficient was lower than that obtained by extrapolating the curve for the pure red solutions to the concentration under consideration. It was therefore possible to estimate the amount of the red form which had disappeared. When, however, this method was applied to solutions at 80° and 97°, where a high concentration of blue form was present, it was realised that the results were meaningless; at the higher concentrations at these temperatures, the molecular extinction coefficient of a point on the more refrangible side of the band characteristic of the red form decreased with increase of concentration, passing through a minimum and finally reaching a value greater than that which would be expected were the solution entirely in the red form. It is therefore evident that the band from the blue form overlaps that from the red over its entire span. In solutions where the colour change had proceeded to only a small extent the effect of this overlapping would be negligible if the absorption of the blue form at the wave-length considered (4800 Å. and 4600 Å.) were small. At concentrations and temperatures where the blue form is in greater concentration, the effect is greater, and a point is reached where the band produced by the red form is weaker than the general absorption of the blue form.

Since it was thus impossible to follow the reaction by examining the blue–green band, the absorption in the red region caused by the blue form was considered. The absorption of this band was followed in a solution saturated at 90° at temperatures up to 110°. Two wave-lengths were chosen, 5900 Å. and 6000 Å., where absorption by the red form would be so low as to be negligible, and the extinction coefficients at these points were determined (Table II). The points at lower temperatures, 60° and 80°, were obtained by considering the absorption of the most concentrated solutions used at these temperatures. The results indicated the growth of the blue form with temperature to the maximum value reached at 100°. It was now necessary to find the concentration of blue form corresponding with this value, which involved the determination of the extinction coefficient of pure blue cobalt chloride.

FIG. 1.

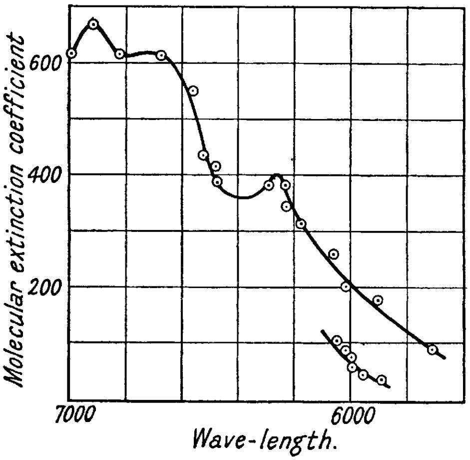


FIG. 2.

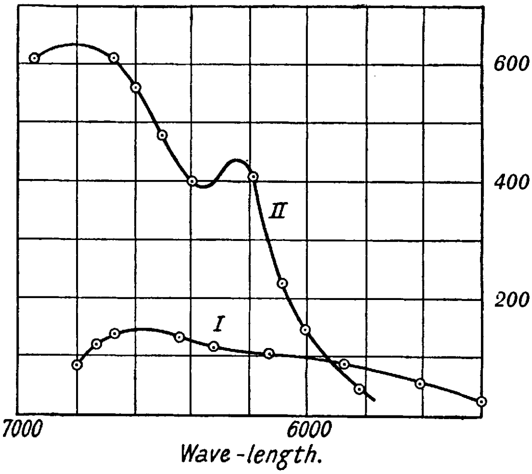


TABLE II.

Temp.	60°	80°	97°	100°	110°
Extinction at 5900 Å.	0·88	0·90	1·45	3·28	3·28
Extinction at 6000 Å.	1·20	1·28	2·03	6·53	6·53

The theories of the colour change would each postulate that in hydrochloric acid solutions the salt is present entirely in the blue form. A solution of convenient concentration was therefore prepared in constant-boiling acid. The molecular extinction coefficient of this solution appeared to be independent of the amount of acid present, so the reaction had evidently proceeded to completion. The results are plotted in Fig. 1, the curve for an aqueous solution at 110° being shown in the same diagram. It can be seen that above 6000 Å. the ordinates of the curve for the acid solution are approximately double those for the aqueous solution.

Unfortunately, it was impossible to complete the curve for concentrated aqueous solutions at 110° since a cell length suitable for measurements of the high extinctions could not be obtained with greater accuracy than 50%. The points which were obtained may be in error to the extent of 10%, since at these concentrations an unknown error is introduced when the solutions (at ordinary temperatures almost completely solid) were poured into the absorption cell, evaporation and crystallisation being the chief causes. The results lend support to the view that aqueous solutions contain a maximum of 50% " blue phase " of cobalt chloride.

