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Bidentate Linkage Isomerization and Phosphate Hydrolysis in (Triphosphato)tetraamminecobalt(III)

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The isomerization and phosphate-hydrolysis reactions of the two linkage isomers of (triphosphato)tetraamminecobalt(III) containing six- and eight-membered chelate rings have been investigated by phosphorus-31 NMR and by visible spectroscopy. In aqueous solution the isomerization reaction between the β,γ- and α,γ-complexes has an equilibrium constant of 0.07 favoring the β,γ-complex at 40.0 °C, pH 6.5. Thermodynamic parameters for the isomerization determined from the dependence of the equilibrium constant upon temperature are $\Delta H° = 5.6$ kcal/mol and $\Delta S° = 16$ cal/(mol K). The first-order rate constants for phosphate hydrolysis in the two isomers are 3.0×10^{-6} and 6.5×10^{-6} s^{-1} for the β,γ-complex and the α,γ-complex, respectively, at 40.0 °C, pH 6.5. The rates of phosphate hydrolysis for the two isomers are nearly identical despite the difference in stability of the two chelate rings of different size.

Previous papers[1-5] have demonstrated the usefulness of (dihydrogen triphosphato)tetraamminecobalt(III) in the study of the interactions between the triphosphate ligand and metal ions. The linkage isomers β,γ-Co(NH$_3$)$_4$H$_2$P$_3$O$_{10}$ (**1**), referred to in this paper as the β,γ-complex, and α,γ-Co-(NH$_3$)$_4$H$_2$P$_3$O$_{10}$ (**2**), referred to as the α,γ-complex, have been characterized by phosphorus-31 NMR[3,5] and X-ray diffraction studies[6-8] as bidentate triphosphato complexes with six- and eight-membered chelate rings, respectively.
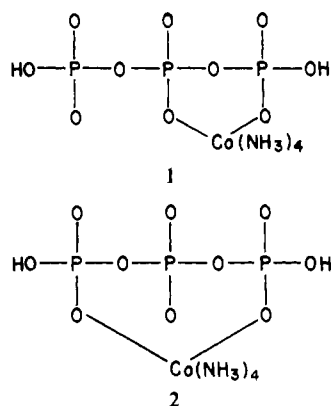
These complexes are of interest due to the isomerization reaction which interconverts the two isomers. Linkage-isomerization reactions are in themselves unusual, and the involvement of bidentate ligands in these reactions is extremely rare.[9-11] This paper reports thermodynamic data on the isomerization reaction between the α,γ- and β,γ-complexes. The involvement of triphosphate as the coordinating ligand makes the results relevant to biochemical systems in which the mode of binding of biological phosphates may affect the rate of enzymatic catalysis.

The rate of phosphate hydrolysis may be dependent on the inherent ring strain present in phosphate-containing rings.[11-13]

Since the isomers of Co(NH$_3$)$_4$H$_2$P$_3$O$_{10}$ differ only as a result of the different sizes of chelate rings, they present a unique opportunity to study the effects of ring strain on phosphate-hydrolysis reactions of metal complexes.

Experimental Section

General Procedures. The cation- and anion-exchange resins used were BioRad AG 50W-X2 and AG 1-X2, 100–200 mesh. All pH measurements were made on an Orion Model 701A digital pH meter fitted with a research grade microcombination electrode. Standardization of the electrode was made with the appropriate NBS buffer solution. UV–visible spectra were taken on a Cary 219 spectrophotometer.

Synthesis of β,γ-Co(NH$_3$)$_4$H$_2$P$_3$O$_{10}$ and α,γ-Co(NH$_3$)$_4$H$_2$P$_3$O$_{10}$. Elemental analysis, phosphorus-31 NMR, and X-ray crystal structures have previously been reported for these complexes.[3,5,7,8] A revised procedure for their preparation was necessary to produce a workable yield of the α,γ-complex.

