

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, OHIO STATE UNIVERSITY]

THE ABSORPTION SPECTRA OF COBALTOUS COMPOUNDS. III. THE PYRIDINE AND QUINOLINE COMPLEXES AND SOLUTIONS

BY WALLACE R. BRODE

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In the earlier papers of this series^{1,2} the absorption spectra of cobaltous chloride, bromide and iodide, in solution in the corresponding halogen acids, were measured (Fig. 1). The data presented in these papers showed the cobalt and halogen atoms to be definitely bound together. The change in molecular weight in going from chloride to bromide to iodide caused a proportional shift in the position of the absorption band. No attempt was made to distinguish between the effect produced by the solvent and that produced by the halogen in combination with the cobalt, since each halide was measured in solution in the corresponding halogen acid. By an application of composite curve analysis,³ the absorption bands were found to be resolvable into a series of component bands of multiple integral frequency. The same series of multiples appeared in the analysis of the absorption band of each of the cobalt halides, but the frequency of any given component band was different, as was also the frequency interval, between the component bands, for the chloride, bromide and iodide.

A discussion of the various theories concerning the color changes of cobalt solutions and molecular configuration of cobalt halides will not be undertaken until additional data have been obtained. However, certain more important papers bearing on the experimental work involved must of necessity be considered. A good review of much of the literature on this subject is to be found in a recent paper by Bassett.⁴ Hantzsch⁵ has shown, in a study of the absorption spectra of cobalt chloride in pyridine, that the color change from pink to blue, caused by the application of heat to the pyridine solution, is similar to that of an aqueous solution of cobalt chloride. The absorption spectrum of the blue pyridine solution indicated the possible existence of a composite curve, similar to that shown in the case of cobalt chloride in hydrochloric acid. A preliminary examination of the absorption spectra of hot solutions of cobalt chloride, cobalt bromide and cobalt iodide, in pyridine, made by Dr. R. A. Morton and the author⁶ at the University of Liverpool, gave the results similar

¹ Brode, *Proc. Roy. Soc.*, 118A, 286 (1928).

² Brode and Morton, *ibid.*, 120A, 21 (1928).

³ Brode, *Bur. Standards J. Research*, 2, 520 (1929).

⁴ Bassett, *J. Chem. Soc.*, 1784 (1930).

⁵ Hantzsch, *Z. anorg. Chem.*, 159, 273 (1926).

⁶ Then a Fellow of the John Simon Guggenheim Memorial Foundation.

to those indicated in Fig. 2. These results were only qualitative in nature, due to the relatively high temperatures required to produce a reasonable concentration, particularly for the iodide salt. Recent observations on these cobaltous halides in quinoline (Fig. 2) have given quantitative data, since the blue solutions are stable at room temperature, so that solutions of a definite concentration of the cobalt halide can be easily measured at a constant temperature. Although there is a marked difference in the molecular weight and other physical properties of the two solvents, pyridine and quinoline, absorption bands of nearly identical shape and frequency were obtained for each of the three halides. This

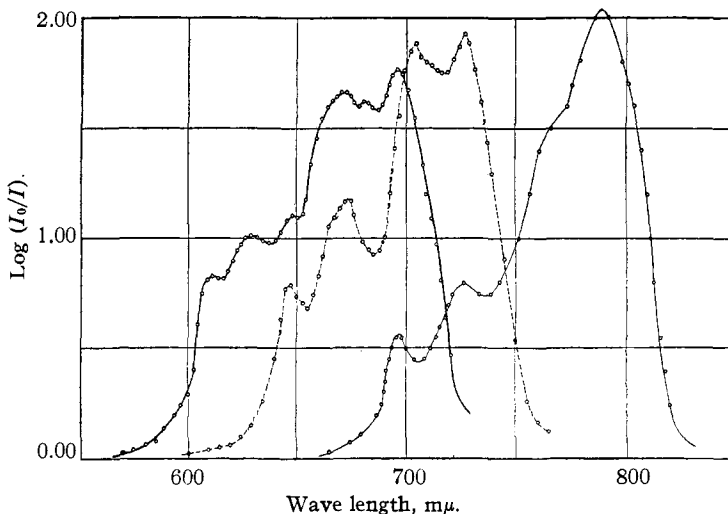


Fig. 1.—The absorption spectra of cobaltous halides in their corresponding halogen acids: —, CoCl_2 in HCl ; - - - - -, CoBr_2 in HBr ; — · — · —, CoI_2 in HI .

would indicate an absence of solvent effect and the probability that neither pyridine nor quinoline is directly bound to the cobalt. On the other hand, the change in shape and frequency position of the absorption bands with a change of the halogen would indicate that there must be a direct connection between the cobalt and the halogen atoms.

