the complete association for the first step. The Shedlovsky method[24] for a uni-univalent electrolyte was used to determine K_{a2}.

The conductance results obtained for three electrolytes are summarized in Table II, together with those for some electrolytes for comparison. The Stokes hydrodynamic radii are also given.

Discussion

The extended Jenkins-Monk method used here involves several important assumptions, especially (i) the use of the limiting law for conductivities and activity coefficients and (ii) the estimation of $\lambda_0(MX^+)$ using Stokes' law. Table III gives the derived parameters resulting from changes in the above assumptions for the perchlorate. Although the association constants in nitrobenzene are hardly influenced by the equations used for activity coefficients, K_{a2} depends on Λ_0 and the ratio of $\lambda_0(MX^+)$ to $\lambda_0(^1/_2M^{2+})$.

Consistent values of λ_0 for the tetraphenylborate and perchlorate were obtained (Table II). The estimation of λ_0 of monovalent ion-paired species remains controversial in the conductance analysis of bi-univalent electrolytes.[25] A λ_0 value of 7.5 for the ion pair $[Ni([14]aneN_4)]I^+$ was estimated from $\lambda_0(I^-) = 20.4$ S cm^2 mol^{-1} and $\Lambda_0\{[[Ni([14]aneN_4)]I]I\} = 27.9$, this leading to 0.4 for the ratio of $\lambda_0\{Ni([14]aneN_4)]I^+\}$ to $\lambda_0\{^1/_2[Ni([14]aneN_4)]^{2+}\}$. Thus, the use of eq 3 for $\lambda_0\{[Ni([14]aneN_4)]ClO_4^+\}$ does not seem unreasonable in view of the slightly larger ClO_4^- compared to I^-.

A square-planar (diamagnetic)-octahedral (paramagnetic) equilibrium is known to exist for Ni(II) chelate cations with macrocyclic ligands in water,[8] but it was reported that the $[Ni([14]aneN_4)]^{2+}$ salts are diamagnetic in methanol.[11] The basicity of solvent molecules is greatly responsible for the position of the equilibrium. Although the donor number (19.0) of methanol, as a measure of basicity,[13] is comparable with that (18.0) of water, the difference between equilibria in water and in methanol may be due to that in the steric factor. Considering the low donor number (4.4) of nitrobenzene, it appears that the $[Ni([14]aneN_4)]^{2+}$/nitrobenzene interaction is electrostatic in nature and very weak, and the cation is not functioning as an octahedral form. This view is consistent with the perchorate and iodide behavior discussed below.

The association constants in Table II drastically change from the tetraphenylborate to the iodide. Generally, most salts of tetraphenylborate are completely dissociated in nitrobenzene[14] due to its low density of surface charge with aromatic character of the benzene rings.[26] It is noteworthy that $[Ni([14]aneN_4)](ClO_4)_2$ is greatly associative, as compared to other uni-univalent electrolytes with active hydrogen atoms such as Bu_3HNClO_4[27] and $[Co(acac)_2(en)]ClO_4$[28] (acac = 2,4-pentanedione anion; en = ethylenediamine); the K_{a1} value of $[Fe(phen)_3](ClO_4)_2$[14] (phen = 1,10-phenanthroline) is only 39 for K_{a1} where there is no hydrogen bond possibility. When å is 0.4 nm, which corresponds to the contact distance between Ni(II) and ClO_4^-, the Fuoss equation of electrostatic association predicts only 500 for K_{a1} and 9 for K_{a2}.

The X-ray analysis of the perchlorate of the [(5(*SR*),7(*RS*),12(*RS*),14(*SR*))-tetramethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) complex[29] established that in the orange isomer the two perchlorate ions are disposed in the axial position and hydrogen bonded to the cation through N-H···O-Cl hydrogen bonds (N···O = 0.31 nm) but no perchlorate oxygen is directly bonded to nickel. The large association constants for the perchlorate supports the view that even in nitrobenzene such axial approach of the perchlorate ions to nickel is effectively enhanced through N-H···O-Cl hydrogen bonds since nitrobenzene is of low basicity. The perchlorate ion is not usually regarded as a hydrogen-bond acceptor.[30,31] However, the hydrogen-bond donor properties of the N-H protons of ethylenediamine-like ligands disposed in square-planar fashion are very important even in the association phenomena of the perchlorate ion.

