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Behavior of Octaaquobis(μ-hydroxo)dichromium(III) in Strong Perchloric Acid and Perchlorate Solutions

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A study was made of the behavior of octaaquobis(μ-hydroxy)dichromium perchlorate in high concentrations of perchloric acid and in sodium and magnesium perchlorate with the NMR "inert probe" method. It was shown that *p*-dioxane behaves as an inert probe in aqueous solutions of chromium complexes and its proton peak broadenings represent the second coordination sphere interactions. The peak broadening due to the dimer is always less than that of the hexaaquochromium(III) monomer under all conditions studied. At high acid and salt concentrations the peak broadenings increase linearly with viscosity at a constant chromium concentration but are different for the acid as compared for the two salts. The increase is linear through the region in which the dimer changes color, and therefore it is included that the color change is not due to the loss of one of the hydroxo bridges as proposed earlier. In addition it is shown that the peak broadening of a known monobridged complex is nearly the same as for a monomer of the same type of ligands, indicating that there is not structural change for the aquo dimer at high acid concentrations. Magnetic susceptibility studies for the aquo dimer give the spin-only value, indicating little or no spin–spin interaction. It is suggested that the color change in the aquo dimer at high acid concentrations may be due to the formation of an inner-sphere perchlorato complex.

The behavior of aquo chromium(III) ions in aqueous solutions of varying pH has been the subject of much study. It has long been known that at low pH the stable species is $Cr(H_2O)_6^{3+}$ while at pH values above 1 it behaves as a Brønsted acid with a pK of 3.8 at 25 °C.[2,3] The complex exchanges bound oxygen atoms very slowly, with a half-life of approximately 40 h,[4] while the protons are rapidly exchanged with the surrounding water molecules.[5] The addition of sodium hydroxide causes further ionization and polymerization. When the molar ratio of hydroxide to chromium is greater than 1.0, precipitation occurs, but even when precipitation is avoided by addition of less than the critical amount of hydroxide ion, there is a slow hydrolysis occurring over a period of hours as indicated by decrease of the pH with time.[6-8] Even without the addition of hydroxide there is a slow polymerization that results when solutions of chromium perchlorate of nitrate are refluxed for a period of time. Analysis shows that both a blue aquo dimer and green aquo trimer are formed. These have been isolated, and their properties have been studied.[9]

There has been considerable study of the properties of the dimer,[10,11] and it has been shown that the ion is quadruply charged, although in solution, ion pairing reduces this to 3+. The accepted structure is that of a bis(μ-hydroxo) bridge between the chromium atoms on the basis of five exchanging oxygen atoms per chromium atom and a static magnetic susceptibility equivalent to six unpaired electrons.[1] A single oxo-bridged structure known in other complexes shows a spin of less than three unpaired electrons per chromium atom, which decreases with decreasing temperature. However, in one study[11] it was found that in strong perchloric acid solution there is a color change from blue to green and this was interpreted as a shift from the bis- to the mono(μ-hydroxo) structure. If the resultant structure has a linear bridge, a change in magnetic properties would be expected, caused by interaction between the chromium atoms. A nonlinear bridge structure would be much more difficult to detect since no change in magnetic susceptibility would be expected, but this was shown to be unlikely in the present work.

In this work the "inert probe" NMR technique was used as described earlier.[12] Essentially the method consists of adding a small amount of a species containing nonlabile protons that does not enter the first coordination sphere of a complex ion in solution. Since there is no exchange, only second coordination sphere and bulk solvent effects are observed and it has been shown that proton peak broadenings are only sensitive to gross structural changes of the complex ion but not to the loss of gain of a proton. Since the loss of a hydroxo bridge is a gross structural change, the method seemed ideally suited to the question of whether a structural change occurred at high acid strength.

