$MeQ)_2]_2O$ is not stable during a prolonged electrolysis and dissociates to give $Fe^{II}(2\text{-}MeQ)_2OH^-$ as the final product. This behavior is consistent with the absence of known examples of stable oxo-bridged binuclear species of iron(II).

The iron(II) complex, FeQ_2, is oxidized to $Fe^{III}Q_3$ by molecular oxygen. Because only 0.25 mol of O_2 is required/mol of iron(II), oxygen must undergo a four-electron reduction. $Fe^{II}Q_2$ also is oxidized to $Fe^{III}Q_3$ by H_2O_2, but the stoichiometry is not certain. The subsequent addition of OH^- causes the reduction of the iron(III) product species.

The marked decrease in the concentration of O_2^- which occurs upon addition of a small amount of $Fe^{II}Q_2$ implies that the iron complex has a catalytic effect on the decomposition of O_2^-. A similar effect has been observed for the manganese(II)–8-quinolinol complex, MnQ_2.[16] The iron complexes appear to be present only in their tris-chelated forms (–0.60-V couple), which indicates that the solution combination is basic. An oxidation peak at +0.050 V indicates the presence of peroxide ion in the product solution.

From the above results and the fact that peroxide does not have an effect on the electrochemistry of the $Fe^{III}Q_3$ complex, new complexes (such as a peroxo-bridged dimer) apparently are not formed.

Because of the apparent catalytic effect of the $Fe^{II}Q_2$ complex for the decomposition of O_2^- and the redox effects of H_2O_2 and OH^- on the iron–8-quinolinol complexes, additional studies are planned to elucidate the redox mechanisms.

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Registry No. FeQ_3, 14514-43-3; FeQ_2, 15213-83-9; $[Fe(2\text{-}MeQ)_2]O_2$, 51331-59-0; $Fe(2\text{-}MeQ)_2OH$, 61477-50-7.

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Linkage Isomers of Pentaammineruthenium–Hypoxanthine Complexes[1]

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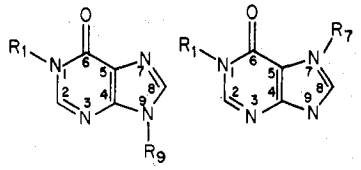
The synthesis of N_3, N_7, and N_9 linkage isomers of a series of pentaammineruthenium(II)– and -(III)–hypoxanthine complexes is reported. Physical measurements of these compounds were made to gain information which might be employed in separating and identifying the metabolites of heavy metals which bind to nucleic acids or their constituent bases. The ruthenium(III) complexes exhibit broad ligand to metal charge-transfer transitions which can be used to assign the isomers. Reduction potentials for these complexes over a broad pH range are presented and are also of use in identifying the complexes. Measurements of the pK_a values of the complexes are reported and were utilized in separating the linkage isomers. A novel N_3 to N_9 isomerization of one of the complexes has been observed to be acid catalyzed.

Introduction

Interactions between transition metals and nucleic acids or their constituent bases have recently been the subject of considerable research. Topics of investigation have tended to center on (1) the role of metals in nucleic acid metabolism,[2-5] (2) the development of new transition metal antitumor agents and the elucidation of their biochemical mechanisms,[6-11] and (3) the selective labeling of nucleic acid bases by heavy metals as an aid in x-ray structure determinations or to facilitate the sequencing of nucleic acids by electron microscopy.[12-15] Other areas of interest have been previously summarized.[16]

Many studies of metal ion interactions with nucleic acids or their constituent bases have been complicated by the availability of numerous metal binding sites. Various spectroscopic (IR,[17] Raman,[18] ESR,[19] NMR,[20-23] CD,[25] UV,[26] visible[16]) and physical methods[27-30] have been employed in efforts to determine the point(s) of metal association. Previous studies with ruthenium–purine complexes indicated that the charge-transfer transitions exhibited by these compounds might be of use in ascertaining the binding site.[31-32] For example, DNA stained with $(NH_3)_5Ru^{III}$ exhibits a charge-transfer absorption band maximum similar to that of $Guo(NH_3)_5Ru^{III}$ indicating preferential binding of the metal to the guanine residues. However, this type of correlation can only be used to determine which bases coordinate the metal ion. Since each base may have several possible binding sites, there remains the additional problem of which sites are involved on a particular base.

The present study was initiated with the goal of synthesizing a series of stable pentaammineruthenium–purine complexes in which the metal binding site could be unequivocally established and to investigate the physical properties of these compounds in order to identify those which might be useful in assigning metal association sites. In particular, we hoped to establish the effect the point of metal attachment has on the ligand to metal charge-transfer (LMCT) bands evident in the electronic spectra of the ruthenium(III)–purine complexes.[16,32] It has been suggested that the energies of these transitions would, to a first approximation, be independent of the coordination site but that the intensities would be site dependent.[31] The relative effect of the metal ion on the acidities of ionizable purine protons has also been used as an indicator of the metal binding site,[14,33] the rule of thumb being that the increase of the acidity of a given proton (relative to the free ligand) is inversely dependent upon the distance between the metal center and the ionizable proton. The



Hypoxanthine

Complex		Metal binding site	Deprotonation site	R_1	R_7	R_9
Ru(III)	Ru(II)					
7-[Hyp](III)	7-[Hyp](II)	7		H		H
7-[Hyp,9⁻](III)	7-[Hyp,9⁻](II)	7	9	H		
7-[Hyp,1⁻,9⁻](III)	7-[Hyp,1⁻,9⁻](II)	7	1, 9			
9-[Hyp](III)	9-[Hyp](II)	9		H	H	
9-[Hyp,7⁻](III)	9-[Hyp,7⁻](II)	9	7	H		
9-[Hyp,1⁻,7⁻](III)	9-[Hyp,1⁻,7⁻](II)	9	1, 7			
7-[1MeHyp](III)	7-[1MeHyp](II)	7		Me		H
7-[1MeHyp,9⁻](III)	7-[1MeHyp,9⁻](II)	7	9	Me		
9-[1MeHyp](III)	9-[1MeHyp](II)	9		Me	H	
9-[1MeHyp,7⁻](III)	9-[1MeHyp,7⁻](II)	9	7	Me		
3-[7MeHyp](III)	3-[7MeHyp](II)	3		H	Me	
3-[7MeHyp,1⁻](III)	3-[7MeHyp,1⁻](II)	3	1		Me	
9-[7MeHyp](III)	9-[7MeHyp](II)	9		H	Me	
9-[7MeHyp,1⁻](III)	9-[7MeHyp,1⁻](II)	9	1		Me	
7-[Ino](III)	7-[Ino](II)	7		H		Rib
7-[Ino,1⁻](III)	7-[Ino,1⁻](II)	7	1			Rib
7-[1MeIno](III)	7-[1MeIno](II)	7		Me		Rib
7-[IDP](III)	7-[IDP](II)	7		H		RDP
7-[IDP,1⁻](III)	7-[IDP,1⁻](II)	7	1	H		RDP