The β,γ-complex, **1**, and the α,γ-complex, **2**, are synthesized by the reaction of [Co(NH$_3$)$_4$(H$_2$O)$_2$]$^{3+}$ with sodium triphosphate followed by the separation of the two isomers by anion-exchange chromatography. A 20 mM solution of the aquo complex is generated by the reaction of 2.58 g of [Co(NH$_3$)$_4$CO$_3$]NO$_3$·^{1}/$_2$H$_2$O in a 10% excess (22 mL) of 1 M HNO$_3$ followed immediately by dilution to 500 mL. The aquo complex is slowly added to a solution of 3.5 g of Na$_5$P$_3$O$_{10}$ dissolved in 100 mL of water. The resulting solution is adjusted to pH 6.5 with 1 M KOH, and the solution is then mechanically stirred. The reaction solution changes from a cloudy white mixture in the initial minutes of the reaction to a deep red solution containing an oily precipitate. The precipitate formed in the initial minutes dissolves over the course of 24 h of continuous vigorous stirring. A total reaction time of 48 h has proven to be the optimum time interval for greatest yields of the triphosphato complex. After the alloted time interval the solution is removed from the reaction vessel and adjusted to pH 8.0. The solution is then charged onto a 3 × 48 cm anion-exchange column which has been pretreated with 0.10 M ethylenediamine–HCl buffer at pH 8.0. After the reaction solution is passed through the column, chromatography with 0.10 M pyridine–HCl buffer at pH 5.0 produces five major bands. The first two are the ortho- and pyrophosphato complexes of cobalt(III) and may be discarded. The slower moving β,γ-complex and trailing α,γ-complex are then collected in turn. The last band has been identified as the tridentate triphosphato complex Co(NH$_3$)$_3$H$_2$P$_3$O$_{10}$ and can also be discarded. The complexes of interest are then individually concentrated on two smaller anion-exchange columns and eluted with 0.05 M HCl. Addition of 1 vol of ethanol to the resulting solutions followed by storage at −20 °C yields long needlelike red crystals for the β,γ-complex in 72 h and a fine pink powder for the α,γ-complex in 24 h. The overall yield of β,γ-complex is 50% while the yield for the α,γ-complex is 9%.

Kinetics. The phosphate hydrolysis of the two linkage isomers was followed by monitoring the total production of the orthophosphate anion by the method previously described.[1,14] The technique involves

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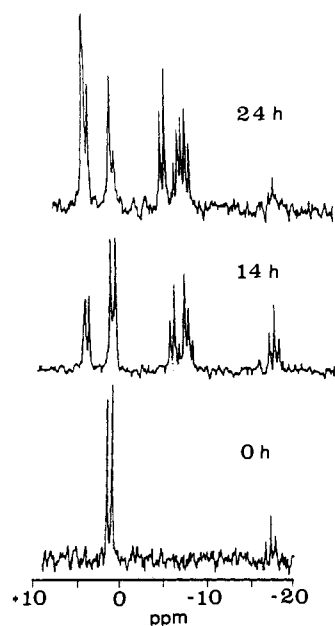(14) Chen, P.; Toribara, T.; Warner, H. *Anal. Chem.* **1956**, *11*, 1756.

Figure 1. Phosphorus-31 NMR spectra of α,γ-Co(NH₃)₄H₂P₃O₁₀ at pH 6.5, 40 °C, showing the results of hydrolysis and isomerization to the β,γ-complex.

the reduction of the cobalt(III) complexes by acidic vanadium(II) followed by the removal of the labile metal ions by cation-exchange chromatography and the analysis for the orthophosphate anion by a spectrophotometric phosphomolybdate method.[14] All experiments were maintained at an ionic strength of 1.0 M by tetramethylammonium nitrate. A thermostated reaction cell was maintained at constant temperature within 0.05 °C by a water jacket. The desired pH was reached and maintained with delivery of 1 M KOH or 1 M HNO₃ into the reaction solution from a microsyringe drive unit. At suitable time intervals 50-μL samples were removed and analyzed for orthophosphate ion. Only the initial portion of the reaction was monitored so that isomerization would not affect the results.