Experimental Section

All starting chromium salts other than the perchlorates were of chemically pure grade from J. T. Baker & Co. Sodium perchlorate hydrate of 95+% purity was obtained from Fisher Scientific Co. The magnesium perchlorate was analytical grade from G. Frederick Smith Co. while the calcium perchlorate hexahydrate and chromium perchlorate, both greater than 99% pure, came from Ventron Corp. Deuterioperchloric acid was of 68% concentration in deuterium oxide and the deuterium oxide, 99+% pure, came from Wilmad Glass Co. Dioxane and methylene chloride were of spectral grade and were obtained from Matheson Coleman and Bell.

Octaaquobis(μ-deuterioxo)dichromium(III) perchlorate was prepared as described in the literature.[13,14] The final dimer solution as prepared always contained monomer and trimer in addition to the dimer, and for this reason each batch was analyzed. The total chromium in the solution was determined and the mixture separated by elution from a 20-cm column of Dowex 50W-X8 100–200 mesh ion-exchange resin. Elution of the separated monomer and dimer was obtained with use of a 0.5 M calcium perchlorate/0.01 M perchloric acid solution. The two fractions were analyzed for chromium, and the amount of trimer plus any higher polymers was determined by difference from the total chromium. Chromium analysis was carried out by oxidation to chromate followed by titration with Fe(II) as described in the literature.[15]

Hexaamminechromium(III) nitrate and the deuterated acid erythrochromium(III) nitrate were prepared with use of the methods described in ref 16. Analyses were obtained from Galbraith Lab-

(1) Taken from I. Ostrich, Ph.D. Thesis, Villanova University. Present address: Negev Phosphate Co., Dimona, Israel.
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oratories, Knoxville, TN. Anal. Calcd for the hexamminechromium(III) nitrate: Cr, 15.28; H, 5.33; N, 37.06. Found: Cr, 15.15; H, 5.47; N, 36.87. Calcd for acid erythrochromium(III) nitrate: Cr, 15.28; H, 5.33; N, 37.06. Found: Cr, 16.66; H, 5.16; N, 31.58.

Stock solutions were prepared by dissolving the appropriate chromium salt in deuterium oxide. In addition to the three chromium salts described above, solutions of hexaaquochromium(III) perchlorate were also used. For the NMR measurements the stock solutions were added with 1.0-mL syringes to 1.00-mL volumetric flasks that were previously weighted and were weighed again after additions. Dilution to the mark with deuterium oxide permitted the calculation of both the molality and the molarity of each solution. When methylene chloride was used as the "inert probe", the solution was saturated by addition of excess methylene chloride and allowed to stand for 24 h with occasional shaking. When dioxane was used as the "inert probe", the chromium stock solutions contained approximately 10% by volume of the dioxane and the same procedure was followed. Since each sample contained roughly 0.1–0.3 mL of stock solution, the resultant dioxane concentration varied from 1 to 4.5% for each sample.

The pD of the various chromium solutions was adjusted by the addition of sodium deuterioxide solution, prepared by the addition of small pieces of metallic sodium to deuterium oxide. The resultant solutions were standarized by titration against potassium biphthalate that had been dried for 3 h at 120 °C.

Sodium perchlorate solutions were prepared by dissolving the salt in 25 mL of deuterium oxide. The solution was evaporated to about 10 mL and more deuterium oxide added back to the original volume. This process was repeated twice more to remove the water of hydration. The resultant solution gave a negative test for chloride ion as shown by silver nitrate and a negative potassium iodide–starch test for chlorate ion, chlorite ion, chlorine dioxide, and chlorine.

The magnesium perchlorate solutions were prepared by adding a known amount of the salt to a 10-mL volumetric flask and diluting to the mark with deuterium oxide.

NMR solutions of varying pD were prepared by addition of the chromium stock solutions containing dioxane and of sodium deuterioxide solution to 1.00-mL volumetric flasks followed by dilution to the mark with deuterium oxide and weighing. In the cases of the hexaammine and erythro salts a drop of concentrated deuterioperchloric acid was added to prevent deuterolysis. Samples were immediately placed in the NMR sample in the NMR sample tubes and stored at 0 °C until used. Solutions of varying salt or acid concentrations were prepared by adding weighed amounts to the 1.00-mL volumetric flasks and diluting with deuterium oxide. Solutions of varying dioxane concentrations were prepared by addition of weighed amounts of dioxane to the stock solutions and diluting with deterium oxide to the mark on the volumetric flasks.

