Contribution from the Department of Chemistry,
Baylor University, Waco, Texas 76703

Synthesis and Chromium(II) Reduction of an Aminoethylphosphonic Acid Complex of Cobalt(III)

MARIANNA ANDERSON BUSCH and DAVID E. PENNINGTON*

Received March 22, 1976 AIC60222F

The first inert complex of an aminoalkylphosphonic acid, $Co(NH_3)_5(1\text{-}AEPH_n)^{(2+n)+}$, has been prepared where 1-AEP is 1-aminoethylphosphonic acid and $n = 0$ or 1. The complex is quite inert to substitution, undergoes reversible protonation with $pK_a = 3.2 \pm 0.2$, and reacts with chromium(II) via a one-electron, inner-sphere mechanism. The rate law is of the form: rate = $(k_0 + k_{-1}/[H^+])[Co(NH_3)_5(1\text{-}AEPH_n)^{(2+n)+}][Cr^{2+}]$, where $k_0 = (1.4 \pm 0.1) \times 10^{-1}\ M^{-1}\ s^{-1}$ and $k_{-1} = (3.5 \pm 0.7) \times 10^{-2}\ s^{-1}$ at 25 °C and $\sum[ClO_4^-] = 1.0$ M. The rate law can be interpreted in terms of a mechanism in which the deprotonated form of the complex $Co(NH_3)_5(1\text{-}AEP)^{2+}$ is substantially more reactive than the protonated form $Co(NH_3)_5(1\text{-}AEPH)^{3+}$. An alternate mechanism is also considered.

Introduction

Amino acids play a vital role in many body functions and readily coordinate to certain transition metals forming a wide variety of well-known complexes. The phosphorus analogues of amino acids, the aminoalkylphosphonic acids, have also been identified in a variety of life forms,[1] including man.[2] Like their amino acid counterparts, aminoalkylphosphonic acids can participate in transamination reactions[3] and can be substituted for alanine in the diet of rats, although resulting in higher blood pressure and increased fat and nitrogen content in the liver as compared to the case of control animals.[4] However, the origin and function of these compounds in the human body have not been determined.

In the area of transition metal chemistry only the interactions of aminoalkylphosphonic acids with labile metal ions have been investigated. Wozniak et al.[5] have surveyed the stability constants and ionization constants of 2-aminoethylphosphonic acid with the divalent metal ions of Ca, Mg, Co, Ni, Zn, and Cu. The observed stabilities increase in the order given. Martell and co-workers[6] have investigated the chelating ability of various multidentate aminoalkylphosphonic acids with the divalent metal ions of Ca, Mg, Mn, Co, Ni, Cu, and Zn. Our preparation of $Co(NH_3)_5(1\text{-}AEPH_n)^{(2+n)+}$ where 1-AEP is 1-aminoethylphosphonic acid and $n = 0$ or 1 represents the first inert metal complex of aminoalkylphosphonic acids where specific metal–ligand interactions can be studied in solution without the complication of fast ligand exchange.

A variety of phosphato complexes of cobalt(III) have been synthesized, but few quantitative data are avaiable for their reduction by chromium(II). Schmidt and Taube[7] prepared and characterized a series of phosphato and methyl phosphato complexes of the pentaamminecobalt(III) class. With the exception of the trimethyl phosphate, these complexes were found to be quite stable to acid and reacted rapidly with solutions of Cr^{2+} with efficient transfer of the phosphate group. The kinetics of these reactions were later reinvestigated by Candlin, Halpern, and Trimm,[8] who derived rate constants for the Cr(II) reduction of each of the individual $RoPO_4$, $RoPO_4H^+$, $RoPO_4H_2^{2+}$, and $RoPO_4H_3^{3+}$ species (Ro = $Co(NH_3)_5$) using the acid dissociation constants reported by Schmidt and Taube.[7] The details of the Cr(II) reactions with the substituted methyl phosphato complexes have never been fully worked out.

Lincoln and Stranks[9] have prepared bidentate complexes of the type $Co(en)_2PO_4$ and $Co(NH_3)_4PO_4$ where en is ethylenediamine. These were found to undergo rapid and reversible interconversion to the monodentate forms $Co(en)_2(H_2O)PO_4$ and $Co(NH_3)_4(H_2O)PO_4$ with significant concentrations of the bidentate complexes persisting only in the pH range 5.5–7.5. Lincoln and Purnell[10] later prepared phosphato complexes of the amminebis(ethylenediamine)cobalt(III) type which were stable to acid at room temperature. Reactions with Cr^{2+} were not investigated.

The recent investigation by Green, Taylor, and Sykes[11] into the reduction of the bridged μ-amido-μ-phosphato-bis[tetraamminecobalt(III)] species represents the only other detailed kinetic study of the reaction of phosphatocobalt(III) complexes with Cr^{2+}. The reduction was found to proceed in two stages, each involving the attack of Cr(II) and reduction of Co(III).

Due to the lack of quantitative data on the Cr(II) redox reactions of phosphorus-containing complexes of Co(III), the present investigation has included a complete kinetic study of the reaction of the $Co(NH_3)_5(1\text{-}AEPH_n)^{(2+n)+}$ complexes with Cr^{2+}. In addition to quantitatively defining the effect of 1-aminoethylphosphonic acid on the rate and possibly the mechanism of Cr(II)–Co(III) reactions, the product of the reaction has been identified as a 1:1 chromium–1-aminoethylphosphonic acid complex. There is currently a high level of interest in the bioinorganic chemistry of chromium(III)–amino acid complexes,[12] and compounds similar to this product could, also, prove to be of some biochemical interest.

Experimental Section

Materials. Chromium(II) perchlorate solutions were prepared by reduction of chromium(III) perchlorate in 0.1 M perchloric acid with lightly amalgamated zinc. The reduction was carried out in an oxygen-free container through which prepurified argon was passed. The argon used was passed through a heated copper catalyst (BASF) at 120 °C to remove traces of oxygen. The chromium(II) solutions were stored under an argon atmosphere in serum bottles capped with self-sealing rubber stoppers.

Lithium perchlorate was prepared by reacting perchloric acid with lithium carbonate. The product was recrystallized three times to remove trace impurities.

Dowex 50W-X8 and 50W-X2 cation-exchange resins (H^+ form, 50–100 mesh) were treated as previously described.[13] Conversion to the Li^+ form was accomplished by treatment with a solution of recrystallized lithium hydroxide followed by water until the effluent was neutral; this was followed by treatment with 1 M lithium perchlorate and finally water until the effluent no longer produced a precipitate with potassium sulfate.

