The X_{11}/ω_1 ratios, 2.32×10^{-3} for ^{16}O and 2.44×10^{-3} for ^{18}O, are in the range found for other metal–ligand stretching modes.[20]

Summary

RR scattering of **1** is dominated by the symmetric Fe–O–Fe stretching mode, ν_s, at 530 cm^{-1}, enhanced via coupling with O → Fe CT transitions. Its excitation profile reveals two CT transitions, at ~405 and ~525 nm, suggested to originate in the two O^{2-} p_π orbitals and terminate in the Fe^{III} d_π orbitals. When maximally enhanced, the ν_s mode supports detectable combination bands with modes at 275 and 104 cm^{-1}. The latter even forms a difference band with ν_s, which loses intensity at low temperature, as required. A progression in ν_s overtones out to $5\nu_s$ is observed, from which accurate harmonic frequency and anharmonicity constants are calculated. The asymmetric Fe–O–Fe stretch, ν_{as} = 754 cm^{-1}, is detectable but very weak; being of B_2 symmetry, it is enhanced only by vibronic mixing. Its overtone, being of A_1 symmetry, is Franck–Condon-allowed, has greater intensity, and also forms a subsidiary series with ν_s. Assignments of other low-frequency modes to Fe–N(pyrazole) and Fe–O(acetate) stretching and Fe–O–Fe and O–C–O(acetate) deformations are suggested on the basis of a normal-coordinate analysis. Of particularly interest are the assignments of moderately strong bands at 275 and 104 cm^{-1} to Fe–N(pyrazole) stretching and (mainly) Fe–O–Fe bending, respectively. The 3-cm^{-1} ^{18}O shift of the 275-cm^{-1} band is due to coupling between the Fe–N(pyrazole)$_{trans}$ and Fe–O_{bridge} bonds. By analogy, the ^{18}O-sensitive 292-cm^{-1} band of azidomethemerythrin is reassigned to the Fe–N(histidine)$_{trans}$ stretch.

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Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Pentaammineruthenium(II/III) Imidazole and Imidazolate Complexes of 2-Carboxylatoimidazole and 2-Imidazolecarboxaldehyde

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$(NH_3)_5RuL^{2+}$ and $(NH_3)_5RuL^{3+}$ complexes of 2-substituted imidazoles, L = 2-carboxylatoimidazole ($2CO_2imH^-$) and 2-imidazolecarboxaldehyde (2CHOimH), have been prepared and characterized by UV–visible spectroscopy, potentiometric titration, and differential-pulse voltammetry. An aldehyde carbonyl/hydrate equilibrium was detected for the free 2CHOimH ligand by ^1H NMR and UV–visible methods. Above pH ≅7 the R = CHO derivative is highly favored over the hydrate, R = $CH(OH)_2$ ($K \leq 7 \times 10^{-4}$ M^{-1} for hydration). Protonation at N3 of 2CHOimH induces hydration (K = 143 at pH 3.17). Thus 2CHOimH is less hydrated than 4-formylpyridine (pfp) by at least 2 orders of magnitude while $2CHOimH_2^+$ is more extensively hydrated than $Hpfp^+$ ($K \sim 3$) by 1 order of magnitude. Coordination of either $(NH_3)_5Ru^{2+}$ or $(NH_3)_5Ru^{3+}$ with $2CO_2imH^-$ or 2CHOimH enhances the acidity of the pyrrole hydrogen. Results determined in this work show that the effects of an organic ring substituent and the coordinated Ru center are virtually additive on stabilizing the imidazolato form ($Ru^{III} > Ru^{II}$; R = CHO > R = CO_2^-). pK_a's for the complexes are as follows (T = 22 °C): $(NH_3)_5Ru^{III}(2CO_2imH)^{2+}$, 7.95 ± 0.05; $(NH_3)_5Ru^{III}(2CH(OH)_2imH)^{3+}$, 5.65 ± 0.05; $(NH_3)_5Ru^{II}(2CHOimH)^{2+}$, ~8.8 compared to the free ligand pK_a's of 10.7 ($2CO_2imH^-$) and 10.5 (2CHOimH). $(NH_3)_5Ru^{II}L$ complexes exhibit two MLCT transitions that establish a π-acceptor order for 2-substituted imidazoles with R = CHO > CO_2^- ≫ H. These MLCT bands occur at 367 nm ($\epsilon = 2.0 \times 10^3$ M^{-1} cm^{-1}) and 420 nm ($\epsilon = 4.6 \times 10^3$ M^{-1} cm^{-1}) for $(NH_3)_5Ru^{II}(2CO_2imH)^+$ and 467 nm ($\epsilon = 4.6 \times 10^3$ M^{-1} cm^{-1}) and 583 nm ($\epsilon = 1.5 \times 10^3$ M^{-1} cm^{-1}) for $(NH_3)_5Ru^{II}$-$(2CHOimH)^{2+}$. These are attributed to $\pi^*_{ring} \leftarrow \pi d$ and $\pi^*_R \leftarrow \pi d$ transitions. The strong π-acceptor character of 2CHOimH (comparable in magnitude to pyrazine) is further established by the $E°$ for $(NH_3)_5Ru(2CHOimH)^{3+/2+}$ of 0.322 V. The LMCT bands ($\pi d \leftarrow (\pi_1)_L$ and $\pi d \leftarrow (\pi_{2,n})$) of the $(NH_3)_5Ru^{3+}$ complexes establishes the π-donor order of 2-substituted imidazoles of R = $CH(OH)_2 > CH_3 > H > CO_2^-$. $(NH_3)_5Ru^{III}(2CO_2im)^+$ dissociates by an I_d-type mechanism with k_d = (1.35 ± 0.03) × 10^{-4} s^{-1}; μ = 2.0 M NaCl, and T = 22 °C. Substitution of $2CO_2imH^-$ on $(NH_3)_5RuOH_2^{2+}$ is slower than substitution of imH; a steric rate reduction of ca. 240 times is implicated after correction for the 10-fold rate increase for anionic vs. neutral ligands. The influence of $(NH_3)_5Ru^{2+}$ and $(NH_3)_5Ru^{3+}$ on 2CHOimH as a ligand is similar to their influence on pfp; Ru^{III} strongly favors the hydration of either ligand while the substantial π-acceptor character of R = CHO favors the carbonyl form for Ru^{II}. The effect is particularly noteworthy for 2CHOimH because imidazoles are generally poor π-acceptors; incorporation of R = CHO introduces the capacity of the imidazole ring to stabilize soft metal centers via a π-acceptor role.

Introduction

Imidazole (Him) and the imidazolate ion (im^-) are of considerable interest in their role as ligands for transition-metal centers in small molecule coordination compounds or in active sites of metalloproteins and metalloenzymes. In the biopolymers the metal center attachment is produced through the amino acid residue histidine. The imidazole ligand appears in a wide variety of redox active and metabolic enzymes, particularly those with Cu(II), Zn(II), Mn(II), or Fe(II) active centers. The modified imidazole, benzimidazole, acts as an axial base in the dietary required vitamin B-12 unit, which contains Co(III). Polymer-supported N-heterocycles, including the pyridines and imidazoles, are being used as a means of supporting redox-active centers for chemical separations of costlier trace metals and as active surfaces for derivatized electrode purposes. For these reasons, the studies of the metal–imidazole interaction in terms of affinity properties and the manner in which the imidazole moiety will affect the redox properties and stabilities of the oxidation states of a given metal center impinges widely on the research areas of biochemistry, coordination chemistry, and homogeneous catalysis.

