34. *The Cobalt Halide and Thiocyanate Complexes in Ethyl-alcoholic Solution.*

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The change of colour from pink to blue, which occurs on addition of hydrogen chloride to solutions of cobaltous nitrate in mixtures of ethyl alcohol and water, was studied. It was found that the stability of the blue complexes increases gradually with the alcohol concentration and that the concentration of hydrogen chloride causing half of the maximum absorption in the red range of the spectrum decreases linearly with the alcohol concentration of the medium. These facts led us to a photometric and conductometric study of the complexes in absolute alcohol. The bromo-, iodo-, and thiocyanato-complexes were also studied, and complete analogy in the composition of all complexes found. Conductometric experiments indicate that compounds are formed in the ratio Co : X = 1 : 2 (X = Cl, Br, I, or SCN), and photometric experiments using Job's method of continuous variations prove definitely that in the presence of excess X^- ions, complex ions $[CoX_4]^{--}$ are formed. The decoloration of blue solutions of cobaltous chloride by mercuric chloride is shown to be due to the formation of $[HgCl_4]^{--}$ ions.

Many investigations have been made of the change of colour of solutions of cobaltous chloride under the action of heat, halides, alcohol, sulphuric acid, or other reagents. The bromide, iodide, and thiocyanate of cobalt behave similarly. These changes have been attributed to changes in solvation of the cobalt ion (Jones, *Z. physikal. Chem.*, 1910, **74**, 325; Houston, *Physikal. Z.*, 1913, **14**, 424) or in its co-ordination number (Hill and Howell, *Phil. Mag.*, 1924, **48**, 833; Hantzsch, *Z. anorg. Chem.*, 1917, **166**, 237), and to the formation of complex compounds $[CoX_n]^{(n-2)-}$, X being a halogen or thiocyanate ion (Donnan and Bassett, *J.*, 1902, **81**, 939; Groh, *Z. anorg. Chem.*, 1925, **146**, 305; Howell and Jackson, *J.*, 1936, 1268; 1937, 621; Brintzinger and Retanarat, *Z. anorg. Chem.*, 1935, **223**, 106; Kiss, Czokan, and Richter, *Chem. Abstr.*, 1942, **36**, 2803). Spectroscopic evidence (Macwalter and Barratt, *J.*, 1934, 517) showed that the same blue compound exists in aqueous and in ethyl-alcoholic solutions containing a high concentration of hydrogen chloride. In aqueous solution the blue compounds are unstable and are formed only at high concentration of halogen ions; in ethyl-alcoholic solution, however, the compounds are rather stable. This fact led us to the study of the composition of the coloured halogeno-complexes in ethyl-alcoholic solution by measurements of electrical conductivity and light absorption. In a number of photometric measurements, Job's method of continuous variations as adopted by Vosburgh and Cooper (*J. Amer. Chem. Soc.*, 1941, **63**, 437) for the study of complex ions was used. The method consists of making a number of mixtures of solutions of equal molarity of the two reactants, A and B, and measuring the optical densities of the mixtures at certain pre-selected wave-lengths. If the extinction coefficients of the reactants are negligible, the optical density is a maximum or minimum for the mixture in which the two reactants have been brought together in the proportions in which they react. Even if the reactants combine in different ratios, and stable compounds AB_n, AB_m . . . , AB_z are formed, the maxima or minima of optical density occur at the ratios $x = n, m \ldots, z$ provided particular wave-lengths are selected. The wave-length at which the molar extinction coefficient of AB_z (the compound with the highest index z) exceeds that of the next lower compound AB_y as much as possible is most suitable for determining the composition of AB_z.

The method of continuous variations is not suitable for determining the composition of the cobalt halide complexes in aqueous solution, owing to their low stability in this medium. On the other hand, it proved possible to determine the ratio Co : X in the alcoholic systems, and from these data conclusions may be drawn about the composition of the complexes in aqueous solution.

EXPERIMENTAL.

For the determination of the extinction coefficients a Hellige " pan photometer " equipped with a set of glass colour filters was used. The depth of the light-absorbing layer was 1 or 5 mm. according to the intensity of the colour of the solution.

The conductivity of the solutions was measured by means of the Leeds and Northrup Wheatstone bridge with an A.C. galvanometer as null instrument. The current was 50 cycles. A small cell holding about 3 c.c. was used. Its constant was determined by means of N/50-potassium chloride at 25°. The accuracy of these measurements was $\pm 0{\cdot}5\%$.

