(23) H. B. Abrahamson, C. C. Frazier, D. S. Ginley, H. B. Gray, J. Libienthal, D. R. Tyler, and M. S. Wrighton, *Inorg. Chem.*, **16**, 1554 (1977).
(24) C. T. Enos, G. L. Geoffroy, and T. H. Risby, *J. Chromatogr. Sci.*, **15**, 83 (1977).
(25) J. C. Kotz, J. V. Petersen, and R. C. Reed, *J. Organomet. Chem.*, **120**, 433 (1976).
(26) B. M. Peake, B. H. Robinson, J. Simpson, and D. J. Watson, *Inorg. Chem.*, **16**, 405 (1977).
(27) C. E. Strouse and L. F. Dahl, *J. Am. Chem. Soc.*, **93**, 6032 (1971).
(28) B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J. Organomet. Chem.*, **67**, C75 (1974).
(29) G. L. Geoffroy, R. Henderson, and W. L. Gladfelter, unpublished results; H. D. Kaesz, private communication.

(30) M. S. Wrighton, *Top. Curr. Chem.*, **65**, 37 (1976), and references therein.
(31) (a) D. S. Breslow and R. F. Heck, *Chem. Ind. (London)*, 467 (1960); (b) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961); (c) R. F. Heck, *ibid.*, **85**, 651 (1963).
(32) B. H. Byers and T. L. Brown, *J. Am. Chem. Soc.*, **99**, 2527 (1977).
(33) $PhCCo_3(CO)_9$ was recently reported to catalyze the hydroformylation of 1- and 2-pentene (R. C. Ryan, C. U. Pittman, and J. P. O'Connor, *J. Am. Chem. Soc.*, **99**, 1986 (1977)), and an intermediate similar to **3** was suggested. No declusterification was observed, however, implying that hydrogen transfer to the apical PhC group does not readily occur in this cluster. Consistent with this notion, we have observed that $PhCCo_3(CO)_9$ is completely inert to photolysis even under an H_2 atmosphere.

Phosphorus-31 NMR Studies of Complexes of Adenosine Triphosphate, Adenosine Diphosphate, Tripolyphosphate, and Pyrophosphate with Cobalt(III) Ammines[1a]

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The complexes $Co(NH_3)_nHATP$ (n = 2, 3, or 4) and $[Co(NH_3)_nADP]$ (n = 4 or 5) have been prepared and isolated in solution. The complexes $Co(en)_2HP_2O_7$, $Co(NH_3)_nHP_2O_7$ (n = 4 or 5), and $Co(NH_3)_nH_2P_3O_{10}$ (n = 3 or 4) have been synthesized and crystallized. These and other phosphato complexes have been examined by ^{1}H and ^{31}P NMR. The ^{31}P NMR spectra of the simpler phosphato complexes provide definitive evidence of pyrophosphate both as a monodentate and as a bidentate ligand and of tripolyphosphate both as bidentate and as a tridentate ligand. In these simpler complexes chemical shift differences between the coordinated phosphates and the corresponding free ligands range from −7 to −14 ppm and provide a basis for the assignment of the spectra of $[Co(NH_3)_4ATP]^-$, in which ATP is entirely bidentate, and of $[Co(NH_3)_3ATP]^-$, in which a mixture of bidentate and tridentate isomers is observed. Sufficient differences in the chemical shifts of diastereomers of the nucleotide complexes make it possible to distinguish differences between the spectra of the two isomers of bidentate $[Co(NH_3)_4ATP]^-$ and of bidentate $Co(NH_3)_4ADP$ and among the spectra of the four isomers of tridentate $[Co(NH_3)_3ATP]^-$.

Introduction

The substitution-inert complexes between chromium(III) and ATP[2] prepared by DePamphilis and Cleland[3] have been used with considerable success to elucidate the kinetic mechanism of yeast hexokinase[4] and other enzymes.[5] In addition, chromium(III)–nucleotide complexes are of some value in determining the state of coordination of the nucleotide substrate with enzymes such as hexokinase, for which the β,γ-bidentate complexes show substrate activity.[4,6] Unfortunately, efforts to crystallize the isomers of CrATP have been unsuccessful, and the paramagnetism of d[3] chromium(III) precludes fruitful NMR studies as a means of structure determination. This paper describes the preparation in solution, characterization, and NMR spectra of diamagnetic substitution-inert complexes of cobalt ammines: $Co(NH_3)_4HATP$, $Co(NH_3)_3HATP$, and $Co(NH_3)_2HATP$. The tetraammine and the triammine exhibit substrate activity with yeast hexokinase[1] and can be used as models to establish the coordination state of the naturally occurring MgATP complex as it binds to the enzyme.

The desire for a definitive interpretation of the ^{31}P and ^{1}H NMR spectra of the ATP complexes described here demanded the preparation and characterization of simpler phosphato complexes for which assignment of the NMR spectra was straightforward; these complexes would serve as a good basis for chemical shift–coordination state correlations. Several phosphato complexes of cobalt amines have previously been reported. These include $Co(NH_3)_5PO_4$,[7,8] $Co(NH_3)_4PO_4$,[9] $[Co(NH_3)_4H_2O(HPO_4)]ClO_4$,[9] $Na[Co(NH_3)_5P_2O_7]$,[7] $Co(en)_2PO_4$,[10] and $[(NH_3)_4Co-\mu-(NH_2,HPO_4)-Co(NH_3)_4](NO_3)_3$.[11] Minimal characterization in solution of the product

of the reaction between $[Co(NH_3)_4(H_2O)_2]^{3+}$ and $P_3O_{10}^{5-}$ has also been presented.[12] Interest in these complexes has been centered on the rates of formation, ring opening, and hydrolysis, but very little NMR data have been reported. The NMR spectra of complexes previously prepared are also recorded so that eventual correlations between O–P–O bond angles and chemical shifts of coordinated phosphates might be made. Such a correlation has recently been made for uncoordinated phosphates.[13]

The complexes of pyrophosphate and tripolyphosphate reported here provide data on the same metal coordination sphere as contained in the nucleotide complexes. Crystal structures of these complexes are of direct value in revealing for coordinated phosphates the spatial relationships which give rise to substrate activity for enzymes that accept the cobalt(III)–nucleotide complexes as substrates.

Experimental Section

Analytical Procedures. Elemental microanalyses of solid materials were performed by Galbraith Laboratories, Knoxville, Tenn. For solution samples, cobalt was determined spectrophotometrically[14] as cobalt(II) after reduction by stannous chloride,[8] the Kjeldahl method was used for nitrogen determination, and phosphorus was estimated spectrophotometrically as phosphomolybdate.

Previously Reported Complexes. The method of Schmidt and Taube[8] was used to prepare $[Co(NH_3)_5PO_4]\cdot2H_2O$ from commercially obtained $[Co(NH_3)_5H_2O]Cl_3$. An attempt to prepare $Co(en)_2PO_4$ as described by Lincoln and Stranks[10] but from *trans*-$[Co(en)_2Cl_2]Cl$[15] instead of the perchlorate salt, yielded a material which exhibited a visible spectrum in agreement with that reported but which had a ^{31}P NMR chemical shift not displaced from free orthophosphate ion at the same pH. The nature of the species actually prepared was not further investigated. A sample of $[(NH_3)_4Co-\mu-(NH_2,HPO_4)-Co-$

$(NH_3)_4](NO_3)_3 \cdot H_2O^{11}$ was kindly supplied by A. G. Sykes.

