acetone situation is apparently much more complicated. Even at the point of equilibrium of tetrahydrated and trihydrated solids, the solvent–salt ratio is only 4.3, and in the region of the dihydrate solid phase it drops to about 3. One must either invoke a decrease in coördination number, or, preferably, consider the possibility that coördination number 6 is maintained by coördination between molecules (*e. g.*, through the nitrate groups) to give polymers of some sort in solution. In agreement with this possibility, the liquid phases are found to be extremely viscous in this region of the phase diagram. X-Ray investigation of these liquids may be expected to give evidence for "super-arrangement" found even in aqueous uranyl nitrate and thorium nitrate systems[11] which are much more dilute (*ca.* 15–20 to one, solvent to salt).

Summary

1. The system cobalt nitrate–water–acetone at 25° shows as equilibrium solids the hexahydrate, tetrahydrate, trihydrate, dihydrate and (probably) the diacetonate.

2. Several methods of preparation of the tetrahydrate are given, its apparent melting point is determined to be 84°, and its place in the cobalt nitrate–water binary system is indicated.

3. The system cobalt nitrate–water–*t*-butyl alcohol at 25° shows as equilibrium solids the hexahydrate, the tetrahydrate-dialcoholate, the trihydrate-trialcoholate, dihydrate-tetraalcoholate and the anhydrous tetraalcoholate.

4. Solvation of the cobalt nitrate in the alcohol solution and polymerization in the acetone solution are suggested as explanations of the liquid phase behavior.

CHICAGO, ILL. RECEIVED MARCH 15, 1950

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[11] Prins, *J. Chem. Phys.*, **3**, 72 (1935).

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Spectrophotometric Investigation of Cobaltous Nitrate in Organic Solvents[1]

BY LEONARD I. KATZIN AND ELIZABETH GEBERT

The spectacular color changes of some cobalt salts (*e. g.*, the chloride) between a salmon-red color and a pure blue, have been known and have attracted interest for many years. Some years ago two extremes of interpretation became differentiated. The one holds that the principal basis for the color change is a change in the hydration of the cobalt, the lower hydrate corresponding to the blue form. The second school holds that the effect is due to formation of a chemical complex, such as $CoCl_4^{--}$. Various hybridizations of these extreme views have of course been proposed.

The data on the halide behavior have been extrapolated to the color changes of other cobalt salts so that the tendency has been to interpret all colors as gradations between the red and blue forms, and hence often as semi-quantitative measures of the degree of admixture of the two forms. An assumption implicit in this procedure is that all tendencies toward visual bluishness represent the same structural alterations and presumably the same spectral changes. This implies further that a given intermediate color should be represented as a mixture of two spectra, that characteristic of the pure red form and that characteristic of the pure blue form.

It will be the endeavor of this paper to demonstrate that not only is all visual bluishness not due to mixture of a blue spectrum (typified by the chloride blue) with the water red spectrum, but that the halide blue spectrum is not typical of all cobaltous complexes, and at least one of them has a spectrum little different from the water red spectrum. Further, as might be anticipated, it will be shown that the complexing–hydration views of these changes are not independent.

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 nitrate was the chemically pure hexahydrate, usually desiccated to various degrees over sulfuric acid. Cobalt perchlorate was prepared from the carbonate and perchloric acid, and recrystallized twice. Chemically pure lithium nitrate was dried in the oven, at about 95°. Tetrabutylammonium nitrate was kindly prepared for us by Dr. Louis Kaplan, from silver nitrate and tetrabutylammonium iodide.

Dioxane was prepared in dry form by distillation over sodium. Periodic tests were made for peroxide content with potassium iodide. Anhydrous methanol was prepared from commercial anhydrous methanol by treatment with magnesium metal turnings, and distillation. *t*-Butyl alcohol was prepared by distilling the commercial anhydrous solvent over sodium, and sometimes by fractional freezing. The other solvents were commercial products. All were analyzed for water content by titration with Karl Fischer reagent, using an electrical end-point determination.[1a] The standard used for the reagent was sodium acetate trihydrate.

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 electrodeposition procedures. A few were performed by

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[1] Presented in part at meeting of the American Chemical Society, San Francisco, Calif., March 28–April 1, 1949.

[1a] Katzin and Sullivan, *J. Phys. & Colloid Chem.*, in press; Atomic Energy Commission Declassified Document No. 2537.

