Reactions of μ-Hydroxo-dicobalt(III) Complexes. Part X.[†] Kinetic Studies of the Reaction of the μ-Amido-μ-hydroxo-bis[tetra-amminecobalt(III)] Complex with Phosphate Ions in Aqueous Perchloric Acid Solutions and the Characterisation of the μ-Amido-μ-phosphato-bis-[tetra-amminecobalt(III)] Complex

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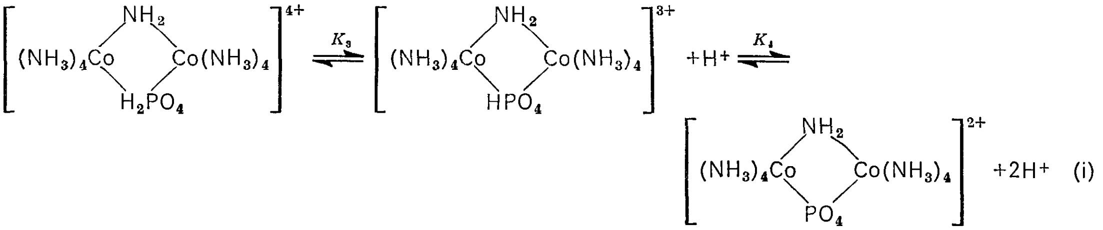
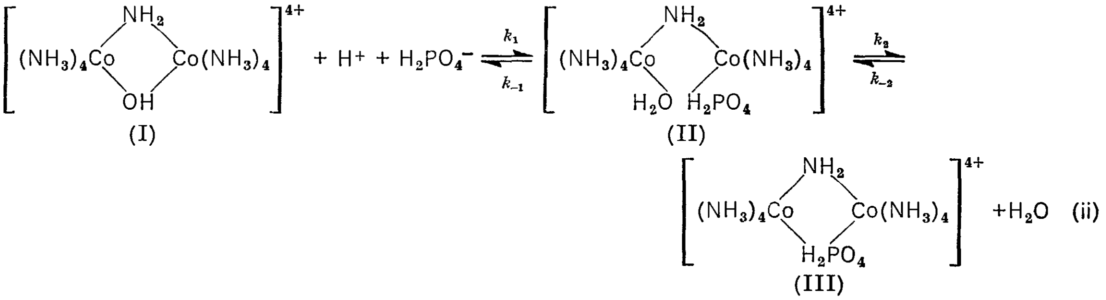
The nitrate salt of the μ-amido-μ-hydrogenphosphato-bis[tetra-amminecobalt(III)] complex and the bromide salt of the corresponding μ-amido-μ-phosphato-complex have been prepared and characterised. First and second acid dissociation constants of H_3PO_4 have been determined by potentiometric titration and $pK_1 = 0{\cdot}9$ and $pK_2 = 5{\cdot}8$ at 25 °C and $I = 2{\cdot}0$M ($NaClO_4$). Acid dissociation constants for the phosphato-complexes [equation (i)] have also been determined and, at 25 °C, $pK_3 = 1{\cdot}5_2$ [$I = 2{\cdot}0$M ($NaClO_4$)] and $pK_4 = 6{\cdot}0 \pm 0{\cdot}1$ [$I = 0{\cdot}1$M($LiClO_4$)]. The kinetics of the interconversion of complexes (I) and (III) [equation (ii)] have been studied at $I = 2{\cdot}0$M ($NaClO_4$).





The intermediate (II) has not been isolated and behaves as a transient. Rate constants k_r (= $k_{-1}k_{-2}/k_2$) for the reverse reaction (40—55 °C) give an [H⁺] dependence of the form $k_r([H^+] + K_3)/[H^+]K_3 = p + q[H^+]$. At 25 °C (extrapolated) values of p and q are $0{\cdot}23 \times 10^{-3}$ l mol⁻¹ s⁻¹ and $0{\cdot}57 \times 10^{-4}$ l² mol⁻² s⁻¹ respectively, and activation parameters have been obtained for both constants. For the forward reaction (20—35 °C), the conversion (I) ⟶ (II) is rate determining and pseudo-first-order rate constants, k_f, may be expressed as $k_f = k_{1a}[H^+][H_2PO_4^-] + k_{1b}[H^+][H_3PO_4]$, with small contributions from a term in $[H_2PO_4^-]^2$. At 25 °C: $k_{1a} = 1{\cdot}18 \times 10^{-3}$ l mol⁻¹ s⁻¹, $\Delta H_{1a}^‡ = 19{\cdot}5 \pm 0{\cdot}7$ kcal mol⁻¹, and $\Delta S_{1a}^‡ = -6{\cdot}5 \pm 2{\cdot}3$ cal K⁻¹ mol⁻¹; and $k_{1b} = 8{\cdot}54 \times 10^{-5}$ l² mol⁻² s⁻¹, $\Delta H_{1b}^‡ = 14{\cdot}3 \pm 0{\cdot}8$ kcal mol⁻¹, and $\Delta S_{1b}^‡ = -29{\cdot}2 \pm 2{\cdot}8$ cal K⁻¹ mol⁻¹.

SIEBERT[1] has isolated the complexes $[Co(NH_3)_4PO_4],2H_2O$ and $[Co(NH_3)_4(H_2O)(HPO_4)]ClO_4,2H_2O$ and proposed structures in which the phosphato-group is bidentate and monodentate respectively. Schmidt and Taube[2] prepared crystalline $[Co(NH_3)_5PO_4],2H_2O$ and studied its aquation and base hydrolysis in aqueous solution. Lincoln and Stranks[3] have studied extensively the nature of phosphato-cobalt(III) complexes in the ammine and ethylenediamine series, showing conclusively that phosphate ion can co-ordinate to a cobalt(III) centre as a monodentate or bidentate ligand. The aquation and base hydrolysis reactions[3,4] of these complexes have also been studied and it has been possible to identify rate constants for the aquation of mono-, di-, and tri-protonated phosphato-species.[‡] In this paper details are presented of the preparation of the μ-amido-μ-phosphato-bis[tetra-amminecobalt(III)]complex in its monoprotonated and unprotonated forms (as the nitrate and bromide salts respectively) and the identification of a diprotonated form in acidic solution. I.r. and u.v.–visible spectra and molecular formulae, as determined by elemental analyses, support μ-phosphato-structures. The complexes are analogous to the μ-amido-μ-sulphato-[5] and μ-amido-μ-selenato-complexes[6] reported previously.

[†] Part IX, ref. 6.

[‡] Throughout the papers phosphate represents the ion PO_4^{3-}.

[1] H. Siebert, *Z. anorg. Chem.*, 1958, **296**, 280.

[2] W. Schmidt and H. Taube, *Inorg. Chem.*, 1963, **2**, 698.

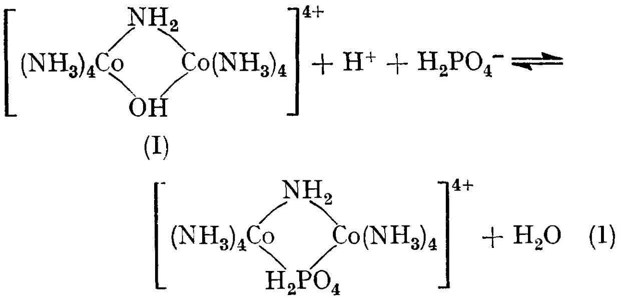
[3] (*a*) S. F. Lincoln and D. R. Stranks, *Austral. J. Chem.*, 1968, **21**, 37; (*b*) S. W. Foong, M.Sc. Thesis, University of Adelaide, 1968; (*c*) S. F. Lincoln and D. R. Stranks, *Austral. J. Chem.*, 1968, **21**, 57.

[4] (*a*) S. F. Lincoln and D. R. Stranks, *Austral. J. Chem.*, 1968, **21**, 67; (*b*) *ibid.*, p. 1745; (*c*) *ibid.*, p. 1733; (*d*) S. F. Lincoln, J. Jayne, and J. P. Hunt, *Inorg. Chem.*, 1969, **8**, 2267.