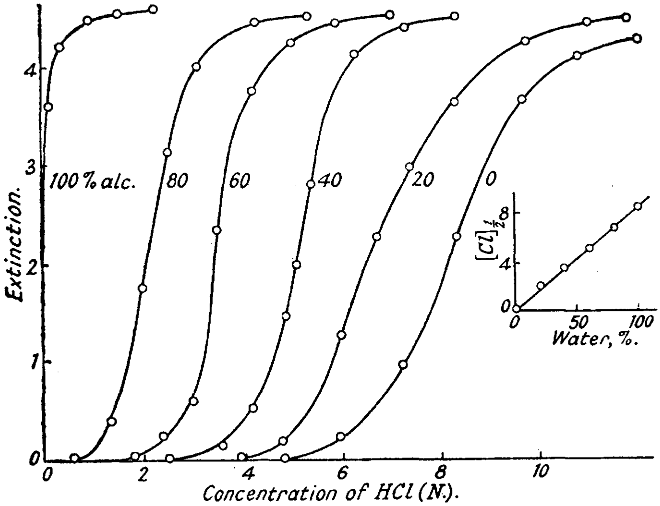
Solutions of $CoCl_2$, $ZnCl_2$, $CdCl_2$, $HgCl_2$, $Hg(OAc)_2$, NaI, and NH_4SCN were made by dissolving the anhydrous salts in absolute alcohol. Cobaltous nitrate dihydrate was prepared by dehydration of the hexahydrate at 74°. Complete dehydration of cobaltous nitrate by this method is not possible owing to partial decomposition. The dried product was dissolved in absolute alcohol, and the solution filtered. Solutions of hydrogen chloride and bromide were prepared by passing the dry gases through absolute alcohol.

The Cobalt Chloride Complexes in Ethyl Alcohol–Water Mixtures.—In order to study the stabilising influence of alcohol on the cobalt chloro-complexes, different amounts of hydrogen chloride were added to solutions of cobaltous nitrate in alcohol–water mixtures, and the absorption of the solutions in the red range of the spectrum measured (filter 6600 A.). The results are plotted in Fig. 1. It is seen that in water the blue compound is not formed at concentrations of hydrogen chloride lower than 5N, whereas in absolute alcohol the blue colour appears even at the smallest concentration of chloride. In the alcohol–water mixtures the minimum concentration of chloride necessary to cause complex formation decreases with increasing alcohol concentration. In all media the extinction coefficient reaches the same maximum value and further addition of hydrogen chloride causes no change. Only in water was the maximum not completely reached. If the concentration of hydrogen chloride causing half of the maximum absorption, $[Cl]_{1/2}$, is plotted against the water concentration, a straight line is obtained, which passes nearly through the origin (see straight-line graph, Fig. 1). This implies that at this absorption the ratio between chloride and water is the same in the different media.

Conductivity Measurements.—In order to determine the composition of the complexes between cobalt and halide ions, the conductivity of a series of solutions of constant halide or thiocyanate concentration and varying concentrations of cobaltous nitrate was measured. The results are shown in Fig. 2. A conductivity minimum at the molar ratio $R = Co : X = 1 : 2$ is common to all the curves. The initial decrease in conductivity is due to complex formation, and the minimum indicates the formation of a compound containing Co and X in the ratio 1 : 2. It cannot be inferred from these curves whether complexes of lower Co : X ratio exist, as the conductivity curve does not consist of straight lines, but is U-shaped. On the right side of the minimum no further breaks in the conductivity curves, which might indicate the presence of cation complexes, are observed. Here, the increase in conductivity with further additions of cobaltous nitrate is smaller than one would expect from the conductivity of pure solutions of the latter. This may be due to the higher viscosity of the solutions containing the halogen or thiocyanate complexes.