The r_s value of 0.59 nm for $[Ni([14]aneN_4)]I^+$ is nearly the same as the sum of diameter of I^- and the radius of Ni^{2+}. This suggests that the I^- ion is oriented next to the nickel(II). This selective orientation with the large association constants is not what would be expected an ion pair. Such selective orientation may be obtained by either a hydrogen-bonding interaction or a charge-transfer complex. The iodide is light orange in nitrobenzene, although very weak because of its low solubility, but this color does not necessarily support the latter because unfortunately the iodide ion itself also gives a charge-transfer-to-solvent spectrum with a light orange color in nitrobenzene.[33]

Registry No. $[Ni([14]aneN_4)](BPh_4)_2$, 88730-77-2; $[Ni([14]aneN_4)](ClO_4)_2$, 15220-72-1; $[Ni([14]aneN_4)]I_2$, 88730-78-3.

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Preparation and Characterization of Rhodium(III) Polyphosphate Complexes

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ATP, ADP, PP, and other di- and triphosphates exist in the living cell as Mg(II) complexes, and it is in this form that they participate in biochemical processes. Mg(II) complexes undergo rapid ligand exchange, and thus the various stereoisomers and/or structural isomers of a given Mg(II) polyphosphate complex exist in solution in rapid equilibrium.

Independently, Mildvan and Cleland introduced the concept of using exchange-inert metal ions in place of Mg(II) for the preparation of stable metal-polyphosphate complexes for use in kinetic, spectroscopic, and stereochemical studies.[1,2] α,β,γ-Tridentate metal complexes of ATP and PPP have been prepared as well as β,γ-bidentate M(ATP), α,β-bidentate M(ADP) and M(PP), γ-monodentate M(ATP) and β-monodentate M(ADP) and M(PP).[3] The two exchange-inert metal ions that have been used in this capacity are Cr(III) and Co(III). The Cr(III) complexes are potentially useful as paramagnetic probes and the Co(III) species as diamagnetic

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probes. Aqua Cr(III) complexes are redox stable. Thus, polyphosphate complexes, prepared with Cr(III), closely resemble the naturally occurring $Mg(H_2O)_n$(polyphosphate) complexes. This is not true for the Co(III) complexes, where NH_3 ligands (or their equivalent) must occupy coordination positions not taken by the polyphosphate. The NH_3 ligands are not well accepted by enzymes, and the unfortunate result is that few enzymes bind or react with the Co(III) complexes.[4] This means that, in general, the Co(III) complexes are not good diamagnetic probes for active-site NMR and ESR distance measurement studies, nor do they serve as probes of enzyme stereospecificity and structural specificity. Furthermore, at and above pH 7 the Co(III) complexes undergo facile reduction, releasing Co(II) and the polyphosphate ligand.[5,6] The presence of either of these species in the NMR or ESR sample can give rise to misleading results.

$Rh(H_2O)_6^{3+}$ is diamagnetic and unlike $Co(H_2O)_6^{3+}$ is redox stable. As a result, $Rh(H_2O)_n$(polyphosphate) complexes should prove superior to their $Co(NH_3)_n$ analogues as enzyme-active-site probes. Moreover, unlike the Cr(III) and Co(III) complexes, those of Rh(III) may be used as heavy-atom probes in enzyme X-ray crystallographic studies. Owing to these superior features, in the present study we have prepared and characterized a series of Rh(III) polyphosphate complexes.

