distance for the bonded sulfur atom in the monodentate ligand is 2.453 (2) Å, which is somewhat shorter than the range of 2.488 (2)–2.530 (2) Å for the remainder of the sulfur atoms adjacent to the arylimido ligand. The corresponding distance for the sulfur atom trans to that ligand is, however, 2.645 (2) Å, which represents a substantial trans effect and the first observation of the trans influence of any imido ligand in compounds with a potential 19-electron configuration.[5] Finally, the distance between the molybdenum atom and the unbound sulfur atom of the monodentate ligand is 5.434 (2) Å while the distance between this sulfur atom and the molybdenum atom in the adjacent molecule is also greater than 5 Å. In general, there are no unusual nonbonded contacts in the structure.

Distances and angles within the arylimido and bidentate dithiophosphate ligands are in good agreement with those found in $Mo_2O_3(S_2P(OC_2H_5)_2)_4$,[6] $Mo_2O_3(NH)(S_2P(OC_2H_5)_2)_2$,[7] and $[Mo(NC_6H_4CH_3)(\mu_3\text{-}S)(S_2P(OC_2H_5)_2)]_4$.[2] The unique distances and angles associated with the PS_2 group in the monodentate dithiophosphate ligand can be seen, however, by comparing them to the corresponding parameters in the bidentate ligands. While the average value of the P–S distances in the bidentate ligands is 2.002 Å, these distances in the monodentate ligand are 2.035 (2) Å (for the sulfur atom bound to the metal) and 1.940 (2) Å (for the unbound sulfur atom). The latter corresponds well with the average value of 1.94 Å from 16 separately determined crystallographic distances which we have found in the literature[8] for P=S bonds. The monodentate nature of this ligand has also allowed the S–P–S bond angle to open slightly to a value of 110.7 (1)° whereas the corresponding values in the bidentate ligands are 105.6 (1) and 106.4 (1)°.

The potential 19-electron configuration of $Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)_3$ and the stereochemical consequences of this configuration have been discussed elsewhere.[1] A brief synopsis with additional comments on similar compounds is appropriate, however. Predictions are based on an effective atomic number rule or, ultimately, the minimization of antibonding energies. A linear arylimido ligand is a 4-electron donor with a $Mo{\equiv}N$ linkage while a bent ligand is a 2-electron donor with a $Mo{=}N$ linkage.[9] The rule can be used, for example, to exclude ionic variants of $Mo(NC_6H_5)Cl_2(S_2CN(C_2H_5)_2)_2$ and to predict one bent and one linear arylimido ligand in $Mo(NC_6H_5)_2(S_2CN(C_2H_5)_2)_2$. These predictions are in accord with the observed structures.[4,9]

Results which are more pertinent to $Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)_3$ are also available. The 18-electron configuration in $Nb(NC_6H_4CH_3)(S_2CN(C_2H_5)_2)_3$ suggests a structure with a coordination number of 7 and a linear arylimido ligand. The actual structure has been shown[10] to be a pentagonal bipyramid with an apical arylimido ligand which is nearly linear. In contrast, $Re(NC_6H_4CH_3)(S_2CN(CH_3)_2)_3$, a compound with a potential 20-electron configuration, can achieve the favored 18-electron configuration either by adopting a coordination of 7 with a bent arylimido ligand or by adopting a coordination number of 6 with a linear arylimido ligand and a monodentate dithiocarbamate ligand. Unambiguous NMR evidence[11] indicates the presence of one monodentate dithiocarbamate ligand and, therefore, a coordination number of 6. Identical structural options are open to $Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)_3$ because of its potential 19-electron configuration, and the 6-coordinate compound is again found as shown herein.

The coordination geometries of $MoO_2(S_2CN(C_3H_7)_2)_2$,[12] $MoOCl_2(S_2CN(C_2H_5)_2)_2$,[13] and $NbO(S_2CN(C_2H_5)_2)_3$[14] mimic those of the arylimido compounds described above because the oxo ligand can also serve as a 2- or a 4-electron donor. Since $MoO(S_2CN(C_2H_5)_2)_3{}^+$ is a pentagonal bipyramid with an apical oxo ligand,[15] it is probably safe to infer the same geometry for $Mo(NC_6H_5)(S_2CN(C_2H_5)_2)_3{}^+$.[16] If so, the additional configurational electron in $Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)_3$ had remarkable structural consequences.

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Registry No. $Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)_3$, 72967-91-0.

