

## The Preparation and Reactivity of Bidentate Phosphato Complexes of Cobalt(III). *Cis*-[Co(cyclen)PO<sub>4</sub>], *Cis*-[Co(en)<sub>2</sub>PO<sub>4</sub>] and the *p*-(Nitrophenylphosphato)-bisethylenediaminecobalt(III) Cation

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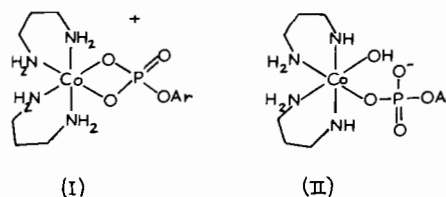
Received July 17, 1982

The preparation of *cis*-[Co(cyclen)PO<sub>4</sub>] and the *p*-nitrophenylphosphatobisethylenediaminecobalt(III) cation are described (cyclen = 1,4,7,9-tetra-azacyclododecane). *Cis*-[Co(cyclen)PO<sub>4</sub>] undergoes rapid ring opening in acidic or basic solution to give the monodentate phosphato species. Loss of monodentate phosphate in acidic solution follows a rate expression of the form  $k_{obs} = k_O + k_H[H^+]$  where  $k_O = 5 \times 10^{-4} \text{ s}^{-1}$  and  $k_H = 4.05 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C and  $I = 0.49 \text{ M}$  (NaClO<sub>4</sub>). The acid-catalysed reaction displays a solvent deuterium isotope effect  $k_{D_2O}/k_{H_2O}$  of ca. 1.4 consistent with a mechanism involving a rapid pre-equilibrium protonation followed by rate determining loss of monodentate phosphate. For [Co(en)<sub>2</sub>PO<sub>4</sub>] in acidic solution, both ring opening of the phosphato ring and loss of monodentate phosphate show a first order dependence on the hydrogen ion concentration and solvolytic pathways are of negligible importance. For ring opening  $k_H = 2 \text{ M}^{-1} \text{ s}^{-1}$  and for loss of monodentate phosphate  $k_H = 1.1 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C and  $I = 0.19 \text{ M}$  (NaClO<sub>4</sub>). Loss of monodentate phosphate from the complex [Co(cyclen)OH(OPO<sub>3</sub>)]<sup>-</sup> also takes place in basic solution and the reaction shows a first order dependence on the hydroxide ion concentration with  $k_{OH} = 2.7 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C and  $I = 0.49 \text{ M}$  (NaClO<sub>4</sub>). For loss of monodentate phosphate from [Co(en)<sub>2</sub>OH(OPO<sub>3</sub>)]<sup>-</sup>  $k_{OH} = 1.4 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ , while for ring opening of bidentate phosphate in [Co(en)<sub>2</sub>PO<sub>4</sub>],  $k_{OH}$  is ca.  $1.75 \text{ M}^{-1} \text{ s}^{-1}$ .

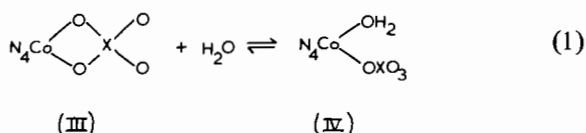
### Introduction

Organic phosphates and polyphosphates are essential to life processes [1], and an understanding of their hydrolysis and related phosphoryl transfer reactions is of great importance. In biological systems these reactions are catalysed by enzymes which in many cases require metal ions (Mg<sup>II</sup>, Mn<sup>II</sup>, Ca<sup>II</sup>, Zn<sup>II</sup> etc.) for activity [2–8]. There has been much speculation as to the precise role of these ions in the mechanism of enzymic phosphate ester hydrolysis.

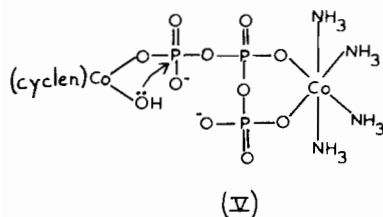
Proposals based on polarisation of electron density, induction of steric strain and the presence of metal bound nucleophiles have all been advanced to account for the rate increases observed in the enzymic reactions. In recent years there has been a marked upsurge in interest in studying the hydrolysis of polyphosphates and phosphate esters in the coordination sphere of kinetically inert cobalt(III) complexes, in an effort to delineate possible mechanisms for these metal ion promoted reactions [9–16]. For example, chelated *p*-nitrophenyl phosphate in the complex (I) undergoes base hydrolysis some 10<sup>9</sup> fold faster than the uncoordinated ester [9]. The reaction competes with ring opening of the chelated ester to give the monodentate *p*-nitrophenylphosphate complex (II). This latter reaction presumably proceeds by an S<sub>N</sub>1CB pathway. X-ray work [9] has established that there is considerable strain in the four-membered phosphato chelate ring of [Co(en)<sub>2</sub>PO<sub>4</sub>], and ring opening readily occurs in acidic and basic solution.



Unlike carbonato complexes surprisingly little work has been published on the synthesis and reactivity of phosphato complexes. Lincoln and Stranks [17] in 1968 carried out pioneering work with [Co(en)<sub>2</sub>PO<sub>4</sub>] and [Co(NH<sub>3</sub>)<sub>5</sub>PO<sub>4</sub>]. With bidentate oxyaniono cobalt(III) complexes the possibility of an equilibrium between monodentate and bidentate oxyaniono species exists. Thus for an XO<sub>4</sub> ligand the equilibrium (1) may occur.