Triply distilled water was used to prepare all stock solutions for the stoichiometric and kinetic measurements and for the recrystallization of reagents and treatment of cation-exchange resins. 1-Aminoethylphosphonic acid was prepared according to the procedure of Chambers and Isbell.[14] $Co(NH_3)_5CO_3^+$ was prepared as the nitrate salt from $Co(NO_3)_2$ and $(NH_4)_2CO_3$ in concentrated aqueous ammonia.[15] All other chemicals were purchased as reagent grade and used as received.

Preparation of Complexes. The complex $Co(NH_3)_5(1\text{-}AEP)^{2+}$ was prepared by the addition of $Co(NH_3)_5CO_3^+$ to an aqueous solution of 1-aminoethylphosphonic acid (1 g) at room temperature until the pH of the mixture was approximately 7. The resulting solution was heated at 50–60 °C for 30 min and evaporated to dryness on a rotary evaporator. The orange residue was heated strongly on a steam bath for several hours yielding a purple-red solid as the final product. The complex of interest was separated as a bright red solution from several other minor reaction products by elution from a 20–30-cm cation-exchange column (Dowex 50W-X2, Li^+ form) using 0.8–1.0 M $LiClO_4$. No attempt was made to measure the yield, but it appears to be on the order of 50% or greater. Other products of this reaction were not identified. In acid solution $Co(NH_3)_5(1\text{-AEP})^{2+}$ undergoes reversible protonation yielding $Co(NH_3)_5(1\text{-AEPH})^{3+}$.

These complexes, like the analogous phosphate ester complexes,[7] are extremely soluble in water and could not be precipitated by any of a variety of anions including $B(C_6H_5)_4^-$. However, for redox studies it was not essential to prepare a solid compound, especially since the complex $Co(NH_3)_5(1\text{-AEP})^{2+}$ appears to be quite stable in neutral solution and could be stored in the dark at room temperature for up to 3 months without any detectable change in spectral or redox properties. Furthermore, careful purification according to the method previously described always produced solutions of the complex with identical spectral and redox characteristics. The Co–(1-AEP) bond is also quite stable to acid, and in 1.0 M $HClO_4$ no loss of 1-AEP could be detected spectrophotometrically over a 24-h period.

Because the complexes could not be precipitated, chemical analysis gave only ratios of elements and ligands. Anal. Calcd for $Co(NH_3)_5(1\text{-AEPH}_n)^{(2+n)+}$: Co:P:$NH_3$ = 1:1:5. Found: Co:P:NH_3 = 1:(0.99 ± 0.02):(4.9 ± 0.1). The presence of the aminophosphonic acid ligand was verified by a positive ninhydrin test. The charges on the complexes were inferred from the concentration of $LiClO_4$ required to elute the species from the cation-exchange column when compared to other known complexes of similar charge and from the behavior of the complexes in acid and neutral solution.

Analyses. The total chromium content of solutions was determined spectrophotometrically as CrO_4^{2-} (ϵ 4815 M^{-1} cm^{-1} at 372 nm).[16] If Co was present, a dark brown precipitate formed which was removed by filtration through Whatman No. 42 filter paper. In cases where Co and Cr were both present in the original sample, the results of the spectrophotometric determination were compared to those obtained using atomic absorption and found to be in agreement. Analysis by atomic absorption was carried out according to standard procedures.[17]

The concentrations of chromium(II) solutions were determined by oxidation with an excess of iron(III) followed by titration of the iron(II) produced with standard potassium dichromate.[18a]

Stock solutions of perchloric acid were standardized by titration with sodium hydroxide to a phenolphthalein end point.

To determine the acidity of chromium(II) solutions and avoid interference from $Cr(OH)_3$ formation in a direct titration, a known volume of chromium(II) solution was injected into an excess of rapidly stirred, aqueous bromine using a calibrated syringe. Excess bromine was expelled by a stream of air, and $Cr(H_2O)_5Br^{2+}$ was converted to the tris(oxalato) complex by heating for 2–3 h with a sixfold excess of potassium oxalate. The cooled solution was titrated potentiometrically with standardized sodium hydroxide.[18b]

Stock solutions of lithium perchlorate were standardized by gravimetric determination of the perchlorate concentration using tetraphenylarsonium chloride[19] or by adsorbing an aliquot of the solution onto a cation-exchange column (Dowex 50W-X8, H^+ form) and determining the acid eluted by titration with sodium hydroxide to a phenolphthalein end point. For a given solution, the results of both methods agreed within experimental error.

The total cobalt content of solutions was determined by heating an aliquot of the sample in dilute alkali to destroy the complex followed by the formation of a complex with ammonium thiocyanate and extraction into a hexyl alcohol–ether mixture.[20] The blue cobaltothiocyanato color was measured spectrophotometrically at 600 nm and compared to a series of standards.

The total phosphorus content of solutions was determined by heating an aliquot of the sample in dilute alkali to destroy the complex and converting the phosphorus to orthophosphate by the addition of ammonium persulfate. Excess persulfate was removed by boiling the solution for 15 min. The orthophosphate was converted to molybdovanadophosphoric acid,[21] and the color allowed to develop for 30 min. The yellow molybdovanadophosphoric acid color was immediately measured spectrophotometrically at 460 nm and compared to a series of standards. If chromium was present, it was removed as the hydroxide prior to the addition of persulfate by filtering the alkaline solution through Whatman No. 42 filter paper. Cobalt does not interfere with the determination if the concentration does not exceed 100 ppm.[21]

The number of ammine ligands in the complex was determined by a modified Kjeldahl method for NH_3.[22] Under identical conditions 1-aminoethylphosphonic acid does not release ammonia.

Reactions with Ninhydrin. Dilute solutions of the cobalt or chromium complexes were made basic by the addition of a few drops of concentrated sodium hydroxide, and the solution was heated until all of the ammine groups were evolved as NH_3. The cooled solution was filtered through Whatman No. 42 filter paper to remove solids, and the filtrate was approximately neutralized by the addition of a slight excess of hydrochloric acid. Excess acid was removed by slow addition of sodium bicarbonate until the evolution of CO_2 ceased. One milliliter of a solution of 0.2 mg of ninhydrin in 50 ml of water was added, and the solution was heated to boiling. Intense violet colors resulted, comparable to the color produced when 1-aminoethylphosphonic acid was treated with ninhydrin.[14] Under identical conditions, complexes like $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_5CO_3^+$ gave negative ninhydrin tests.