Recent research in our laboratory has revealed a rather striking range of kinetic, physical, and spectral influences of the imidazole or its imidazolate form on the chemistry of its complexes. For example, chemical shift patterns for the ^1H and ^{13}C NMR resonances in diamagnetic imidazole complexes such as the $(NH_3)_5Co^{III}L$ series show clear differences from those of the related pyridine derivatives.[1,2] The d^n configuration of the metal center exhibits a marked influence, greater than the ionic potential, on the pK_a of the pyrrole ring proton of imidazoles; the effect has

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been studied for Cr(III), Fe(III), Co(III), Rh(III), Ru(III), and Ir(III).[3-5] The imidazoles produce the theoretical maximum value for the quadrupole splitting parameter of low-spin C_{4v} complexes in the $(CN)_5Fe^{II}L^{2-}$ series (the first such measurement).[6] Presence of one or more imidazoles markedly influences the existence and intensity of N-superhyperfine ESR coupling to all N donors, saturated or aromatic, in a Cu(II) complex.[7] The Fe(III) and Ru(III) imidazole and imidazolates exhibit in the visible region strong LMCT bands[8] that are enhanced by resonance Raman.[9] The studies reported in this paper examine the influence of a substituent in the 2-position of the imidazole ring with R = CHO or CO_2^- toward $(NH_3)_5Ru^{2+}$ and $(NH_3)_5Ru^{3+}$. The results are supported by parallel studies in a companion paper for the $(CN)_5Fe^{3-}$ and $(CN)_5Fe^{2-}$ series.[10]

However, the metal–imidazole π-interactions as perturbed by the withdrawing functional groups, R = CHO and CO_2^-, are more clearly drawn for the Ru(II) and Ru(III) cases because the ammonia spectator ligands do not compete for π density with the imidazole or imidazolate. The resultant spectral observations are more directly related to the π-bonding influences than when a CN^- competitor ligand is present. In the course of the work the interrelationship of 2-imidazolecarboxyaldehyde (2CHOimH) and 2-carboxylatoimidazolate ($2CO_2imH^-$) with 4-formylpyridine (pfp) and isonicotinic acid became apparent. Interesting comparisons with the $(NH_3)_5Ru(pfp)^{2+/3+}$ complexes as studied previously by Zanella and Taube[11] have evolved.

The imidazole ring is quasi-aromatic due to the presence of a pyrrole hydrogen at N1. It has a resonance energy estimated to be 14.2 kcal/mol[12a] compared to 31.9 kcal/mol for the aromatic pyridine.[12b] Imidazole rings are generally poor π-acceptors and very good π-donors while the pyridines behave in the reverse fashion: good π-acceptors and poor π-donors. These influences of imidazoles and pyridines toward metal centers in general have been particularly well established by using the $(NH_3)_5RuL^{3+/2+}$ and $(CN)_5FeL^{2-/3-}$ series.[3-10]

With the pyridine family of ligands a marked change in ligand character may be achieved by changing ring substituents, particularly in the 2- or 4-positions. The MLCT spectra of the $(NH_3)_5Ru^{II}L^{2+}$ and $(CN)_5Fe^{II}L^{3-}$ shift to longer wavelengths with electron-withdrawing groups and toward higher energy with electron-releasing groups.[14,15] This is taken as evidence of increased π-donation from $(NH_3)_5Ru^{2+}$ or $(CN)_5Fe^{3-}$ into the π^* level of the pyridine ring as perturbed by the substituent. Although pyridine, itself, is a poor π-donor, incorporation of the $-\ddot{N}R_2$ functionality alters the properties of the resultant ring (dmapy) such that its chemical behavior is more closely aligned with the classic behavior of imidazoles and pyrazoles as good π-donors.[6,16-18]

The substituent influence on coordinated imidazoles has not been studied extensively as there are few commercially available, simple substituted imidazoles other than the methylated derivatives. An anticipated, but small influence, has been observed for R = CH_3 on the various spectral properties of the $(NH_3)_5RuL^{3+/2+}$ or $(CN)_5FeL^{2-/3-}$ series. The 4-nitroimidazole case was recently examined by Eaton and Watkins for the $(CN)_5Fe^{3-}$ series.[19] Presence of this intensely withdrawing group (R = NO_2) altered the capacity of the imidazole ring to accept π-electron density so much that both Fe(II) and Fe(I) stable species were characterized.[19] In this paper we show that less strong withdrawing groups of more common, biologically relevant strength can switch the imidazole chromophore into a strong π-acceptor, but the same ligand retains the good π-donor character of the parent or imidazolate ring.

Experimental Section

Reagents. $[(NH_3)_5RuCl]Cl_2$ was prepared by standard laboratory procedures. The $(NH_3)_5Ru^{II}(imidazole)^{n+}$ complexes of 2-carboxylatoimidazolate and 2-imidazolecarboxaldehyde were prepared by reduction of $(NH_3)_5RuCl^{2+}$ over Zn/Hg under an Ar blanketing gas. The $(NH_3)_5RuOH_2^{2+}$ solution was transferred to an Ar-purged ligand solution. The Ar was scrubbed of trace O_2 by passage of the gas through Cr(II) scrubbing towers prior to bubbling the Ar through the Ru(II) solutions. 2-Imidazolecarboxaldehyde was obtained from Aldrich. 2-Carboxylatoimidazolate was synthesized as described in a companion paper.[10] Ru(III) complexes were prepared by oxidation of the Ru(II) species with O_2.

Instrumentation. Ultraviolet–visible spectra were obtained with a Varian-Cary 118C spectrophotometer. Solutions were placed in quartz cells that were flushed with Ar and sealed with rubber septa. Solutions of Ru(II) complexes were transferred to the cells by syringe techniques. ^1H NMR spectra were recorded on a WH-300 Burker spectrometer at 300.0 MHz. Electrochemical data were recorded with an IBM EC-225 voltammetric analyzer using the conventional three-electrode assembly. The reference electrode was a NaCl saturated calomel electrode; the working electrode was a glassy-carbon disk. pH measurements were made on an Orion 701 pH meter with a combination glass/SCE minielectrode. The pH meter was calibrated with standard commercial phosphate (6.86), borate (9.18), biphthalate (4.01) and tris (10.40) buffers.

Ion-Exchange Separation. Cationic $(NH_3)_5Ru^{III}L$ derivatives were isolated from Dowex 50W-X8 resin in the Na^+ form. Complexes were eluted with washes of 0.10, 0.50, 1.00, 2.00, or 4.00 M NaCl solutions with pH adjustment (HCl or NaOH) to control whether the imidazole or imidazolato complexes were to be isolated.

