form metal hydrides and methane as the stable products.[10] The similarity between this reaction and the mechanism we have proposed is obvious, but formation of a stable hydride in a solvent of low dielectric constant would support only the gross features of a hydride mechanism for the exchange.

A comparison between the rates of reaction for the various isotopic hydrogen species is shown in Fig. 3. Isotope effects are undoubtedly partly responsible for the different slopes, but other factors are also present. The exchange of HD may produce either H_2 or HD by reaction with a solvent proton, so the disappearance of HD represents only about half the rate at which it reacts. The higher rate for parahydrogen as compared with deuterium may be due to some conversion by perturbations too low in energy to produce exchange. Thus the positive identification of the isotope effect will be complicated, and we are able to say at present only that it is probably not very large.

LOS ANGELES, CALIF.

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[10] H. Gilman, A. L. Jacoby and H. Ludman, THIS JOURNAL, **60**, 2336 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OKLAHOMA A. AND M. COLLEGE]

Aquo and Chloro Complexes of Cobalt(II) and Nickel(II) in 2-Octanol[1]

BY W. D. BEAVER, L. E. TREVORROW, W. E. ESTILL, P. C. YATES AND T. E. MOORE

RECEIVED APRIL 15, 1953

A study has been made of the extent of chloro and aquo complexing of cobalt(II) and nickel(II) in 2-octanol solutions. Spectrophotometry was employed to identify the complexes and to estimate their stability. Evidence for the existence of $CoCl^+$, $CoCl_2$, $CoCl_3^-$ and $CoCl_4^-$ was obtained. Results of varying the water concentration in solutions of constant cobalt and chloride concentration showed stoichiometric reaction of two water molecules with $CoCl_2$ leading to the formation of a monochloro complex and further reaction of approximately eleven water molecules with $CoCl^+$ leading to an aquated cobalt species, presumably Co^{++}_{aq}. Evidence is presented for the formation of a single unstable colored chloro complex of nickel. Both cobalt and nickel chlorides may be polymerized in 2-octanol. These results may be significant in regard to the separation of cobalt and nickel chlorides through the extraction of cobalt chloride by 2-octanol.

Increasing attention is being given to the chemistry of inorganic salts in non-aqueous solvents largely as a result of interest in liquid–liquid extraction procedures.[2] However, of the numerous salt solvent-pair combinations investigated, only a few have been studied intensively in an effort to interpret the nature of the interactions occurring in the non-aqueous phase.

Garwin and Hixson[3] have reported the separation of $CoCl_2$ from $NiCl_2$ by the selective extraction of $CoCl_2$ into 2-octanol. Good separation factors coupled with high extractibility of the cobalt salt were found only if the aqueous phase contained a high concentration of HCl or $CaCl_2$ as an extraction-promoting agent. This extraction system has been studied in these laboratories, and since the octanol-rich phases at equilibrium have been shown to contain considerable amounts of the promoting agent and water as well as $CoCl_2$, it seemed desirable to investigate the nature and extent of complexing which occurs in octanol between these components of the system.

Experimental

Materials.—Anhydrous $NiCl_2$ and $CoCl_2$ were prepared by repeated grinding and heating the corresponding recrystallized C.P.-grade hydrated salts at 120° in air. Care was taken to use only those materials in each case which contained a negligible amount of the other metal. C.P. anhydrous LiCl was further dried for 24 hours at 120° before use.

Anhydrous octanol solutions of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ were obtained by metathesis of anhydrous octanol solutions of $AgClO_4$ and $CoCl_2$ or $NiCl_2$. Preliminary experiment showed that metathesis at room temperature of equivalent quantities of these salts resulted in a quantitative precipitation of AgCl. Anhydrous nickel and cobalt perchlorates could not be prepared by vacuum dehydration of the perchlorate hydrates.

"Anhydrous" octanol (Matheson Company's best grade) was found by Karl Fischer analysis to have no more than 0.002% water and was used without further drying.

Analytical Methods.—Water determinations were made by the Karl Fischer[4] method employing a dead-stop end-point.

Chloride analysis was done by a modified Volhard titration using alcoholic silver nitrate and aqueous potassium thiocyanate in the back titration. The operations were carried out directly in the octanol solutions without prior back extraction into water.