Solid bidentate carbonato ions of the type  $[\text{CoN}_4\text{CO}_3]^+$  are well established, but the aquocarbonato species analogous to (IV) has not been isolated in the solid state, although it occurs as an intermediate in the hydrolysis of such complexes in acidic and basic solution. As a preliminary to studies of the hydrolysis of phosphate esters and polyphosphates on cobalt(III) we required information on the hydrolytic stability of bidentate and monodentate orthophosphate on cobalt(III). Studies with complexes such as  $[\text{Co}(\text{en})_2\text{PO}_4]$  are complicated by isomerisation of the product  $\text{cis-}[\text{Co}(\text{en})_2(\text{OH}_2)_2]^{3+}$  or  $\text{cis-}[\text{Co}(\text{en})_2(\text{OH})_2]^+$  complexes to the corresponding *trans*-isomers. Such isomerisations can be avoided by the use of  $[\text{Co}(\text{cyclen})\text{PO}_4]$  since cyclen (1,4,7,10-tetraazacyclododecane) gives only *cis*-complexes with cobalt(III) [20]. Norman and Cornelius [18] have recently found that the hydrolysis of  $\beta,\gamma\text{-}[\text{Co}(\text{NH}_3)_4\text{H}_2\text{P}_3\text{O}_{10}]$  in which the triphosphate ion is coordinated as a bidentate undergoes rapid hydrolysis (triphosphate  $\rightarrow$  pyrophosphate) in the presence of the cobalt(III) complex of cyclen. The results are consistent with a mechanism involving coordination of the free end of the phosphate chain in the  $\text{Co}(\text{NH}_3)_4\text{H}_2\text{P}_3\text{O}_{10}$  by the cyclen complex to form a dinuclear species (V) followed by internal attack on the phosphate chain by coordinated hydroxide. Recently it has also been shown that the hydrolysis of the acetyl



phosphate monoanion is significantly catalysed by the exchange-inert hydroxo complex  $[(\text{NH}_3)_5\text{CoOH}]^{2+}$  ( $k_{\text{MOH}} = 2.9 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  at  $25^\circ\text{C}$ ) which operates by a nucleophilic pathway involving attack at the carbonyl carbon [19].

## Experimental

The complex  $[\text{Co}(\text{en})_2\text{PO}_4] \cdot \text{H}_2\text{O}$  was prepared from *trans*- $[\text{CoCl}_2(\text{en})_2]\text{Cl}$  essentially as described by Lincoln and Stranks [17] for the perchlorate salt. Cyclen was prepared as previously described [21]. *p*-Nitrophenylphosphatobis(ethylenediamine)cobalt(III) chloride ( $[\text{Co}(\text{en})_2\text{O}_3\text{POC}_6\text{H}_4\text{NO}_2]\text{Cl}$ ) was prepared as follows. *Trans*- $[\text{CoCl}_2(\text{en})_2]\text{Cl}$  (0.57 g) and sodium *p*-nitrophenyl phosphate were mixed into a paste using a few drops of water. The paste was warmed for a few minutes at *ca.*  $60^\circ\text{C}$  and then diluted to about  $10 \text{ cm}^3$  with water. Further heating for 5–10 min at  $60\text{--}70^\circ\text{C}$  resulted in the precipitation of a pink complex

which was filtered off. The product was washed with some cold water, ethanol then ether and dried *in vacuo*. *Anal.* Calc. for  $\text{C}_{10}\text{H}_{20}\text{O}_6\text{N}_5\text{PClCo}$ ; C, 27.8; H, 4.7; N, 16.2. Found: C, 27.5; H, 4.6; N, 16.4%. *p*-Nitrophenylphosphatobis(trimethylenediamine)cobalt(III) perchlorate was prepared as previously described [9], as was *cis*- $[\text{CoBr}_2(\text{cyclen})]\text{Br}$  [20].

The complex *cis*- $[\text{Co}(\text{cyclen})\text{PO}_4] \cdot \text{H}_2\text{O}$  was prepared as follows. *Cis*- $[\text{CoBr}_2(\text{cyclen})]\text{Br}$  (0.48 g) was mixed into a paste with  $\text{Na}_3\text{PO}_4$  (0.1 g) using a few drops of water and warmed at *ca.*  $50^\circ\text{C}$  for 5 min. The red paste obtained was diluted to  $25 \text{ cm}^3$  with water and heated for *ca.* 2 hours at  $60\text{--}70^\circ\text{C}$ . The volume of the solution was reduced to *ca.*  $2 \text{ cm}^3$ . Addition of excess ethanol precipitated the pink product (if an oil is formed, a solid can be obtained by trituration with ethanol). The complex was purified by dissolving in the minimum volume of hot water, and filtering. Cooling in ice followed by the addition of ethanol reprecipitated the product which was washed with ethanol, then ether and dried *in vacuo*. *Anal.* Calc. for  $\text{C}_8\text{H}_{20}\text{N}_4\text{O}_4\text{PCo} \cdot \text{H}_2\text{O}$ ; C, 27.9; H, 6.4; N, 16.3. Found: C, 27.4; H, 6.2; N, 16.1%.