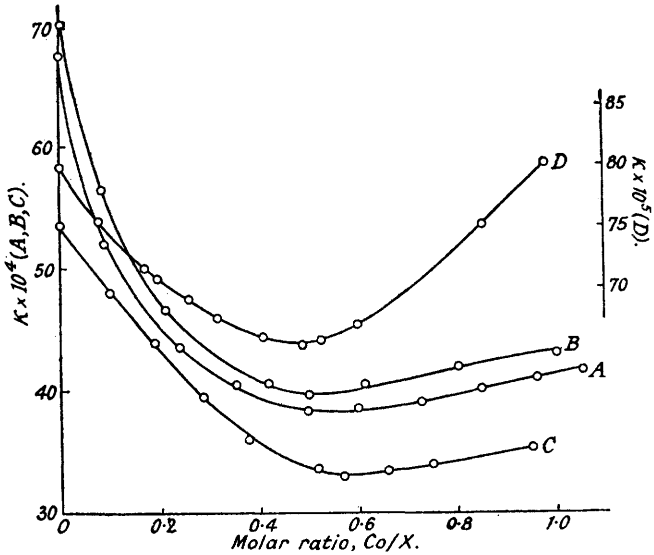
Generally, the results of measurements of conductivity in alcoholic solution do not lend themselves to interpretation as easily as those obtained in aqueous systems. As in alcohol the dissociation of many electrolytes is not complete, equivalence points cannot be determined by linear extrapolation. From our measurements the composition of anion complexes cannot be determined, but the occurrence of a distinct conductivity minimum at the molar ratio Co : X = 1 : 2 shows that compounds are formed at this ratio. The number of solvent molecules in the co-ordination sphere or the degree of association of these complexes cannot be determined by conductometric experiments. The compounds are not autocomplexes, for their spectra are different from those of the ions $[CoX_4]^{--}$ (see later). Solid alcoholates $CoCl_2,2EtOH$

FIG. 1.



Extinction (filter 6600 A.) *of solutions of* 0·01M-*cobaltous chloride and hydrogen chloride in ethyl alcohol–water mixtures at room temperature. All values calculated for* 1 *cm. of absorbing solution. Half-extinction concentration of hydrogen chloride plotted against alcohol concentration.*

FIG. 2.

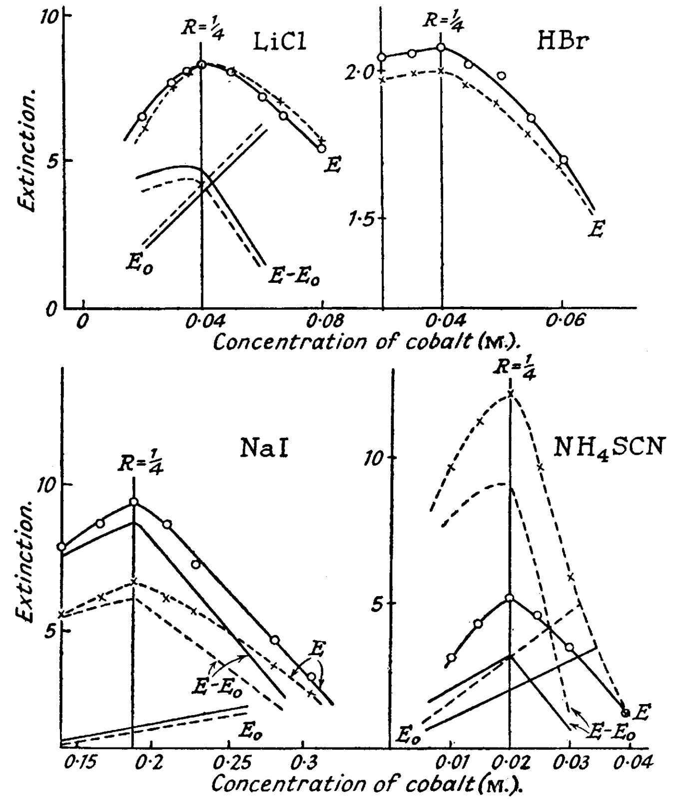


Specific conductivity κ *in absolute alcohol at* 0° *plotted against molar ratio* Co/X : $Co(NO_3)_2$ + (*A*) 0·72N-HCl, (*B*) 0·72N-HBr, (*C*) 0·5N-NaI, (*D*) 0·05N-NH_4SCN.

and $CoCl_2,3EtOH$ are reported in the literature. If we assume that the number of solvent molecules in the co-ordination sphere is equal in the solid and dissolved salts and also that the co-ordination number 5 is improbable, it may be assumed that the complexes present in solution are of the composition $[CoCl_2(EtOH)_2]$ or, generally, $[CoX_2(EtOH)_2]$, *i.e.*, undissociated, solvated molecules.