Nickel was estimated colorimetrically by a modification of a procedure described by Snell[5] employing the color of bis-(dimethylglyoximo)-nickel in methanol–pyridine mixtures. The octanol solutions were treated directly with alcoholic dimethylglyoxime and then diluted with pyridine. Standards were prepared over the expected concentration range of $NiCl_2$ and the optical densities compared at 360 mμ.

Procedures.—Spectrophotometric measurements were made employing a Beckman DU spectrophotometer at 30° with 1-cm. Corex cells. Solutions of optical densities greater than 1.5 were studied by decreasing the light path to 0.1 cm. by means of quartz spacers inserted in the cells.

Solubility determinations of $NiCl_2$ in LiCl–octanol mixtures were performed on a series of 30 solutions in which the LiCl concentration varied from 0.04 to 1.5 molal. The solutions were shaken first at 50° for several hours and then at 30° for over two weeks. Excess $NiCl_2$ was separated, the solutions were analyzed for nickel and chloride, and the absorption spectrum was obtained.

Treatment of Data.—Interaction between $Co(ClO_4)_2$ and LiCl was studied by the method of continuous variations developed by Job[6] and others.[7] Interactions between $CoCl_2$

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[1] Presented in part at the 8th Southwest Regional Meeting of the American Chemical Society, Little Rock, Ark., 1952. Supported under Contract AT(11-1)-71 No. 1 with the U. S. Atomic Energy Commission.

[2] H. M. Irving, *Quarterly Rev.*, **5**, 200 (1951).

[3] L. Garwin and A. N. Hixson, *Ind. Eng. Chem.*, **41**, 2303 (1949).

[4] J. Mitchell, Jr., and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

[5] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," 3rd Ed., Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 345.

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

[7] L. I. Katzin and E. Gebert, THIS JOURNAL, **72**, 5464 (1950).

and LiCl and between $CoCl_2$ and H_2O were investigated by the usual spectrophotometric methods.[8,9]

A combination of solubility and spectrophotometric methods similar to those described by Gordon and Shreyer[10] was attempted in the $NiCl_2$–LiCl–octanol system. However, the very viscous nature of concentrated LiCl solutions in octanol caused great difficulty in assuring the establishment of equilibrium with solid $NiCl_2$, and hence only a more or less qualitative discussion of this system seems justified. Interaction between chloro complexes of $NiCl_2$ and H_2O could not be extensively investigated because of the almost complete destruction of the complex at very low water concentrations accompanied by precipitation of a solid phase.

Results

Figure 1 is a plot showing the effect of the addition of varying amounts of LiCl on the spectra of anhydrous $Co(ClO_4)_2$ solutions. The concentration of $Co(ClO_4)_2$ was held constant (8×10^{-4} *M*) while the LiCl was varied from 0 to 0.8 *M*. LiCl does not absorb in the spectral region studied, and the absorption of $Co(ClO_4)_2$ is virtually negligible in comparison to the high absorption of chloro complexes. For clarity in presentation many of the LiCl/$Co(ClO_4)_2$ ratios are not included in Fig. 1.

At wave lengths between 470 and 580 mμ, the absorption increases with addition of LiCl until a 2:1 LiCl/$Co(ClO_4)_2$ ratio is attained. Thereafter, it steadily decreases up to the highest ratios (1000:1) investigated.

Although it is not evident from the figure owing to the large plotting scale adopted, a similar phenomenon occurs in the neighborhood of 630 mμ with the maximum absorption at a 50:1 ratio. Beyond 650 mμ and in the neighborhood of 620 mμ, the absorption increases continuously at all ratios studied.

Three points of crossing of these curves, or isosbestic points, located at 585, 605 and 620 mμ, include all curves having ratios between 2:1 and 50:1 with higher ratios deviating from these points progressively, while one isosbestic point at 645 mμ includes all ratios higher than 50:1 but no lower ones.

These features of the spectra indicate at least three absorbing entities, one reaching a maximum concentration at a 2:1 ratio having isosbestic points at 585, 605 and 620 mμ with a second absorbing entity which attains a concentration maximum at a 50:1 ratio, and a third entity having an isosbestic point at 645 mμ with the second and which apparently reaches no concentration maximum even at a 1000:1 ratio. The isosbestic points at 585, 605 and 620 mμ also show that little of the highest complex exists below 10:1 ratio since appreciable deviations of the curves from the isosbestic points do not occur below this ratio.