Supplementary Material Available: Listings of observed and calculated structure amplitudes, anisotropic thermal parameters, hydrogen positional and thermal parameters, and bond distances and angles (34 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of the (4-Hydroxyphenyl phosphato)pentaamminecobalt(III) Ion

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Internal ligand-to-metal electron transfer initiated by the action of an external oxidant on the ligand has received much less attention than the inner- and outer-sphere mechanistic types. Taube's 1970 review of induced electron-transfer reactions[1] cites only 15 references, and little additional work in this area has appeared since then. French and Taube's pioneering study of the action of Ce(IV) on (pyridinemethanol)pentaamminecobalt(III) ions[2] exposed many of the important mechanistic questions concerning the induced electron-transfer effect. More recently, highly efficient induced electron transfer has been reported in the Ce(IV) oxidation of $(NH_3)_5Co^{III}$ complexes of α-hydroxy acids.[3]

We have initiated studies of induced electron transfer linked to the interaction of one-electron oxidants with cobalt(III) complexes of hydroquinone esters. A semiquinone phosphate intermediate is generated in the two-electron oxidation of (4-hydroxyphenyl)phosphoric acid (HQ-*P*) to orthophosphate and 1,4-benzoquinone.[4] Coordinated benzosemiquinone

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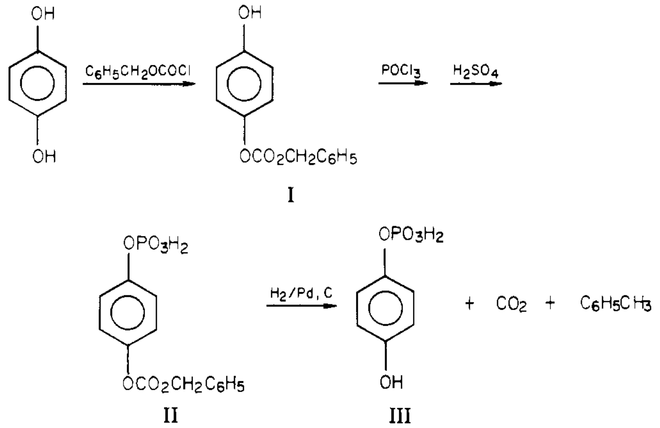
phosphate presumably has the option of transferring an electron internally to cobalt(III) or externally to the free radical initiator. Our ultimate objective is the complete understanding of factors affecting the efficiency of induced electron transfer in hydroquinone ester complexes. In this paper, we concentrate on the synthesis and characterization of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion, which has proved to be quite challenging. Preliminary studies of internal electron transfer induced by Ce(IV) also are presented.

Experimental Section

Materials. Reagent grade chemicals were used throughout, and solutions were prepared with doubly or triply distilled water. The method of Basolo and Murmann[5] was used to prepare $[Co(NH_3)_5CO_3](NO_3)$ and $[Co(NH_3)_5H_2O](ClO_4)_3$. A procedure quite similar to that described by Mac-Coll and Beyer[6] was followed in the synthesis of $[Co(NH_3)_5Me_2SO](ClO_4)_3 \cdot 2H_2O$. SP-Sephadex-C-25-120 cation-exchange resin (Sigma) was used in all chromatographic experiments. A ceric sulfate stock solution in 1 N H_2SO_4 was prepared from $Ce(HSO_4)_4$ (G. F. Smith). Anaerobic solutions were prepared by purging with chromous-scrubbed nitrogen in serum-capped containers.

Preparation of (4-Hydroxyphenyl)phosphoric Acid and Barium 4-Hydroxyphenyl Phosphate Hydrate. Literature procedures are available for the synthesis of (4-hydroxyphenyl)phosphoric acid and its salts.[7,8] The yields we obtained from these methods were not sufficient for the preparation of the target cobalt(III) complex, so a new synthetic route was devised.



A 90% yield of monocarbobenzoxyhydroquinone (I) (mp 119–121 °C; lit.[9] 120–120.5 °C) was obtained from the reaction of benzyl chloroformate (Aldrich) with hydroquinone under a N_2 atmosphere.[9] So that high yields of this intermediate could be obtained reproducibly, benzyl chloroformate was added dropwise to the vigorously stirred hydroquinone solution over a 2–3-h time period and the reaction was allowed to proceed for at least 12 h.

Monocarbobenzoxyhydroquinone monophosphoric acid (II) was prepared from the reaction of $POCl_3$ with I in pyridine, followed by hydrolysis of the phosphoryl chloride product. In a typical preparation, 38.7 g (0.16 mol) of I was dissolved in 30 mL of freshly distilled, dried pyridine, and the solution was cooled to 0 °C in an ice–salt bath. Phosphorus oxychloride (28.5 g, 0.19 mol) was then added dropwise to the stirred, cooled solution over a period of 1 h, maintaining the temperature at less than 25 °C. Pyridinium hydrochloride was removed from the reaction mixture by filtration after overnight storage at 0 °C. The pale yellow supernatant was hydrolyzed through the slow addition of 300 mL of 6 N H_2SO_4, with vigorous stirring and continuous cooling in an ice bath to hold the temperature below 16 °C. Subsequently, the phosphate ester was extracted from the reaction mixture by shaking with 3–4 150-mL portions of chloroform. The solvent was removed from the combined extracts on a rotary evaporator, leaving behind a 90% yield (based on I) of the crude product (II), a viscous, amber oil. This compound was not purified further, but the presence of both carbobenzoxy (carbonyl absorption at 1765 cm^{-1}) and phosphate (broad, strong bands between 800 and 1200 cm^{-1}) functional groups was confirmed by infrared spectra of the neat compound smeared between KBr plates.