Experimental Section

General Considerations. NMR spectra were recorded at 25 °C by using either a Varian XL-100 (operating at 40.51 MHz for ^{31}P) or an IBM WP200SY (operating at 81.02 MHz for ^{31}P) NMR spectrometer. ^{31}P NMR samples contained 0.3 mM EDTA in 10% D_2O while ^{13}C NMR samples contained 1 mM EDTA in 40% D_2O. ^{31}P chemical shifts are reported in ppm downfield (+) or upfield (−) from a 0.1 M D_3PO_4 external standard while ^{13}C chemical shifts are reported in ppm downfield from an internal trimethylsilane standard. CD spectra were recorded by using a Jasco 500-C spectropolarimeter and UV/visible absorption spectra by using a Perkin-Elmer 552 spectrophotometer. Molar extinction coefficients are based on elemental analysis data or adenosine content, which in turn is based upon absorptivity at 260 nm (ϵ = 15 400). Elemental analyses were carried out by Galbraith Laboratories, Knoxville, TN. High-pressure liquid chromatography was carried out by using an IBM LC/9533 liquid chromatograph or Beckman 330 chromatograph, an Altex C-18 reverse-phase analytical column (25 cm) or Whatman C-18 reverse-phase preparative column (50 cm) and 0.10 M potassium methanesulfonate at pH 2.2 as an isocratic eluant. The cycloheptaamylose (1.3 × 250 cm) column was prepared and chromatography carried out as previously described.[7] A solution of $[Rh(H_2O)_6](ClO_4)_3$ was prepared according to the method of Jørgensen,[8] adjusted to pH 3.5 with KOH, and then filtered to remove crystalline $KClO_4$. All enzymes, nucleotides, buffers, and Dowex and Sephadex resins were purchased from Sigma Chemical Co. $Rh(H_2O)_3Cl_3$ was purchased from Alfa Chemical Co. The Dowex resins were bleached with Br_2 as previously described.[7]

$Rh(H_2O)_4PP$ (1). Fifty milliliters of 20 mM $[Rh(H_2O)_6](ClO_4)_3$ at pH 3.5 was added to 50 mL of 20 mM PP that had been adjusted to pH 3 with use of Dowex 50-X2 (H^+) resin. The mixture was heated at 80 °C for 20 min. The resulting solution was cooled and then rinsed through a 1.8 × 17 cm Dowex 50-2X (H^+) column at 4 °C with deionized H_2O. The pH of the yellow eluate was adjusted to 5.0 with 1 M KOH, and then it was loaded onto a 1.8 × 17 cm Dowex 1-X2 (Cl^-) column. The column was first washed with deionized water and then the desired product eluted with 10 mM HCl (a side product, $Rh(PP)_2$, remains bound to the column) (yield 50%). The spectral properties of $Rh(H_2O)_4PP$ at pH 2.0 are as follows: visible absorption λ_{max} = 329 nm (ϵ = 71) and 413 nm (ϵ = 80), λ_{min} = 368 nm (ϵ = 39) and 282 nm (ϵ = 21); P-31 NMR +5.6 ppm (s). Crystals were obtained from concentrated solutions of $Rh(H_2O)_4PP$ stored at pH 3.0 (4 °C) and dried over P_2O_5. Anal. Calcd for $[Rh(H_2O)_4HP_2O_7]\cdot 2H_2O$: H, 3.4; P, 16.1; Rh, 26.7. Found: H, 3.2; P, 15.6; Rh, 26.7. Analysis for Cl, whose presence would indicate that the HCl salt had been crystallized, revealed that none was present.

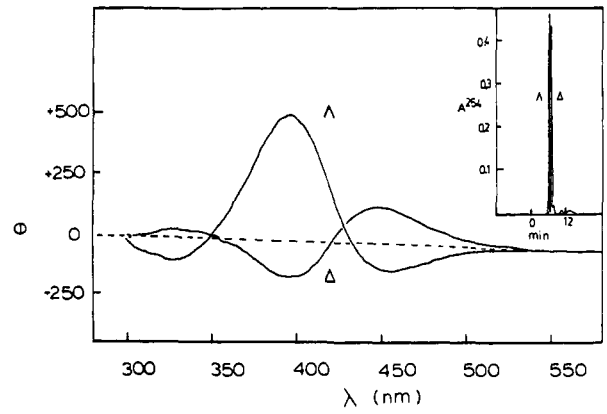

Figure 1. CD spectra of the Λ and Δ α,β-bidentate $Rh(H_2O)_4ADP$ screw-sense isomers at pH 3. The inset shows the reverse-phase HPLC trace of the two isomers (see Experimental Section for details).

