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The Preparation of [Cotn$_2$PO$_4$] and [CotrpnPO$_4$] and Kinetics of Phosphato Complex Formation from the Highly Reactive [Cotn$_2$(OH)(H$_2$O)]$^{2+}$ and [Cotrpn(OH)(H$_2$O)]$^{2+}$ Cations

SALAH S. MASSOUD*

Department of Chemistry, Faculty of Science, Alexandria University, Alexandria (Egypt)

and RONALD M. MILBURN

Department of Chemistry, Boston University, Boston, MA 02215 (U.S.A.)

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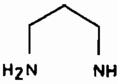
Abstract

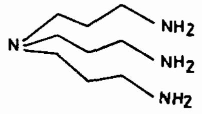
The complexes [Cotn$_2$PO$_4$]·2H$_2$O and [CotrpnPO$_4$]·5H$_2$O have been prepared and characterized. The kinetics of the anation reactions of [Co(N$_4$)(OH)(H$_2$O)]$^{2+}$ by phosphate was studied for the two systems (N$_4$) = tn$_2$ and trpn, at pH 6.5, 25 °C and μ = 1.0 M. The results are consistent with S_N1_{IP} mechanism involving rapid preequilibrium ion-pair formation, followed by a slow substitution step. The reactivity of [Co(N$_4$)(OH)(H$_2$O)]$^{2+}$ for phosphate complex formation decreases in the order trpn > tn$_2$ > en$_2$.

Introduction

Marked labilization is associated with the six-membered ring systems in tetraaminecobalt(III) species. The tripodal tetraamine 3,3′,3″-triaminotripropylamine (trpn) ligand, N(CH$_2$CH$_2$CH$_2$NH$_2$)$_3$ offers a system with a fixed *cis* geometry [1–3], as well as an extremely labile octahedral complex with respect to substitution reactions [1], when compared to those species derived from the bis(ligand) 1,3-diaminopropane (tn), NH$_2$CH$_2$CH$_2$CH$_2$NH$_2$ [1, 4, 5].



(tn)



(trpn)

The aquahydroxo(tetraamine)cobalt(III) cations, [Co(N$_4$)(OH)(H$_2$O)]$^{2+}$ with (N$_4$) = tn$_2$ or trpn have been found to have large catalytic effects on promoting the hydrolysis of ADP (adenosine 5′-diphosphate) and ATP (adenosine 5′-triphosphate) [6–9], and of phosphate esters [10, 11]. Also, the corresponding dihalo species [CotrpnX$_2$]$^+$ (X = F, Cl or Br) [1] and *trans*-[Cotn$_2$Cl$_2$]$^+$ [4, 5] exhibit high rates for substitution reaction, significantly greater than those observed for the [Coen$_2$X$_2$]$^+$ complex ions. In addition to the role of these complexes in catalysis, and because phosphate is one of the byproducts resulting from the hydrolysis of ATP [6–8, 12, 13], ADP [9], phosphate monoesters [10, 11, 14] or triphosphate [12, 15–18] by Co(N$_4$)(aq) species (the term 'aq' refers to (H$_2$O)$_2$, (OH)(H$_2$O) or (OH)$_2$, depending on pH, and charges omitted for simplicity), more information on the general characteristics and the kinetics of complex formation of Co(N$_4$)(aq) with phosphate is needed.

In general two mechanisms exist for cyclization of the oxyanions such as phosphate, carbonate and sulphate with cobalt(III) complexes. These mechanisms may involve substitution at the metal via the monocoordinated oxyanion with the displacement of coordinated solvent, or attack by coordinated solvent at the oxyanions, or the protonated form, of the dangling monodentate [19]. Therefore in this paper, the anation reactions of [Co(N$_4$)(OH)(H$_2$O)]$^{2+}$ ((N$_4$) = tn$_2$ or trpn) by phosphate are examined at pH 6.5, 25 °C and μ = 1.0 M, and the phosphato product of each reaction was isolated and characterized.