Photometric Measurements.—The table shows the extinction coefficients of alcoholic solutions of M/10-cobaltous nitrate, and of M/10-cobaltous chloride alone and in the presence of a large excess of hydrogen chloride. The medium was absolute alcohol. It is seen that the extinction of cobaltous chloride cannot be interpreted as a mere superposition of those of rose cobaltous nitrate and of the blue compound formed in excess of hydrogen chloride; it has a spectrum of its own. On the other hand, spectra of solutions containing Co and X in the ratio 1 : 3 can be interpreted as a superposition of cobaltous nitrate, CoX_2, and CoX_2 in the presence of a large excess of X^- ions. It was therefore assumed that complexes containing cobalt and X in the ratio 1 : 3 do not exist.

FIG. 3.



Extinction of mixtures of x *c.c. of* $Co(NO_3)_2$ *and* (10 — x) *c.c. of halide solution of concentration* c *for filters* 6600 *and* 6900 A. *The straight lines* E_0 *are calculated on the assumption that a compound at the ratio* R = Co/X = 1/2 *is formed, but does not react with excess halide :* LiCl, c = 0·2M; HBr, c = 0·2M; NaI, c = 0·95M; NH_4SCN, c = 0·1M.

———————————— 6900 A.
– – – – – – – – – – – – 6600 A.

Extinction coefficients in absolute alcohol for different filters.

		Extinction coefficient, *E*, at :				
Composition of solution. A. :	6900.	6600.	5700.	5500.	5300.	5000.
1 C.c. 0·1M-Co(NO$_3$) + 9 c.c. EtOH	2	1	5	17	20	24
1 C.c. 0·1M-$CoCl_2$ + ,, ...	133	148	89	39	29	12
,, + 9 c.c. 2·25N-HCl...	588	462	62	15	10	6

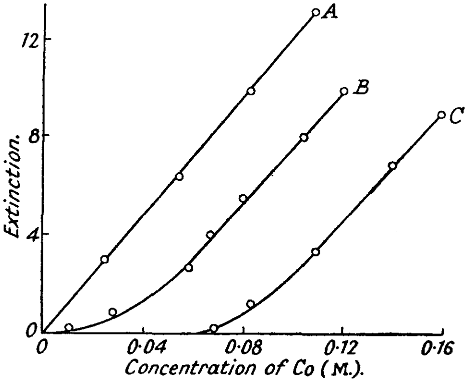
Fig. 3 shows the extinction coefficients *E* at wave-lengths 6900 and 6600 A. of solutions containing cobaltous nitrate and different halides. The sum of the molar concentrations of cobalt and X is equal in all solutions of a particular series. From these curves the difference $E - E_0$ (E_0 = the extinction coefficient of the solution containing Co and X in the ratio 1 : 2) was calculated and plotted in the same diagram. *The latter curves have a distinct maximum at the ratio* Co : X = 1 : 4, *showing that compounds* *are formed at this ratio.* Only the curves for bromide are not very clear : the curves showing E against cobalt concentration have a maximum at the ratio Co : Br = 1 : 4, but the $E - E_0$ curve has no maximum.

The Action of Mercuric, Zinc, and Cadmium Compounds on Alcoholic Solutions of Cobaltous Chloride.—Although phase studies of the systems $CoCl_2$–MCl_2–H_2O (where M = Hg, Zn, or Cd) were made (Bassett and Croucher, *J.*, 1930, 1784; Benrath, *Z. anorg. Chem.*, 1927, **163**, 396) the reaction between cobaltous chloride and the other chlorides had apparently not been investigated in solution. We studied the disappearance of the blue colour of alcoholic solutions of cobaltous chloride when added to different amounts of mercuric, zinc, and cadmium salts in alcoholic solution by measuring the absorption of the solutions so formed. The solutions do not turn blue at first, but only after a certain quantity of cobaltous chloride has been added.

Fig. 4 shows the absorption coefficients (filter 6600 A.) of pure alcoholic solutions of $CoCl_2$ (A) and of mercuric salts to which different amounts of pure alcoholic solution of cobaltous chloride were added (B, C). At large concentrations of cobaltous chloride the curves eventually become parallel, and from the distance between the parallel curves the amount of cobaltous chloride which reacts with the mercuric compound can be calculated. It is seen that cobaltous chloride combines with mercuric chloride and acetate in the ratios Co : Hg = 1 : 1 and 1 : 2, respectively, which suggests the formation of complex ions $HgCl_4^{--}$. The same conclusion was reached by measuring the absorption at 6900 A.

Similar experiments were carried out with cadmium and zinc chloride, and from the distance between the curves we calculated the ratios $CoCl_2$: $CdCl_2$ = 1 : 1·3 and $CoCl_2$: $ZnCl_2$ = 1 : 1·4.