$Rh(H_2O)_4(P)_2$ (2). A 5.5-mL solution containing 22 mM $Rh(H_2O)_4PP$, 22 mM $MgCl_2$, 15 mM K^+MES (MES = 2-(*N*-morpholino)ethanesulfonate) (pH 5.3) was added dropwise at 25 °C over a 10-min period to a 3.3-mL solution containing 0.4 mM yeast inorganic pyrophosphatase, 40 mM $MgCl_2$, and 121 mM K^+MES (pH 6.0). As the reaction proceeded, a yellow precipitate was formed, which was collected by centrifugation. The precipitate, redissolved in 10 mM HCl, showed a singlet at +15.0 ppm (^{31}P NMR spectrum) and λ_{max} at 416 nm, a shoulder at 325 nm, and λ_{min} at 372 nm (visible absorption spectrum). The product was reprecipitated by adjusting the pH of solution to 6, washed with H_2O, and dried over P_2O_5 (96% overall yield). Anal. Calcd for $[Rh(H_2O)_4(HP_2O_8)Mg(H_2O)_6]\cdot 4H_2O$: H, 4.9; Mg, 4.3; P, 10.8; Rh, 18.0. Found: H, 4.7; Mg, 4.8; P, 10.4; Rh, 17.8. Analysis for Cl revealed that none was present.

$Rh(H_2O)_3PPP$ (3). Fifty milliliters of 20 mM $[Rh(H_2O)_6](ClO_4)_3$ at pH 3 was combined with 50 mL of 20 mM PPP at pH 3 and the resulting solution heated at 80 °C for 25 min. After the solution was cooled, the pH was adjusted to 5 with KOH and then it was absorbed onto a 1 × 40 cm Dowex 1-X2 (Cl^-) column at 4 °C. The column was first washed with ca. 200 mL of deionized water to elute nonanionic Rh(III) complexes and then washed with ca. 300 mL of 0.1 M py-HCl (pH 5). The resin with the yellow band that was chromatographed down the column during the py·HCl elution was transfered to a second column, washed with 10 mM HCl, and then eluted with 50 mM HCl (yield 35%). The visible absorption spectrum of $Rh(H_2O)_3PPP$ at pH 3 is characterized by λ_{max} at 415 and 325 nm and λ_{min} at 372 nm and the ^{31}P NMR spectrum by a doublet (J = 20 Hz) at +6.3 ppm and triplet at −5.4 ppm.

$Rh(H_2O)_4ADP$ (4). Fifty milliliters of 20 mM $[Rh(H_2O)_6](ClO_4)_3$ at pH 3 was combined with 50 mL of 20 mM ADP at pH 3 and the resulting solution heated at 80 °C for 25 min. After the solution was cooled, the pH was adjusted to 2 with HCl and the solution was absorbed onto a 1.7 × 40 cm Dowex 50-X2 (H^+) column at 4 °C. After the column was wahsed with ca. 600 mL of deionized water, two yellow bands had separated. The resin of the first (top) band was removed to a second column and slowly (to focus) rinsed with 0.3 M $HClO_4$. The pH of the yellow eluate was adjusted to 3 with $KHCO_3$, and then the eluate was filtered to remove crystalline $KClO_4$ (yield 20%). The spectral properties of $Rh(H_2O)_4ADP$ at pH 3 are as follows: visible absorption λ_{max} = 409 nm (ϵ = 120) and 315 nm (ϵ = 126), λ_{min} = 364 nm (ϵ = 70); ^{31}P NMR +3 ppm (d, α-P) and +8 ppm (d, J = 21 Hz, β-P). The ^{13}C NMR (decoupled) spectral data for ADP at pH 2 are as follows: 150 (C-6), 148 (C-4), 145 (C-2), 142 (C-8), 118 (C-5), 88 (C-1′), 84 (C-4′), 75 (C-2′), 70 (C-3′), 65 ppm (C-5′). The ^{13}C NMR spectral data for $Rh(H_2O)_4ADP$ measured under these same conditions are as follows: 150 (C-6), 149 (C-4), 145 (C-2), 143 (C-8), 119 (C-5), 89 (C-1′), 84 (C-4′), 75 (C-2′), 70