The carbobenzoxy protecting group was removed from II by hydrogenolysis.[9] Palladium on activated charcoal catalyst was added to a solution of II in 95% ethanol, and the mixture was stirred under a hydrogen atmosphere for several days. After removal of the catalyst by filtration, the solvent was taken off on a rotary evaporator, yielding a yellow oil. Hydrogenolysis was continued to completion, as determined by the absence of the 1765-cm^{-1} infrared absorption of the carbobenzoxy group. The overall yield of III was 65%, based on hydroquinone.

Although Andrews reports a solid form of (4-hydroxyphenyl)phosphoric acid,[8] we could not convert our crude oil to a crystalline product in good yield. A white crystal was obtained by dissolving the oil in the minimum amount of Me_2SO at 50–60 °C, followed by cooling to 0 °C and precipitation with cold distilled water. More than 50% of the hydroquinone phosphate product was lost in this purification procedure. The crude oil, containing only small amounts of ethanol and water impurities, was used therefore in the synthesis of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion.

So that it could be confirmed that (4-hydroxyphenyl)phosphoric acid was the product of our synthesis, a portion of the crude oil was converted to a crystalline barium salt, $Ba[HOC_6H_4OPO_3] \cdot H_2O$. The oil (19.15 g) was dissolved in 100 mL of water, and the solution was filtered to remove a small amount of insoluble material. The solution was then adjusted to pH 7 with $NH_3(aq)$ and mixed with a slight (10%) excess of barium acetate to give a white precipitate. This solid was collected on a sintered-glass filter, washed with cold 95% ethanol, and dried in vacuo for 6 h; the yield was 12.6 g. Anal. Calcd for $Ba[HOC_6H_4OPO_3] \cdot H_2O$: C, 20.98; H, 2.05; P, 9.02. Found: C, 21.00; H, 1.95; P, 9.04. IR: 3350 (s, br), 1630 (m), 1510 (s), 1475 (m), 1390 (w), 1230 (s, br), 1085 (s, br), 930 (m, shoulder), 900 (s), 820 cm^{-1} (m). UV: ϵ_{275}(max) 1765 M^{-1} cm^{-1} (1 N $HClO_4$).

Analyses. The perchlorate content of stock $LiClO_4$ solutions was determined gravimetrically.[10] The ceric sulfate stock solution was standardized against As_2O_3.[11]

Kitson's method was used to assay cobalt in chromatographic fractions.[12] Complexes were degraded to Co_2O_3 by boiling in alkaline solution. Enough HCl was then added to convert the oxide to $Co^{2+}(aq)$. A standard curve for the spectrophotometric assay (625 nm) was generated from the analysis of $Co^{2+}(aq)$ solutions prepared from the metal. The method of Gould and Taube[13] was used to determine $[Co^{II}]$ in solutions containing cerium. A constant volume (5 mL) of test solution in 1 N H_2SO_4 was diluted to 25 mL with concentrated HCl after quenching excess Ce(IV) with hydroquinone. The absorbance at 695 nm was then determined and compared, as before, with a standard curve.

The 4-hydroxyphenyl phosphate content in cobalt complexes was determined by two methods. In the first, complexes were boiled in alkaline solution, resulting in the oxidative cleavage (by O_2) of the ligand to 1,4-benzoquinone and orthophosphate. The spectrophotometric method (460 nm) of Kitson and Mellon[14] was then used to assay orthophosphate, using K_2HPO_4 solutions as standards. Full-color development was not achieved until 48 h after ammonium vanadate and ammonium molybdate were added to orthophosphate solutions. The second method for determining hydroquinone phosphate complexed to cobalt(III) involved complete hydrolysis to $[(NH_3)_5CoH_2O]^{3+}$ and free ligand at 70 °C (vide infra). The phosphate ester was quantitatively separated from cobalt by absorption of the product solution onto a 1 × 10 cm cation-exchange column. A_{275} was then measured to give [HQ-*P*] after adding sufficient $HClO_4$ to the column effluent to bring $[H^+]$ to ca. 1 M.

The number of ammine ligands in cobalt complexes was found through a modified Kjeldahl analysis.[15] The complex was decomposed with excess NaOH in a Kjeldahl flask attached to a distillation

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assembly. The resulting solution was boiled for 40 min to distill NH_3 into a collection flask containing a known amount of hydrochloric acid. Excess HCl was then titrated to a bromocresol green end point with standard NaOH.

