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Synthesis and Hydrolysis of the Pentammine(diethylphosphato) Cobalt(III) Cation. Comments on the Reaction of $[Co(NH_3)_5OH]^{2+}$ with Neutral Phosphate Esters

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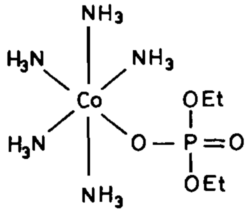
Recent work in these laboratories [1, 2] has shown that simple non-labile mono-aquo metal complexes function as general base catalysts in the hydrolysis of neutral phosphate and phosphonate esters in dilute aqueous solution. In order to elaborate on these studies, consideration has been given to the reaction of $[Co(NH_3)_5OH]^{2+}$ with 4-nitrophenyldiethylphosphate (PNPDEP). A general base catalytic (GBC) mechanism will yield free (uncomplexed) diethylphosphoric acid in solution, while direct nucleophilic displacement would give the complex $[Co(NH_3)_5(DEP)]^{2+}$ (where DEP is the monoanion of diethylphosphoric acid). Accordingly the complex $[Co(NH_3)_5(DEP)]^{2+}$ (I) has been synthesized and its hydrolysis characteristics studied. The determined rates of aquation and base hydrolysis were typical for anionopentammine cobalt(III) complexes.



I

Experimental

All reagents used were the purest available. Diethylphosphoric acid was supplied by Kodak and 4-nitrophenyldiethylphosphate (PNPDEP) was synthesized by the reaction of diethylchlorophosphate with dry sodium 4-nitrophenate in toluene [2, 3]. (**Caution**: PNPDEP should be handled with care as it exhibits anticholinesterase activity.) The cobalt complex $[Co(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ was synthesized as described by Sargeson *et al.* [4].

$[Co(NH_3)_5(DEP)](CF_3SO_3)_2$ (I)

0.71 g diethylphosphoric acid (4.6 mmol) and 2.72 g $[Co(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ (4.6 mmol) were dissolved in ~50 ml absolute ethanol. To this was added 0.5 g of triethylamine, and the whole was refluxed for 30 min under dry nitrogen. After reflux, the solution was reduced under vacuum at 45 °C to ~2 ml in volume, filtered through a no. 3 glass sinter and left for several days under dry nitrogen at −10 °C. Pink microcrystals formed, were collected by filtration, washed with 0.5 ml ice cold propan-2-ol and vacuum dried over silica-gel. The product was extremely soluble in H_2O, MeOH and EtOH and recrystallization proved impracticable. *Anal.* Calc. for $C_6H_{25}N_5F_6O_8PS_2Co$: C, 12.79; H, 4.47; N, 12.43. Found: C, 12.10; H, 4.23; N, 11.76%. The visible absorption spectrum in 0.1 M HNO_3 gave λ_{max} (ϵ (mol^{-1} cm^{-1})): 505(53) and 355(43). The visible spectrum was unchanged in the pH range 1–10 indicating no ionizable protons in this range. IR spectra in KBr discs indicated strong P–O ethyl stretching modes at 970 and 1058 cm^{-1} which were not apparent in the starting materials. ^{31}P NMR spectra were run on a Jeol FX60 FT instrument at room temperature. They were consistent with the structure I for the title compound. NMR solutions were 1:1 (v/v) H_2O/D_2O (D_2O to provide lock signal) and were 0.05 M in EDTA to prevent line broadening by any paramagnetic cobalt(II) species. All spectra were referenced to external H_3PO_4. pH was adjusted by the addition of 1 M NaOH and all solutions were ~20 mM with respect to phosphorus. UV–Vis kinetic measurements were made using an LKB 4050 spectrophotometer fitted with a data logger and scanning measurements were made on a Shimadzu UV 240 instrument. Reactions were initiated by adding a few milligrams of solid $[Co(NH_3)_5(DEP)]^{2+}$ to a 1 cm spectrophotometer cell maintained at 35(±0.1) °C. All kinetics were carried out at $I = 0.1$ mol dm^{-3} ($Li(CF_3SO_3)$).

