tography. Under these conditions, however, the chelate was not eluted and the test was discontinued after several hours. Another attempt with the column temperature at 80° was similarly unsuccessful. Apparently the complex is strongly solvated by dibutyl-*d*-tartrate, inasmuch as it was readily eluted from the silicone grease column at 30°. A final attempt was made at 110°, but at this temperature dibutyl-*d*-tartrate bled rapidly from the column, so the experiments were discontinued.

It was concluded that it will be necessary to use an optically active liquid that is less volatile and/or polar than dibutyl-*d*-tartrate if gas–liquid chromatography is to be successful in separating optical isomers of inner complexes.

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Studies on Phosphato and Methyl Phosphato Complexes of the Pentaamminecobalt(III) Class

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A method of preparing the compound $Co(NH_3)_5PO_4{\cdot}2H_2O$ is described. The compound dissolves to form solutions in which PO_4^{-3} is directly bound to $Co(NH_3)_5^{+3}$. Dissociation of PO_4^{-3} is slow in acidic solution so that the affinity of the bound PO_4^{-3} for H^+ in each of the three stages of association can be measured. These measurements have been made and, in addition, the equilibrium quotient governing the replacement of bound $H_2PO_4^-$ by H_2O has been determined. Evidence is presented for substantial outer-sphere affinity of $Co(NH_3)_5H_2O^{+3}$ for $H_2PO_4^-$. Methods of preparing $Co(NH_3)_5PO_4(CH_3)_3^{+3}$ and $Co(NH_3)_5PO_4(CH_3)_2^{+2}$ in solution are described. The former ion aquates and hydrolyzes rapidly with bond-breaking at both Co–O and P–O positions, but without ester hydrolysis. $Co(NH_3)_5PO_4(CH_3)_2^{+2}$ aquates and hydrolyzes much less rapidly, and again without ester hydrolysis. In the reaction of $Co(NH_3)_5PO_4H_2^{+2}$ or of $Co(NH_3)_5PO_4(CH_3)_2^{+2}$ with Cr^{+2}, the phosphate group is transferred, but when $Co(NH_3)_5PO_4(CH_3)_3^{+3}$ reacts no transfer takes place, and in this system the reaction with Cr^{+2} waits on the formation of $Co(NH_3)_5OH_2^{+3}$.

Methods[1,2] for the preparation of phosphato complexes of the pentaammineCo(III) class have been described, but later workers[3,4] have expressed doubt that the preparations were successful. Daniel and Salmon[4] state that they were unable to prepare a solid phase containing the species $Co(NH_3)_5PO_4$. In this paper we report a method for the preparation of $Co(NH_3)_5PO_4{\cdot}2H_2O$; our investigations of acidified solutions of this compound show that PO_4^{-3} is indeed bound to the residue $Co(NH_3)_5^{+3}$. Our experience leads us also to doubt that Duff and Duval and Duval actually had the phosphatopentaammine Co(III) complex in hand, and we think it likely that phosphate salts containing $Co(NH_3)_5OH^{+2}$ or $Co(NH_3)_5OH_2^{+3}$ as cations actually were prepared by them. It seems necessary at the outset to correct the erroneous statement made by one of us[5] that the phosphato complex is very labile, a statement which was based on the assumption that Duff's procedure actually leads to the inner-sphere complex.

In addition to describing the conditions which we found optimum for the preparation of the phosphato complex, we describe methods for the preparation of $Co(NH_3)_5PO_4(CH_3)_3^{+3}$ in trimethylphosphate and of $Co(NH_3)_5PO_4(CH_3)_2^{+2}$ in water. Compounds of both ions appear to be remarkably soluble and our efforts to prepare pure solids were unsuccessful. The equilibria involving the association of H^+ with $Co(NH_3)_5PO_4$ in each of the three stages were studied, and the equilibrium quotient for the replacement of H_2O from $Co(NH_3)_5H_2O^{+3}$ by $H_2PO_4^-$ has been measured. The aquation and hydrolysis of the phosphate complexes have been investigated as well as the reaction of each of the complexes with Cr^{+2}. Of particular interest to us was the possibility that electron transfer through phosphate or through the dimethyl complex leads to activation effects analogous to those observed in the reaction of Cr^{+2} with complexes of organic half-esters.[6] Such activation effects have been eliminated as possibilities in some of the systems, but they remain as possibilities in others which have not been studied directly.

Experimental

Materials.—$Co(NH_3)O_5H_2(ClO_4)_3$[7] and $Co(NH_3)_5Br_3$[8] were prepared by standard methods. A solution containing Cr^{+2} was produced by electrolytic reduction of Cr^{+3} in acid perchlorate

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(2) R. Duval and C. Duval, *Compt. rend.*, **189**, 573 (1929).

(3) R. Klement, *Z. anorg. allgem. Chem.*, **156**, 237 (1926).

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(8) $Co(NH_3)_5Br_3$ was supplied by Dr. M. Green.

solution. A solution containing $NaPO_4(CH_3)_2$[9,10] was prepared by the hydrolysis of $(CH_3)_3PO_4$ in aqueous NaOH. All other chemicals were commercial products of good quality and were used without further purification.

Analyses.—Cobalt[11] was determined in the +2 state by measuring the extinction of the solution in concentrated HCl at $\lambda = 650$ mμ. Co(III) complexes were reduced for analysis using $SnCl_2$ in aqueous HCl at 70°. The Kjeldahl method[12] was used for the determination of NH_3. Chromium was determined spectrophotometrically[13] as CrO_4^{-2}, CH_3OH by a slight modification of Boos' method,[14] and phosphate gravimetrically.[15]

Mass spectrometric determinations of O^{18}/O^{16} ratios were made on samples of CO_2 obtained from the oxygen-containing material by the method of Anbar and Guttman.[16]

Results

A. The Preparation of a $Co(NH_3)_5PO_4$ Compound.—The affinity of phosphate for the pentaamminecobalt(III) residue in an intermediate range of acidity is high enough so that there is no difficulty in preparing a solution containing $Co(NH_3)_5PO_4H_2^{+2}$ at fairly high concentration. The only difficulty in preparing a pure compound is met in separating the desired complex from $Co(NH_3)_5OH_2^{+3}$ and from other components of the solution. However, the displacement of phosphate from the first coördination sphere of the cobalt complex in acid or mildly alkaline solution is slow enough so that an ion-exchange separation is feasible, and the method to be described makes use of such a procedure.