Experimental

1,2-Diaminoethane (en) and 1,3-diaminopropane (tn) were purchased from Aldrich Chemical Co. and were used without further purification. The 3,3′,3″-triaminotripropylamine tetrahydrochloride hemihydrate (trpn·4HCl·$\frac{1}{2}$H$_2$O) was obtained from Strem Chemical Co. All other chemicals were reagent grade quality.

Caution: The perchlorate complexes should be treated as potentially explosive, and always require precautions, including limitations in the amounts handled.

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*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

General Techniques

Electronic spectra and kinetics of complex formation of [$Cotn_2PO_4$] were carried out with a Cary 210 spectrophotometer. The kinetics of anation of [$Cotrpn(OH)(H_2O)]^{2+}$ by phosphate was studied by a Durrum-D110 stopped-flow spectrophotometer in conjunction with a Tektronix oscilloscope for visual display of the reaction trace. pH measurements were made using an Orion Research pH meter model 601 with a combined pH electrode (4 M KCl–sat.Ag/AgCl) from Fisher Scientific Company. The elemental analyses for the phosphato complexes were performed by Galbraith Laboratories, Knoxville, TN, U.S.A.

Preparation of Complexes

[$Cotn_2PO_4$]·$2H_2O$

This complex was prepared by dissolving 2.0 g of *trans*-[$Cotn_2Cl_2$]Cl·$3\frac{1}{2}H_2O$ [20] and 2.0 g of $Na_3PO_4 \cdot 2H_2O$ in water (15 ml). The purple solution was heated at 80 °C, with stirring for 3 h, during which the volume of the solution was reduced to ≃5 ml. Upon cooling, and after the addition of an equal volume of methanol, the rose precipitate separated out was filtered off. Recrystallization was achieved by dissolving the product in a minimum volume of warm water, filtering and reprecipitating with methanol. The precipitate was collected by filtration, washed with cold water, methanol and ether, and then air dried (yield 25%). *Anal.* Calc. for [$Co(C_3H_{10}N_2)_2PO_4$]·$2H_2O$: C, 21.31; H, 7.15; N, 16.57. Found: C, 21.45; H, 7.15; N, 16.57%. This complex was previously prepared as a tetrahydrate using a different procedure [20].

[$CotrpnPO_4$]·$5H_2O$

To 0.5 mmol of finely powdered [$Cotrpn\text{-}CO_3$]$ClO_4 \cdot H_2O$ [2], 0.6 ml of 6 M $HClO_4$ was added; this was followed by heating at 60 °C for 5 min. The resulting solution was treated with H_3PO_4 (0.5 mmol), diluted to 6 ml, the pH was adjusted to 7.0 by 2 M KOH, and then heated at 60 °C for 15 min. The product which separated out, after standing *in vacuo* over P_4O_{10} for 3 days, was treated with anhydrous methanol (10 ml). The undissolved $KClO_4$ was filtered off and the filtrate was reduced to a small volume by a rotary evaporator. The crude solid was redissolved in 5 ml of anhydrous methanol and after filtration the solvent was allowed to evaporate at room temperature. Further recrystallization was achieved from ethanol (yield 50%). *Anal.* Calc. for [$Co(C_9H_{24}N_4)PO_4$]·$5H_2O$: C, 25.01; H, 7.93; N, 12.96; P, 7.12; Co, 13.6. Found: C, 24.92; H, 7.86; N, 12.71; P, 7.12; Co, 12.5%.

[$Coen_2PO_4$]·$2H_2O$

This complex was prepared from *trans*-[$Coen_2Cl_2$]Cl, essentially as described for the perchlorate salt [21].

Kinetic Measurements

All rates were measured at 25 °C under pseudo first-order conditions using excess phosphate.