All NMR spectra were recorded on a modified Varian A-60 instrument fitted with an A-60A probe. The instrument was tuned for each sample, with care taken to balance the curvature of the field, and the rf field was adjusted to be below saturation. Spectra were run at a low recording speed to prevent broadening. The chemical shifts and peak widths reported are the average of at least three determinations having a variation of less than 5% in the peak width. Spectra were also taken the next day and/or several days later and the chemical shifts and peak widths compared. In all cases where no chemical reactions were expected, the values determined at the later time agreed with the original within the specification of the instrument.

The instrument was calibrated with a 6% tetramethylsilane sample in chloroform and the temperature of the probe measured by the peak separation of an ethylene glycol standard solution. Peak widths were measured as the value at half-height of the signal while chemical shifts of methylene chloride were measured as the shift from that of dioxane used as an external standard. Dioxane shifts were measured relative to an arbitrary zero frequency. All sample tubes were 5-mm precision bore type, and the internal standard was a sealed capillary.

All pH measurements were made with a Corning Model 10 or a Fisher Acumat Model 220 pH meter. A Fisher Model 13-369-94 micro combination glass electrode filled with a 4 M sodium chloride was used. Potassium chloride could not be used due to the formation of insoluble potassium perchlorate at the glass frit of the electrode.

Results and Discussion

In the present work *p*-dioxane was used as the "inert probe" rather than the methylene chloride used in earlier work.[12]

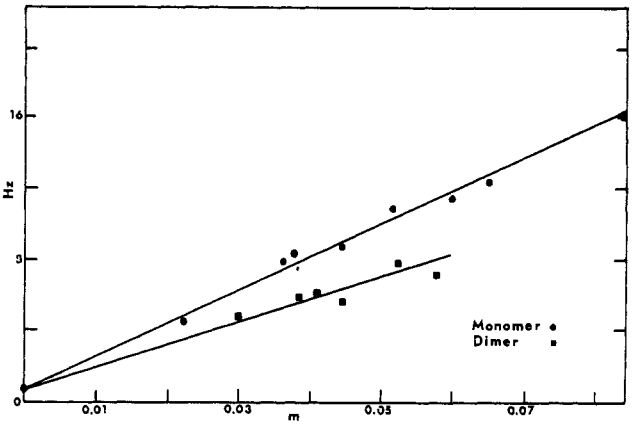

Figure 1. Plot of proton peak widths (in hertz) as a function of the aquo chromium monomer and dimer molalities.

Dioxane has the great advantage that it is miscible with water, thus allowing higher concentrations to be used, in comparison to that for methylene chloride. However, it was necessary to show that dioxane will function in the same manner as methylene chloride. Toward this end a series of varying concentrations of chromium(III) perchlorate and the aquo dimer were run with a constant amount of dioxane and the proton peak widths measured. The results are shown in Figure 1, and it can be seen that the peak widths increase proportionally to the monomer and dimer concentrations in the same manner as was shown earlier with methylene chloride. It would not be expected that the dioxane proton peak broadenings would be the same as those for methylene chloride since the rotational correlation times of the two molecules are different and the larger number of protons on dioxane would result in a different residence time in the second coordination sphere. The behavior of the dioxane is in agreement with earlier work,[17] which showed that, in water–dioxane mixtures, the water preferentially solvates up to the limit of salt solubility.

The effect of varying dioxane concentration on the peak width at a fixed chromium concentration was tested, and it was found that there was no change for dioxane concentrations varying between 0.7 and 2.03% by weight. This result together with that described above gives the conclusion that there is an equlibrium distribution of dioxane between the second coordination sphere and the bulk solution in the concentration range used in the present work.