The reaction to form the phosphato complex was carried out in a solution made up of 55 ml. of H_2O, 4 ml. of concentrated H_3PO_4, 16 g. of NaH_2PO_4, and 10 g. of $Co(NH_3)_5OH_2(ClO_4)_3$. The mixture was heated at 70–80° for approximately 1 hr., then it was cooled and poured through the resin bed. Good results were obtained with Dowex 50W-X4 in the hydrogen form contained in a column 22 mm. in diameter and 250 mm. in length. After the solution had been passed through the column, the resin bed was washed with water. Separation of the phosphato complex from the aquo is particularly easy in dilute alkali, which converts the phosphato complex to a neutral species, and the aquo to the dipositive cation. A solution 0.05 *M* in NaOH is an effective eluent; if the eluent is much more concentrated in alkali, the cobalt complex is decomposed.

The most concentrated portions of the eluate totalling about 1 l. were combined and were treated with 100 ml. of concentrated NH_3 and 500 ml. of C_2H_5OH. Crystallization is complete after several hours in the freezing compartment of a refrigerator. The crystals were gathered by filtration, and washed with ice water, C_2H_5OH, and ether. The salt was recrystallized from a concentrated solution in 1 *M* $HClO_4$, using NH_3 to bring about supersaturation, adding it to incipient crystallization, then cooling to complete the process. The crystals were gathered and washed as described above. The analysis of the material dried at room temperature is reported below.

	Found	Theor. for $Co(NH_3)_5PO_4 \cdot 2H_2O$
Co	21.38	21.42
P	11.24	11.26
N	25.32	25.46

The yield following this procedure is *ca.* 25%.

Intense drying reduces the water content of the compound, but we did not find it possible to prepare the monohydrate or the anhydrous material. When the crystals are ground to a fine powder, they become somewhat hygroscopic.

The compound is only sparingly soluble in water, but it is readily brought into solution by acid, which converts the complex to protonated forms.

B. The Preparation of $Co(NH_3)_5PO_4(CH_3)_3^{+3}$.—The affinity of $Co(NH_3)_5^{+3}$ for $(CH_3)_3PO_4$ in water is too low and the complex is too labile for the preparation in water to be practicable, but solutions of the complex in trimethyl phosphate can be made up without difficulty. The reaction

$$\underline{Co(NH_3)_5Br_3} + 3AgClO_4 + (CH_3)_3PO_4 = Co(NH_3)_5PO_4(CH_3)_3(ClO_4)_3 + \underline{3AgBr}$$

(formulas for solid phases are underlined) proceeds substantially to completion at 50° in 10 hr. without side reactions. Water must be rigorously excluded for otherwise the aquo complex is formed. The solvent was dried using $CaSO_4$, and the $AgClO_4$ by heating it at 225°. The mixture was made up in a drybox using as reaction vessel a centrifuge tube fitted with a ground glass stopper. A 20% excess of $AgClO_4$ was used, and when this excess was objectionable, Ag^+ was precipitated using dry NaBr. The product solutions were quite concentrated (in a typical preparation 3 mmoles of $Co(NH_3)_5Br_3$ in 4 ml. of $(CH_3)_3PO_4$ was used) and centrifugation proved to be more practical than filtration as a means of separating the solid phase.

Many anions were tried as precipitants for $Co(NH_3)_5PO_4(CH_3)_3^{+3}$ but none was completely successful. Chloride, bromide, and many others fail because they replace the ester from the Co(III) residue. It appears, however, that when $(NH_4)_2CrO_4$ dissolved in CH_3OH is used the solid phase which forms contains the ester complex intact; at least the solution of the solid in water shows a change in spectrum with time which corresponds to that known to take place for the ester complex. However not enough work was done with the solid phase to characterize it completely.

It is of interest to note that the dimethyl sulfoxide complex can be prepared in a manner analogous to that described for the phosphate ester complex, but $AgClO_4$ in acetonitrile fails to remove Br^- from $Co(NH_3)_5Br^{+2}$.

C. The Preparation of Aqueous Solutions of Co-

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TABLE I

EXTINCTION COEFFICIENTS OF PHOSPHATO COMPLEXES OF THE PENTAAMMINECOBALT(III) CLASS

λ,	ϵ^a for ligand					
mμ	PO_4	PO_4H	PO_4H_2	PO_4H_3	$PO_4(CH_3)_2$	$PO_4(CH_3)_3$
580	33.8	23.6	16.3	17.8	14.0	13.5
560	59.4	45.3	35.6	32.5	30.5	27.0
540	83.0	68.2	54.8	45.8	48.6	40.7
520	88.8	77.0	63.5	51.3	57.8	46.3
500	74.8	68.4	59.0	47.1	54.8	43.6
480	53.4	51.1	46.8	40.7	44.8	38.0
460	34.0	33.7	33.1	32.8	32.8	31.0
440	21.4	20.0	19.8	22.0	20.0	21.1
420	20.2	12.9	10.6	13.5	10.4	12.1
400	39.8	19.0	9.5	12.4	9.0	10.8
380	66.3	44.0	26.5		23.7	19.6
360	73.8	61.5	47.3		45.7	34.0
340	63.2	44.4	37.7		42.7	38.4
320	>90	32.0	13.6		25.0	20.1
300		>90	6.7		18.0	8.8
λ_{max}	525	521	517.5	519.5	517	520
ϵ_{max}	90.0	77.8	63.7	51.6	58.1	46.3
λ_{max}	364	359	356		325.5	347
ϵ_{max}	73.9	61.6	48.3		48.3	39.2

[a] $\epsilon = 1/cd \log I_0/I$ where the concentration is in moles/l. and d is in cm.