Kinetics of anation of [$Cotn_2(OH)(H_2O)]^{2+}$ by phosphate

A stock solution of 0.01 M [$Cotn_2(OH)(H_2O)]^{2+}$ was prepared by dissolving a weighed sample of *trans*-[$Cotn_2(OH)(H_2O)](ClO_4)_2$ [20] and $NaClO_4$ (to adjust ionic strength) in deionized distilled water. The pH of the solution was adjusted to 6.5, immediately before use, with NaOH or $HClO_4$ using a glass stick ('dotting', the volume changes were negligible) [7]. Thermostated aliquots of the complex were added rapidly to equal volumes of equilibrated phosphate solution of appropriate concentration (0.025–0.075 M KH_2PO_4) preadjusted to pH 6.5. The final complex concentration, after mixing, was 5×10^{-3} M, with $\mu = 1.0$ M. The reaction mixture was rapidly transferred to a thermostated 1 cm quartz cell. The change in absorbance at 536 nm was monitored as a function of time. The wavelength used is one at which substantial differences in absorbances exist between the reactants and products.

Kinetics of anation of [$Cotrpn(OH)(H_2O)]^{2+}$ by phosphate

Separate solutions of KH_2PO_4 (0.025–0.300 M) were prepared and the pH was adjusted to 6.5 as described above. The diaqua complex ion [$Cotrpn(H_2O)_2]^{3+}$ was generated by treating a weighed sample of [$CotrpnCO_3$]$ClO_4 \cdot H_2O$ (0.50 mmol) [2] with 0.6 ml of 6 M $HClO_4$ followed by heating at 60 °C for 5 min. Then, $NaClO_4$ and water were added to give a solution of final complex concentration 0.01 M. The pH of the solution was adjusted to 6.5 immediately before use; these solutions should not be kept for long periods of time [3]. The phosphate and complex solutions were equilibrated at 25 °C and introduced separately into thermostated storage syringes of an automated stopped-flow assembly. Runs were made in the usual fashion at wavelength 550 nm. All pseudo first-order rate constants, calculated from the stopped-flow oscilloscope traces, are reported as the average of at least two kinetic runs.

Results and Discussion

Chelate Structure

The phosphato cobalt(III) complexes [$Cotn_2PO_4$]·$2H_2O$ and [$CotrpnPO_4$]·$5H_2O$ were prepared by the reaction of *trans*-[$Cotn_2Cl_2$]Cl·$3\frac{1}{2}H_2O$ with Na_3PO_4 and the reaction of [$Cotrpn(H_2O)_2]^{3+}$ with H_3PO_4, respectively. The spectral features of the isolated phosphato complexes together with [Co-

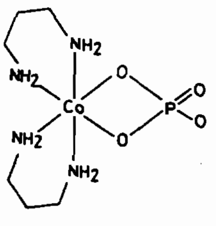
TABLE 1. Electronic spectra of diaqua- and phosphato(tetraamine)cobalt(III) complexes

Complex	Medium	$\lambda_{max}(\epsilon)^a$	$\lambda_{max}(\epsilon)$	Reference
cis-$[Cotn_2(H_2O)_2](ClO_4)_3 \cdot H_2O$	0.1 M $HClO_4$	506(53.5)	362(65.4)	22
$[Cotn_2PO_4] \cdot 2H_2O$	H_2O	536(108.0)	369(99.7)	this work
$[Cotrpn(H_2O)_2](ClO_4)_3 \cdot 2H_2O$	0.1 M $HClO_4$	530(57)	369(90.8)	3
$[CotrpnPO_4] \cdot 5H_2O$	H_2O	550(114.5)	373(104.0)	this work
cis-$[Coen_2(H_2O)_2]^{3+}$	0.05 M HNO_3	492(80.9)	355(60)	23
$[Coen_2PO_4] \cdot H_2O$	H_2O	529(112)	377(98)	24

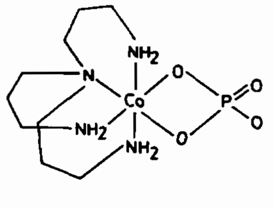
$^a\lambda$ in nm and ϵ in M^{-1} cm^{-1}.