Results and Discussion

Free Ligand Spectra. The $Li(2CO_2imH)$ salt in aqueous solution exhibits two main transitions in the UV region at 247 and 330 nm ($\epsilon_{330}/\epsilon_{247} = 0.035$); the details of the aqueous solution spectrum of $2CO_2imH^-$ are reported in a companion paper.[10] The intense transition at 247 nm ($\epsilon = 1.22 \times 10^4\ M^{-1}\ cm^{-1}$) is assigned to the lowest $\pi \rightarrow \pi^*$ transition of the imidazole ring structure for $2CO_2imH^-$. This band shifts to 244 nm upon protonation of the pyridine N of $2CO_2imH^-$ at pH 7.26. The $\pi \rightarrow \pi^*$ transition is further shifted to 236 nm at pH ≤ 2 upon protonation of the R = CO_2^- substituent.[10] The transition at 330 nm is assigned to a separate $n \rightarrow \pi^*$ transition of the carboxylate chromophore. The 330-nm transition is reduced in intensity upon protonation of the R = CO_2^- unit. The intensity of the band at pH 1.00 where the CO_2^- group is ca. 60% protonated is 41.6% of its maximum value above pH ≤ 6 in the deprotonated range. Above pH $\cong 9.5$ the pyrrole hydrogen at N1 undergoes deprotonation. The two main transitions for $2CO_2im^{2-}$ appear at 248 and 336 nm.[10]

The spectrum of the 2CHOimH ligand in water exhibits the spectral changes as a function of pH as shown in Figure 1. Two features are noted in the pH range below 9: an intense $\pi \rightarrow \pi^*$ transition assigned to the imidazole ring structure in conjugation with R = CHO is evident at 286 nm, and a minor feature is observed at 211 nm (pH 7.60). Upon protonation of the imidazole ring for 2CHOimH, the feature at 211 nm grows in intensity at the expense of the ring $\pi \rightarrow \pi^*$ transition at 286 nm, which shifts

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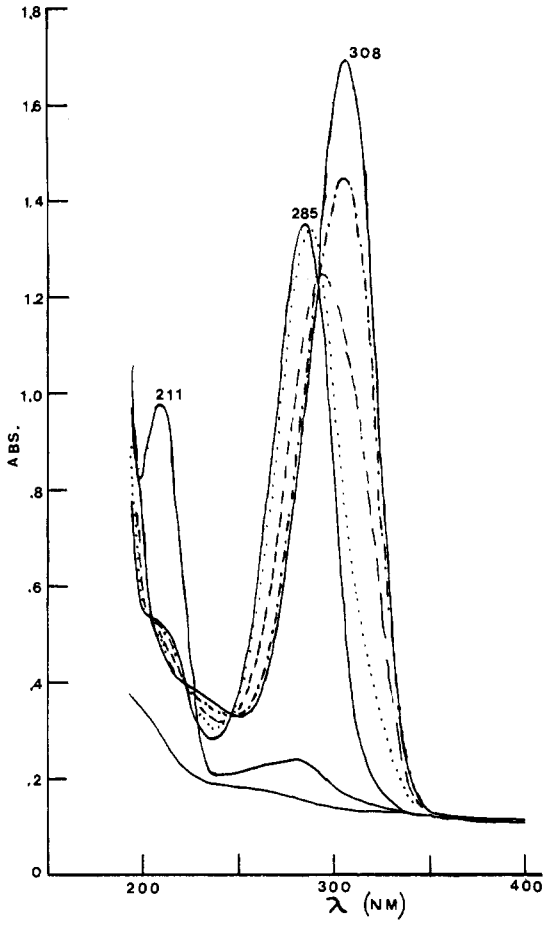
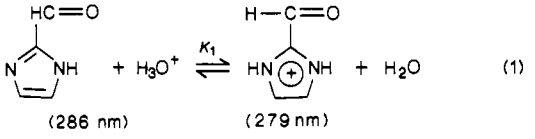


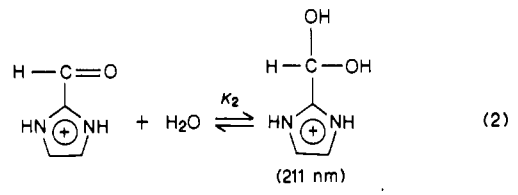
Figure 1. UV spectra of 2CHOimH as a function of pH. (—, peak at 308 nm) pH 11.48; (–·–) pH 11.04; (– –) pH 10.50; (···) pH 9.80; (—, peak at 285 nm) pH 7.60; (—, peak at 211 nm) pH 3.17; lowest curve, cell blank.

to 279 nm for the protonated $2CHOimH_2^+$ ion. The protonation of the ring, followed by increase in the 211-nm intensity and decrease of the 286-nm intensity, exhibits isosbestic behavior at 205, 222, and 246 nm.

The known hydration equilibrium for the related 4-formylpyridine, which favors R = $CH(OH)_2$ over R = CHO when $(NH_3)_5Ru^{3+}$ or H^+ is coordinated at the pyridine nitrogen,[11] provides the proper model for protonation of the 2CHOimH ligand according to the equilibria in eq 1 and 2. If nearly equivalent



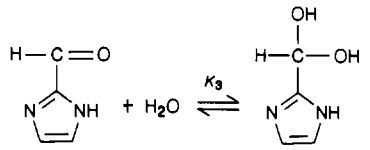
(1)



(2)

extinction coefficients of the $\pi \rightarrow \pi^*$ transitions are assumed for the ring-protonated and -deprotonated carbonyl forms, the extinction coefficient of the hydrate, $2CH(OH)_2imH_2^+$, is ca. 1.7-fold lower than the ring-protonated carbonyl form. Then K_2 is 143 (T = 22 °C, pH 3.17).

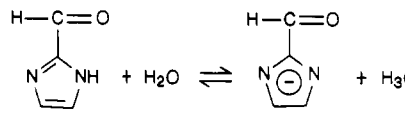
The conclusions made on the $2CO_2imH^-$ and 2CHOimH ligands with UV–visible methods are supported by ^{13}C and ^1H NMR spectra. The ^{13}C NMR spectra of $2CO_2imH^-$ exhibits singlets with chemical shifts at 165.1 (CO_2^-), 143.6 (C2), and 123.8 ppm (C4, C5).[10] Its ^1H spectrum displays a singlet at δ 7.28 for the C4H, and C5H pair.[10] The 2CHOimH proton resonances were examined as a function of pH and solvent. A 0.1 M solution of 2CHOimH (pD ≥8) exhibited two singlets, one at δ 9.10 (CHO) and another of twice the integration at δ 6.80 (C4H, C5H). No evidence for any hydrate form, R = $CH(OH)_2$, is observed. Thus the hydration of the 2CHOimH in its neutral form (eq 3) has K_3



(3)

≪ 0.01 at pD ≥7 as measured by the ^1H NMR and the UV–visible data. Assuming equal ϵ's for the $\pi \rightarrow \pi^*$ transitions of the free carbonyl form and the hydrate, K_3 is calculated to be ≤6.7 × 10^{-4} at pH 7.60 from the UV data. When 2CHOimH was dissolved in either D_2O or Me_2SO-d_6 and acidified with CF_3C-OOH, a significant amount of the hydrate form was readily apparent in the ^1H NMR spectrum. Resonances for the $2CHOimH_2^+$ ion occurs as singlet at δ 9.78 (CHO) and δ 7.69 (C4H, C5H). Note that both resonances are shifted downfield by the σ-withdrawing effect of H^+ residing on the N3 position. New singlet resonances appear at δ 7.60 (area 2; C4H, C5H) and δ 6.08 ($CH(OH)_2$). The ^1H resonance for the hydrates of pfp occur with chemical shifts of δ 6.02 and 6.23 for pfp–hydrate and $Hpfp^+$–hydrate, respectively.[11] Zanella and Taube's values for the equilibrium constants,[11] expressed as the ratio of the hydrate/carbonyl form for the pfp case, are $K'_3 \cong 0.7$ (T = 37 °C); $K'_3 < 0.1$ (25 °C) and $K'_3 \geq 3$ (35 °C) where the primed constants are the related equilibria for pfp as shown for 2CHOimH by eq 2 and 3. Therefore, two effects are noted. K_3 for 2CHOimH is at least 2 orders of magnitude smaller than K'_3 for pfp, meaning that the extent of hydration of the neutral free ligand is much less for 2CHOimH than for pfp. Protonation of the ring proton for both 2CHOimH and pfp promotes an increase in the amount of the hydrate form. $2CHOimH_2^+$ ($K \sim 84$) is more extensively hydrated than $Hpfp^+$ ($K \sim 3$) by 1 order of magnitude.