When one compares the absorption spectra of the cobaltous halides in pyridine solution with those of the same salts in concentrated halogen acids one notes a marked difference. The shift in the position of the absorption band toward the red end of the spectrum as one goes from chloride to bromide to iodide is much greater in acid solution than in the pyridine or quinoline solution. It will also be noted that for any given halide as, for example, the chloride, the absorption band in acid solution is of lower frequency than for the same salt in pyridine or quinoline.

These larger differences in frequency and the general displacement to lower frequency values in acid solution may be attributed to either of the following causes: (a) to the direct combination of the cobalt atom with a greater number of halogen atoms, or (b) to the effect of the solvent medium which in the acid solution is different for each salt studied.

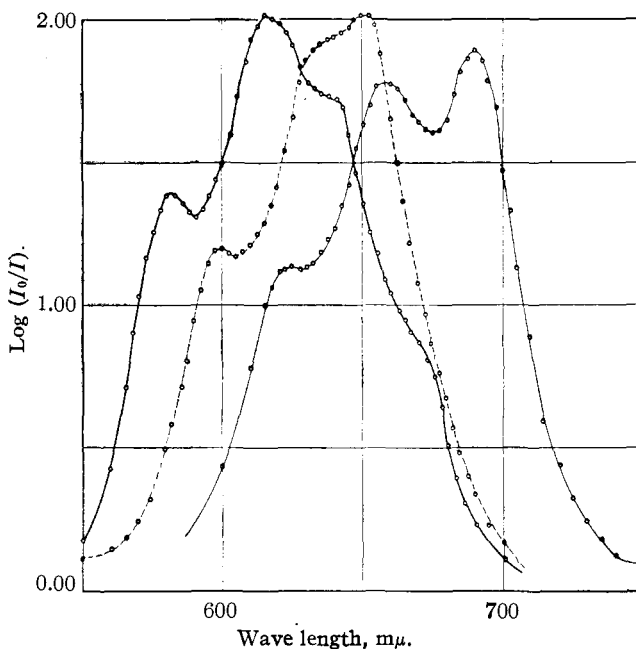


Fig. 2.—The absorption spectra of cobaltous halides in quinoline: ———, CoCl_2 ; - - - - -, CoBr_2 ; ———, CoI_2 . (Identical or nearly identical curves were obtained from cobalt quinolinium halides in quinoline and cobalt halides and cobalt pyridinium halides in pyridine.)

From the above observations it would seem that one has to deal here with two distinct systems of vibrations:⁷ that characteristic of the acid solution and that characteristic of solution in an organic base such as pyridine or quinoline. In the present state of our knowledge of these composite absorption bands it is not possible to say whether the differences between the two series of absorption bands are due to a change in the component members. When the data from the halogen acid series (which will be referred to as the "HX" system) and the pyridine-quinoline series (which will be referred to as the "Py-Q" system) are compared on a

⁷ For purposes of comparison and discussion, a system will be defined as an electronic configuration which produces a series of absorption bands that remain similar in shape and multiple relations even though the mass of the molecule may be changed, *i. e.*, by a change from Cl to Br to I.

frequency scale in place of the wave length scale as used in this paper, it will be noted that either of the above possibilities would be supported by the data.

