2,2′-bpy)$RuOH_2]^{2+}$, 89486-25-9; $Ru(trpy)Cl_3$, 72905-30-7; [(trpy)(bpy)RuCl]Cl, 89463-54-7; [(trpy)(bpy)RuCl](PF_6), 83572-47-8; [(trpy)(bpy)RuO]$(ClO_4)_2$, 89463-57-0; [(trpy)(4,4′-$(MeO)_2$-2,2′-bpy)RuCl]Cl, 89463-58-1; (bpy)(2,6-pyridinedicarboxylato)RuCl, 89486-26-0; $(bpy)RuCl_4$, 63338-26-1; $[(trpy)(bpy)Ru^{III}–OH]^{2+}$, 81971-63-3; $[(trpy)(bpy)Os^{III}–OH]^{2+}$, 89463-59-2; $[(trpy)(bpy)Os^{IV}{=}O]^{2+}$, 89463-60-5; $[(trpy)(bpy)Ru^{III}–OH_2]^{3+}$, 89463-61-6; $[(trpy)(bpy)Os^{III}–OH_2]^{3+}$, 89463-62-7.

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Influence of the Metal Centers on the pK_a of the Pyrrole Hydrogen of Imidazole Complexes of $(NH_3)_5M^{3+}$, M(III) = Co(III), Rh(III), Ir(III), Ru(III)

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Received August 19, 1983

The pK_a's at 298 K, μ = 0.10 (NaCl), and the temperature dependence (273–343 K) for the deprotonation of the pyrrole NH of several imidazoles coordinated to $(NH_3)_5M^{3+}$ moieties (M = Co^{III}, Rh^{III}, Ir^{III}, Ru^{III}) are reported. A greater importance of d^n configuration over ion size is found. Data summarized for various systems are as follows (ligand, M (pK_{298}, $\Delta H_a°$ in kcal/mol, $\Delta S_a°$ in eu)): imidazole = imH, Co^{III} (9.99, 14.0 ± 0.5, 1.3 ± 1.6), Rh^{III} (9.97, 13.6 ± 0.3, 0.1 ± 1.3), Ir^{III} (10.05, 13.4 ● 0.3, 1.2 ± 1.0), Ru^{III} (8.9, 10.0 ± 0.8, 3.7 ± 1.2); 2-methylimidazole = 2-MeimH, Co^{III} (10.67, 17.8 ± 0.7, 11.2 ± 2.4); 2,4(5)-dimethylimidazole = 2,5-Me_2imH, Co^{III} (11.04, 13.4 ± 0.5, 5.3 ± 1.6), Ru^{III} (10.20, 13.2 ± 0.6, −2.1 ± 1.6). ^1H NMR spectra of low-spin d^6 complexes of imidazoles and ring-methylated imidazoles are discussed for Co^{III}, Rh^{III}, Ir^{III}, and Ru^{II}. C-2 and remote ring, C-5, substituents are shifted downfield relative to the free imidazole ligand in the order $H^+ > Co^{III} > Rh^{III} > Ir^{III}$. The C-4 position is influenced competitively by σ-withdrawal ring substituents and TIP effects for Co^{III}. Assignments of the remote isomer for $(NH_3)_5M(2,5\text{-}Me_2imH)^{3+}$ (M = Co^{III}, Ru^{III}) are made from the ^1H NMR spectra of the Co^{III} and Ru^{II} complexes. The Ru^{III} complexes of 2,5-Me_2imH and the imidazolate form (2,5-Me_2im^-) both exhibit LMCT spectra. The imidazolato form has three bands at 655, 377, and 272 nm, proposed for $\Pi_1 \rightarrow \Pi_d$, $\Pi_2 \rightarrow \Pi_d$, and $n \rightarrow \Pi_d$ transitions, where Π_1, Π_2, and n are the highest HOMO's of the imidazolato ring.