The empirical formulas of the two lower complexes were established by the continuous variation plots shown in Figs. 2B and 2C. Variations conducted at 610, 600 and 570 mμ have maxima at a 0.66/0.33 mole fraction ratio of LiCl to $Co(ClO_4)_2$ corresponding to an empirical formula of $CoCl_2$, while those at 640, 660 and 670 mμ have maxima at LiCl/$Co(ClO_4)_2$ mole fraction ratio of 0.75/0.25 indicating a trichloro complex. Vosburgh and Cooper's[11] modified *y* function for systems containing more than one absorbing reactant was used in constructing the latter plot since the absorption of $CoCl_2$ at these wave lengths is appreciable. Extinction coefficients of $CoCl_2$ necessary for evaluating this function were obtained from anhydrous $CoCl_2$–octanol solutions. It is unlikely that the higher complex causes much deviation of the maximum from stoichiometric values since it is obviously much weaker than the second complex.

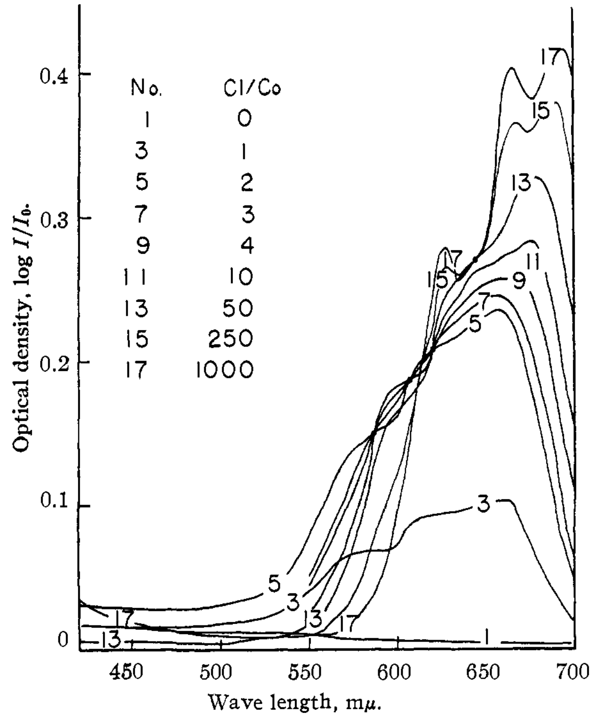

Fig. 1.—Absorption spectra at 30° of LiCl–$Co(ClO_4)_2$ mixtures in 2-octanol. $Co(ClO_4)_2 = 8 \times 10^{-4}$ *M* in 1.00-cm. Corex cell.

Since complex ion formation usually occurs in a stepwise fashion, the variation shown in Fig. 2A was designed as a test for the presence of a monochloro complex. In this study the components were $CoCl_2$ and $Co(ClO_4)_2$. The results showed a maximum interaction at a 1:1 ratio with the formation of an absorbing entity having an extinction coefficient less than half that of $CoCl_2$. Conventionally this entity would be written as a ($CoCl^+$) complex although polymeric structures conforming closely with the stoichiometry of the reaction are also possible. It should be pointed out, however, that the existence of extensively dissociated compounds in a solvent of such low dielectric constant and high viscosity is improbable, and the formulation of simple complex ions is a matter of convenience only.

The ($CoCl^+$) and $CoCl_2$ complexes were too stable in anhydrous octanol to enable an estimate of their stability constants to be made from spectrophotometric data; however, the ($CoCl_3^-$) complex was sufficiently unstable to enable a calculation of its stability constant. Accordingly a logarithmic plot of the concentration ratio ($CoCl_3^-$)/($CoCl_2$) against (Cl^-) was made from the data in Fig. 1 over LiCl/$Co(ClO_4)_2$ ratios between 2:1 and 50:1. The extinc-

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(8) S. M. Edmonds and N. Birnbaum, THIS JOURNAL, **63**, 1471 (1941).

(9) W. D. Kingery and D. N. Hume, *ibid.*, **71**, 2393 (1949).