Phosphorus-31 NMR Spectroscopy. Phosphorus-31 NMR spectra were recorded by using a Bruker WP-80 instrument on solutions containing 30% D₂O as a signal lock. Chemical shifts are reported relative to an external standard of 85% H₃PO₄. Experiments were run with a pulse width of 1.6 μs and a delay time of 2 s. Typically 500 pulses were accumulated to generate each spectrum. All samples were 0.10 M in Na₂EDTA to prevent line broadening by traces of paramagnetic metal ions. Spectra for all samples were recorded at ambient probe temperature (29 °C).

Thermodynamic Measurements. Equilibrium constants were calculated from the equilibrium concentrations of the β,γ-complex and the α,γ-complex. The determination of the equilibrium concentrations involved the quantitative separation of the equilibrated solution of the isomers by anion-exchange chromatography. In a typical experiment a 25 mM solution of the β,γ-complex was added to a reaction cell and adjusted to pH 6.5 by the addition of 1 M KOH. At the selected time intervals 30.0-mL aliquots were removed for analysis. Each aliquot was charged onto a 20 × 3.5 cm column of anion-exchange resin. The complexes were then eluted with 0.10 M pyridine–HCl buffer at pH 5.0. The solution coming off of the column was monitored by using a Gilson Holochrome column monitor, and the absorbance at 519 nm was recorded by using a strip-chart recorder. The quantitatively separated isomers were collected, and their individual concentrations were determined by the absorbance at 519 nm where the molar absorptivities are 70.2 and 66.7 M⁻¹ cm⁻¹ for the α,γ- and β,γ-isomers. Apparent equilibrium constants were then calculated from eq 1.

$$K_{app} = \frac{[\alpha,\gamma\text{-Co(NH}_3)_4\text{H}_n\text{P}_3\text{O}_{10}]^{n-2}}{[\beta,\gamma\text{-Co(NH}_3)_4\text{H}_n\text{P}_3\text{O}_{10}]^{n-2}} \quad (1)$$

Results

Potentiometric titrations for the two isomers yielded pK values of 2.3 ± 0.1 and 5.7 ± 0.1 for the β,γ-complex, **1**, and 3.6 ± 0.1 and 5.3 ± 0.1 for the α,γ-complex, **2**, at 40.0 °C

Table I. Rate Constants for Hydrolysis of Free Triphosphate, β,γ-Co(NH₃)₄H₂P₃O₁₀, and α,γ-Co(NH₃)₄H₂P₃O₁₀ at 40 °C and I = 1.0 M

pH	10⁶k, s⁻¹		
	HₙP₃O₁₀ᵃ	β,γ-isomerᵇ	α,γ-isomerᶜ
0	265	202	
0.65	58	35	39
2.0	7.5	4	15
4.0	1.6ᵈ	2.0	2.3
5.0	1.5		1.8
6.0	0.3	5.0	1.7
6.5		3.0	6.5
7.0	0.31ᵈ	1.0	5.4
9.0	0.02	3.0ᵉ	3.8ᵉ

ᵃ Greenfield, S.; Cliff, M. "Analytical Chemistry of the Condensed Phosphates"; Wiley: New York, 1975; p 23. ᵇ Reference 2. β,γ-Complexes were 25 mM in 1 M tetramethylammonium nitrate. ᶜ Concentrations of α,γ above pH 4.0 were 25 mM. Concentrations of α,γ below pH 4.0 were 10 mM to prevent rapid precipitation of the α,γ-complex. ᵈ Extrapolated from data at 60 °C: Van Wazer, J. R.; Griffith, E. J.; McCullough, J. F. *J. Am. Chem. Soc.* **1955**, *77*, 287. ᵉ Decomposition of β,γ and α,γ-complexes above pH 9.0 prevents studies at higher pH.

and 1.0 M ionic strength maintained by tetramethylammonium nitrate. No protonation steps at lower pH could be observed.