Kinetic Measurements. The kinetics of acid hydrolysis of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion was followed at 519 nm. Anaerobic solutions were incubated at 70.0 ± 0.2 °C. Aliquots were removed at various times with a gas-tight syringe and quenched in an ice bath. Room-temperature spectra were then measured in the interval 400–600 nm. Observed first-order rate constants (k_{obsd}) were derived from the slopes of linear $\ln (A_t - A_\infty)$ vs. time plots. Reported values generally are the average of three determinations.

Instrumentation. UV–visible spectra were recorded on a Cary 17 spectrophotometer, thermostating the cell compartment at 25.0 °C for spectrophotometric titrations. A Perkin-Elmer Model 457 spectrophotometer was used for infrared measurements. An Ionalyzer Model 801 meter, calibrated against pH 4, 7, and 10 standards, was used to make pH measurements. The uncertainty in pH readings is estimated to be ±0.05 unit. Chromatographic separations were carried out at 3–4 °C in a Masterbilt cold case. A Lauda Model B-1 bath was used to thermostat solutions in kinetic and induced electron-transfer studies.

Results

Synthesis of the (4-Hydroxyphenyl phosphato)pentaamminecobalt(III) Ion. The approach of Busch and Pennington[16] was adopted in the synthesis of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion, $[Co(NH_3)_5(O_3POC_6H_4OH)]^+$. $[Co(NH_3)_5CO_3](NO_3)$ (2.0 g, 7.6 mmol) was slowly added, over a period of 1 h, to a stirred solution of (4-hydroxyphenyl)phosphoric acid (4.3 g, 22 mmol) in ca. 3 mL of water at room temperature. Another 2–3 mL of water was then added, and the mixture was heated at 65–70 °C for 1.5 h. The color of the solution changed from red-orange to deep red over this interval, and evolution of CO_2 was complete within 0.5 h. The reaction mixture was then cooled to room temperature, diluted to 1000 mL (pH 6.1), and applied to two 2.5 × 20 cm cation-exchange columns equilibrated with 0.05 M $LiClO_4$ (pH 6).

Seven bands were identified upon elution of these columns with $LiClO_4$ at pH 6. Elution with 0.2 M $LiClO_4$ brought a small amount of a yellow component off of the column. A red-violet fraction (30% of total cobalt), assigned to $[Co(NH_3)_5(O_3POC_6H_4OH)]^+$, was then eluted with 0.3 M $LiClO_4$. Subsequent minor fractions eluted by 0.3 M $LiClO_4$ were, in order of elution, yellow-brown and pink. A purple component was then eluted with 0.5 M $LiClO_4$ before collecting the next major fraction, $[(NH_3)_5CoH_2O]^{3+}$ (60% of total cobalt), identified from its absorption maxima at 492 and 345 nm. Finally, a highly unstable pink band was eluted with 1.0 M $LiClO_4$.

The red-violet fraction eluted by 0.3 M $LiClO_4$ exhibited an absorption maximum at 519 nm and well-defined shoulders near 360 and 275 nm. Attempts to crystallize this complex by cooling or the addition of nonaqueous solvents were unsuccessful. Cobalt and phosphate analyses of material isolated from four independent preparations gave a Co:P ratio of 1:1.00 (±0.02). A single ammonia analysis gave the result Co:NH_3 = 1:5.04 (±0.04). These analyses clearly support our assignment of the red-violet fraction to $[Co(NH_3)_5(O_3POC_6H_4OH)]^+$.

Other preparative routes to $[Co(NH_3)_5(O_3POC_6H_4OH)]^+$ were examined, but none bettered the 30% yield achieved through the above procedure. Comparable yields were observed in the reaction of III with $[Co(NH_3)_5Me_2SO]^{3+}$ in dimethyl sulfoxide at 50–55 °C. Again, numerous side products were observed on chromatographing product mixtures.