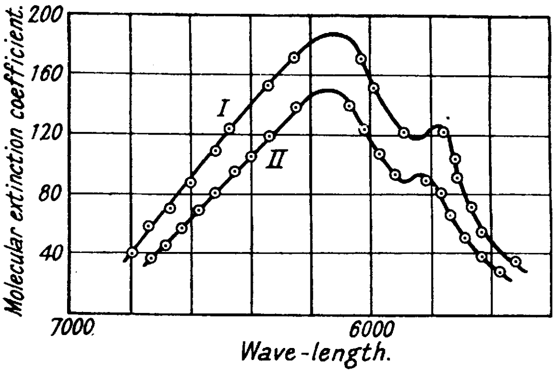
An attempt was then made to determine whether in other solvents in the absence of added chloride ions the equilibrium ever proceeded beyond 50%.

(b) *Alcoholic solutions.* The work of Gròh and Schmidt (*loc. cit.*) confirms the theory in such a striking manner that some amplification seemed desirable. The alcoholic solution was 0·01*M*, and Fig. 2 (Curve I) shows the absorption curve obtained. The value of the maximum is considerably lower than in the case of the ethyl-alcoholic solutions used by Gròh, but this is explained by his theory that in ethyl alcohol the reaction $2CoCl_2 \longrightarrow CoCl_4'' + Co^{\cdot\cdot}$ has not proceeded to completion. He found that dilution produced wide deviations from Beer's law. Our solution was considerably more dilute than his.

This solution was now saturated with hydrogen chloride, prepared from sulphuric acid and ammonium chloride pellets and dried with phosphoric oxide. Since a change in volume occurred, it was necessary to redetermine the concentration before measuring the absorption. The curve (Fig. 2, Curve II) is almost identical with that for cobalt chloride in aqueous hydrochloric acid, except that the whole band has been moved in the direction of lower frequencies. This curve confirms Gròh's value of 609 for the maximum of absorption of the pure blue form.

(c) *Pyridine solutions.* A study of the work of Brode showed that pyridine and quinoline solutions of cobalt chloride absorbed as strongly as hydrochloric acid solutions. Since this is not in agreement with the complex-ion theory, which adequately explains the reaction in aqueous and in alcoholic solution, a more detailed examination was made.

FIG. 3.



In a preliminary experiment a solution of cobalt chloride in acetone was prepared (in which according to Gròh the auto-complex formation has proceeded almost to completion), and to this drops of pyridine were added. If Brode's curves are correct, the solution should become twice as blue as before, and observations in a colorimeter appeared to confirm this view. However, when a spectrophotometric examination was made, a curve (Fig. 3, Curve I) was obtained where the maximum of absorption is only 180, *i.e.*, complex formation had proceeded only a little further than with ethyl alcohol.

The explanation of the results with the colorimeter is now clear. Since the pyridine solution of cobalt chloride absorbs nearer the blue region of the spectrum, its effect on the eye is different from that of an acetone solution, and it appears to be denser. On the other hand, in spite of the fact that pyridine solutions of cobalt chloride fall into line with the complex-ion theory, there are some notable differences. All other organic solvents produce absorption curves whose maxima lie near 6600 Å., but the maximum for pyridine solutions is considerably lower, as has been indicated (6070 Å.). Furthermore, Hantzsch has shown that the electrical properties of these solutions are different from those of solutions in other organic solvents.

Experiments were then made with redistilled pyridine which had been thoroughly dried by standing in contact with freshly heated baryta for several weeks, and then distilled from baryta. In all these experiments, since cobalt chloride is almost completely insoluble in pyridine, acetone (dried by standing over calcium chloride) was used as diluent.