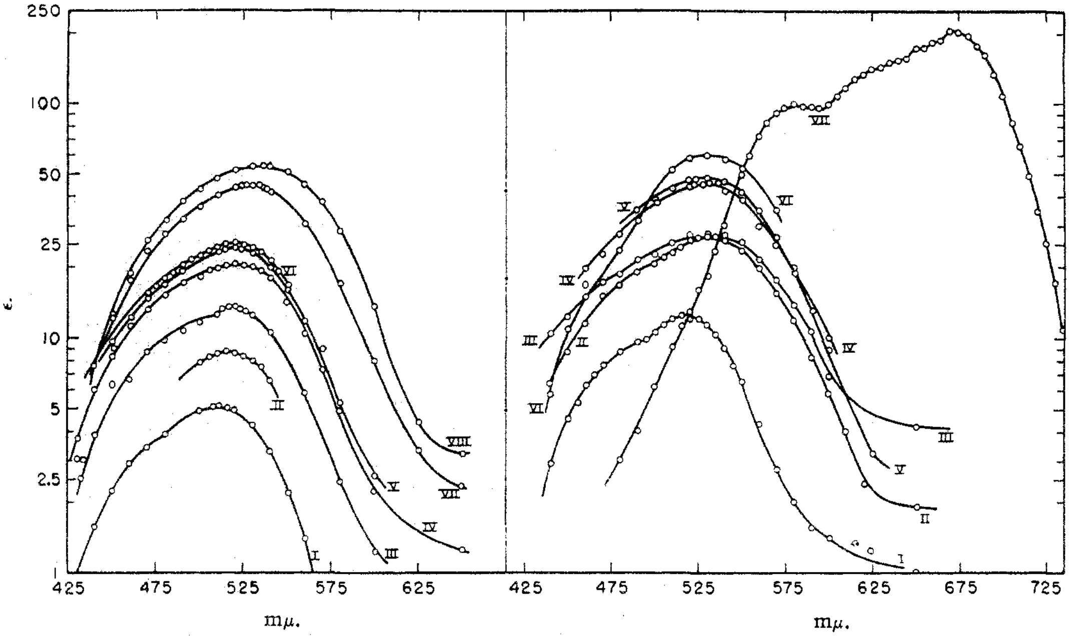

Fig. 1.—Absorption curves for cobaltous nitrate in various solvents. Fig. 1a: curve I, 0.1 *M* salt in water; II, 0.05 *M* salt in methyl alcohol (0.08% water); III, 0.01 *M* salt in isobutyl alcohol; IV, 0.03 *M* salt in *n*-propyl alcohol (1% water); V, 0.01 *M* salt in *n*-butyl alcohol; VI, 0.02 *M* salt in ethyl alcohol (0.02% water); VII, 0.01 *M* salt in isopropyl alcohol; VIII, 0.01 *M* salt in *t*-butyl alcohol. Fig. 1b: I, 0.06 *M* salt in ethylene glycol (0.2% water); II, 0.03 *M* salt in dioxane (0.01% water); III, 0.01 *M* salt in diethyl cellosolve; IV, 0.003 *M* salt in methyl isobutyl ketone; V, 0.01 *M* salt in *s*-butyl alcohol; VI, 0.01 *M* salt in acetone (0.5% water); VII, $CoCl_2$ in *t*-butyl alcohol.

ignition to Co_3O_4. In most cases the stock solutions were also analysed for water.

It is a pleasure to acknowledge our indebtedness to Mr. James C. Sullivan for assistance in preliminary experiments, and to Mr. John Ferraro for analytical assistance.

Experimental

Effects of Solvent.—Solutions of cobaltous nitrate in organic solvents show a magenta color whose intensity is a function of the concentration and the solvent. The shading is toward red rather than the blue end. The color change is minimal in methanol, and increases with heavier solvents. Additions of small increments of water to the solutions (*e. g.*, in acetone or *t*-butyl alcohol) alter the appearance of the solutions toward that of the water solution, and when the water content has reached 10% by volume, differences are practically indistinguishable. Figure 1 shows the absorption spectrum of cobaltous nitrate in a number of alcohols, acetone, methyl isobutyl ketone, dioxane and ethylene glycol diethyl ether (diethyl "cellosolve") as well as in water. The molar extinction coefficient is plotted on a logarithmic scale to maintain detail in the curves. The absorption in the red falls off gradually. The water content of the solvent used is indicated in each case. The spectrum of cobaltous chloride in acetone is given for comparison. The banded structure of the chloride spectrum has been reported by others.[2]

Effects of Water.—The quantitative effects of stepwise addition of water to the cobaltous nitrate are shown for the solutions in acetone, *t*-butyl alcohol, and dioxane (Fig. 2). All three solvents show qualitatively similar behavior—depression of the absorption coefficient, with the greater effects in the first few per cent. of water added. In detail, the *t*-butyl alcohol solutions show the greatest sensitivity to traces of water, and the dioxane solutions the least. From about 6–8% by volume of water to 20% by volume, the absorption coefficients are highest in the dioxane solution and lowest in the *t*-butyl alcohol solutions. It is clear that the effect of water is not primarily one of altering the dielectric constant, since the order of dielectric constants is dioxane < *t*-butyl alcohol < acetone.

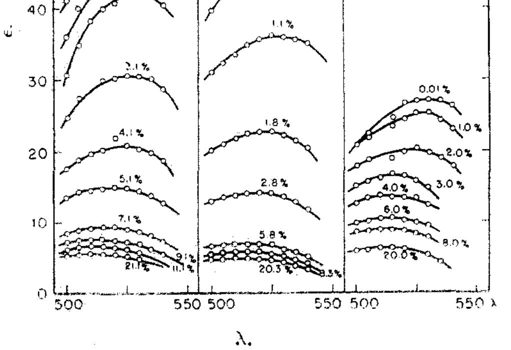

Fig. 2.—Extinction of cobalt nitrate in acetone, *t*-butyl alcohol and dioxane as function of water content of solvent.

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[2] Jones and Uhler, *Am. Chem. J.*, **37**, 126, 207 (1907); Groh, *Z. anorg. allgem. Chem.*, **146**, 305 (1925); Hantzsch, *ibid.*, **159**, 273 (1927); Brode, *Proc. Roy. Soc.* (*London*), **A118**, 286 (1928).

Furthermore, the dielectric constant of 80% dioxane is 10.7, while that of anhydrous *t*-butyl alcohol is 9.9, and the dielectric constant of 80% *t*-butyl alcohol (16.5) is less than that of anhydrous acetone (19.1).[3] On the other hand, comparison of the absorption in water solution with that in methyl, ethyl, isopropyl and *t*-butyl alcohols (the water-miscible alcohols) shows that there is in the higher dielectric constant region a correlation with dielectric constant, but with a constant in the neighborhood of 20 or less other factors (*e. g.*, activity coefficient of water) becomes important. This is borne out by the positions of the solutions in water-immiscible alcohols, in which water activity coefficients must be high, and dioxane (see below).

Composition of Complex.—The presumption is, from these data, that one is dealing with complex formation facilitated by lowering of the dielectric constant, and that the process of complex formation with nitrate ion is somehow reversed by water. A corollary of this hypothesis is that addition of nitrate ion should induce formation of additional complex, unless the process is already complete. In correspondence, addition of an equi-molal amount of tetrabutylammonium nitrate to solutions of cobaltous nitrate in acetone, *t*-butyl alcohol or dioxane, produces a rise in extinction coefficient. To obtain a stoichiometric formula for the complex, the method of "continuous variations" elaborated by Job[4] is useful. The method is based upon the readily verified relation that on mixing two reagents forming an additive complex, to a fixed total formal concentration, the concentration of the complex is a maximum when the reagents are in the stoichiometric proportion in which they appear in the complex. Plotting a suitable property of the complex against concentration of reagents should give a maximum at the ratio corresponding to the formula of the complex.