$(NH_3)_5PO_4(CH_3)_2{}^{+2}$.—The preparation of the dimethyl phosphato complex can be accomplished in moderately acidic solution. The affinity of $(CH_3)_2PO_4{}^-$ for $Co(NH_3)_5{}^{+3}$ is probably not much less than that of $H_2PO_4{}^-$, and the ester ion survives heating in the acid solution quite well. In fact the principal Co(III) contaminant in the solution after heating to bring about substitution is the aquo ion rather than the monomethyl ester or the phosphato complex. Ion exchange again was used as the means of separating the desired complex from other Co(III) species. Although the charges of the species $Co(NH_3)_5OH_2{}^{+3}$ and $Co(NH_3)_5PO_4(CH_3)_2{}^{+2}$ differ, the separation, at least as a preparative method, is quite difficult to achieve.

The solution used for the conversion of $Co(NH_3)_5OH_2{}^{+3}$ to $Co(NH_3)_5PO_4(CH_3)_2{}^{+2}$ was about 0.3 M in the aquo perchlorate and 3 M in the dimethyl phosphato species. Perchloric acid was added to bring the pH into the range of 1 to 3. The solution was heated at 75° for approximately 45 min., and after cooling it was poured through a column containing resin (Dowex 50-X4) in the acid form, the column then being purged with water. Na, Ca, Sr, Ba, and La perchlorates, at various concentrations, were tried as eluents, and we finally settled on 0.7 M $Ca(ClO_4)_2$ as the most suitable. Using this eluent, a resin bed about 20 cm. high and 1.2 cm. in diameter, a flow rate of 2 to 3 ml./min. resulted in a workable compromise between the demands of good separation and a reasonably good production rate. At best, solutions 0.03 M in the diester complex were eluted. For experiments in which a high concentration of $Ca(ClO_4)_2$ was undesirable, K_2SO_4 was added in an amount equivalent to Ca^{+2}, and the $CaSO_4$ and $KClO_4$ which formed were removed by filtration.

Attempts to precipitate the Co(III) ion failed with the group of more than thirty anions which were used and which included $B(C_6H_5)_4{}^-$. Since for our applications it was not essential to prepare a solid compound, our research on this point was again not exhaustive. We are confident that the solutions did contain $Co(NH_3)_5PO_4(CH_3)_2{}^{+2}$ as the dominant Co(III) species on the basis of the following evidence. The spectra of the species $Co(NH_3)_5OH_2{}^{+3}$ and $Co(NH_3)_5PO_4$ are known to be very sensitive to acidity in the pH range 1 to 11, and that of $Co(NH_3)_5PO_4CH_3{}^+$ is expected to be as sensitive to acid as is $Co(NH_3)_5PO_4H^+$ (*vide infra*). Only those preparations were considered satisfactory which showed no change with acidity in the absorption spectrum covering the wave length range 600 to *ca.* 300 mμ. Analysis of a solution for Co, PO_4, and CH_3OH (after hydrolysis) showed them to be present in the ratio 1 to 1 to 1.85–1.96.

D. The Extinction Coefficients of the Phosphatopentaamminecobalt(III) Species.—The values of extinction coefficients covering the range from 580 to 300 mμ at intervals of 20 mμ are recorded in Table I. The results of the experiments to be reported in a later section were used in selecting the conditions of acidity. These were: for $Co(NH_3)_5PO_4$, 0.01 M NaOH; for $Co(NH_3)_5PO_4H^+$, NaOAc–HOAc buffer at pH 5.5; for $Co(NH_3)_5PO_4H_2{}^{+2}$, 0.1 M $HClO_4$; for $Co(NH_3)_5PO_4H_3{}^{+3}$, 11.6 M $HClO_4$ or 18 M H_2SO_4; for $Co(NH_3)_5PO_4(CH_3)_2{}^{+2}$, 0.05 M $HClO_4$; for $Co(NH_3)_5PO_4(CH_3)_3{}^{+3}$, $(CH_3)_3PO_4$. Even in the strongly acid solutions used to measure the spectrum of $Co(NH_3)_5PO_4H_3{}^{+3}$, loss of phosphate from the coördination sphere is very slow ($t_{1/2}$ several hours at room temperature).

E. Aquation and Hydrolysis Reactions.—It already has been mentioned that loss of phosphate from $Co(NH_3)_5$ PO_4 even in strongly acid solution is quite slow. The success of the preparative method which depends on using dilute alkali as eluent shows that hydrolysis is also quite slow (*i.e.*, $t_{1/2}$ of the order of hours). Measurements on the rate of approach to equilibrium for phosphate substitution in $H_3PO_4/H_2PO_4{}^-$ buffer mixtures are described in the next section, and further discussion of the rates of substitution in the Co(III)–$H_2PO_4^-$ system will be deferred.

With the ester complexes, it is interesting to learn to what extent ester hydrolysis accompanies formation of the aquo complex. The spectrum of the product of the aquation of $Co(NH_3)_5PO_4(CH_3)_3^{+3}$ in acid solution corresponds within experimental error to that of the aquo complex. At most, a few per cent of the dimethyl phosphate complex is formed. In the alkaline hydrolysis also, the principal reaction is hydrolysis of the metal complex rather than of the ester moiety. Consideration of the method used for the preparation of $Co(NH_3)_5PO_4(CH_3)_2^{+2}$ and of the observation that little $Co(NH_3)_5PO_4CH_3^+$ is formed shows that ester hydrolysis in the complex is slow in acid solution. A direct determination of CH_3OH after alkaline hydrolysis showed that less than 3% of the total reaction takes place by ester hydrolysis.

Several experiments were undertaken to measure the rate of aquation of $Co(NH_3)_5PO_4(CH_3)_3^{+3}$. They were done by diluting the solution of the complex in $(CH_3)_3PO_4$ with an aqueous acidic solution containing $NaClO_4$ to make up the ionic strength. In two experiments, each with the initial complex concentration at 1×10^{-2} *M*, the ionic strength adjusted to 0.5, and the temperature at 25.0°, the specific rates of aquation, *k*, were found to be 1.50×10^{-2} and 1.47×10^{-2} min.$^{-1}$ at 0.1 and 0.4 *M* $HClO_4$, respectively (the dilution with water reduced the concentration of $(CH_3)_3PO_4$ to *ca.* 0.2 *M*). The hydrolysis in alkaline solution is very rapid. In one case the solution was acidified within 1 min. after the alkali was added (9.5×10^{-3} *M* after dilution) yet spectrophotometric analysis showed that hydrolysis already had been completed. A single experiment was done on the aquation of the tributyl phosphate complex. Under conditions comparable to those used for the the methyl, *k* was observed to be 8.3×10^{-3} min.$^{-1}$.