## Kinetics

The reactions were monitored spectroscopically using a Gilford 2400S spectrophotometer thermostatted by circulating water. Ring opening and loss of monodentate phosphate from  $[\text{Co}(\text{en})_2\text{PO}_4]$  in acidic solutions was monitored at 530 nm (absorbance decrease). Perchloric acid solutions adjusted to  $I = 0.19 \text{ M}$  with  $\text{NaClO}_4$  were the reaction medium employed. Loss of monodentate phosphate from *cis*- $[\text{Co}(\text{en})_2\text{OH}(\text{OPO}_3)]^-$  in sodium hydroxide solutions (adjusted to  $I = 0.49 \text{ M}$  with  $\text{NaClO}_4$ ) were monitored at 530 nm (absorbance decrease). Loss of monodentate phosphate from *cis*- $[\text{Co}(\text{cyclen})\text{OH}_2(\text{OPO}_3\text{H})]$  in perchloric acid solutions was monitored at 250 nm (absorbance decrease). Solvent deuterium isotope effects were studied using HCl (or DCl) solutions in  $\text{H}_2\text{O}$  (or  $\text{D}_2\text{O}$ ;  $>99.9\%$   $\text{D}_2\text{O}$ ). Loss of monodentate phosphate from *cis*- $[\text{Co}(\text{cyclen})\text{OH}(\text{OPO}_3)]^-$  in sodium hydroxide solutions was monitored at 250 nm (absorbance decrease). Values of  $k_{\text{obs}}$  (the observed first-order rate constant) were derived from the absorbance data using a microcomputer.

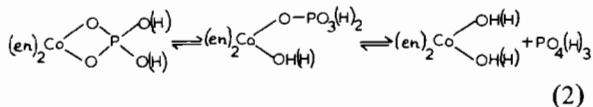
Routine ultraviolet–visible spectra including interval scan spectra were determined on a Perkin-Elmer 402 instrument. Infrared spectra were obtained on a Perkin-Elmer 457 spectrophotometer using KBr discs.  $^1\text{H}$  n.m.r. spectra were measured using a Perkin-Elmer R32 instrument at 90 MHz. Solutions in  $\text{D}_2\text{O}$  were employed with NaTMS as internal reference.  $^{31}\text{P}$  n.m.r. spectra were obtained on a Bruker WP80 instrument at 32.44 MHz with  $\text{Na}_3\text{PO}_4$  as reference and  $\text{D}_2\text{O}$  as solvent.

Activity coefficients were determined using the Davies' equation [22].

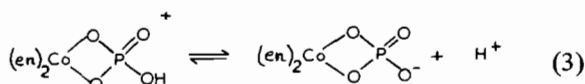
## Results and Discussion

The reaction of *trans*-[CoCl<sub>2</sub>(en)<sub>2</sub>]Cl with Na<sub>3</sub>PO<sub>4</sub> gives [Co(en)<sub>2</sub>PO<sub>4</sub>]·H<sub>2</sub>O as the crimson monohydrate which can be dehydrated at 80–90 °C for 1 hour. The symmetry of a bidentate phosphato ligand is C<sub>2v</sub>. Frequencies assigned to the phosphate ligand are ν<sub>1</sub> 915 cm<sup>-1</sup> and ν<sub>3</sub> 902, 1050, 1087 cm<sup>-1</sup>. The splitting of the ν<sub>3</sub> fundamental into three bands confirms the C<sub>2v</sub> symmetry of the bidentate phosphato ligand. In D<sub>2</sub>O the <sup>31</sup>P signal occurs 634 Hz upfield from external Na<sub>3</sub>PO<sub>4</sub> at 32.44 MHz (δ = 19.54 ppm). The electronic spectrum of an aqueous solution of [Co(en)<sub>2</sub>PO<sub>4</sub>] has λ<sub>max</sub> 529 nm (ε = 112 M<sup>-1</sup> cm<sup>-1</sup>) and λ<sub>max</sub> 377 nm (ε = 98 M<sup>-1</sup> cm<sup>-1</sup>).

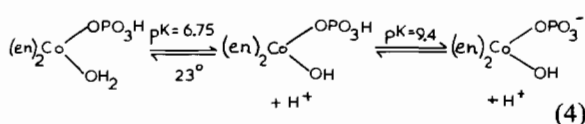
When the solution is acidified, the spectrum rapidly changes to that of [Co(en)<sub>2</sub>H<sub>2</sub>O(HPO<sub>4</sub>)]<sup>+</sup>. The two maxima shift to shorter wavelength and there is a decrease in the extinction coefficients to 511 nm (ε = 108 M<sup>-1</sup> cm<sup>-1</sup>) and 366 nm (ε = 84). If the pH is readjusted to 5–7 the spectral change is reversed. On standing or heating acidified solutions of [Co(en)<sub>2</sub>(H<sub>2</sub>O)(HPO<sub>4</sub>)]<sup>+</sup> the maxima and extinction coefficients move to those characteristic of *cis*-[Co(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> namely 492 nm (ε = 81) and 359 nm (ε = 63) [23]. The spectral data are consistent with the series of equilibria (eq. 2),



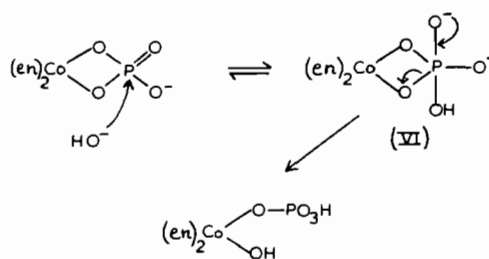
Lincoln and Stranks have shown [17] that the equilibrium (3) has pK<sub>a</sub> 4.25 at 5 °C



For the ring-opened complex the corresponding pK<sub>a</sub> values are shown for the equilibria (4)



Hydrolysis of Co(en)<sub>2</sub>OH<sub>2</sub>(PO<sub>4</sub>) in all acidic and basic media containing H<sub>2</sub>O<sup>18</sup> gives phosphate of natural <sup>18</sup>O abundance [17], confirming that the reaction proceeds entirely by a mechanism involving Co–O bond cleavage. Acid hydrolysis of chelate phosphate in [Co(en)<sub>2</sub>PO<sub>4</sub>] has also been shown to involve purely Co–O cleavage, however in 0.25 M NaOH some 35% O–P cleavage occurs [17]. In basic solution it appears that ring opening can occur by both an S<sub>N</sub>1CB process and by direct nucleophilic attack on phosphorus presumably to give a phosphorane intermediate (VI), Scheme 1.



