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Spectrophotometric Studies of Cobaltous Chloride¹

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From the almost one hundred years of scientific investigation of the colors of cobalt salts there has resulted no general agreement yet as to the basis of the change between red and blue of such a salt as cobaltous chloride. Not only is there still discussion between adherents of the "complex ion" school of interpretation, and the "dehydration" school, but even in the camp of the complex ion proponents there is not agreement as to the probable formula of the complex. Thus, most recently, Robinson and Brown² concluded, from studies in aqueous salt solutions, that the blue complex is a dichloro cobalt complex; Wormser³ believes, on the basis of conductivity results, that the complex is a trichloro complex in acetone, while Barbinok⁴ and Bobtelsky and Spiegler⁵ deduce from application of the method of "continuous variations" introduced by Job⁶ that the complex is a tetrachloro complex.

Since the variety of techniques used in the above papers alone might lead to different interpretations, and since our earlier work with the cobalt nitrate system⁷ had shown formation of a dinitrato complex, the chloride system was investigated. In order to avoid ambiguity, the investigation was conducted spectrophotometrically.

Procedure.—Spectrophotometric measurements were made with the Beckman model DU quartz spectrophotometer. The density scale of the instrument was calibrated with standards obtained from the National Bureau of Standards. Density settings were found reproducible to 0.002 density unit.

The cobalt chloride used was the chemically pure hexahydrate. Cobalt perchlorate was prepared from the carbonate and perchloric acid, and recrystallized twice. Chemically pure lithium chloride was dried in the oven at *ca.* 90°. Pyridinium chloride was the Eastman Kodak Co. product, boiled with benzene until the solid chloride formed. The solids $\text{Co(Py)}_2\text{Cl}_2$, $\text{Co(Py)}_6\text{Cl}_2$ and $(\text{HPy})_2\text{CoCl}_4$ were those prepared by Katzin, Ferraro and Gebert.⁸

Anhydrous alcohols were prepared from the commercial anhydrous products by treatment with sodium metal (magnesium turnings for methanol) and distillation. Tetrahydrofuran was purified

for us by Dr. George Gibson. The other solvents used were commercial pure products. All were analyzed for water content by titration with Karl Fischer reagent, using an electrical end-point determination, and the apparatus of Zerban and Sattler.⁹ The standard used for the reagent was sodium acetate trihydrate.¹⁰

Stock solutions were made of the salts in the desired solvents, and aliquot dilutions were made for spectrophotometric study. The concentrations of the cobalt salts were determined by analysis for cobalt by standard electro-deposition procedures. In most cases the stock solutions were also analyzed for water.

We are indebted to Mr. John R. Ferraro for analytical assistance.

Experimental

Cobaltous Chloride Spectrum.—Cobaltous chloride in methanol gives a pink solution, with a hint of blue color; in more concentrated solutions, the blue tinge becomes more marked. In all the higher alcohols, and acetone, it shows a pure blue color. In the absorption curves of the corresponding solutions, shown in Fig. 1, the logarithm of the extinction coefficient is plotted to facilitate comparison of curves. So far as revealed by the logarithmic curves, the absorption spectra of the solutions in the higher alcohols are identical in shape and differ only in the maximum extinction coefficients attained. The spectrum of the solution in acetone is seen to differ in several respects from the alcohol curves. Within the series, therefore, there are apparent three sorts of deviations from the water spectrum—that shown by methanol, that shown by the higher alcohols and that shown by acetone.

Effects of Added Chloride.—Additions of lithium chloride to solutions of cobalt chloride in methanol intensify the blue color. Solutions in acetone or the higher alcohols remain blue. Spectrophotometric investigation of the acetone solutions shows, however, that the absorption does not remain unchanged. The behavior is summarized in Fig. 2. Addition of small portions of concentrated aqueous hydrochloric acid to a solution of cobalt chloride in acetone (0.7–10% by volume) gives a spectrum showing peaks at 625, 635, 665 and 690–695 $\text{m}\mu$, with an inflection at 610 $\text{m}\mu$. The picture is essentially the same as for addition of excess lithium chloride to cobalt chloride in acetone, with there being a question as to whether the pair of peaks at 625 and 635 $\text{m}\mu$ as compared to the single lithium chloride-induced peak at 625–630 $\text{m}\mu$ indicates a significant difference.

The methanol solution is less responsive to added chloride (Fig. 3). However, with 20 equivalents of LiCl there are sharply defined a peak at 595 $\text{m}\mu$ and one at 670–675 $\text{m}\mu$, in addition to the still large peak at 530 $\text{m}\mu$. With isopropyl alcohol, 66 equivalents of LiCl produce little obvious change. Inspection shows, however, that the 575 $\text{m}\mu$ peak has been replaced by one at 595 $\text{m}\mu$, the peak at 615 $\text{m}\mu$ is no longer distinguishable, and the long wave length peak has been shifted from 660 to 675 $\text{m}\mu$. The shape of the curve is hardly distinguishable from that for the methyl alcohol solution with 20 equivalents of LiCl ,

(1) Presented in part at the American Chemical Society meeting in Atlantic City, September, 1949.

(2) R. A. Robinson and J. B. Brown, *Trans. Proc. Roy. Soc. New Zealand*, **77**, 1 (1948).

(3) Y. Wormser, *Bull. soc. chim. France*, 395 (1948).

(4) M. C. Barbinok, *J. Phys. Chem. (USSR)*, **22**, 1100 (1948).

(5) M. Bobtelsky and K. S. Spiegler, *J. Chem. Soc.*, 143 (1949).

(6) P. Job, *Ann. chim.*, [10] **9**, 113–134 (1928).

(7) L. I. Katzin and E. Gebert, *THIS JOURNAL*, **72**, 5455 (1950).

(8) L. I. Katzin, J. R. Ferraro and E. Gebert, *ibid.*, **72**, 5471 (1950).

(9) F. W. Zerban and L. Sattler, *Ind. Eng. Chem., Anal. Ed.*, **18**, 138 (1946).

(10) L. I. Katzin and J. C. Sullivan, *J. Phys. & Colloid Chem.*, in press; A. E. C. Declassified Document No. 2537.