The major part of this work was directed toward the behavior of the dimer complex at high acid and salt concentrations. As expected, under these conditions the proton peak widths showed broadenings with increasing salt or acid concentrations at constant chromium concentrations. It was recognized long ago[18] that the broadening is due to the increase in solution viscosity, but it is of interest to note that the broadenings due to added magnesium and sodium perchlorates are roughly similar and larger than that due to added perchloric acid. These are shown in Figures 2 and 3 for the aquo monomer and dimer and indicate that ionic charge alone is not the sole factor in broadening. In all cases for a given chromium concentration the peak width of the monomer is greater than that of the dimer and most important there is no sharp break in the dimer peak width curve at high acid and salt concentrations.

As mentioned in the introduction, Thompson[11] observed a color change in the dimer solution from blue-green to green at perchloric acid concentrations in the region of 8 M and

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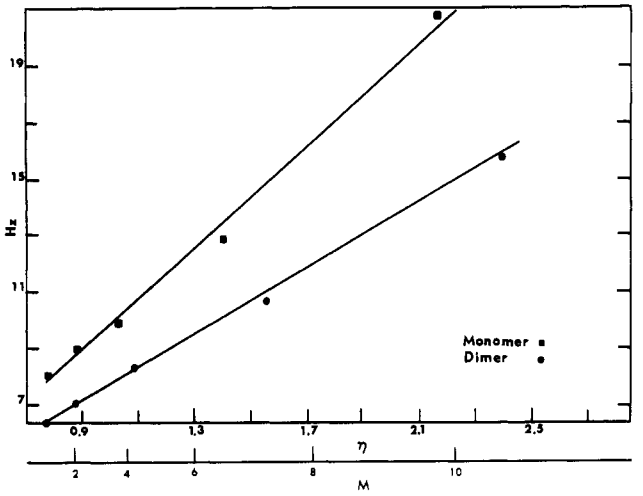


Figure 2. Plot of peak widths (in hertz) in solutions with fixed molarities of the aquo monomer and dimer as a function of the viscosities and molarities of solutions having high concentrations of deuterioperchloric acid.

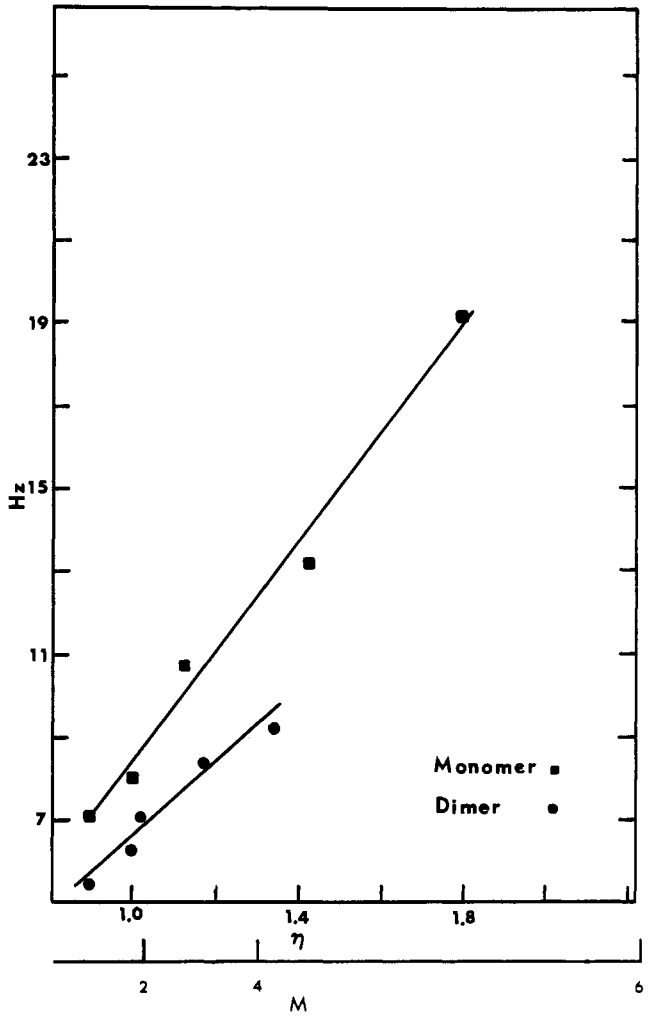


Figure 3. Plot of peak widths (in hertz) in solutions with fixed molalities of the aquo monomer and dimer as a function of viscosities and molarities of solutions having high concentrations of sodium perchlorate.

suggested that this is due to the opening of one of the hydroxo bridges to form a monobridged species. If this were the case, it is a significant structural change and it would be expected that there would be a break in the plot of peak width vs. perchloric acid concentration for the dimer in this concentration range, but as noted above, no such break was observed.