FIG. 4.



Extinction (*filter* 6600 A.) *of solutions of cobaltous chloride and mercuric chloride and acetate in absolute alcohol at room temperature* : (*A*) $CoCl_2$; (*B*) $CoCl_2$ + 0·044M-$HgCl_2$; (*C*) $CoCl_2$ + 0·044M-$Hg(OAc)_2$.

Discussion.—From the photometric data it may be concluded that, in the presence of a sufficient excess of halogen or thiocyanate ions, the ratio Co : X in the complex ions formed in alcoholic solution is 1 : 4. As the spectra of alcoholic and aqueous solutions of cobaltous chloride containing an excess of hydrogen chloride are nearly equal (Richter, *Chem. Abstr.*, 1939, **33**, 4126; Macwalter and Barratt, *loc. cit.*), the same compound exists also in aqueous solution. On the other hand, the spectra of aqueous solutions of cobaltous chloride containing an excess of hydrogen chloride and of solid anhydrous Cs_3CoCl_5 are identical (Schultz and Lilec, *J. Amer. Chem. Soc.*, 1942, **64**, 2784). In the latter salt four chlorine atoms are grouped in tetrahedral configuration around the central cobalt ion (Powell and Wells, *J.*, 1935, 359). The co-ordination number of cobalt in the complex ion formed in excess of chloride is therefore 4, and the composition of the ion $[CoCl_4]^{--}$. It may be assumed that also in the bromide, iodide, and thiocyanate complexes no solvent molecules enter the inner shell of the complex ion and the general formula of these ions is $[CoX_4]^{--}$

Apart from these complex ions there also exist complex compounds containing cobalt and X in the ratio 1 : 2. These compounds are formed at lower halogen concentrations or even when the anhydrous salts CoX_2 are dissolved in absolute alcohol. Their spectra are different from the spectrum of $[CoX_4]^{--}$ and are not a superposition of the spectra of cobaltous and $[CoX_4]^{--}$ ions. Their existence was proved by measurements of conductivity.

The measurements of the extinction coefficient in alcohol–water mixtures (Fig. 1) show that, whereas in water a high concentration of chloride is necessary to replace the water in the co-ordination sphere, the introduction of chloride is facilitated in the alcohol–water mixtures. This is due to the smaller concentration of water and the association between alcohol and water molecules. In absolute alcohol the chloride ion enters the co-ordination sphere immediately and therefore the reaction between chloride and cobaltous ion is nearly quantitative.

The constancy of the ratio $[Cl]_{1/2}/H_2O$ bears an interesting relation to the findings of Howell and Jackson (*loc. cit.*), who investigated the action of chlorides on aqueous solutions of cobaltous chloride. From measurements of the viscosity and optical absorption of the solutions they conclude that the ratio between the concentrations of chloride and water in the medium determines the structure of the co-ordination sphere.

The different theories put forward to explain the colour change of aqueous solutions of cobaltous chloride on addition of halides or thiocyanates, alcohols, or other organic solvents, sulphuric acid, or even on heating are actually correlated. The colour change was explained by changes in solvation, co-ordination number, and complex formation. We think that the deep colour is characteristic of the covalent bond between cobalt and X, which causes deformation of the electronic orbits. In aqueous solutions there is equilibrium between two actions : (*a*) the tendency of the halogen ions to form a covalent bond (between the 4*s* electrons of the cobalt and the *p* electrons of the halogen), and (*b*) the shielding action of the molecular dipoles of water which prevent this approach.

Factors enhancing the covalent-bond forming tendency (*e.g.*, increasing the concentration of halogen ions) or weakening the shield of water molecules (*e.g.*, the addition of organic solvents of lower dielectric constant than water, or of dehydrating agents such as sulphuric acid, or a rise in temperature) transform the ionised cobaltous salts into covalent compounds of deep colour. In the covalent compounds the distance between Co and X is smaller than in the solvated pink compounds. Whereas in the pink compounds the co-ordination number of cobalt is 6, there is room for only four radicals X if the latter are bound to the central cobalt by a covalent bond. Thus the formation of the covalent compounds implies desolvation, change in co-ordination number, and deformation of the electronic orbits resulting in change of colour and magnetic properties (Datta, *Physikal. Ber.*, 1934, **15**, 1323, 1910).

The authors wish to acknowledge the assistance of Mr. N. Sternberg in this investigation.

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