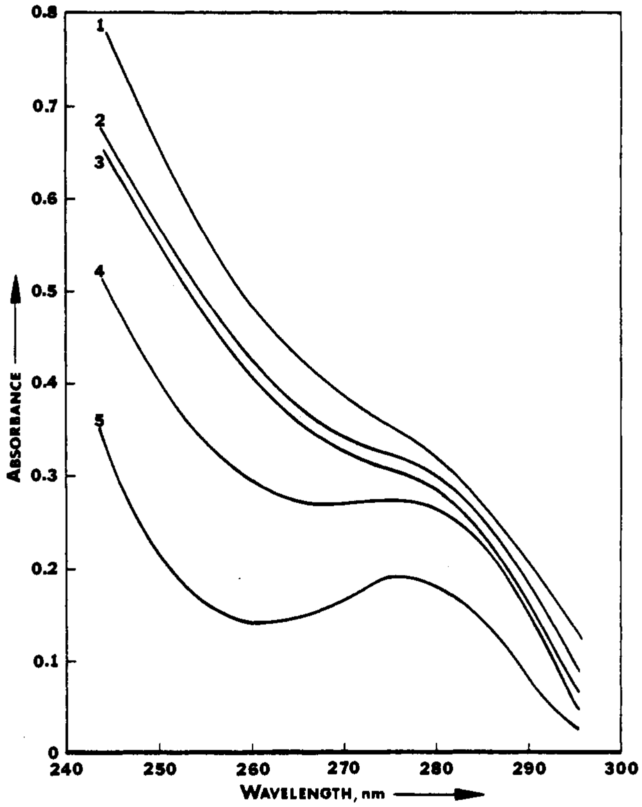

Figure 1. Ultraviolet spectra of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion ($[Co^{III}]$ = 0.154 mM, $\sum[ClO_4^-]$ = 0.05 M, 25 °C): (1) pH 9.10, (2) pH 7.55, (3) pH 5.55, (4) pH 3.25, (5) pH 1.05.

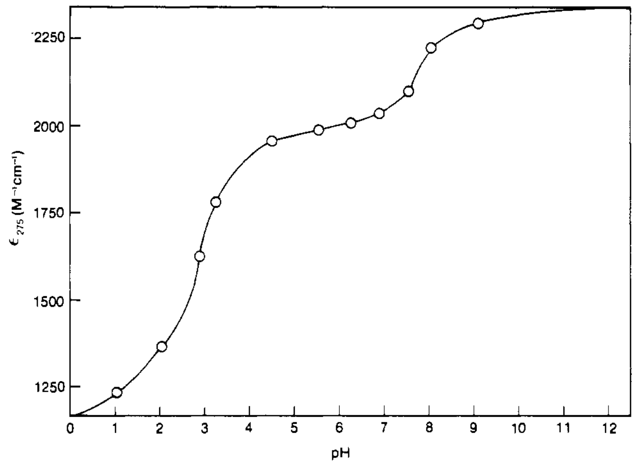

Figure 2. Spectrophotometric titration of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion at 275 nm ($[Co^{III}]$ = 0.154 mM, $\sum[ClO_4^-]$ = 0.05 M, 25 °C).

Acid Ionization Constants. Spectrophotometric titrations were performed to determine the first (phosphate O–H) and second (phenolic O–H) acid ionization constants of $[Co(NH_3)_5(OP(O)(OH)OC_6H_4OH)]^{2+}$. The ultraviolet spectrum of this complex is quite sensitive to changes in pH (Figure 1). Figure 2 shows the pH dependence of A_{275} at 25 °C. The pH of solutions was adjusted with $HClO_4$ or NH_3(aq) while the perchlorate ion concentration was held constant at 0.05 M through the addition of $LiClO_4$.

The acid ionization constants K_1 and K_2 were derived from separate nonlinear least-squares analyses of the two titration curves evident in Figure 2, with the extinction coefficients of the protonated and ionized species and the acid ionization constant as the parameters to be fitted in each case. Results of this analysis are pK_1 = 2.83 ± 0.05, pK_2 = 7.75 ± 0.10,

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[16] Busch, M. A.; Pennington, D. E. *Inorg. Chem.* **1976**, *15*, 1940.

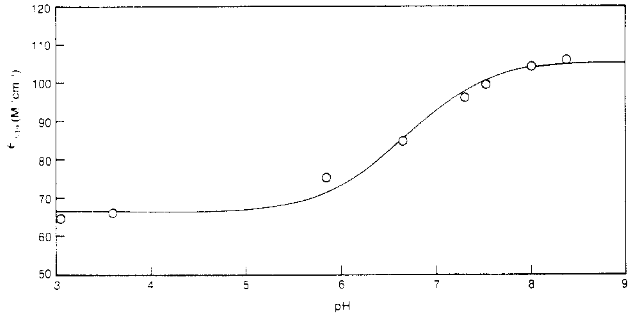

Figure 3. Spectrophotometric titration of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion at 519 nm ([Co^{III}] = 0.584 mM, $\sum[ClO_4^-]$ = 1.00 M, 25 °C).

$\epsilon_{275}(+2)$ (1.24 ± 0.02) × 10^3 M^{-1} cm^{-1}, $\epsilon_{275}(+1)$ (1.98 ± 0.02) × 10^3 M^{-1} cm^{-1}, and $\epsilon_{275}(0)$ (2.31 ± 0.02) × 10^3 M^{-1} cm^{-1}, where the numbers in parentheses directly behind refer to the charge of the complex ion derived from the ionization of $[Co(NH_3)_5OP(O)(OH)OC_6H_4OH]^{2+}$.