An additional important equilibrium occurs for 2CHOimH at high pH as shown in eq 4. We estimate the pK_a for equilibrium



(4)

4 to be 10.5 on the basis of the appearance of the new $\pi \rightarrow \pi^*$ transition at 308 nm. The spectrum is fully shifted at pH 11.5 and is shifted halfway with a broader, weighted average curve at pH 10.50. Data for the $(NH_3)_5Ru^{III}(2CHOimH)^{3+}$ complex reported in another section suggests the free ligand pK_a would be in the 10.5–10.9 range (see below); therefore, both estimates are in reasonable agreement with the same value (pK_a = 10.5).

The infrared spectrum of the Li(2COimH) salt has been reported in a companion paper;[10] the $\nu_{CO_2^-}$ occurs at 1601 cm^{-1}.[10] The infrared spectrum of the 2CHOimH ligand exhibits a very weak ν_{CO} at 1620 cm^{-1} and ν_{CH} (aldehyde) at 2825 cm^{-1}. H bonding is known to have a strong effect on ν_{CO}, shifting the position to 1666 cm^{-1} for salicylaldehyde (below 1700 cm^{-1}). The ν_{CO} for 2CHOimH shows very strong H bonding; the solid may be an extended H-bonded polymer as it is very slow to dissolve in water.

$(NH_3)_5Ru^{2+}$ and $(NH_3)_5Ru^{3+}$ Complexes of $2CO_2imH^-$. When a solution containing 2.67 × 10^{-3} M $(NH_3)_5RuOH_2^{2+}$ and 4.75 × 10^{-2} M $2CO_2imH^-$ was prepared under Ar, a new bright yellow species having two maxima at 367 and 420 nm grew in over several hours (Figure 2). Kinetic data were collected at 475 nm in a 1.00-cm cell. A first-order kinetics program (VAINF2), which allows for a reiterated estimate of A_∞ for the reaction to achieve the best fit to the actual data, was used to determine a rate constant of 8.44 × 10^{-3} M^{-1} s^{-1} for eq 5. The substitution of the unhindered

$$(NH_3)_5RuOH_2^{2+} + 2CO_2imH^- \rightarrow (NH_3)_5Ru(2CO_2im)^+ \quad (5)$$

imidazole ligand occurs with a rate constant of 0.20 M^{-1} s^{-1}.[20]

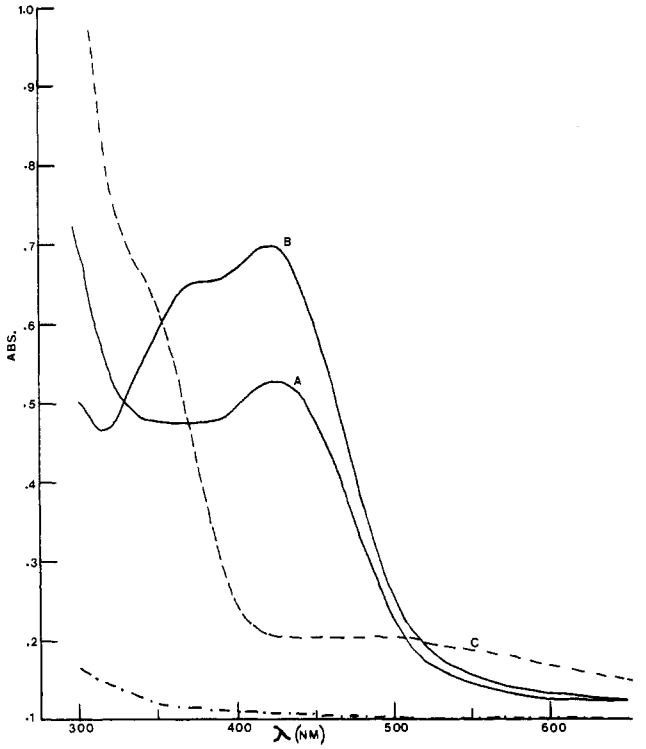


Figure 2. UV–visible spectra of $[(NH_3)_5Ru^{II}(2CO_2imH)]^+$: (A) $[Ru(II)]_{tot} = 2.67 \times 10^{-3}$ M, $[2CO_2imH^-]_{tot} = 4.75 \times 10^{-2}$ M, 0.10-cm cell, $T = 22$ °C, 5 h; (B) same conditions as spectrum A obtained at 8 h; (C) oxidation of solution used for spectrum B with O_2.

Anions substitute about 10 times faster in unhindered substitution reactions with $(NH_3)_5RuOH_2^{2+}$ compared to neutral ligands; the substitution rate for $2CO_2imH^-$ should be about 2 M^{-1} s^{-1} without a steric correction. The relative rates imply a steric reduction in rate of about 240 times. The $(NH_3)_5Ru(imH)^{2+}$ complex exhibits transitions only in the ultraviolet region; a double maximum is observed at 255 and 280 nm with ϵ's of 2.51×10^3 M^{-1} cm^{-1}. The band at 420 nm in the $(NH_3)_5Ru(2CO_2imH)^+$ spectrum is slightly more intense ($\epsilon_{420} = 2.24 \times 10^3$ M^{-1} cm^{-1}; $\epsilon_{367} = 2.02 \times 10^3$ M^{-1} cm^{-1}). The existence of a reasonably intense transition shifted into the visible region implicates an MLCT transition as the cause of this band. For comparison, the pyridine complex, $(NH_3)_5Ru(py)^{2+}$, has its MLCT transition at 408 nm with $\epsilon = 7.77 \times 10^3$ M^{-1} cm^{-1}. It is reasonable that the extended conjugation of the R = CO_2^- 2-substituted ligand should produce a red shift in this transition relative to that for R = H.

When O_2 was admitted to the solution by stirring in air, a light violet solution ($\lambda_{max} = 540$ nm) was obtained at pH 9.50. The solution changes to a light yellow one ($\lambda_{max} = 430$ nm) if the pH is adjusted to 6.72 with HCl. The oxidation process required about 5 min for completion (eq 6 and 7). A spectrophotometric titration

$$4(NH_3)_5Ru(2CO_2imH)^+ + O_2 + 4H^+ \rightarrow 2H_2O + 4(NH_3)_5Ru(2CO_2imH)^{2+} \quad (6)$$

$$(NH_3)_5Ru(2CO_2imH)^{2+} \rightleftarrows (NH_3)_5Ru(2CO_2im)^+ + H_3O^+ \quad (7)$$

using the appearance of the 540-nm band of the imidazolato complex, $(NH_3)_5Ru(2CO_2im)^+$, gave a pK_a value of 7.95 ± 0.05 for $(NH_3)_5Ru^{III}(2CO_2imH)^{2+}$. The coordination of $(NH_3)_5Ru^{3+}$ to imidazole lowers the pK_a for the N1H from 14.2 (free ligand) to 8.9 (complex), yielding a decrease in the pK_a of 5.3 units. The presence of R = CO_2^- lowers the pK_a of the free ligand $2CO_2imH^-$ by the influence of delocalization in spite of the additional −1 charge (see the section about the ligand). The free ligand pK_a at N1H is ca. 10.7. Assuming the presence of the anionic R = CO_2^- group would negate the effect of the positive Ru(III) center by about 2.5 pK units, one would expect the pK_a of the coordinated $2CO_2imH^-$ ligand to be about 7.9, in reasonable agreement with the experimental value.