Determination of the Equilibrium Constant K_a. A standardized solution of the cobalt(III) complex was prepared in triply distilled water, and the perchlorate concentration was adjusted to 1 M with lithium perchlorate. Carbon dioxide free argon was bubbled through the solution for 30 min, and the temperature was adjusted to 25.0 °C by thermostating in a water bath. While a stream of prepurified argon was maintained through the solution, the pH of the mixture was measured on a Beckman pH meter (expanded scale), which had been calibrated at 25 °C using Beckman buffer solutions pH 7.00, 4.01, and 10.01. The pK_a was calculated from the measured pH and the total cobalt concentration of the solution assuming coordination through oxygen and that the amino group on the phosphonic acid is 100% protonated. Within experimental error (±0.05 pH unit) the pH at 15.0 and 35.0 °C was equal to the value obtained at 25.0 °C.

Independent verification of the pK_a value was obtained by measuring the variation of the molar absorptivity of the complex with hydrogen ion concentration in 1.0 M lithium perchlorate–perchloric acid mixtures. The solutions were rendered carbon dioxide free by deaereation with a stream of argon and thermostated at 25.0 °C in the cell compartment of a Cary Model 14 recording spectrophotometer. After temperature equilibration was reached, the absorbances of the cobalt(III) solutions vs. blanks of the same lithium perchlorate–perchloric acid composition were measured at 517 nm. Observed molar absorptivities were compared to those calculated by assuming the pK_a value determined potentiometrically and found to be in good agreement.

Stoichiometric Measurements. Reaction vessels were serum bottles covered with self-sealing caps. All manipulations were performed under an atmosphere of prepurified argon. A known volume of chromium(II) solution was added by means of a calibrated hypodermic syringe, equipped with a stainless steel needle, to a deaereated solution of the cobalt(III) complex (10% excess) containing the desired amount of lithium perchlorate and enough perchloric acid to neutralize the ammonia released and leave the solution about 0.05 M in acid. After completion of the reaction (at least 10 half-lives) oxygen was admitted to the vessel and the reaction mixture was adsorbed onto a 30-cm cation-exchange column (Dowex 50W-X8, H^+ form). Most of the cobalt(II) was eluted using a solution with $[Li^+]$ = 0.95 M and $[H^+]$ = 0.05 M. Unreacted cobalt(III) remained adsorbed on the top of the column, but a green reaction product was readily eluted using a solution with $[Li^+]$ = 1.95 M and $[H^+]$ = 0.05 M. This complex was collected quantitatively and analyzed for chromium and phosphorus.

Kinetic Measurements. The desired amounts of the cobalt(III) complex, lithium perchlorate, and perchloric acid were added to a 5-cm cylindrical, spectrophotometric cell. The cell was covered with a self-sealing rubber cap, and oxygen was removed by means of a stream of prepurified argon. The cell was then placed in the thermostated (±0.1 °C) cell compartment of a Cary Model 14 recording spectrophotometer. After temperature equilibration was reached, the desired amount of chromium(II) solution was added by means of a calibrated syringe.

Kinetic measurements were obtained by continuously observing the decrease in absorbance at 355.5 nm. A tenfold or greater excess of chromium(II) over cobalt(III) gave strictly first-order reactions in all cases over at least 2–3 half-lives (about 75–88% of the reaction). Rate constants were obtained from the slopes of plots of ln $(A_t - A_\infty)$ vs. time where A_t and A_∞ are the absorbances at times t and approximately 8–10 half-lives, respectively. The rates were not influenced by changing the wavelength at which the absorbance decrease was monitored (477 and 465 nm) or by the further addition of Zn^{2+} which

Table I. Comparison of the Absorption Maxima (nm), Molar Absorptivities (M^{-1} cm^{-1}), and Acid Dissociation Constants for Various Phosphorus-Containing Complexes of the Pentaammine- and Bis(ethylenediamine)cobalt(III) Classes and Other Relevant Species[a]

Species	λ_{max} (ϵ_{max})	λ_{max} (ϵ_{max})	pK_a
$Co(NH_3)_5(1\text{-AEPH})^{3+}$ [b]	513 (61.3)	353 (52.8)	3.2 ± 0.2
$Co(NH_3)_5(1\text{-AEP})^{2+}$ [b]	517 (69.4)	359 (61.2)	
$Co(NH_3)_5(OPO_3H_3)^{3+}$ [c]	519.5 (51.6)		−0.67[d]
$Co(NH_3)_5(OPO_3H_2)^{2+}$ [c]	517.5 (63.7)	356 (48.3)	3.6 ± 0.1
$Co(NH_3)_5(OPO_3H)^{+}$ [c]	521 (77.8)	359 (61.6)	8.5 ± 0.1
$Co(NH_3)_5(OPO_3)$[c]	525 (90.0)	364 (73.9)	
cis-$Co(en)_2NH_3(OPO_3H_3)^{3+}$ [e]	508 (81.7)	355 (69.0)	
cis-$Co(en)_2NH_3(OPO_3H_2)^{2+}$ [e]	508 (89.8)	355 (76.9)	3.20 ± 0.05
cis-$Co(en)_2NH_3(OPO_3H)^{+}$ [e]	510 (101.5)	357 (86.4)	7.85 ± 0.05
cis-$Co(en)_2NH_3(OPO_3)$[e]	513 (112.5)	362 (96.2)	
trans-$Co(en)_2NH_3(OPO_3H_3)^{3+}$ [e]	513 (56.2)	351 (52.1)	
trans-$Co(en)_2NH_3(OPO_3H_2)^{2+}$ [e]	511.5 (60.8)	352 (55.6)	3.00 ± 0.05
trans-$Co(en)_2NH_3(OPO_3H)^{+}$ [e]	515.5 (74.9)	353 (66.7)	7.73 ± 0.05
trans-$Co(en)_2NH_3(OPO_3)$[e]	521 (90.5)	357 (76.5)	
$Co(en)_2(OH_2)(OPO_3H_2)^{2+}$ [f]			3.10 ± 0.05
$Co(en)_2(OH_2)(OPO_3H)^{+}$ [f]	511 (107.6)	366 (83.8)	9.40 ± 0.05
$Co(NH_3)_5[OP(OCH_3)_3]^{3+}$ [c]	520 (46.3)	347 (39.2)	
$Co(NH_3)_5[OPO(OCH_3)_2]^{2+}$ [c]	517 (58.1)	325.5 (48.3)	
H_3PO_4 [g]			1.72
$H_2PO_4^-$ [g]			5.92
HPO_4^{2-} [g]			12.5