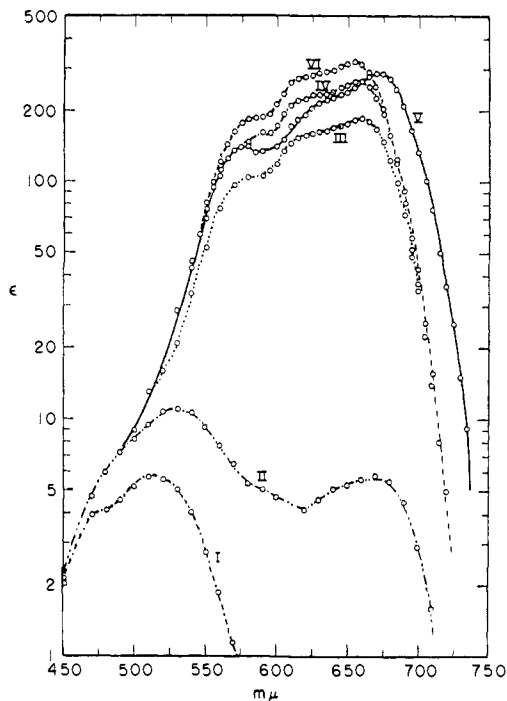


Fig. 1.—Absorption spectrum of cobalt chloride in various solvents: I, H_2O (identical with $\text{Co}(\text{ClO}_4)_2$ in methanol); II, methanol; III, ethanol; IV, isopropyl alcohol; V, acetone; VI, *t*-butanol.

aside from the absorption (in the methanol) below *ca.* 570 $\text{m}\mu$.

Nature of Absorbing Species: Cl:Co ratios.—The differences in the spectra in the various solvents and under the varied conditions indicate that more than one species of absorbing entity is involved. The results of adding lithium chloride make it seem that the differences are concerned at least in part with differences in the ratio of chloride to cobalt in the absorbing body.

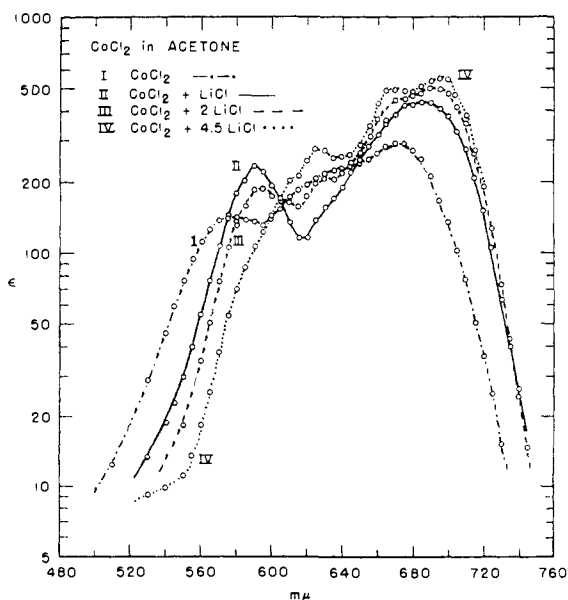


Fig. 2.— CoCl_2 in acetone with additions of LiCl .

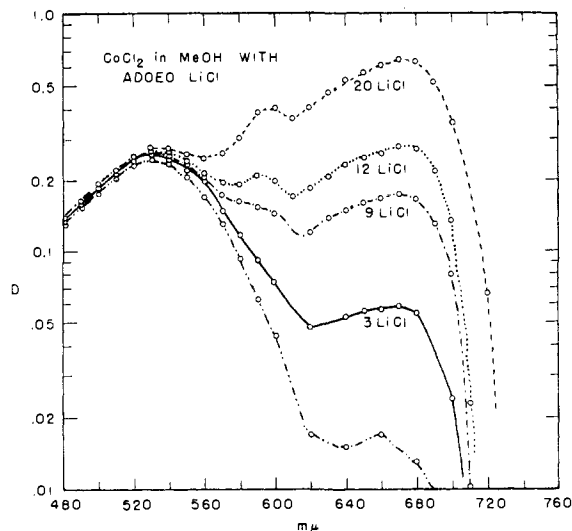


Fig. 3.— CoCl_2 in methanol with additions of LiCl .

The association of definite portions of the observed spectra with entities having definite Cl:Co ratios is possible through the method of "continuous variations" originated by Job.⁸ The method is based upon the relation that mixing two reagents which form an additive complex, to a fixed total formal concentration gives a maximum concentration of the complex when the reagents are in the stoichiometric proportion in which they appear in the complex. Katzin and Gebert⁷ have developed the case for the appearance of more than one complex. They found that the maximum of the lowest complex, which may be designated AB_n , came at a reagent ratio $B:A$ lower than the value n , and the highest complex reached a maximum at a reagent ratio greater than the composition ratio. An intermediate complex, if it exists, achieves its maximum approximately at its composition ratio, depending on the properties of the other complexes. Using the differences in absorption spectra of the complexes to detect them, and restricting ourselves here to the case in which all the complexes absorb more strongly than the uncomplexed material A , a system with but two complexes will show a peak in excess optical density (over that of the reagents singly) somewhere between the concentration peaks of the two complexes. Where one of the complexes absorbs much more strongly than the other, the maximum in excess density will fall close to the maximum concentration point of the absorbing complex. With three complexes in the system, the middle one absorbing less than either the lowest and highest, one will find two peaks and a minimum in the excess density values. In the special case that the first complex is strong enough that at concentrations used in the experiments it is essentially completely associated, one may use M molar AB_n and B as reagents, instead of A and B , and the complex AB_{n+p} will then give a maximum at the reagent ratio p . This method is useful to improve "resolution" of higher complexes.

By use of cobalt perchlorate and lithium chloride as the reagents, one may apply the method to the methanol system (Fig. 4). In the neighborhood of 665 $\text{m}\mu$, the excess density is at its peak near a Cl:Co ratio of 3:1; in the neighborhood of 530 $\text{m}\mu$, the peak comes at 2:1 or below, and at 570–590 $\text{m}\mu$ the peak comes at 2:1 or above. These results are consistent with the presence of complexes of the cobalt and chloride composition CoCl_2 and CoCl_3^- . There is dominant absorption of the former around 530 millimicrons, and of the latter in the region around 665 $\text{m}\mu$. Both absorb in the range 570–590 $\text{m}\mu$ (and perhaps higher), while the form of CoCl_2 composition absorbing at 570 $\text{m}\mu$ may be different than that absorbing at 530 $\text{m}\mu$.