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(C-3′), 66 ppm (C-5′). The UV CD spectrum of $Rh(H_2O)_4ADP$ at pH 5 was characterized by a λ_{max} at 260 nm ($[\theta] = -3600$) and closely resembled that of ADP ($\lambda_{max} = 260$ nm, $[\theta] = -3000$) measured under the same conditions. The $Rh(H_2O)_4ADP$ diastereoisomers were separated by HPLC using a reverse-phase preparative column, 100 mM potassium methanesulfonate (pH 2.2), and a flow rate of 4 mL/min. The retention times of the two isomers present in roughly equal molar amounts were 6.6 and 7.5 min.

The CD spectra of the pure isomers are shown in Figure 1. In order to assign tentatively the α-P configuration of these isomers, the relative retention times of the $Co(NH_3)_4ADP$ screw-sense isomers (7.3 and 8.3 min) and $Cr(H_2O)_4ADP$ screw-sense isomers (7.0 and 8.0 min) having known configurations were measured.[7] In each case the first isomer eluted had the Λ configuration as determined with use of CD spectral techniques and the second isomer had the Δ configuration.

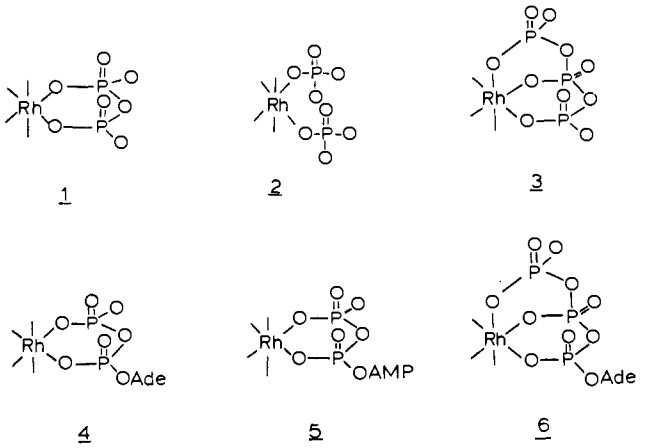
$Rh(H_2O)_nATP$ (5,6). Fifty milliliters of 20 mM $[Rh(H_2O)_6](ClO_4)_3$ at pH 3 was combined with 50 mL of 20 mM ATP at pH 3 and the resulting solution heated at 80 °C. After the solution was cooled, the pH was adjusted to 2 with HCl and then the solution was chromatographed on a 1.7 × 40 cm Dowex 50-X2 (H^+) column with deionized water as eluant (4 °C). The $Rh(H_2O)_nATP$ was chromatographed down the column as a broad yellow band and was collected by using a fraction collector. The $Rh(H_2O)_nATP$-containing fractions were combined, concentrated in vacuo (25 °C) to 5 mL, and chromatographed on a 1.7 × 100 cm G-10 Sephadex column at 4 °C in order to remove contaminating adenosine monophosphate (10 mM K^+MES (pH 5.5) as eluant). The visible spectrum of $Rh(H_2O)_nATP$ (pH 5.5) showed maxima at 327 nm ($\epsilon = 72$) and at 415 nm ($\epsilon = 62$) and λ_{min} at 376 nm ($\epsilon = 32$). The ^{13}C NMR (decoupled) spectral data for ATP at pH 5.0 were determined to be as follows: 154 (C-6), 151 (C-2), 148 (C-4), 140 (C-8), 118 (C-5), 88 (C-1′), 84 (C-4′), 75 (C-2′), 70 (C-3′), 66 ppm (C-5′). The ^{13}C NMR (decoupled) spectral data for $Rh(H_2O)_nATP$ under these same conditions were determined to be as follows: 154 (C-6), 152 (C-2), 149 (C-4), 141 (C-8), 119 (C-5), 88 (C-1′), 84 (C-4′), 75 (C-2′), 71 (C-3′), 67 ppm (C-5′). The UV CD spectrum of $Rh(H_2O)_nATP$ at pH 5 was characterized by λ_{max} at 255 nm ($[\theta] = -4600$) and closely resembled that of ATP ($\lambda_{max} = 255$ nm, $[\theta] = -4000$) measured under the same conditions. The ^{31}P NMR spectrum measured at pH 3.9 revealed the presence of β,γ-bidentate $Rh(H_2O)_4ATP$ (**5**) (t, −11.5 ppm, α-P; t, −8.6 ppm, β-P; d, +7.6 ppm, γ-P) and α,β,γ-tridentate $Rh(H_2O)_3ATP$ (**6**) (m, −7.5 ppm, β-P; m, +0.6 ppm, α-P; m, +8.0 ppm, γ-P). The bidentate:tridentate isomer ratio was 4:1 in the case of a reaction mixture obtained by heating reactants for 2 min (10% yield of $Rh(H_2O)_nATP$) and 1:1 in the case of a reaction mixture heated for 30 min (20% yield of $Rh(H_2O)_nATP$); only the tridentate isomer was observable in reaction mixtures heated for 3.5 h (25% yield of $Rh(H_2O)_3ATP$).