Figure 1. Abbreviations for complexes used in this work. (Rib = ribose; Ino = 6-hydroxy-9-β-D-ribofuranosylhypoxanthine; RDP = 5′-ribose diphosphate; IDP = 5′-inosine diphosphate.)

systematic study of the acidities of the linkage isomers reported here indicates that relative changes in pK_a values for specific protons upon purine coordination are useful in assigning linkage isomers.

Reference to Figure 1 will acquaint the reader with the abbreviations for the complexes utilized in this work. The abbreviations include all of the necessary structural and protonation information about a particular complex except the $(NH_3)_5Ru$ group which is common to all. Standard biochemical abbreviations are used for the ribofuranosyl derivatives of hypoxanthine, inosine (Ino), and 5-inosine diphosphate (IDP). The crystal and molecular structures of 7-[Hyp](III), 9-[Hyp](III), and 9-[7MeHyp](III) have been determined by x-ray methods and will be reported elsewhere. Otherwise, the table of Figure 1 anticipates the assignment of linkage isomers which is considered in the Discussion.

Experimental Section

Chemicals and Reagents. Chloropentaammineruthenium(III) chloride was prepared by refluxing hexaammineruthenium(III) chloride, obtained from Matthey Bishop, Inc., in 6 M HCl for 4 h followed by crystallization from 0.1 M HCl.[35] Standard acids, bases, lithium chloride, buffer solutions, and ion-exchange resins were prepared according to previously reported methods.[16,32] Inosine, hypoxanthine, and inosine 5′-triphosphate were obtained from the Aldrich Chemical Co., deoxyinosine was purchased from Nutritional Biochemicals Corp., and 1-methylhypoxanthine and 7-methylhypoxanthine were bought from Cyclo Chemical. 1-Methylinosine was prepared by the method of Jones and Robins.[36] All ligands were used without further purification. Microanalyses were performed by the Stanford Microanalytical Laboratory, Stanford, Calif.

Equipment. Spectra were recorded on Cary Model 15 or 118 spectrophotometers. Electrochemical measurements were made on a cyclic voltammetry apparatus using a platinum button (Beckman) or a hanging drop mercury electrode (Brinkmann) as the indicator electrode and a standard calomel reference electrode. Measurements of pH were made with a Metrohm combination glass electrode on a Beckman Expandomatic pH meter standardized with Beckman buffers.

Synthesis of Compounds. Complexes with inosine and 1-methylinosine were prepared by allowing an argon-purged solution of chloropentaammineruthenium(III) trifluoroacetate to react with a 10% excess of the ligand at pH 3–5 over zinc amalgam for about 30 min. The zinc amalgam was then removed and the solution was oxidized by bubbling air through it for at least 1 h. The products were separated on a 6-cm Bio-Rex 70 column eluted with increasing concentrations (0.2–1.0 M) of ammonium acetate. Usually only a single red band was evident in this step; however, preparations that had been allowed to stand in strong acid for long periods showed an additional band containing the corresponding hypoxanthine complex. The ammonium acetate eluent was eliminated by subsequent ion exchange on a short 3-cm Ag-50 (Bio-Rad) column eluted with 1 M HCl to wash through the ammonium acetate and then 3–4 M HCl to elute the complex. The eluate was rotoevaporated to dryness, filtered, evaporated again, and then dissolved in a minimum of water. Ethanol was either added directly or added by diffusion to induce crystallization. Crystals were collected and washed with water–ethanol before storing in a desiccator. Anal. Calcd for $[(Ino)(NH_3)_5Ru]Cl_3 \cdot H_2O$: C, 20.75; N, 21.77; H, 5.05; Cl, 18.37. Found: C, 20.89; N, 21.53; H, 4.82; Cl, 18.02. Calcd for $[(1MeIno)(NH_3)_5Ru]Cl_3 \cdot H_2O$: C, 22.28; N, 21.26; H, 5.27; Cl, 17.94. Found: C, 22.46; N, 21.40; H, 5.32; Cl, 18.10.

The N_7 and N_9 linkage isomers of hypoxanthine and (1-methylhypoxanthine)pentaammineruthenium(III) chloride were prepared by similar methods. The isomers were separated on a Bio-Rex column with the N_7-bound complex eluting first and a small amount of a red, highly charged species, possibly a purine-bridged biruthenium complex adhering to the top of the column. Numerous unidentified bands were often in evidence in the chromatographic separation of preparations with the 1-methylhypoxanthine ligand. Impurities in the ligand are suspected as the source of these bands. The 7-[Hyp](III) complex could be prepared as the sole product of the reaction using deoxyinosine as the starting ligand and subsequently hydrolyzing off the deoxyribose. This was accomplished by subjecting the air-oxidized reactant solution to an additional ion-exchange chromatography step on an Ag-50 column eluted with HCl to hydrolyze the sugar moiety and eliminate a small amount of highly charged impurity. Analysis for N_7-$[(Hyp)(NH_3)_5Ru]Cl_3 \cdot 1.5H_2O$ was determined by a crystal and molecular structure determination by x-ray diffraction. Anal. Calcd for N_9-$[(Hyp)(NH_3)_5Ru]Cl_3 \cdot H_2O$: C, 13.44; N, 28.23; H, 4.74; Cl, 23.81; Ru, 22.6. Found: C, 13.45; N, 28.34; H, 4.63; Cl, 23.81; Ru, 22.1. Calcd for N_7-$[(1MeHyp)(NH_3)_5Ru]Cl_3 \cdot 3H_2O$: C, 14.51; N, 25.38; H, 5.47; Cl, 21.41; Ru, 20.3. Found: C, 14.49; N, 25.91; H, 5.06; Cl, 20.85; Ru,

20.4. Calcd for N_9-[(1MeHyp)$(NH_3)_5$Ru]$Cl_3 \cdot H_2O$: C, 15.64; N, 27.36; H, 5.06; Cl, 23.08; Ru, 21.9. Found: C, 15.27; N, 27.39; H, 4.93; Cl, 22.73; Ru, 21.8.