Oxygen exchange between $Co(NH_3)_5H_2O^{+3}$ and water[8,17] is slow compared to aquation or hydrolysis of the complex, hence it is possible to do tracer experiments to learn the position of bond breaking. The experiments were done using the trimethyl phosphato complex at normal enrichments in O^{18} enriched solvent. The product aquo ion was precipitated as the bromide salt; after drying the salt the coördinated water was liberated by heating, and the isotopic composition was determined by the Anbar and Guttman[16] method. For the aquation experiments, the reaction was allowed to proceed for between seven and eight half-lives. In three independent experiments, the isotopic composition of the aquo ion neglecting isotopic fractionation effects corresponded to 84.4 ± 1% bond breaking at the Co–O position. When a correction is made for the exchange of the aquo ion with solvent, the % bond-breaking at the Co–O position is calculated as about 80. In alkaline solution, hydrolysis is very rapid compared to exchange[17] and no correction for exchange of the product complex is necessary. For these experiments, the % bond breaking at the Co–O position is calculated as 88 ± 1.

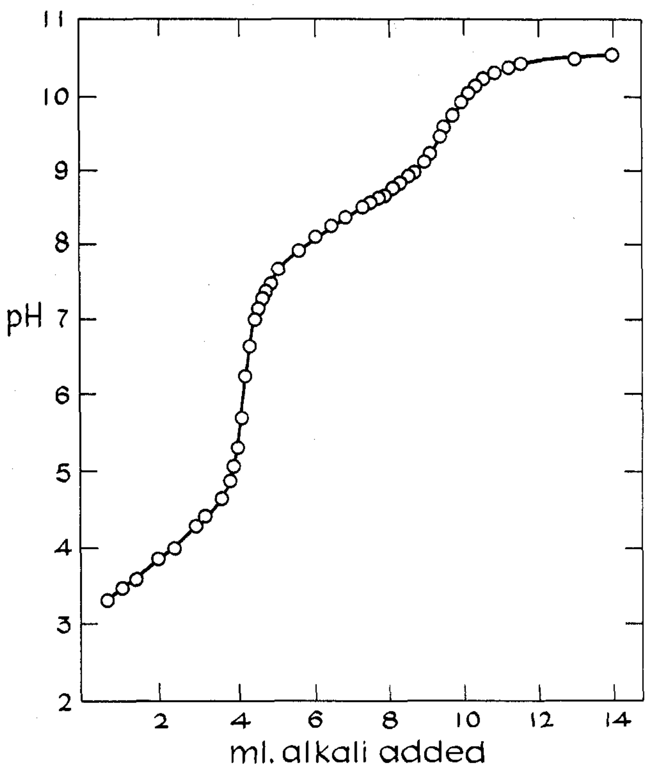

Fig. 1.—Titration curve for $(NH_3)_5CoPO_4H_2$.

The rate of aquation of $Co(NH_3)_5PO_4(CH_3)_2^{+2}$ is very slow. No direct study of the rate was made but it is reasonable to expect it to be comparable to that observed for $Co(NH_3)_5PO_4H_2^{+2}$. In 0.01 *M* NaOH, hydrolysis is complete in 24 hr. The product spectrum was that of the hydroxo complex (or aquo on acidifying), and no CH_3OH could be detected in the final solution even when the hydrolysis was done in 1 *M* $Ca(ClO_4)_2$ (pH ~ 8) solution.

F. Equilibria in Solutions of the Phosphatopentaamminecobalt(III) Complex.—It is of interest to investigate the affinity for H^+ of PO_4^{-3} bound to the $Co(NH_3)_5^{+3}$ residues. Approximate equilibrium quotients for the reactions

$$Co(NH_3)_5PO_4H^+ = Co(NH_3)_5PO_4 + H^+ \qquad (1)$$

$$Co(NH_3)_5PO_4H_2^{+2} = Co(NH_3)_5PO_4H^+ + H^+ \qquad (2)$$

were obtained by potentiometric titration using a Coleman pH meter. Both the solution to be titrated and the alkali solution used were 1 *M* in $NaClO_4$; the Co(III) complex was used at 0.025 *M*. The titration curve which was obtained is shown in Fig. 1. Inspection of the curve shows that two stages of association with H^+ take place in the pH range covered. Analysis of the curves yields 8.50 ± 0.05 and 3.60 ± 0.05 for the two p*K* values. We associate these with reactions 1 and 2, respectively. This connection is not justified on the basis of the data given, but other considerations leave little doubt that it is correct. As will be shown, a third stage of association can be demonstrated in very strong acid; the correspondence of the spectrum of the product of the association with that of $Co(NH_3)_5PO_4$-

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(17) H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **80**, 2642 (1958).

$(CH_3)_3^{+3}$ leaves little doubt that the product is $Co(NH_3)_5PO_4H_3^{+3}$. The assignment made also explains the correspondence of the spectrum of the complex in 0.1 *M* H^+, where it is presumed to have the formula $Co(NH_3)_5PO_4H_2^{+2}$, with that of $Co(NH_3)_5PO_4(CH_3)_2^{+2}$.

Our assignment of equilibrium quotients to reactions 1 and 2 leads to the conclusion that at pH >9, $Co(NH_3)_5PO_4$ is the dominant form of the phosphato complex; in the range of 8 to 4, $Co(NH_3)_5PO_4H^+$ predominates, and in the range below 3, $Co(NH_3)_5PO_4H_2^{+2}$ predominates. As will be shown in the account following, at very low pH further association of H^+ with the complex takes place.