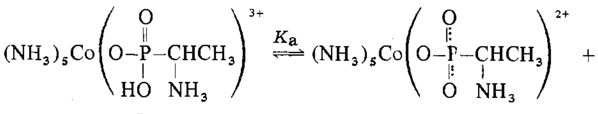
[a] Temperature 25 °C and $\mu = 1.0$ except where noted otherwise. [b] This work. $\Sigma[ClO_4^-] = 1.0$ M. [c] Reference 7. [d] $\mu = 3$. [e] Reference 10. [f] Reference 9; temperature 23 °C. [g] Reference 7; $\mu = 2$.

is present as a secondary product of the chromium(II) preparation. Measurements were made at various hydrogen ion concentrations at 15.9, 20.4, 25.0, 29.6, and 34.2 °C with $\sum[ClO_4^-] = 1.0$ M (lithium perchlorate).

Results

The $Co(NH_3)_5(1\text{-AEPH}_n)^{(2+n)+}$ Complex in Solution. The visible absorption spectrum of $Co(NH_3)_5(1\text{-AEPH}_n)^{(2+n)+}$ depends on the acidity of the solution. The values of the molar absorptivities for the two absorption maxima observed in the range 650–300 nm for the conditions $\sum[ClO_4^-] = 1.0$ M and $[H^+] = 5.2 \times 10^{-8}$ and 0.5 M, respectively, are listed in Table I. These appear to be limiting values for low and high acidity and are assumed to correspond to the $Co(NH_3)_5(1\text{-AEP})^{2+}$ and $Co(NH_3)_5(1\text{-AEPH})^{3+}$ complexes, respectively.

The absorption spectra of these aminophosphonic acid complexes correspond quite closely to several analogous phosphatopentaamminecobalt(III) complexes prepared by Taube et al.[7] and the phosphatoamminebis(ethylenediamine)cobalt(III) complexes prepared by Lincoln and Purnell.[10] A comparison of these data in Table I strongly suggests that the 1-aminoethylphosphonic acid ligand is bound to the central metal through an oxygen–cobalt bond rather than through a nitrogen–cobalt bond and that changes in the spectrum of the complex with changes in hydrogen ion concentration can be ascribed to protonation and deprotonation of the remaining P–OH group (eq 1). The latter assumption



I II (1)

is further supported by the fact that the changes in the spectrum of $Co(NH_3)_5(1\text{-AEPH}_n)^{(2+n)+}$ with changes in acidity are fast relative to the time of mixing and completely reversible over the pH range studied.

The Equilibrium Constant, K_a. By analogy with other amino acids and amino acid complexes,[24] the amine pK_a is expected to be much larger than that of the P–OH group. If the amine group on the aminophosphonic acid is essentially 100% protonated over the pH range of interest, then K_a for P–OH can be estimated by simply measuring the pH of a standardized solution of $Co(NH_3)_5(1\text{-AEPH}_n)^{(2+n)+}$ at a known temperature with $\sum[ClO_4^-] = 1.0$ M (lithium perchlorate).

The hydrolysis of $Co(NH_3)_5(1\text{-AEP})^{2+}$ in water leads to a slightly basic solution according to eq 2. The equilibrium

$$Co(NH_3)_5(1\text{-AEP})^{2+} + H_2O \overset{K_b}{\rightleftharpoons} Co(NH_3)_5(1\text{-AEPH})^{3+} + OH^- \quad (2)$$

expression for the hydrolysis reaction can be solved for K_a in terms of K_w, the total cobalt concentration $[Co^{III}]_t$, and the measured pH in the conventional manner. At 25.0 °C a solution containing 2.36×10^{-3} mol/l. of cobalt and $\sum[ClO_4^-] = 1.0$ M had a pH of 7.28 ± 0.05 (expanded scale) yielding a value of 3.2 ± 0.2 for pK_a. By comparison, uncomplexed 1-aminoethylphosphonic acid has a pK_a for acid dissociation of the second P–OH group equal to approximately 5.7 ± 0.2 as estimated from the titration curve with 0.1 N sodium hydroxide.[14] As expected, replacement of the proton on one P–OH group by the pentaamminecobalt(III) group increases the acidity of the remaining P–OH group. The acid dissociation constant of the aminophosphonic acid complex is compared in Table I with the acid dissociation constants of other relevant species.

Scan spectra obtained on solutions of the $Co(NH_3)_5(1\text{-AEPH}_n)^{(2+n)+}$ complexes for a variety of pH values and identical cobalt content show well-defined isosbestic points at 418 ± 2 and 472 ± 3 nm. These results are not inconsistent with the presence of the two species I and II in solution.

Independent verification of the pK_a value was obtained by measuring the molar absorptivities of an equilibrium mixture of the $Co(NH_3)_5(1\text{-AEPH}_n)^{(2+n)+}$ complexes at 517 nm at different hydrogen ion concentrations (25 °C, $\sum[ClO_4^-] = 1.0$ M). The molar absorptivities observed are the weighted averages of the molar absorptivities of the protonated species I and deprotonated species II where the brackets indicate

$$\epsilon_{obsd} = \{\epsilon_I[Co(NH_3)_5(1\text{-AEPH})^{3+}] + \epsilon_{II}[Co(NH_3)_5(1\text{-AEP})^{2+}]\}/[Co^{III}]_t$$

concentrations. The values for ϵ_I (61.1 M^{-1} cm^{-1}) and ϵ_{II} (69.4 M^{-1} cm^{-1}) were assumed to be the molar absorptivities at 517 nm measured for solutions with $\sum[ClO_4^-] = 1.0$ M and $[H^+] = 0.5$ and 5.2×10^{-8} M, respectively. A wavelength of 517 nm was chosen to maximize the change in ϵ_{obsd} with acidity. The curve in Figure 1 was calculated from ϵ_I and ϵ_{II} using the pK_a value measured potentiometrically. The experimentally determined molar absorptivities can be seen to agree well with the calculated values, suggesting that the potentiometric determination of K_a is reasonably accurate and not inconsistent with the postulation that the hydrogen ion concentration in solution is the result of the protonation and deprotonation of only one functional group (P–OH) rather than of two