A 519-nm spectrophotometric titration carried out as before at 25.0 °C, but with $\sum[ClO_4^-]$ = 1.00 M, is shown in Figure 3. A single titration curve, assigned to the K_2 ionization, is evident between pH 3.05 and 8.38. The visible absorption maximum is invariant within this interval. The parameters obtained from the nonlinear least-squares analysis of the data are pK_2 = 6.69 ± 0.11, $\epsilon_{519}(+1)$ 67 ± 2 M^{-1} cm^{-1}, and $\epsilon_{519}(0)$ 105 ± 2 M^{-1} cm^{-1}.

Kinetics and Stoichiometry of Acid Hydrolysis. A study of the kinetics and stoichiometry of the anaerobic acid hydrolysis reaction of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion was carried out at 70 °C, $\sum[ClO_4^-]$ = 1.00 M ($HClO_4$, $LiClO_4$). Spectra run over a period of 8 h showed that $[Co(NH_3)_5H_2O]^{3+}$ accounts for at least 99% of the cobalt product of this reaction. Thus, the absorption maximum shifted from 519 to 492 nm, and the equilibrium A_{492} value accorded well with that calculated from the initial Co(III) concentration and the extinction coefficient of $[Co(NH_3)_5H_2O]^{3+}$ (ϵ_{492} 51.0 M^{-1} cm^{-1}). A Co(II) analysis carried out on the products of acid hydrolysis ([Co^{III}]$_0$ = 2.34 mM) at pH 1.9 showed that a small amount (0.70%) of cobalt(II) was produced, presumably from the intramolecular oxidation of the hydroquinone phosphate ligand.

Assays for free 4-hydroxyphenyl phosphate were carried out on the products of acid hydrolysis at pH 0.02, 0.45, and 1.62. Ultraviolet spectra of cobalt-free product solutions showed that the ratio of free HQ-*P* produced per cobalt atom is 1.02 (±0.06):1. This result confirms the stoichiometry of the reactant and also shows that a negligible amount of HQ-*P* is lost to oxidation or ester hydrolysis at 70 °C on the time scale of the aquation reaction.

Figure 4 shows the result of kinetic studies of acid hydrolysis at 70 °C in the pH interval 0.02–4.62. The sigmoidal k_{obsd} vs. pH plot is readily understood in terms of a mechanism involving simultaneous hydrolysis of two species, AH (rate constant k_{AH}) and A (rate constant k_A), related by a rapid acid ionization preequilibrium (ionization constant K_{AH}). The rate law expected on this basis is

$$k_{obsd} = (k_{AH}[H^+] + k_A K_{AH})/([H^+] + K_{AH}) \quad (1)$$

An excellent nonlinear least-squares fit of the data to this equation was attained, yielding the parameters k_A = (0.50 ± 0.02) × 10^{-4} s^{-1}, k_{AH} = (1.34 ± 0.03) × 10^{-4} s^{-1}, and pK_{AH} = 1.82 ± 0.07.

Induced Electron Transfer. The anaerobic oxidation of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion by Ce(IV) in 1 N H_2SO_4 was studied at 25.0 °C. Freshly purified complex eluted from SP-C-25 resin with 1 N H_2SO_4 was used in these experiments. Sufficient Ce(IV) stock solution was rapidly injected (gas-tight syringe) into stirred solutions of the complex (0.30 mM) to give Ce:Co ratios of 10.0, 13.3, 20.0, 23.3, and 33.3. The efficiency of induced electron transfer observed was quite low, as the % Co(II) findings (±1%) on the product solutions were 9, 8, 8, 6, and 5, respectively. The Ce(IV) oxidation of the cobalt complex is complete shortly after mixing, consistent with kinetic studies of the oxidation of the free ligand under the same conditions (k = 9.5 × 10^4 M^{-1} s^{-1}).[17]

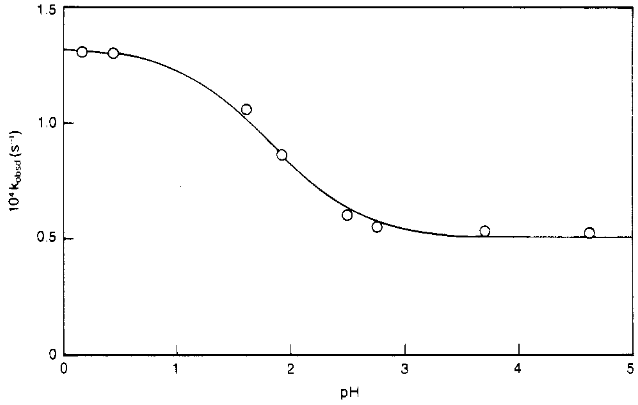

Figure 4. pH dependence of the rate of acid hydrolysis of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion ([Co^{III}] = 0.978 mM, $\sum[ClO_4^-]$ = 1.00 M, 70 °C).