Results and Discussion

The purpose of the present study was to prepare and characterize a series of Rh(III) polyphosphate complexes that are to be used in ensuing studies to probe enzyme-active sites.[9] The general synthetic method employed was modeled after that used previously for the preparation of Cr(III) polyphosphate complexes. Specifically, dilute solutions of $[Rh(H_2O)_6](ClO_4)_3$ and polyphosphate at pH 3 were heated at 80 °C. Relatively longer reaction times, however, were required for the formation of Rh(III) polyphosphate complexes (ca. 30 min) than were required for the corresponding Cr(III) species.[7]

P^1,P^2-Bidentate $Rh(H_2O)_4PP$ (**1**) was obtained in pure form in 50% yield while tridentate $Rh(H_2O)_3PPP$ (**3**) was obtained in 35% yield. Both complexes were conveniently purified from the crude reaction mixture with use of Dowex 1 anion-exchange chromatography. Bidentate $Rh(H_2O)_4PP$ was converted quantitatively to $Rh(H_2O)_4(P)_2$ (**2**) in the presence of Mg^{2+}-activated yeast inorganic pyrophosphatase. $Rh(H_2O)_4PP$ was crystallized from a concentrated aqueous solution while $Rh(H_2O)_4(P)_2$ was precipitated from an aqueous solution containing $MgCl_2$ as the Mg^{2+} salt.

α,β-Bidentate $Rh(H_2O)_4ADP$ was obtained pure in 20% yield with use of Dowex 50 cation-exchange chromatography.



Cycloheptaamylose column chromatography, which had proven effective in the separation of the α-P screw-sense isomers of $Cr(H_2O)_4ADP$ and $Co(NH_3)_4ADP$, did not result in the resolution of the $Rh(H_2O)_4ADP$ configurational isomers.[7,10] On the other hand, reverse-phase HPLC techniques, which had been previously used to separate the β-P screw-sense isomers of β,γ-bidentate $Cr(H_2O)_4ATP$,[11] were found effective in the separation of the $Rh(H_2O)_4ADP$ isomers (see Figure 1). The CD spectra of the purified isomers are shown in Figure 1. The first isomer to elute from the HPLC column shows a significantly greater ellipticity at 400 nm than does the second isomer. The $Cr(H_2O)_4ADP$ isomers similarly do not show mirror-image CD spectra, but rather the Δ isomer shows ca. half the ellipticity at the λ_{max} as that of the Λ isomer.[7] In order to assign tentatively the configuration of the $Rh(H_2O)_4ADP$ isomer at α-P, the relative configurations of the corresponding $Cr(H_2O)_4ADP$ and $Co(NH_3)_4ADP$ isomers were correlated with their relative HPLC elution positions with use of CD spectral techniques. The Λ isomers of the Cr(III) and Co(III) complexes eluted in front of the corresponding Δ isomers, and on this basis the Λ configuration was tentatively assigned to the Rh(III) isomer that gave the shortest retention time and the Δ configuration to the isomer that showed the longest retention time (see Figure 1).