The comparison of the extinction coefficients for the phosphato complex in 11.6 *M* $HClO_4$ or 18 *M* H_2SO_4 (see column headed H_3PO_4 in Table I) with those observed when 0.1 *M* $HClO_4$ is the medium shows a marked difference between the sets of values. The agreement of the spectra observed in 11.6 *M* $HClO_4$ and 18 *M* H_2SO_4 shows that in the very acidic media a limiting form of the complex is reached and we take this to be $Co(NH_3)_5PO_4H_3^{+3}$ (*vide supra*). The equilibrium quotient for the reaction

$$Co(NH_3)_5PO_4H_3^{+3} = Co(NH_3)_5PO_4H_2^{+2} + H^+ \quad (3)$$

can be determined from measurements of the extinction coefficients at constant μ in media intermediate in acidity between 0.1 and 11.6 *M* $HClO_4$. The data obtained in such a study are reported in Table II. The equilibrium quotient is calculated from the relation

$$K_3 = \frac{(A - A_3)(H^+)}{(A_2 - A)}$$

where A, A_3, and A_2 are the absorbances of the solution and of the limiting forms for $Co(NH_3)_5PO_4H_3^{+3}$ and $Co(NH_3)_5PO_4H_2^{+2}$, respectively. A_2 was obtained as a plateau in the plot of A against (H^+) in the acidity range at about 0.1 *M*.

TABLE II[a]

THE EQUILIBRIUM QUOTIENT K_3 FOR THE REACTION $Co(NH_3)_5PO_4H_3^{+3} = Co(NH_3)_5PO_4H_2^{+2} + H^+$

$(HClO_4)$	A	$(A - A_3)$	$(A_2 - A)$	K_3
11.6	0.480			
18.[b]	.480			
3.00	.550	70	43	4.9
1.00	.572	92	21	4.7
0.60	.580	100	13	4.6
.30	.586	106	7	4.6
.10	.593			
			Mean	4.7

[a] $\mu = 3.0$ using $NaClO_4$ except for the solution at 11.6 *M* $HClO_4$ and 18 *M* H_2SO_4; temp. = 25 ± 0.2°; A = optical density at λ = 520 mμ. [b] H_2SO_4.

A spectrophotometric study was made of the equilibria obtaining in solutions containing $Co(NH_3)_5OH_2^{+3}$, $Co(NH_3)_5PO_4H_2^{+2}$, $H_2PO_4^-$, and H_3PO_4. If outer sphere association of $Co(NH_3)_5OH_2^{+3}$ and $H_2PO_4^-$ can be neglected, the dominant equilibrium is

$$Co(NH_3)_5PO_4H_2^{+2} + H_2O = Co(NH_3)_5OH_2^{+3} + H_2PO_4^- \quad (4)$$

The relative amounts of the two forms of Co(III) can be determined by measurements of extinction of solutions at a wave length at which the two forms have different extinction coefficients.

The reaction mixtures contained H_3PO_4 and NaH_2PO_4 at concentrations high compared to that of Co(III); $NaClO_4$ was added to adjust the ionic strength to 1.0. Measurements at 25° were made from time to time to learn the rate of approach to equilibrium, and the solutions were kept at temperature for approximately six half-lives. The rate of approach to equilibrium is much faster at the higher temperatures 37.5 and 50.2° and the solutions were stored at these temperatures for 40 and 24 days, respectively, a time ample to ensure equilibration in each case.

The compositions of the solutions are recorded in Table III, and the spectrophotometric history for the solutions at 25° in Table IV.

TABLE III

COMPOSITION OF THE SOLUTIONS USED FOR EQUILIBRIUM STUDIES[a]

	Solution			
	A	B	C	D
(H_3PO_4)	0.20	0.20	0.20	0.20
(NaH_2PO_4)	.10	.20	.50	.20
$(NaClO_4)$	.90	.80	.50	.80

[a] The concentration of the complex was 1.00×10^{-3} *M;* for solutions A, B, and C, the aquo complex was used and for D the phosphato.

TABLE IV

APPROACH TO EQUILIBRIUM IN THE PHOSPHATO-AQUO SYSTEM[a]

Time,	Absorbance of solution			
days	A	B	C	D
0	0.412	0.412	0.412	0.669
8	.436	.448	.476	.621
20	.462	.485	.529	.598
36	.483	.516	.557	.562
55	.500	.531	.564	.550
79	.505	.537	.569	.541

[a] Temp., 25°; ionic strength, 1.00; absorbances are recorded at λ = 520 mμ.

Solutions B and D differ only in that the aquo complex was used as the starting material for B and the phosphato for D. The solutions approach the same value of absorbance, thus ensuring that equilibrium was reached and that the concentrations of Co(III) were indeed the same. The equilibrium quotient then can be calculated using the equilibrium absorbance, and the initial absorbances for the aquo and phosphato ions. For the solutions left to equilibrate at the higher temperatures, the absorbance measurements were also made at 25°; no appreciable re-equilibration took place in the course of measurements.

The results of the calculations of the equilibrium quotients assuming that reaction 4 describes the system are reported in Table V.

The equilibrium quotients are by no means independent of the concentration of $H_2PO_4^-$. The variation is qualitatively the same as is observed in SO_4^{-2}–$Co(NH_3)_5OH_2^{+3}$ [18] when the analogous data are treated in a

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[18] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **78**, 15 (1956).

TABLE V

RESULTS OF TEST CALCULATIONS OF EQUILIBRIUM QUOTIENTS FOR REACTION 4 AT μ = 1.00; STOICHIOMETRIC (H_3PO_4), 0.2 *M*

	K_4' calcd. for		
($H_2PO_4^-$)[a]	25.0°	37.5°	50.2°
0.114	0.175	0.137	0.108
.207[b]	.204	.163	.130
.507	.316	.257	.207

[a] Corrected for the contribution by the dissociation of H_3PO_4.
[b] Solutions B and D yielded identical values at the three temperatures.

similar manner. As was done for that system, we ascribe the variation to outer-sphere association. The variation in K_4' as calculated for Table V comes about because both $Co(NH_3)_5OH_2^{+3}$ and $Co(NH_3)_5OH_2^{+3}\cdot H_2PO_4^-$ have the same extinction coefficients in the visible range of the spectrum and not all the complex counted as the aquo ion really has that form.