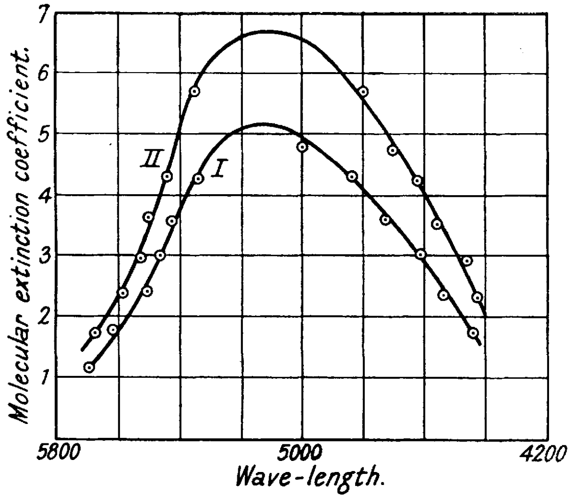
The solution of the dried materials was examined (Fig. 3, Curve II); 1·4% of water was now added and the absorption curve redetermined. An increase in absorption had occurred, for the curve obtained was coincident with that from undried pyridine (Fig. 3, Curve I). Continued addition beyond this point caused no further increase in absorption, and when 4% of water had been added definite signs of the red form appeared. This effect is peculiar to the pyridine solutions, since normally the addition of water immediately causes the red form to appear.

The explanation of this anomalous behaviour may be connected with the formation of a complex ion $CoCl_2(OH)_2''$ (see p. 523). It is obvious that any hypotheses based upon colour changes in pyridine solution are open to doubt, since these solutions do not undergo the same reactions as solutions in other organic solvents.

II. *Cobalt Bromide Solutions.*—A brief examination of cobalt bromide solutions has been made to determine whether this salt behaves in a similar manner to the chloride. Gròh and Schmidt's method for cobalt chloride was employed. Since they had observed that in acetone solutions the reaction $2CoCl_2 \longrightarrow CoCl_4'' + Co^{\cdot\cdot}$ has proceeded to completion, the problem consisted in determining the absorption curves of a solution of cobalt chloride in acetone, and of the same solution after saturation with hydrogen bromide. The curve obtained closely resembled that of cobalt chloride in hydrochloric acid, the maximum absorption coefficient being in each case just over 600. The maximum absorption in the absence of hydrobromic acid was in the region of 6600 Å., and the absorption coefficient was approximately 300. Thus the effect of hydrobromic acid on the absorption of cobalt bromide runs parallel to that of hydrochloric acid on cobalt chloride.

III. *Cobalt Fluoride Solutions.*—None of the previous investigations in this field has dealt with the absorption spectrum of cobalt fluoride. Houston and Brode (*locc. cit.*) mentioned that no colour change took place in these solutions, an observation sufficiently anomalous to warrant further investigation. Brode has indicated that the absorption of the " blue form " moves nearer the red as the halogen atom becomes heavier, so the absorption of the complex ion in the fluoride should be nearer the blue than in cobalt chloride solutions. It might in these circumstances be superimposed on the blue–green absorption band characteristic of the ion of cobalt. If this were so, no colour change would occur, but merely an increase in depth of tint.

FIG. 4.



The cobalt fluoride was prepared by heating the carbonate with hydrofluoric acid in a lead dish on a water-bath, and allowed to crystallise. (Boiling caused formation of insoluble oxyfluoride.) A dilute solution of this salt in water was examined photometrically and a curve (Fig. 4, Curve I) similar to that for the other cobalt salts was obtained. At 75°, however, the extinction coefficient increases by 35% (Fig. 4, Curve II). By analogy with the aqueous solutions of cobalt chloride, this would not be expected unless it is assumed that another complex has been formed, and that its absorption curve is superimposed on that of the ions present in the cold solution. The effect of temperature would then be that the total absorption of the ordinary form would decrease, owing to the formation of the new complex, but the final effect on the absorption curve would be an increase, since it has been shown in the other cases that the extinction coefficient of the " blue " complex is much greater than that of the simple ion. It thus appears that the effect of temperature on aqueous solutions of cobalt fluoride may be analogous to its effect on the chloride, with the exception that the absorption of the " blue " form lies in the same region as that of the " red " form.

The effect in organic solvents. Since cobalt fluoride is almost completely insoluble in most organic solvents, the work was restricted, but a solution was prepared in methyl alcohol. In this solvent the reaction $2CoX_2 \longrightarrow CoX_4'' + Co^{\cdot\cdot}$ has not proceeded very far, so these solutions could not be regarded as favourable to complex formation. It was found, however, that pyridine could be added to the solution without precipitation, and an absorption curve was plotted for this solution. Table III shows that the extinction coefficient has increased far in excess of any possible physical variation due to the solvent (pyridine 75%, methyl alcohol 25%).