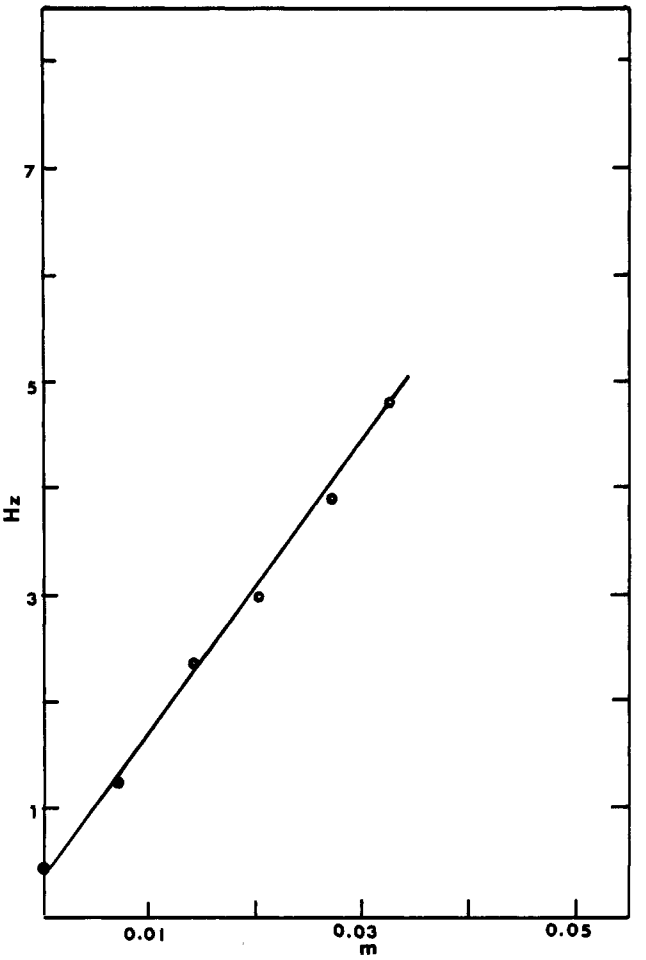


Figure 4. Plot of peak widths (in hertz) as a function of the molality of hexaamminechromium(III) nitrate.

Table I. Absorbance at the Maxima for Mono- and Dichromium Species

species	λ, nm	ε	λ, nm	ε
$Cr(H_2O)_6^{3+}$	574	13.4	407	15.6
$Cr(H_2O)_5(ClO_4)^{2+}$	580		412	
$Cr_2(H_2O)_8(OH)_2^{4+}$	580	17.3	416	20.3
green species	582	18.2	424	29.4

Another method of determination of the structure of the aquo dimer is to compare the relative peak widths of the aquo monomer and dimer with that a chromium complex having a known monobridged structure. This was done by comparing the relative peak widths of hexaamminechromium(III) nitrate with that of the acid erythrochromium(III) nitrate, $(NH_3)_5Cr{-}OH{-}Cr(NH_3)_4H_2O$. The latter was chosen because it is the only known ion having a monohydroxo bridged that is similar to the aquo dimer and stable in aqueous solution. It was necessary to compare it to the hexaamminechromium(III) complex since there will be differences between water and ammonia molecules in their effect on the second coordination sphere. The peak broadenings of the dioxane due to these species are shown in Figures 4 and 5, and the values for the slopes of all four species are given in Table I. It can be seen that the peak widths of the two ammine complexes are nearly the same while those for the two aquo complexes differ considerably. The similarity between the aquo monomer and the two ammine complexes is accidental and should not be considered.