Discussion

Stoichiometric evidence strongly supports our assignment of the red-violet band eluted from SP-C-25 resin to the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion. The position of the $^1T_{1g} \leftarrow {}^1A_{1g}$ ligand field transition at 519 nm is consistent with findings on $[(NH_3)_5CoO_3POC_6H_5]^+$ (518 nm)[18] and other (phosphato)pentaamminecobalt(III) ions.[16] The low yield attained and difficulty of obtaining a solid are a severe liability in our preparative method. Work is continuing on alternative synthetic routes in nonaqueous solvents to eliminate the predominant $[Co(NH_3)_5H_2O]^{3+}$ side product.

The pK_1, pK_2, and pK_3 (phenolic O–H) values of (4-hydroxyphenyl)phosphoric acid are 1.4, 6.14, and 10.4, respectively.[19,20] Ionization constants (25 °C, I = 1.0 M) of H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-} are enhanced by factors of 2 × 10^2, 2 × 10^2, and 6 × 10^3, respectively, upon coordination to $(NH_3)_5Co^{III}$.[21] On this basis, we assign the pK_1 and pK_2 values calculated from the ultraviolet spectrophotometric titration to the ionization of the phosphate and phenolic O–H groups in $[Co(NH_3)_5OP(O)(OH)OC_6H_4OH]^{2+}$. The complex chromatographs as a 1+ cation at pH 6, consistent with this assignment. Relative to the free acid, Δ(p*K*) values for the first and second ionization steps of the complex are −3.3 and −2.6, respectively. The p*K* value of 6.69 derived from the 519-nm spectrophotometric titration may also be assigned to the phenolic O–H ionization, considering the influence of the secondary salt effect at higher ionic strength.

Our rate data on the hydrolysis of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion indicate that the hydroxyphenyl substituent has little effect on the behavior of the phosphate leaving group. The dependence of k_{obsd} on [H$^+$] is explained by assigning k_{AH} to the aquation of

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$[(NH_3)_5CoOP(O)(OH)OC_6H_4OH]^{2+}$ and k_A to the reaction of the corresponding monovalent cation, derived from the ionization of the phosphate O–H group. The pK_{AH} value obtained from the kinetic measurements at 70 °C, $\sum[ClO_4^-] = 1.0$ M, is smaller than pK_1 calculated from the 275-nm spectrophotometric titration at 25 °C, $\sum[ClO_4^-] = 0.05$ M, by about 1.0 unit. This difference appears reasonable, considering the enhancements in acid strength expected with increasing temperature and ionic strength.

The rate constants k_A and k_{AH} are comparable to those reported for the aquation of $[(NH_3)_5CoOPO_3H]^+$ (3.5×10^{-5} s^{-1}) and $[(NH_3)_5CoOPO_3H_2]^{2+}$ (4.5×10^{-4} s^{-1}) (70 °C, $I = 1.0$ M ($NaClO_4$)),[22] respectively. The ratio of rate constants for hydrolysis of 2+ and 1+ ions at 70 °C is somewhat larger in the phosphato system (13) than in the hydroxyphenyl phosphato system (2.7). This small difference may reflect the electron-donating capability of the C_6H_4OH substituent, resulting in the partial neutralization of positive charge added to the coordinated phosphate group through protonation. Finally, it may be noted that the absence of phosphate ester hydrolysis accompanying the aquation of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion is consistent with the observations of Schmidt and Taube on Co(III)-complexed dimethyl and trimethyl phosphate.[21]

Our preliminary results demonstrate that induced electron transfer occurs in the reaction of the (4-hydroxyphenyl phosphato)pentaamminecobalt(III) ion with Ce(IV) and that the trend in % Co(II) with increasing [Ce(IV)] is as expected from the competition between external and internal oxidants for a semiquinone phosphate intermediate. Unfortunately, the low Co(II) yields prevent us from quantitatively estimating the ratio of rate constants for electron transfer from this intermediate to Co(III) and Ce(IV). Weaker oxidants such as $Mo(CN)_8^{3-}$ will be employed in future studies of induced electron transfer in hydroquinone ester complexes in the hope that higher Co(II) yields will be attained.

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Registry No. I, 74206-92-1; II, 80963-06-0; III, 940-75-0; $[Co(NH_3)_5(O_3POC_6H_4OH)]^+$, 80964-53-0; $Ba[HOC_6H_4OPO_3]$, 80963-07-1; $POCl_3$, 10025-87-3; $[Co(NH_3)_5CO_3](NO_3)$, 15244-74-3.