[Co(NH₃)₂(H₂O)₂Cl₂]Cl. A light green diammine complex of cobalt(III) tentatively formulated as $[Co(NH_3)_2(H_2O)_2Cl_2]Cl$ can be prepared from $K[Co(NH_3)_2(NO_2)_4]^{16}$ by substituting the latter for $[Co(NH_3)_3(NO_2)_3]$ in the procedure previously used[17] to make $[Co(NH_3)_3(H_2O)Cl_2]Cl$. The elemental analysis indicates possible contamination of the product with $K[Co(NH_3)_2(NO_2)_4]$. Anal. Calcd for $[Co(NH_3)_2(H_2O)_2Cl_2]Cl \cdot 9H_2O$: N, 7.05; Cl, 26.76; Co, 14.83. Found: N, 7.69; Cl, 25.49; Co, 14.67.

General Procedure for Other Complexes. The synthesis of Co(NH₃)₄HATP, Co(NH₃)₃HATP, Co(NH₃)₂HATP, Co(NH₃)₅ADP, Co(NH₃)₄ADP, Co(NH₃)₅HP₂O₇, Co(NH₃)₄HP₂O₇, Co(en)₂HP₂O₇, Co(NH₃)₄H₂P₃O₁₀, and Co(NH₃)₃H₂P₃O₁₀ use as starting materials cobalt complexes containing the desired amines: $[Co(NH_3)_5CO_3]NO_3$,[18] $[Co(NH_3)_4CO_3]NO_3$,[19] $trans$-$[Co(en)_2Cl_2]Cl$,[15] $[Co(NH_3)_3(H_2O)Cl_2]Cl$,[17] and $[Co(NH_3)_2(H_2O)_2Cl_2]Cl$. The carbonato complexes are first dissolved in 10% excess 1 M hydrochloric acid to generate the aquo complexes. Aqueous solutions 0.01 M in the appropriate cobalt complex and in Na₂H₂ATP, Na₂HADP, K₄P₂O₇, or Na₅P₃O₁₀ are adjusted to pH 3 with dilute hydrochloric acid or potassium hydroxide solution and are heated 10 min at 80 °C. The crude product solutions are filtered if necessary to remove solid material and charged onto columns of either cation- or anion-exchange resin, as noted. The specific resins used are AG50W-X2 cation-exchange resin, H⁺ form, 100–200 mesh, and AG1-X2 anion-exchange resin, Cl⁻ form, 100–200 mesh. Chromatography of the nucleotide complexes is done in the cold, and solutions of these complexes are stored near 0 °C.

ATP Complexes. Due to the subtleties in the purification of Co(NH₃)₄HATP, specific volumes of solutions routinely used are reported. For a 500-mL preparation a column of cation-exchange resin 2.5 × 20 cm is used. After the product solution is passed through the column, at least 1000 mL of water is passed through to move the product below the nearly colorless band containing Na⁺ and K⁺. The top red band then contains $[Co(NH_3)_4(H_2O)_2]^{3+}$ and this resin is removed by pipet. Chromatography with 1000–3000 mL of 0.1 M lithium formate, pH 2.8, moves Co(NH₃)₄HP₂O₇, closely followed by Co(NH₃)₃HATP, with the pH front. The large red band containing Co(NH₃)₄HATP moves more slowly, and when it is well separated from the other bands, it is pipetted into a second column 1.5 cm in diameter containing 2 cm of fresh cation-exchange resin. The product is eluted with 0.3 M aniline and the aniline is extracted three times with five volumes of diethyl ether. This procedure yields a solution which contains the ATP complex as a zwitterion at its isoionic pH 3.3 and which contains no other ions. Anal. Calcd for Co(NH₃)₄C₁₀H₁₃N₅O₁₃P₃: Co/N/P, 1.00/9.00/3.00. Found: Co/N/P, 1.00/8.81/3.10; yield 50%.

The crude product solution of Co(NH₃)₃HATP is absorbed on cation-exchange resin and the product is eluted with 0.1 M lithium formate, pH 3.5. The pH of the solution coming off the column is adjusted to 2 with hydrochloric acid, the complex is absorbed on a second column, and the product is eluted slowly with 0.3 M aniline. The aniline is extracted as above. On storage of the solution near 0 °C Co(NH₃)₃HATP comes out of solution over a period of weeks as a flocculent precipitate. The lavender solid can be collected, washed with water, and dried over P₄O₁₀, but decomposition to unknown products occurs within a few weeks. The solid is sparingly soluble in water, but dissolves in dilute acid or base. Due to the instability of the solid, spectra were recorded using the solution as initially prepared. Anal. Calcd for Co(NH₃)₃C₁₀H₁₃N₅O₁₃P₃: Co/N, 1.00/8.00. Found: Co/N, 1.00/8.07; yield 80%.

The diammine complex Co(NH₃)₂HATP is purified by the same chromatographic procedure as is the triammine. Elution with aniline solution causes discoloration of the column due to apparent oxidation of the aniline by cobalt(III) for both the diammine and the triammine. For the triammine this reaction is negligible for slow chromatography if the aniline is extracted immediately, but for the diammine only the front edge of the band on the column is spared decomposition; yield 3%.

Attempts were made to prepare monodentate ATP complexes by using a pentaamminecobalt complex and by shortening the heating time with a tetraammine. Although in both instances compounds exhibiting the expected chromatographic behavior resulted, the ³¹P NMR spectra showed many peaks and were not readily interpreted. Apparently the monodentate complexes form but decompose within a few hours.

ADP Complexes. The product solution of Co(NH₃)₄ADP is charged onto cation-exchange resin, and the column is washed well with water. A small red band forms beneath the Na⁺ region. By analogy with the chromium(III) system,[3] this band is probably Co(NH₃)₄(ADP)₂. The top red band containing Co(NH₃)₄ADP and $[Co(NH_3)_4(H_2O)_2]^{3+}$ is pipetted to a second column, and the product is eluted with 0.3 M aniline. The aniline is extracted with diethyl ether to give a solution of Co(NH₃)₄ADP in 55% yield.

The purification of Co(NH₃)₅ADP uses cation-exchange resin, and reaction by-products are eluted with 0.1 M lithium acetate, pH 4.5. Subsequent elution with 0.3 M aniline elutes an unknown orange species followed by a red complex tentatively identified as Co(NH₃)₅ADP by its visible spectrum. The aniline is extracted with diethyl ether. Unfortunately a 0.03 M solution formed a weak gel not amenable to characterization by NMR.

Pyrophosphato Complexes. Chromatography of the crude product solution of Co(NH₃)₅HP₂O₇ on cation-exchange resin reveals an unidentified violet band absorbing below the K⁺ band. This violet band is eluted cleanly with 0.1 M lithium formate, pH 3.5. The product is then eluted in a broad but discrete band by 0.3 M aniline, and the aniline is extracted with diethyl ether. Red crystals form immediately in concentrated solutions and over a period of several weeks of storage near 0 °C in more dilute solutions. The crystals are filtered off, washed with water and diethyl ether, and dried under vacuum over P₄O₁₀. Anal. Calcd for $[Co(NH_3)_5HP_2O_7] \cdot H_2O$: H, 5.38; N, 20.78; Co, 17.48; P, 18.38. Found: H, 5.33; N, 20.55; Co, 17.20; P, 18.69; yield 7%.