The three consecutive phosphorus-31 NMR spectra in Figure 1 were taken at 0, 14, and 24 h intervals on the α,γ-complex in aqueous solution at 40.0 °C and pH 6.5 to identify the species present during the isomerization reaction. The bottom spectrum in Figure 1 is that of the α,γ-complex initially present. As previously reported,[3] the doublet at 1 ppm arises from the two terminal phosphorus atoms of the triphosphato ligand and the triplet at −18 ppm from the center (uncoordinated) phosphorus. The spectrum after 14 h again shows the doublet and triplet at 1 and −18 ppm from the α,γ-complex; however, along with these peaks three new sets of peaks have arisen. The doublets at 5 ppm and at −3 ppm and the triplet at −8 ppm match the spectrum of the β,γ-complex.[3,5] The two doublets arise from the coordinated (5 ppm) and uncoordinated (−3 ppm) terminal phosphates, while the triplet is an unresolved double doublet from the uncoordinated center phosphate. Thus the spectra provide direct evidence for the isomerization of the original α,γ-complex, **2**, to the β,γ-complex, **1**. Singlets at 4.4, 0.9, and −7.0 ppm have previously been assigned to Co(NH₃)₄HₙP₂O₇, HₙPO₄, and HₙP₂O₇, respectively, and are consistent with the known products of the hydrolysis of the triphosphato ligand.[1] The spectrum of the solution after 24 h is shown as the top spectrum in Figure 1 and represents the total equilibration of the isomers. The peaks for the α,γ-complex, **2**, and the β,γ-complex, **1**, are still present, but the peaks from the products of triphosphate hydrolysis have greatly increased.

Ion-exchange separation of the isomers in totally equilibrated solutions was used to determine the concentrations of the isomers at equilibrium and thereby the apparent equilibrium constants for the β,γ- to α,γ-isomerization. At pH 6.5 values of K_{app} were determined to be 0.035, 0.052, 0.070, and 0.11 at 19.0, 30.5, 40.0, and 50.2 °C. At all temperatures studied the β,γ-complex is favored, but increasing temperatures shift the equilibrium in the direction of the α,γ-complex. From these data thermodynamic parameters for the isomerization have been calculated to be $\Delta G°$ = 1.6 kcal/mol, $\Delta H°$ = 5.6 kcal/mol, and $\Delta S°$ = 13 cal/(mol K).

First-order rate constants for the initial portion of the hydrolysis reaction of the triphosphato ligand at 40 °C for the two isomers over the pH range of 0.65–9.0 are reported in Table I along with rate constants for the free ligand. Over the entire pH range studied the rates of hydrolysis of the two linkage isomers differ only slightly. At low pH the rates of

hydrolysis of the complexes are slower than the rate for the free ligand. At high pH the rate for the free ligand drops sharply while the rates for the complexes remain nearly constant.

Discussion

The yield of the α,γ-complex at pH 6.5 has been increased fivefold over the yield originally reported[3] at pH 3.0. The increased yield of the α,γ-complex compared to the β,γ-complex is attributed to the different state of protonation of the incipient phosphate ligand. The relevant pK value would be that for a monodentate γ-complex [Co(NH$_3$)$_4$(H$_2$O)-HP$_3$O$_{10}$]$^{2-}$, which is a likely intermediate in the formation of either isomer. Although no such complex has been isolated, the monodentate complex γ-Co(NH$_3$)$_5$H$_2$P$_3$O$_{10}$ has been prepared in this laboratory. The highest phosphate pK for this complex is 6.7 and should reflect protonation of the terminal uncoordinated phosphate.[17] Such protonation in the tetra-ammine would discourage coordination of the terminal phosphate group and favor a formation of the β,γ-complex. The different yields at pH 6.5 and 3.0 are consistent with the pK value determined for the pentaammine. Higher pH values might increase still further the relative yield of the α,γ-isomer, but the absolute yield would fall due to the autoreduction of the starting cobalt(III) complex.