The similarity of the two ammine complex peak widths can be explained on the basis of two competing effects. An analysis based on molecular models, taking into account the X-ray work of Yevitz and Stanko,[19] shows that only 9 of the 16 faces of

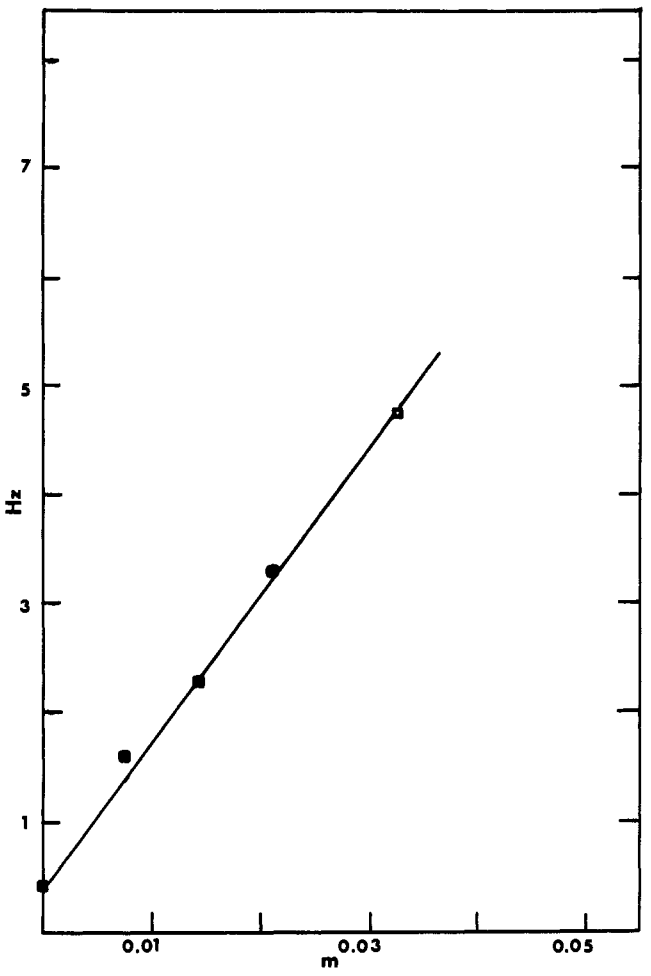


Figure 5. Plot of peak widths (in hertz) as a function of the molality of erythrochromium(III) nitrate.

the erythro complex are open to dioxane approach compared with the openess all 16 faces of the two hexaammine ions. In addition the Cr–Cr distance is about 3.91 Å, giving a ellipsoidal molecule, which would have a longer rotational correlation time than the monomers. This increase in correlation time compensates for the loss in accessibility to the faces, giving approximately the same broadening for both species.

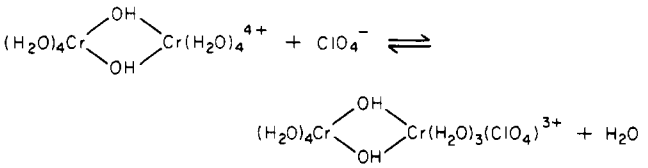
In the case of the aquo dimer structural analysis shows that only eight of the faces are open to the dioxane, and this loss in accessibility is only partially compensated by the increase in correlation time of the dimer. Thus the two dimers behave differently compared with the similar monomer. Again, if there was a structural change at high acid concentration, the peak widths of the aquo dimer would have been expected to approach the monomer values as was found in the ammine complexes.

During the present work the susceptibility of the dimer was measured with use of the Evans method.[20] Correction for the diamagnetic susceptibilities of all of the species present is solution was made by using tabulated values.[21] The values for the monomer and dimer found were 3.94 and 3.89 μ_B, respectively. The value for the monomer is somewhat higher than the spin-only value but within experimental error. The dimer value indicates clearly that there is no interaction between chromium ions across the hydroxyl bridges and is well above the value of 3.75 μ_B obtained by Thompson. This rules out any effect of spin–spin interactions on the peak broadenings of the aquo dimer. Although the susceptibility of the erythro complex was not determined during this work, the general similarity of the peak broadening compared to that of the aquo dimer suggests no strong spin–spin interaction although some may be present. It would be necessary to carry out a variable-temperature study to settle this point.