In a recent article Percival and Wardlaw⁸ have described the preparation of cobalt pyridinium and cobalt quinolinium halides, to which they

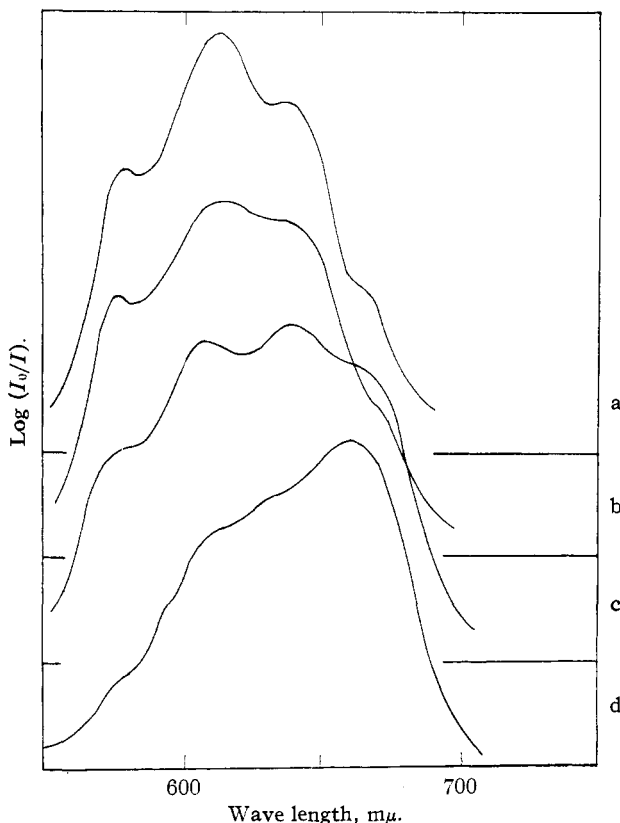


Fig. 3.—(a) The absorption spectra of cobaltous chloride-pyridine complex (CoPy_2Cl_2) in CHCl_3 ; (b) CoPy_2Cl_2 in $\text{CHCl}_3 + \text{C}_2\text{H}_5\text{OH}$; (c) CoPy_2Cl_2 in $\text{C}_2\text{H}_5\text{OH}$; (d) $(\text{PyH})_2\text{CoCl}_4$ (cobaltous pyridinium chloride) in $\text{C}_2\text{H}_5\text{OH}$.

have assigned a constitution involving the CoCl_4'' ion. The blue cobalt solutions have been associated by many writers with the possible existence of this ion in solution. The above-mentioned compounds are, however, among the first to be isolated in which such a group has been formulated for a solid substance. The general method of preparation of these compounds was to mix in an alcoholic solution, pyridine (or quinoline) hydrochloride (bromide or iodide) with an equimolecular amount of the corre-

⁸ Percival and Wardlaw, *J. Chem. Soc.*, 1505 (1929).

sponding cobaltous halide. The cobalt pyridinium (or quinolinium) halide formed by this reaction was filtered off and recrystallized from alcohol. All of these compounds crystallized with ease from alcohol, yielding needle-shaped crystals in the case of the pyridine derivatives and plates in the case of the quinoline derivatives. Because of the possibility of confusion of these compounds with those described in the following paragraph, analyses were made on these complexes and the results of Percival and Wardlaw were confirmed.

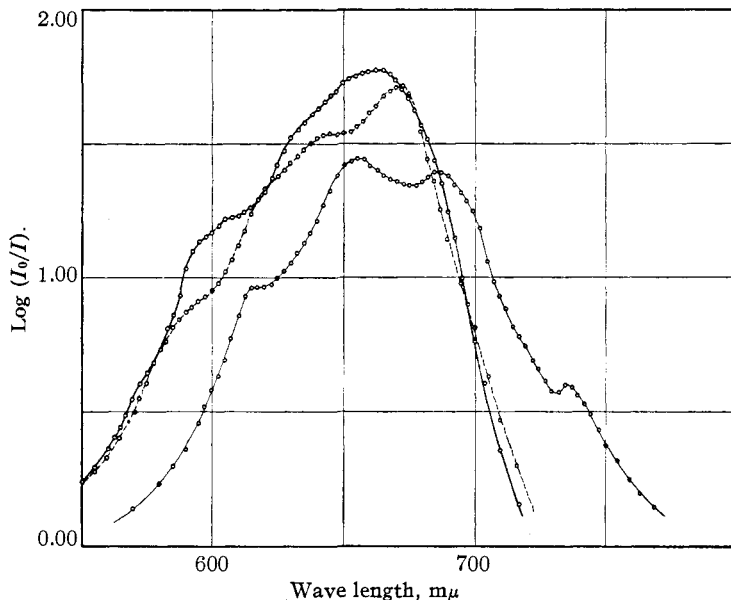
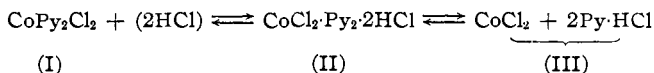


Fig. 4.—The absorption spectra of cobalt quinolinium halogen complexes $((QH)_2CoX_2)$ in absolute ethyl alcohol: $X = Cl$, ———; Br , - - - - -; and I , — · — · —. The cobalt pyridinium complexes gave identical curves.