[5] M. B. Stevenson, A. G. Sykes, and R. S. Taylor, *J. Chem. Soc.* (*A*), 1970, 3214.

[6] S. W. Foong and A. G. Sykes, *J.C.S. Dalton*, 1973, 504.

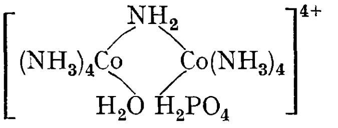
Acid dissociation constants determined for the two protonated species confirm the existence of three distinct forms in solution. Kinetic studies on the formation of the μ-amido-μ-dihydrogenphosphato-complex (III) from the μ-amido-μ-hydroxo-complex (I) and the reverse reaction [equation (1)] have similar features



(I)

(III)

to those reported earlier for the reactions with sulphate and selenate ions. The formation of an aquo-intermediate (II), as a transient, is believed to occur. We



(II)

do not exclude the possibility of H_3PO_4 as a reactant by writing $H_2PO_4^-$ in (1).

RESULTS

Preparation and Characterisation of Binuclear Phosphatocobalt(III) *Complexes*.—Changes occurred in the u.v.–visible spectra of a solution of the μ-amido-μ-hydroxo-complex (520 nm, ε 149 l mol^{-1} cm^{-1}) on addition of various concentrations (0·5, 1·0, and 1·5M) of phosphoric acid, and two new intense peaks were observed at 538 and 370 nm. Reaction was essentially complete at [HClO$_4$] $\geqslant$ 0·5M and $[PO_4^{3-}]_T \geqslant$ 1·0M. The nitrate salt of the μ-amido-μ-hydrogenphosphato-complex was readily precipitated on addition of ammonium nitrate, but the bromide salt could not be similarly obtained. However when a solution of the nitrate complex was adjusted to pH 9 and ammonium bromide added, the bromide salt of the μ-amido-μ-phosphato-complex was obtained (details as in the Experimental section).

A solution of the nitrate salt (10^{-3}M) in distilled water had a pH of 3—4 and that of the bromide salt had a pH of 7—8. The spectra of the two complexes in distilled water were different with peaks at 372 (ε 553) and 538 nm (ε 374 l mol^{-1} cm^{-1}) for the nitrate salt, and 378 (ε 530) and 542 nm (ε 370 l mol^{-1} cm^{-1}) for the bromide salt. However, when the salts were dissolved in 0·1M-HClO$_4$ their spectra were coincident [370 (ε 603), 538 nm (ε 375 l mol^{-1} cm^{-1})]. The observations are consistent with the existence of species with diprotonated, monoprotonated, and unprotonated phosphato-ligands, depending on the pH of the solution. The protonation equilibria are reversible. Figure 1 shows the spectra of species which are predominant in the stipulated pH ranges. Absorption maxima occur at similar wavelengths to those observed for the μ-amido-μ-sulphato-complex and its selenato-analogue (Table 1), and similar structures are envisaged. Protonation of the bridging ligand effects the intensity of the band at *ca.* 370 nm in the case of the μ-sulphato- and μ-phosphato-complexes but does not significantly affect the band at *ca.* 540 nm.

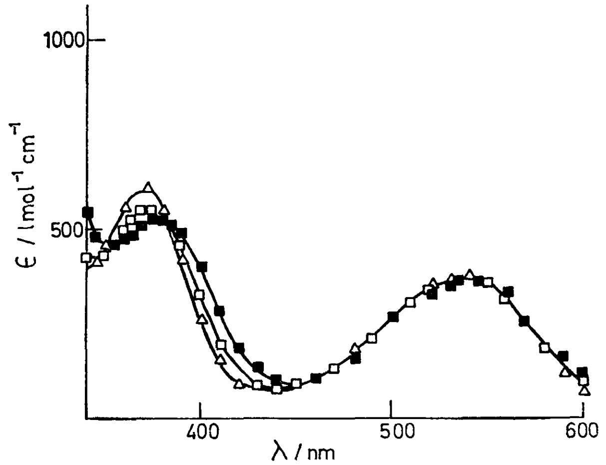


FIGURE 1 U.v.–visible absorption spectra of the μ-amido-μ-phosphato-complex, (III), at pH 9 (■), pH 3 (□), and [HClO$_4$] = 2·0M (△). The spectra correspond to the unprotonated, monoprotonated, and diprotonated forms

Figure 2 shows i.r. spectra of μ-phosphato- and μ-hydrogenphosphato-complexes in the frequency range 1200—800 cm^{-1}, in which the ν_1 and ν_3 bands of the phosphate group lie. The free phosphate anion has T_d symmetry, with four fundamental frequencies of which ν_1, at 980—970 cm^{-1}, is i.r.-inactive and ν_3 is at 1082—1080 cm^{-1} (Table 2). The

TABLE 1

Absorption coefficients (ε) at maxima in the u.v.–visible spectra of $\mu(NH_2,YO_4^{n-})$ complexes, protonated and unprotonated forms, where YO_4^{n-} is a bridging oxo-anion

Complex	$\lambda_{max.}$ nm	ε l mol^{-1} cm^{-1}	$\lambda_{max.}$ nm	ε l mol^{-1} cm^{-1}
$[(NH_3)_4Co\cdot\mu(NH_2,SeO_4)\cdot Co(NH_3)_4]^{3+}$ [a]	370	674	542	310
$[(NH_3)_4Co\cdot\mu(NH_2,SO_4)\cdot Co(NH_3)_4]^{3+}$ [b,c]	367	630	538	362
$[(NH_3)_4Co\cdot\mu(NH_2,HSO_4)\cdot Co(NH_3)_4]^{4+}$ [d]	364	760	536	375
$[(NH_3)_4Co\cdot\mu(NH_2,ClO_4)\cdot Co(NH_3)_4]^{4+}$ [e]	360	*ca.* 850	544	*ca.* 350
$[(NH_3)_4Co\cdot\mu(NH_2,PO_4)\cdot Co(NH_3)_4]^{2+}$ [f]	378	530	542	370
$[(NH_3)_4Co\cdot\mu(NH_2,HPO_4)\cdot Co(NH_3)_4]^{3+}$ [g]	372	553	538	374
$[(NH_3)_4Co\cdot\mu(NH_2,H_2PO_4)\cdot Co(NH_3)_4]^{4+}$ [b]	370	603	538	375

[a] In 0·01M-HClO$_4$; ref. 6. [b] In 0·1M-HClO$_4$. [c] Ref. 5. [d] In 15M-H$_2$SO$_4$; R. S. Taylor, Ph.D. Thesis, Leeds University, 1970. [e] In 12·2M-HClO$_4$; ref. 7. [f] At pH 9. [g] At pH 3.

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[7] A. G. Sykes and R. S. Taylor, *J. Chem. Soc.* (*A*), 1970, 1424.

splitting of the latter for the binuclear phosphato-complexes is consistent with C_{2v} symmetry, frequencies being increased by 20—65 cm^{-1} for the monoprotonated species which is to be expected for a protonated phosphate group.[8] Also, the ν_1 band is at a lower frequency than that of the unprotonated phosphato-complex. Similar effects are observed with mononuclear monodentate phosphato-complexes (Table 2), where ν_3 increases by *ca.* 20—50 cm^{-1} and ν_1 decreases from 934 to 877 cm^{-1}. The extra band at 1082 cm^{-1} for the $[H_2O(NH_3)_4CoOPO_3H]^+$ complex, not assigned by Lincoln and Stranks,[3a] may arise from distortion of the C_{3v} symmetry of the monodentate phosphato-ligand. Monoprotonation of the phosphato-group and/or H-bonding to the vicinal OH_2 group in this complex may produce a similar effect to that of a bidentate phosphate ligand with cobalt(III). Hence, it is not surprising that C_{2v} symmetry is indicated from the i.r. spectrum. It is concluded that the solid samples of the binuclear complexes which have been isolated here contain bridging phosphate ligands, that of the nitrate being monoprotonated while that of the bromide salt is unprotonated.