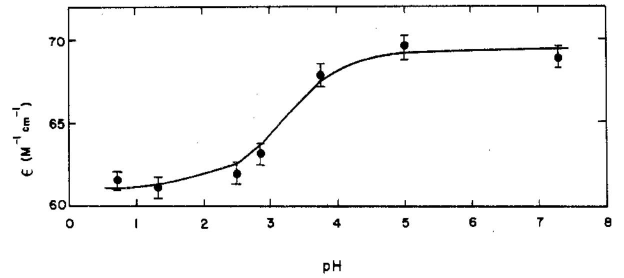


Figure 1. Variation of molar absorptivity of $Co(NH_3)_5$-(1-$AEPH_n)^{(2+n)+}$ with acid concentration in 1.0 M $LiClO_4$-$HClO_4$ at 25.0 °C, 517 nm. The solid line was calculated using the pK_a value measured potentiometrically. The experimental points are the observed molar absorptivities at different acidities.

functional groups (P–OH and $-NH_3^+$).

The complexes appear to be quite inert to substitution and remain stable in solution for long periods without undergoing acid hydrolysis. Base hydrolysis can be observed if the pH exceeds 9 or 10 at room temperature, but in dilute alkali at 25 °C, the half-life for the reaction is estimated to still be on the order of 1 h or more.

Stoichiometry of the Cr(II)–Co(III) Reaction and the Cr(III) Product. The reaction of Cr^{2+} with the $Co(NH_3)_5(1\text{-}AEPH_n)^{(2+n)+}$ complexes appears to involve 1:1 stoichiometry with efficient transfer of the 1-AEP ligand to chromium(III) (a one-electron, inner-sphere mechanism). As much as 94% of the theoretically expected amount of Cr(III) can be readily eluted from a cation-exchange column under conditions which do not lead to elution of $Cr(H_2O)_6^{3+}$. Spectral scans of the green Cr(III) complex taken after several kinetic runs indicated an absorption maximum at about 420 nm, which is typical of oxygen-bound, monosubstituted Cr(III) complexes. For example, $Cr(H_2O)_5(H_nPO_4)^{3-n}$, $Cr(H_2O)_5(H_2PO_2)^{2+}$, and $Cr(H_2O)_5OSO_3^+$ exhibit second absorption maxima at 420, 420, and 417 nm, respectively.[7,25,26] Eluent concentrations required for convenient separation of $Cr(1\text{-}AEPH_n)^{(2+n)+}$ and Cr^{3+} produced solutions of $Cr(1\text{-}AEPH_n)^{(2+n)+}$ which were too dilute for an accurate determination of the molar absorptivity.

An analysis of the complex for chromium and phosphorus gave a ratio of 1.0:(0.96 ± 0.04). This complex also gives an intense violet color when treated with ninhydrin according to the method previously described. Since a solution of 2.0 M cation concentration is required to elute the complex (Experimental Section), the Cr(III) species probably contains the protonated form of the 1-AEP ligand giving the complex a 3+ charge. A 2+ charge would require only about 1.0 M cation concentration for elution.[27]

The positive ninhydrin test obtained by treatment of the Cr(III) complex must be due to aminophosphonic acid complexed to chromium. Uncomplexed aminophosphonic acid having a 0 or 1+ charge in 0.05 M acid would be eluted well before the more highly charged Cr(III) species.

Kinetics of the Cr(II)–Co(III) Reaction. Kinetic data for the reduction of $Co(NH_3)_5(1\text{-}AEPH_n)^{(2+n)+}$ by Cr^{2+} at 25.0 °C in 0.49 M $HClO_4$ with $\sum[ClO_4^-] = 1.0$ M are summarized in Table II. Since individual kinetic runs were clearly pseudo first order for at least 2–3 half-lives, the second-order rate constants k^{2d} were calculated for each experiment from the relationship $k_{obsd} = k^{2d}[Cr(II)]$. With the exception of the experiments at lowest Cr^{2+} concentration (5.0×10^{-3} M) all the values of k^{2d} are equal within experimental error. Addition of Zn^{2+} equal to twice the Cr^{2+} concentration can also be seen to have no significant effect on the reaction rate (experiment 10) when compared to an experiment conducted at the same Cr^{2+} concentration without added Zn^{2+} (experiment 1). Slightly low values of k^{2d} at $[Cr(II)] = 5.0 \times 10^{-3}$ M can be accounted for if a small amount of air oxidation occurred for these low levels of chromium during manipulation of the solutions.

Table II. Kinetic Experiments for the Chromium(II) Reduction of $Co(NH_3)_5(1\text{-}AEPH_n)^{(2+n)+}$, $n = 0$ and 1[a]

Expt	$10^2[Cr^{2+}]$, M (no. of runs)	$10^3 k_{obsd}$ s⁻¹	$10k^{2d}$, M⁻¹ s⁻¹
1	0.5 (4)	0.951 ± 0.008	1.90 ± 0.01
2	1.0 (3)	2.21 ± 0.05	2.21 ± 0.05
3	2.0 (2)	4.54 ± 0.05	2.27 ± 0.01
4	4.0 (2)	9.2 ± 0.2	2.30 ± 0.04
5	6.0 (3)	13.8 ± 0.6	2.3 ± 0.1
6[b,c]	2.0 (1)	4.62	2.31
7[b,d]	2.16 (1)	4.94	2.29
8[d,e]	2.16 (1)	5.16	2.39
9[d]	2.16 (2)	4.8 ± 0.2	2.33 ± 0.03
10[f]	0.50 (2)	0.97 ± 0.09	2.0 ± 0.1

[a] Temperature 25 °C, $\Sigma[ClO_4^-] = 1.0$ M, $[H^+] = 0.49$ M, $[Co^{III}]_t = 5.0 \times 10^{-4}$ M, and measurements made at 355.5 nm except where noted otherwise. Errors represent one standard deviation. [b] Measurements at 477 nm. [c] $[Co^{III}]_t = 2.0 \times 10^{-3}$ M. [d] $[Co^{III}]_t = 2.16 \times 10^{-3}$ M. [e] Measurements at 465 nm. [f] Concentration of Zn^{2+} increased to 10^{-2} M.