Scheme 1

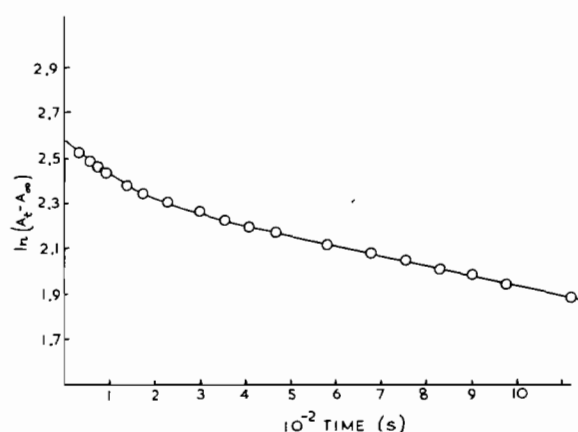
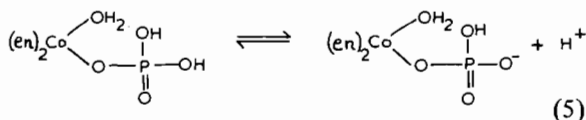


Fig. 1. Two step reaction of *cis*-[Co(en)<sub>2</sub>PO<sub>4</sub>] in 9.3 × 10<sup>-4</sup> M HClO<sub>4</sub> monitored at 530 nm and 25 °C.

Similarly at pH 6.8 and 25 °C there is 40% P–O bond cleavage in the ring opening step.

Hydrolysis of *cis*-[Co(en)<sub>2</sub>PO<sub>4</sub>] was studied using 9.3 × 10<sup>-4</sup>–1.3 × 10<sup>-2</sup> M solutions of HClO<sub>4</sub> adjusted to I = 0.19 M. At low acidities two consecutive reactions could be detected at 530 nm, Fig. 1. Analysis of the data gave the values of k<sub>obs</sub> (the observed rate constants at constant acidity) listed in Table I. The initial fast reaction is assigned to the ring opening step and the slower reaction to loss of monodentate phosphate. For both reactions values of k<sub>obs</sub> are directly proportional to the hydrogen ion concentration with k<sub>H</sub> = k<sub>obs</sub>/[H<sup>+</sup>]. Figure 2 illustrates the data for the loss of monodentate phosphate. For the equilibrium (5)



pK<sub>a</sub> = 3.10 at 23 °C [17]. At the lowest acidity used the pH = 3.10 and at the highest acidity pH = 1.95 (using γ = 0.86, calculated from the Davies' equation at I = 0.19 M). Acid catalysis could result from the reactions, Scheme 2, with decomposition occurring via the zwitterion (VII) to generate a five coordinate intermediate on cobalt(III) and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. The present results provide no evidence for solvolytic displacement.

TABLE I. Reactions of  $[\text{Co}(\text{en})_2\text{PO}_4]$  in Acidic Solutions at 25 °C and  $I = 0.19 \text{ M}$  ( $\text{NaClO}_4$ ).\*

$10^3 [\text{HClO}_4]$ (M)	$10^3 k_{\text{obs}}^{\text{b}}$ ( $\text{s}^{-1}$ )	$k_{\text{H}}^{\text{b}}$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$10^3 k_{\text{obs}}^{\text{a}}$ ( $\text{s}^{-1}$ )	$k_{\text{H}}^{\text{a}}$ ( $\text{M}^{-1} \text{s}^{-1}$ )
0.93	0.75	0.8	1.72	1.9
2.81	3.51	1.3	5.47	2.0
4.68	5.24	1.1	10.02	2.1
6.34	7.17	1.1		
8.42	10.02	1.2		
11.23	13.43	1.2		
13.10	16.99	1.3		

\* $k^{\text{a}}$  relates to ring opening;  $k^{\text{b}}$  relates to loss of monodentate phosphate. Reactions studied at 530 nm.