The $(NH_3)_5Ru^{III}(2CO_2im)^+$ complex was reasonably stable at pH 9.5; it was separated from excess free ligand by means of ion-exchange on Dowex 50W-4X resin in the Na^+ form. Free ligand was eluted with 1.0 M NaCl adjusted to pH 9. The complex moved slowly with 1.0 M NaCl. In order to avoid resin phase decomposition, the washed product was eluted with 2.0 M NaCl. The eluted ion had a spectrum with the same 540-nm maximum. The position of this band is diagnostic of the $(NH_3)_5Ru^{III}$–imidazolates and it is assigned as the $d\pi \leftarrow (\pi_1)_L$ LMCT transition corresponding to the 550-nm transition of $(NH_3)_5Ru^{III}(im)^{2+}$.[8,9,21] The LMCT nature of the assigned transitions of the Ru^{III} complexes of this paper and our prior reports[8,9,21] have been supported by INDO/S calculations by Krogh-Jespersen and Schugar.[23] The influence of the R = CO_2^- in the 2-position, acting as a withdrawing group, is detected by the 10-nm shift to higher energy for the $(NH_3)_5Ru(2CO_2im)^+$ complex. The ion-exchanged complex was used to confirm the presence of the 430-nm band for $(NH_3)_5Ru(2CO_2imH)^{2+}$, but a long tailing band with a component of lower intensity exists for this ion at ~510 nm. This transition may be due to a weak $\pi_{CO_2} \rightarrow d\pi$ interaction, also of the LMCT type.

The ion-exchanged $(NH_3)_5Ru(2CO_2im)^+$ solution was adjusted to pH 11.10 in order to ensure that formation of the imidazolato form was complete. Repetitively scanned spectra from 700 to 400 nm revealed a steady decrease in the 540-nm band. The dissociation of the $(2CO_2im^{2-})$ ligand is implied as shown in eq 8 and 9. The first-order rate constant for this dissociation process was

$$(NH_3)_5Ru^{III}(2CO_2im)^{2+} \rightleftarrows [(NH_3)_5Ru\cdots(2CO_2im)^{2+}] = \text{int} \quad (8)$$

$$\text{int} \rightarrow (NH_3)_5RuOH^{2+} + 2CO_2imH^- \quad (9)$$

found to be $k_d = (1.35 \pm 0.03) \times 10^{-4}$ s^{-1} ($T = 25$ °C, $\mu = 2.0$ M NaCl). The products of the reaction were shown to be $(NH_3)_5RuOH^{2+}$ and $(NH_3)_5RuCl^{2+}$ in the early phases of the dissociation process, prior to the ultimate decomposition of the unstable ruthenium(III) pentaammines under basic conditions. On longer reaction times, the ruthenium red polymers were observed. The dissociative nature of the mechanism is implicated by the presence of both OH^- and Cl^- incorporated in the product. As the intermediate loses recognition of its $2CO_2im^{2-}$ leaving group, any species in the solvent cage may be trapped. Therefore at 2.0 M NaCl both the ion-paired Cl^- nearby the overall positive $(NH_3)_5Ru(2CO_2im)^+$ complex and solvent cage water are trapped.

$(NH_3)_5Ru^{2+}$ and $(NH_3)_5Ru^{3+}$ Complexes of 2CHOimH. The $(NH_3)_5Ru(2CHOimH)^{2+}$ complex forms when $(NH_3)_5RuOH_2^{2+}$ is injected into a ligand solution of 2CHOimH under Ar. The solution is purple to the eye. The free ligand UV–visible and ^1H NMR spectra show that at a pH >7 virtually all of the ligand is in the carbonyl form for 2CHOimH. $(NH_3)_5Ru^{2+}$ is known to back-bond into strongly π-accepting ligands including the 4-formylpyridine (pfp) ligand. Zanella and Taube have shown that the carbonyl form is strongly stabilized for pfp by its coordination to $(NH_3)_5Ru^{2+}$ due to the conjugated interaction of R = CHO with the pyridine ring.[11] By contrast the $(NH_3)_5Ru^{3+}$ serves only the same role as H^+; this strongly favors the hydration of pfp. Like $(NH_3)_5Ru^{II}(2CO_2imH)^+$, $(NH_3)_5Ru(2CHOimH)^{2+}$ is oxidized by admission of O_2. Oxidation is complete in about 2 min. Spectra of the Ru(III) complex of $(NH_3)_5Ru^{III}(2CHOimH)^{3+}$ are given in Figure 3 as a function of pH. Two bands are observed in the typical pattern of the Ru(III)–imidazoles. The band at 465 nm is assigned as the $d\pi \leftarrow (\pi_{2,n})_L$ LMCT transition while the lower intensity broad band at ca. 690

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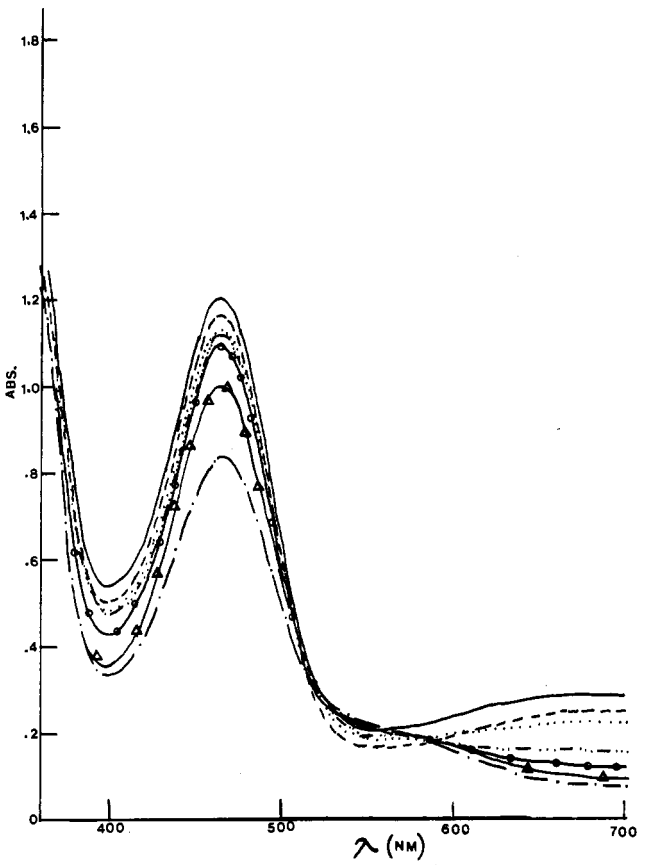


Figure 3. Spectrophotometric titration of $(NH_3)_5Ru^{III}(2CH(OH)_2imH)^{3+}$ (curve, pH): (—, 8.70); (--, 6.70); (···, 5.89); (-···-, (5.41); (○, 4.95); (△, (3.50); (-·-, 2.00). T = 22 °C, and $[Ru^{III}]_{tot}$ = 2.00×10^{-3} M,; Data (not shown) were also collected at pH values of 8.04, 7.50, 4.55, 4.00, and 2.90.