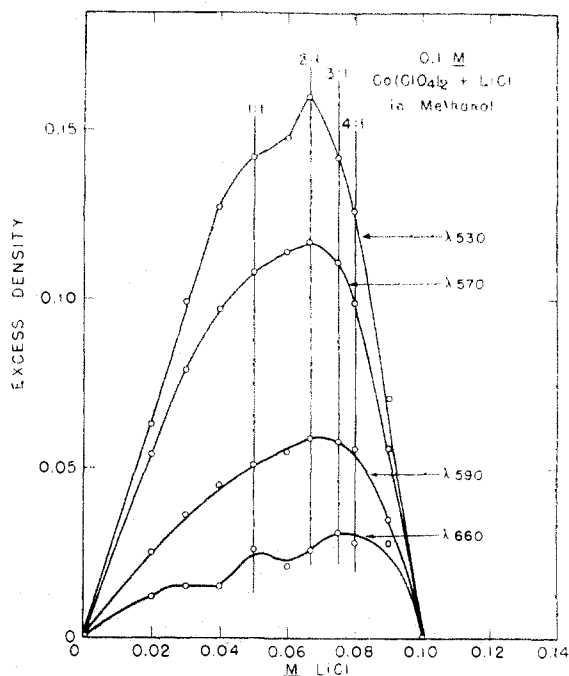


Fig. 4.—Continuous variations test in methanol.

In similar fashion (see Fig. 5), the ethanol solutions show the influence of a 2:1 chloride-to-cobalt ratio at 515 $m\mu$, with most of the absorption being due to this body; absorption at 570–595 $m\mu$ showing contributions from both 2:1 and 3:1 bodies; and from 620–700 $m\mu$, the dominance of absorption due to the 3:1 chloride-to-cobalt entity. There is a suggestion of a weak 4:1 con-

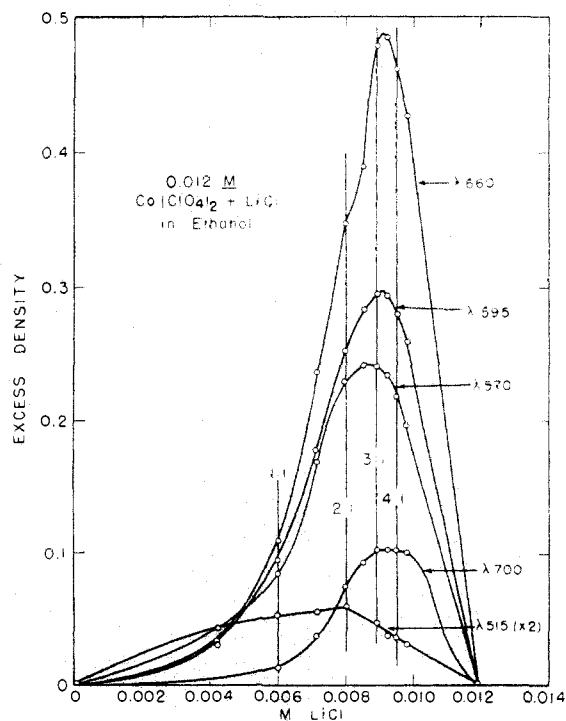


Fig. 5.—Continuous variations test in ethanol.

tribution at 700 $m\mu$. The fact that around 575 $m\mu$ there is strong absorption due to a 2:1 body, with the absorption at this wave length much stronger than at 530 $m\mu$, the reverse of the methanol situation, gives basis for the statement that in methanol two 2:1 bodies are represented, but in different proportions than in the case of the higher alcohols. The picture in isopropyl alcohol is in all respects similar with somewhat sharper differentiation of the CoCl_2 absorption at 570 $m\mu$, and the 3:1 absorption at 590 $m\mu$. The 3:1 absorption shows through 680 $m\mu$.

As might be expected from the variations of the spectrum on addition of LiCl to CoCl_2 in acetone, the experiments with cobalt perchlorate and LiCl in that solvent (Fig. 6) show the absorption at 570 and 620 $m\mu$ to be due to a CoCl_2 entity, while 650 to 670 $m\mu$ show both the 2:1 and higher absorptions to be involved. The absorption from 689–700 $m\mu$ shows a progressively increasing influence of a 4:1 entity. As expected also, the 620 $m\mu$ region shows the 4:1 absorption since the 3:1 has a minimum here. Experiments with CoCl_2 and LiCl show even more precisely the combined influence of CoCl_3^- and CoCl_4^{2-} entities at 620 $m\mu$, and the influence of the latter from 650 $m\mu$ on. It therefore is clear that the successive spectral changes in acetone represent spectra of 2:1, 3:1 and 4:1 $\text{Cl}:\text{Co}$ entities, respectively.

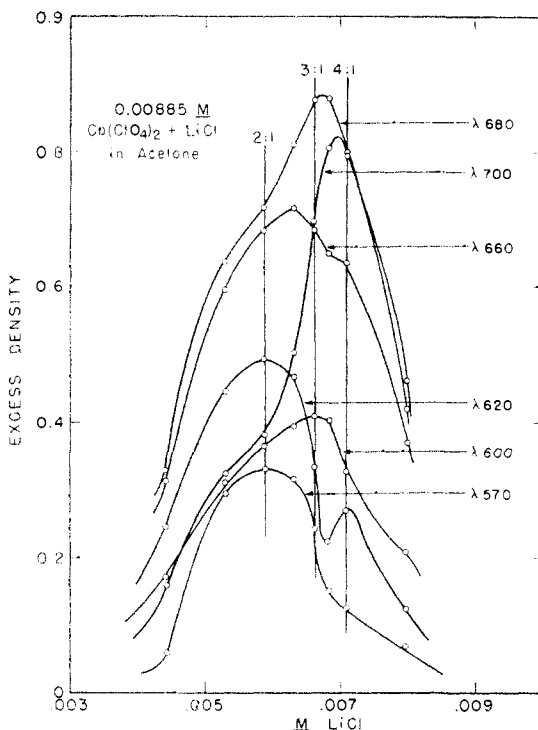


Fig. 6.—Continuous variations test in acetone.