(10) S. Gordon and J. M. Shreyer, *ibid.*, **74**, 3169 (1952).

(11) W. C. Vosburgh and G. R. Cooper, *ibid.*, **63**, 437 (1941).

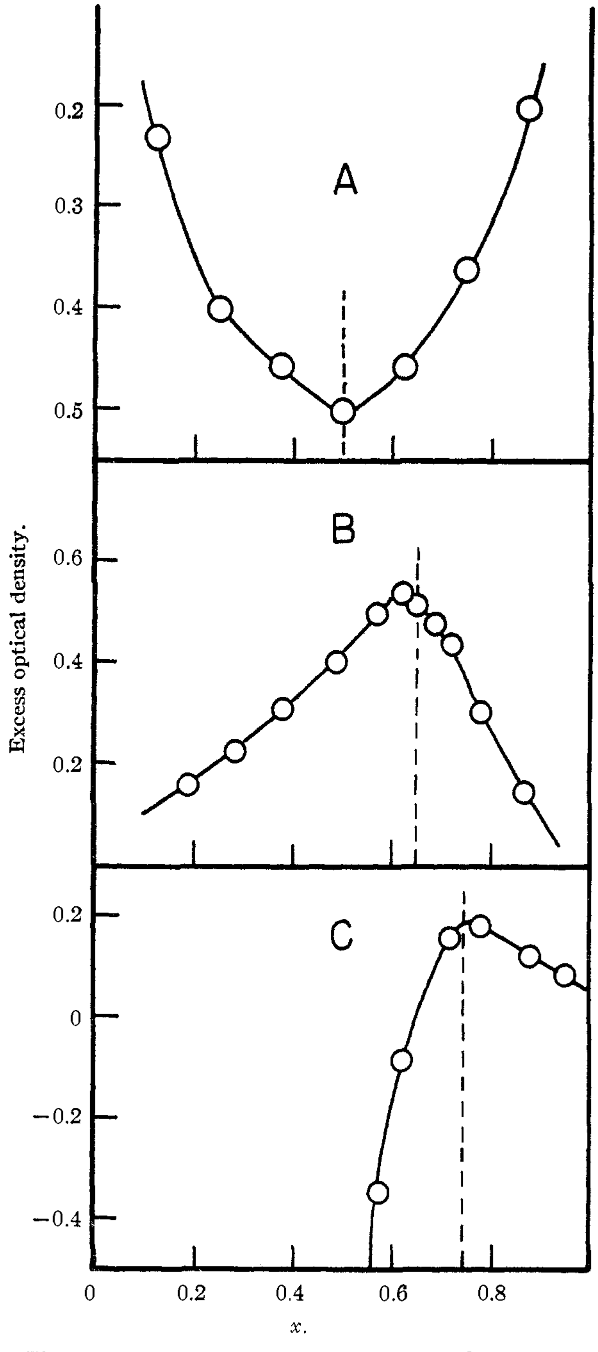
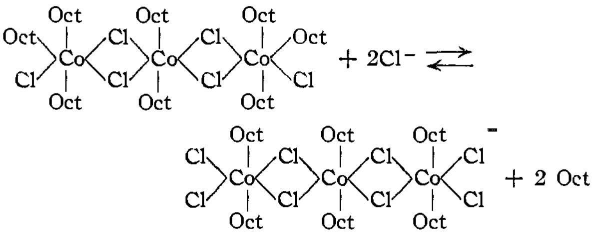


Fig. 2.—Continuous variation study at 30°: A, λ 660 mμ, $CoCl_2 = 1.6 \times 10^{-3}\, x\, M$, $Co(ClO_4)_2 = 1.6 \times 10^{-3} (1 - x)\, M$; B, λ 570 mμ, $LiCl = 1.56 \times 10^{-2}\, x\, M$, $Co(ClO_4)_2 = 1.56 \times 10^{-2} (1 - x)\, M$; C, λ 640 mμ, $LiCl = 1.56 \times 10^{-2}\, x\, M$, $Co(ClO_4)_2 = 1.56 \times 10^{-2} (1 - x)\, M$.

tion coefficient of $CoCl_2$ in octanol was used to estimate the concentration of this complex in the neighborhood of 585 mμ where it is the principal absorbing entity. Successive approximations were employed to correct for absorption of the second complex and after a short series of such approximations, concentrations of $CoCl_2$ and the second complex were obtained which gave constant extinction coefficient values for the second complex at all wave lengths studied. These concentrations were then used in the logarithmic plot.