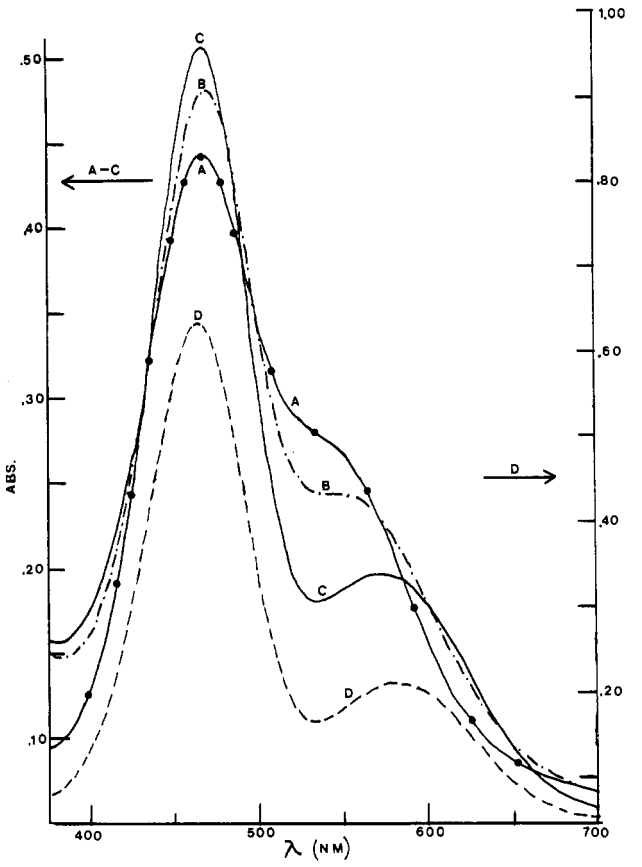


Figure 4. Spectrophotometric titration of $(NH_3)_5Ru^{II}(2CHOimH)^{2+}$. ($[Ru^{II}]_{tot} = 1.37 \times 10^{-3}$ M, 0.10-cm cell, T = 22 °C): (A) pH 9.20; (B) pH 8.15; (C) pH 7.55; (D) pH 3.30. Data were also collected at pH 5.68 and 4.42, but are not shown for clarity.

nm is assigned to $d\pi \leftarrow (\pi_1)_L$, which is the C-based to $d\pi$ transition of LMCT type. The spectrophotometric titration using the 690 nm band defines the pK_a of the $(NH_3)_5Ru^{3+}$ coordinated to 2CHOimH as being 5.65 ± 0.05. As discussed in the section concerning the free ligand spectra, this value shows the pK_a is lowered by about 5 pK units by the presence of the $(NH_3)_5Ru^{3+}$ moiety.

The fact that the 2-methylimidazolato complex has its $d\pi \leftarrow (\pi_1)_L$ transition at 620 nm and its $d\pi \leftarrow (\pi_{2,n})_L$ transition at 367 nm, it appears that the R substituent in the 2-position of the ring of the $(NH_3)_5Ru^{3+}$ complex of 2CHOimH is *more electron releasing than* CH_3, rather than being more withdrawing than CH_3. Also the position of the $d\pi \leftarrow (\pi_1)_L$ band at 690 nm for the $2CHOim^-$ ligand is at a longer wavelength than the R = CO_2^- substituent, e.g., the coordinated $2CO_2im^{2-}$ case described previously. Since the σ_p constant of –CHO (0.22) is much larger than that for $-CO_2^-$ (σ_p = 0.0), it can be argued that the LMCT band for the carbonyl form of $2CHOim^-$ ought to occur at higher energy than the LMCT bands for $2CO_2im^{2-}$. The reconciliation of these results may be achieved if it is assumed that coordination of $(NH_3)_5Ru^{3+}$ favors the hydrate form, R = $CH(OH)_2$, just as it does in the pfp case of Zanella and Taube.[11] Therefore it is the authors' conclusion that both the 2CHOimH ligand and its imidazolate are present in the hydrate form for its $(NH_3)_5Ru^{III}L$ complex.

Coordination of $(NH_3)_5Ru^{2+}$ ought to favor the carbonyl form of 2CHOimH. Since the carbonyl form of the free ligand is greatly favored above pH ~6, synthesis of the $(NH_3)_5Ru^{II}(2CHOimH)^{2+}$ complex from the free ligand solution should produce the coordinated complex in the carbonyl form. The stabilization of the Ru(II) oxidation state relative to the Ru(III) state in $(NH_3)_5Ru(2CHOimH)^{3+/2+}$ vs. $(NH_3)_5Ru(imH)^{3+/2+}$ is implicated by the differential-pulse voltammogram of the 2CHOimH complex, which exhibits its peak potential at 0.322 V vs. NHE. This compares to a potential of 0.079 V for the $(NH_3)_5Ru(imH)^{3+/2+}$ couple and 0.077 V for the $2CH_3imH$ analogue.[22a] The 0.322 V potential for the $(NH_3)_5Ru(2CHOimH)^{2+/3+}$ couple falls between the 0.305 V potential of the pyridine complex and the 0.49 V potential for the pyrazine complex.[22b] Since both pyridine and pyrazine act only as π-acceptors toward $(NH_3)_5Ru^{2+}$ and as very poor π-donors toward $(NH_3)_5Ru^{3+}$, the result for the $(NH_3)_5Ru(2CHOimH)^{3+/2+}$ couple requires that 2CHOimH acts as a very good π-acceptor ligand, better than pyridine.

The visible spectrum of the $(NH_3)_5Ru(2CHOimH)^{2+}$ complex (Figure 4) exhibits some changes with pH that are at first curious. Shepherd and Taube noted that for even the parent $(NH_3)_5Ru(imH)^{2+}$ complex that the spectrum alters with pH >9, suggesting dissociation of the pyrrole hydrogen at N1.[20] Since the imidazolato form of even the free ligand 2CHOimH, e.g. $2CHOim^-$, is encountered at 3.5 pK units lower than imidazolate itself (pK_a = 14.2), then it should not be surprising that the $(NH_3)_5Ru^{2+}$ center will increase the acidity of the pyrrole hydrogen at N1 for 2CHOimH. The effect should be attenuated relative to the influence of the $(NH_3)_5Ru^{3+}$ moiety for two reasons. The Ru(II) charge is lower by one unit, which should translate into two-thirds of the effect for Ru(III). This would promote a lowering of the pK_a of the $(NH_3)_5Ru(2CHOimH)^{2+}$ complex by 5.0 units relative to that of the free ligand. However, the degree to which π back-bonding increases the basicity of the 2CHOimH ring should account for as much as a 2–3 pK unit shift toward a higher pK. The predicted net effect would be a pK_a of ~9 for the complex, depending on the balance of the charge influence of the M^{II} centers and the amount of π back-donation.

Examination of the spectrum (Figure 4) shows two bands at pH 9.20 of the MLCT type, present as a principal band at 467 nm and a shoulder at 550 nm. Since these transitions are MLCT in origin, the intensity of the transition is logically lower for the anionic imidazolato form, $2CHOim^-$, than for the neutral