Thus, at constant acidity the reaction is clearly first order in Cr^{2+} over a 1.0×10^{-2} to 6.0×10^{-2} M range and first order in total cobalt(III) over a 5.0×10^{-4} to 2.16×10^{-3} M range (experiment 9). This is consistent with the rate law $-d[Co^{III}]_t/dt = k^{2d}[Cr(II)][Co(NH_3)_5(1\text{-}AEPH_n)^{(2+n)+}]$ where $[Co(NH_3)_5(1\text{-}AEPH_n)^{(2+n)+}] = [Co^{III}]_t = [Co(NH_3)_5(1\text{-}AEP)^{2+}] + [Co(NH_3)_5(1\text{-}AEPH)^{3+}]$.

The reaction rate is strongly influenced by changes in acidity. As shown in Table III, an increase in hydrogen ion concentration markedly decreases k_{obsd} and k^{2d}. Plots of k^{2d} vs. $[H^+]^{-1}$ for a variety of temperatures are nicely linear with nonzero intercepts. The dependence of k^{2d} upon hydrogen ion concentration is therefore given by eq 3 where k_0 represents

$$k^{2d} = k_0 + k_{-1}/[H^+] \tag{3}$$

an acid-independent pathway and k_{-1} represents an acid-dependent pathway for the reaction. Values for k_0 and k_{-1} at various temperatures are given in Table IV.

Discussion

On the basis of results presented earlier the inner-sphere redox reaction between $Co(NH_3)_5(1\text{-}AEPH_n)^{(2+n)+}$ and chromium(II) can be represented by

$$\begin{aligned}&Co(NH_3)_5(1\text{-}AEPH_n)^{(n+2)+} + Cr^{2+}(aq) + 5H^+ \\ &\rightarrow Cr(H_2O)_5(1\text{-}AEPH_n)^{(n+2)+} + Co^{2+}(aq) + 5NH_4^+\end{aligned} \tag{4}$$

From the stoichiometry and the rate law ($-d \ln [Co^{III}]_t/dt = (k_0 + k_{-1}/[H^+])[Cr^{II}]$) it is possible to formulate at least two mechanisms for the reaction.

Mechanism I. The reactions for this mechanism are

$$Co(NH_3)_5(1\text{-}AEPH)^{3+} \leftrightarrows Co(NH_3)_5(1\text{-}AEP)^{2+} + H^+ \quad K_a \tag{5}$$

$$Co(NH_3)_5(1\text{-}AEP)^{2+} + Cr^{2+}(aq) \xrightarrow{H^+} \text{products} \quad k_a \tag{6}$$

$$Co(NH_3)_5(1\text{-}AEPH)^{3+} + Cr^{2+}(aq) \xrightarrow{H^+} \text{products} \quad k_{ah} \tag{7}$$

Equation 5 has been shown to be a rapid, reversible reaction for which $K_a = (6 \pm 1) \times 10^{-4}$ M; hence the dominant form of the complex under the conditions of all kinetic experiments is $Co(NH_3)_5(1\text{-}AEPH)^{3+}$. However, for mechanism I, the dominant kinetic term for the redox process involves the deprotonated form $Co(NH_3)_5(1\text{-}AEP)^{2+}$ even at the highest acidity (0.83 M). The empirical constant k_{-1} ($(3.5 \pm 0.7) \times 10^{-2}$ s⁻¹ at 25 °C) = k_aK_a from which $k_a = (6 \pm 2) \times 10$ M⁻¹ s⁻¹ can be calculated.[28] This is to be compared to $k_{ah} = k_0 = (1.4 \pm 0.1) \times 10^{-1}$ M⁻¹ s⁻¹ for the protonated complex under

Table III. Kinetic Experiments for the Chromium(II) Reduction of $Co(NH_3)_5(1\text{-}AEPH_n)^{(2+n)+}$, $n = 0$ and 1, for Various Acidities and Temperatures[a]

Temp, °C	$[H^+]$, M	$10^2 k_{obsd}$, s^{-1}	$10k^2$[d], $M^{-1}\ s^{-1}$
15.9	0.125	0.424	2.12
15.9	0.077	0.572	2.86
15.9	0.056	0.760	3.80
15.9	0.042	1.01	5.06
20.4	0.490	0.308	1.54
20.4	0.125	0.546	2.73
20.4	0.077	0.830	4.15
20.4	0.056	1.11	5.53
25.0	0.826	0.384	1.92
25.0	0.826	0.388	1.94
25.0	0.490	0.454	2.27
25.0	0.490	0.454	2.27
25.0	0.232	0.632	3.16
25.0	0.133	0.734	3.67
25.0	0.125	0.810	4.05
25.0	0.100	0.920	4.60
25.0	0.100	0.910	4.55
25.0	0.081	1.23	6.16
25.0	0.077	1.20	6.00
25.0	0.067	1.28	6.42
25.0	0.067	1.33	6.63
25.0	0.059	1.46	7.28
25.0	0.053	1.60	7.98
25.0	0.050	1.79	8.95
25.0	0.050	1.74	8.72
29.6	0.490	0.652	3.26
29.6	0.200	0.954	4.77
29.6	0.133	1.02	5.12
29.6	0.100	1.35	6.76
29.6	0.081	1.50	7.52
34.2	0.490	0.798	3.99
34.2	0.200	1.17	5.84
34.2	0.133	1.41	7.07
34.2	0.100	1.64	8.19
34.2	0.077	1.88	9.42

[a] $[Co^{III}]_t = 5.0 \times 10^{-4}$ M, $[Cr^{II}] = 2.0 \times 10^{-2}$ M. Measurements made at 355.5 nm for all experiments.

Table IV. Rate Constants for the Chromium(II) Reductions of $Co(NH_3)_5(1\text{-}AEPH_n)^{(n+2)+}$, $n = 0$ and 1, at Various Temperatures[a]

Temp, °C	$10(k_0 = k_{ah})$,[b,c] $M^{-1}\ s^{-1}$	$10^2 k_{-1}$, s^{-1}	$10^{-1} k_a$,[b] $M^{-1}\ s^{-1}$	$10^{-6} k_h$,[c,d] $M^{-1}\ s^{-1}$
15.9	0.5 ± 0.2	1.9 ± 0.1	3.2 ± 0.6	4.8 ± 0.2
20.4	0.9 ± 0.2	2.5 ± 0.2	4.2 ± 0.8	6.2 ± 0.5
25.0	1.4 ± 0.1	3.5 ± 0.7	6 ± 2	9 ± 2
29.6	2.5 ± 0.3	4.1 ± 0.4	7 ± 1	10 ± 1
34.2	3.2 ± 0.2	4.9 ± 0.2	8 ± 1	12.2 ± 0.5

[a] Errors calculated according to ref 28. [b] Mechanism I. [c] Mechanism II. [d] Error in k_h determined by considering only the error in k_{-1}.

specific reaction rate conditions.