The values for the apparent equilibrium constant for the isomerization of the chelation isomers of the (dihydrogen triphosphato)tetraaminecobalt(III) complex reveal that the β,γ-complex, **1**, is the thermodynamically preferred species. The thermodynamics are reflected in the yield of each isomer in the synthesis (50% β,γ- and 7% α,γ-complex). The $\Delta G°$ value of 1.6 kcal/mol closely matches values reported for the ring-strain energy of other chelating complexes.[11,15] As-

signment of this free energy change as due to ring strain, however, would ignore the different energies of hydration of the isomers which would contribute to the difference in free energy change between the two triphosphato–metal complexes.

A positive entropy change is observed for the transformation of the β,γ-complex, **1**, to the α,γ-complex, **2**. Apparently the mobility of the eight-membered ring formed in the α,γ-complex contributes more to the entropy than the mobility of the six-membered ring formed in the β,γ-complex. A decrease in the ordering of solvent molecules in the overall solvation shell would be expected to accompany the increased mobility of the phosphate ring. The combination of these effects explains the entropy increase in the β,γ- to α,γ-isomerization.

The mobility of the ring can also effect the degree of ring strain experienced by each isomer. Flexing and puckering of the ring are accepted as internal factors for decreasing the entropy of the ring system and in turn the ring strain of that system.[15,16] Apparently the α,γ-complex has a mechanism for the partial relief of internal ring strain imposed by the formation of an eight-membered chelate ring.

A large difference in the ring-strain energies between the two isomers would certainly be reflected in their rates of phosphate hydrolysis. The similarity of the hydrolysis rates of the β,γ- and α,γ-complexes suggests that ring strain is not a major contributing factor in determining the rates of hydrolysis.

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Magnetic Circular Dichroism Spectra for the Intense UV Bands of the Tetrachloro- and Tetrabromoplatinate(II) Ions

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Electronic absorption and magnetic circular dichroism (MCD) spectra are reported for PtCl$_4$$^{2-}$ in acetonitrile solution in the UV region from 3.9 to 5.1 μm^{-1} and in methanol solution from 3.9 to 5.0 μm^{-1}. Absorption and MCD spectra are also reported for PtBr$_4$$^{2-}$ in acetonitrile solution from 2.9 to 5.1 μm^{-1}. The two intense bands observed for PtCl$_4$$^{2-}$ at 4.25 (shoulder) and 4.41 μm^{-1} in acetonitrile have associated with them negative and positive A terms, respectively. The bands observed for PtBr$_4$$^{2-}$ at 3.62 and 4.75 μm^{-1} in acetonitrile also exhibit negative and positive A terms, respectively. These bands together with some other features are assigned to a combination of ligand-to-metal charge-transfer (LMCT) and d $\rightarrow$ p (5d $\rightarrow$ 6p on Pt) transitions. Comparisons are made with the spectra of AuCl$_4$$^-$ and AuBr$_4$$^-$.

Introduction

In contrast to the weaker, low-energy ligand field (LF) bands, where band assignments seem well established,[2,3] the interpretation of the intense bands in the UV spectra above

4.0 μm^{-1} for PtCl$_4$$^{2-}$ and above 3.0 μm^{-1} for PtBr$_4$$^{2-}$ has presented difficulties. There has been a lack of agreement as to assignment in spite of considerable experimental and theoretical work. Two types of electronic excitation have been proposed for these intense bands: allowed d $\rightarrow$ p transitions and ligand-to-metal charge-transfer (LMCT) transitions. The former are visualized as excitation from the occupied 5d orbitals of Pt(II) (labeled b$_{2g}$(xy), e$_g$(xz, yz), and a$_{1g}$(z^2) in D_{4h} symmetry) to the empty out-of-plane π MO (a$_{2u}$), which is mainly 6p$_z$ (z axis is taken perpendicular to the molecular

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