Percival and Wardlaw did not refer to the work of Hantzsch,⁵ Reitzenstein⁹ or Grossmann,¹⁰ who prepared similar compounds by the interaction of cobaltous halides with pyridine or quinoline in alcohol solution. These authors have assigned formulas of the general type $Co(C_5H_5N)_2X_2$ and $Co(C_8H_7N)_2X_2$ to such compounds. The relation between these cobalt halogen complexes may well be represented by the equation



According to Percival and Wardlaw the formula for compound (II) should be written as $(PyH)_2CoCl_4$. Since compounds of both types (I)

⁹ Reitzenstein, *Ann.*, **282**, 275 (1894).

¹⁰ Grossmann, *Ber.*, **37**, 1256 (1904).

and (II) can be recrystallized from alcohol solutions without change in composition and since both give blue solutions, a study of their absorption spectra should offer valuable information with regard to the nature of these complexes. The cobalt chloride-pyridine complex (Compound I) gave in alcohol an absorption spectrum quite similar to the absorption spectrum of cobalt chloride in pyridine (Fig. 3). While the band intensities of the former did not exactly correspond with those (Fig. 2) of cobalt chloride in pyridine or quinoline, their frequency positions were the same, and it was further shown that the band intensities could be altered without changing the position of the bands by the use of other solvents

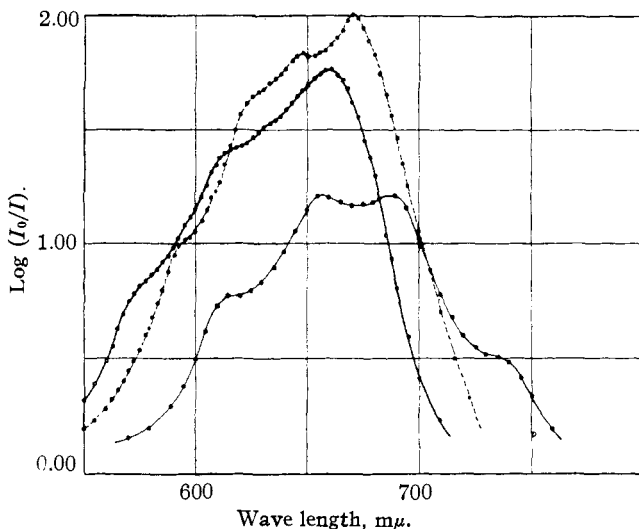


Fig. 5.—The absorption spectra of cobaltous halides in ethyl alcohol: Cl, ———; Br, - - - - -; and I, — · — · —.

such as ligroin and chloroform. In these latter solvents there is a general sharpening of the bands while in alcohol there seems to have been a broadening and flattening of the bands. The same effects were noted in a study of the absorption spectra of the quinoline complex, which, though of a markedly different color from the pyridine complex in the crystalline state, gave an almost identical absorption spectrum in alcohol solution.

The absorption spectra of the cobaltous pyridinium and quinolinium chlorides (II), bromides and iodides (Fig. 4) in alcohol were quite different from the absorption spectra of the corresponding cobalt halides in pyridine and quinoline. A comparison of the curves of these pyridinium and quinolinium complexes in alcohol with those of the corresponding cobalt halides in alcohol (Fig. 5) showed that for the same halogen nearly identical absorption spectra were obtained. These facts suggest a reaction similar

to that indicated from (II) to (III) in the above equation, and that the cobalt halide absorption spectrum in alcohol was not influenced by the pyridinium or quinolinium chloride present. An exact analysis of the curves is not possible due to the broad flat nature of the component portions of the alcohol bands. There is some question as to whether there is a distinct alcohol system of absorption, similar to the "HX" and "Py-Q" systems or whether the curve (Fig. 4) is formed by an equilibrium between the "HX" and "Py-Q" systems. The addition of very small amounts of quinoline to a solution of cobalt chloride in alcohol produces the absorption spectra characteristic of cobalt chloride in quinoline, (Fig. 7), and in a like manner the addition of small amounts of hydrochloric acid and lithium chloride to the neutral alcohol solution of cobalt