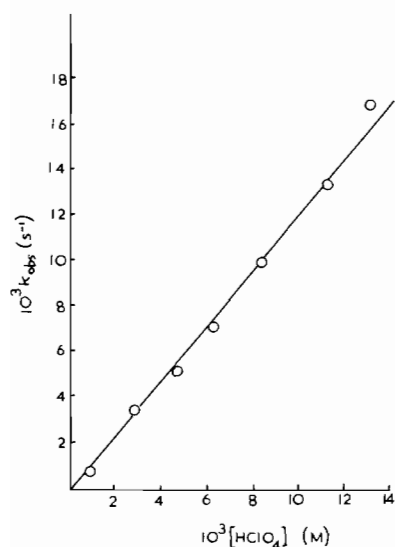
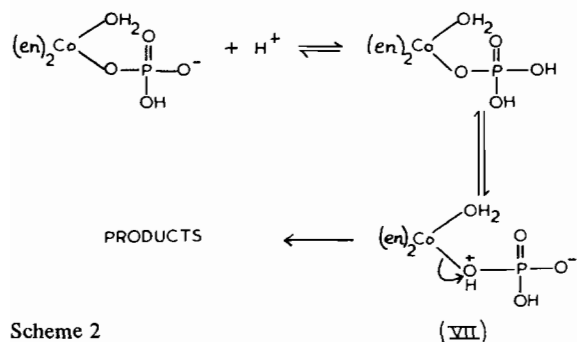


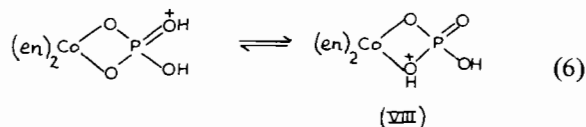
Fig. 2. Loss of monodentate phosphate in  $[\text{Co}(\text{en})_2\text{OH}_2(\text{OPO}_3\text{H}_2)]^{2+}$  in the pH range 3.10–1.95 at 25 °C and  $I = 0.19 \text{ M}$ .



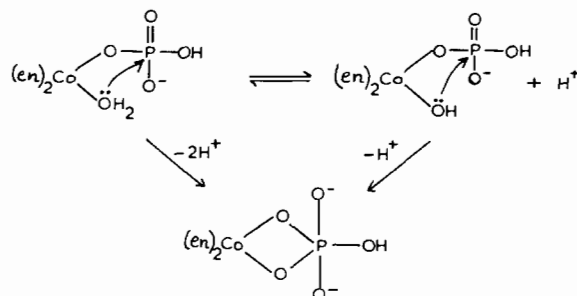
Scheme 2

Scheme 2 involves a rapid pre-equilibrium protonation followed by slow loss of monodentate phosphate. Such a reaction should show a solvent deuterium isotope effect  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} > 1$ . An isotope effect  $k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}} = 1.4$  is observed with the cyclen analogue (see later).

At 25 °C it was also possible to study the acid catalysed ring opening step using  $\text{HClO}_4$  solutions in the range  $4.7 \times 10^{-3}$ – $1.0 \times 10^{-3} \text{ M}$  (pH 2.4–pH 3.1). Values of  $k_{\text{obs}}/[\text{H}^+]$  are constant giving  $k_{\text{H}} = 2.0 \text{ M}^{-1} \text{ s}^{-1}$ , Table I. Since  $\text{p}K_{\text{a}} \sim 4.2$  for the equilibrium (3) this data refers to the acid catalysed ring opening of  $[\text{Co}(\text{en})_2\text{OPO}_3\text{H}]^+$  which probably involves the zwitterionic species (VIII), equation (6).



Ring closure of the monodentate phosphato species in the pH range 5–7 may involve attack of coordinated water or hydroxide ion at the phosphorus centre, Scheme 3. Such reactions have been well studied in



Scheme 3

similar complexes involving N-coordinated amino-acids and amino-acid esters [24]. In this context it is interesting to note that the hydrolysis of acetyl phenyl phosphate monoanion is significantly catalysed by  $[(\text{NH}_3)_5\text{CoOH}]^{2+}$  which operates by a nucleophilic pathway involving attack at the carbonyl carbon [19].

Loss of monodentate phosphate from  $\text{cis-}[\text{Co}(\text{en})_2\text{OH}(\text{OPO}_3)]^-$  also takes place in basic solution. Table II lists values of  $k_{\text{obs}}$  at  $I = 0.49 \text{ M}$  ( $\text{NaClO}_4$ ) over the range of sodium hydroxide concentrations  $9.4 \times 10^{-3} \text{ M}$  to  $4.68 \times 10^{-1} \text{ M}$ . Values of  $k_{\text{obs}}$  are directly proportional to  $[\text{OH}^-]$  with  $k_{\text{OH}} = 1.4 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C, Table II. Loss of monodentate phosphate is expected to occur by an  $\text{S}_{\text{N}}1\text{CB}$  process. Lincoln and Stranks have studied the base hydrolysis of the chelated phosphato complex and quote  $k = 1.75 \text{ M}^{-1} \text{ s}^{-1}$  for ring opening at 22.5 °C and  $I = 1 \text{ M}$  [17]. Ring opening in basic conditions gives some 35% P–O cleavage and 65% Co–O cleavage. Direct nucleophilic attack on phosphorus to give the phosphorane (VI) presumably leads to P–O cleavage and the  $\text{S}_{\text{N}}1\text{CB}$  process to Co–O cleavage. As a result,  $k_{\text{OH}} = k_{\text{CB}} + k_{\text{P}}$  (where  $k_{\text{CB}}$  relates to the conjugate base pathway and  $k_{\text{P}}$  to attack on phosphorus) and

TABLE II. Loss of Monodentate Phosphate from *cis*-[Co(en)<sub>2</sub>OH(OPO<sub>3</sub>)]<sup>-</sup> in Basic Solution at 25 °C and I = 0.49 M (NaClO<sub>4</sub>).<sup>a</sup>

$10^3$ [NaOH] (M)	$10^3 k_{\text{obs}}$ (s <sup>-1</sup> )	$10^2 k_{\text{OH}}$ (M <sup>-1</sup> s <sup>-1</sup> )
9.4	0.14	1.5
18.7	0.30	1.6
28.1	0.35	1.2
37.4	0.53	1.4
93.6	1.33	1.4
187.1	2.66	1.4
280.6	3.83	1.4
374.2	5.00	1.3
467.8	6.30	1.3

$k_{\text{OH}} = 1.4 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$

<sup>a</sup> Reaction studied at 530 nm.