On a column of cation-exchange resin Co(NH₃)₄HP₂O₇ and the unreacted cobalt complex form two adjacent red-violet bands. The pyrophosphato complex is eluted with 0.3 M aniline. Upon extraction of the aniline with diethyl ether, red-violet needles form. These crystals are filtered off and recrystallized by dissolution in 0.3 M aniline followed by ether extraction. The crystals are washed with water and diethyl ether and dried over P₄O₁₀. Anal. Calcd for $[Co(NH_3)_4HP_2O_7] \cdot 2H_2O$: H, 5.07; N, 16.57; Co, 18.33; P, 17.08. Found: H, 4.94; N, 17.02; Co, 18.33; P, 16.93; yield 50%.

In the purification of Co(en)₂HP₂O₇ on cation-exchange resin, washing with water reveals the product as a dark red band which forms below several minor bands of undetermined composition. After sufficient washing to separate the dark red band from the other components, the resin above this band is removed. The product is eluted with 0.3 M aniline and is recrystallized as described for the tetraammine. Anal. Calcd for $[Co(H_2NCH_2CH_2NH_2)_2HP_2O_7] \cdot 2H_2O$: C, 12.32; H, 5.43; N, 14.36; Co, 15.11; P, 15.88. Found: C, 12.19; H, 5.49; N, 14.52; Co, 14.85; P, 16.25; yield 25%.

Tripolyphosphato Complexes. Solutions containing the tripolyphosphato complexes are adjusted to pH 7 with potassium hydroxide solution and charged onto anion-exchange resin. Chromatography with 0.1 M hydrochloric acid adjusted to pH 5 with pyridine washes through unreacted material. Some Co(NH₃)₄HP₂O₇ may be present and moves off the column in a broad band. Preparations of the tetraammine contain triammine formed by loss of coordinated ammonia during heating, and preparations of the triammine may contain tetraammine due to impurities[20] in the Co(NH₃)₃(NO₂)₃[21] from which the $[Co(NH_3)_3(H_2O)Cl_2]Cl$ used in the synthesis is prepared. Upon continued chromatography with the pyridine–hydrochloric acid solution, the tripolyphosphato complexes slowly separate with the red tetraammine moving more rapidly than the lavender triammine. The resin containing the pure complex is removed to a second column and the product is eluted with 0.05 M hydrochloric acid. One volume of ethanol is added to the tetraammine solution and two volumes to the triammine solution. Crystals are harvested after several weeks of storage at 20 °C, washed with ethanol and diethyl ether, and dried over P₄O₁₀. Solid Co(NH₃)₄H₂P₃O₁₀ is not stable indefinitely at room temperature; after several months the ³¹P NMR spectrum shows an extraneous line in the region where free orthophosphate ion would be expected. Anal. Calcd for $[Co(NH_3)_4H_2P_3O_{10}] \cdot H_2O$: H, 4.03; N, 14.01; Co, 14.73; P, 23.23. Found: H, 3.70; N, 14.18; Co, 14.74; P, 23.16; yield 25%. Calcd for Co(NH₃)₃H₂P₃O₁₀: H, 3.04; N, 11.51; Co, 16.15; P, 25.46. Found: H, 3.44; N, 11.05; Co, 15.15; P, 25.58; yield 35%.

NMR Spectra. Proton and ³¹P NMR spectra were determined using a Bruker HX90E spectrometer operating at 90 MHz for proton and 36.44 MHz for phosphorus in the pulsed mode. Transients were accumulated in and transformed by a Nicolet 1080 computer. For ³¹P spectra the solutions used contained 20–50% deuterium oxide and

Table I. UV–Visible Spectra of Phosphatocobalt Amines[a]

Complex	λ_{max}, nm (ϵ, M^{-1} cm^{-1})		
[Co(NH$_3$)$_5$P$_2$O$_7$]$^-$		358 (56.2)	520 (69.5)
[Co(NH$_3$)$_4$P$_2$O$_7$]$^-$		372 (55.1)	522 (70.5)
[Co(en)$_2$P$_2$O$_7$]$^-$		369 (76.9)	512 (106)
[Co(NH$_3$)$_4$P$_3$O$_{10}$]$^{2-}$		366 (54.9)	518 (66.7)
[Co(NH$_3$)$_3$P$_3$O$_{10}$]$^{2-}$		375 (64.1)	561 (67.9)
Co(NH$_3$)$_4$HATP	257 (16 900)	366 (56.0)	518 (68.1)
Co(NH$_3$)$_3$HATP	257 (18 500)	374 (74.2)	548 (76.8)
Co(NH$_3$)$_2$HATP	257 (22 100)	382 (87.0)	560 (66.6)
Co(NH$_3$)$_4$ADP	257 (15 500)	359 (67.9)	517 (63.9)
Co(NH$_3$)$_5$ADP	257 (15 400)[b]	353 (58.9)[b]	513 (71.0)[b]

[a] Phosphato complexes in aqueous 0.1 M NaHCO$_3$, pH 8. Nucleotide complexes at their isoionic pH (3.3 for ATP complexes; 6.5 and 7.4 for ADP tetra- and pentaammine). [b] The molar absorptivity at 257 nm was assumed to be 15 400 M^{-1} cm^{-1} on the basis of the adenine absorption, and those at 353 and 513 nm were calculated from the relative absorbance.

were routinely passed through columns of Chelex 100 immediately before use to remove paramagnetic impurities. Line widths of 2–3 ___ were achieved by this technique. Due to the need for higher resolution to observe the fine structure in the spectra of the nucleotide complexes, their spectra were run in the presence of 0.1 M EDTA. Because the phosphate-bridged dinuclear complex has a +2 charge under the conditions used and thus does not readily pass through Chelex, its spectrum was also run in the presence of EDTA. The phosphorus spectra were routinely proton decoupled, although decoupling made a noticeable difference in the spectra only for the nucleotide complexes. Phosphorus chemical shifts are referenced to an external standard of 1 M H$_3$PO$_4$. Within experimental error this standard has the same chemical shift as 85% H$_3$PO$_4$, but the ^{31}P NMR spectrum of 1 M H$_3$PO$_4$ is a much narrower line.

Results

Syntheses and Characterization. The selection of the conditions used for the syntheses of the newly prepared complexes was based upon conditions previously used successfully for chromium(III) complexes.[3] Sampling of the reaction solution at various time intervals from 1 to 16 min served to demonstrate that maximal yield for Co(NH$_3$)$_4$HATP was reached at about 8 min. Since most of the complexes can be obtained in reasonable yield by the procedures described, no attempt was made to determine the optimal conditions for their preparation.

The identities of the simpler phosphato complexes are established by elemental analysis and chromatographic behavior. The spectral results to be presented are all consistent with the formulations given. The identity of those nucleotide complexes for which chemical anaylsis has not been obtained is confirmed by spectral measurements and by the successful characterization of other complexes prepared by analogous procedures. The designation of the number of water molecules has been omitted for Co(NH$_3$)$_3$HATP and Co(NH$_3$)$_2$HATP. This omission is made in recognition of the presence of bidentate and tridentate isomers which contain different numbers of water molecules in the inner coordination sphere.

UV–Visible Spectra. The major features of the ultraviolet and visible spectra of the complexes prepared here are presented in Table I. The maxima at 257 nm are characteristic of adenine and have molar absorptivities approximating those of the free nucleotides. Spectra of the simpler phosphato complexes were recorded immediately after dissolution. Overnight standing at pH 8 results in a significant amount of decomposition and apparent reduction to cobalt(II) for the lower ammine complexes, but negligible decomposition occurs in 1–2 h.