This simple relationship is complicated if more than one complex is formed. Vosburgh and Cooper[5] have pointed out a few properties of special cases of the system forming two complexes, but have not given the general relationships, which allow one to use the method to greater advantage. We have therefore elaborated the derivations for the case of three complexes which are to be investigated by spectrophotometric means, as follows. As in the basic experiment, one considers equimolar starting solutions, of concentration M, of reactants A and B. When one mixes these in the proportion x volumes of B and $(1 - x)$ volumes of A, without appreciable volume change, it is assumed that the following equilibria are established

$$\mathrm{A} + n\mathrm{B} \rightleftharpoons \mathrm{AB}_n \qquad (1)$$

$$\mathrm{AB}_n + p\mathrm{B} \rightleftharpoons \mathrm{AB}_{n+p} \qquad (2)$$

$$\mathrm{AB}_{n+p} + q\mathrm{B} \rightleftharpoons \mathrm{AB}_{n+p+q} \qquad (3)$$

If w represents the concentration of free reagent B, and c_0, c_1, c_2 and c_3, those of the uncomplexed reactant A and the three successive complexes, respectively, the following equations may be written

$$c_0 = M(1 - x) - c_1 - c_2 - c_3 \qquad (4)$$

$$w = Mx - nc_1 - (n + p)c_2 - (n + p + q)c_3 \qquad (5)$$

$$c_0w^n = k_1c_1 \qquad (6)$$

$$c_1w^p = k_2c_2 \qquad (7)$$

$$c_2w^q = k_3c_3 \qquad (8)$$

If one considers the usual case of spectrophotometric observation at a wave length at which reactant B is colorless, the increase Δ in the optical density D due to formation of complexes between A and B may be formulated as

$$\Delta = \epsilon_0c_0 + \epsilon_1c_1 + \epsilon_2c_2 + \epsilon_3c_3 - \epsilon_0M(1 - x) \qquad (9)$$

where the subscripts of the molal extinction coefficients ϵ indicate the form of A to which they refer. The experimental values of Δ when plotted against x will yield a curve intersecting the abscissa at zero and unity; the curve in between must possess one or more maxima and minima—that is, the derivative of Δ with respect to x will be equal to zero at one or more points. The relation of these points to the composition of the complexes is the subject of the following discussion.

Algebraic combination of the differentiated form of equation (9) with equations (4) through (8) and their derivatives, gives

$$\left(\frac{x}{1 - x}\right) = n + \frac{p((\epsilon_2 - \epsilon_0)c_2 + (\epsilon_3 - \epsilon_0)c_3) + q(\epsilon_3 - \epsilon_0)c_3}{(\epsilon_1 - \epsilon_0)c_1 + (\epsilon_2 - \epsilon_0)c_2 + (\epsilon_3 - \epsilon_0)c_3}\left[1 + \frac{n(c_1 + c_2 + c_3) + p(c_2 + c_3) + qc_3}{M(1 - x)}\right] - \frac{p(p + n)(c_2 + c_3) + q(q + n + 2p)c_3}{M(1 - x)} \qquad (10)$$

This equation represents the locus of the values of $(x/1 - x)$ for which $\mathrm{d}\Delta/\mathrm{d}x = 0$.

The special cases derived from this general equation are instructive. When c_2 and c_3 are zero (*i. e.*, only one complex exists), the relation reduces to Job's case, $x/(1 - x) = n$. When three complexes exist, and one is the only colored substance present in the system (or is the only form differing in absorption from the parent reagent), the maximum density change will appear at the maximum in concentration of the complex. Setting this relation in equation 10 successively for the three complexes (*i. e.*, taking only one of the three $(\epsilon - \epsilon_0)$ terms at a time as different from zero) one gets for the reagent ratio at which the successive complexes reach maximum concentration

$$\left(\frac{x}{1 - x}\right)_1 = n - \frac{p(p + n)(c_2 + c_3) + q(q + n + 2p)c_3}{M(1 - x)} \qquad (11)$$

$$\left(\frac{x}{1 - x}\right)_2 = (n + p) + \frac{npc_1 - q(n + p + q)c_3}{M(1 - x)} \qquad (12)$$

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[3] Harned and Owen, "Physical Chemistry of Electrolytic Solutions," ACS Monograph No. 95, Reinhold Publ. Corp., New York, N. Y., 1943, page 118.

[4] Job, *Ann. chim.*, [10] **9**, 113 (1928).

[5] Vosburgh and Cooper, THIS JOURNAL, **63**, 437 (1941)

and

$$\left(\frac{x}{1-x}\right)_3 = (n+p+q) + \frac{n(p+q)c_1 + q(n+p)c_2}{M(1-x)} \qquad (13)$$

Equation (11), when c_3 is taken as zero, becomes identical with the single maximum point derived by Vosburgh and Cooper.[5] These relations may be summarized briefly as follows. When a single complex is formed, its maximum occurs at its formal composition ratio, n. When two complexes are formed, the first reaches its maximum concentration at a reagent ratio below the formal value, n, for this complex, and the concentration of the second is a maximum at a reagent ratio somewhat above the formal ratio, $(n + p)$, for the second complex. When three complexes are involved, the lowest is at a maximum below its formal ratio n, the highest is a maximum above its formal composition ratio $(n + p + q)$, and the intermediate complex is a maximum approximately at its ratio, $(n + p)$, the exact location depending on the formulas and dissociation constants of the complexes in the given system.

In the case of the system with two complexes, equation (10) may be written

$$\left(\frac{x}{1-x}\right) = n - \frac{p(n+p)c_2}{M(1-x)} + \frac{pc_2}{\left(\frac{(\epsilon_1-\epsilon_0)}{(\epsilon_2-\epsilon_0)}\right)c_1 + c_2}\left[1 + \frac{n(c_1+c_2)+pc_2}{M(1-x)}\right] \qquad (14)$$

where the quantity

$$(x/1-x) = n - p(n+p)c_2/M(1-x) \qquad (15)$$

represents the location of the maximum value of c_1. The parenthetical quantity in equation (14) is always positive. It will be seen that so long as $(\epsilon_1 - \epsilon_0)/(\epsilon_2 - \epsilon_0)$ is positive, the peak value of Δ is restricted to the $(x/1 - x)$ values between the two complex concentration maxima. The exact shape of the Δ *vs.* x curve in this area cannot be determined without further information. For example, if the first complex is strong, and the two complex extinctions are the same, there may be an extremely flat peak of Δ. When the ratio $(\epsilon_1 - \epsilon_0)/(\epsilon_2 - \epsilon_0)$ is negative, however, the $(x/1 - x)$ values are no longer restricted to the region between the complex concentration peaks, and it is possible to demonstrate that in some cases at least there will be both a definite maximum and a definite minimum in the Δ *vs.* x curve *i. e.*, two places where $d\Delta/dx = 0$.

Thus for example consider the case when $(\epsilon_1 - \epsilon_0)$ is negative and numerically equal to $(\epsilon_2 - \epsilon_0)$, and both complexes are strong enough to be almost completely associated at $(x/1 - x) = n$ and $(x/1 - x) = (n + p)$, respectively. The first additions of the reagent will give a negative value of Δ; in the region of the peak in c_2, Δ will have a positive value; therefore at an intermediate point the two effects compensate ($\Delta = 0$) and there are necessarily two places where $d\Delta/dx = 0$, one a maximum and one a minimum.