In the present study isoionic $Rh(H_2O)_nATP$ was prepared by heating of $[Rh(H_2O)_6](ClO_4)_3$ with ATP followed by chromatographic separation on a Dowex 50 H^+ cation-exchange column. β,γ-Bidentate $Rh(H_2O)_4ATP$, α,β,γ-tridentate $Rh(H_2O)_3ATP$, and adenosine monophosphate coelute from the column. The relative ratio of these three species was found to be dependent on the reaction time. Adenosine monophosphate and the tridentate complex predominate at reaction periods exceeding 30 min, and the bidentate complex predominates at a reaction period of 2 min. The adenosine monophosphate is easily removed from $Rh(H_2O)_nATP$ by gel filtration chromatography. The assignment of the α,β-bidentate and α,β,γ-tridentate structures to these complexes is based upon the similarities between the ^{31}P NMR spectral properties observed for these complexes and those of the corresponding β,γ-bidentate $Co(NH_3)_4ATP$ and α,β,γ-tridentate $Co(NH_3)_3ATP$ complexes.[12]

In an earlier paper the preparation of $[Rh(H_3ATP)(H_2O)_4]Cl_2$ (from rhodium trichloride), in which ATP acts as a bidentate ligand coordinating through N(7) and one of the phosphate oxygen atoms, was reported.[13] Very little

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(12) The structural assignments given to $Rh(H_2O)_4PP$, $Rh(H_2O)_4(P)_2$, $Rh(H_2O)_3PPP$, and $Rh(H_2O)_4ADP$ are also based in part upon the similarities that exist between the ^{31}P NMR spectral properties of these complexes and those reported for the corresponding $Co(NH_3)_n$ complexes.[5,14]

structural evidence for this complex was provided, however, by the authors. Previous studies with Cr(III) and Co(III) complexes of ADP and ATP have shown that N(7) and N(1) of the heterocyclic ring does not insert into the coordination sphere of the metal ion. In order to ensure that this was also the case with RhATP and RhADP, we examined both the absorption and elliptical properties of the adenine ring present in the complexes and found that they were no different from those of the adenine ring of uncomplexed ADP and ATP. In addition, Rh(III) coordination to these nucleotides does not alter the ^{13}C NMR spectral properties and therefore we feel confident that only the phosphoryl oxygens serve as ligands in these complexes.

It is interesting to note the difference in behavior of the Rh(III), Co(III), and Cr(III) ATP complexes. $Cr(NH_3)_3(H_2O)$ATP and $Cr(H_2O)_4$ATP are stable bidentate complexes. $Cr(H_2O)_4$ATP converts to what is believed to be the α,β,γ-tridentate complexes only under strongly acidic conditions.[7,15] $Co(NH_3)_3(H_2O)$ATP is not stable but spontaneously converts to the α,β,γ-$Co(NH_3)_3$ATP tridentate complex.[15] Bidentate $Rh(H_2O)_4$ATP, on the other hand, can be transformed to the tridentate complex by heating it at pH 3 or by allowing it to stand at 4 °C (pH 2-5) over a period of several days. Preliminary studies indicate that both the α,β,γ-tridentate $Rh(H_2O)_3$ATP and the β,γ-bidentate $Rh(H_2O)_4$ATP stereoisomers (whose presence is apparent from the ^{31}P NMR spectra of the given structural isomer) can be resolved on both cycloheptaamylose columns and reverse-phase HPLC columns. Efforts to purify the individual stereoisomers are currently under way.