$k_{\text{CB}}/k_{\text{P}} = 65/35$ . These equations give  $k_{\text{CB}} = 1.14 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{\text{P}} = 0.61 \text{ M}^{-1} \text{ s}^{-1}$ . Both pathways make a significant contribution to the ring opening step.

#### *Cis*-[Co(cyclen)PO<sub>4</sub>] · H<sub>2</sub>O

The complex *cis*-[Co(cyclen)PO<sub>4</sub>] · H<sub>2</sub>O was readily prepared by the reaction of *cis*-[CoBr<sub>2</sub>(cyclen)] Br with Na<sub>3</sub>PO<sub>4</sub>. The i.r. spectrum of the complex has a very strong band at 1065 cm<sup>-1</sup> assigned to ν<sub>3</sub> of the chelate PO<sub>4</sub> group (*cf.* 1050 cm<sup>-1</sup> in the ethylenediamine derivative). Aqueous solutions of the complex do not show time dependent changes of the visible spectrum which has λ<sub>max</sub> 530 nm (ε = 174 M<sup>-1</sup> cm<sup>-1</sup>) and 365 nm (ε = 140 M<sup>-1</sup> cm<sup>-1</sup>). The spectral parameters are very comparable to those of [Co(en)<sub>2</sub>PO<sub>4</sub>] where λ<sub>max</sub> = 529 (ε = 112) and 377 nm (ε = 98) [17]. *Cis*-[Co(cyclen)PO<sub>4</sub>] undergoes rapid ring opening in acidic solution to give the monodentate complex. Loss of monodentate phosphate was studied using perchloric acid solutions in the range 3.86 × 10<sup>-3</sup> M to 9.7 × 10<sup>-2</sup> M at I = 0.49 M and 25 °C, Fig. 3. Values of k<sub>obs</sub> obtained are summarised in Table III.

TABLE III. Loss of Monodentate Phosphate from *cis*-[Co(cyclen)OH<sub>2</sub>(OPO<sub>3</sub>H)] in Acidic Solution at 25 °C and I = 0.49 M (NaClO<sub>4</sub>).

$10^3$ [HClO <sub>4</sub> ] (M)	$10^3 k_{\text{obs}}$ (s <sup>-1</sup> )
3.86	0.70
7.7	0.75
9.7	0.85
19.3	1.27
38.6	2.13
58.0	2.85
74.7	3.66
97.0	4.32

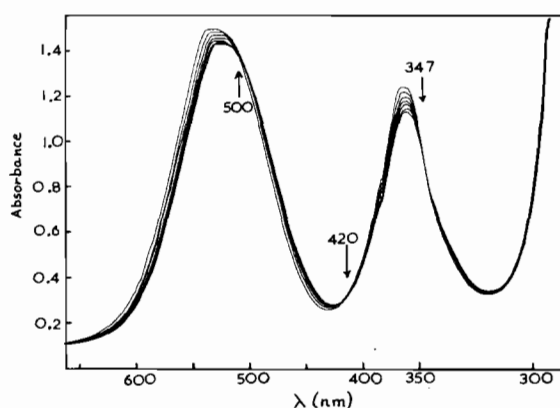


Fig. 3. Absorbance changes for loss of monodentate phosphate from [Co(cyclen)OH<sub>2</sub>(OPO<sub>3</sub>H)] in 0.01 M HClO<sub>4</sub> at 25 °C. The time interval between scans is 1 min. The reaction displays isosbestic points at 500, 420 and 347 nm.

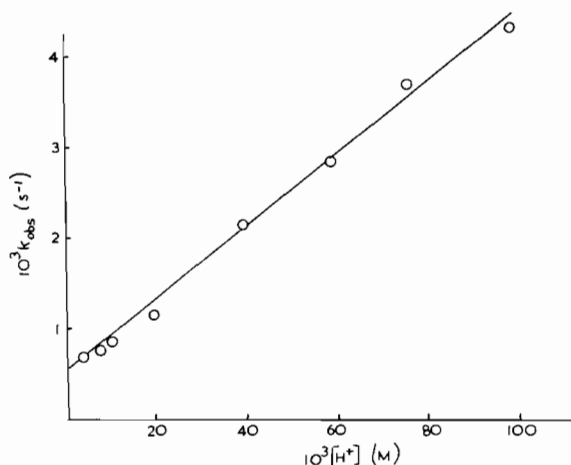
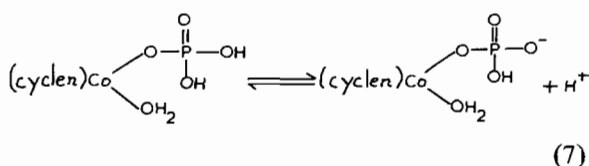


Fig. 4. Plot of  $k_{\text{obs}}$  versus  $[\text{H}^+]$  for the loss of monodentate phosphate from *cis*-[Co(cyclen)OH<sub>2</sub>(OPO<sub>3</sub>H)].