It is interesting that the protonated form of the 1-AEP complex and that of the corresponding phosphato complex[8] are redox active in contrast to certain carboxylato complexes of cobalt(III).[27,29] Presumably, the protonation of the carboxylato groups blocks the formation of a bridged activated complex by tying up the lead-in carbonyl oxygens, whereas the phosphato moieties can accommodate one or two protons without tying up the phosphoryl oxygen lead-in group. However, it must be noted that deprotonation does not significantly enhance the reaction of the bridged complex μ-amido-μ-phosphatobis[tetraamminecobalt(III)] with Cr^{2+}.[11]

Mechanism II. Mechanism II can be written by combining reaction 7 with reactions 8 and 9. This mechanism differs from mechanism I with regard to the site of proton loss and also assumes that $Co(NH_3)_5(1\text{-}AEP)^{2+}$ is not reactive. The empirical parameter $k_0 = k_{ah}$ remains unchanged, whereas k_{-1} now equals $k_h K_h$.

$$Cr^{2+}(aq) + H_2O \rightleftarrows CrOH^+ + H^+ \quad K_h \tag{8}$$

$$CrOH^+ + Co(NH_3)_5(1\text{-}AEPH)^{3+} \rightarrow \text{products} \quad k_h \tag{9}$$

A reasonable order of magnitude for K_h for Cr^{2+} can be obtained from the following consideration. A variety of values for the hydrolysis constants of both Fe^{3+} and Fe^{2+} have been reported[30] with $K_h(Fe^{2+}) < K_h(Fe^{3+})$ by about four orders of magnitude in 1.0 M $NaClO_4$ at 25 °C. The hydrolysis constant for Cr^{3+} has been reported as 4.2×10^{-5} in 1.0 M $NaNO_3$ at 25 °C.[31] Assuming that $K_h(Cr^{3+})$ exceeds $K_h(Cr^{2+})$ by the same order of magnitude as in the iron system, $K_h(Cr^{2+})$ can be estimated as roughly 4×10^{-9} for 1.0 M $LiClO_4$ at 25 °C. In Table IV are listed values of k_h for mechanism II derived on the basis of the above assumptions and the further assumption that K_h would not vary substantially over the temperature range of this investigation. The fastest inner-sphere Cr^{2+} reductions occur with rate constants of about 10^6–10^7 $M^{-1}\ s^{-1}$,[32] so the magnitudes of the k_h values obtained in this way are not unreasonable.

The above mechanisms need not be mutually exclusive. If both reactions 6 and 9 are operative, then $k_{-1} = k_a' K_a + k_h' K_h$. However, it is not possible to obtain independent values of k_a' and k_h'.

Activation Parameters. Activation parameters for the various rate constants k were derived from plots of ln k vs. $1/T$ and the relationships $E_a = \Delta H^\ddagger + RT$ and $A = [\kappa T k_B/h] \exp(\Delta S^\ddagger/R)$ where the transmission coefficient κ was assumed to be 1, k_B = Boltzmann's constant, and h = Planck's constant. Values of $\Delta H^\ddagger$ (kcal/mol) and $\Delta S^\ddagger$ (cal/(deg mol)) are as follows: from k_{ah}, 16 ± 2 and −7 ± 4; from k_a (assuming mechanism I), 8 ± 2 and −21 ± 6, from k_a (assuming mechanism II), 8.3 ± 0.6 and +3 ± 2, respectively.[28] It should be noted that while both $\Delta H_a^\ddagger$ and $\Delta S_a^\ddagger$ derived from k_a (mechanism I) are consistent with activation parameters obtained for other inner-sphere Cr^{2+} reactions, $\Delta S_h^\ddagger$ derived from k_h (mechanism II) is much too positive.[32] However, since the activation parameters for k_a and k_h both reflect assumed ΔH values of zero for K_a and K_h and $\Delta S_h^\ddagger$ is highly dependent on an assumed value of K_h, no further comment on them will be made.

It is not immediately obvious how to account for the activation parameters for k_{ah}; $\Delta H_{ah}^\ddagger$ is somewhat higher and $\Delta S_{ah}^\ddagger$ somewhat less negative than is usually observed in inner-sphere Cr^{2+} reductions of this type.[32] The rate constant, k_{ah}, is however, the same or nearly the same order of magnitude as the rate constants obtained for Cr^{2+} reactions with a variety of acetato and substituted acetato[29] as well as glycinato and substituted glycinato[24] complexes of pentaamminecobalt(III), all of which have been shown to be the result of inner-sphere mechanisms, but with more typical activation parameters.

Comparison with Other Phosphorus-Containing Pentaamminecobalt(III) Complexes. Table V summarizes the available data on the chromium(II) reductions of pentaamminecobalt(III) complexes having phosphorus-containing ligands. The dramatic decrease in the rate of Cr^{2+} reduction with protonation of the 1-aminoethylphosphonic acid ligand (entries 6 and 7) observed in this work (mechanism I) is entirely in accord with earlier findings.[7,8] Statistical corrections to account for the number of equivalent sites available for attack by Cr^{2+} have been made in entries 1, 2, and 6 to facilitate a comparison of the rate constants.