The N_9 and N_3 linkage isomers of [7MeHyp](III) were similarly prepared. Preparations employing an excess of ligand usually exhibited only the two linkage isomers on chromatographic separation. The N_3 isomer, which appeared as an orange band on the carboxylate resin column eluted with ammonium acetate, eluted well before the yellow N_9 isomer. When less than a stoichiometric amount of ligand was used, a highly charged species usually adhered to the top of the column. The N_9 isomer could be isolated as a solid according to the method given for the other hypoxanthine complexes. Similar attempts to isolate the N_3 isomer by slow crystallization from acidic solutions invariably resulted in crystals of the N_9 isomer. Rapid precipitation rendered samples contaminated with the N_9 isomer. Solids prepared by either method usually gave elemental analyses similar to the calculated values. Pure solutions of the N_3 isomer in 0.1 M LiCl could be prepared by transferring the band containing the desired product to a 3-cm Bio-Rex 70 column which was eluted with water followed by 0.05 M HCl. The acid containing the complex was neutralized with LiOH as it eluted from the column. The resultant solution was concentrated by rotoevaporation and then adjusted to 0.1 M with a standard LiCl solution. The ruthenium concentration of these solutions was determined by atomic absorption. Anal. Calcd for N_9- and N_3-[(7MeHyp)$(NH_3)_5$Ru]$Cl_3 \cdot H_2O$: C, 15.64; N, 27.36; H, 5.03; Cl, 23.08; Ru, 21.9. Found for N_3 isomer contaminated with small amount of N_9 isomer derived from N_3 isomer: C, 15.57; N, 27.56; H, 4.87; Cl, 22.81; Ru, 22.0. Found for N_9 isomer: C, 15.27; N, 27.39; H, 4.93; Cl, 22.73; Ru, 21.8.

(Inosine diphosphate)pentaammineruthenium(III) was prepared using inosine 5′-triphosphate as the starting material by a method similar to that used to synthesize the inosine complex. Products were separated by a single ion-exchange chromatography on a 10 cm Ag-50 column. Two red bands were evident. The first band eluted with 1–2 M HCl and is believed to be that of the inosine triphosphate complex. The second band containing the inosine diphosphate complex was rotoevaporated to dryness and redissolved in water, and the mixture was filtered. The complex was then crystallized from a concentrated aqueous solution at pH 4. Anal. Calcd for (IDP)$(NH_3)_5$Ru: C, 19.05; N, 20.00; H, 4.67; P, 9.83; Ru, 16.0. Found: C, 19.11; N, 19.87; H, 4.69; P, 10.10; Ru, 15.0.

Physical Measurements. Electronic spectra were recorded and molar absorptivities determined by previously reported methods. The values of pK_a were determined spectrophotometrically for the ruthenium compounds at $\mu = 0.1$ according to standard techniques.[16,37] Reduction potentials were determined by cyclic voltammetry using techniques stated elsewhere.[32] Formal potentials were measured at half the distance between the anodic and cathodic peaks. Peak separations were generally around 65 mV and were usually no greater than that measured for the hexaammineruthenium(III)–hexaammineruthenium(II) couple under the same conditions. The reduction potential for the hexaammineruthenium(III) complex was measured as 59 mV on this system.

Results

Synthesis. Preparations with inosine ligands usually gave a single product. Small amounts of a highly charged red species present in some preparations were probably due to hypoxanthine impurities. The presence of two products when 5′-inosine triphosphate was used as the purine ligand was due to the formation of both the inosine diphosphate complex, which was isolated as a solid, and a similar complex of lower charge which eluted first from the cation-exchange column and is presumably the corresponding triphosphate complex. Preparations with deoxyinosine which were allowed to sit in acid (1–6 M HCl) for several hours invariably yielded 7-[Hyp](III) as the sole product as initially determined by structural analysis by x-ray diffraction[34] and subsequently by UV–visible spectra. The hypoxanthine complex was also evident as an impurity when solutions of 7-[Ino](III) were allowed to stand in acid.

At least two products were observed with hypoxanthine derivatives which did not have an alkyl substituent at N_9. Preparations with these ligands often exhibited a highly charged red species which did not elute from the carboxylate resin ion-exchange column with 1 M ammonium acetate. The amount of this red species increased in proportion to the excess quantity of ruthenium present in the reaction mixture. Several other bands were often evident in chromatographic separations on carboxylate resin columns with preparations involving hypoxanthine and 1-methylhypoxanthine. A red-purple band containing the N_7-bound isomers of these two ligands eluted first in 0.4 M ammonium acetate. A red and an orange-yellow band eluted with 0.4–0.6 M ammonium acetate. These two bands were poorly separated and were often collected together and treated as a single fraction in subsequent steps invariably yielding 9-[Hyp](III) as the single product.

Preparations with the 7-methylhypoxanthine ligand usually yielded two distinct bands on the carboxylate resin column. A red band which eluted first was determined to contain 3-[7MeHyp](III). A yellow band which eluted with 0.6 M ammonium acetate was comprised of the N_9 isomer. All attempts to isolate the N_3 isomer as a pure solid resulted in contamination with the N_9 isomer, in spite of the excellent chromatographic separation.