2CHOimH ligand. As the pH is lowered from 9.20 to 3.30 the intensity of the 467-nm region increases, and a new band emerges on the low-energy side of the band. The final maximum position of the resolved long wavelength band is at 583 nm. The ratio of the extinction coefficients ($\epsilon_{467}/\epsilon_{583}$) is 3.0; $\epsilon_{467} \sim 4.6 \times 10^3$ M^{-1} cm^{-1}. The spectral changes in the 500–650-nm region are reversed if the pH is adjusted back up to 9.7 from 3.30. Fifteen-minute intervals were used for pH adjustment and filling Ar-flushed cells. Therefore any hydration-related equilibrium such as might occur in the vicinity of pH 3.3 is probably established more rapidly than would be detected by these techniques. But the favoring of the carbonyl form by Ru(II)'s presence and the fact that the free ligand shows significant hydration only below pH 5 implies that the dominant form of the complex in the pH >4.4 to pH <7.8 range is the neutral 2CHOimH complex. The presence of a significant absorption, caused by the imidazolato form, $(NH_3)_5Ru(2CHOim)^+$, in the spectrum with pH $\geq$7.8 indicates at least 1.7 pK unit of increased acidity for $(NH_3)_5Ru(2CHOimH)^{2+}$, e.g. p$K_a \geq 8.8$. In this manner one calculates that the back-bonding into 2CHOimH is nearly as significant as in the $(NH_3)_5Ru(pz)^{2+}$ complex where a 2.8 pK unit increase in basicity of the ring is observed. However imidazoles are not as aromatic as the pyridines and pyrazines so the extent of $d\pi-\pi^*$ mixing with imidazoles should be less. The experimental results imply that the Ru(II) 2+ charge wins out against back-donation relative to its effect on pyrazine. It might also be noted that the proton resides at a greater distance from Ru(II) in the six-membered pyrazine ring than for the five-membered imidazole ring system. The Ru(II) positive charge influence should be more strongly sensed at the pyrrole hydrogen. Apparently this influence is even experienced for the parent $(NH_3)_5Ru(imH)^{2+}$ system (loc. cit.). In spite of the smaller π back-bonding to the imidazoles, the influence of the R = CHO substituent in 2CHOimH is sufficient to cause a significant increase in the π-acceptor character for the imidazole ring. The implications concerning the pK_a of $(NH_3)_5Ru(2CHOimH)^{2+}$ as being a result of reasonably high π-donation of the metal compared with the $(NH_3)_5Ru(pz)^{2+}$ complex is in harmony with the observed $(NH_3)_5Ru(2CHOimH)^{3+/2+}$ couple at 0.322 V compared with 0.49 V for the pyrazine case. The pyrazine can only stabilize the Ru(II) side of the couple by π-accepting, while 2CHOimH can stabilize both the Ru(II) side by π-accepting and the Ru(III) side by π-donating. The power of π-donation will be further enhanced for the hydrate form favored by Ru(III). Therefore the net influence of the π-acceptor property of 2CHOimH will be suppressed relative to that of pyrazine as evidenced by the electrochemical data.

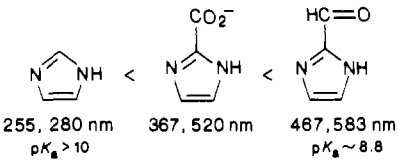
Comparisons with $(CN)_5Fe^{II}L^{3-}$ and $(CN)_5Fe^{III}L^{2-}$ Complexes. The pentacyanoferrate(II/III) analogue complexes with L = $2CO_2imH$ and 2CHOimH are the subject of a complete companion paper.[10] However a few salient points can be made that amplify the studies of the $(NH_3)_5Ru^{II}L^{2+}$ and $(NH_3)_5Ru^{III}L^{3+}$ complexes of this report. The $2CO_2imH^-$ ligand does not bind to the $(CN)_5Fe^{3-}$ chromophore and binds only weakly ($K_f \sim 35$ M^{-1}) for the $(CN)_5Fe^{2-}$ moiety. This is the effect of charge repulsion for the $(CN)_5Fe^{2-/3-}$ cases. The results of this report show that $2CO_2imH^-$ coordinates successfully with both $(NH_3)_5Ru^{2+}$ and $(NH_3)_5Ru^{3+}$. The rates of dissociation of the Fe(III) complexes $(CN)_5FeL^{2-}$ are significantly more rapid than for their $(NH_3)_5RuL^{3+}$ counterparts. This is indicative of dissociative or I_d mechanisms for the ligand substitution reactions. This process involves separation of negative charge from metal center as the leaving group bond is stretched in the transition state. This barrier is much greater for the positive Ru(III) center in $(NH_3)_5Ru^{3+}$ than for the overall anionic unit, $(CN)_5Fe^{2-}$. All of the imidazolato complexes $(CN)_5Fe^{III}(Rim)^{3-}$ convert rather rapidly (minutes time scale) to the aquated $(CN)_5FeOH^{3-}$ complex. The $(CN)_5Fe(2CO_2im)^{4-}$ dissociation is too rapid for conventional spectroscopy[10] while $(NH_3)_5Ru(2CO_2im)^+$ dissociates over several hours.

Stable complexes with the neutral ligand 2CHOimH are found for all four cases: $(CN)_5Fe^{2-/3-}$ and $(NH_3)_5Ru^{3+/2+}$. The electrochemistry of the 2CHOimH complex compared with that of the pyrazine ligand implies a substantial π-acceptor character for 2CHOimH that is not possessed by the parent imH ring. MLCT transitions of $\epsilon > 10^3$ M^{-1} cm^{-1} are observed for both the $(CN)_5Fe(2CHOimH)^{3-}$ and $(NH_3)_5Ru(2CHOimH)^{2+}$ complexes. The respective positions of the main MLCT band (454 nm for Fe^{II}, 467 nm for Ru^{II}) are strikingly similar to the 452-nm MLCT band of $(CN)_5Fe(pz)^{3-}$[14] and the 472-nm MLCT band of $(NH_3)_5Ru(pz)^{2+}$[13] in support of a π-accepting character of 2CHOimH comparable to pyrazine!

The similarity of the spectra of the $(CN)_5Fe(2CO_2imH)^{2-}$ and $(CN)_5Fe(2CHOimH)^{2-}$ complexes suggests no preferential hydration of 2CHOimH when coordinated to $(CN)_5Fe^{2-}$, but the evidence here supports hydration when $(NH_3)_5Ru^{3+}$ is coordinated. The shift to the hydrate form when $(NH_3)_5Ru^{3+}$ or H^+ coordinates to 2CHOimH, but not for $(CN)_5Fe^{2-}$, does suggest that σ-withdrawal through the bond system will promote a greater charge on the R = CHO carbon center. This influence promotes nucleophilic addition of water. The existence of two MLCT transitions for both the $(CN)_5Fe(2CHOimH)^{3-}$ and $(NH_3)_5Ru(2CHOimH)^{2+}$ complexes is compatible with $\pi_{CO}^* \leftarrow \pi d$ (M(II)) at the lower energy of the two overlapped bands and $(\pi_1^*)_L \leftarrow \pi d$ (M(II)) for the higher energy band. π_{CO}^* and $(\pi_1^*)_L$ represent the antibonding levels of the R = CHO chromophore and the C-based imidazole ring MO.

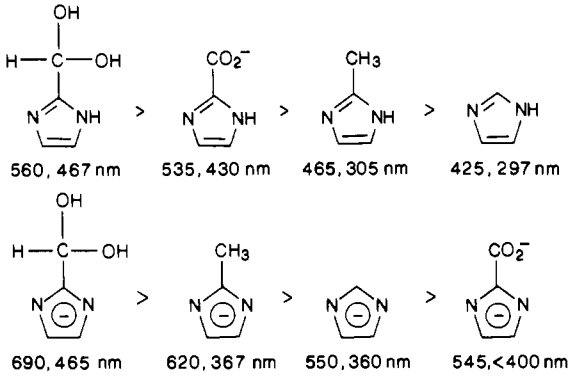
Conclusions

The imidazole series of ligands has been shown to be tunable in its ability to act as a π-acceptor or a π-donor depending upon the nature of the substituent in the 2-position. Imidazole, itself, acts as a relatively poor π-acceptor. The MLCT bands for the Ru(II) pentaammines indicate the π-acceptor order as shown (MLCT band positions are listed below each ring):