Entries 2 and 6 and entries 3 and 7 have similar phosphoryl oxygen environments, except that an OH group in the phosphato complexes has been replaced by an aminoalkyl

Table V. Comparison of the Rates of Chromium(II) Reduction of Various Phosphorus-Containing Pentaamminecobalt(III) Complexes[a]

Entry	Oxidant	k, M^{-1} s^{-1}	Ref
1	$RoOPO_3$[b]	1.6×10^9	*c*
2	$RoOPO_3H^+$ [b]	4.2×10^3	*c*
3	$RoOPO_3H_2^{2+}$	3×10^{-1}	*c*
4	$RoOPO_3H_3^{3+}$	3×10^{-1}	*c*
5	$RoOPO(OCH_3)_2$	2.5×10^{-2}	*d*
6	$Ro(1\text{-AEP})^{2+}$ [b]	3×10	*e*
7	$Ro(1\text{-AEPH})^{3+}$	1.4×10^{-1}	*e*

[a] Temperature 25 °C, $\mu = 1.0$, Ro = $Co(NH_3)_5^{3+}$. [b] Corrected for the statistical factor by dividing the rate constant k by the number of equivalent sites available for Cr^{2+} attack. [c] Reference 8. [d] Reference 7. [e] This work.

group in the 1-AEP complexes. The monohydrogen complex (entry 2) thus has a lower Coulombic and steric barrier to reduction than the more bulky 1-AEP complex (entry 6) and a higher rate (100 times) of reduction by Cr^{2+}. On the other hand, the rate constants for the reduction of the dihydrogen complex (entry 3) and the protonated 1-AEP complex (entry 7) are within a factor of 2, but both are nearly a factor of 10 greater than the rate observed for the dimethyl ester complex (entry 5) in which two OH groups have been replaced by methoxy groups. Clearly there must be substantial steric constraints for this last complex in achieving the bridged, activated complex.

Acknowledgment. The authors thank Mrs. Connie Stovall for the preparation of the 1-aminoethylphosphonic acid used in this work and Professor A. F. Isbell for providing an infrared spectrum and sample of the purified compound. The authors are grateful to the Robert A. Welch Foundation for financial support of this research and to the National Science Foundation (Grant No. GP-8248) for matching funds for the purchase of the Cary 14 spectrophotometer.

Registry No. $Co(NH_3)_5(1\text{-AEPH})^{3+}$, 59388-98-6; $Co(NH_3)_5CO_3^+$, 15844-68-5; Cr^{2+}, 22541-79-3; 1-aminoethylphosphonic acid, 6323-97-3.

References and Notes

(1) (a) J. M. LaNauze, H. Rosenberg, and D. C. Shaw, *Biochim. Biophys. Acta*, **212**, 332 (1970); (b) C. R. Liang and H. Rosenberg, *ibid.*, **156**, 437 (1968); (c) J. S. Kittredge, A. F. Isbell, and R. R. Hughes, *Biochemistry*, **6**, 289 (1967); (d) T. Matsubara and A. Hayashi, *Biochim. Biophys. Acta*, **296**, 171 (1973); (e) H. Shimizu, Y. Kakimoto, T. Nakajuma, A. Kanazana, and I. Sano, *Nature (London)*, **207**, 1197 (1965); (f) M. Kandatsu and M. Horiguchi, *Agric. Biol. Chem.*, **29**, 781 (1965).

(2) (a) J. A. Alhadeff and G. D. Davis, Jr., *Biochemistry*, **9**, 4866 (1970); (b) J. A. Alhadeff and G. D. Davis, Jr., *Biochim. Biophys. Acta*, **244**, 211 (1971); (c) E. D. Korn, D. G. Dearborn, H. M. Fales, and E. A. Sokoloski, *J. Biol. Chem.*, **248**, 2257 (1973).

(3) E. Roberts, D. G. Simonsen, M. Horiguchi, and J. Kittredge, *Science*, **159**, 886 (1968).

(4) S. H. Kim, J. N. Cho, and Y. J. Kim, *Hanguk Yongyang Hakhoe Chi*, **2**, 173 (1969); *Chem. Abstr.*, **75**, 3445 (1971).

(5) M. Wozniak, J. Nicole, G. Tridot, and A. Verbert, *Chim. Anal. (Paris)*, **54**, 147 (1972).

(6) K. S. Rajan, I. Murase, and A. E. Martell, *J. Am. Chem. Soc.*, **91**, 4408 (1969).

(7) W. Schmidt and H. Taube, *Inorg. Chem.*, **2**, 698 (1963).

(8) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

(9) S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, **21**, 37, 57, 67 (1968).

(10) S. F. Lincoln and A. L. Purnell, *Inorg. Chem.*, **10**, 1254 (1971).

(11) M. Green, R. S. Taylor, and A. G. Sykes, *J. Inorg. Nucl. Chem.*, **33**, 2157 (1971).

(12) W. Mertz, E. W. Toepfer, E. E. Roginski, and M. M. Polansky, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **33**, 2275 (1974).

(13) L. D. Brown and D. E. Pennington, *Inorg. Chem.*, **10**, 2117 (1971).

(14) J. R. Chambers and A. F. Isbell, *J. Org. Chem.*, **29**, 832 (1964).

(15) G. G. Schlessinger, "Inorganic Laboratory Preparations", Chemical Publishing Co., New York, N.Y., 1962, p 211.

(16) G. W. Haupt, *J. Res. Natl. Bur. Stand.*, **48**, 414 (1952).

(17) "Analytical Methods for Atomic Absorption Spectrophotometry", Perkin-Elmer Corp., Norwalk, Conn., March 1973; see section on Cr standard conditions.

(18) (a) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis", 3d ed, Macmillan, New York, N.Y., 1952, p 579; (b) W. J. Blaedel and J. J. Panos, *Anal. Chem.*, **22**, 910 (1950).

(19) H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 186, 269 (1939).

(20) N. H. Furman, Ed., "Standard Methods of Chemical Analysis", Vol. I, 6th ed, Van Nostrand, Princeton, N.J., 1962, pp 389–390.

(21) R. E. Kitson and M. G. Mellon, *Ind. Eng. Chem.*, **16**, 379 (1944).

(22) Reference 18a, p 536.

(23) B. B. Owen, *J. Am. Chem. Soc.*, **56**, 24 (1934).

(24) R. Holwerda, E. Deutsch, and H. Taube, *Inorg. Chem.*, **11**, 1965 (1972).

(25) J. H. Espenson and D. E. Binau, *Inorg. Chem.*, **5**, 365 (1966).

(26) J. E. Finholt, R. W. Anderson, J. A. Fyfe, and F. G. Caulton, *Inorg. Chem.*, **4**, 43 (1965).

(27) J. R. Ward and A. Haim, *J. Am. Chem. Soc.*, **92**, 475 (1970).

(28) Error analysis was performed according to standard equations for determining the propagation of errors and the least-squares fit to a straight line (equal or unequal uncertainities in the data points): P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, N.Y., 1969, Chapters 4 and 6.

(29) M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971).

(30) *Chem. Soc., Spec. Publ.*, **No. 17**, 52–54 (1964).

(31) Reference 30, p 49.

(32) R. G. Linck, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, **9**, 303–352 (1972).