Table I. Ligand to Metal Charge-Transfer Transitions of Pentaammineruthenium(III)–Hypoxanthine Complexes[a]

Ligand	Visible ν_{max}, $cm^{-1} \times 10^3$	Visible ϵ, M^{-1} cm^{-1}	UV ν_{max}, $cm^{-1} \times 10^3$	UV $\epsilon \times 10^{-3}$, M^{-1} cm^{-1}
3-[7MeHyp]	21.7	491	32.1	1.40
7-[Ino]	22.0	267	32.8	1.08
7-[1MeIno]	22.0	295	32.8 sh	1.03
7-[IDP]	22.2	250	32.5	1.09
7-[Hyp]	21.7	316	33.3	1.33
7-[1MeHyp]	21.6	340	33.4	1.15
9-[Hyp]	23.1	101	31.9	1.83
9-[1MeHyp]	22.8	120	31.4	1.61
9-[7MeHyp]	22.7	134	31.4	2.24
3-[7MeHyp,1^-]	19.1	1630	30.2	2.40
7-[Ino,1^-]	19.1	330	28.5 sh	0.59
			33.0 sh	1.20
9-[7MeHyp,1^-]	19.4	325	28.5	1.50
7-[IDP,1^-]	19.4	283	33.3	1.17
7-[Hyp,9^-]	18.9	859	28.0	2.02
7-[1MeHyp,1^-]	18.8	916	27.7	1.82
9-[Hyp,7^-]	20.5	164	28.0	4.14
9-[1MeHyp,7^-]	20.1	184	27.6	4.1
7-[Hyp,1^-,9^-]	17.0	1170	24.9	1.14
			32.0	2.00
9-[Hyp,1^-,7^-]	17.4	264	25.3	3.20
			32.7	1.10

[a] Neutral-ligand spectra taken in 0.1 M HCl. Deprotonated-ligand spectra taken in 0.1 M LiCl at a pH at least 2 units above the pK_a value. sh = shoulder.

Spectra. The spectrophotometric properties of the various ruthenium(III)–hypoxanthine complexes are summarized in Tables I and II. In general, the ruthenium(III) compounds exhibited a broad absorption band in the visible region, a second broad band in the near-ultraviolet, and a third absorption in the ultraviolet. The spectra of the ruthenium(III) complexes varied as a function of pH with the near-ultraviolet and visible absorptions usually shifting toward lower energy and increasing in intensity with decreasing acid concentration. The single exception to this in the normal pH range was the 1-methylhypoxanthine complex which contains no easily ionizable protons. Isosbestic points were normally observed on varying the pH in the region of a well resolved pK_a. Complexes with hypoxanthine as the ligand exhibited a new band in the near-ultraviolet region at high pH.

The ruthenium(II) complexes usually showed broad absorptions in the near-ultraviolet (Table III) and a second area of more intense absorption in the ultraviolet (Table II). Several of the neutral ligand complexes appeared to have two broad

Table II. Ligand π–π^* Transitions of Pentaammineruthenium–Hypoxanthine Complexes[a]

Ligand	Ru(III) λ_{max}, nm	Ru(III) $\epsilon \times 10^{-3}$, M^{-1} cm^{-1}	Ru(II) λ_{max}, nm	Ru(II) $\epsilon \times 10^{-3}$, M^{-1} cm^{-1}
3-[7MeHyp]	215 sh	12	253	13.1
	235	9.0		
	255	9.7		
7-[Ino]	249	10.1	246	11.7
7-[1MeIno]	252	9.51	247	10.7
7-[IDP]	249	10.7		
7-[Hyp]	247	10.3	245	11.6
7-[1MeHyp]	249	9.4	245	10.9
9-[Hyp]	251	10.6	254	12.0
9-[1MeHyp]	237 sh	10.7	257	15.8
	248	10.9		
9-[7MeHyp]	232 sh	11.6	234 sh	13
	251	12	254	15.6
3-[7MeHyp,1⁻]	263	9.6	256	13.0
7-[Ino,1⁻]	260	10.0	251	11.6
9-[7MeHyp,1⁻]	264	13.5	258	16.5
7-[IDP,1⁻]	261	9.86		
7-[Hyp,9⁻]	237 sh	7.59	255	11.7
	255	9.69		
7-[1MeHyp,9⁻]	240 sh	7.4	255	10.8
	256	8.90		
	296	1.51		
9-[Hyp,7⁻]	240	13.0	258	12.8
	252 sh	12.7		
9-[1MeHyp,7⁻]	241	12.2	252	13.1
	254 sh	11.2		
7-[Hyp,1⁻,9⁻]	261	9.7	257	12.8
9-[Hyp,1⁻,7⁻]	240	9.9	258	12.8
	257	12.6		

[a] Spectra taken at $\mu = 0.1$ in LiCl at a pH adjusted with HCl or LiOH to a value 2 units above or below the pertinent pK_a. sh = shoulder; i = inflection point.

Table III. Metal to Ligand Charge-Transfer Transitions of Pentaammineruthenium(II)–Hypoxanthine Complexes[a]

Ligand	λ_{max}, nm	$\epsilon \times 10^{-3}$, M^{-1} cm^{-1}
3-[7MeHyp]	357	2.2
7-[Ino]	370	2.25
	400 sh	1.98
7-[1MeIno]	367	2.33
7-[Hyp]	360	2.28
	395 sh	1.93
7-[1MeHyp]	358	2.5
	395	1.9
9-[Hyp]	348	2.12
	400 sh	1.2
9-[1MeHyp]	340	2.5
9-[7MeHyp]	349	2.37
	385 sh	2.0
3-[7MeHyp,1⁻]	360	2.5
7-[Ino,1⁻]	305 sh	2.5
	362	1.82
9-[7MeHyp,1⁻]	361	2.3
7-[Hyp,9⁻]	328	2.32
7-[1MeHyp,9⁻]	344	2.7
9-[Hyp,7⁻]	345	2.33
9-[1MeHyp,7⁻]	351	2.17
	395 sh	1.53
7-[Hyp,1⁻,9⁻]	300	2.61
	348 sh	1.9
9-[Hyp,1⁻,7⁻]	298	2.29
	342 sh	1.65

[a] Neutral-ligand spectra taken in 0.1 M HCl. Deprotonated-ligand spectra taken in 0.1 M LiCl at least 2 units above the pK_a value. sh = shoulder; i = inflection point.

overlapping bands in the near-ultraviolet. The poor resolution of these bands and their proximity to the more intense ultraviolet absorption made it difficult to determine the variation in the energies and intensities of these bands as a function of pH. In general, however, these absorptions increased in energy with increasing pH.