Results and Discussion

Initial spectral scans at 40 °C and pH 11.0 (Fig. 1) showed that a slow reaction, presumably release of diethylphosphate anion (later confirmed by ^{31}P NMR), occurred and could be monitored at 496 or 360 nm, wavelengths of maximum absorption change. However, slow decomposition of the complex occurred at the pHs necessary to see any reaction within a reasonable time period. This decomposition manifests itself in slight absorbance increases in the 600–700 nm range of the spectrum as seen also in Fig. 1. As a result of this, only initial rate constants could be obtained over 1–1.5 half lives. These were calculated by exponential curve fitting routines based on the algorithm of Gampp [5]. Values at 2.5, 5.0 and 7.5 millimolar hydroxide ion concentrations are given in Table I.

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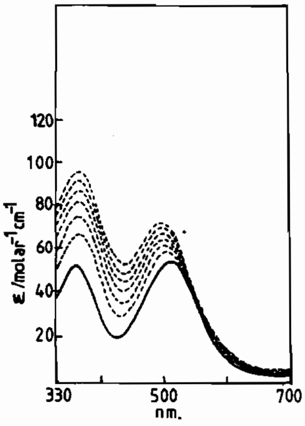

Fig. 1. Repeat scan spectrum for reaction of $[Co(NH_3)_5(DEP)]^{2+}$ in aqueous solution at 40 °C and $I = 0.1$. Time interval is 7 min and pH = 11.0.

TABLE I. Rate Constants for the Hydrolysis of $[Co(NH_3)_5(DEP)]^{2+}$ by Aqueous Base at 35 °C and $I = 0.1$ mol dm^{-3}

$10^3 \times [OH]$ (mol dm^{-3})	$10^2 \times k_{obs}$ (s^{-1})	
	496 nm	360 nm
2.5	2.44	2.41
5.0	4.65	4.99
7.5	6.80	7.60

As can be seen, reasonably reproducible rates result which give a mean second order rate constant for reaction (1)

$$[Co(NH_3)_5(DEP)]^{2+} + OH^- \longrightarrow [Co(NH_3)_5OH]^{2+} + DEP^- \qquad (1)$$

The value deduced for k_{OH} at 35 °C and $I = 0.1$ mol dm^{-3} is 9.6 mol^{-1} dm^2 s^{-1}. A value for the first order spontaneous aquation rate by H_2O (k_{aq}) in 0.1 M CF_3SO_3H has also been measured and has a value under similar conditions of $\sim 2 \times 10^{-5}$ s^{-1}. These values serve to illustrate the stability, with respect to ligand substitution, of complex I in aqueous solution. An approximate half-life for the stability of the complex at pH 7.5 can be calculated from eqn. (2)

$$k_{calc} = k_{aq} + k_{OH}\,OH \qquad (2)$$

Inserting the experimentally determined values of k_{aq} and k_{OH}, a half life for solvolysis at pH 7.5 and 35 °C is predicted to be about 6 h; the value is of the order expected for solvolysis of pentammine cobalt(III) complexes [6]. Some data are available on the corresponding dimethylphosphato cobalt(III) complex which has been synthesized by Schmidt and Taube [7]. This complex was not isolated as a solid but was characterized by ion chromatography and UV–Vis spectroscopy in aqueous solution. A detailed kinetic study was not carried out but the aquation of the dimethylphosphate ester complex was said to be very slow and might be expected to be similar for that of the complex $[Co(NH_3)_5H_2PO_4]^{2+}$ where a k_{aq} value of 2.18×10^{-7} s^{-1} has been reported [8] at 25 °C.

Results of ^{31}P NMR experiments are shown in Figs. 2, 3 and 4. Figure 2a shows the spectrum of diethylphosphate ($\delta = 0.80$) while Fig. 2b shows that of $[Co(NH_3)_5(DEP)]^{2+}$ under the same conditions ($\delta = 7.81$). Figure 3 then clearly shows the appearance of free ester when complexed DEP is treated with base at room temperature. There is no indication of intermediate product formation.