Similarly, for the case with three complexes, where there is an alternation of signs of the respective extinction differences, one may find three places where $d\Delta/dx = 0$. In fact, if the extinctions of the first and third complexes are equal, a value for $(\epsilon_2 - \epsilon_0)$ distinctly smaller than that for the first and third complexes should give a minimum ($d\Delta/dx = 0$) even though the sign of Δ remains unchanged.

A case which is of interest is the one in which the starting substance is AB_n, rather than A. Equation (5) then becomes altered to

$$w = nM(1-x) + Mx - nc_1 - (n+p)c_2 - (n+p+q)c_3$$

and its derivative becomes correspondingly altered. Equations 4, and 6–8, remain unchanged. Investigating the condition for a maximum in c_1 (*i. e.*, $dc_1/dx = 0$), one finds it met by the equation

$$Mx = -n^2c_0 - p^2c_2 - (p+q)^2c_3$$

Since the right-hand side of this equation is always negative, it can be satisfied only by negative values of the left-hand side. Negative values of x mean only that there is no point above the starting ratio of B to A (*i. e.*, n) at which $dc_1/dx = 0$. This is in agreement with the location of the c_1 peak in the previous case (see equation (11)). A peak in the value of c_2 is found to come at

$$(x/1-x) = p - q(p+q)c_3/M(1-x) \qquad (16)$$

when c_0 is negligible at this point, and at slightly lower values when it cannot be neglected. It is seen that a peak or minimum value for Δ in this experiment cannot be found unless a complex AB_{n+p} forms in the system. In the case that the first complex, AB_n, is sufficiently strong that the absorption of the solution for the experimental cases is closely given by $\epsilon_1M(1 - x)$, and the free A concentration is essentially nil, the situation reduces to the parent experiment with reagents A' ($= AB_n$) and B to give complexes $A'B_p$, $A'B_{p+q}$, and so forth. An equation for the general case can be derived in fashion similar to the derivation of equation (10), but will contain a dilution function of the optical density of the parent solution which can be evaluated only for special cases such as the one just discussed.

One may now return to the cobaltous nitrate experiment. The formal extinction coefficient of 0.01 molal cobaltous nitrate in acetone or *t*-butyl alcohol, and that for the solution diluted ten-fold with dry solvent, agree within experimental error. This gives presumptive basis to apply the criterion stated above. More data presented below will support this. Performing the continuous variations experiment with equimolal solutions of cobaltous nitrate and tetrabutylammonium nitrate one may follow the excess optical density as a function of the added nitrate. In Fig. 3 are shown such plots for acetone and *t*-butyl alcohol solutions. The property plotted is the excess in optical density over that due to the cobalt nitrate by itself. It is seen that the curves peak at a ratio 1:1, indicating a trinitrato cobalt complex. It is therefore clear that a complex with ratio of nitrate to cobalt higher than 2 exists, and that if cobaltous nitrate is very little dissociated in these solutions, as the data indicate,

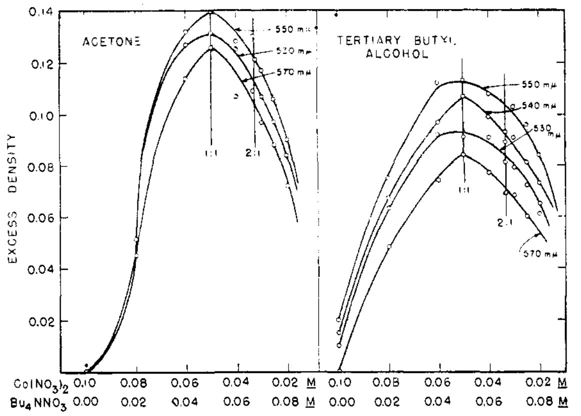

Fig. 3.—Demonstration of formation of trinitrato complex of cobalt by method of continuous variations. Reactants–cobalt nitrate and tetrabutylammonium nitrate. Data for solvent *t*-butyl alcohol have ordinate scale zeros adjusted to separate curves.

the ratio of nitrate to cobalt in this higher complex is 3. It is pertinent also that if one substitutes lithium nitrate for the tetrabutylammonium nitrate in the above experiments, one obtains the same results for the solution in acetone, but in *t*-butyl alcohol one finds that the addition of lithium nitrate has no effect. This will be referred to again below.

If the spectral differences between aqueous and organic solutions of cobalt nitrate are due to formation of nitrate complex, and the absorption data show little difference between acetone and *t*-butyl alcohol of comparable dryness, it becomes necessary to explain why dioxane solution shows such a (comparatively) low extinction coefficient. If instead of a single portion of tetrabutylammonium nitrate, one adds twice the molar equivalent, to 0.005 *M* dioxane solution of cobaltous nitrate containing only water of crystallization, droplets of a denser liquid phase separate out which contain most of the cobalt nitrate. Similarly, if one attempts to make too concentrated a solution of cobaltous nitrate hexahydrate in dioxane, one obtains separation of two liquid phases. It is therefore likely that the activity coefficient of water in the dioxane is considerably higher than in either acetone or tertiary butyl alcohol, which would explain the lower extinction at comparable water concentrations.

Lower Complexes.—The experiment using cobaltous nitrate and tetrabutylammonium nitrate in the continuous variations test, although revealing the existence of a trinitrato complex, does not give direct evidence of undissociated cobalt nitrate, or a possible mononitrate complex. Without this information it is not possible to be certain to what extent the shift in absorption on dissolving cobalt nitrate in the organic solvent is due to disproportionation to trinitrato complex. Tests were therefore made using cobalt perchlorate in organic solvents. It was found, however, that although the change was less intense, the color of the perchlorate solutions was shifted in fashion similar to that of the nitrate. This symptom of complex formation with the perchlorate complicated the anticipated experiments in the visible, so attention was turned to the ultraviolet. Preliminary experiments had shown that the intensity of absorption in the ultraviolet, due in aqueous solution to the nitrate ion, was greatly increased in the organic solutions, and that the absorption fell off with addition of water similarly to the absorption in the visible. Since acetone absorbs in this region of the ultraviolet, further experiments were all carried out in *t*-butyl alcohol solution.