Although the reactions leading to the Rh(III) polyphosphate complexes are quite simple to carry out, the yields are generally low owing to competing side reactions. In the case of the preparation of $Rh(H_2O)_4$PP the low yield is in part due to the intermolecular reaction of the monodentate $Rh(H_2O)_5$PP complex with a second Rh(III) ion to form Rh_2PP (which passes through the Dowex 1 column) or with a second PP ion to form $Rh(PP)_2$ (which remains bound to the Dowex 1 column after the acid wash). These processes compete with the intramolecular insertion of the uncomplexed phosphoryl group. Likewise, the yield of $Rh(H_2O)_4$ADP is limited by intermolecular reactions of the β-monodentate $Rh(H_2O)_5$ADP complex, which compete with bidentate complex formation. The formation of tridentate $Rh(H_2O)_3$PPP is accompanied by generation of PP, P, $Rh(H_2O)_n$P, and $Rh(H_2O)_4$PP as determined by ^{31}P NMR analysis of the crude reaction mixture. The predominant Rh(III)-containing side product formed during the $Rh(H_2O)_n$ATP reaction passes through the Dowex 50 H^+ cation-exchange column in the first void volume and is probably $Rh(ATP)_2$.

Unlike the reactions involving $Cr(H_2O)_6^{3+}$, those with $Rh(H_2O)_6^{3+}$ are not amenable to base catalysis. Specifically, attempts to prepare the rhodium complexes in solutions at pH 5 leads to immediate precipitation of the Rh(III), presumably as the hydroxide.

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Electrochemical Studies of [Bis(acetylacetone) ethylenediiminato]oxovanadium(IV), VO(acen), and Its Thio Analogue, VS(acen)

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Although the vanadyl ion Schiff base complex VO(acen) (H_2acen = the Schiff base of acetylacetone and ethylenediamine) has been of interest for many years, its sulfur analogue, VS(acen), has only recently been synthesized.[1,2] The thiovanadyl compound is formed by treating the oxo analogue with B_2S_3 in rigorously dry methylene chloride. The thio complex is quite oxygen sensitive in solution and readily reverts back to the oxo analogue. Electronic, IR, and ESR spectra have been reported for both complexes.[2] Crystallographic studies of VO(acen)[3,4] show its structure to be a rectangular pyramid with the terminal oxygen atom at the apex. The structure of VS(acen) has recently been reported[5] and is quite similar to that of VO(acen) except for the V=O and V=S bond lengths. The V=S bond (2.061 Å) is closer to a single bond in length. Their structures are shown in Figure 1.

We present here an electrochemical study of these compounds and a correlation between their electrochemical behavior and their structures.

Experimental Section

Cyclic voltammetric measurements were made with a Princeton Applied Research Model 173 three-electrode potentiostat and a Model 175 universal programmer. The voltammograms were recorded on a Houston Instruments Model 2000 Omnigraphic X-Y recorder or a Tektronix Type 549 storage oscilloscope. Controlled-potentional electrolysis was carried out with the above potentiostat and a Princeton Applied Research Model 179 digital coulometer.

The working electrode for cyclic voltammetry was a Beckman platinum-inlay electrode. A platinum-mesh electrode was used for controlled-potential electrolysis. The auxiliary electrode was a small piece of platinum foil separated from the cell solution by a fine-porosity frit. The reference electrode consisted of a Ag/AgCl electrode in aqueous tetramethylammonium chloride (Aldrich) with the concentration adjusted to make the electrode potential 0.000 V vs. SCE. The reference electrode junction was a small soft-glass cracked bead sealed into a Pyrex tube. The electrode was positioned in a Luggin capillary in the cell assembly.

Most experiments were carried out in a Vacuum Atmospheres Co. Model HE-43-2 glovebox with an HE 493 Dri-train, under a dry-nitrogen atmosphere. A simple electrochemical cell open to the box atmosphere was used. Experiments with H_2S gas were carried out in an all-glass cell constructed from standard taper 60/50 inner and outer ground-glass joints. The electrodes were positioned in the cell cap by means of several smaller ground-glass joints. Prepurified nitrogen was flushed through the cell during use.

Spectrophotometric measurements were made on a Hewlett-Packard 8450A UV/vis spectrophotometer. IR spectra were recorded on a Perkin-Elmer 683 IR spectrophotometer.

Reagents. High-purity dimethyl sulfoxide (0.011% water), acetonitrile (0.003% water), and methylene chloride (0.003% water) were obtained from Burdick and Jackson Laboratories and deoxygenated before use. Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium bromide (Aldrich) and perchloric acid as previously described[6] and used as the supporting electrolyte.

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