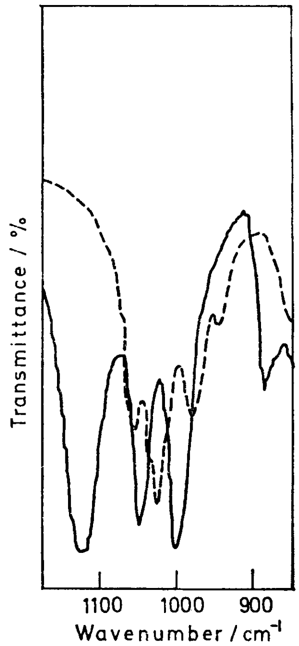
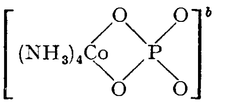
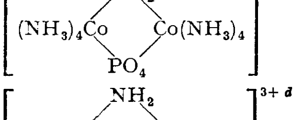
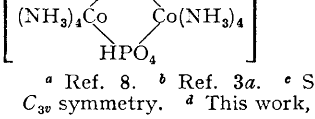


FIGURE 2 I.r. spectra (KBr discs) of the complexes $[(NH_3)_4Co{\cdot}\mu(NH_2,PO_4){\cdot}Co(NH_3)_4]Br_2$ (– – – –) and $[(NH_3)_4Co{\cdot}\mu(NH_2,HPO_4){\cdot}Co(NH_3)_4](NO_3)_3$ (——)

TABLE 2

Evidence for a bridging phosphate ligand from i.r. spectra: a comparison of frequency assignments for some cobalt(III) phosphato-complexes

Species	Symmetry	$\frac{\nu_1}{cm^{-1}}$	$\frac{\nu_3}{cm^{-1}}$
PO_4^{3-} [a]	T_d	980	*ca.* 1082
$[Co(NH_3)_6]PO_4$ [b]	T_d	970w	965—1035
$[(NH_3)_5CoOPO_3]$ [b]	C_{3v}	934m	980s 1030s
$[H_2O(NH_3)_4CoOPO_3H]^+$ [b]	C_{2v} [c]	877m	1010s 1055vs 1082s
 [b]	C_{2v}	900m	920s 1045s 1110s
 2+ [d]	C_{2v}	950m	980ms 1030s 1060ms
 3+ [d]		887m	1000s 1050s 1125s

[a] Ref. 8. [b] Ref. 3*a*. [c] Shows distortion from expected C_{3v} symmetry. [d] This work, determined in KBr discs.

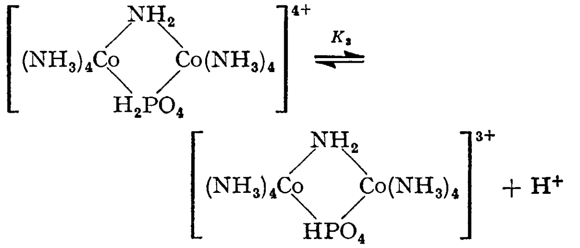
Acid Dissociation Constants for Phosphoric Acid.—Acid dissociation constants for phosphoric acid have previously been measured in perchlorate media, with $I = 0{\cdot}1$—$1{\cdot}0$M $(NaClO_4)$.[9] Since the present work was carried out at $I = 2{\cdot}0$M, values of K_1 and K_2 were redetermined by

$$H_3PO_4 \overset{K_1}{\rightleftharpoons} H_2PO_4^- + H^+ \qquad (2)$$

$$H_2PO_4^- \overset{K_2}{\rightleftharpoons} HPO_4^{2-} + H^+ \qquad (3)$$

potentiometric titration (details as in the Experimental section). Mean values at 25 °C and $I = 2{\cdot}00 \pm 0{\cdot}05$M $(NaClO_4)$ are $pK_1 = 0{\cdot}9 \pm 0{\cdot}04$ and $pK_2 = 5{\cdot}8$. A titration carried out at 45 °C showed no appreciable difference in p*K* values from those at 25 °C. Consequently the latter were used at all temperatures investigated in the kinetic experiments (*i.e.* $\Delta H_0 \simeq 0$ over this comparatively small temperature range[9]). Thus in the range of $[H^+]$ used ($0{\cdot}1$ — $2{\cdot}0$M), the only significant phosphate species present are $H_2PO_4^-$ and H_3PO_4, and the formation constant for H_3PO_4, $K_F = (1/K_1)$, is $7{\cdot}94 \pm 0{\cdot}5$ l mol^{-1} at $I = 2{\cdot}00 \pm 0{\cdot}05$M $(NaClO_4)$ and 25—45 °C.

Acid Dissociation Constants for the Binuclear Phosphato-complex.—The first acid dissociation constant, K_3 [equation (4)], was determined spectrophotometrically. Thus an



(4)

equation of the form (5) can be derived, where OD_{obs} is the

$$\frac{1}{OD_1 - OD_{obs}} = \frac{1}{OD_1 - OD_2}\left(\frac{K_3}{[H^+]} + 1\right) \qquad (5)$$

observed absorbance and OD_1 and OD_2 are absorbances of the mono- and di-protonated complexes respectively. A value of K_3 was obtained from plots of $(OD_1 - OD_{obs})^{-1}$ against $[H^+]^{-1}$. Figure 3 illustrates these plots at 25 and 40 °C and $\lambda = 410$ nm (the wavelength at which the greatest change in optical density occurred) and values of pK_3 are $1{\cdot}5_2$ and $1{\cdot}5_3$ respectively at $I = 2{\cdot}0$M $(NaClO_4)$. The second acid dissociation constant, K_4 [equilibrium (6)],

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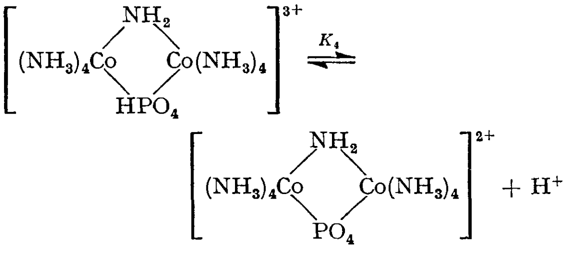
[8] D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.*, 1954, 493.

[9] ' Stability Constants of Metal-ion Complexes,' Chem. Soc. Special Publ. No. 17, 1964; No. 25, 1971.

was determined by pH titration. A solution (20 ml) of the μ-amido-μ-hydrogenphosphato-complex (3 × 10^{-3}M) at I = 0·1M ($LiClO_4$) was titrated against 0·2M-NaOH solution at 25 °C. Figure 4 illustrates the titration curve and the corresponding first-derivative plot. The pK_a of the complex was evaluated from the approximation (7), such

$$\mathrm{pH} = \mathrm{p}K_4 + \log\frac{[\mu(\mathrm{PO_4})]}{[\mu(\mathrm{HPO_4})]} \qquad (7)$$

that pK_4 = pH when half the equivalent of sodium hydroxide has been added. The method was sufficiently accurate for the purposes of this work. The value of pK_4 obtained was 6·0 ± 0·1 at 25 °C and I = 0·1M ($LiClO_4$). Since a precise value of K_4 is not required in our treatment, this quantity was not determined at I = 2·0M ($NaClO_4$).



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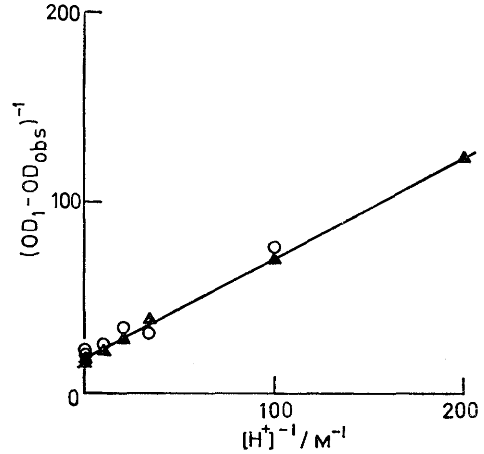

FIGURE 3 Determination of the acid dissociation constant K_3 [equation (4)] from absorbance (OD) measurements at 410 nm [equation (5)]. The temperature variation from 25 (▲) to 40 °C (○) produces no significant effect, I = 2·0M ($NaClO_4$)

Kinetics of the Reverse of Reaction (1).—Temperatures of 40—55 °C were used to investigate the reverse of reaction (1). Runs were followed spectrophotometrically at λ = 538 nm, which is a peak for the μ-amido-μ-phosphato-complexes. Pseudo-first-order plots of log (OD_t − OD_∞) against time for the disappearance of complex (III) were linear to 60—75% completion, OD_∞ values being calculated assuming the final product to be the μ-amido-μ-hydroxo-complex (I) {ε 142 l mol^{-1} cm^{-1} with [H^+] = 0·1M, ε 148 l mol^{-1} cm^{-1} with [H^+] = 2·0M at 538 nm}. Subsequently the plots curved owing to the decomposition of (I). Runs were followed to at least 40% completion. First-order rate constants, k_r, were calculated from the linear portion of the plots (Table 4) and when [H^+] was varied from 0·1 to 2·0M, I = 2·0M ($NaClO_4$), k_r showed a dependence on [H^+].