The ultraviolet absorptions summarized in Table II are similar in energy and intensity to those exhibited by the free ligands. These absorptions are usually slightly more intense for the ruthenium(II) complexes than for the corresponding ruthenium(III) species.

Electrochemistry. Formal potentials as measured by cyclic voltammetry are reported in Table IV. The observed separation between the anodic and cathodic peaks indicates that the couples are reversible. In all cases, differences in reduction potential between the neutral and deprotonated ligand complexes were approximately those expected from the differences in pK_a values between the ruthenium(III) and ruthenium(II) complexes (see Table V).

pK_a Measurements. pK_a values determined spectrophotometrically for the loss of a proton from the various ruthe-

Table IV. Formal Reduction Potentials of Ruthenium(III)- and -(II)-Hypoxanthine Complexes, $\mu = 0.1$

Couple	E_f vs. NHE, V
3-[7MeHyp] (III–II)	0.25[a]
3-[7MeHyp,1⁻] (III–II)	0.07[c]
7-[Ino] (III–II)	0.24[a]
7-[Ino,1⁻] (III–II)	0.14[c]
7-[1MeIno] (III–II)	0.24[a,b]
7-[Hyp] (III–II)	0.21[a,b]
7-[Hyp,9⁻] (III–II)	−0.03[c]
7-[Hyp,1⁻,9⁻] (III–II)	−0.13[d]
7-[1MeHyp] (III–II)	0.21[a]
7-[1MeHyp,9⁻] (III–II)	−0.02[c]
9-[Hyp] (III–II)	0.19[a,b]
9-[Hyp,7⁻] (III–II)	−0.03[c]
9-[Hyp,1⁻,7⁻] (III–II)	−0.11[d]
9-[1MeHyp] (III–II)	0.19[a]
9-[1MeHyp,7⁻] (III–II)	−0.04[c]
9-[7MeHyp] (III–II)	0.19[a,b]
9-[7MeHyp,1⁻] (III–II)	0.12[c]

[a] 0.01 M HCl, 0.09 M LiCl. [b] 0.001 M HCl, 0.099 M LiCl. [c] Glycine, LiOH, LiCl buffer, pH 9. [d] 0.1 M LiOH.

Table V. pK_a Measurements at 25° C

Pentaammineruthenium–Hypoxanthine Complexes

Metal binding site	Ligand	Deprotonation site	pK_a Ru(III)	pK_a Ru(II)	ΔpK_a[a]	ΔpK_a[b]
N_3	7MeHyp	N_1	4.82	8.1	3.3	3.2
N_7	Hyp	N_9	3.87	7.8	3.9	4.0
N_7	1MeHyp	N_9	3.95	7.8	3.9	3.9
N_7	Ino	N_1	6.59	8.3	1.7	1.7
N_9	7MeHyp	N_1	7.46	8.4	0.9	1.2
N_9	Hyp	N_7	4.15	7.6	3.5	3.7
N_9	1MeHyp	N_7	4.20	7.7	3.5	3.8
N_7	Hyp^-	N_1	9.30	11.0	1.7	1.7
N_9	Hyp^-	N_1	10.00	11.4	1.4	1.4

Free Ligands[c]

Ligand	Deprotonation site	pK_a	Ligand	Deprotonation site	pK_a
Hypoxanthine	N_1	8.9	7-Methylhypoxanthine	N_1	9.0
Hypoxanthine	N_7 or N_9	12.1			
1-Methylhypoxanthine	N_7 or N_9	8.9	Inosine	N_1	8.7

[a] Difference in the pK_a values for the Ru(III) and Ru(II) complexes measured spectrophotometrically. [b] Difference in the pK_a values for the Ru(III) and Ru(II) complexes determined from electrochemical measurements. [c] Reference 38.

nium(II) and -(III) complexes are reported in Table V. Protonations were reversible for the ruthenium(III) complexes over the time span of the pK_a determinations. Ruthenium(II) complexes were considerably less stable and isosbestic points were often lost at high pH. Solutions of both ruthenium(II) and -(III) complexes discolored when allowed to stand at high pH for extended periods. Those complexes which were able to deprotonate at a site on the hypoxanthine ring proximal to the metal center exhibited greater stability at high pH than those which could not. As has been observed with the corresponding guanine and xanthine complexes,[16,32] the addition of a ruthenium(III) center has a marked effect on the acidity of the purine ring protons. For example, the acidity constant of 7-methylhypoxanthine is increased by a factor of 10^4 over that of the free ligand upon binding pentaammineruthenium(III) at the N_3 site. Coordination of ruthenium(II) increases the acidity of the ligand much less markedly, e.g., only 0.9 in the pK_a value for 3-[7MeHyp](II) relative to the free ligand. Due to the difficulty in measuring the pK_a values of the air and pH-sensitive ruthenium(II) complexes spectrophotometrically, a verification of these values was obtained by determing the ΔpK_a between the Ru(III) and Ru(II) complexes electrochemically. The similarities in these values indicate that the reported pK_a values are accurate.

Discussion

Structure. The ruthenium binding site in the compounds 7-[Hyp$(NH_3)_5$Ru]Cl_3, 9-[Hyp$(NH_3)_5$Ru]Cl_3, and 9-[7MeHyp$(NH_3)_5$Ru]Cl_3 has been determined by x-ray diffraction studies.[34] Assignments of the coordination site in all other N_7- and N_9-bound complexes were made on the basis of spectral similarities to one of these complexes. Reference to Table I shows that the similarity in spectra of complexes assigned the same binding site embraces both energies and molar absorptivities. This similarity holds equally well when the ligand is deprotonated at a given site. For several complexes it is also possible to assign the binding sites by eliminating those sites which are blocked by alkyl groups, sterically hindered or chemically unlikely. For example, the ligand 1-methylinosine is expected to bind ruthenium only at N_7 since the N_1 and N_9 sites are alkylated and the ribose sterically hinders attack by a bulky metal ion at N_3. At neutral or low pH inosine and inosine diphosphate are also expected to coordinate ruthenium at N_7. Metal ions will bind at the N_1 of hypoxanthine and guanine ligands only when this site is deprotonated at high pH. Similarly, at low pH 7-methylhypoxanthine can coordinate the metal only at N_3 or N_9. When the imidazole ring is not alkylated, the proton can tautomerize between N_7 and N_9 making both sites available. Hypoxanthine and 1-methylhypoxanthine can, therefore, coordinate pentaammineruthenium(II) at N_3, N_7, or N_9 under the reaction conditions given. Substitution of the N_1 proton by a ruthenium ion to form a binuclear diruthenium–hypoxanthine species may account for the highly charged red species that were present in several of the preparations. This highly charged material appeared to increase with pH and decreasing amount of ligand. Similar binuclear species have been observed with platinum–purine complexes.[17]