Although the plot was perfectly linear at all wave lengths for all $LiCl/Co(ClO_4)_2$ ratios between 2:1 and 50:1, the slope of the line was 0.67 instead of 1.00 as required by the simple reaction $CoCl_2 + (Cl^-) \rightleftarrows (CoCl_3^-)$.

This deviation of slope could arise either from variations in the neglected activity coefficient ratio $\gamma_{(CoCl_3^-)}/\gamma_{(CoCl_2)}\gamma_{(Cl^-)}$ or by virtue of the existence of $CoCl_2$ as a polymeric bridged complex. For example occurrence of the reaction



would be consistent with the observed slope and still be well within the possible experimental error in locating the continuous variation maxima in Fig. 2B. A bridged structure similar to the type shown is exhibited in the solid state by $CoCl_2{\cdot}2H_2O$,[12] and it would not be surprising to find an analogous structure in a weakly basic solvent of low dielectric constant such as octanol.

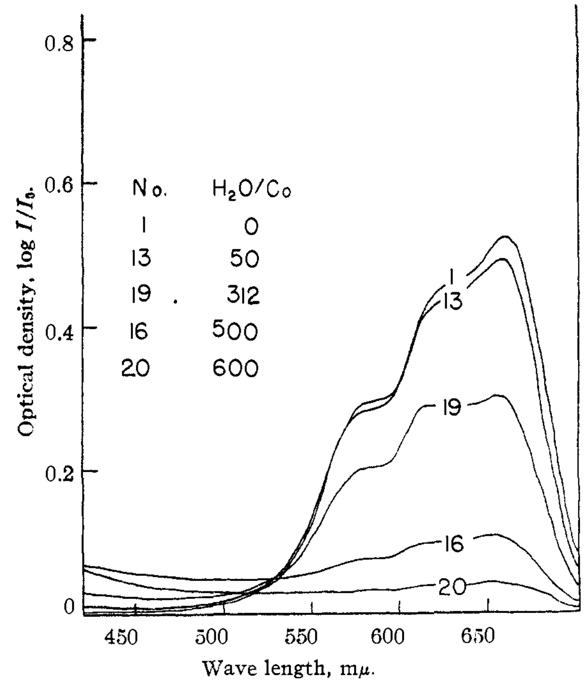


Fig. 3.—Absorption spectra at 30° of $CoCl_2$–H_2O mixtures in 2-octanol. $CoCl_2 = 1.6 \times 10^{-3}\, M$ in 1.00-cm. Corex cell.

Figure 3 shows that the effect of the addition of water on the spectrum of $CoCl_2$ in octanol is to decrease the absorption peaks without altering the other characteristics of the spectrum. Accordingly it was assumed that competition of water with chloride for coördination positions around the cobalt was occurring, leading to the formation of

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[12] B. K. Vainshtein, *Doklady Akad. Nauk S.S.S.R.*, **68**, 301 (1949).

hydrated lower chloro complexes. The data were therefore fitted to the hypothetical reaction

$$CoCl_2 + nH_2O \rightleftharpoons CoCl(H_2O)_n^+ + Cl^-$$

The extinction coefficient of $CoCl_2$ was assumed to be that found in anhydrous systems, while that of $CoCl(H_2O)_n^+$ was taken as equal to the value obtained at the minimum in the variation plot of Fig. 2A. By a series of successive approximations, values of

$$k_2 = \frac{(CoCl_2)(H_2O)^n}{(CoCl(H_2O)_n^+)(Cl^-)}$$

were calculated. Good agreement of the data with this expression was obtained with $n = 2$. The inverse first power variation with chloride ion concentration was checked by extending the studies to $LiCl–Co(ClO_4)_2–H_2O$–octanol mixtures at fixed water concentrations but varying chloride concentrations. At 0.1 and 0.3 *M* water concentrations constant values of k_2 identical with those found in the $CoCl_2–H_2O$–octanol systems were obtained. At 0.5 *M* water concentration k_2 was constant but about 30% smaller numerically than in the previous cases. These *k* values and concentration ranges are listed in Table I.