Since pK_3 = $1{\cdot}5_2$ at 25—40 °C, it is necessary to make allowances for the presence of the mono- as well as the di-protonated complex. Equation (8), the simplest form

$$k_r([\mathrm{H}^+] + K_3)/K_3 = l + m[\mathrm{H}^+] \qquad (8)$$

of the hydrogen-ion dependence, was found to be not applicable (Figure 5). The appearance of this Figure suggests that l does not make a significant contribution and that a term in [H^+]^2 may be effective. The data in fact give a good fit to equation (9) (see Figure 6). The replace-

$$k_r([\mathrm{H}^+] + K_3)/[\mathrm{H}^+]K_3 = p + q[\mathrm{H}^+] \qquad (9)$$

ment of $NaClO_4$ by $LiClO_4$ to adjust the ionic strength, and the replacement of the bromide for the nitrate salt of the μ-amido-μ-phosphato-complex, did not produce any sig-

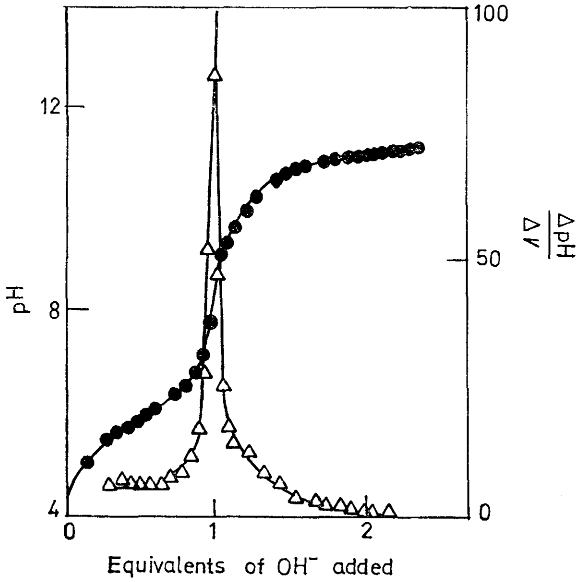

FIGURE 4 Determination of the acid dissociation constant K_4 [equation (6)] by pH titration: (●), titration curve (left-hand scale); (△), first-derivative plot (right-hand scale) [I = 0·1M ($LiClO_4$)]

TABLE 3

Acid dissociation constants for some cobalt(III) phosphato-complexes

Species	Temp. °C	pK		
$[(NH_3)_4Co{\cdot}\mu(NH_2,H_2PO_4){\cdot}Co(NH_3)_4]^{4+}$	25	1·52 (pK_3) [a]	6·0 (pK_4) [b]	
$[Co(en)_2PO_4H]^+$	5		4·25 [c]	
$[Co(tn)_2PO_4H]^+$	5		4·12 [d]	
$[(NH_3)_5CoOPO_3H_3]^{3+}$			3·60 [f]	8·50 [f]
PO_4H_3	25	0·67 [e]—0·9 (pK_1) [a]	5·8 (pK_2) [a]	12·5 [e]

[a] This work; I = 2·0M ($NaClO_4$). [b] This work; I = 0·1M ($LiClO_4$). [c] Ref. 3*a* (en = ethylenediamine); I = 1·0M ($NaClO_4$). [d] Ref. 3*b* (tn = trimethylenediamine); I = 0·16M ($NaClO_4$). [e] Ref. 2; I = 1M ($NaClO_4$). [f] Ref. 2; I = 3M ($NaClO_4$) and 25 °C.

TABLE 4

Pseudo-first-order rate constants, k_r, for the reaction (III) $\longrightarrow$ (I) at $I = 2{\cdot}0$M (NaClO$_4$). The nitrate salt of the binuclear phosphato-complex was used except where stated

Temp. °C	10^4[Complex] [a] M	[H$^+$] M	$10^5 k_r$ s^{-1}	$10^3 k_r([H^+] + K_3)/[H^+]K_3$ l mol^{-1} s^{-1}
40	4·13	0·1	3·05	1·20
	4·29 [b]	0·1	3·47	1·37
	4·58	0·5	3·67 [c]	1·16
	4·20	1·0	4·45	1·36
	4·76	1·5	5·80	1·72
	4·62	2·0	6·31	1·89
	4·48	2·0	8·16	2·45
45	3·97 [b]	0·1	5·18	2·05
	4·36 [b]	0·5	7·64 [c]	2·41
	5·56	1·0	9·86	3·01
	15·54 [b]	1·5	12·00	3·62
	4·33 [b]	1·5	11·60	3·50
	17·35	2·0	14·10	4·23
	4·48	2·0	14·30	4·29
50	4·88	0·1	7·84	3·10
	2·87 [b]	0·5	12·20 [c]	3·84
	5·03	0·5	11·90 [c]	3·75
	4·48	0·75	15·20	4·69
	3·18 [b]	0·75	12·10 [c]	3·73
	4·48	1·0	16·70	5·09
	3·02 [b]	1·0	16·30 [c]	4·97
	3·20 [b]	1·5	19·70 [c]	5·94
	3·43 [b]	2·0	22·70	6·81
	3·04 [b]	2·0	24·30	7·29
	4·69	2·0	25·20	7·56
55	4·90	0·1	12·50	4·95
	4·03 [b]	0·5	19·20 [c]	6·05
	4·27	1·0	25·30 [c]	7·72
	5·22	1·5	33·60	10·14
	4·30	2·0	41·00	12·30

[a] Total concentration. [b] Bromide salt used. [c] $I = 2{\cdot}0$M (LiClO$_4$).

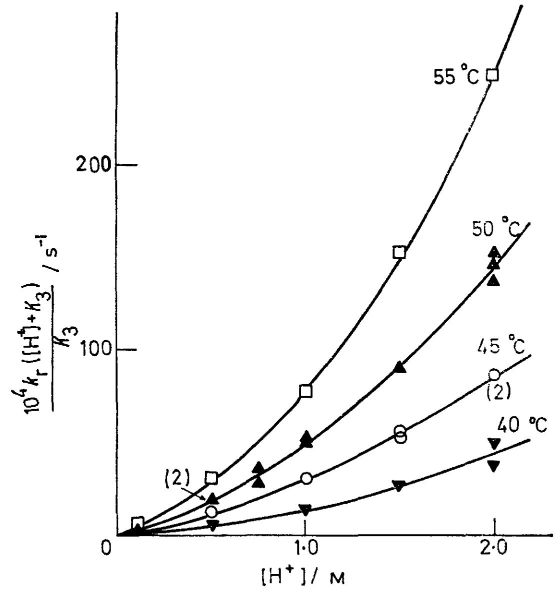

FIGURE 5 Dependence of k_r on [H$^+$] for the reaction of the μ-amido-μ-phosphato-complex [equation (8) is not applicable], $I = 2{\cdot}0$M (NaClO$_4$–LiClO$_4$)

nificant effect. Values of p and q at the different temperatures were evaluated by an unweighted least-squares program and are shown in Table 5 together with extrapolated values at lower temperatures. Activation parameters were determined by use of a non-linear least-squares treatment in which each data point [10] was given equal weighting. The values so obtained are $\Delta H_p^\ddagger = 18{\cdot}4 \pm 1{\cdot}5$ kcal mol^{-1}, $\Delta S_p^\ddagger = -13{\cdot}5 \pm 4{\cdot}6$ cal K^{-1} mol^{-1}, $\Delta H_q^\ddagger = 27{\cdot}3 \pm 2{\cdot}5$ kcal mol^{-1}, and $\Delta S_q^\ddagger = 13{\cdot}6 \pm 7{\cdot}8$ cal K^{-1} mol^{-1}. Both p and q are composite terms, the identity of which will be considered in the Discussion section.