Proton NMR. Table II summarizes the 90-MHz proton NMR spectra of the ammine hydrogens for many of the complexes prepared here. The data in Table II are for 0.1 M DCl solutions, but experiments with solutions at pH 8 showed

Table II. Ammine Proton NMR Spectra of Phosphatocobalt Ammines[a]

Complex[b]	Chem shift,[c] ppm		Peak area ratio, cis:trans
	Cis	Trans	
[Co(NH$_3$)$_5$H$_2$PO$_4$]$^{2+}$	0.22	−0.93	4.0
[Co(NH$_3$)$_5$H$_3$P$_2$O$_7$]$^{2+}$	0.49	−0.80	4.3
[Co(NH$_3$)$_4$H$_2$P$_2$O$_7$]$^+$	0.73	−0.32	1.2
[Co(NH$_3$)$_4$H$_3$P$_3$O$_{10}$]$^+$	0.81	−0.29	1.1
	0.88		
Co(NH$_3$)$_3$H$_2$P$_3$O$_{10}$	0.17		
Co(NH$_3$)$_4$HATP	0.81	−0.23	d
	0.88	−0.47	
Co(NH$_3$)$_3$HATP	0.18		

[a] Phosphato complexes in 0.1 M DCl in D$_2$O; nucleotide complexes in D$_2$O at isoionic pH. [b] Probable predominant ionic form is given. [c] Positive values are downfield (by convention) from [Co(NH$_3$)$_6$]$^{3+}$. [d] Not directly measurable due to overlap from ribose hydrogen atoms.

changes in chemical shift of 0.1 ppm or less for cis ammine hydrogens of the two pyrophosphato complexes. The trans ammine hydrogens of these complexes exchange with solvent too rapidly at pH 8 to be observed by the techniques used here. The conclusion that the lower field peaks correspond to the cis ammine hydrogens is in agreement with previously reported assignments[22] for related complexes. Consistent with this assignment is the observation that the positions of both the cis and trans ammine hydrogen peaks move downfield as the number of phosphate groups cis to the given ammine increases. The cis ammine hydrogens of [Co(NH$_3$)$_4$H$_3$P$_3$O$_{10}$]$^+$ are not equivalent and appear as two broad overlapping peaks. The trans ammine hydrogens appear as one broad peak at pH 1, but as two overlapping peaks 0.08 ppm apart at pH 3.

Proton NMR spectra of Co(NH$_3$)$_4$HATP at pH 3 are shown in Figure 1. The pH of the solution for the lower spectrum was first raised to 9 with potassium hydroxide for 10 min to exchange the ammine hydrogens and then lowered to 3 with hydrochloric acid. The peaks labeled a and b correspond, respectively, to the hydrogens on C-8 and C-2 of the adenine ring. The positions of these peaks are shifted only slightly from those in free ATP at the same pH, but the peak of the hydrogen on C-8 appears to be broadened. The peaks labeled c arise from the hydrogen on the 1' carbon of the ribose and are essentially unshifted also. The cis ammine hydrogens are expected on the basis of the spectra of the other tetraammine complexes in Table II to occur in the region labeled d. The presence of the remainder of the ribose hydrogens in this area precludes a definitive assignment, but one or both of the tallest peaks in this area of the upper spectrum can be attributed to the cis ammine hydrogens. The two peaks labeled e are the trans ammine hydrogens and correspond closely in position to those observed in the simpler phosphato complexes. The chemical shift difference between these two peaks is constant in the range 0.007–0.07 M Co(NH$_3$)$_4$HATP.

Phosphorus-31 NMR. Phosphorus-31 NMR spectra recorded for available simple phosphato complexes of cobalt ammines are summarized in Table III. The phosphorus resonance for [Co(en)$_2$P$_2$O$_7$]$^-$ was also measured and found to occur 0.04 ppm upfield from the analogous tetraammine complex.

The assignment of the spectra may readily be made on the basis of the splitting patterns observed and the chemical shift differences between free and coordinated ligands. In [(NH$_3$)$_4$Co-μ-(NH$_2$,PO$_4$)·Co(NH$_3$)$_4$]$^{2+}$ and [Co(NH$_3$)$_5$HPO$_4$]$^+$ the phosphorus resonances are shifted more than −11 ppm from free orthophosphate ion in the same state of protonation, and this difference is taken as an indication that large coordination chemical shifts may be expected for phosphorus atoms in coordinated phosphates. In [Co(N-

Table III. ^{31}P NMR Spectra of Phosphatocobalt Ammines[a]

Complex	Chem shift, ppm[b]	Multi-plicity[c]	Coupling const, Hz[d]	Coordination chem shift[e]
[(NH$_3$)$_4$Co-μ-(NH$_2$,-PO$_4$)-Co(NH$_3$)$_4$]$^{2+}$	−17.0	s		−11.7
[Co(NH$_3$)$_4$HPO$_4$]$^+$	−14.2[f]	s		−11.2
[Co(NH$_3$)$_5$P$_2$O$_7$]$^-$	1.6	d	21.5	0.0
	−5.6	d	21.5	−7.2
[Co(NH$_3$)$_4$P$_2$O$_7$]$^-$	−4.7	s		−10.4
[Co(NH$_3$)$_4$P$_3$O$_{10}$]$^{2-}$	−4.2	d	15.9	−9.2
	5.1	d	19.8	0.1
	9.1	dd	16.0, 19.7	−10.4
[Co(NH$_3$)$_3$P$_3$O$_{10}$]$^{2-}$	−4.2	d	16.4	−9.1
	5.6	t	16.2	−13.9

^{a} 0.1 M in 0.1 M NaHCO$_3$, pH 8, to fully deprotonate phosphates. ^{b} Relative to 1 M H$_3$PO$_4$. ^{c} s = singlet, d = doublet, t = triplet, dd = double doublet. ^{d} Precision is ±0.2 Hz. ^{e} Ppm, upfield from corresponding phosphorus resonance in free ligand in the same state of protonation. ^{f} pH 7.5.

H$_3$)$_5$P$_2$O$_7$]$^-$ the phosphorus atom which has a coordination chemical shift of −7.2 ppm can be assigned as the atom in the coordinated phosphate and the one with negligible displacement is in the noncoordinated phosphate. The two phosphorus atoms in [Co(NH$_3$)$_4$P$_2$O$_7$]$^-$ are equivalent and the large shift from free pyrophosphate confirms that both phosphate groups are coordinated to cobalt. Three distinct phosphorus atoms are observed for [Co(NH$_3$)$_4$P$_3$O$_{10}$]$^{2-}$. The doublet which is shifted −9.2 ppm from the resonance of the phosphorus atom in the terminal position of free tripolyphosphate ion represents the phosphorus atom in the coordinated terminal phosphate. The other doublet is shifted only 0.1 ppm and corresponds to the phosphorus atom in the noncoordinated terminal phosphate. The resonance of the middle phosphorus atom is split by each of the terminal phosphorus atoms and appears as the double doublet. The shift of −10.4 ppm from the middle phosphorus atom of free tripolyphosphate ion indicates that the middle phosphate in [Co(NH$_3$)$_4$P$_3$O$_{10}$]$^{2-}$ is in the coordination sphere of the cobalt. In [Co(NH$_3$)$_3$P$_3$O$_{10}$]$^{2-}$ the splitting pattern may be used to assign the doublet to the terminal phosphorus atoms and the triplet to the middle one. Once again large shifts from the free ligand are found upon coordination of the phosphates.

The coordination chemical shifts listed in the last column of Table III are measured from the corresponding position in the spectrum of the free phosphate ligand in the same state of protonation in order to show only the effect of coordination to the cobalt. The suitability of expressing the shifts in this manner is verified by the low values observed for the phosphorus atoms in the phosphate residues not bound directly to the cobalt in [Co(NH$_3$)$_5$P$_2$O$_7$]$^-$ and [Co(NH$_3$)$_4$P$_3$O$_{10}$]$^{2-}$.