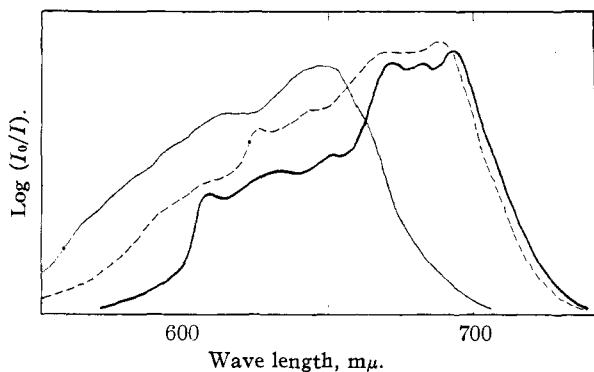


Fig. 6.—The absorption spectra of CoCl_2 ; in concentrated HCl , ———; in a 3% solution of LiCl in alcohol, - - - - -; and in ethyl alcohol, — · — · —.

chloride produces absorption spectra which are characteristic of cobalt chloride in hydrochloric acid (Fig. 6). Gróh¹¹ made a study of this latter reaction and concluded that the alcohol solution of cobalt chloride contained equimolecular amounts of Co^{++} and CoCl_4^{--} ions and that the change in color on addition of the halogen containing salt such as lithium chloride is due to an increase in the concentration of the CoCl_4^{--} ion with a corresponding decrease in the amount of the Co^{++} ion, the latter ion being responsible for the pink color of cobalt solutions. The data here presented would seem to indicate a change in the nature of the blue absorption spectrum rather than a mere intensification of the alcohol bands, and hence does not support Gróh's proposed mechanism. As another example of difference of intensity of components of the same system under different conditions, the changes in intensities of the 595 $m\mu$ and 695 $m\mu$ bands are worth noting.

¹¹ Gróh, *Z. anorg. Chem.*, **162**, 321 (1927); **146**, 305 (1925).

The addition of small amounts of halogen ions, either as quinolinium chloride or free hydrochloric acid, had no apparent effect on the absorption bands of cobaltous chloride in quinoline. Also, the addition of quinolinium chloride to the alcohol solution of cobalt chloride had no effect on the absorption band, indicating that all of the cobalt ions have the same amount of halogen.