Let R, O, and P represent the concentration of the aquo ion, of the outer-sphere complex, and the inner-sphere form, respectively, then

$$\frac{(\mathrm{R} + \mathrm{O})(H_2PO_4^-)}{(\mathrm{P})} = K_4' \qquad (5)$$

and

$$K_4' = K_4 + K_0(H_2PO_4^-) \qquad (6)$$

where

$$K_4 = \frac{(\mathrm{R})(H_2PO_4^-)}{(\mathrm{P})} \text{ and } K_0 = (\mathrm{O})/(\mathrm{P})$$

The linear variation of K_4' with ($H_2PO_4^-$) required by eq. 6 is exhibited by the data when they are plotted. The values of the parameters K_4 and K_0 determined from the plots are summarized in Table VI. The parameters fit the data well enough so that the average deviation of the experimental points from the requirements of the equations is less than 1%. K_0 and K_4 are almost equally sensitive to errors in the measurements; they are probably accurate to only 5 to 10%.

TABLE VI

VALUES OF K_0 AND K_4 AT VARIOUS TEMPERATURES

	K_0	K_4
25.0	0.37	0.12_7
37.5	.31	$.10_0$
50.2	.25	$.07_8$

The equilibrium quotient K_7 for the reaction

$$Co(NH_3)_5OH_2^{+3}\cdot H_2PO_4^- = Co(NH_3)_5OH_2^{+3} + H_2PO_4^- \qquad (7)$$

is given by the ratio K_4/K_0, and the value at 25° is 0.35. With a value this large for the dissociation constant of a complex ion it cannot be claimed that the stability has been measured accurately. However, the data are accounted for satisfactorily by assuming a species of the formula $Co(NH_3)_5OH_2^{+3}\cdot H_2PO_4^-$, and it is likely that a 1:1 species of this kind does make a substantial contribution to the stoichiometry of the system.

The inner-sphere complex becomes more stable relative to $Co(NH_3)_5OH_2^{+3}$ and $H_2PO_4^-$ as the temperature rises. ΔH for reaction 4 (where $Co(NH_3)_5OH_2^{+3}$ now does not include the outer-sphere form) is calculated from the variation of K_4 with temperature as -3.7 ± 0.3 kcal. and $\Delta S = -16.7$ e.u. The inner-sphere complex increases in stability also relative to the outer-sphere form as the temperature rises. ΔH for the reaction

$$Co(NH_3)_5PO_4H_2^{+2} + H_2O = Co(NH_3)_5OH_2^{+3}\cdot H_2PO_4^-$$

is calculated as -3.0 ± 0.3 kcal. and ΔS as -12.0 e.u.

Though the prime interest in this study was not the kinetics of the processes, the rate data presented in Table IV seem worthy of analysis. The approach to equilibrium in each case is pseudo first order as is expected since $H_2PO_4^-$ is much in excess of Co(III). The values of k (where k is the specific rate for the approach to equilibrium based on a plot of log $(A - A_\infty)$ against time) for solutions A, B, C, and D are 2.75×10^{-5}, 3.3×10^{-5}, 4.6×10^{-5}, and 3.3×10^{-5} min.$^{-1}$, respectively. Since the changes forward and reverse are pseudo first order, if the system is well behaved the values of k for solutions B and D should, as observed, be identical.

The kinetic data are treated in relation to the mechanism

$$Co(NH_3)_5PO_4H_2^{+2} + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co(NH_3)_5OH_2^{+3} + H_2PO_4^-$$

cognizance being taken of the fact that the equilibrium corresponding to reaction 7 is established rapidly. Adopting the symbols P, R, and O as defined earlier, and letting ($H_2PO_4^{-2}$) = (C), total Co(III) = (S), we have the rate law

$$-\frac{\mathrm{d(P)}}{\mathrm{d}t} = k_1(\mathrm{P}) - k_2(\mathrm{R})(\mathrm{C})$$

This equation leads to the integrated form

$$[(\mathrm{P}) - (\mathrm{P}_\infty)] = [(\mathrm{P}_0) - (\mathrm{P}_\infty)]e^{-at}$$

where

$$a = k_1 + \frac{k_2K_7(\mathrm{C})}{K_7 + (\mathrm{C})}$$

The coefficient a is equal to the specific rate as measured experimentally for the rate of approach to equilibrium. Thus a plot of these specific rates against $K_7(\mathrm{C})/[K_7 + (\mathrm{C})]$ yields k_1 as intercept and k_2 as slope. The value of $K_7(\mathrm{C})/[K_7 + (\mathrm{C})]$ for solutions A, B = D, and C are 0.086, 0.130, and 0.205. When the plot is constructed k_1 is found to be $1.5_5 + 10^{-5}$ min.$^{-1}$ and k_2 is 13×10^{-5} M^{-1} min.$^{-1}$. The equilibrium quotient computed for the rate-determining reaction as the ratio k_1/k_2 is 0.12, to be compared to 0.13 obtained by direct measurement.

G. The Reactions with Cr^{+2}.—The reaction of Cr^{+2} with the phosphato complex even in acid solution is very rapid. When an equivalent amount of Cr^{+2} is added to 0.01 *M* complex in 0.05 *M* $HClO_4$, the reaction is complete in *ca.* 10 sec. at 25°. Phosphate transfers efficiently and more than 90% of the Cr(III) can be eluted readily from a cation exchange column under conditions which do not lead to elution of $Cr(H_2O)_6^{+3}$. The Cr(III)–phosphate complex has absorption maxima at 420 and 590 mμ (410 and 575 mμ for $Cr(H_2O)_6^{+3}$).