Cobalt perchlorate in *t*-butyl alcohol was optically clear in the vicinity of 300 millimicrons, the location of the nitrate ion peak. Cobaltous nitrate showed an extinction (based on the cobalt concentration) of about 200 at this wave length. The absorption curve is shown in Fig. 4, and can be seen to be a modified nitrate ion curve.

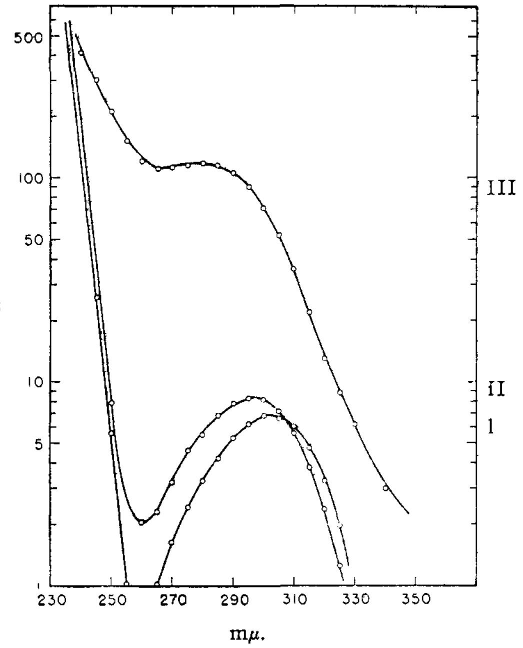

Fig. 4.—Variation of absorption of nitrate group: I, LiNO$_3$ in 50% *t*-butyl alcohol; II, LiNO$_3$ in 100% *t*-butyl alcohol; III, LiNO$_3$ + Co(ClO$_4$)$_2$ in 100% *t*-butyl alcohol.

Further investigation showed that addition of a small portion of lithium nitrate to cobalt perchlorate in the alcohol solution gave this modified spectrum with extinction

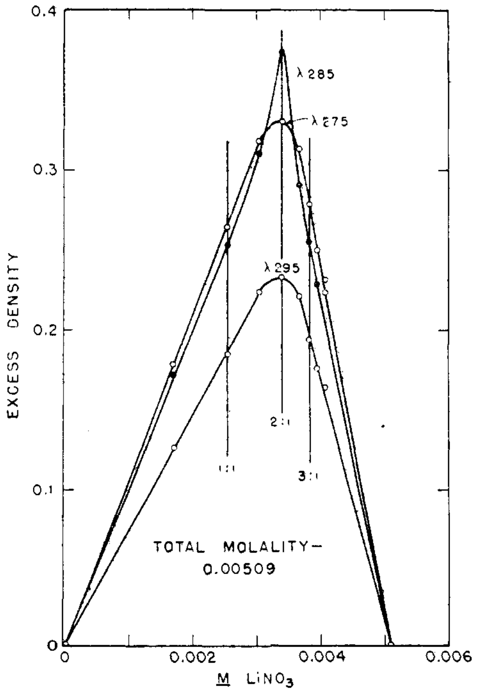

Fig. 5.—Continuous variations test, Co(ClO$_4$)$_2$ and LiNO$_3$ in *t*-butyl alcohol.

coefficient (per nitrate) identical with that if the solute were cobalt nitrate alone. This shows that the complex is strong. Application of the continuous variations test using lithium nitrate and cobalt perchlorate shows that the complex forms with two nitrates per cobalt (Fig. 5).

If one adds lithium nitrate to a solution of cobaltous nitrate (rather than perchlorate) in *t*-butyl alcohol, the absorption of the solution in the ultraviolet is just the sum of the absorptions due to the two components. This duplicated the behavior in the visible, noted above. When tetrabutylammonium nitrate (expected to be more highly ionized) is used instead of lithium nitrate, there appears an excess of optical density above that of the components. Free nitrate ion therefore seems to be necessary for the reaction. Use of tetrabutylammonium nitrate and cobaltous nitrate in the continuous variations experiment gives an indication of an excess density peak at the expected 1:1 ratio, but the excess density is small, and confusing irregularities may also occur in the curve, possibly because of the small values involved.

It is possible to evaluate the extent of disproportionation of simple solutions of cobaltous nitrate by estimating a value for the complex dissociation constant

$$K_1 = (\mathrm{NO_3^-})(\mathrm{Co(NO_3)_2})/(\mathrm{Co(NO_3)_3^-}) \qquad (17)$$

This can be done through measurements of the optical density, as at 285 millimicrons, of solutions with a constant concentration of cobaltous nitrate and variable portions of tetrabutylammonium nitrate. *t*-Butyl alcohol is used as solvent because of the absorption of acetone. The dissociation constant of tetrabutylammonium nitrate calculated for *t*-butyl alcohol of dielectric constant 10.0 from the data of Bien, Kraus and Fuoss[6] for the salt in anisole ($D = 4.28$) is 8.51×10^{-5}. The nitrate ion concentration can then be approximated by the value 8.51×10^{-5}. $(\mathrm{Bu_4NNO_3})/(\mathrm{Bu_4N^+})$, assuming that the amount of tetrabutylammonium ion present is equal to the amount of trinitratocobalt formed. The last can be estimated from the following relation. If two substances present to formal concentrations c_1 and c_2, possessing molal extinction coefficients ϵ_1 and ϵ_2 react in equimolal ratio to give a product of extinction ϵ_3 in concentration c_3, the value of c_3 is given by

$$c_3 = (D - \epsilon_1 c_1 - \epsilon_2 c_2)/(\epsilon_3 - \epsilon_1 - \epsilon_2)$$

where D is the optical density of the final solution. Knowing the extinction coefficients it is possible to calculate K_1 by the approximate equation

$$K_1 = 8.51 \times 10^{-5}\, x(c_2 - c_3)/c_3\, x(c_1 - c_3)/c_3 \qquad (17a)$$

Even though it is known only that $\epsilon_3 > (\epsilon_1 + \epsilon_2)$, an order of magnitude estimation of K_1 can be made sufficiently well for our purposes. As a first approximation, one may assume that the absorption at 285 millimicrons is proportional to the number of nitrate groups coördinated to each cobalt atom, making the value of $(\epsilon_3 - \epsilon_1 - \epsilon_2)$ approximately 110. Using this value in calculations for a series of data (see Table I) gives a grouping of K_1 values around 1×10^{-3}, with a factor of 3 between the extreme values. Smaller values of K_1 (stronger complexing) would be shown with smaller values of $(\epsilon_3 - \epsilon_1 - \epsilon_2)$; however with values as small as 50, the data would show greater than 100% formation of trinitrato complex. As a practical limit, the value 55 may be used. The constants obtained with this value scatter considerably more than in the previous case (Table I), while the median values found for the constant are only 0.25 to 0.1 as large as for the first calculation. Thus, even without exact values for K_1, the conclusion seems justified that the trinitrato complex in *t*-butyl alcohol is so much weaker than the dinitrate form that disproportionation of cobaltous nitrate is probably insignificant, and that the color difference between aqueous cobaltous nitrate and alcoholic cobaltous nitrate is due primarily to the undissociated salt in the latter. Since the behavior in the visible for the acetone solution is very much the same as for the *t*-butyl alcohol, and the absorption is similar, the same conclusion seems applicable.