The presence of other fluorides. The colour change in cobalt chloride and bromide is effected by the addition of other chlorides whose tendency to form complexes is not as great as is that of cobalt chloride. Only qualitative experiments could be carried out with cobalt fluoride, since those fluorides of other elements which were sufficiently soluble to cause the effect exerted

TABLE III.

Extinction coeff.	Wave-length.	Extinction coeff.	Wave-length.	Extinction coeff.	Wave-length
6·5	5770; 4310	12·6	5540; 4515	20·0	4660
8·5	5700; 4400	14·5	5430; 4580	22·75	5270; 4690
10·5	5580; 4440	17·0	5390; 4580	25·0	5190; 4820

a solvent action on the glass. It was, however, shown that sodium and potassium fluorides produced a darkening in colour in aqueous solutions of cobalt fluoride. On the other hand, hydrofluoric acid produced no change. This acid being weak, its concentration of fluoride ions is very much smaller than in solutions of the alkali salts.

DISCUSSION.

From the above experiments, it appears that the equilibrium Co (red) $\rightleftarrows$ Co (blue) never exceeds 50% in water, alcohol, acetone, or pyridine in the absence of a common ion. It would seem that in each case Donnan and Bassett's theory satisfactorily explains the facts, since, when the reaction has reached completion, only half the cobalt is in the form of the blue complex. Addition of a common ion will cause the remainder of the cobalt to change to the blue form. However, there is no such limiting condition in equations built up on the basis of hydration.

In all red solutions of cobalt salts, a single band of absorption with a head at 5100 Å. is produced. The intensity of the band is approximately the same in all cases. The band is attributed to the cobalt ion. In the blue solutions of cobalt halides in their corresponding acids, a complex band appears whose wave-length becomes greater as the weight of the anion increases. However, the general form and intensity of the band is the same. This would indicate that the absorber contains the anion, but is of the same form in all solutions, *i.e.*, a complex ion.

Solutions of cobalt halides in organic solvents (except pyridine) produce bands approximately in the same position as those from aqueous solutions in the corresponding halogen acid. This would be expected if the complex ion is formed. The intensities of the bands in these solvents and in water are never more than one-half of that of the corresponding band in the halogen acid, in accordance with the relevant scheme. Donnan and Bassett's migration experiments (p. 517) show that the complex is negative.

Hill and Howell's theory (see p. 518) embodies the principles of both the complex-ion and the hydrate theory, being essentially similar to the former but different in its applications. In aqueous solution the assumption would be of two species $Co(H_2O)_4^{\cdot\cdot}$ and $Co(H_2O)_6^{\cdot\cdot}$—an assumption which we have been unable to verify. However, Howell's physical experiments may be interpreted on the basis of the complex-ion theory.

The present work has shown that pyridine solutions of cobalt chloride are anomalous, as regards both the position of the absorption band and the effect of the addition of water. It is possible that in basic solvents the blue colour may be attributed to some absorber containing water. The curve is similar in form to that of cobalt chloride in other solvents, which leads to the belief that there is a complex-ion in this case, possibly $CoCl_2(OH)_2''$. The lighter hydroxyl groups would then explain the shift of the curve in the direction of lower frequencies.

Brode has shown that the bands in pyridine and quinoline solutions of cobalt halides do not show such great shifts with increasing weight of halogen as is the case with the corresponding halogen acid. This would seem to show that the halogen plays a less important part in the quinoline complex than in the halogen acid complex, *e.g.*, $CoX_2(OH)_2''$ as compared with CoX_4''. It is not impossible that, for pyridine solutions, Hantzsch's view is correct, the pseudo-salt formed being $CoCl_2Py_2$. Conductivity data support the view, and so to some extent does the work of Rohde and Vogt.

A similar study to the above conducted on a solution of cobalt thiocyanate should prove illuminating. Aqueous solutions of this salt at room temperature pass from red to blue as the concentration is increased, and it would be expected that the equilibrium $2Co(CNS)_2 \longrightarrow Co^{\cdot\cdot} + Co(CNS)_4''$ would have proceeded to completion at a much lower temperature than with aqueous cobalt chloride solutions. The lower temperatures involved would make the investigation easier, and it might be possible to apply the law of mass action.

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