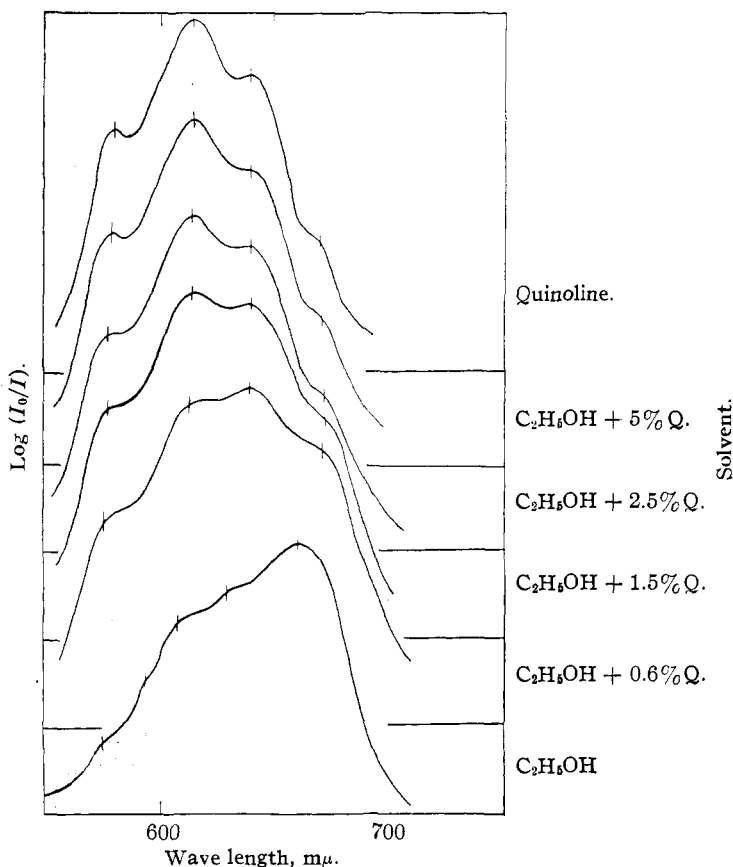


Fig. 7.—The change from the alcohol absorption to the "Py-Q" system of absorption caused by the addition of quinoline to a solution of CoCl_2 in ethyl alcohol.

If the alcohol solutions are to be considered as representing an intermediate or equilibrium state between the "HX" and "Py-Q" systems, then it should be possible to go directly from one system to another by the addition of one solvent to a cobalt solution of the other. A few of the curves obtained from nearly fifty solutions of varying concentration of hydrochloric acid and quinoline are presented in Fig. 8. These curves

were selected to show representative conditions and transition stages.

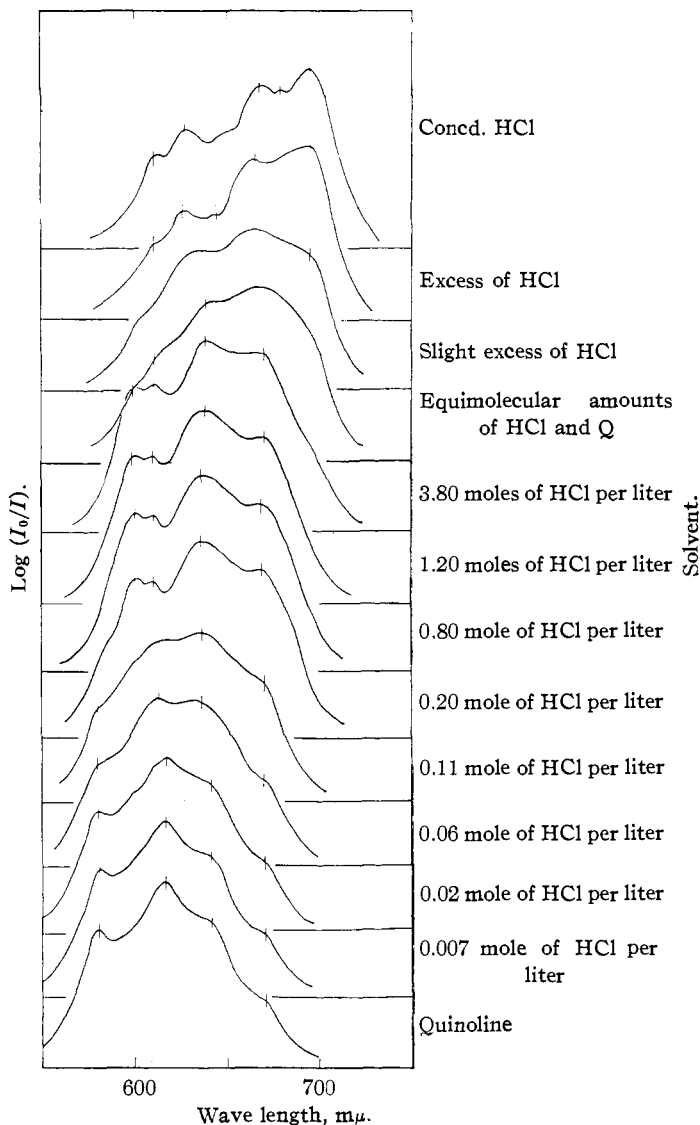


Fig. 8.—The change from the "Py-Q" system, through the "intermediate" system to the "HX" system, caused by the addition of HCl to a solution of CoCl_2 in quinoline. (The curves in this figure are only a few of the some fifty curves, observed at various Q-HCl concentrations. They have been chosen to show characteristic stages or transition points in the change of the absorption systems. The concentration of CoCl_2 in all solutions was approximately 0.0043 mole per liter.)

Over a considerable concentration range there is no apparent effect on the general nature of this intermediate absorption band, and only after a concentration of acid in excess of the quinoline is reached do the "HX" or acid system bands appear. While the intermediate band obtained in this "HX"—"Py-Q" equilibrium is not identical with the alcohol band, the close similarity in position and shape, allowing for some solvent effect, would argue for the existence of an "intermediate" system of absorption as well as for the "HX" and "Py-Q" systems.