At high water concentrations, the absorption of $CoCl_2$ in octanol–water mixtures is reduced below that of the 1:1 complex, and this suggested the possible further interaction

$$CoCl(H_2O)_2^+ + mH_2O \rightleftharpoons Co(H_2O)_{m+2}^{++} + Cl^-$$

Using again the value of the extinction coefficient of the 1:1 complex obtained from the variational study of Fig. 2A together with that of $Co(H_2O)_{m+2}^{++}$ derived from solutions of $Co(ClO_4)_2$ in aqueous octanol, calculations of the concentration ratio of $CoCl(H_2O)_2^+$ to $Co(H_2O)_{m+2}^{++}$ were made by successive approximations. The values of this ratio together with experimental values of the water and chloride concentrations (corrected for that assumed to be a part of the complexes) were substituted into the equation

$$k_1 = \frac{(CoCl(H_2O)_2^+)(H_2O)^m}{(Co(H_2O)_{m+2}^{++})(Cl)^-}$$

It was found that a plot of log (H_2O) against log $(Co(H_2O)_{m+2}^{++})(Cl^-)/(CoCl(H_2O)_2^+)$ was linear and had a slope corresponding to $m = 11$. The surprisingly large value of 13 for the apparent hydration of Co^{++} in these aqueous octanol solutions (*ca.* 1 *M* in H_2O) is supported by the similarity of the spectra and hydration number to those of $Co(ClO_4)_2$ in octanol–water mixtures found by Yates, *et al.*[13] Values of k_1 and the applicable concentration ranges are given in Table I.

Evidence of complex formation in the $NiCl_2$–octanol system was the development of a blue color in solutions containing high concentrations of either HCl or LiCl. Examination of the spectra showed two symmetric absorption peaks at $\lambda = 650$ and $\lambda = 720$ mμ which progressively increased in intensity with increase in LiCl concentration at approximately constant $NiCl_2$ concentration.

TABLE I

Complex	System[a]	Conditions	Reaction[b] and equilibrium concn. constants	
		H_2O from 0.72 to 1.04 *M*		
$Co(H_2O)_{13}^{++}$	(1)	H_2O/Co ratio from 450 to 650	(a)	72
		H_2O from 0 to 0.5 *M*		
$CoCl(H_2O)_2^+$	(1)	H_2O/Co ratio from 0 to 312.5	(b)	3.2×10^2
	(2)	Cl/Co ratio from 2 to 6		
		H_2O = 0.5 molar	(b)	57
		H_2O = 0.3 molar	(b)	3.8×10^2
		H_2O = 0.1 molar	(b)	4.1×10^2
$CoCl^+$	(4)	Anhydrous		
	(3)	Cl/Co ratio from 1 to 1000	(c)	1.0×10^2
$CoCl_2$	(1)	H_2O from 0 to 0.5 *M* H_2O/Co ratio from 0 to 312.5		
	(2)	Cl/Co ratio from 1 to 250		
	(4)	All regions		
$CoCl_3^-$	(3)	Cl/Co ratio from 2.5 to 1000	(c)	1.0×10^2
	(2)	Cl/Co ratio from 10 to 1000		
$CoCl_4^{--}$	(3)	Cl/Co ratio from 100 to 1000		
	(2)	Cl/Co ratio from 100 to 1000		

[a] (1) $CoCl_2–H_2O$–octanol; total cobalt constant at 1.6×10^{-3} *M;* (2) $Co(ClO_4)_2–LiCl–H_2O$–octanol; total cobalt constant at 1.6×10^{-3} *M;* (3) $Co(ClO_4)_2$–LiCl–octanol; total cobalt constant at 8×10^{-4} *M;* (4) $Co(ClO_4)_2–CoCl_2$–octanol; total cobalt constant at 1.6×10^{-3} *M.* [b] (a) $Co(H_2O)_{13}^{++} + Cl^- \rightleftarrows CoCl(H_2O)_2^+ + 11H_2O$; (b) $CoCl(H_2O)_2^+ + Cl^- \rightleftarrows CoCl_2 + 2H_2O$; (c) $CoCl_2 + Cl^- \rightleftarrows CoCl_3^-$.