Experiments were done to learn whether oxygen exchange between PO_4^{-3} and water accompanies the reduction of $Co(NH_3)_5PO_4H_2^{+2}$ by Cr^{+2}, and whether exchange is catalyzed when the resulting Cr(III)–PO_4^{-3} complex is left in contact with Cr^{+2} for an extended period of time. The reaction was conducted in an O^{18}-enriched solution containing $HClO_4$ at 0.05 *M* and Cr^{+2} and $Co(NH_3)_5PO_4H_2^{+2}$ at 0.04 and 0.02 *M*, respectively. Immediately after reaction, an aliquot was treated to recover phosphate as Ag_3PO_4 (the work-up of the solution involved oxidation of Cr(III) to CrO_4^{-2} by H_2O_2 in NaOH, removal of Co as the solid oxide or hydroxide, precipitation of CrO_4^{-2} as the Tl(I) salt in acidic medium, and finally precipitation of Ag_3PO_4). Other aliquots were similarly treated at later intervals. Isotopic analyses on the first sample and samples after 48 and 144 hr. showed O^{18}/O^{16} ratios of 4.04×10^{-3}, 4.05×10^{-3}, and 4.06×10^{-3}, to be compared to 4.07×10^{-3} for the blank. The solvent as used showed a ratio of O^{18} to O^{16} of 16.40×10^{-3}. It is clear that no appreciable activation of the phosphate for exchange accompanies its participation as a bridging group in the reaction.

The reduction of $Co(NH_3)_5PO_4(CH_3)_3^{+3}$ by Cr^{+2} proceeds slowly and at a rate which is independent of (H^+). The rate is independent of the concentration of Cr^{+2} at least in the range investigated, 2×10^{-3} to 8×10^{-3} *M;* the reaction is first order in Co(III), and the value of *k* which was found, 1.5×10^{-2} min.$^{-1}$, is within experimental error the same as that observed in the aquation. The product of the reaction is $Cr(H_2O)_6^{+3}$. It is clear that reduction of the complex by Cr^{+2} is very slow, and at the levels of Cr^{+2} used, the reagent must wait for the formation of $Co(NH_3)_5OH_2^{+3}$.

The reaction of $Co(NH_3)_5PO_4(CH_3)_2^{+2}$ with Cr^{+2} is independent of (H^+) in the range of acidity from 0.1 to 0.5 *M*. The reaction when Cr^{+2} is in excess is nicely first order in the complex. No experiments were done specifically to learn the order with respect to Cr^{+2}, but since the reaction with Cr^{+2} is much more rapid than any hydrolysis or aquation processes for the complex, it is highly likely that it is first order also in Cr^{+2}. The specific rate calculated for $Cr^{+2} + Co(III) \rightarrow$ as the rate determining step is 1.5 M^{-1} min.$^{-1}$ at 25° and $\mu = 0.5$ ($NaClO_4$). The product is a Cr(III) complex rather than $Cr(H_2O)_6^{+3}$.

Our interest in the reaction was principally to learn whether ester hydrolysis accompanies the reaction of the complex with Cr^{+2}, but many features of this line of investigation are still unclear. Boos' method for CH_3OH does not respond to $Co(NH_3)_5PO_4(CH_3)_2^{+2}$ or to $(CH_3)_2PO_4^-$, and in no case was appreciable CH_3OH observed before reaction with Cr^{+2}. In some cases, but not in all, CH_3OH was detected, the equivocal statement applying whether analysis was made directly after reaction with Cr^{+2} or after the product mixture was poured through cation exchange resin. The largest amount we detected corresponds to hydrolysis of 55% of the ester. The conclusion seems definite that the intrinsic reaction $Cr^{+2} + Co(NH_3)_5PO_4(CH_3)_2^{+2}$ does not produce CH_3OH; there is a possibility that some adventitious ingredient in addition promotes the production of alcohol, the possibility that a minor component of the Co(III) solution present in amounts varying from preparation to preparation does respond, and other possibilities as well. Further work on the system is called for and will be undertaken.

Comments

Equilibrium Aspects.—The data on the affinity of the bound phosphate for H^+ make it possible to assess the influence of the residue $Co(NH_3)_5^{+3}$ in enhancing the acidity of H_3PO_4, $H_2PO_4^-$, and HPO_4^{-2}. The relevant data are set forth in Table VII. The residue $Co(NH_3)_5^{+3}$ is observed to enhance the acidity in each of the first two stages of dissociation by a factor of about 200, and in the third stage, by a factor approximately 30 times as great. Another comparison, though not independent of those made, nevertheless seems worth making explicitly: of the effect which $Co(NH_3)_5^{+3}$ and H^+ have in promoting the acidity of other OH groups in the molecule. This involves comparing $Co(NH_3)_5PO_4H_2^{+2}$ with H_3PO_4 and $Co(NH_3)_5PO_4H^+$ with $H_2PO_4^-$. When allowance is made for the statistical factors, H^+ is more effective than $Co(NH_3)_5^{+3}$ by a factor of about 50 in the first stage and about 200 in the second stage. In either case the influence of H^+ relative to $Co(NH_3)_5^{+3}$ is much less than is exerted when the two acid promoting centers are on the oxygen which bears the dissociable proton (the ratio of acidities for H_3O^+ and $Co(NH_3)_5OH_2^{+3}$ is approximately 10^7). It also should be mentioned that the effect of $Co(NH_3)_5^{+3}$ in promoting the acidity is not as great as that reported for Al^{+3}—the acid dissociation constant of $AlPO_4H_2^+$ is given as 8×10^{-3}.[19]

TABLE VII
ACID DISSOCIATION OF BOUND AND FREE PHOSPHORIC ACIDS[a]

	Bound	Free
H_3PO_4	4.7^b	1.9×10^{-2c}
$H_2PO_4^-$	2.2×10^{-4}	1.2×10^{-6d}
HPO_4^{-2}	3.2×10^{-9}	$\sim 5 \times 10^{-13}$

[a] $\mu = 1.0$ except where noted otherwise. [b] $\mu = 3.0$. [c] B. J. Thamer, *J. Am. Chem. Soc.*, **79**, 4298 (1957). [d] Determined by potentiometric titration with the method used for the phosphato complex.