Nature of the Water Effect.—The obvious hypothesis for the effect of water addition to the organic solutions is that the nitrate ion coördinated displaces solvent or water groups which are coördinated to the cobaltous ion (as in dilute aqueous solution), and the effect of water addition is to reverse the process. In dry organic solvents of low dielectric constant, the competitive position of the nitrate ion (because of electrostatic attraction) is such that essentially complete association of the salt results. Addition of water has two effects: the lesser is an increase in the dielectric constant; the more important is the introduction into the solution of a very strong electron donor, which is capable of effectively displacing the nitrate ion even at moderate dielectric constants.

One may, for the earliest additions of water to the organic solution, set up the reaction

$$\mathrm{Co(NO_3)_2 \cdot}x\mathrm{H_2O} + a\mathrm{H_2O} \rightleftharpoons \mathrm{Co(NO_3)^+ \cdot}(x + a)\mathrm{H_2O} + \mathrm{NO_3^-} \qquad (18)$$

with an appropriate equation for the second dissociation step. If the constant for the second step is large, the two reactions will not be distinguishable from

$$\mathrm{Co(NO_3)_2 \cdot}x\mathrm{H_2O} + b\mathrm{H_2O} \rightleftharpoons \mathrm{Co(H_2O)^{++}}\,(x + b) + 2\mathrm{NO_3^-} \qquad (19)$$

since water is in large excess. The corresponding equilibrium constants are of the form

$$[\mathrm{H_2O}]^a K_5 = \frac{[\mathrm{Co(NO_3)(H_2O)^+}_{(x+a)}][\mathrm{NO_3^-}]}{[\mathrm{Co(NO_3)_2(H_2O)}_x]}, \text{ and} \qquad (20)$$

$$[\mathrm{H_2O}]^b K_6 = \frac{[\mathrm{Co(H_2O)^{++}}_{(x+b)}][\mathrm{NO_3^-}]^2}{[\mathrm{Co(NO_3)_2(H_2O)}_x]} \qquad (21)$$

and in either case a plot of the logarithm of the right-hand side of the equation against the logarithm of the water concentration (ignoring the complication of uncertain activity coefficients) might give a line whose slope would be equal to the power of the water concentration. One is able

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(6) Bien, Kraus and Fuoss, This Journal, 56, 1860 (1934).

TABLE I

DISSOCIATION CONSTANT OF $Co(NO_3)_3^-$ COMPLEX IN *t*-BUTYL ALCOHOL

Formal concn. Co	Formal concn. Bu_4NNO_3	Opt. density at 285 mμ	Concn. $Co(NO_3)_3^{-a,b}$	$K_1 \times 10^{4b}$	Concn. $Co(NO_3)_3^{-a,c}$	$K_1 \times 10^{4c}$
0.00182	....	0.335	....	...	....	...
	0.183×10^{-3}	.343	0.9×10^{-4}	20	1.3×10^{-4}	5
	$.364 \times 10^{-3}$	.351	1.7×10^{-4}	9	2.7×10^{-4}	1.6
	$.727 \times 10^{-3}$	.355	2.0×10^{-4}	18	3.1×10^{-4}	5.6
	1.45×10^{-3}	.368	3.2×10^{-4}	14	4.9×10^{-4}	4.6
	1.82×10^{-3}	.377	3.0×10^{-4}	11	6.4×10^{-4}	2.9
	2.73×10^{-3}	.389	5.0×10^{-4}	10	7.8×10^{-4}	2.8
	3.64×10^{-3}	.410	6.9×10^{-4}	6	10.9×10^{-4}	1.4
	4.09×10^{-3}	.413	7.1×10^{-4}	6.5	11.3×10^{-4}	1.4
.00176	....	(0.387)[d]	....	...	....	...
	1.84×10^{-3}	0.416	2.0×10^{-4}	54	4.0×10^{-4}	10.2
	3.68×10^{-3}	.457	5.2×10^{-4}	13	10.0×10^{-4}	1.7
	5.52×10^{-3}	.473	6.0×10^{-4}	14	11.6×10^{-4}	1.7
	7.36×10^{-3}	.495	7.4×10^{-4}	11	14.4×10^{-4}	0.8
.00312	....	.656	....	...	....	...
	3.46×10^{-3}	.753	0.82×10^{-3}	7.6	15.1×10^{-4}	1.2
	6.92×10^{-3}	.814	1.29×10^{-3}	5.3	23.6×10^{-4}	0.5
	10.40×10^{-3}	.844	1.45×10^{-3}	6.1	26.5×10^{-4}	.4
.00273	....	.613	....	...	....	...
	2.76×10^{-3}	.688	0.59×10^{-3}	11	11.6×10^{-4}	1.5
	5.52×10^{-3}	.747	1.04×10^{-3}	5.8	20.4×10^{-4}	0.5
	6.90×10^{-3}	.753	1.04×10^{-3}	7.8	20.4×10^{-4}	.7
	8.28×10^{-3}	.779	1.23×10^{-3}	6,0	24.2×10^{-4}	.26
	9.66×10^{-3}	.790	1.28×10^{-3}	6.3	25.3×10^{-4}	.17

[a] $\epsilon_{Bu_4NNO_3} = 4$. [b] $(\epsilon_3 - \epsilon_1 - \epsilon_2) = 110$. [c] $(\epsilon_3 - \epsilon_1 - \epsilon_2) = 55$. [d] Estimated, taking $\epsilon_{Co(NO_3)_2} = 220$.

to evaluate the necessary quantities, as above, through the nitrate ion absorption in the two forms, and the solution composition. Data for a typical experiment are shown in Table II. Stepwise additions of water were made to a solution of cobaltous nitrate in *t*-butyl alcohol. The optical densities at 285 millimicrons and 1 centimeter path length were then translated into concentrations of coördinated and free nitrate ion, and the equilibrium constants calculated, using $\epsilon_{NO_3} = 114$ for the nitrate bound to cobalt, in anhydrous alcohol. As is seen from the log–log plot (Fig. 6) the calculation on the basis of equation 21 gives a reasonably good straight line over a range of 10^4 in value of the constant, and a slope corresponding to 3.3 for the power of the water concentration. Since the number of moles of water per liter is rather different from that for *t*-butyl alcohol, some effect of difference between concentration on volume basis, and mole ratios, might influence the relation of high-water to low-water points, either in deviation of points from the line, or slope of the line. However, calculation on the basis of mole ratio of water (to allow for water–alcohol competition) rather than percentage or molality, fails to alter the relations significantly (Fig. 6, line II).