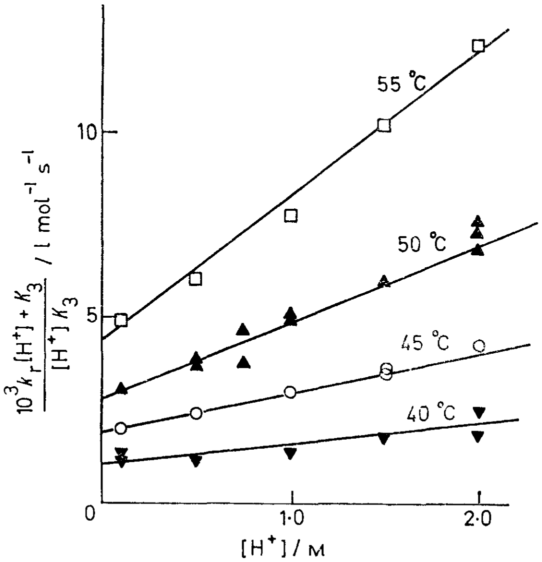

FIGURE 6 Dependence of k_r on [H$^+$] for the reaction of the μ-amido-μ-phosphato-complex [equation (9) is applicable], $I = 2{\cdot}0$M (NaClO$_4$–LiClO$_4$)

Kinetics of the Forward Reaction.—For most conditions of [H$^+$] and total phosphate, [PO$_4^{3-}$]$_T$, the reaction did not proceed to completion and it was necessary to apply a correction for the reverse reaction. Since it was possible that free phosphate ions would have some effect on the latter (studied in the previous section in the absence of phosphate ions), the forward reaction was investigated under conditions where the correction for the rate of the reverse reaction was small (<10%), and any error introduced negligible. Thus concentrations were in the ranges [H$^+$] = 0·7—2·0M and [PO$_4^{3-}$]$_T$ = 0·4—2·0M, and the temperature 20—35 °C. Ionic strengths were calculated by

TABLE 5

Variation of constants p and q with temperature for the reverse reaction, $I = 2{\cdot}0$M (NaClO$_4$)

Temp. °C	$10^3 p$ l mol^{-1} s^{-1}	$10^4 q$ l^2 mol^{-2} s^{-1}
20	0·13 ± 0·03 [a]	0·25 ± 0·07 [b]
25	0·23 ± 0·05 [a]	0·57 ± 0·15 [b]
30	0·39 ± 0·07 [a]	1·24 ± 0·31 [b]
35	0·64 ± 0·13 [a]	2·63 ± 0·49 [b]
40	1·09 ± 0·30	4·87 ± 2·9
45	1·86 ± 0·06	11·7 ± 0·4
50	2·69 ± 0·19	22·4 ± 1·5
55	4·22 ± 0·28	39·3 ± 2·3

[a] Obtained by extrapolation of a plot of log (p/T) against $1/T$. [b] Obtained by extrapolation of a plot of log (q/T) against $1/T$.

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[10] Low Alamos Report LA2367, 1959 and Addenda by R. H. Moore and R. K. Zeigler. We are grateful to Dr. T. W. Newton for sending us details of this program.

allowing for dissociation of H_3PO_4 into H^+ and $H_2PO_4^-$ ions; formation of the ions HPO_4^{2-} and PO_4^{3-} was assumed to be negligible. Runs were followed spectrophotometrically at $\lambda = 538$ nm. Absorbance (OD_∞) readings were measured after 8 half-lives and pseudo-first-order plots of log ($OD_\infty - OD_t$) against time for the appearance of the $\mu(NH_2,H_2PO_4)$ complex were linear to $>80\%$ completion. Pseudo-first-order rate constants, k_{obs}, were evaluated, and corrected for the reverse reaction assuming $k_{obs} = k_f + k_r$, where k_f is the pseudo-first-order rate constant for formation of the μ-amido-μ-dihydrogenphosphato-complex.

TABLE 6

Pseudo-first-order rate constants, k_f, for the conversion (I) $\longrightarrow$ (II), $I = 2{\cdot}0$M ($NaClO_4$), and values of k_{corr} [defined as in the left-hand side of equation (14)], using the perchlorate salt of complex (I)

Temp. °C	10^4[Complex] M	$[PO_4^{3-}]$ M	$[H^+]$ M	10^4k_{obs} s^{-1}	10^4k_r s^{-1}	10^4k_f s^{-1}	10^3k_{corr} $l^2\ mol^{-2}\ s^{-1}$
20	1·35	1·00	1·00	1·82	0·06	1·76	1·14
	1·41	1·50	1·00	2·93	0·06	2·87	1·07
	1·36	2·00	1·00 ^{a}	4·52	0·06	4·46	1·14
	1·27	1·00	1·25 ^{a}	1·95	0·06	1·89	1·22
	1·27	1·50	1·25 ^{a}	3·27	0·06	3·21	1·23
	1·36	2·00	1·25 ^{a}	4·75	0·06	4·69	1·20
	1·54	0·70	1·50 ^{a}	1·39	0·07	1·32	1·32
	1·35	1·00	1·50	2·03	0·07	1·96	1·26
	1·47	1·50	1·50	3·50	0·07	3·43	1·33
	1·27	1·00	1·75 ^{a}	2·31	0·07	2·24	1·48
	1·36	1·50	1·75 ^{a}	3·73	0·07	3·66	1·44
	1·27	2·00	1·75 ^{a}	5·41	0·07	5·34	1·42
	1·54	0·70	2·00	1·60	0·07	1·53	1·54
	1·40	1·00	2·00	2·30	0·07	2·23	1·45
	1·36	1·50	2·00	3·86	0·07	3·79	1·49
	1·35	2·00	2·00	5·66	0·07	5·59	1·51
25	1·73	2·00	0·70	5·88	0·10	5·78	1·61
	1·80	1·00	1·00	2·89	0·10	2·79	1·94
	1·44	1·50	1·00	4·62	0·10	4·52	1·86
	1·42	2·00	1·00	6·67	0·10	6·57	1·84
	1·74	1·00	1·50	3·40	0·12	3·28	2·27
	1·86	1·50	1·50	5·41	0·12	5·29	2·21
	1·60	2·00	1·50	7·66	0·12	7·54	2·14
	1·65	0·70	1·75	2·37	0·13	2·24	2·33
	1·59	0·40	1·94	1·39	0·13	1·26	2·44
	1·47	0·70	1·94	2·50	0·13	2·37	2·47
	1·76	1·00	1·94	3·84	0·13	3·71	2·59
	1·72	1·50	1·94	6·13	0·13	6·00	2·55
	1·26	2·00	1·94	8·50	0·13	8·37	2·44
30	1·64	1·00	1·00	4·46	0·18	4·28	3·13
	1·64	1·50	1·00	7·25	0·18	7·07	3·16
	1·49	2·00	1·00	10·19	0·18	10·01	3·07
	1·49	1·00	1·50	5·07	0·21	4·86	3·48
	1·37	1·50	1·50	8·44	0·21	8·23	3·67
	1·44	2·00	1·50	11·87	0·21	11·66	3·62
	1·40	1·00	1·75	5·57	0·22	5·53	3·99
	1·44	2·00	1·75	12·72	0·22	12·50	3·91
	1·54	0·70	2·00	4·14	0·24	3·90	4·21
	1·37	1·00	2·00	5·88	0·24	5·64	4·06
	1·37	1·50	2·00	9·51	0·24	9·27	4·17
	1·37	2·00	2·00	13·39	0·24	13·15	4·15
35	1·31	1·00	1·00	7·37	0·32	7·05	5·18
	1·60	1·62	1·00	12·95	0·32	12·63	5·16
	1·40	2·00	1·00 ^{a}	16·70	0·32	16·38	5·09
	1·60	2·00	1·00	16·81	0·32	16·49	5·14
	1·60	1·00	1·50	8·61	0·38	8·23	5·96
	1·60	1·62	1·50	14·95	0·38	14·57	5·93
	1·60	2·00	1·50	19·31	0·38	18·93	5·92
	1·47	0·70	1·75 ^{a}	6·17	0·41	5·76	6·22
	1·47	0·70	2·00	6·58	0·44	6·14	6·62
	1·55	1·00	2·00	9·42	0·44	8·98	6·46
	6·99	1·00	2·00	9·47	0·44	9·03	6·50
	1·40	1·62	2·00	16·95	0·44	16·51	6·79
	1·31	2·00	2·00	21·50	0·44	21·06	6·66

^{a} $I = 2{\cdot}0$M ($LiClO_4$).