$en_2PO_4]$, presented in Table 1 and depicted in Fig. 1, are very similar. The positions of the two λ_{max} of the diaqua complex ions $[Co(N_4)(H_2O)_2]^{3+}$ are shifted to longer wavelengths upon complexation with phosphate. Furthermore, at pH ≈6.5 and initial $[H_2PO_4^-]/[Co(N_4)(aq)]$ concentration ratios up to 30, the product spectrum was identical to that formed at the 1:1 molar ratio.

The four membered bidentate phosphato chelate ring was established by X-ray structure determination in $[Coen_2PO_4] \cdot H_2O$ [14] and by the ^{31}P NMR spectra of solutions prepared from the orthophosphate and $Cotn_2(aq)$ [25]. The latter study has shown that the major species formed over the pH range 6–9 is $[Cotn_2PO_4]$ in which the phosphate group is acting as a bidentate ligand in the four membered chelate ring [25]. Thus the phosphato chelate ring in $[Cotn_2PO_4]$ and $[CotrpnPO_4]$ complexes can be represented as shown below.



$(Cotn_2PO_4)$



$(Co\,trpn\,PO_4)$

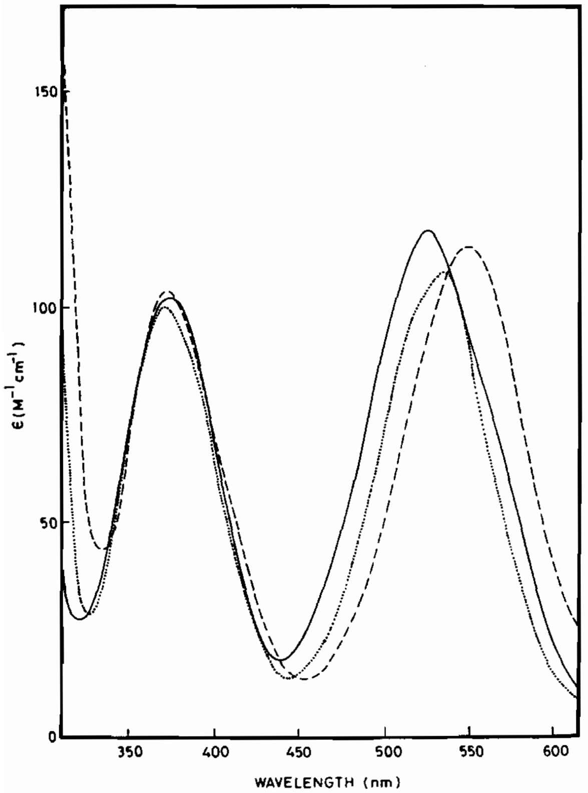
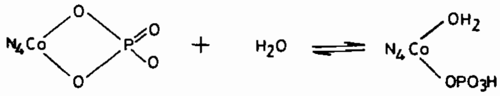


Fig. 1. Absorption spectra of $[Co(N_4)PO_4]$ complexes in aqueous medium: (——), $N_4 = en_2$; (·······), $N_4 = tn_2$; (– – –), N_4 = trpn.

With phosphato cobalt(III) complexes, an equilibrium between the monodentate and the bidentate phosphato species exist, i.e. an equilibrium (1) may occur [19, 26, 27].



(1)

The diaqua-, aquahydroxo- and dihydroxo(tetraamine)cobalt(III) complex ions are related by the acid–base equilibria shown in reactions (2) and (3).

$$[Co(N_4)(H_2O)]^{3+} + H_2O \overset{K_1}{\rightleftharpoons} [Co(N_4)(OH)(H_2O)]^{2+} + H_3O^+ \quad (2)$$

$$[Co(N_4)(OH)(H_2O)]^{2+} + H_2O \overset{K_2}{\rightleftharpoons} [Co(N_4)(OH)_2]^+ + H_3O^+ \quad (3)$$

We have determined the values of pK_1 and pK_2 by potentiometric titrations. These values are 4.78 and 7.22 (25 °C, $\mu = 0.5$ M) for $(N_4) = tn_2$, under conditions where *cis–trans* isomerization had already proceeded to equilibrium level [22]. The corresponding values are 4.82 and 7.52 (25 °C, $\mu = 0.1$ M) respectively, for (N_4) = trpn [3]. Thus, it can be assumed that the aquahydroxo complex is the major reactive species in the middle pH range.