A plot of  $k_{\text{obs}}$  versus the hydrogen ion concentration is linear with a positive intercept, Fig. 4, indicating that  $k_{\text{obs}} = k_{\text{O}} + k_{\text{H}}[\text{H}^+]$ . The slope of the line gives  $k_{\text{H}} = 4.05 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  and the intercept  $k_{\text{O}} = 5 \times 10^{-4} \text{ s}^{-1}$  with a correlation coefficient of 0.998. The spectrum of the final product obtained is identical to that of *cis*-[Co(cyclen)(OH<sub>2</sub>)<sub>2</sub>]<sup>3+</sup>, Table IV. The pK<sub>a</sub> for the equilibrium (7)



is likely to be *ca.* 3, similar to the value obtained for the analogous bisethylenediamine complex, and acid catalysis is expected to occur essentially as shown in Scheme 2. At the lowest acidities employed 3.86 × 10<sup>-3</sup> M HClO<sub>4</sub> the pH is *ca.* 2.5 (using γ = 0.86 at

TABLE IV. Electronic Spectra of Cyclen Complexes.<sup>a</sup>

Complex	$\lambda_{\max}$ (nm)	$\epsilon$ ( $M^{-1} \text{ cm}^{-1}$ )
<i>cis</i> -[Co(cyclen)PO <sub>4</sub> ]	530	174
	365	140
<i>cis</i> -[Co(cyclen)(OH <sub>2</sub> ) <sub>2</sub> ] <sup>3+</sup>	496	209
	348	157
<i>cis</i> -[Co(cyclen)(OH) <sub>2</sub> ] <sup>+</sup>	540	185
	350	157

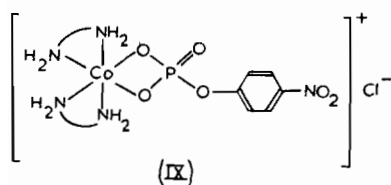
<sup>a</sup>The spectra of *cis*-[Co(cyclen)(OH)<sub>2</sub>]<sup>+</sup> and *cis*-[Co(cyclen)(OH<sub>2</sub>)<sub>2</sub>]<sup>3+</sup> were generated by base hydrolysis of *cis*-[Co(cyclen)Br<sub>2</sub>]<sup>+</sup>Br followed by acidification to pH 1 for the diaquo complex.

$I = 0.49 M$ ). The  $k_0$  term probably represents the spontaneous hydrolysis of the [Co(cyclen)OH<sub>2</sub>(OPO<sub>3</sub>H)]<sup>+</sup> species.

The present results lend credence to the mechanism shown in (V) suggested by Norman and Cornelius [18] to account for the cobalt(III)cyclen promoted hydrolysis of Co(NH<sub>3</sub>)<sub>4</sub>H<sub>2</sub>P<sub>3</sub>O<sub>10</sub>. This reaction displays a pH rate profile indicating the participation of an ionising group with a  $pK_a$  of *ca.* 8, assigned to a water molecule in the monodentate phosphato complex. The present results indicate that at  $[\text{OH}^-] = 1.93 \times 10^{-2} M$  and  $I = 0.49 M$  (pH *ca.* 12.2) the half life of the monodentate phosphato species is about 27 minutes. At pH 10.2 (the maximum pH employed by Norman and Cornelius) the half life will be *ca.*  $2.7 \times 10^3$  minutes and thus such a complex will be sufficiently long lived to participate in the reaction.

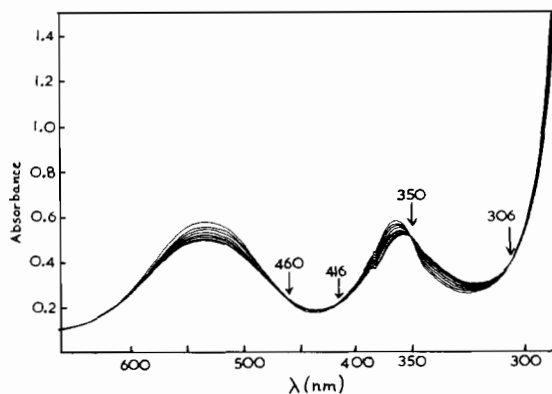
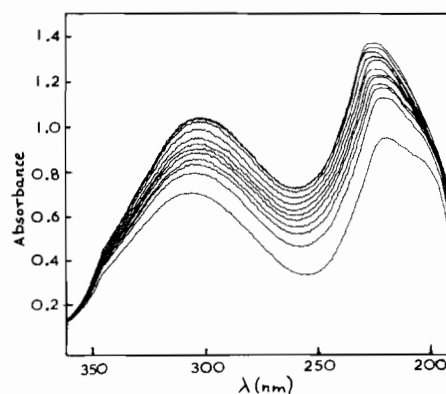
#### *p*-Nitrophenylphosphatobisethylenediaminecobalt(III)

Reaction of sodium *p*-nitrophenyl phosphate with *trans*-[CoCl<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup>Cl in concentrated aqueous

TABLE V. Solvent Deuterium Isotope Effect for the Acid Catalysed Loss of Monodentate Phosphate from [Co(cyclen)OH<sub>2</sub>(OPO<sub>3</sub>H)]<sup>+</sup>.