Binding by ruthenium(II) to the oxygen site of hypoxanthine ligands is unlikely since neutral oxygen exhibits a high lability on ruthenium as well as a low affinity. While coordination to the C_8 of hypoxanthine is a possibility for ruthenium(II)–ammine species, no such complexes were isolated. The spectra and reduction potentials of none of the complexes are consistent with C_8 coordination nor is the elemental analysis of any of the compounds in keeping with the loss of the trans ammonia, which has been invariably observed in all the ammineruthenium carbon-bound complexes isolated to date.[32,40]

Since only two compounds were formed in the reaction with 7-methylhypoxanthine as the ligand, one can safely assume that these represent the N_3- and N_9-bound complexes. Previous studies have shown that the acidity of a given purine ring proton increases as the distance between the proton and the metal center decreases. Therefore, tentative assignments of the N_3 and N_9 complexes were made on the basis of their relative acidities, i.e., the complex with the lower pK_a should have the metal center closer to the N_1 deprotonation site and so was assigned as the N_3-bound isomer. The structure of the N_9-bound species has since been verified by x-ray diffraction techniques[34] causing the second complex to be assigned as N_3 bound by simple elimination. Also the charge-transfer bands of the 3-[7MeHyp](III) complex are significantly more intense than those for similar complexes known to be N_7 or N_9 bound. Finally, the reduction potential for the 3-[7MeHyp](III) complex is higher than those for similar N_7 and N_9 complexes. This is consistent with the metal center being on the pyrimidine rather than the imidazole ring, since the pyrimidine(pentaammine)ruthenium(III) complex has a greater reduction potential than the corresponding imidazole complex.[31,40]

The isomerization of the complex assigned as 3-[7MeHyp](III) to the N_9-bound form implies that the metal center is in close proximity to the N_9 site prior to isomerization. Substitution of nitrogen ligands on ruthenium(III)–ammine complexes normally occurs very slowly. For example, the loss of ammonia from $(NH_3)_6Ru^{III}$ proceeds with a half-life of approximately 3.1 years in chloride media.[41] The N_3 to N_9 linkage isomerization of the 3-[7MeHyp](III) complex occurs with a half-life of approximately 5 h at pH 3. At higher pH, where the pyrimidine ring is deprotonated, this isomerization proceeds much more slowly and solutions of the N_3-bound complex can be preserved at pH 7 and 4 °C for long periods. Protonation of the anionic ligand appears to decrease the basicity of the N_3 site sufficiently so that the ruthenium moves over to the more electron-rich N_9. Space-filling models indicate that the lone pair of the N_9 impinges on an octahedral face of the metal ion coordinated at N_3. Thus the steric arrangement around the metal center combined with the relative changes in the basicity of the N_3 vs. the N_9 site on protonation at N_1 facilitates the N_3 to N_9 isomerization.

Spectra. The two broad absorption bands exhibited by ruthenium(III)–purine complexes in the visible and near-ultraviolet regions have been previously interpreted as ligand to metal charge-transfer bands (LMCT) arising from separate π orbitals on the purine to a half-filled $d\pi$ level on the ruthenium. The increases in intensity and differing bathochromic shifts for the two transitions on deprotonation of the purine support this conclusion.[16,32] If this interpretation is correct and the additional assumptions are made that the donor and acceptor orbitals are the same and remain nearly constant in energy regardless of the ruthenium binding site, then the charge-transfer bands of the various linkage isomers are expected to be similar in energy. However, the electric dipoles of the ground and excited states should vary between the linkage isomers so that the intensities of these bands should be a function of the coordination site. Thus the energies of the LMCT bands recorded in Table I are quite similar for a series of linkage isomers with neutral hypoxanthine ligands or with hypoxanthine derivatives deprotonated at the same site. This is particularly apparent in the series 3-[7MeHyp,1^-](III), 7-[Ino,1^-](III), and 9-[7MeHyp,1^-](III) in which the energies vary by only 300 cm^{-1} but the molar absorptivities extend over a fivefold range.

Similarly the visible LMCT transitions of the fully deprotonated complexes 7- and 9-[Hyp^{2-}](III) differ by an order of magnitude in intensity but only by 400 cm^{-1} in energy. These complexes also exhibit a third band in the near-ul-

traviolet which is consistent with the above LMCT interpretation, if it is assumed that the double deprotonation of the ligand raises the energy of the π molecular orbitals on the purine sufficiently to allow a LMCT from a third lower lying ligand level. The presence of a dianionic ligand should also, to a lesser extent, elevate the energies and remove the degeneracies of the ruthenium d orbitals allowing the additional interpretation of the third band as a $d \rightarrow d$ transition. The possibility of this band arising from a $d \rightarrow d$ transition may be eliminated since such an absorption would be expected to occur at a much lower energy. The absorption at 32000 cm^{-1} might be attributed to a $d \rightarrow d$ transition since this is in the region expected for $10Dq$ of an ammineruthenium(III) complex (34000 cm^{-1});[39] however, the intensity is a bit higher than might be expected for such a transition even in an ion of such low symmetry.[42]

The absorption bands recorded in Table II for the series of Ru(II) complexes are typical of pentaammineruthenium(II) coordinated to aromatic molecules with low-lying π^* orbitals. These absorptions can be attributed to $d \rightarrow \pi^*$ metal to ligand charge-transfer (MLCT) transitions. Since $d-\pi^*$ backbonding plays an important role in the chemistry of pentaammineruthenium(II) ions, no simple interpretation of the energies and intensities of these bands as a function of binding site can be made. Appreciable mixing of the metal and ligand orbitals of π symmetry is expected to occur and it is likely that the extent of this mixing is a function of the availability of the π^* purine orbitals at a given binding site. Furthermore, several of the complexes exhibit overlapping MLCT bands which complicates their assignment and interpretation.