The 36.4-MHz ^{31}P{^{1}H} (see footnote 23) NMR spectrum of Co(NH$_3$)$_4$ADP is shown in Figure 2. The assignment of the doublet on the left as P$_\beta$[24] and the multiplet on the right as P$_\alpha$ is based upon the similar relative chemical shifts in ADP. The coordination chemical shifts on the order of −10 ppm for
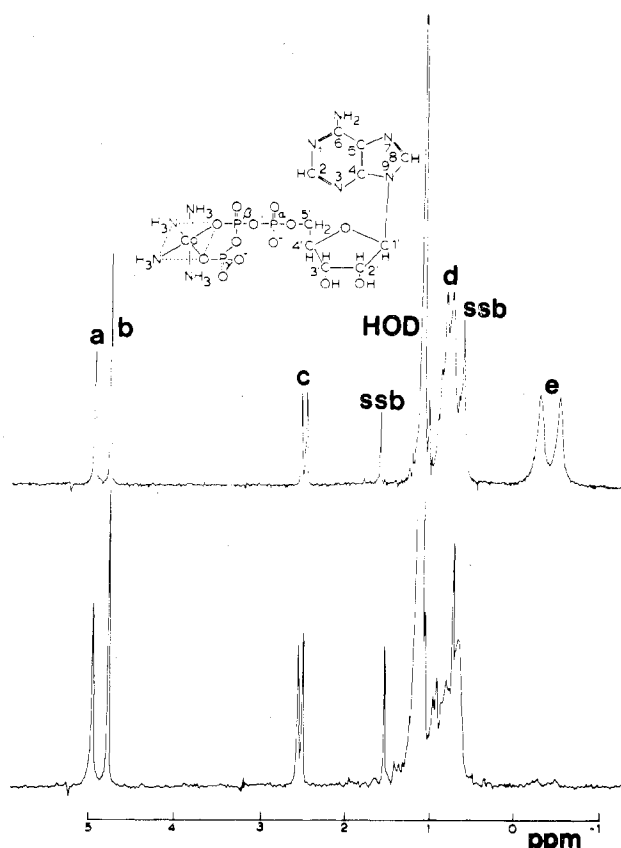

Figure 1. Proton NMR spectra of Co(NH$_3$)$_4$HATP in D$_2$O at isoionic pH 3.3. The ammine hydrogens have been exchanged with solvent for the lower spectrum: a, hydrogen on C-8; b, hydrogen on C-2; c, hydrogen on C-1′; d, cis ammine hydrogens and hydrogens on C-2′ to C-5′; e, trans ammine hydrogens; ssb, spinning sideband. Chemical shift scale relative to [Co(NH$_3$)$_6$]$^{3+}$.
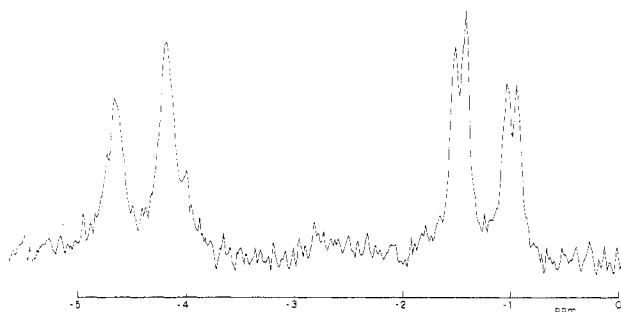

Figure 2. The 36.4-MHz ^{31}P{^{1}H} spectrum of Co(NH$_3$)$_4$ADP at pH 8, showing on the right the chemical shift difference between the doublets of the α phosphorus atoms of the two diastereomers. Chemical shift scale relative to 1 M H$_3$PO$_4$.

both P$_\alpha$ and P$_\beta$ as given in Table IV reveal that ADP acts as a bidentate ligand. For this α,β-bidentate complex of ADP two isomers are possible. These isomers correspond to the

Table IV. ^{31}P NMR Spectra of Nucleotide Complexes of Cobalt Ammines at pH 8[a]

	Chem shift,[b] ppm				Coupl const, Hz		Coordination chem shift,[c] ppm			
	P$_\alpha$[d]	P$_\alpha$[e]	P$_\beta$	P$_\gamma$	$J_{\alpha,\beta}$	$J_{\beta,\gamma}$	P$_\alpha$[d]	P$_\alpha$[e]	P$_\beta$	P$_\gamma$
[Co(NH$_3$)$_4$ATP]$^-$		10.9	10.4	−4.0	20	16		0.4	−10.4	−9.9
[Co(NH$_3$)$_3$ATP]$^-$	1.0	11.0	8.2	−4.7	17.4, 17.0 20.5, 18.8[f]	16	−9.5	0.5	−12.5	−9.9
[Co(NH$_3$)$_4$ADP]	−1.1		−4.3		18.0		−11.5		−10.0	

^{a} P$_\alpha$ indicates the phosphorus atom closest to adenosine. P$_\beta$ and P$_\gamma$ are the successively remote phosphorus atoms. See Figure 1. ^{b} Relative to 1 M H$_3$PO$_4$. ^{c} Measured from the corresponding phosphorus resonance for the free ligand in the same state of protonation. ^{d} Phosphorus in coordinated phosphate. ^{e} Phosphorus in noncoordinated phosphate. ^{f} Values for the four tridentate isomers. See text.
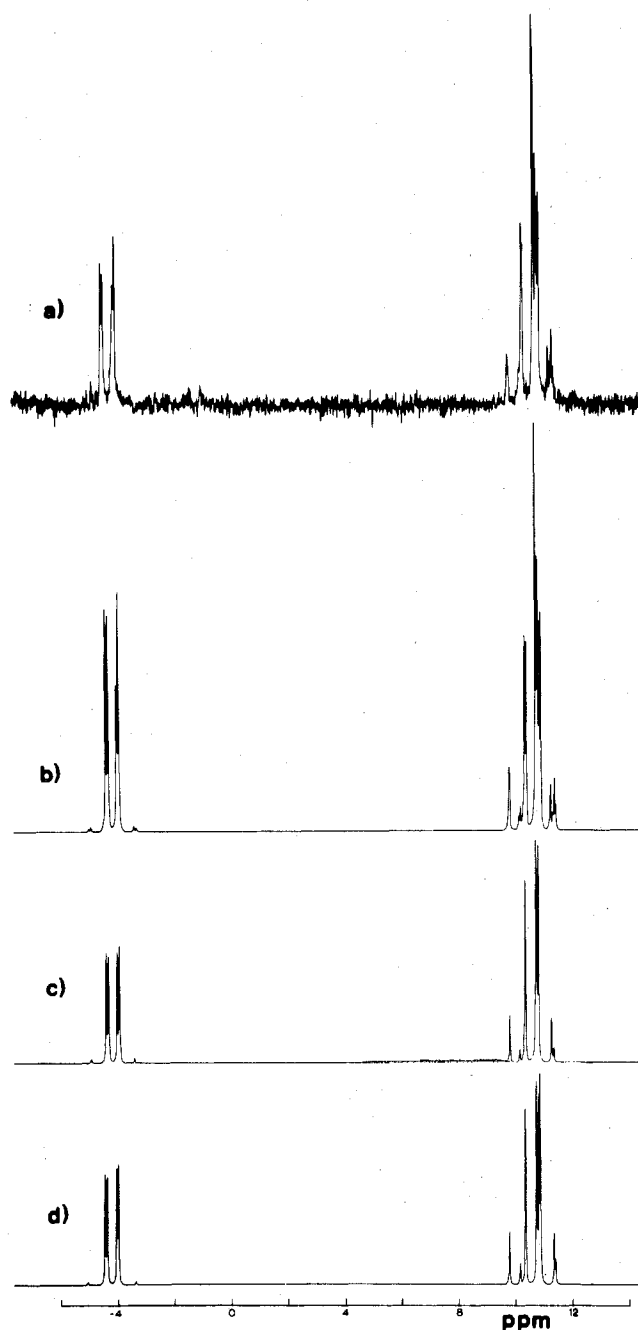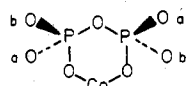
Figure 4. The 36.4-MHz $^{31}P\{^1H\}$ spectrum of $[Co(NH_3)_3ATP]^-$ at pH 8. From left to right the groups of peaks represent P_γ, P_α, P_β (all coordinated) and P_α (noncoordinated). Expanded portion shows doublets representing P_α for all four tridentate isomers. Chemical shift scale relative to 1 M H_3PO_4.