Given the stability of $[Co(NH_3)_5DEP]^{2+}$ in aqueous solution at neutral pH, some comment can be

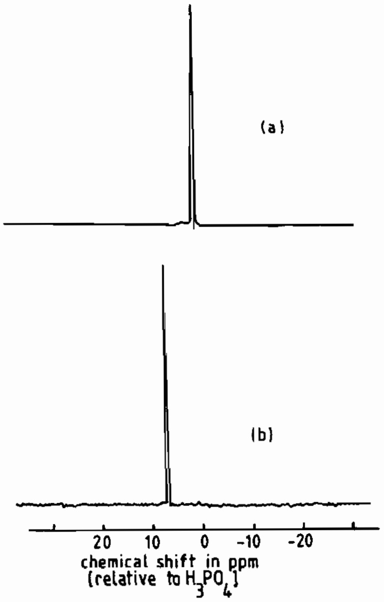

Fig. 2. ^{31}P NMR spectra of (a) diethylphosphoric acid and (b) $[Co(NH_3)_5(DEP)]^{2+}$ at 20 millimolar concentration and pH 11.3. Room temperature.

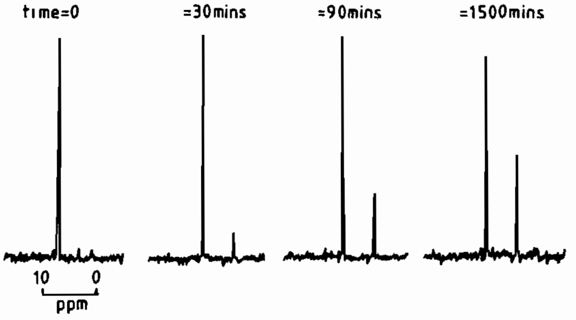

Fig. 3. ^{31}P NMR spectra of reaction of $[Co(NH_3)_5(DEP)]^{2+}$ with OH^- at pH 11.3 and room temperature.

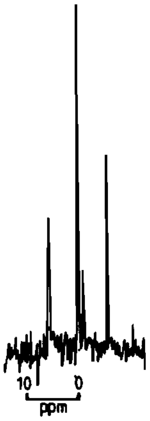

Fig. 4. ^{31}P NMR spectrum of reaction of 20 mM [Co(NH_3)$_5$-OH] with DNPDEP at pH 7.3 (both 20 mM) at 35 °C for 4 h.

made on the mechanism of the reaction of pentamminehydroxo cobalt(III) with *p*-nitrophenyldiethylphosphate (and related compounds). The half life for this reaction at pH 7.3 with the concentration of cobalt complex and phosphate ester being approximately equal to 20 millimolar is expected to be about 0.8 h at 35 °C. Thus, if direct nucleophilic attack of the phosphorus ester is the dominant pathway in the reaction, formation of complexed DEP should be observable in the ^{31}P NMR spectrum.

Conversely, if a general base catalyzed pathway is the preferred mechanism, then free DEP should be observable in the ^{31}P NMR spectrum (Fig. 4) of a 20 mM solution both in $[Co(NH_3)_5H_2O]^{2+}$ and *p*-nitrophenyldiethylphosphate which has been equilibrated at 35 °C for 4 h at pH 7.3 (pH-stat). The spectrum shows the presence of both complexed DEP ($\delta = 7.62$) and uncomplexed DEP ($\delta = 0.71$) with probably some free *p*-nitrophenyldiethylphosphate present ($\delta = -0.42$) indicating that both GBC and nucleophilic pathways occur. The predominant product is, however, uncomplexed diethylester, suggesting that general base catalysis under these conditions is the preferred pathway, though direct nucleophilic attack also contributes to the overall hydrolysis of the *p*-nitrophenyldiethylphosphate ester. Clearly a knowledge of the rate of anation of $[Co(NH_3)_5HO]^{2+}$ by diethylphosphate is required for a complete analysis of the interaction, although studies in this laboratory reveal no significant anation reaction to be observable under the experimental conditions employed. Additionally in Fig. 4, a fourth phosphorus species is apparent at 6.66 ppm upfield of H_3PO_4. This signal is puzzling, but is well pronounced and is not present in the starting materials. The most obvious candidate to cause this resonance is tetraethylpyrophosphate which could arise from the nucleophilic attack of free diethylphosphate anion on coordinated DEP. Certainly inductive effects of the metal center would make the coordinated phosphorus center more susceptible to nucleophilic attack. The ^{31}P NMR spectrum of tetraethylpyrophosphate does occur well upfield of H_3PO_4 (~13 ppm in $CDCl_3$ [9]). Further work is underway to establish the exact nature of this unexpected fourth species but, nevertheless, the results confirm the function of the metal complex as a general base catalyst in the hydrolysis of neutral phosphate esters.

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