[HCl] or [DCl] ( <i>M</i> )	$10^3 k_{\text{obs}}(\text{DCl})$ ( $s^{-1}$ )	$k_{\text{D}}$ ( $M^{-1} s^{-1}$ )	$10^3 k_{\text{obs}}(\text{HCl})$ ( $s^{-1}$ )	$k_{\text{H}}$ ( $M^{-1} s^{-1}$ )	$k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$
58.0	5.50	0.086	4.29	0.065	1.3
38.6	4.27	0.098	3.02	0.065	1.5

$k_{\text{H}} = (k_{\text{obs}} - k_0)/[\text{H}^+]$ ;  $k_{\text{D}} = (k_{\text{obs}} - k_0)/[\text{D}^+]$  where  $k_0 = 5 \times 10^{-4} s^{-1}$ . Note  $k_{\text{D}}/k_{\text{H}} = k_{\text{D}_2\text{O}}/k_{\text{H}_2\text{O}}$ .

Fig. 5. Loss of monodentate phosphate from *cis*-[Co(cyclen)-OH(OPO<sub>3</sub>)]<sup>-</sup> in 0.05 *M* NaOH at 25 °C. The time interval between scans is 2 min.Fig. 6. Spectral changes observed for *cis*-[Co(en)<sub>2</sub>O<sub>3</sub>POC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>]<sup>+</sup> in aqueous solution at 25 °C. The time interval between scans is 3 min.

solutions gives *cis*-[Co(en)<sub>2</sub>O<sub>3</sub>POC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>]<sup>+</sup>Cl (IX). The complex has only limited water solubility. The i.r. spectrum (KBr disc) has the characteristic aromatic ring absorptions at 1590 and 1510  $\text{cm}^{-1}$  with a strong band at 1350  $\text{cm}^{-1}$  due to the  $\nu(\text{NO}_2)$  symmetrical vibration. Strong absorption due to P–O occurs at *ca.* 1120  $\text{cm}^{-1}$  (br). Dilute aqueous solutions of the complex show complex time dependent changes in the 200–350 nm range, Fig. 6. These spectral changes are probably associated with ring

TABLE VI. Loss of Monodentate Phosphate from *cis*-[Co(cyclen)OH(OPO<sub>3</sub>)]<sup>-</sup> in Basic Solution at 25 °C and I = 0.49 M (NaClO<sub>4</sub>).<sup>a</sup>

10 <sup>3</sup> [NaOH] (M)	10 <sup>3</sup> k <sub>obs</sub> (s <sup>-1</sup> )	10 <sup>2</sup> k <sub>OH</sub> (M <sup>-1</sup> s <sup>-1</sup> )
19.3	0.43	2.2
38.6	0.91	2.4
58.0	1.52	2.6
74.7	2.29	3.1
96.6	2.68	2.8
193.0	5.23	2.7
290.0	8.14	2.8
380.0	10.71	2.8
483.0	13.39	2.8

$k_{OH} = 2.7 \times 10^{-2} M^{-1} s^{-1}$

<sup>a</sup> Reaction monitored at 250 nm.

opening and concomitant isomerisation of the *cis* to the *trans* product Sargeson *et al.* [9] have shown that *cis*-[Co(pn)<sub>2</sub>O<sub>3</sub>POC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>]<sup>+</sup> hydrolyses in the pH range 6.5–13.5 to give *ca.* 35% *p*-nitrophenol and ~65% monodentate *p*-nitrophenyl phosphate. The ester hydrolysis is accelerated 10<sup>9</sup> fold relative to the uncoordinated ester in basic solution. We have also observed that solutions of *cis*-[Co(pn)<sub>2</sub>O<sub>3</sub>POC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>]<sup>+</sup> in 'tris' buffer pH 8.12 clearly show the release of *p*-nitrophenoxide at 400 nm ( $\epsilon = 18,700 M^{-1} cm^{-1}$  for the ion at 400 nm and pK<sub>a</sub> for the phenol = 7.15). No evidence for the release of *p*-nitrophenol was observed with *cis*-[Co(en)<sub>2</sub>O<sub>3</sub>POC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>]<sup>+</sup>. In basic solution it appears that the only significant reactions are ring opening and loss of the monodentate phosphate ester by S<sub>N</sub>1CB processes, with concomitant isomerisation of *cis* to *trans*-isomers.

X-ray work indicates considerable strain in the 4-membered phosphato chelate ring of [Co(en)<sub>2</sub>PO<sub>4</sub>] and presumably similar strain will be present in the phosphate ester derivative. In the *cis*-[Co(pn)<sub>2</sub>O<sub>3</sub>POC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>]<sup>+</sup> complex there will be some compensation for this strain due to the more flexible inert ligand. As a result ring opening is expected to be more rapid with the bisethylenediamine derivative. Hydrolysis of uncoordinated *p*-nitrophenyl phosphate is extremely slow with  $k = 1.4 \times 10^{-9} s^{-1}$  at pH 10.2 [25].

<sup>1</sup>H n.m.r. measurements also indicate that *p*-nitrophenyl phosphate is completely lost from the complex in acidic solution. The <sup>1</sup>H n.m.r. spectrum of an authentic sample of *p*-nitrophenyl phosphate in 0.1 M DCl in D<sub>2</sub>O has a typical AB quartet in the aromatic region with two doublets centred at 7.34  $\delta$  and 8.22  $\delta$  (J = 8 Hz). A solution of *cis*-[Co(en)<sub>2</sub>O<sub>3</sub>-

POC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>]<sup>+</sup> in 0.1 M DCl in D<sub>2</sub>O gives an identical n.m.r. spectrum indicating that complete hydrolysis of the complex had occurred in the time required for the measurement (*ca.* 15 min).

### Acknowledgement

We wish to thank the SERC for financial support and the award of a postdoctoral fellowship to one of us (R.B.).

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