Kinetics of Anation of $[Co(N_4)(OH)(H_2O)]^{2+}$ by Phosphate

The kinetics of phosphato complex formation for $[Cotn_2(OH)(H_2O)]^{2+}$ and $[Cotrpn(OH)(H_2O)]^{2+}$ were conducted under pseudo first-order conditions using excess phosphate, which also served as an effective buffer. The pH of the reaction mixture was strictly constant throughout the course of the reaction. All rate constants were measured at 25 °C and pH 6.5, in media of ionic strength 1.0 M $(NaClO_4)$. The pseudo first-order rate constants, k_{obs}, which were obtained from a linear least-squares analysis of the plot of $\ln(A_\infty - A_t)$ versus t, where A_t and A_∞ are the absorbances of the reacting solution at time t and after four half-lives, are collected in Table 2. The final absorbances, A_∞ were calculated from the known spectrum of $[Cotn_2PO_4]$ and $[CotrpnPO_4]$.

TABLE 2. Variation of k_{obs} for the reactions of aquaamine-cobalt(III) complexes with phosphate, determined at pH 6.5, 25 °C, μ = 1.0 M and $[Co(N_4)(OH)(H_2O)]^{2+}$ = 5 mM

(N_4)	$[PO_4]_T$ (mM)	k_{obs} (s^{-1})
tn_2	12.50	3.40×10^{-3}
	18.75	4.43×10^{-3}
	25.00	4.93×10^{-3}
	31.25	5.43×10^{-3}
	37.50	5.79×10^{-3}
trpn	12.50	0.30
	25.00	0.40
	37.50	0.51
	50.00	0.55
	75.00	0.60
	100.0	0.69
	150.0	0.73

Plots of $1/k_{obs}$ vs. $1/[PO_4]_T$ give straight lines with correlation coefficients r = 0.998 for $[Cotn_2(OH)(H_2O)]^{2+}$ and r = 0.993 for $[Cotrpn(OH)(H_2O)]^{2+}$, respectively.

Values of k_{obs} increase with increasing phosphate concentration, and tend to limiting values at high phosphate concentrations. These data are consistent with an interchange mechanism involving the formation of a precursor outer-sphere species in a rapid preequilibrium, followed by rate determining interchange between outer and inner sphere ligands. Thus, the anation of $[Co(N_4)(OH)(H_2O)]^{2+}$ by phosphate can be considered to occur via an ion-pair S_N1_{IP} mechanism, analogous to the system where $(N_4) = en_2$ studied by Lincoln and Stranks [24].

In terms of the presumed reactive species, the process may be represented as follows

$$[Co(N_4)(OH)(H_2O)]^{2+} + HPO_4^{2-} \overset{\text{very fast, } K_{IP}}{\rightleftharpoons} [Co(N_4)(OH)(H_2O)^{2+}\cdot HPO_4^{2-}] \quad (4)$$

$$[Co(N_4)(OH)(H_2O)^{2+}\cdot HPO_4^{2-}] \xrightarrow{k} [Co(N_4)(OH)(OPO_3H)] + H_2O \quad (5)$$

$$[Co(N_4)(OH)(OPO_3H)] \xrightarrow{\text{fast}} [Co(N_4)PO_4] + H_2O \quad (6)$$

For pseudo first-order conditions of excess phosphate and constant pH, the rate of the reaction is given by

$$\frac{d[Co(N_4)(OH)(OPO_3H)]}{dt} = k_{obs}C_t$$

$$= k[Co(N_4)(OH)(H_2O)^{2+}\cdot HPO_4^{2-}] \quad (7)$$

where C_t is the total analytical concentration of the complex including the hydroxoaqua and ion-pair species. In this suggested mechanism, it can be shown that

$$k_{obs} = \frac{kK_{IP}[PO_4]_T}{1 + K_{IP}[PO_4]_T} \quad (8)$$

K_{IP} is the conditional overall ion-pair equilibrium constant for association of the hydroxoaqua cation with the phosphate anion, $[PO_4]_T$ represents the total concentration of the phosphate. According to eqn. (8) and at high phosphate concentration, $K_{IP}[PO_4]_T \gg 1$, a limiting rate will be observed. Equation (8) can be rearranged into the more appropriate form

$$\frac{1}{k_{obs}} = \frac{1}{kK_{IP}} \times \frac{1}{[PO_4]_T} + \frac{1}{k} \quad (9)$$