In summary of this series of experiments one may say that there seem to be at least two sets of spectra attributable to CoCl_2 entities. One is characterized by the 530 $m\mu$ peak found for CoCl_2 in methyl alcohol. Another is characterized by the peaks at 575 $m\mu$, and 615–620 $m\mu$ found in the higher alcohols. The peak at about 660 $m\mu$ in the alcohols is probably also due to this entity, but determination of this is complicated by the heavy absorption in the same region of the CoCl_3^- complex, which may mask the assignment of the absorption to CoCl_2 . Similarly, in acetone the assignment of the 575 $m\mu$ absorption to CoCl_2 is definite; there is a CoCl_2 absorption near 620 $m\mu$ but not at the precise wave length at which it is found in the alcohols, and there is perhaps a little more direct evidence that the long wave length peak at 675 $m\mu$ is attributable to CoCl_2 . This then is definitely different in wave length

from the alcohol long wave length peak. The general picture of the spectra leads the authors to favor the latter view.

Similarly, the CoCl_3^- spectra in the alcohols and in acetone have the absorption peak at $595 \text{ m}\mu$ in common, with the second peak being at $675 \text{ m}\mu$ in the alcohols, and at $685 \text{ m}\mu$ in acetone. In the latter case especially the possibility of a small contribution to this peak from a higher complex cannot be completely ruled out, but from the evidence is undoubtedly quite minor. For the spectrum of the CoCl_4^- group we have given evidence solely from the acetone system; identical results for this and the lower Cl:Co ratios have been obtained with an ether, tetrahydrofuran. The sole point of difference seems to be that the CoCl_4^- form is a little harder to produce, a detectable amount of the CoCl_3^- entity still being present at an 8 to 1 ratio of lithium chloride to cobalt chloride.

A question basic to the interpretation of the spectra found is that of the degree of disproportionation of a solution of CoCl_2 in alcohol or acetone, since it is possible that the differences between the two spectra might be due to the variation in degree of disproportionation. A spectrum that might be attributed to a pure CoCl_2 absorption could afford a resolution of this question. It is therefore interesting that the spectrum of CoCl_2 in quinoline (Fig. 7) shows essentially only two peaks, at 575 and $615\text{--}620 \text{ m}\mu$, with slight inflections at 640 and about $660 \text{ m}\mu$. Pyridine (Fig. 7) shows a mixture of quinoline and methanol spectra. If one makes the assumption that the quinoline spectrum is pure CoCl_2 spectrum, and the spectrum of $\text{CoCl}_2 + \text{LiCl}$ in acetone is pure CoCl_3^- spectrum, mixtures of these in the proper proportions should reproduce the alcohol and acetone pictures. In actuality, this turns out to be impossible.

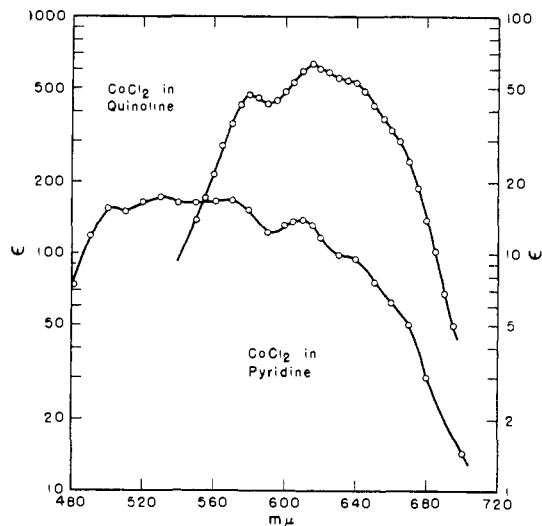


Fig. 7.—Spectra of CoCl_2 in quinoline and in pyridine.

Solvation Effects.—In what has been presented to this point, in addition to the differences between the acetone and alcohol spectra for CoCl_2 , there is the distinctive spectrum for CoCl_2 in methanol, and the spectra for CoCl_2 in quinoline and in pyridine. These differences, from the evidence of the method of continuous variations presented above, must be attributed in the main to the influence of groups other than Cl^- interacting with the cobalt in the solution, *i. e.*, the solvent molecules.

Further differences are indicated on addition of lithium chloride to the solutions. In the case of acetone, a spectral change is induced on the addition of one equivalent of chloride which in the alcohols is found only on addition of gross excesses of chloride, and which still differs in detail from the corresponding acetone picture. Finally, addition of excess LiCl or HCl to CoCl_2 in acetone or tetrahydrofuran produces a spectral change which is not given by

much larger excesses of lithium chloride in the alcohols. Thus there is evidence for a solvation effect of another kind, namely, apparent interference in the reaction between cobalt and chloride. The fact that alcohols from methyl through tertiary butyl evidence this difference shows it is not primarily a function of dielectric constant, but of structural groups.

Interesting data come from comparison of solvents in mixtures. Addition of a rather small amount of pyridine or quinoline to a CoCl_2 solution in acetone gives a noticeable spectral change (Fig. 8). Investigation of the rela-

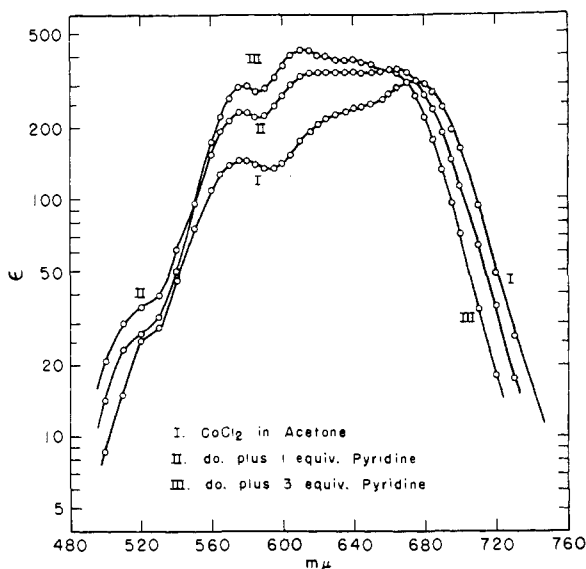


Fig. 8.—Effect of pyridine on CoCl_2 spectrum in acetone.

tions by the method of continuous variations shows that the effect involves products with one and two molecules of base per cobalt atom, respectively (Fig. 9). The effect of the one-pyridine product seems most marked. If to the CoCl_2 reactant solution is added an equivalent of LiCl , again addition of the pyridine will produce a spectral altera-