The 36.4-MHz $^{31}P\{^1H\}$ NMR spectrum for $[Co(NH_3)_4ATP]^-$ at pH 8 is shown as curve a in Figure 3, and the chemical shifts are recorded in Table IV. The peaks in the left multiplet are shifted from the γ phosphorus of free ATP by −9.9 ppm. The assignment of this multiplet as P_γ is confirmed by comparison with the coordination chemical shift of −9.2 ppm seen for the phosphorus atom in the coordinated, terminal phosphate of $[Co(NH_3)_4P_3O_{10}]^{2-}$. The right multiplet is shifted by −10.4 and 0.4 ppm, respectively, from P_β and P_α of free ATP. These values agree well with the coordination chemical shifts of −10.4 and 0.1 ppm for the analogous phosphorus atoms in $[Co(NH_3)_4P_3O_{10}]^{2-}$. These data are definitive evidence that the complex $[Co(NH_3)_4ATP]^-$ is a β,γ-coordinated, bidentate species.

In spite of its complexity, the spectrum in Figure 3 provides strong evidence of the presence of both isomers of $[Co(NH_3)_4ATP]^-$. These two diastereomers are analogous to those for $Co(NH_3)_4ADP$ and differ from each other in their configuration about the β phosphorus atom. The simulated spectrum presented as curve b of Figure 3 closely approximates the experimental spectrum. This simulation represents the superposition of the spectra labeled c and d, which correspond to the individual isomers. Each of these latter spectra is an ABX pattern in which A and B are tightly coupled and "virtual coupling" of X to A is observed. For curve c the parameters used in the simulation are $\nu_A = 50$, $\nu_B = 69$, $\nu_X = 595$ Hz and $J_{AB} = 20$, $J_{AX} = 0$, $J_{BX} = 16$ Hz. For curve d the parameters are the same except for $\nu_A = 45$ and $\nu_B = 68$ Hz.

In the triammine complex $[Co(NH_3)_3ATP]^-$ many more isomers are present. The 36.4-MHz $^{31}P\{^1H\}$ NMR spectrum at pH 8 is shown in Figure 4. Four envelopes of peaks can be observed. On the basis of the shifts for the phosphato complexes, they can be assigned from left to right as coordinated P_γ, coordinated P_α, coordinated P_β, and noncoordinated P_α. The tridentate isomers contribute to the peaks of the coordinated P_α, P_β, and P_γ, while the β,γ-bidentate isomers contribute to the peaks of noncoordinated P_α, coordinated P_β, and coordinated P_γ. The coordination chemical shifts corresponding to this assignment are given in Table IV and correspond closely to those observed for the complexes $[Co(NH_3)_3P_3O_{10}]^{2-}$ and $[Co(NH_3)_4P_3O_{10}]^{2-}$ which serve as models for the tridentate and bidentate ATP complexes, respectively.

Four diastereomers of tridentate $[Co(NH_3)_3ATP]^-$ are possible and correspond to attachment of adenosine to the oxygen atoms labeled a, b, c, and d in the diagram

Figure 3. (a) The 36.4-MHz $^{31}P\{^1H\}$ spectrum of $[Co(NH_3)_4ATP]^-$ at pH 8. (b) Simulated spectrum approximating curve a. (c, d) Simulated spectra of individual isomers. Simulations used parameters given in text and a line width of 1 Hz. The peaks on the left correspond to the γ phosphorus atom and those on the right to the tightly coupled α and β phosphorus atoms. Chemical shift scale relative to 1 M H_3PO_4.

attachment of adenosine to the oxygen atoms labeled a or b in the structure

The two isomers are characterized by different absolute configurations about the α phosphorus atom and are diastereomers since adenosine itself is asymmetric. A chemical shift difference of 4 Hz between the isomers is observed in the doublets of P_α. A single doublet with broadened lines is found for P_β and indicates a smaller difference of about 0.5 Hz between the resonances of P_β for the two isomers.
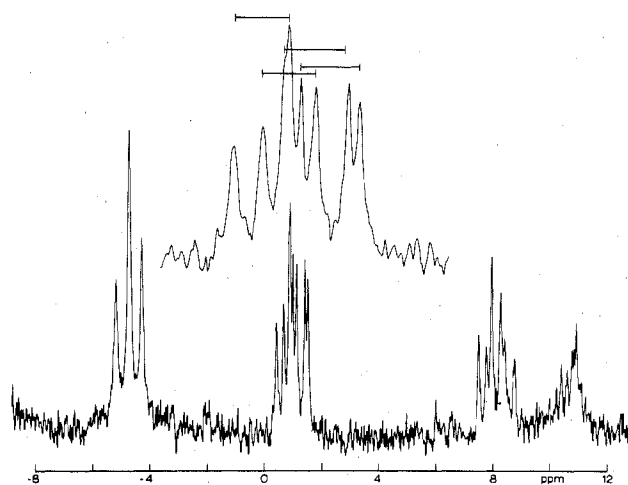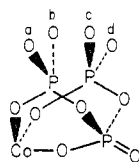
These isomers are characterized by different absolute configurations about P_α and P_β. An expansion of the peaks for coordinated P_α shown in Figure 4 reveals the presence of all four diastereomers. Seven lines can be distinguished, and the shoulder on the third line from the left is taken as evidence of an eighth line. One of the possible pairings is shown with bars in Figure 3 and gives four doublets with coupling constants of 17.4, 17.0, 20.5, and 18.8 Hz, from top to bottom.

Discussion

Phosphorus-31 NMR. Apparently all previous ^{31}P NMR studies of metal binding to simple phosphates have been restricted to labile systems in which the spectra give information descriptive of an average of all species present in solution. The information obtained here is in sharp contrast to such studies; the cobalt(III) ammines are substitution inert and each spectrum is representative of discrete species in solution. The ^{31}P NMR spectra obtained here are thus open to a more rigorous interpretation.

The chemical shifts observed in the ^{31}P NMR spectra of the phosphato complexes provide definitive evidence for coordination of the phosphates to cobalt. The shifts from the free ligand are of larger magnitude and in the opposite direction compared with those which occur upon protonation of phosphates. For example,[25] the chemical shift for orthophosphate ion moves upfield by 6 ppm as the pH is lowered until H_3PO_4 is the predominant species. The changes in chemical shift upon coordination of phosphates to cobalt are of similar magnitude to those observed for systems involving Zn^{2+} or UO_2^{2+}. Cooperman[26] studied the ^{31}P NMR spectra of substituted phosphates and found a chemical shift change of −8.5 ppm upon coordination of Zn^{2+} to the α phosphate of tetraamminophosphonyl phosphate. In a study of nucleotide binding to UO_2^{2+}, Rich, Agarwal, and Feldman[27] found coordination chemical shifts as large as −5.0 ppm for the β phosphorus of ATP. In the present study, the observed coordination chemical shifts range from −7.2 to −13.9 ppm for phosphorus atoms in coordinated phosphate residues.