Values of k_f obtained are shown in Table 6. Some runs at 45 °C, where decomposition of complex (I) is significant, showed considerable curvature over the last 80% of the reaction, and did not fit the interpretation of the data applied at lower temperatures. For this reason the highest temperature considered was 35 °C.

We should expect this system to behave like the analogous sulphate [5] and selenate ion [6] studies, with a dependence as in (10) (see Figure 7). This equation may be written in

$$k_f = k_{1a}[H^+][H_2PO_4^-] + k_{1b}[H^+][H_3PO_4] \quad (10)$$

terms of $[PO_4^{3-}]_T$ and K_F as in equation (11), where $[PO_4^{3-}]_T$ is given by equation (12). At a given (total)

$$k_f(1 + K_F[H^+])/[H^+][PO_4^{3-}]_T = F = k_{1a} + k_{1b}K_F[H^+] \quad (11)$$

$$[PO_4^{3-}]_T = [H_3PO_4] + [H_2PO_4^-] \quad (12)$$

phosphate concentration, plots of F against $[H^+]$ were linear, but when $[PO_4^{3-}]_T$ was varied a series of closely parallel lines was obtained. Also, as in previous studies, the intercepts of the ordinate gave a linear dependence on anion concentration (Figure 8). Only at 25 °C was it possible to identify any deviations from linearity of plots of the intercepts against $[PO_4^{3-}]_T$ such as occurred in the sulphate ion study. The data are therefore adequately represented by equation (13) which includes a further term,

$$k_f(1 + K_F[H^+])/[H^+][PO_4^{3-}]_T = k_{1a} + k_{1b}K_F[H^+] + c[PO_4^{3-}]_T \quad (13)$$

$c[PO_4^{3-}]_T$. Such a term is indicative of a dependence on $[PO_4^{3-}]_T^2$ or, possibly, $[HPO_4^{2-}]^2$ in the rate law (10). Values of c were obtained from the gradients of plots in Figure 7 and are listed in Table 7.

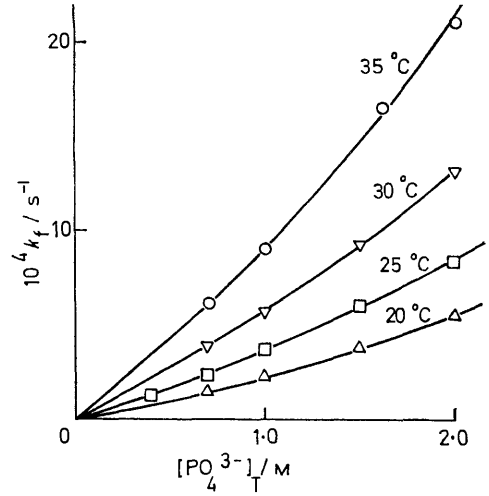


FIGURE 7 Variation of the pseudo-first-order rate constant k_f with $[PO_4^{3-}]_M$ in the reaction of the μ-amido-μ-hydroxo-complex with phosphate ions, $[H^+] = 2{\cdot}0M$ (except for points at 25 °C, when $[H^+] = 1{\cdot}94M$) and $I = 2{\cdot}0M$ ($NaClO_4$–$LiClO_4$)

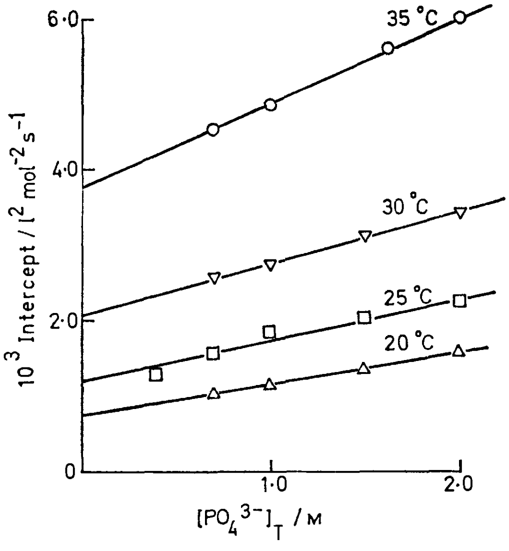


FIGURE 8 Dependence of the intercept of equation (11) on total phosphate-ion concentration; $I = 2{\cdot}0M$ ($NaClO_4$–$LiClO_4$). The gradient corresponds to a further term in c

TABLE 7

Variation of rate constants, k_{1a} and k_{1b}, for the forward reaction, and the parameter c with temperature, $I = 2{\cdot}0M$ ($NaClO_4$)

Temp. °C	10^3k_{1a} $l^2 mol^{-2} s^{-1}$	10^5k_{1b} $l^2 mol^{-2} s^{-1}$	$10^3 c$ $l^3 mol^{-3} s^{-1}$
20	0·73 ± 0·04	4·94 ± 0·30	0·43
25	1·18 ± 0·06	8·54 ± 0·47	0·55
30	2·07 ± 0·09	13·12 ± 0·67	0·70
35	3·71 ± 0·09	18·30 ± 0·74	1·12

Equation (13) can be rearranged to give (14), where we write the left-hand side of equation (14) as k_{corr} (Table 6).

$$k_f(1 + K_F[H^+])/[H^+][PO_4^{3-}]_T - c[PO_4^{3-}]_T = k_{1a} + k_{1b}K_F[H^+] \quad (14)$$

The value of K_F used throughout was 7·94 l mol⁻¹ for 20—35 °C. Figure 9 shows a plot of k_{corr} against $[H^+]$. Values of k_{1a} and k_{1b} were obtained from this plot using a least-squares program and are shown in Table 7. Activation

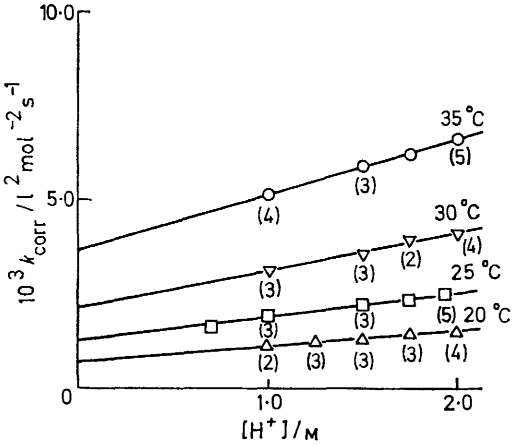


FIGURE 9 Variation of the rate constant k_{corr} [the left-hand side of equation (14)] with $[H^+]$ for reaction of the μ-amido-μ-hydroxo-complex with phosphate ions, $I = 2{\cdot}0M$ ($NaClO_4$–$LiClO_4$). Figures in parentheses indicate the number of runs averaged

TABLE 8

Summary of kinetic data for the forward (k_{1a} and k_{1b}) and reverse (a, b, and b') reactions, $I = 2{\cdot}0M$ ($NaClO_4$)