The comparison of the affinity of phosphate for a residue such as $Co(NH_3)_5^{+3}$, in which the binding is restricted to a single oxygen of the phosphate with the more labile tripositive ions, is also of interest. Lanford[20] and Kiehl report $FePO_4H^+$ as the predominant form of the Fe(III)–PO_4^{-3} complex in the dilute acid range and give the value 2.2×10^9 for the equilibrium quotient governing the association of Fe^{+3} with HPO_4^{-2}. The equilibrium quotient for the corresponding reaction of $Co(NH_3)_5^{+3}$ with HPO_4^{-2} is only 1.4×10^3. The relatively high affinity exhibited by Fe^{+3} for HPO_4^{-2} suggests that the structure is different from that of the Co(III) complex, specifically that HPO_4^{-2} is bound in a

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(19) N. Bjerrum and C. R. Dahm, *Z. physik. Chem. Bodenstein Festband*, 627 (1931).

(20) O. E. Lanford and S. T. Kiehl, *J. Am. Chem. Soc.*, **64**, 291 (1942).

chelate form; the high acidity of $AlPO_4H_2^{+2}$ compared to $Co(NH_3)_5PO_4H_2^{+2}$ suggests the possibility of chelation in the Al(III) system also.

The high stability of the complex $Co(NH_3)_5OH_2^{+3}\cdot H_2PO_4$ which is indicated by our work is surprising. The outer-sphere affinity of $H_2PO_4^-$ for $Co(NH_3)_5OH_2^{+3}$ is not much less than that of SO_4^{-2}.[18] The heat effects for the two systems also are remarkably similar, the similarity extending to the detail that ΔH for the formation of the outer-sphere complex from the free ions is almost zero. Also the entropy change for the collapse of the outer-sphere ion to the inner-sphere form is very nearly the same in the two cases (+13 for the sulfato and +12 for the acid phosphato). It seems likely that the similarity arises from compensating effects. Although the net charge of $H_2PO_4^-$ is less than that of SO_4^{-2}, more negative charge is concentrated on the nonprotonated oxygens of $H_2PO_4^-$ than on the oxygens of SO_4^{-2}.

The Aquation and Hydrolysis Reactions.—An extremely interesting result is the great lability of the $Co(NH_3)_5\text{–}PO_4(CH_3)_3^{+3}$ complex; this, together with the fact, not explicitly mentioned before, that many of the ammine Co(III) compounds are very soluble in $(CH_3)_3PO_4$, suggests the use of $Co(NH_3)_5PO_4(CH_3)_3^{+3}$ as an intermediate in the preparation of complexes of the pentaammine class using $(CH_3)_3PO_4$ as a solvent. It is interesting also that the lability is not localized at the Co(III) center, but as was shown by the tracer results, about 20% bond breaking takes place at the phosphorus center. In the trimethyl phosphate complex, each of the oxygens carries a group. The bond breaking on phosphorus does not take place at the P–O linkage bearing the CH_3 groups, but rather at the linkage bearing the $Co(NH_3)_5^{+3}$ group, in spite of the fact that the inductive effect of CH_3^+ is much greater than that of $Co(NH_3)_5^{+3}$ (CH_3^+ is expected to be rather similar to H^+).

The greater lability of the trimethyl complex compared to the dimethyl or phosphato complex is not unexpected, and it can be ascribed to the inductive effect of the additional CH_3^+ group. But it is surprising that the rate of aquation of the phosphato complex in very strong acid, when the phosphate is completely protonated, is considerably less than that of the trimethyl ester in water. The difference can in part be ascribed to the low activity of H_2O in the very acidic solvent. But even when allowance is made for this, the comparison suggests that the species $Co(NH_3)_5PO_4H_3^{+3}$ does not take advantage of the possibility of redistributing the protons from their normal equilibrium positions in forming the activated complex for reaction. If proton redistribution were indeed involved or required, a much greater rate for the protonated complex would be expected than for $Co(NH_3)_5PO_4(CH_3)_3^{+3}$, which cannot readily redistribute CH_3^+.

Having the approximate measurements of the outer-sphere association of $Co(NH_3)_5OH_2^{+3}$ with another ligand, the comparison of the first-order interchange processes for a group of outer-sphere complexes takes on additional significance. The first-order interchange specific rates for $Co(NH_3)_5OH_2^{+3}\cdot H_2O$,[7,17] $Co(NH_3)_5OH_2^{+3}\cdot SO_4^{-2}$,[21] and $Co(NH_3)_5OH_2^{+3}\cdot H_2PO_4^-$[22] are 3.5×10^{-4}, 1.1×10^{-4}, and 4.6×10^{-5} min.$^{-1}$, respectively. It is not true for this series, as appears to be approximately true for some dipositive aquo ions, that the first-order interchange processes are independent of the incoming group,[23] and a substantial kinetic influence of the incoming group is indicated. This is in line with views which Adamson[24] has expressed on the nature of the substitution process.

The Reactions with Cr^{+2}.—The rates of reaction of Cr^{+2} with $Co(NH_3)_5PO_4(CH_3)_3^{+3}$, $Co(NH_3)_5PO_4(CH_3)_2^{+2}$, and $Co(NH_3)_5PO_4H_2^{+2}$ increase in that order, and the order is readily rationalized. The bridged-activated complex which provides the reaction path for the second and third complexes is not possible for the first. Electron transfer to the complex would require electron tunneling through the intact coördination shells, a process which already has been shown to be slow in the reaction of Cr^{+2} with $Co(NH_3)_6^{+3}$.[25] The ion $Co(NH_3)_5PO_4H_2^{+2}$ can rapidly lose a proton (or two) prior to reaction with Cr^{+2}, and this may well account for the much higher rate observed for it compared to $Co(NH_3)_5PO_4(CH_3)_2^{+2}$.

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(21) H. Taube and F. A. Posey, *J. Am. Chem. Soc.*, **75**, 1463 (1953).

(22) k_2 in the rate term $k_2(H_2PO_4^-)(Co(NH_3)_5OH_2^{+3})$ is 13×10^{-5} M^{-1} min.$^{-1}$ at 25°; the quotient governing equilibrium 7 is 0.35.

(23) M. Eigen, "Advances in the Chemistry of Coördination Compounds," The Macmillan Co., New York, N. Y., 1961.

(24) A. W. Adamson, *J. Am. Chem. Soc.*, **80**, 3183 (1958).

(25) A. Zwickel and H. Taube, *ibid.*, **83**, 793 (1961).