The conclusions drawn concerning the mode of coordination of the simple phosphates are the same conclusions which could be made based upon the known number of ammines about the cobalt.[28] Taken as a whole they form a solid basis for interpretation of ^{31}P NMR spectra of phosphates bound to cobalt in systems for which isolation of crystalline species is not readily achieved. These results find their first application in the assignments of the spectra of nucleotide complexes of cobalt ammines which have been given.

The most significant results to come from this work are the ^{31}P NMR spectra showing differences among the individual isomers of the nucleotide complexes. The complex Co-$(NH_3)_4$ADP has only two possible α,β-bidentate isomers, and the spectrum can be readily assigned by inspection. The overlapping of the resonances from the α and β phosphorus atoms in $[Co(NH_3)_4ATP]^-$ complicates the spectrum, but a detailed analysis is still possible for the mixture of isomers. In $[Co(NH_3)_3ATP]^-$ four tridentate isomers are possible for a facial configuration of the phosphates, and all of these are clearly visible in the peaks of the α phosphorus. The β and γ phosphorus regions of $[Co(NH_3)_3ATP]^-$ are complicated by the presence of the bidentate isomers. Four bidentate isomers are possible for a facial configuration of the ammines and four for a meridional configuration. Even if one arrangement of the ammines is predominant, the β and γ

phosphorus regions correspond to the superposition of the spectra of eight species. The region of the noncoordinated α phosphorus could be due to as few as four species if one ammine configuration predominates, but the lower abundance of the bidentate isomers makes resolution in this region more difficult to achieve.

The measured values of coupling constants for the phosphato complexes are of interest for comparison with other reports. Glonek et al., in their study of ^{31}P NMR spectra of polyphosphates,[29] noted a trend in the coupling constants between terminal and penultimate phosphorus atoms. As the chain length of the polyphosphates decreases, the coupling constant increases from 17.5 Hz for long-chain polyphosphates to 20.6 Hz for tripolyphosphate. The two coupling constants measured here between a phosphorus atom in a coordinated phosphate and one in an adjacent, noncoordinated phosphate increase further from 19.8 Hz for tripolyphosphate ion in $[Co(NH_3)_4P_3O_{10}]^{2-}$ to 21.5 Hz for pyrophosphate ion in $[Co(NH_3)_5P_2O_7]^-$ and are consistent with the reported trend. The values of phosphorus–phosphorus coupling constants are observed to decrease upon coordination of phosphates to cobalt. Values of near 16 Hz have been obtained for coupling constants between phosphorus atoms in adjacent, coordinated phosphates in both of the tripolyphosphato complexes prepared here. These values are significantly less than the reported[29] value of 20.6 Hz for free tripolyphosphate ion. Decreases in coupling constants have previously been observed upon coordination of Mg^{2+} to phosphates.[30]

Proton NMR. The observed peak area ratios in the proton NMR spectra are consistent with the expected patterns[22] of two peaks with relative area of 4.0 for a pentaammine and 1.0 for a cis tetraammine. Since trans ammine hydrogens are known to exchange more rapidly than cis ammine hydrogens,[31] the modest deviations from these values as seen in Table II may be attributed to partial isotopic exchange with solvent.

In the complex $Co(NH_3)_4$HATP a chemical shift difference between sets of trans ammine hydrogens can be observed. The source of this difference could be the chemical difference between the two trans ammines or the two peaks could arise from the two isomers. Inasmuch as a chemical shift difference between trans ammines is observed in $Co(NH_3)_4H_2P_3O_{10}$, the source of the shift difference in $Co(NH_3)_4$HATP is evidently the chemical shift difference between the two trans ammines rather than the subtle differences between the two diastereomers. The broadening of the H-8 resonance could arise either from intramolecular interactions or from a small chemical shift difference between isomers. The results presented here do not provide a basis for a conclusion concerning the actual source of the broadening.

Concluding Remarks. All of the simple phosphato complexes prepared here are crystalline and several x-ray structures are completed or are in progress.[32] The greatest value of these complexes may be realized only after the structures are completed. Due to the inert coordination sphere of cobalt(III), structural parameters determined in the solid state may be reasonably expected to differ only slightly from those which exist in solution. Gorenstein[13] has shown a correlation between O–P–O bond angle and ^{31}P NMR chemical shift for a number of phosphate esters. If such a correlation could be extended to cobalt complexes, ^{31}P NMR would be a powerful tool for determining the solution geometry of phosphates bound to cobalt in complexes which are useful for the understanding of biochemical systems.

Note Added in Proof. The two diastereomers of Co-$(NH_3)_4$ATP have been separated by using yeast hexokinase in the presence of glucose to convert one to $Co(NH_3)_4$(glucose 6-phosphate)ADP and to convert this product (after separation from the inactive isomer on a column of cross-linked cyclo-

heptaamylose) back to the active isomer of Co(NH$_3$)$_4$ATP. By treatment with HIO$_4$, followed by aniline at pH 5, Co-(NH$_3$)$_4$ATP isomers are degraded to Co(NH$_3$)$_4$H$_2$P$_3$O$_{10}$ without loss of chirality. The CD of each enantiomer at 550 nm is the same in sign as that of the parent nucleotide, and x-ray analysis of a crystal of Co(NH$_3$)$_4$H$_2$P$_3$O$_{10}$ from the inactive isomer of Co(NH$_3$)$_4$ATP (negative CD) shows that it corresponds to attachment of AMP in position b of the first diagram given above.[32] The active isomer (positive CD) corresponds to attachment of AMP in position a. The ^{31}P NMR spectra are in excellent agreement with the simulated ones in Figure 3, with (c) being the active and (d) the inactive isomer.

The diastereomers of Co(NH$_3$)$_4$ADP separate cleanly on the cycloheptaamylose column, with the one whose α-phosphate is farthest downfield in Figure 2 coming off first and having a negative CD band at 540 nm. The second isomer (positive CD) probably corresponds in structure to attachment of adenosine in position a of the diagram. This work will be reported in detail at a later date.