The simplicity of the spectral features pointed to the existence of no more than one colored species other than $NiCl_2$. As a consequence of the relatively low values obtained for the optical density at all except the highest $LiCl/NiCl_2$ concentration ratios, an attempt was made to study the formation of less highly colored complexes by solubility measurements. The results of solubility determinations on three series of solutions having different equilibration times, all over two weeks, showed a 30-fold variation between series and serious scatter of the data within any single series indicative of failure to reach equilibrium with the solid phase. Nevertheless the variations in the absorption spectra allow some interesting conclusions to be drawn about this system.

If the apparent extinction coefficient ϵ_A is defined as the ratio of the observed optical density to the analytical $NiCl_2$ concentration, then it is easily shown that for a series of association reactions, *e.g.*

$$NiCl_2 + LiCl \longrightarrow LiNiCl_3$$
$$LiNiCl_3 + LiCl \longrightarrow Li_2NiCl_4$$

in a solvent where the dissociation of $NiCl_2$ is negligible and only nickel-containing species have appreciable absorption, ϵ_A is given by

$$\epsilon_A = \frac{\epsilon_0 + \epsilon_1 k_1(LiCl) + \epsilon_2 k_1 k_2(LiCl)^2 + \cdots}{1 + k_1(LiCl) + k_1 k_2(LiCl)^2 + \cdots} \quad (1)$$

where ϵ_0, ϵ_1, ϵ_2 are, respectively, the extinction coefficients of $NiCl_2$, $LiNiCl_3$ and $Li_2(NiCl_4)$ and k_1, k_2. . .are the formation constants of each from the next lower species. Although eq. 1 requires ϵ_A to be independent of the concentration of $NiCl_2$ this was not found experimentally.

A plot of ϵ_A as the ordinate against the LiCl concentration for the three series of solutions revealed that for each series the values of ϵ_A were approximately linear with respect to the LiCl concentration, but that the lines were widely divergent. The slope of the curve corresponding to the lowest average nickel content (1.7×10^{-2}

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[13] P. C. Yates, R. Williams, R. Laran and T. E. Moore, THIS JOURNAL, 75, 2212 (1953).

molal) was 40 times greater than that of the highest (3.5×10^{-3} molal).

A reasonable explanation lies in the assumption of polymerization reactions competitive with the association reactions already referred to. For a reaction of the type

$$y(\mathrm{NiCl_2}) \rightleftharpoons (\mathrm{NiCl_2})_y$$

the expression for ϵ_A becomes

$$\epsilon_A = \frac{\epsilon_0 + \epsilon_1 k_1(\mathrm{LiCl}) + \epsilon_2 k_1 k_2(\mathrm{LiCl})^2 + y\epsilon_p k_p(\mathrm{NiCl_2})^{y-1}}{1 + k_1(\mathrm{LiCl}) + k_1 k_2(\mathrm{LiCl})^2 + y k_p(\mathrm{NiCl_2})^{y-1}} \quad (2)$$

where ϵ_p and k_p refer to the extinction coefficient and formation constant of the polymer. If the polymer is much less highly colored than the complexes so that ϵ_p is small by comparison with ϵ_1 and ϵ_2, the results found are consistent with the qualitative predictions of eq. 2. That ϵ_p is comparatively small is shown by the fact that the lowest values of ϵ_A are associated with the highest values of $NiCl_2$ and the lowest values of LiCl.

The rapid decrease in ϵ_A for relatively small changes in $NiCl_2$ content indicates that the tendency to form chloro complexes is small compared to the polymerization reaction since the extinction coefficients of the chloro complexes (estimated from the solutions of lowest $NiCl_2$ and highest LiCl content) are probably in excess of 200. By comparison with $CoCl_2$ in octanol $NiCl_2$ forms the weaker chloro complexes although both salts may exist partly as polymerized species.

The results of this investigation agree qualitatively with the observations of Katzin and Gebert[14] on isopropyl and *t*-butyl alcohol solutions of $CoCl_2$ in the identification of chloro complexes having 2 and 3 chlorine atoms per cobalt. The failure to find evidence of a $CoCl_4^=$ complex by these authors was doubtless because of the more limited range of chloride-to-cobalt concentration ratios studied. Spectral characteristics reported for $CoCl_4^=$ in acetone correspond closely to those of the highest chloro complex found in octanol.