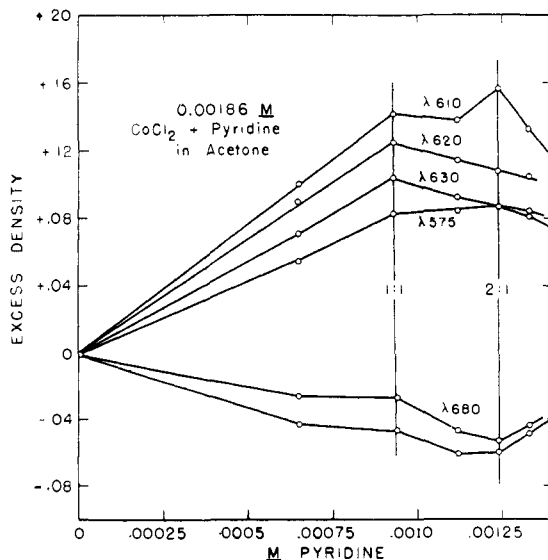


Fig. 9.—Continuous variations test, effect of pyridine on CoCl_2 in acetone.

tion (Fig. 10) which the method of continuous variations ascribes mainly to a single molecule of the base with a very minor portion due to a product containing two pyridines.

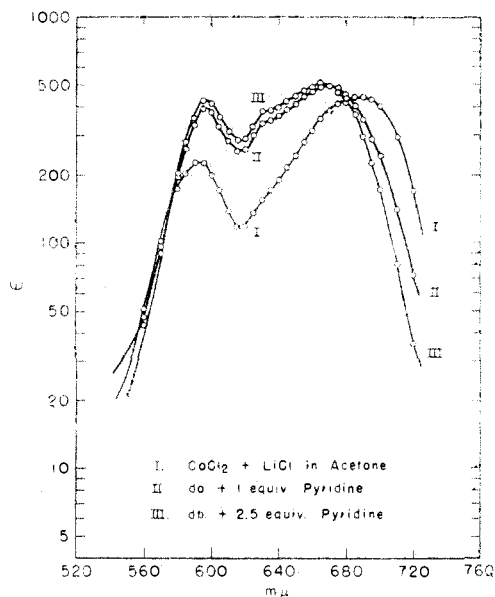


Fig. 10.—Pyridine effect on spectrum of $\text{CoCl}_2 + \text{LiCl}$ in acetone.

If, to a cobalt chloride solution containing excess lithium chloride, so that it is characterized by the spectrum attributed to the CoCl_4^{2-} complex, one now adds pyridine, a different alteration of spectrum occurs. The spectrum attained this time becomes indistinguishable from that where only one equivalent of LiCl has been used and a single molecule of pyridine seems to be involved in the principal change (Fig. 11). Investigation of the reactant solution ($\text{Co}(\text{ClO}_4)_2 + \text{pyridine}$) against lithium chloride solution shows that the $575 \text{ m}\mu$ peak is due to CoCl_2 , and the $595 \text{ m}\mu$ peak to CoCl_3^- , and there is no clear indication of the formation of CoCl_4^{2-} complex. In this case, therefore, there is obvious competition between pyridine and the fourth chloride to be complexed, with the equilibrium largely displaced in favor of the pyridine.

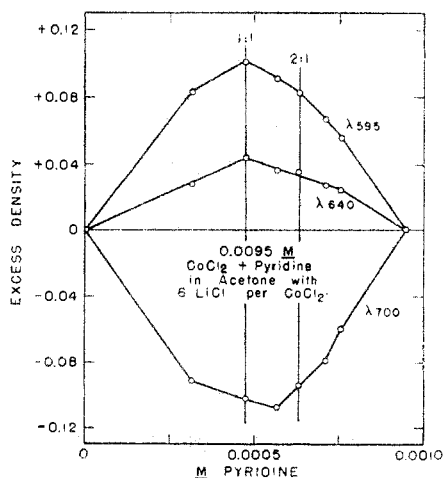


Fig. 11.—Continuous variations test, effect of pyridine on CoCl_4^{2-} spectrum.

The spectral changes found on adding pyridine to cobalt chloride solutions in the isopropyl alcohol are small, the extinction values at any given wave length changing very little. As a consequence, application of the method of continuous variations is difficult. There seems to be indication here of two complexes, one with one or two pyridines involved, and one with some relatively large number, probably greater than 4. In *t*-butyl alcohol the complexes involve one pyridine and possibly two pyridines also.

The effects of addition of alcohol to the acetone solutions is small, and visible only with concentrations of the order of 5–10% by volume. The effects of water, in the range of 1 per cobalt, could not be studied reliably, since for solutions of the order of 0.001 M for spectrophotometric observation it would be essential to keep the water below a tenth of this, or 0.02% . The analytical method, with acetone, is inadequate for these requirements. In the ranges of higher water concentration, however, the effects are significant. Their direction is indicated in Fig. 12, where the solute is CoCl_2 . The absorption peak normally at $675 \text{ m}\mu$ is shifted toward lower wave lengths, and the $575 \text{ m}\mu$ absorption is decreased, more than the over-all lowering in absorption intensity. The spectrum approaches in some ways the spectrum of the CoCl_3^- entity, allowing for the alteration in position of the long wave length peak. Addition of lithium chloride to the solution containing water verifies this, since the $595 \text{ m}\mu$ peak of the CoCl_3^- entity is sharpened, and the spectrum clarified. In *t*-butyl alcohol addition of water lowers the absorption intensity without changing the shape.

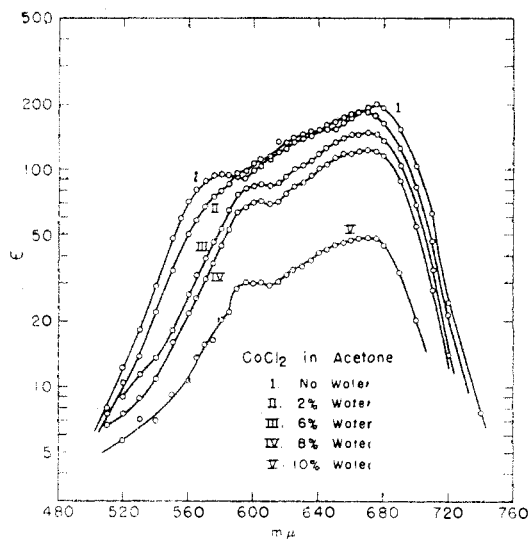


Fig. 12.—Effect of water on spectrum of CoCl_2 in acetone.