Reduction Potentials. The reduction potentials summarized in Table IV are reversible on the time scale employed to measure them. The formal potentials vary little as a function of the metal binding site. However, the differences between the reduction potentials of the various linkage isomers are significant and, for the neutral-ligand complexes, follow the order $N_3 > N_7 > N_9$. The reduction potential for a pentaammineruthenium(III) ion on the pyrimidine ring of a purine might be expected to be a bit higher than if it were on the imidazole ring. The more electron-deficient pyrimidine would be expected to function as a slightly better π-electron acceptor and thus delocalize electron density away from Ru(II) via the d orbitals and thereby stabilize it relative to ruthenium(III).[31,40] In all cases, deprotonation of the hypoxanthine ligand lowers the reduction potential of the complex. Ligand deprotonation decreases the magnitude of the reduction potential as the distance between the metal center and the deprotonation site decreases. Deprotonation at N_1 results in decreases in reduction potentials of approximately 0.18, 0.10, and 0.07 V when the metal is at N_3, N_7, or N_9, respectively. Deprotonation on the imidazole ring when the metal is also coordinated to this moiety decreases the reduction potential by approximately 0.23 V.

pK_a Values. As has been noted for other purines, the increase in the acidity of the hypoxanthine ligand is a function of the proximity of the metal ion to the deprotonation site. For the series of Ru(III) complexes the pK_a for deprotonation at N_1 is decreased by 4.2, 2.1, and 1.5 for metal coordination at N_3, N_7, and N_9, respectively. Coordination of Ru(III) on the imidazole decreases the pK_a value for the loss of a proton from this ring by approximately 4.8 units. Coordination of Ru(II) to hypoxanthine increases the acidity of the ligand to a lesser extent. The pK_a for deprotonation at N_1 is decreased by 0.9, 0.4, and 0.6 for Ru(II) coordination at N_3, N_7, and N_9, respectively. When the Ru(II) ion is bound to the imidazole ring, the pK_a value of the imidazole ring proton is decreased by approximately 1.2.

The physical measurements of the pentaammineruthenium(II)- and -(III)–hypoxanthine linkage isomers reported here should facilitate the identification and separation of metal–purine complexes in the future. Identification of the isomers can be made on the basis of the intensity of the LMCT in the visible region, with the molar absorptivity of these bands decreasing in the order N_3, N_7, N_9. The relative increase in acidity of hypoxanthine ligand upon coordination to ruthenium(III) is also a function of the binding site and can be used to assign linkage isomers, and a careful consideration of the charge of the complex as a function of pH allows the separation of these complexes by ion-exchange chromatography. It should also be noted that the acid-catalyzed N_3 to N_9 isomerization of 3-[7MeHyp$(NH_3)Ru^{III}$] may be the cause of previous failures to isolate and characterize N_3-coordinated metal–purine complexes.

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Registry No. N_7-[(Hyp)$(NH_3)_5Ru^{III}$], 61483-55-4; N_7-[(Hyp)$(NH_3)_5Ru^{II}$], 61483-56-5; N_7-[(Hyp,9^-)$(NH_3)_5Ru^{III}$], 61483-57-6; N_7-[(Hyp,9^-)$(NH_3)_5Ru^{II}$], 61483-58-7; N_7-[(Hyp,1^-,9^-)$(NH_3)_5Ru^{III}$], 61483-59-8; N_7-[(Hyp,1^-,9^-)$(NH_3)_5Ru^{II}$], 61483-60-1; N_9-[(Hyp)$(NH_3)_5Ru^{III}]Cl_3$, 61483-61-2; N_9-[(Hyp)$(NH_3)_5Ru^{II}$], 61483-62-3; N_9-[(Hyp,7^-)$(NH_3)_5Ru^{III}$], 61483-63-4; N_9-[(Hyp,7^-)$(NH_3)_5Ru^{II}$], 61483-64-5; N_9-[(Hyp,1^-,7^-)$(NH_3)_5Ru^{III}$], 61483-65-6; N_9-[(Hyp,1^-,7^-)$(NH_3)_5Ru^{II}$], 61483-66-7; N_7-[(1MeHyp)$(NH_3)_5Ru^{III}]Cl_3$, 61491-41-6; N_7-[(1MeHyp)$(NH_3)_5Ru^{II}$], 61483-67-8; N_7-[(1MeHyp,9^-)$(NH_3)_5Ru^{III}$], 61483-68-9; N_7-[(1MeHyp,9^-)$(NH_3)_5Ru^{II}$], 61483-69-0; N_9-[(1MeHyp)$(NH_3)_5Ru^{III}]Cl_3$, 61483-70-3; N_9-[(1MeHyp)$(NH_3)_5Ru^{II}$], 61483-71-4; N_9-[(1MeHyp,7^-)$(NH_3)_5Ru^{III}$], 61483-72-5; N_9-[(1MeHyp,7^-)$(NH_3)_5Ru^{II}$], 61483-73-6; N_3-[(7MeHyp)$(NH_3)_5Ru^{III}]Cl_3$, 61483-74-7; N_3-[(7MeHyp)$(NH_3)_5Ru^{II}$], 61483-75-8; N_3-[(7MeHyp,1^-)$(NH_3)_5Ru^{III}$], 61505-85-9; N_3-[(7MeHyp,1^-)$(NH_3)_5Ru^{II}$], 61483-92-9; N_9-[(7MeHyp)$(NH_3)_5Ru^{III}]Cl_3$, 61483-76-9; N_9-[(7MeHyp)$(NH_3)_5Ru^{II}$], 61483-77-0; N_9-[(7MeHyp,1^-)$(NH_3)_5Ru^{III}$], 61483-78-1; N_9-[(7MeHyp,1^-)$(NH_3)_5Ru^{II}$], 61483-79-2; N_7-[(Ino)$(NH_3)_5Ru^{III}]Cl_3$, 61483-80-5; N_7-[(Ino)$(NH_3)_5Ru^{II}$], 61477-68-7; N_7-[(Ino,1^-)$(NH_3)_5Ru^{III}$], 61477-69-8; N_7-[(Ino,1^-)$(NH_3)_5Ru^{II}$], 61477-70-1; N_7-[(1MeIno)$(NH_3)_5Ru^{III}]Cl_3$, 61477-71-2; N_7-[(1MeIno)$(NH_3)_5Ru^{II}$], 61477-72-3; N_7-[(IDP)$(NH_3)_5Ru^{III}$], 61477-73-4; N_7-[(IDP,1^-)$(NH_3)_5Ru^{III}$], 61477-74-5.