The nature of the color change observed in the work of Thompson and in the present work for the aquo dimer at high perchloric acid concentrations cannot be decided with certainty, but more recent work by Jones and Bjerrum[22] on the hexaaquo monomer suggests an explanation. These workers observed that at high perchloric acid concentrations an inner-sphere perchlorato complex is formed according to

$$Cr(H_2O)_6^{3+} + ClO_4^- \rightleftharpoons Cr(H_2O)_5(ClO_4)^{2+} + H_2O$$

We suggest the analogous reaction for the dimer:



Both complexes are green with a half-life of formation for the monomer of about 70 min at 20 °C compared with about 15 min for the dimer. Visible–UV spectral data for the two species from the two workers are given in Table I below. As can be seen from the data both green species show a shift of several nanometers to longer wavelengths for both bands. No absorbance values are available for the green monomer although a calculated curve shows little change for ϵ at both bands. From the spectral data it can be argued that both green species undergo similar changes and hence are perchlorato complexes.

In the case of the sodium perchlorate additions no color change of the solutions up to the highest salt concentrations were observed. However, an inspection of the viscosity concentration data showed that the highest salt concentration was on the order of 4 M which is well below the 8 M acid concentration where color change was observed, and hence the lack of color change is not surprising.

The major objection to the proposed inner-sphere complex is the observation of Thompson that the green compound is held more tightly on the Dowex 50W-4X resin than the more highly charged blue aquo dimer. However, Whitney and Diamond[23] have shown that, in high perchloric acid concentrations, factors other than ionic charge play an important role, affecting distribution coefficients on ion-exchange resins. It was observed that $Fe(H_2O)_6^{3+}$ is much more strongly held than $Cr(H_2O)_6^{3+}$ even though both ions are of similar size. Thse workers argue that the difference is due to the fact that some of the labile water molecules in the iron complex are removed and the resultant smaller ion can enter the resin pores more easily than does the chromium complex, which only slowly exhanges water molecules. As additional evidence for this argument they observed that the chromium ion distribution coefficient gradually increases over a period of weeks.

In the present work, if a perchlorato inner-sphere complex is formed with the dimer, it would have a lower symmetry than does the starting dimer and presumably lose water molecules more readily. Supporting this argument is the difference in half-lives for the monomer and aquo dimer described above and the general observation that mixed-ligand chromium complexes have more rapid exchange kinetics than do those containing only single species. Thus the partially dehydrated perchlorato inner-sphere complex could enter the resin pores

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more readily than the aquo dimer and the increased binding resulting from this behavior would more than offset the higher charge of the latter. The argument proposed here could be tested by observing whether the distribution coefficient of the aquo dimer increases with time, but no such experiments have been reported.

Conclusions

In the present work it was shown that *p*-dioxane is a suitable "inert probe" for the study of the second coordination sphere of complex ions. It was used to study the behavior of the octaaquobis(μ-hydroxo)dichromium(III) perchlorate acid and perchlorate salt solutions. The peak broadening of the dioxane is less for the dimer compared to that for the hexaaquochromium(III) ion under all conditions studied, and this was attributed to exclusion of the dioxane from some of the dimer faces in the second coordination sphere. The difference between the calculated and expected broadening for the dimer due to the exclusion is probably due to the longer correlation time for rotation of the dimer compared to that for the monomer. The magnetic susceptibility of the dimer gives a spin-only value for the chromium ions, indicating no interaction across the bis(μ-hydroxo) birdges. It is postulated that, at high acid concentrations, the color change of the dimer is due to an inner-sphere perchlorato complex.

Registry No. Cr, 7440-47-3; *p*-dioxane, 123-91-1; $Cr_2(H_2O)_8(OH)_2^{4+}$, 23852-05-3.