Since a number of complexes of cobalt chloride and pyridine are known in the solid state, and since solids alleged to have the CoCl_4^{2-} unit have also been prepared, it is of interest to look at their spectra in solution. The compounds $\text{CoCl}_2 \cdot 2\text{Py}$, $\text{Co}(\text{Py})_6\text{Cl}_2$ and $(\text{HPy})_2\text{CoCl}_4$ were chosen for this purpose.

The dipyrnidinium cobalt tetrachloride is soluble in acetone and alcohols, but not appreciably soluble in chloroform or benzene. The absorption spectrum in both alcohols and acetone was that of the equivalent mixture of cobaltous chloride and lithium chloride, *i. e.*, the spectrum of the CoCl_2 entity in the alcohols, and the spectrum of the CoCl_3^- entity with a trace of CoCl_4^{2-} in acetone. The CoCl_4^{2-} grouping which has been demonstrated crystallographically in Cs_3CoCl_5 ¹¹ and which is believed by Percival and Wardlaw¹² to be present in the dipyrnidinium compound, does not seem to survive into solution. The

(11) H. M. Powell and A. F. Wells, *J. Chem. Soc.*, 359 (1935).
 (12) E. G. V. Percival and W. Wardlaw, *ibid.*, 1505 (1929).

ebullioscopic tests of Percival and Wardlaw indicated a dissociation in solution into 2-3 particles; our evidence confirms this but indicates that the dissociation is not ionic, into pyridinium ions and CoCl_4^- ions, but rather into molecular entities, pyridinium chloride and cobaltous chloride.

In a given solvent, be it alcohol, acetone, chloroform or benzene, the absorption spectra of $\text{CoCl}_2 \cdot 2\text{Py}$ and $\text{Co}(\text{Py})_2\text{Cl}_2$ are indistinguishable. In the alcohols and in acetone, the spectra are indistinguishable from those given by mixtures of cobalt chloride and pyridine in the same proportion. There is further but a small difference between these solutions and those with more pyridines, as would be deduced from the "continuous variations" experiments cited earlier. The greatest difference occurs between the alcohol spectrum and the other spectra; the absorption pictures in acetone, chloroform and benzene for $\text{CoCl}_2 \cdot 2\text{Py}$ are very closely similar (Fig. 13). The order of spectral differences noted, from the alcohols through the hydrocarbon benzene, is also the order of decreasing polarity of molecules, and qualitative confirmation of the evidence obtained from the effects of added chloride of the role of solvent-solute interaction in the complexing picture. If one extrapolates qualitative similarity into semiquantitative relationships, one may say that the solvent-solute interaction in the acetone solution is not much greater than that in the benzene solution, and that therefore, since we expect little or no interaction in the latter, it may be very weak in the former.

Discussion

The various observations can be correlated in terms of variation in kinds and numbers of groups coordinated. The normal salmon-pink of dilute aqueous cobaltous solutions, with absorption centering at $510 \text{ m}\mu$, is due to the hexahydrated cobaltous ion. Cobalt chloride in methanol shows a magenta color with absorption centering at about $535 \text{ m}\mu$. The same color is shown by solid cobalt chloride tetrahydrate,¹³ solid cobalt chloride tetrapyridine, and solutions of cobaltous nitrate in organic solvents.⁷ For both the chloride and the nitrate solutions it has been shown that the absorption is associated with CoX_2 entities, and it seems unmistakable that this color is due to $\text{CoX}_2 \cdot 4\text{Z}$, where Z represents various molecular groups (water, pyridine, methanol, etc.).

The CoCl_2 entity which gives a blue color is presumably different in solvation from the one just discussed, and it is our conclusion that the blue cobalt chloride forms are $\text{CoCl}_2 \cdot 2\text{Z}$. The most direct evidence involves the pyridine-containing solutions. Cobalt chloride in pyridine shows a mixture of "blue," and methanol-like "red" spectra. Dilution of the pyridine, as with acetone, leaves only "blue" spectrum. This blue spectrum is identical to that found on adding two pyridines to the blue CoCl_2 entity of the acetone solution, with the resulting pyridine-containing entity retaining the two chlorides. When one adds pyridine to the CoCl_4^- entity in acetone, a pyridine enters the group by eliminating a chloride. Addition of one pyridine to the CoCl_3^- entity in acetone can be accomplished without displacing a chloride. In addition to this evidence, when cobalt chloride tetrapyridine is treated with benzene, in which it is only slightly

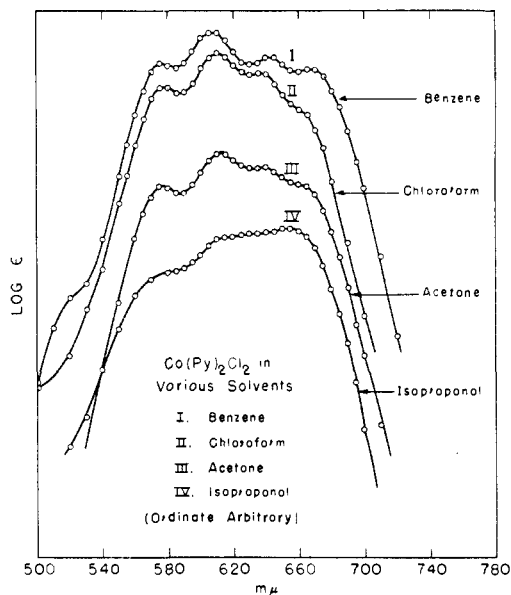


Fig. 13.— $\text{Co}(\text{Py})_2\text{Cl}_2$ in various solvents; comparison of shapes of absorption curves (relative ordinates arbitrary).

soluble, a deposit of blue cobalt chloride dipyridine forms on the undissolved solid,⁸ indicating dissociation of pyridine on solution of the tetrapyridinate; ether, in which the latter is completely insoluble, fails to give this reaction. The benzene solution is blue. If large excesses of lithium chloride are added to cobalt chloride in methanol, in which the red-type spectrum predominates, blue CoCl_2^- spectrum which is found with the higher alcohols appears, but the bulk of the red-type absorption remains.