The water effects in a solution containing 0.2 mole of lithium nitrate per mole of cobalt perchlorate, rather than a simple cobalt nitrate solution, are somewhat different. A plot of the optical density at 285 millimicrons as a function of the water content is shown in Fig. 7. The

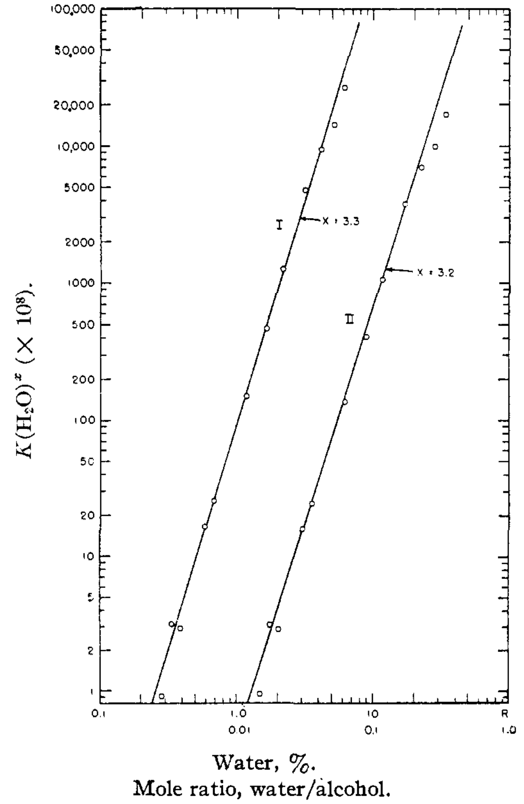

Fig. 6.—Determination of power to which water enters into equation (8).

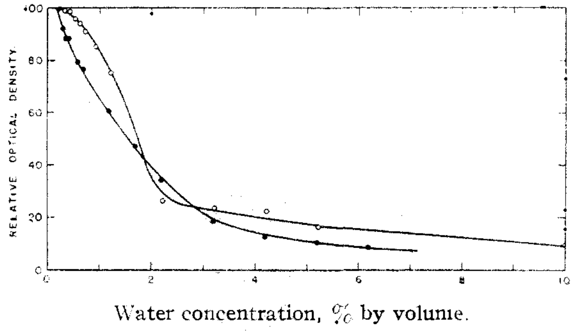

Fig. 7.—Relative optical density at 285 millimicrons as function of increasing water content of *t*-butyl alcohol solution (unity = no water added). I, $Co(NO_3)_2$; II, $LiNO_3 + 5Co(ClO_4)_2$.

optical density has been normalized to unity at the lowest water concentration. The data for the cobaltous nitrate experiment, similarly treated, are given for comparison. Whereas the cobalt nitrate curve drops smoothly and evenly with addition of water, the curvature being concave upward, the curve for the lithium nitrate–cobalt perchlorate mixture is less affected by the first additions of water, suffers a sharp drop between 1 and 2% water, and then levels off somewhat above the nitrate curve. Since the cobalt concentration in the mixed salt experiment is some 8 times that in the cobalt nitrate experiment, being 0.03 *M*, it may be that the concentration of cobalt perchlorate is high enough to affect the free water concentration when the water content is low, deferring the larger effects on the strongly coördinated nitrate to higher water concentrations.

Discussion

From the evidence presented, it is apparent that the difference in the light absorption of dilute aqueous cobaltous salts, and cobalt nitrate in organic solution, rests in formation of undissociated $Co(NO_3)_2$ in the organic media. It is further shown that a trinitrato complex may also be produced in the presence of excess ionic nitrate, since in a medium such as *t*-butyl alcohol formation of the trinitrato complex can be brought about by tetrabutylammonium nitrate, but not by lithium nitrate.

The effects of water and the organic solvent can best be approached from the viewpoint of Bernal and Fowler,[7] according to which the number 6 is to be taken as the normal maximum coördination number for cobaltous ion, and also represents the hydration in water solution. As one adds increasing proportions of an organic base such as *t*-butyl alcohol to an aqueous solution of cobalt nitrate, there will occur competition between water and the organic bases for the solvation positions, and a proportion of the water will be displaced. As the proportion of organic component in the solution increases, the dielectric constant drops, and the electrostatic attraction of oppositely charged ions increases. Eventually the anions in turn become electron donor competitors for the coördination positions around the metal atom, as their effective concentration is increased by their proximity to the cation. In this three-way competition for the coördination positions the position of the nitrate ion becomes very strong by the time the dielectric constant has been reduced to the order of 20, as shown by the apparent strong association of cobalt nitrate in acetone, in which the absorption coefficient in the visible is equal to that for *t*-butyl alcohol, which has a considerably lower dielectric constant. Trinitrato complex may be formed if a free nitrate ion is available to displace another solvent group, but the electrostatic force with three anion groups involved is weaker than with two, and the complex is considerably less stable.