	Rate constant (25 °C)	$\Delta H^‡$ kcal mol⁻¹	$\Delta S^‡$ cal K⁻¹ mol⁻¹
k_{1a}	$1{\cdot}18 \times 10^{-3}$ ($l^2 mol^{-2} s^{-1}$)	19·5 ± 0·7	−6·5 ± 2·3
k_{1b}	$8{\cdot}54 \times 10^{-5}$ ($l^2 mol^{-2} s^{-1}$)	14·3 ± 0·8	−29·2 ± 2·8
$[(a/K_3) + b']$	$0{\cdot}26 \times 10^{-3}$ ($l mol^{-1} s^{-1}$)	18·4 ± 1·5	−13·5 ± 4·6
b/K_3	$0{\cdot}57 \times 10^{-4}$ ($l^2 mol^{-2} s^{-1}$)	27·3 ± 2·5	13·6 ± 7·8
b	$0{\cdot}18 \times 10^{-5}$ ($l mol^{-1} s^{-1}$)	*	

* Since the enthalpy change corresponding to K_3 is small, the activation enthalpy corresponding to b is similar to that for b/K_3.

parameters for k_{1a} and k_{1b}, estimated by a non-linear least-squares treatment [10] where each data point was weighted equally, are $\Delta H_{1a}^{\ddagger} = 19{\cdot}5 \pm 0{\cdot}7$ kcal mol^{-1}, $\Delta S_{1a}^{\ddagger} = -6{\cdot}5 \pm 2{\cdot}3$ cal K^{-1} mol^{-1}, $\Delta H_{1b}^{\ddagger} = 14{\cdot}3 \pm 0{\cdot}8$ kcal mol^{-1}, and $\Delta S_{1b}^{\ddagger} = -29{\cdot}2 \pm 2{\cdot}8$ cal K^{-1} mol^{-1}. Errors arising from K_F and from the uncertainty in values of c have not been included. All activation parameters for both forward and reverse reactions are shown in Table 8.

DISCUSSION

The characterisation of the μ-amido-μ-phosphato-complex and its protonated forms is decisive. Values obtained for the acid dissociation constants K_3 and K_4 are of considerable interest. Table 3 lists pK_a values of some phosphato-cobalt(III) complexes alongside those for phosphoric acid. Of particular concern is whether co-ordination of the phosphato-ligand to a cobalt(III) centre is comparable to protonation of the ligand. Acid dissociation constants show a definite enhancement of the basicity of the phosphate ligand on replacing H$^+$ by the penta-amminecobalt(III) entity. The pK_a values of H_3PO_4 and the diprotonated binuclear phosphato-complex are directly comparable and it is observed that attachment of the phosphato-ligand to two cobalt(III) atoms has approximately the same effect on the basicity of the ligand as monoprotonation. A similar effect is observed in the case of the μ-amido-μ-oxalato-bis[tetra-amminecobalt(III)] complex and oxalic acid.[11] Intermediate behaviour is apparent in mononuclear complexes containing chelated phosphate ligands.

The hydrogen-ion dependence observed for the reverse reaction, equation (9), can be accounted for by considering reactions of diprotonated, μ(H_2PO_4), and monoprotonated, μ(HPO_4), species. By analogy with the μ-sulphato-[5] and μ-selenato-studies,[6] [H$^+$] independent and [H$^+$] dependent paths might be expected as in equation (15), which leads to (16). From Figure 5 it is

$$k_r[(\mu(PO_4)_T] = a[\mu(H_2PO_4)] + b[H^+][\mu(H_2PO_4)] + a'[\mu(HPO_4)] + b'[H^+][\mu(HPO_4)] \quad (15)$$

$$k_r([H^+] + K_3)/K_3 = a[H^+]/K_3 + b[H^+]^2/K_3 + a' + b'[H^+] \quad (16)$$

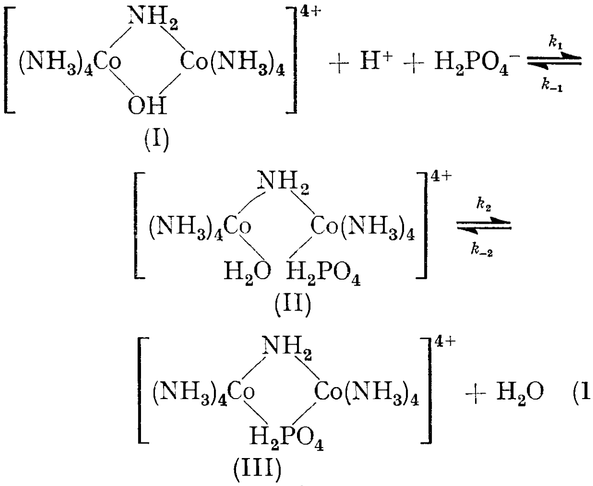
concluded that the [H$^+$] independent term a' makes negligible contribution. Therefore the [H$^+$] dependence can be expressed as in (17). A plot of the left-hand side

$$k_r([H^+] + K_3)/[H^+]K_3 = a/K_3 + b' + b[H^+]/K_3 \quad (17)$$

of (17) against [H$^+$] was linear (Figure 6) and the constants p and q can therefore be identified as $[(a/K_3) + b']$ and b/K_3 respectively. The constant b is $0{\cdot}18 \times 10^{-5}$ l mol^{-1} s^{-1} at 25 °C and $I = 2{\cdot}0$M (NaClO$_4$–LiClO$_4$). Activation parameters for a and b' cannot be evaluated. The enthalpy of activation for b is probably little different from that for b/K_3 and is of similar magnitude to values observed for aquation of mononuclear triprotonated phosphato-complexes.[4a] It is appreciably bigger than similar parameters for the μ-amido-μ-sulphato- ($\Delta H_b^{\ddagger} = 15{\cdot}4$ kcal mol^{-1} and $\Delta S_b^{\ddagger} = -34$ cal K^{-1} mol^{-1}) and μ-amido-μ-selenato-complexes ($\Delta H_b^{\ddagger} = 16{\cdot}4$ kcal mol^{-1} and $\Delta S_b^{\ddagger} = -36{\cdot}3$ cal K^{-1} mol^{-1}).

The overall equilibrium constant K_{12} for the formation of complex (III) from (I) [equation (1)] is given by $K_F k_{1b}/b = 376 \pm 80$ l^2 mol^{-2} at 25 °C and $I = 2{\cdot}0$M. We conclude that it is of the same order of magnitude as that for the selenato-complex (265 l^2 mol^{-2} from spectrophotometric changes), but smaller by an order of magnitude than that for the sulphato-complex ($2{\cdot}24 \times 10^3$ l^2 mol^{-2}).*

As in previous studies involving the μ-sulphato-[5] and μ-selenato-complexes,[6] intermediate formation of complex (II) is necessary to account for the interconversion of complexes (I) and (III) [equation (18)]. All the rate constants defined in this equation are either first order or pseudo-first order. The complex (II) has not been isolated and (as before) no evidence has been obtained for any significant build-up of this intermediate in either the forward or reverse reactions. Assuming stationary-state kinetics for (II), equations (19) and (20) are obtained. Of the two limiting cases we prefer



(18)

$$k_f = k_1k_2/(k_2 + k_{-1}) \quad (19)$$

$$k_r = k_{-1}k_{-2}/(k_2 + k_{-1}) \quad (20)$$

$k_2 > k_{-1}$ to $k_{-1} > k_2$. That is to say that the H_2O ligand attached to a cobalt(III) centre in complex (II) is relatively labile as in the case of the sulphato- and selenato-complexes. This is consistent with the greater stability of oxo-anion (YO_4^{n-}) bridges as compared with halide bridges, for when chloride and bromide ions react with complex (I) the μ-chloro- and μ-bromo-products are less stable and complexes such as (IV) are present in aqueous solutions.[7] Thus, with phosphate ions (as well as those of sulphate and selenate), $k_f = k_1$, $k_r = k_{-1}k_{-2}/k_2$, and $k_2 > k_1$ since there is no build-up of

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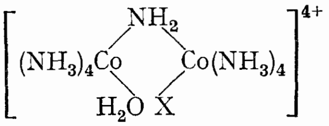
* Values obtained in the sulphate ion study for k_{corr}/k_r (1M-HClO$_4$), k_{1a}/a, and $k_{1b}/(K_{HSO_4}b)$ were $4{\cdot}5 \times 10^3$, $4{\cdot}9 \times 10^3$, and $2{\cdot}3 \times 10^3$ l^2 mol^{-2} respectively (ref. 5). A value of K_{12} of $2{\cdot}24 \times 10^3$ l^2 mol^{-2} was determined spectrophotometrically from equilibrium studies.