The ability of the $(NH_3)_5Ru^{2+}$ moiety to increase the acidity of the N1H on coordination has also been established. The influence of M(III) centers in this regard is better known.[3-5] The d^6 complexes $(NH_3)_5Co^{3+}$, $(NH_3)_5Rh^{3+}$, and $(NH_3)_5Ir^{3+}$ all lower the pK_a of imidazole's pyrrole hydrogen by about 4.2 pK units[23] while $(NH_3)_5Ru^{2+}$ shows a 1.9 pK unit decrease for the 2CHOimH complex. The 45% of the normal influence of a d^6 tripositive metal center for Ru(II) is in reasonable agreement with a predicted $^2/_3$ ratio based on the charges and the absence of π-acceptor character for a Ru(II) center. The d^5 configuration is much more efficient at lowering the pK_a of the N1H of the ring;[3-5] stabilization of the product side of the reaction via π-donation of the imidazolato form of the complex is the accepted reason for this chemical behavior. As with the parent imidazole complex, presence of $(NH_3)_5Ru^{3+}$ causes an additional lowering of the pK by 5 units, as for example in the $(NH_3)_5Ru^{III}(2CO_2imH)^{2+}$ complex. The interesting result, however, is that the influence of the Ru(III) center is *virtually additive* with the influence of an organic ring substituent. The parent free ligand pK_a for imidazole is 14.2. The presence of $(NH_3)_5Ru^{3+}$ plus R = CO_2^- yields a 6.25 pK unit decrease for the N1H position while $(NH_3)_5Ru^{3+}$ plus R = $CH(OH)_2$ yields an 8.55 pK unit decrease. The slight extra advantage of R = $CH(OH)_2$ vs. R = CO_2^- is seen in the difference of these two values: 2.3. On the basis of charges of the dissociating complexes, 3+ for $(NH_3)_5Ru(2CH(OH)_2imH)^{3+}$ and 2+ for $(NH_3)_5Ru(2CO_2imH)^{2+}$, one would anticipate about a 5 pK advantage to the former instead of a 2.3 pK difference. Therefore these results also support a greater stabilization or electron withdrawal by R = CO_2^- compared to that of the aldehyde hydrate, R = $CH(OH)_2$, lending further support to the prior conclusion that all of the Ru(III)-2CHOimH complex is present as the hydrate, R = $CH(OH)_2$, form. $2CO_2imH^-$ and $2CH(OH)_2imH$ (the aldehyde hydrate) act as good π-donors toward $(NH_3)_5Ru^{3+}$. Therefore the position of the LMCT bands that have been observed in our

data is compatible with the following π-donor order for both the neutral ligand and the imidazolato form of the ligand for these rings (LMCT band positions are listed below each ring for the $(NH_3)_5Ru^{III}L$ complex):



It appears that the extra ionic charge of $2CO_2imH^-$ is an advantage in its role of π-donation for the parent imidazole series, but loses importance relative to a full anion charge localized on the five-membered ring. Therefore its position in the π-donor series shifts below im^- and above $2CH_3imH$; the other neutral R substituents remain in their logical electron-releasing order: $CH(OH)_2 \geq CH_3 > H$. Once the imidazolato form is created by deprotonation of the neutral parent ring structure, less assistance is provided by the 2-substituent in lowering the $d\pi \leftarrow (\pi_1)_L$ transition energy. The additional shifts on the π_1-based transition are calculated to be 3364 cm^{-1}, R = $-CH(OH)_2$; 4737 cm^{-1}, R = $-CH_2^-$; 5376 cm^{-1}, R = $-CH_3$; and 5347 cm^{-1}, R = H. Therefore $-CH_3$ is actually the better releasing group toward the anionic ring, compared to R = $-CH(OH)_2$.

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Study of Stereodynamics by Variable-Temperature ^{195}Pt NMR Spectroscopy. Diastereomerism in Platinum(II) Thioether Complexes and Solvent Effects

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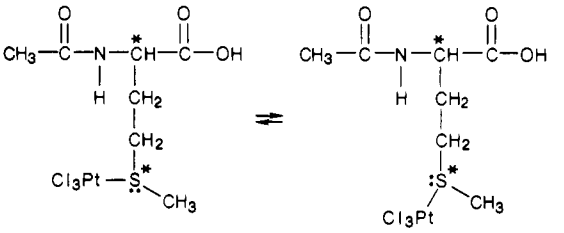
We have synthesized and characterized new $[PtCl_3(thioether)]^-$ complexes with the following thioethers as unidentate ligands: *N*-formyl-DL-homomethionine (FHMetH), *N*-acetyl-L-methionine (AcMetH), *N*-acetyl-*S*-methyl-DL-cysteine (AcMeCysH), DL-3-(methylthio)-1,2-propanediol (MTPD), and DL-3-(methylthio)-2-butanone (MTB). These complexes constitute a series in which the length of the $(CH_2)_x$ chain connecting the chiral carbon and sulfur atoms is varied systematically: x = 3, 2, 1, 1, and 0, respectively. Each of the complexes exists in two diastereomeric forms, which are related by intramolecular inversion of configuration at the coordinated sulfur atom. The diastereomers are clearly evident in the ^{195}Pt NMR spectra, whose dependence on temperature yields the ΔG^* values for inversion. Stereodynamic processes involving all but the simplest thioether ligands and processes resulting in subtle changes in molecular structure proved intractable by the common ^1H and ^{13}C NMR methods. The barrier to inversion depends on the solvating ability of the medium in an interesting way. Small amounts of diglyme in aqueous solution reduce the difference in chemical shifts between the ^{195}Pt NMR peaks of the diastereomers and thus lower the coalescence temperature, but they do not affect the barrier significantly. Large amounts of diglyme, however, lessen the stabilizing effect of hydration upon the thioether complex and lower the barrier. In unidentate complexes, which have flexible structures, the chiral C atom provides virtually no discrimination between the two configurations of the chiral S atom irrespective of the length of the $(CH_2)_x$ chain between the two atoms. Significant discrimination is evident, however, in the bidentate complex *cis*-$[PtCl_2(MeCysH)]$. Steric constraint, such as that provided by chelation, seems to be a prerequisite for chiral discrimination.

Introduction

Inversion of the pyramidal configuration at coordinated chalcogen atoms (S, Se, and Te) has been observed in various metal complexes.[1] Virtually all of these studies are based on the principle that inversion causes an interchange of diastereotopic H atoms in the prochiral CH_2 group and consequently gives rise to the collapse of an AB quartet into a singlet in the ^1H NMR spectrum. Although elegant experiments have been based on this stereochemical principle, reliance on it, and on the corresponding ^1H NMR techniques, has restricted previous studies to complexes containing relatively simple ligands of the $(RCH_2)_2S$ and RCH_2SCH_2R' types and to the corresponding bidentates, for which the collapse of the methylene quartet upon heating is easily discernible.

Stereodynamic studies of metal complexes with biological ligands and, ultimately, with proteins clearly demand a different experimental method. In a previous publication[2] we reported on sulfur inversion in the complex $[PtCl_3(AcMetH)]^-$, the process shown in eq 1. With *N*-acetyl-L-methionine acting as a unidentate


(1)

thioether ligand, this complex is a realistic model for the binding of $PtCl_3^-$ label to the side chain of a methionine residue in proteins. The inversion process even in this relatively simple compound proved intractable by the common methods of ^1H and ^{13}C NMR spectroscopy. The corresponding ^1H and ^{13}C signals of the diastereomers were already coalesced at 278 K. In other words, the ^1H and ^{13}C nuclei proved insufficiently sensitive to the minor structural changes caused by inversion at the sulfur atom.

Owing to the great dependence of the ^{195}Pt chemical shift on the ligand atoms and on the more distant environment,[3-7] ^{195}Pt

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