Thus, according to eqn. (9), plots of $1/k_{obs}$ versus $1/[PO_4]_T$ should give straight lines, with slopes equal to $1/kK_{IP}$ and intercepts equal to $1/k$. The values of k and K_{IP} for the two systems studied are tabulated in Table 3, and are compared with those for $[Coen_2(OH)(H_2O)]^{2+}$ system.

An alternative limiting S_N1 mechanism might also be proposed for the reaction

$$[Co(N_4)(OH)(H_2O)]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(N_4)(OH)]^{2+} + H_2O \quad (10)$$

TABLE 3. Comparison of the ion pairing equilibrium constants (K_{IP}) and the first-order rate constants for inner-sphere outer-sphere interchange (k) for the reactions of aquahydroxo(tetraamine)cobalt(III) complexes with orthophosphate (μ = 1.0 M)

Complex ion	pH	K_{IP} (M^{-1}) (temperature (°C))	k (s^{-1}) 25 °C)
$[Cotn_2(OH)(H_2O)]^{2+}$	6.5	49.5 (25)	8.98×10^{-3}
$[Cotrpn(OH)(H_2O)]^{2+}$	6.5	36.3 (25)	0.85
cis-$[Coen_2(OH)(H_2O)]^{2+a}$	6.94	60 (47.9)	8.99×10^{-6}

^{a}Data extracted from ref. 24.

$$[Co(N_4)(OH)]^{2+} + HPO_4^{2-} \xrightarrow{k_2} [Co(N_4)(OH)(HPO_4)] \qquad (11)$$

which corresponds to the rate eqn. (12).

$$\frac{d[Co(N_4)(OH)(HPO_4)]}{dt} = \frac{k_1k_2[Co(N_4)(OH)(H_2O)^{2+}][HPO_4^{2-}]}{k_{-1} + k_2[HPO_4^{2-}]} = k_{obs}[Co(N_4)(OH)(H_2O)^{2+}] \qquad (12)$$

The latter expression will lead to a limiting rate when $k_2[HPO_4^{2-}] \gg k_{-1}$. However, the importance of ion pairing in reactions between appositely charged ions has been pointed out [24].

The assumption of rapid ring closure via hydroxide substitution (eqn. (6)) is believed to be assisted by 'chelate effect' or 'neighbouring group effect'. The hydroxide group in $[Co(N_4)(OH)(HPO_4)]$ is ligated *cis* to the dangling monodentate phosphato group; a favourable position for intramolecular chelation [28, 29] where the metal is providing a driving force in producing the chelate ring.

It is evident from the data in Table 3 that the reactivity order of the aquahydroxo(tetraamine)cobalt(III) ions for phosphato complex formation is parallel to what has been observed for the aquation of their dihalo species [1, 4] and for the hydrolysis of ATP [6], i.e. the reactivity decreases in the order $Cotrpn^{3+} > Cotn_2^{3+} > Coen_2^{3+}$ and the complex ion $[Cotrpn(OH)(H_2O)]^{2+}$ is $\simeq 10^5$ more reactive than $[Coen_2(OH)(H_2O)]^{2+}$ ion.

In conclusion, the complex Cotrpn(aq) represents a compromise for a system of fixed *cis* geometry, due to the tripodal nature of the trpn ligand, and a fully labile octahedral cobalt(III) species. Furthermore, attention has to be paid to the hydrolysis reactions of phosphate derivatives, especially when reactive cobalt(III) complexes are used in excess, due to the possibility of interaction of these complexes with the phosphate byproduct.

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