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Metal Ion Promoted Hydrophobic Interactions between Nucleotides and Amino Acids. Mixed-Ligand Adenosine 5'-Triphosphate/Metal Ion(II)/L-Leucinate Systems and Related Ternary Complexes[1,2]

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Mixed-ligand complexes of the type $M(ATP)(Aa)^{3-}$, where $M^{2+} = Mn^{2+}$, Cu^{2+}, Zn^{2+}, Cd^{2+}, or Pb^{2+} and $Aa^- =$ alaninate, 2-aminopropionate (α-aminobutyrate), norvalinate, norleucinate, leucinate (leu), or isoleucinate, have been studied by potentiometric pH titrations and ^1H NMR; some earlier results on $M(ATP)(tryptophanate)^{3-}$ have been included for comparison. The potentiometric measurements (with Mn^{2+}, Cu^{2+}, and Zn^{2+}) reveal a slightly higher formation tendency, expressed as $\Delta \log K_M = \log K^{M(ATP)}_{M(ATP)(Aa)} - \log K^{M}_{M(Aa)}$, for the systems with leucinate compared to those with alaninate. This increase in stability is attributed to an intramolecular hydrophobic ligand–ligand interaction between the purine moiety of ATP^{4-} and the isopropyl residue of leucinate. The position of the intramolecular isomeric equilibrium between an "open" and "closed" form, in which the hydrophobic interaction occurs, was estimated: of the ternary $M(ATP)(leu)^{3-}$ complexes with Mn^{2+}, Cu^{2+}, and Zn^{2+} about 41, 21, and ~5% (to ~30%) exist in the folded, i.e. closed, form. The intramolecular aromatic-ring stacking interactions between the purine moiety of ATP^{4-} and the indole residue of tryptophanate (trp^-) in the $M(ATP)(trp)^{3-}$ complexes is (as expected) more pronounced: of the complexes with Mn^{2+}, Cu^{2+}, and Zn^{2+} about 52, 35, and 74% exist in the stacked form. ^1H NMR shift measurements of the mentioned ATP/amino acid systems in the absence and presence of Zn^{2+}, Cd^{2+}, or Pb^{2+} confirmed that such hydrophobic ligand–ligand interactions exist and that they are effectively promoted by the formation of a metal ion bridge between the two reactants; to some extent a promotion can also occur by the polar interactions between the ammonium group of the amino acid and the phosphate chain of the nucleotide. For the metal ion facilitated interaction: the longer the side chain of the aliphatic amino acid, the larger is the upfield shift of the terminal methyl group(s) of the amino acid side chain, resulting from the interaction with the aromatic purine moiety within the ternary complex. The $\Delta G°$ values calculated from the equilibrium constants agree well with the theoretical predictions for such interactions. It is also shown that mixed-ligand complexes of the mentioned kind exist in the physiological pH range and that the formation of a metal ion bridge increases the probability for "recognition" between two species; this result is fascinating regarding the specificity and selectivity observed in nature.

The essential relationships between nucleic acids and amino acids in biological systems are their binding and recognition interactions.[4] The aim of various studies was therefore to characterize amino acid– or protein–DNA interactions and to clarify the binding of nucleotides, which occur as coenzymes in enzymic reactions, to the protein part of the enzymes. Among the possible kinds of interactions are (i) hydrogen bonding between the amino acids and the nucleic acid bases,[5] (ii) polar interactions[6,7] between positively charged ammonium groups of amino acids and negatively charged phosphate groups of nucleotides, (iii) aromatic-ring stacking between the purine or pyrimidine bases and suitable aromatic side-chain residues of the amino acids, like the indole[7-11] or imidazole groups,[12] and (iv) the related hydrophobic interactions.[13-15]

It was also shown that two such interactions may occur simultaneously,[7,10] leading thus to cooperativity. Furthermore, the polar interactions, i.e. the ionic bridge, may be replaced by a metal ion,[7,9,11] leading thus to the formation of ternary

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