Registry No. Co(NH$_3$)$_4$HATP, 63915-26-4; Co(NH$_3$)$_4$ADP, 63937-09-7; Co(NH$_3$)$_5$ADP, 63937-08-6; Co(NH$_3$)$_5$HP$_2$O$_7$, 63915-25-3; Co(NH$_3$)$_4$HP$_2$O$_7$, 63915-24-2; Co(en)$_2$HP$_2$O$_7$, 63915-23-1; Co(NH$_3$)$_3$H$_2$P$_3$O$_{10}$, 63915-22-0; Co(NH$_3$)$_4$H$_2$P$_3$O$_{10}$, 63915-20-8; [Co(NH$_3$)$_5$P$_2$O$_7$]$^-$, 63915-21-9; [Co(NH$_3$)$_4$P$_2$O$_7$]$^-$, 63915-34-4; [Co(en)$_2$P$_2$O$_7$]$^-$, 63915-33-3; [Co(NH$_3$)$_4$P$_3$O$_{10}$]$^{2-}$, 63915-32-2; [Co(NH$_3$)$_3$P$_3$O$_{10}$]$^{2-}$, 63937-07-5; [Co(NH$_3$)$_5$H$_2$PO$_4$]$^{2+}$, 19169-72-3; [Co(NH$_3$)$_5$H$_3$P$_2$O$_7$]$^{2+}$, 63915-31-1; [Co(NH$_3$)$_4$H$_2$P$_2$O$_7$]$^+$, 63915-30-0; [Co(NH$_3$)$_4$H$_3$P$_3$O$_{10}$]$^+$, 63915-29-7; [(NH$_3$)$_4$Co-μ-(NH$_2$,PO$_4$)-Co(NH$_3$)$_4$]$^{2+}$, 34420-25-2; [Co(NH$_3$)$_4$HPO$_4$]$^+$, 64023-30-9; [Co(NH$_3$)$_4$ATP]$^-$, 63915-28-6; [Co(NH$_3$)$_2$(H$_2$O)$_2$Cl$_2$]Cl, 53861-32-8; K[Co(NH$_3$)$_2$(NO$_2$)$_4$], 14285-97-3; [Co(NH$_3$)$_5$CO$_3$]NO$_3$, 15244-74-3; [Co(NH$_3$)$_4$CO$_3$]NO$_3$, 15040-52-5; *trans*-[Co(en)$_2$Cl$_2$]Cl, 14040-33-6; [Co(NH$_3$)$_3$(H$_2$O)Cl$_2$]Cl, 13820-77-4; H$_4$ATP, 3714-60-1; Co, 7440-48-4.

References and Notes

(1) (a) Presented in part at the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., 1976; see Abstracts, No. BIOL 121 and INOR 150. (b) To whom correspondence should be addressed at the Department of Chemistry, Wichita State University, Wichita, Kans. 67208.
(2) ATP = adenosine triphosphate, ADP = adenosine diphosphate, AMP = adenosine monophosphate.
(3) M. L. DePamphilis and W. W. Cleland, *Biochemistry*, **12**, 3714 (1973).
(4) K. D. Danenberg and W. W. Cleland, *Biochemistry*, **14**, 28 (1975).
(5) C. A. Janson and W. W. Cleland, *J. Biol. Chem.*, **249**, 2562, 2567, 2572 (1974); M. I. Schimerlik and W. W. Cleland, *ibid.*, **248**, 8418 (1973); D. A. Armbruster and F. B. Rudolph, *ibid.*, **251**, 320 (1976); J. Bar-Tana and W. W. Cleland, *ibid.*, **249**, 1271 (1974).
(6) D. O. Brummond and W. W. Cleland, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **33**, 1565 (1974), Abstract 1929.
(7) R. Duval, *Ann. Chim. (Paris)*, [10] **18**, 241 (1932).
(8) W. Schmidt and H. Taube, *Inorg. Chem.*, **2**, 698 (1963).
(9) H. Siebert, *Z. Anorg. Allg. Chem.*, **296**, 286 (1958).
(10) S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, **21**, 37 (1968). (b) Since the completion of this work, the crystal structure of Co(en)$_2$PO$_4$ has been reported by B. Anderson, R. M. Milburn, J. M. Harrowfield, G. B. Robertson, and A. M. Sargeson, *J. Am. Chem. Soc.*, **99**, 2652 (1977). These authors also cite a private communication dealing with Co(en)$_2$HP$_2$O$_7$.
(11) J. D. Edwards, S. Foong, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 829 (1973).
(12) C. Stanisav and R. Vatulescu, *Stud. Univ. Babes-Bolyai, Ser. Chem.*, **20**, 11 (1975).
(13) D. G. Gorenstein, *J. Am. Chem. Soc.*, **97**, 898 (1975).
(14) E. Baskerville, *Anal. Chem.*, **21**, 1089 (1949).
(15) J. C. Bailar, *Inorg. Synth.*, **2**, 222 (1946).
(16) G. Schlessinger, *Inorg. Synth.*, **9**, 170 (1967).
(17) G. Schlessinger, *Inorg. Synth.*, **6**, 180 (1960).
(18) F. Basolo and K. Murmann, *Inorg. Synth.*, **4**, 171 (1953).
(19) G. Schlessinger, *Inorg. Synth.*, **6**, 173 (1960).
(20) W. Stanley, S. Lum, and C. S. Garner, *J. Inorg. Nucl. Chem.*, **35**, 3587 (1973).
(21) G. Schlessinger, *Inorg. Synth.*, **6**, 189 (1960).
(22) See, for example, P. Clifton and L. Pratt, *Proc. Chem. Soc., London*, 339 (1963).
(23) The notation {^{1}H} indicates proton decoupled.
(24) In ADP and ATP, P$_\alpha$ indicates the phosphorus atom closest to adenosine. P$_\beta$ and P$_\gamma$ are the successively remote phosphorus atoms. See Figure 1.
(25) K. Moedritzer, *Inorg. Chem.*, **6**, 936 (1967).
(26) B. S. Cooperman, *Biochemistry*, **8**, 5005 (1969).
(27) K. E. Rich, R. T. Agarwal, and I. Feldman, *J. Am. Chem. Soc.*, **92**, 6818 (1970).
(28) Bidentate coordination of individual phosphate residues has been observed in cobalt(III) complexes containing ethylenediamine (see ref 10). In the complexes reported here, when the phosphates are coordinated, only one of the oxygen atoms attached to a given phosphorus atom is coordinated to cobalt.
(29) T. Glonek, A. J. R. Costello, T. C. Myers, and J. R. Van Wazer, *J. Phys. Chem.*, **79**, 1214 (1975).
(30) T. Son, M. Roux, and M. Ellenberger, *Nucleic Acids Res.*, **79**, 1214 (1975).
(31) J. W. Palmer and F. Basolo, *J. Phys. Chem.*, **64**, 778 (1960).
(32) E. Merritt and M. Sundaralingam, to be submitted for publication.

Study of the Reaction of Cobalt(II) and Nickel(II) Benzeneseleninato Complexes with Bidentate Nitrogen Donor Ligands

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The pseudooctahedral bis(benzeneseleninato-*O*)bis(2,2'-bipyridyl) and bis(benzeneseleninato-*O*)bis(1,10-phenanthroline) compounds of cobalt(II) and nickel(II) are obtained by reaction of the complexes M(H$_2$O)$_2$(XPhSeO$_2$)$_2$ (M = Co, Ni; X = H, *p*-Cl, *m*-Cl, *p*-Br, *m*-Br, *p*-CH$_3$, *p*-NO$_2$) with 2,2'-bipyridyl and 1,10-phenanthroline according to eq 1. All the diaquo complexes react with 2 mol of 2,2'-bipyridyl or 1,10-phenanthroline in ethanol to form seleninato-*O* complexes. The newly prepared compounds are characterized on the basis of far-IR and near-IR spectroscopy and electronic spectra, as well as by magnetochemical investigations. A distorted octahedral geometry accounts for the room-temperature spectroscopic properties of these compounds. The nitrogen donor ligands behave always as bidentate. Our cobalt(II) and nickel(II) complexes show *Dq* values in keeping with the proposed structures and with literature data for CoN$_4$O$_2$ and NiN$_4$O$_2$ chromophores.

Introduction

Our interest in the coordination properties of the para- and meta-substituted benzeneseleninic acids as ligands was recently extended to the study of the chemical reactivity and linkage isomers of the coordination compounds of such ligands. Owing to the four possibilities for bonding the RSeO$_2^-$ ligand to coordination centers, the seleninato complexes are particularly suitable as model substances for the study of various isomerization phenomena.

The benzeneseleninato group can behave as a monodentate