Including the blue entities with more than two chlorides per cobalt, one may say that the forms giving blue-type spectra all represent 4-coordinated cobalt, and that the spectral variations are functions of the particular groups bound. Since the same spectrum appears in the several alcohols, which is different from that in acetone and tetrahydrofuran, and different from the blue spectra of pyridine and quinoline-containing solutions, the nature of the coordinating group of the solvent evidently plays an important role in determining the spectral absorption. The spectral data summarized in Table I indicate the characteristic absorption peaks for the various absorbing species.

The blue CoCl_4^- group in Cs_3CoCl_5 has been shown to be tetrahedral.¹¹ A similar group presumably is found in blue $(\text{HPy})_2\text{CoCl}_4$.¹² This compound, when dissolved in acetone or alcohol, is dissociated to give CoCl_2 and CoCl_3^- entities. Addition of more lithium or pyridinium chloride to the acetone solution gives a spectrum attributable to a CoCl_4^- group. There is no *a priori* reason for the configuration of this group in solution to be different from that in the solid. When the group reacts with a single pyridine

(13) L. I. Katzin and J. R. Ferraro, unpublished data.

TABLE I
ABSORPTION MAXIMA FOR Co(II)-Cl COMPLEXES

Bracketed wave lengths indicate small or poorly delineated peaks, detected by inflection points in curves.

Absorbing form	Peaks primarily determined by Cl:Co ratio, $m\mu$	Peaks largely dependent on molecular addenda (X), $m\mu$
Co(H ₂ O) ₆ ²⁺		510
CoX ₄ Cl ₂		525-540
CoX ₂ Cl ₂	575	610-615, 640, 665 (pyridine, quinoline) 615, 655-660 (alcohols) 625-630, 675 (acetone, tetrahydrofuran)
CoXCl ₃ ⁻	595	630, 665 (pyridine, quinoline) [625], [640], 675 (alcohols) [630], 685 (acetone, tetrahydrofuran)
CoCl ₄ ⁻	[615], 625, [640], 670, 700 (LiCl in acetone, tetrahydrofuran) 615, 625, 635, 665, 695 (HCl in acetone)	

molecule, eliminating a chloride in the process, there is no evidence for a possible change in configuration. There is, in fact, no such evidence in the solution behavior in any of the 4-coördination substitutions.

In the case of solid compounds of the type CoCl₂·2Z, however, there are customarily found two crystal forms, differing in color. In the dipyridine and the dihydrate cases, for example, there are a stable violet-colored form, and an unstable blue. On no more evidence than this analogy with some other metallic elements, the assumption has been made that *cis* and *trans* isomers of planar molecular groupings are involved. All tests by magnetic susceptibility criteria have shown behavior attributable to ionic or tetrahedral coördination, rather than the *dsp*² binding of a planar configuration.^{14,15} The sole positive evidence offered is in the case of violet CoCl₂·2Py, in which Cox, Shorter, Wardlaw and Way¹⁶ find X-ray evidence that the four coördinated groups must be in the same plane, and the two pyridines are *trans* to each other (significantly, they were not able to show that the blue form is *cis* planar). Mellor and Coryell¹⁷ point out that the X-ray data are equally well satisfied if the cobalt is octahedrally coördinated with links to chlorides in planes above and below. The violet color in this case would represent a further extension of the magenta color induced by replacement of two waters by the anions. Even in the case of definitely coördinately bound complexes, such as those of nickel, two solid forms not in the relation of *cis* and *trans* isomers

(14) E. D. P. Barkworth and S. Sugden, *Nature*, **139**, 374 (1937).

(15) D. P. Mellor and R. J. Goldacre, *J. Proc. Roy. Soc. N. S. Wales*, **73**, 233 (1940).

(16) E. G. Cox, A. J. Shorter, W. Wardlaw and W. J. R. Way, *J. Chem. Soc.*, 1556 (1937).

(17) D. P. Mellor and C. D. Coryell, *This Journal*, **60**, 1786 (1938).

may be met. Thus, there have been prepared by Lifschitz, Bos and Dijkema¹⁸ isomeric, easily interconvertible, cationic nickel complexes, in which one form is bluish-green and paramagnetic, and the other form yellow and diamagnetic. Likewise, Willis and Mellor¹⁹ have shown that complexes of nickel which are diamagnetic in the solid state may show paramagnetism corresponding to two unpaired electrons in solution.

The paramagnetic Ni(II) complexes are usually taken to have the configuration $3d^84s^24p^6$ (tetrahedral, with *sp*³ binding), and the diamagnetic complexes are assumed to be square (*dsp*²) with configuration $3d^{10}4s^24p^4$. The 4 electrons in the 4*p* shell of this configuration are paired, leaving one orbital vacant. An analogous square Co(II) configuration, because one less electron is available, would have both the 3*d* and 4*p* shells incomplete simultaneously. The tendencies summarized in Hund's rule would lead to a prediction that this sort of configuration in Co(II) should be most unstable, since even in the case of Ni(II) its stability is limited. The evidence already given that the "blue" forms of the cobalt halides are tetrahedral groups may be taken as confirmation.

The relation between the forms with 4 groups coördinated and those with 6 groups is difficult to establish. Co(II) has 7 electrons to use in filling the 3*d*, 4*s*, and 4*p* shells. With the maximum pairing, this leaves only 5 orbitals to hold 6 groups, as in the case of the hexahydrated ion. No good picture of this process has been presented. Magnetic susceptibility studies on the hexahydrated ion have shown values approaching 5 unpaired electrons. Although this result has usually been passed off as 3 unpaired electrons with an unexpectedly high orbital contribution, the susceptibility values could equally well result from the configuration $3d^54s^2$ (a half-filled shell is recognized as a rather stable configuration). Resonance or electrostatic binding could account for the total of 6 groups coördinated; part might fill the vacant 4*p* orbitals. This should be considerably less stable than a true hexacoördinate condition (*e. g.*, Co(III)), so that in solutions of low "base strength" the tetracoördinate condition results, with 4 pairs of electrons coming from the donor groups.