TABLE II

EFFECT OF WATER ON ABSORPTION OF $Co(NO_3)_2$ IN *t*-BUTYL ALCOHOL

$Co(NO_3)_2$ = 0.00176 *M*

Water concn., ml. per 100 ml.	Optical density per cm., at 285 mμ	Concn. $Co(NO_3)_2$ × 10^4	$K_6(H_2O)^b$ × 10^8	Mol ratio H_2O/alc.	$K'_6(H_2O)^{b,a}$ × 10^8
0.188	0.398	17.4$_5$	0.0008	0.0098	0.0008
.288	.367	16.0$_5$	.9	.0151	.9
.338	.351	15.3	3.2	.0177	3.2
.388	.352	15.3$_5$	3.0	.0203	3.1
.588	.316	13.7$_5$	17	.0308	16
.688	.3045	13.2	26	.0362	25
1.188	.241	10.3	150	.0628	140
1.688	.1875	7.9	460	.0895	410
2.188	.1360	5.5$_5$	1,260	.117	1,100
3.188	.0740	2.7$_3$	4,800	.172	3,800
4.188	.0514	1.7	9,500	.228	7,000
5.188	.0408	1.2	15,000	.285	10,000
6.188	.0335	0.7$_2$	27,000	.344	17,000

[a] $K'_6(H_2O)^b =$

$$K_6(H_2O)^b\ x \left[\frac{\text{(moles solvent per liter, dry alcohol)}}{\text{(moles mixed solvent per liter)}}\right]^2.$$

The pattern of replacement of waters, in the competition between water and organic base, is probably the loss first of two waters, then a third, a fourth, and finally the last two as a pair. This behavior is in agreement with the second-power nitrate term in equations 19 and 21, but more direct basis for it is found in the data of Katzin and Ferraro[8] on the ternary systems cobaltous nitrate–water–acetone and cobaltous nitrate–water–*t*-butyl alcohol. The lesser sensitivity to water of solutions of cobalt nitrate in acetone in comparison with those in *t*-butyl alcohol, indicated in Fig. 2, is hereby interpretable as an expression of the lower base strength of the ketone, giving a lower proportion of hexasolvate at low water concentrations than the stronger base, *t*-butyl alcohol. At the lowest water concentrations mainly tetrasolvated (and undissociated) salt is present in the *t*-butyl alcohol solution also. That water comes

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(7) Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

(8) Katzin and Ferraro, THIS JOURNAL, **72**, 5455 (1950).

in at the 3.3 power in equation 21 may be taken to mean that the hexasolvate forming has on the average 3.3 waters in its solvation complement.

That the formation of the hexasolvate results in complete ionization of the salt does not necessarily follow, since even with 10% of water the dielectric constant of *t*-butyl alcohol is less than that of anhydrous acetone. One may picture the nitrates still in the main held to the cation by electrostatic attraction, which situation still gives the proper stoichiometry. The spectrum of the associated cobalt nitrate in the ultraviolet has been taken to be that of a nitrate group with electronic grouping shifted due to coördination,[9] and the change on removal from the coördination sphere should restore essentially the free nitrate spectrum, even if the anion is still held electrostatically to the cation. Similar explanations for the change in absorption on adding low concentrations of water to a solution in a medium of low dielectric constant have been given by Bortini[10] for the case of picric acid, and by Schaefer,[11] and von Halban and Litmanowitsch[12,13] for nitric acid.

The color of cobaltous nitrate in dry acetone or tertiary butyl alcohol, where it forms the undissociated tetrasolvate, is a decided magenta. The blue tinge, however, is not due to a complex spectrum of the type familiar with the cobalt halides, but seems to be due in the main to intensification of the normal cobalt absorption, and a broadening of the peak towards longer wave lengths. (There may also be a long-wave length tail with a small absorption coefficient.) The trinitrato complex shows a spectrum very similar in appearance, with an intensification and a slight shift in the wave length of the peak. The spectra are very like those found in aqueous solutions of cobalt salts to which have been added high concentrations of other soluble salts.[14] Blueness in cobaltous salt colors need not, therefore, indicate complexes of the type giving the blue of the halides, and absence of blue color need not indicate the absence of coördination.

The color behavior of cobalt perchlorate in organic solvents parallels that of the nitrate, but the complex formed seems to be much weaker. This is in agreement with the low coördinating power of perchlorate ion usually found. Experiments in which *t*-butyl alcohol solutions of hydrated cobalt perchlorate (dehydration past the tetrahydrate stage seems to induce decomposition) have been strongly dried further by shaking with anhydrous magnesium perchlorate have produced solutions almost as intensely colored as those of nitrate solutions. The magnesium perchlorate which dissolves in this treatment may have helped increase the completeness of the association reaction by common ion effect also.

The concept of competition between anions and water and other molecular electron donors for coördination positions may throw light also on the differences in common hydration states for different compounds of the same cation. In addition to factors such as crystal lattice energies, the electron donor strength of the anion is important. An anion which is a poor electron donor should make a salt which tends toward greater hydration. The perchlorate anion is not only a poor electron donor but is a large anion. It is therefore seen that perchlorates in general tend to be strong binders of water by combining ready displacement from coördination positions with large ionic size, so that the lattice energy changes accompanying introduction of water into a solid are minimized.

In an oxygenated anion like nitrate, coördination to a cation produces a structural strain, as indicated by the change in absorption spectrum. Such an alteration is shown in general by the transition element nitrates,[9] and may be a factor in the low stability and the difficulty of preparing anhydrous nitrates of the transition elements.[15,16,17] Similarly, in our experience, cobalt perchlorate and nickel perchlorate cannot be dehydrated without decomposition.

Summary

1. Cobalt nitrate dissolved in organic solvents undergoes an absorption spectrum change compared to the aqueous solution (intensification and shift to slightly longer wave lengths) which is attributable to formation of undissociated $CoX_4(NO_3)_2$, where X = solvent groups.
2. On addition of water an equilibrium is established with the hexasolvated form, $CoX_6(NO_3)_2$, whose spectrum is that of cobalt salts in dilute aqueous solution.
3. Addition of nitrate ion in the dry organic solvent may give formation of a weak trinitrato cobalt complex, presumably $CoX_3(NO_3)_3^-$.
4. The qualitative behavior of cobalt perchlorate solutions in organic solvents indicates a parallel type of metal ion–anion–solvent interaction.
5. A relationship of strength of cation–anion interaction to the stability of solid salt solvates is pointed out.

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[9] Katzin, *J. Chem. Phys.*, **18**, 789 (1950).

[10] Bortini, *Z. physik. Chem.*, **87**, 105 (1914).

[11] Schaefer with Niggeman, *Z. anorg. allgem. Chem.*, **97**, 285 (1916).

[12] von Halban, "Contrib. étude structure mol.," Vol. commem. Victor Henri, 1947/48, p. 239–245 (1948).

[13] von Halban and Litmanowitsch, *Helv. Chim. Acta*, **31**, 1963 (1948).

[14] Weyl, *J. Applied Phys.*, **17**, 628 (1946).

[15] Guntz and Martin, *Bull. soc. chim.*, **5**, 1004 (1909).

[16] Marketos, *Compt. rend.*, **155**, 210 (1912).

[17] De Forcrand, *ibid.*, **156**, 1044 (1913).