Experimental

The observations recorded in the figures in this paper, with the exception of Fig. 1, were made on a Bausch and Lomb spectrophotometer which was equipped with a modified DuBoscq colorimeter attachment which permitted the use of all glass cells and the rapid variation of cell thickness by changing the position of the glass plungers. The data are recorded in wave length values expressed in millimicrons (meters $\times 10^{-9}$), as abscissa and in extinction coefficients, expressed as $\log I_0/I$, as ordinates.

Cobalt chloride was prepared by dissolving cobalt carbonate in c. p. hydrochloric acid, recrystallizing from water and drying at 120° in the presence of dry hydrogen chloride. The anhydrous cobalt chloride was kept at 100° in a closed container until used. The sample was analyzed and checked for both cobalt and halogen. The cobalt was determined by the sulfate fusion method and the halogen by the standard silver chloride method.

A convenient means of determining the amount of cobalt present in any sample was to evaporate the solution to a small volume or to dryness and make up to the original volume with concentrated hydrochloric acid. The presence of such impurities as quinolinium hydrochloride, sulfates, nitrates or other halides in small amounts were shown by experiment to have no influence on the absorption bands of the hydrochloric acid solution. The hydrochloric acid solutions follow Beer's law throughout a wide concentration range. Because of its general shape, location and intensity, the band at $625\text{ m}\mu$ was chosen for reference purposes (Fig. 1).

The molecular extinction coefficient for cobalt chloride in concentrated hydrochloric acid was found to be 335.5 at $\lambda = 625\text{ m}\mu$ and this value was used to determine the cobalt content of other solutions. In compounds where the halogen content might vary, such as the pyridine and quinoline complexes, separate halogen determinations were made to insure that the correct compound was being used. The earlier data on the halogen acid solutions¹ were obtained from weighed samples of the supposed hexahydrate. From the above analyses it is shown that the water content was not as supposed, so that the data as published represent the absorption of 0.7225 g. of the anhydrous cobaltous chloride per liter (Fig. 1).

Summary

A spectrophotometric study has been made of cobalt chloride, cobalt bromide and cobalt iodide dissolved in pyridine and quinoline, and the relation between the data observed and those previously presented on the corresponding acid solutions has been discussed. Although the data of this paper are in contradiction to some of the data and theories published or offered by others on the nature of cobalt colors, no attempt has been made to explain the actual constitution of the cobalt complexes. Discussion on this point is reserved for a later paper which will be presented after the publication of the cobalt alkaline solution data.

1. Evidence has been presented to substantiate the existence of three absorption systems in blue cobalt solutions, namely, the halogen acid system, the pyridine-quinoline system and a possible intermediate system.

2. The fact that the cobalt halides gave identical absorption spectra in both pyridine and quinoline supports the theory that the cobalt atom is not directly connected to the pyridine or quinoline molecule, since with the markedly different molecular weights of pyridine and quinoline, one would expect a shift in the absorption bands or a change in the component intensities with such a change in molecular weight. On the other hand, the nature of the holding or partial valence forces in complexes may be such that the effects produced would be too small to observe.

3. The change in frequency of the absorption bands with a change of halogen in the pyridine-quinoline system is similar to that previously observed in the halogen acid system, but of smaller magnitude, indicating a possible cobalt complex involving fewer halogen ions and more ions common to all three compounds.

4. Cobalt pyridinium and quinolinium halogen complexes give in alcohol the same absorption spectra as the pure cobalt halide in alcohol, indicating the non-existence of pyridinium or quinolinium complexes in the alcohol solution.

5. By a change of solvents it has been possible to alter the intensity of components of absorption bands without shifting their frequency position. If identical band positions but different extinction coefficient values are to be taken as indication of equilibrium isomers,¹² then the data presented on the absorption spectra of the cobalt quinoline and pyridine chloride complexes in alcohol and in chloroform would support the contention of Hantzsch⁵ that isomeric forms of these complexes can exist.

COLUMBUS, OHIO

¹² Morton, *J. Chem. Soc.*, 706 (1926).