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Comparative Studies of the Reduction of Bis(2,9-dimethyl-1,10-phenanthrolinediyl-4,7-bis(benzenesulfonato))copper(II) and Bis(2,9-dimethyl-1,10-phenanthroline)copper(II) Ions by Hydroquinone

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Considerable uncertainty currently exists concerning the intrinsic electron-transfer reactivity of cuprous/cupric systems. Widely divergent estimates of the Cu(I,II) self-exchange rate constant (k_{11}) in copper–phenanthroline complexes have been obtained by applying the relative Marcus theory to cross-reaction data.[1–4] Justification of this indirect approach is required, as cross reactions must satisfy the weak-overlap, outer-sphere criterion of the Marcus theory.

A comparison of rate parameters for the hydroquinone (H_2Q) reduction of bis(2,9-dimethyl-1,10-phenanthroline)copper(II) ($Cu(dmp)_2^{2+}$) and bis(2,9-dimethyl-1,10-phenanthrolinediyl-4,7-bis(benzenesulfonato))copper(II) ($Cu(dpmp)_2^{2-}$) ions is presented in this note. Relative Marcus theory is applied, as in our previous work,[4] to estimate the k_{11} values of the $Cu(dmp)_2^{2+/+}$ and $Cu(dpmp)_2^{2-/3-}$ couples. For this application, hydroquinone is a good choice of reductant. Thus, the Marcus relationship successfully correlates rate constants with thermodynamic driving force in the oxidation of substituted hydroquinones by $Cu(dmp)_2^{2+}$ and other one-electron oxidants.[4] Furthermore, apparent self-exchange rate parameters for the $Mo(CN)_8^{3-/4-}$ and $Fe(CN)_6^{3-/4-}$ couples, derived from cross reactions with hydroquinone, are consistent with the experimental rate constant of the $Fe(CN)_6^{4-}$ – $Mo(CN)_8^{3-}$ reaction under the same conditions.[5]

Experimental Section

Materials amd methods described by Clemmer et al.[4] were employed in kinetic studies of the hydroquinone reduction of $Cu(dpmp)_2^{2-}$. The disodium salt of 2,9-dimethyl-1,10-phenanthrolinediyl-4,7-bis(benzenesulfonic acid) (Sigma) was used as received. The oxidant and reductant were prepared in the same sodium acetate buffer (ionic strength = 0.2 M), and, in most runs, the $dpmp^{2-}$ ligand was contained initially in the copper(II) solution.

Hydrogen ion concentrations were derived from pH readings (Brinkmann pH-104 meter) by using relationship 1, based on an

$$-\log [H^+] = pH - 0.12 \qquad (1)$$

activity coefficient of 0.757 for 0.2 M NaOAc.[6] In pH-dependence studies, the total ligand concentration ($[dpmp]_{tot}$) was adjusted to give a $[dpmp^{2-}]/[Cu^{II}]_{tot}$ ratio of 18, taking protonation of $dpmp^{2-}$ to $Hdpmp^-$ into account ($pK_a(Hdpmp^-) = 5.80$).[7] Although formation constants in the Cu^{II}–$dpmp^{2-}$ system are not known, drawing the analogy to the structurally similar Cu^{II}–dmp system indicates that an 18-fold excess of $dpmp^{2-}$ should be adequate to convert 98+% of the available copper(II) into the $Cu(dpmp)_2^{2-}$ ion.[4,8] This assumption was justified by showing that observed rate constants ($[H_2Q] = 1$ mM, pH 6.02) are independent of ligand concentration in the range 20- to 100-fold excess of dpmp over Cu, in agreement with findings on Cu^{II}–dmp solutions.[4]

Formation of $Cu(dpmp)_2^{3-}$ was followed at 483 nm (ϵ_{483} 1.225×10^4 M^{-1} cm^{-1})[7] on a Durrum D-110 stopped-flow apparatus, with the total copper concentration held constant at 10 μM and with at least a 10-fold excess of reductant. Fast and slow increases in 483-nm absorbance were noted in all runs, suggesting the presence of Cu^{II}–$dpmp^{2-}$ complexes other than $Cu(dpmp)_2^{2-}$. The contribution of the slow phase to ΔA_{483} is considerably smaller when the $dpmp^{2-}$ ligand is present initially in the reductant solution, rather than the copper(II) solution. It seems reasonable to conclude, therefore, that the slow phase corresponds primarily to the reduction of Cu^{II}–$dpmp^{2-}$ complexes which are formed slowly on the time scale required for the formation and subsequent reduction of $Cu(dpmp)_2^{2-}$.

Fortunately, the difference in rate between the fast and slow components of ΔA_{483} was sufficiently large to allow the evaluation of observed first-order rate constants for the predominant fast phase (k_{obsd} (fast)) from standard ln $(A_\infty - A_t)$ vs. time or Guggenheim[9] plots. In most runs a reliable A_∞ (fast) was established on the os-

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