References and Notes

(1) Presented in part at the 170th National Meeting of the American Chemical Society, Chicago, Ill., 1975; see Abstracts, No. INOR 187. The major portion of this work was done at Boston University.
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Photochemistry of Transition Metal Hydride Complexes. 2. $[RuClH(CO)(PPh_3)_3]$, $[RuH_2(CO)(PPh_3)_3]$, and $[RuClH(CO)_2(PPh_3)_2]$[1]

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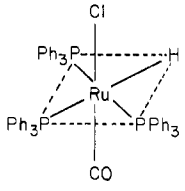
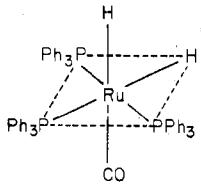
Ultraviolet irradiation of $[RuClH(CO)(PPh_3)_3]$ results in elimination of carbon monoxide and generation of the potent hydrogenation catalyst $[RuClH(PPh_3)_3]$. The reaction occurs with a 313-nm quantum yield of 0.06. The dicarbonyl complex $[RuClH(CO)_2(PPh_3)_2]$ is also formed in the photolysis through the separate reaction of $[RuClH(CO)(PPh_3)_3]$ with part of the photoreleased CO. Irradiation of $[RuH_2(CO)(PPh_3)_3]$ leads to elimination of molecular hydrogen, apparently generating transient $[Ru(CO)(PPh_3)_3]$, and irradiation under a CO atmosphere converts $[RuH_2(CO)(PPh_3)_3]$ quantitatively into $[Ru(CO)_3(PPh_3)_2]$. Photolysis of $[RuClH(CO)_2(PPh_3)_2]$ results in photoisomerization which is slowly reversed in the dark.

Introduction

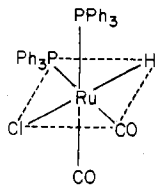
Although transition metal hydride complexes are an important class of compounds in inorganic and organometallic chemistry, the photochemical properties of only a few have been investigated in detail.[2] We have initiated a systematic investigation into the photochemistry of hydride complexes in order to determine what effect the hydride ligand has on the excited-state properties and to determine if, as we now suspect,[2] photoinduced elimination of molecular hydrogen is a general property of di- and polyhydride complexes of all of the transition elements. In this paper we examine the previously well-characterized compounds $[RuClH(CO)(PPh_3)_3]$, **1**,



1



2



3

$[RuH_2(CO)(PPh_3)_3]$, **2**, and $[RuClH(CO)_2(PPh_3)_2]$, **3**. Complexes **1** and **2** are ideally suited for comparison of their photochemistry since **2** is derived from **1** by simple substitution of chloride by hydride.

$[RuClH(CO)(PPh_3)_3]$ is a cream-colored solid and is easily prepared in high yield by the reaction of $RuCl_3 \cdot xH_2O$ with PPh_3 and aqueous HCHO in boiling 2-methoxyethanol.[3] $[RuH_2(CO)(PPh_3)_3]$, a white solid, is prepared by a similar reaction in alcoholic KOH,[3] and $[RuClH(CO)_2(PPh_3)_2]$ derives from $[RuClH(CO)(PPh_3)_3]$ by treatment with CO.[4] The stereochemistry of the isomer of $[RuClH(CO)(PPh_3)_3]$ prepared in this manner, shown in **1**, is suggested by the demonstrated stereochemistry of $[RuClH(CO)(PMe_2Ph)_3]$,[5] by the published crystal structure of $[OsClH(CO)(PPh_3)_3]$,[6] and by the similarity of the infrared spectra of the ruthenium and osmium derivatives.[7] Infrared and NMR data have led to the assignment of the stereochemistries of $[RuH_2(CO)(PPh_3)_3]$[3,8] and $[RuClH(CO)_2(PPh_3)_2]$[4] shown in **2** and **3**. $[RuClH(CO)(PPh_3)_3]$ readily undergoes thermal substitution of the phosphine ligand trans to the hydride[9] and has also been shown[10] to be a catalyst for the isomerization of terminal olefins. Interestingly, $[RuH_2(CO)(PPh_3)_3]$ is apparently inert to substitution of the phosphine ligands.[11] Complexes **1**–**3** are relatively air stable in the solid state but solutions slowly decompose when exposed to air.

Experimental Section

The complexes $[RuClH(CO)(PPh_3)_3]$,[3] $[RuClD(CO)(PPh_3)_3]$,[12] $[RuClH(PPh_3)_3]$,[13] $[Ru(CO)_3(PPh_3)_2]$,[3] $[RuH_2(CO)(PPh_3)_3]$,[3] and $[RuClH(CO)_2(PPh_3)_2]$[4] were prepared by published procedures. Solvents used for measurement of spectra were MC & B Spectroquality, and all other solvents were purified by standard methods. All experiments and manipulations of compounds were conducted under vacuum or under a purified N_2 or Ar atmosphere, unless otherwise specified.

General Irradiation Procedures. Irradiations were conducted at 366 nm using a 450-W Hanovia medium-pressure Hg lamp equipped with Corning Glass 0-52 and 7-37 filters ($I \approx 10^{-8}$ einstein/min), at 313 nm using the same lamp in a Pyrex well with a K_2CrO_4 filter solution, or in a 350-nm Rayonet photoreactor. The complex to be studied was placed in an evacuable quartz UV cell or a Schlenk tube, and after degassing on a vacuum line the appropriate solvent was distilled onto the sample. Solutions for infrared studies were transferred in an inert-atmosphere glovebox to 0.5-mm NaCl solution infrared cells. Solutions were irradiated with the appropriate lamp, and electronic and infrared spectra were periodically recorded.