[11] K. L. Scott, M. Green, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 3651.

complex (II). Also $k_2 > k_{-2}$ to allow the interconversion (I) $\longrightarrow$ (III) to proceed to completion. A comparison of rate constants and activation parameters for hydroxo-bridge cleavage of complex (I) will be made elsewhere.



(IV); X = Cl or Br

The value of K_F determined at $I = 2{\cdot}0 \pm 0{\cdot}05$M ($NaClO_4$) has considerable ($\pm 10\%$) uncertainty. We were unable to observe any temperature dependence in K_F because this uncertainty could not be overcome. We have assumed that ΔH_0 *ca.* 0 for protonation of $H_2PO_4^-$, which is reasonable when comparisons are made with values of ΔH_0 determined at other ionic strengths.[9] At $I \longrightarrow 0$, $\Delta H_0 = 1{\cdot}85 \pm 0{\cdot}05$ kcal mol^{-1} so that the range of values of K_F over 20—35 °C is small. As a test of the feasibility of this approach, an artificial temperature dependence was applied to K_F using $\Delta H_0 = +2$ kcal mol^{-1} at $I = 2{\cdot}0$M ($NaClO_4$), which is probably excessive. The effect on values of k_{1a} and k_{1b} and their activation parameters was then estimated. When the variation ($K_F = 7{\cdot}6$—$8{\cdot}9$ l mol^{-1}) was applied, assuming $K_F = 7{\cdot}94$ l mol^{-1} at 25 °C, $\Delta H_{1a}^{\ddagger} = 19{\cdot}8 \pm 0{\cdot}9$ kcal mol^{-1}, $\Delta S_{1a}^{\ddagger} = -5{\cdot}3 \pm 3$ cal K^{-1} mol^{-1}, $\Delta H_{1b}^{\ddagger} = 15{\cdot}1 \pm 1{\cdot}1$ kcal mol^{-1}, and $\Delta S_{1b}^{\ddagger} = -26{\cdot}5 \pm 3{\cdot}7$ cal K^{-1} mol^{-1}, values which lie within the quoted limits of error of the activation parameters determined without any temperature variation of K_F. The effect on the values of k_{1a} and k_{1b} at different temperatures was not significant.

The curvature of plots of k_t against $[PO_4^{3-}]_T$ (Figure 7) cannot be interpreted as kinetic evidence for ion-pairing between the μ-amido-μ-hydroxo-complex and the anion involved in the bridge-cleavage process. However, as in previous studies, a term in *c* is observed which, in this case, involves two phosphate ions and would seem to imply ion-pairing of one of these at some unreactive site. This produces an effect on the reactivity of the complex. We have not observed a path for attack of the ion $H_2PO_4^-$ on the unprotonated μ-hydroxo-bridge.

EXPERIMENTAL

Samples of the chloride salt of the μ-amido-μ-hydroxo-bis-[tetra-amminecobalt(III)] complex, $[(NH_3)_4Co{\cdot}\mu(NH_2,OH){\cdot}Co(NH_3)_4]Cl_4,4H_2O$, were prepared and converted to the perchlorate salt, $[(NH_3)_4Co{\cdot}\mu(NH_2,OH){\cdot}Co(NH_3)_4](ClO_4)_4,H_2O$, as described elsewhere.[7] The latter salt was used in all kinetic studies.

μ-Amido-μ-phosphato-bis[tetra-amminecobalt(III)] *Complexes.—Nitrate salt.* (Phosphoric acid (1·5M, 4 ml), previously warmed to 40 °C, was added to solid μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] chloride (0·42 g). The mixture was warmed to 50 °C to dissolve all the solid and the solution maintained at 40 °C for 1·5 h, after which it was cooled to room temperature. After cooling in ice, the solution was filtered and the filtrate made 1·5M in ammonium nitrate by addition of the solid salt. A dark red complex crystallised when the solution was kept in the refrigerator overnight. The crystals were collected, washed with ethanol, and dried by suction (crude yield 0·19 g). The product (0·175 g) was recrystallised by dissolving it in the minimum volume of 0·02M-perchloric acid (8 ml) and warming to 50 °C. Ammonium nitrate (0·75 g) was added and the warm solution filtered. Crystals appeared on cooling the filtrate and were collected, washed with ethanol and ether, and dried in air. The *complex* lost one molecule of water of crystallisation by dehydration over P_2O_5 for 11 days {Found: N, 29·5; H, 5·0; H_2O, 2·9. Calc. for $[(NH_3)_4Co{\cdot}\mu(NH_2,HPO_4){\cdot}Co(NH_3)_4](NO_3)_3,H_2O$: N, 29·5; H, 5·10; H_2O, 3·15%}.

Bromide salt. The nitrate salt (0·1 g) was dissolved in the minimum volume of water at 35 °C. The solution was cooled in ice and adjusted to pH 9 by dropwise addition of concentrated ammonia solution (S.G. 0·880). An ice-cold saturated solution of potassium bromide was then added slowly until the first crystals appeared, after which the solution was cooled in ice. Purple needles crystallised and were collected, washed with ethanol and ether, and air dried (yield 62%). The complex was recrystallised by repeating the procedure. Dehydration over P_2O_5 showed that more than four water molecules were lost. The dehydrated *complex* readily regained weight on exposure to the atmosphere {Found: N, 20·4; H, 5·8; Br, 26·2. Calc. for $[(NH_3)_4Co{\cdot}\mu(NH_2,PO_4){\cdot}Co(NH_3)_4]Br_2,5H_2O$: N, 20·5; H, 5·85; Br, 26·0%}. The perchlorate salt could not be isolated by the usual method of adding crystals of silver(I) perchlorate to a saturated solution of the bromide salt.

I.r. studies were carried out on a Perkin-Elmer 457 instrument, samples being prepared in KBr discs. The pH of solutions of the μ-amido-μ-phosphato-complexes was measured using a Radiometer pH meter (type M4d) with Radiometer glass (type G202C) and calomel (type K401) electrodes immersed directly in the solution of complex. The pH meter was calibrated using a phosphate buffer (pH 6·50, Radiometer type 51001) and checked against buffer solutions of pH 3·2 and 1·1. To determine the acid dissociation constants of phosphoric acid, 0·1M-H_3PO_4 solution (35 ml), $I = 2{\cdot}05$M ($NaClO_4$), was titrated against *ca.* 1M-NaOH solution added in 0·1 ml aliquot portions from a microburette. The end-point was determined from Gran-type plots[12] of $(\Delta pH)^{-1}$ against V, the volume of alkali added (in ml). These estimates were required for two computer programs which were used to calculate the pK values. The first program[13] calculated values of pK_1 and pK_2 at each data point on the titration curve. The values quoted here are those obtained when the calculations converged. The second program calculated pK_1 only, in a similar fashion, but gave a mean of pK_1 values calculated over a preselected range. The latter coincided with values obtained using the first program, within the limits of error. The final values of pK_1 and pK_2 quoted are the arithmetic means of values from three titrations at 25 °C. During the titrations I decreased to 2·00M at the second end-point.

Phosphoric acid, perchloric acid, sodium perchlorate, and ammonia solution used were of AnalaR grade purity. Sodium hydroxide for pH titrations was prepared free from dissolved carbonate ions by making a saturated solution of the solid in triply distilled water. Sodium carbonate did not dissolve and the supernatant liquid was diluted

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[12] G. Gran, *Acta Chem. Scand.*, 1950, **4**, 559.

[13] R. K. Wharton and A. G. Sykes, *J.C.S. Dalton*, 1973, 439.

with triply distilled water and stored in a sealed Polythene bottle for no more than 1 day. Lithium perchlorate was prepared by methods previously used in these laboratories. Unicam SP 500 and 800 (recording) spectrophotometers were used in this study.

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