In the recent papers on the cobalt chloride complexes cited earlier, three applied the method of continuous variations, two of them^{4,5} following the blue color, and coming to the conclusion that it was due to CoCl₄⁻. In both cases, apparently, failure to realize the alterations in the continuous variations relations with more than one complex present was partly to blame for missing the other complexes. Barbinok⁴ had no steps intermediate between Cl:Co ratios

(18) I. Lifschitz, J. G. Bos and K. M. Dijkema, *Z. anorg. allgem. Chem.*, **242**, 97 (1939).

(19) J. B. Willis and D. P. Mellor, *This Journal*, **69**, 1237 (1947).

of 2.33 and 4.0; Bobtelsky and Spiegler⁵ explicitly assumed that complexes of the type CoX_3^- did not exist. Conductivity data also gave the latter an indication of a CoX_2 complex in water-alcohol mixtures, but it is not possible to say whether this was the $\text{CoCl}_2 \cdot 4\text{Z}$ or $\text{CoCl}_2 \cdot 2\text{Z}$ complex. Wormser³ followed the electrical conductivity changes rather than colors, and the method of continuous variations gave evidence for a trichloro complex. This means only that this complex is much more highly conducting than the other two. Earlier data of Groh and Schmid²⁰ confirm Wormser's data on the conductivity. Wormser's identification of a spectrum due to a CoCl^+ complex is apparently based on a misinterpretation, engendered in part by her recognition of only the CoCl_3^- complex.

Robinson and Brown² used a different technique, and concentrated aqueous salt solutions. Their identification of $\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2$ as the source of blue color is probably due to not properly interpreting the first-formed "rose" solutions with absorption maximum shifted to 525 μ as due to this entity. A similar rose colored aqueous

(20) J. Groh and R. Schmid, *Z. anorg. allgem. Chem.*, **162**, 321 (1927).

solution has been recognized by other workers.^{21,22} The blue complex dealt with by Robinson and Brown is probably $\text{Co}(\text{H}_2\text{O})_2\text{Cl}_2$; formation of higher complexes seems unlikely in aqueous solution.

Summary

1. The absorption spectra shown by cobalt chloride dissolved in various solvents are shown to be ascribable to the entities $\text{Co}(\text{H}_2\text{O})_6^{++}$, CoX_4Cl_2 , and CoX_2Cl_2 , with colors, respectively, salmon-pink, rose to magenta, and blue.

2. In a solution containing excess chloride (e. g., as LiCl), the blue forms CoX_2Cl_2 , CoXCl_3^- and CoCl_4^{--} may be found, their proportions depending on equilibrium between the metal ion, anions and molecular "bases" (electron donors) present. The spectra characteristic of these forms are described.

3. Evidence is given to show that the various blue forms have tetrahedral groupings of electron donors around the metal atom, and suggestions are made for the electron configurations involved.

(21) A. v. Kiss and M. Gerendas, *Z. physik. Chem.*, **180**, 117 (1937).

(22) W. A. Weyl, *J. Applied Phys.*, **17**, 628 (1946).

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Some New Pyridine Compounds of Cobalt(II) Salts

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The similarity between the hydrates, ammoniates and pyridinates¹ of a number of salts has been observed and commented upon many years ago (e. g., Reitzenstein, 1897,^{1a} and literature quoted therein). With particular respect to cobalt(II) chloride, the hexahydrate, dihydrate and monohydrate are known, as well as the corresponding ammoniates and pyridinates.² Although the tetrahydrate is usually accepted as stable at room temperature only in the form of mixed crystals with MnCl_2 ,³ the tetrammoniate⁴ and the tetrapyridinate² are known. In the case of cobaltous nitrate, the hexahydrate, tetrahydrate,^{5,6} trihydrate and dihydrate are recognized; the literature shows only the hexammonia^{7,8} and the

tetrapyridine^{1,9} compounds. Finally, with the perchlorate, the hexahydrate² is known, formation of a tetrahydrate is certain,¹⁰ and preparation of the corresponding hexammonia,² tetrammonia² and tetrapyridine¹¹ compounds has been reported.

We have confirmed the preparation of the cobalt chloride hexa-, tetra- and dipyridine compounds. In the case of cobalt nitrate, we have prepared all of the pyridine analogs of the hydrates, namely, the hexa-, tetra-, tri- and dipyridinates. In addition, a mixed water-pyridine tetrasolvate, the dihydrate-dipyridinate was prepared. In the case of the perchlorates, the hexapyridinate and tetrapyridinate-dihydrate, a mixed hexasolvate, have been made.

The ready preparation of the stable cobalt chloride tetrapyridinate, and the reported tetrammoniate, are interesting, since one investigator has reported the tetrahydrate to be stable only in the temperature region 48–58°,¹² another has reported its formation at 116°,¹³ and deConinck¹⁴

(1) To save space, and because the compounds are treated as solvates rather than "complexes," the terms hydrate, ammoniate and pyridinate are used instead of aquo coordination compound, ammine coordination compound and pyridine coordination compound. "Cobalt," without further designation, means cobalt(II).

(1a) Reitzenstein, *Z. anorg. Chem.*, **18**, 253 (1898).

(2) Gmelin's "Handbuch der anorganischen Chemie," Cobalt (Sys. No. 58), 8th Ed., Verlag Chemie, Berlin, 1932; Abt. A, p. 275, 301; Abt. B, p. 11, 13, 21, 24.

(3) Stortenbeker, *Z. physik. Chem.*, **16**, 250 (1895).

(4) Clark, Quick and Harkins, *THIS JOURNAL*, **42**, 2483 (1920).

(5) Funk, *Z. anorg. Chem.*, **20**, 393 (1899).

(6) Katzin and Ferraro, *THIS JOURNAL*, **72**, 5451 (1950).

(7) Ephraim and Rosenberg, *Ber.*, **51**, 130 (1918).

(8) Clark and Buchner, *THIS JOURNAL*, **44**, 230 (1922).

(9) Hantzsch with Schlegel, *Z. anorg. allgem. Chem.*, **159**, 273 (1927).

(10) Katzin and Gebert, to appear in *THIS JOURNAL*.

(11) Weinland, Effinger and Beck, *Arch. Pharm.*, **265**, 352 (1927).

(12) Benrath, *Z. anorg. allgem. Chem.*, **220**, 142 (1934).

(13) Bersch, *Sitzber. Akad. Wiss. Wien, math. naturw. Klasse, Abt. II*, **66**, 724 (1867).

(14) deConinck, *Bull. classe sci., Acad. roy. Belg.*, **803**, 1170 (1904).