[14] L. I. Katzin and E. Gebert, THIS JOURNAL, **72**, 5464 (1950).

STILLWATER, OKLAHOMA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA]

Crystal Structures of Americium Compounds[1]

BY D. H. TEMPLETON AND CAROL H. DAUBEN

RECEIVED MAY 25, 1953

The crystal structures of several compounds of americium, element 95, have been determined by the X-ray powder diffraction method. AmF_3 is hexagonal (LaF_3 type) with $a = 4.067 \pm 0.001$ Å. and $c = 7.225 \pm 0.002$ Å. for the pseudo-cell which explains the powder data. AmO_2 is cubic (CaF_2 type) with $a = 5.383 \pm 0.001$ Å. AmOCl is tetragonal (PbFCl type) with $a = 4.00 \pm 0.01$ Å., $c = 6.78 \pm 0.01$ Å. The metal parameter is 0.18 ± 0.01. Am_2O_3 is cubic when prepared at 600° and hexagonal when prepared at 800°. For the cubic form (Mn_2O_3 type) $a = 11.03 \pm 0.01$ Å. The metal parameter is -0.030 ± 0.002. For the hexagonal form (La_2O_3 type) $a = 3.817 \pm 0.005$ Å., $c = 5.971 \pm 0.010$ Å.

In coöperation with Professor B. B. Cunningham and his students, we have been observing the X-ray diffraction patterns of various compounds of americium, element 95. The isolation of americium produced by the beta decay of Pu^{241} has been described by Cunningham.[2] Prior to 1948 the purification was usually terminated when the impurities (chiefly lanthanum) were reduced to one or two per cent. Since that time there have been available americium stocks of much higher purity.[3,4] In this paper we report our results concerning the crystal structures of AmF_3, AmO_2, AmOCl and two forms of Am_2O_3.

The powder diffraction patterns were taken with Cu Kα X-rays ($\lambda = 1.5418$ Å.) in cameras of radius 4.5 cm. The nickel filter was placed between the sample and the film to help diminish the background due to the radiations from the radioactive decay of Am^{241}. When care was taken that the small sample was entirely in the X-ray beam, the background was not troublesome.

Americium Trifluoride.—Americium trifluoride was prepared by Eyring as described elsewhere.[5] Sample A (Table I) was pink in color, like that described by Fried.[6] Sample B was a subsequent preparation which was grey or lavender in color. Its diffraction pattern was almost identical with that of sample A. Sample C was prepared by Dr. J. C. Wallmann from the very pure americium nitrate solution used by Howland and Calvin for their magnetic investigation.[7] Some of this americium was precipitated as the hydroxide and heated with oxygen to 525°. It was then heated in hydrogen fluoride to 715°. The product was pink but after a week, part of it had turned yellow. Sample C consisted of some of this yellow material.

With each of the three samples an excellent powder diffraction pattern was obtained corresponding to the LaF_3-type structure.[8] The unit cell dimensions listed in Table I refer to the hexagonal pseudo-cell containing two americium atoms. This cell accounts for all the diffraction lines observed in the powder patterns. Faint reflections in single crystal patterns[8,9] require an *a* axis which is

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[1] This research was performed under the auspices of the A.E.C.

[2] B. B. Cunningham, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 19.2, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

[3] H. R. Lohr and B. B. Cunningham, THIS JOURNAL, **73**, 2025 (1951).

[4] L. Eyring, H. R. Lohr and B. B. Cunningham, *ibid.*, **74**, 1186 (1952).

[5] E. G. Westrum and L. Eyring, *ibid.*, **73**, 3396 (1951).

[6] S. Fried, *ibid.*, **73**, 416 (1951).

[7] J. J. Howland and M. Calvin, *J. Chem. Phys.*, **18**, 239 (1950).

[8] I. Oftedal, *Z. physik. Chem.*, **B5**, 272 (1929); **B13**, 190 (1931).

[9] We have observed these weak reflections for a single crystal of pure synthetic CeF_3, showing that the effect in tysonite[8] is not due to ordering between the cerium and lanthanum atoms.