Introduction

The inductive influence of a cationic metal center is responsible for many common, but important, chemical phenomena. For example, the hydrolysis and polymerization of simple aqua ions such as $Fe(H_2O)_6^{3+}$ and the Lewis acid catalysis of ions such as H^+, Zn^{2+}, Cu^{2+}, and Al^{3+} on ester hydrolysis and numerous other organic reactions come to mind. The Lewis acid influence operates predominantly through σ withdrawal on the coordinated ligand to promote nucleophilic reactions at positions adjacent to the coordinated atom. If the ligand is protonic as with H_2O, H_2S, imidazoles, pyrazoles, amines, and amides, the inductive effect alters the pK_a of a site of deprotonation. If σ induction only operates to change the pK_a, the influence should attenuate rapidly with bond distance or, for ions of constant charge, the acidity should decrease with size. We set out to examine the applicability of this simple model in terms of the influence of varying the metal center on the pK_a of a coordinated imidazole ligand as a function of ionic potential and d^n configuration. A study of this sort has relevance to biochemical systems and catalysis. In particular, the imidazolate ion, which is produced by deprotonation of imidazole or with amino acids via the side-chain residue of histidine, is of interest in regard to its function as the bridging ligand between Cu(II) and Zn(II) in bovine erythrocyte superoxide dismutase[1] and as a strong base for other enzymes. We recently reported on the affinity of imidazole and imidazolate as ligands toward the low-spin d^5 center $(CN)_5Fe^{2-}$.[2] It was shown for Fe(III) in the $(CN)_5FeL^{2-}$ environment that the influence of the metal ion originates largely from changing the enthalpy of dissociation of the pyrrole N–H bond relative to that of the free ligand.[2,3] The barrier is lowered by ca. 8.8 kcal/mol by coordination to $(CN)_5Fe^{2-}$. Harrowfield et al. have measured the pK_a of $(NH_3)_5Co(imH)^{3+}$ at 25.0 °C as 10.02;[4,5] this is close to the value obtained for $(CN)_5Fe(imH)^{2-}$ (10.93)[2] as well as for the complexes of imidazole with ferrimyoglobin (10.34),[3] cobalamin (10.25),[6] and methylmercuric ion (9.61).[7] It becomes difficult to evaluate the influence of the metal ion for such diverse species where solvation differences are likely for highly charged cations and anions compared with bulky hydrophobic molecules and organometallic ions. Therefore, special influences of particular metal centers become hidden. It is of interest to know if the results for $(CN)_5Fe(imH)^{2-}$ are representative. Comparisons should be made among a related series of ions of the same charge in a constant spectator ligand set where attention could be placed on the chemical nature of the central metal ion. Solubilities and synthetic work suggested that comparisons among the $(NH_3)_5ML^{3+}$ complexes would be the best case. In addition the synthesis of this series has been expedited by the recent reports of Taube and Sargeson[8] concerning the use of trifluoromethanesulfonato (TFMS) complexes of $(NH_3)_5M^{3+}$, M = Co(III), Rh(III), Ir(III), Ru(III), Os(III). The TFMS intermediate complexes are readily obtained from available $[(NH_3)_5MCl]Cl_2$ precursor compounds. With slight modifications to these literature procedures one can prepare the imidazole complexes of Co(III), Rh(III), Ir(III), and Ru(III) in order that chemical trends for this series of ions can be examined. The results of

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these studies are reported here. A related study of the pK_a's of coordinated pyrazoles has been presented but again without a common ligand set and charge of the ion.[21] With the 4-methylimidazole ligand, linkage isomers have been isolated for Co(III) and are described elsewhere.[13,14] These substituted imidazoles have allowed the examination of the influence of ring induction upon the pK_a of a coordinated ligand for Co(III) and Ru(III) cases.

Experimental Section

Synthesis of Co(III) Complexes via $(NH_3)_5Co(Me_2SO)^{3+}$. The $(NH_3)_5Co^{III}$ complexes of 4(5)-methylimidazole (Aldrich), 2,4(5)-dimethylimidazole (Gallard Schlesinger), 1,4-dimethylimidazole,[9] and 1,5-dimethylimidazole[9] (Aldrich) were synthesized as their perchlorate salts by the reaction of $[(NH_3)_5CoOH_2](ClO_4)_3$ with excess ligand in dimethyl sulfoxide solvent at 70–85 °C. Aquapentaamminecobalt(III) perchlorate was prepared by a literature method.[10] $(NH_3)_5CoL^{3+}$ complexes, L = imidazole or one of its CH_3-substituted derivatives, were prepared as in ref 4 with slight modification. The progress of the reaction, forming $(NH_3)_5CoL^{3+}$, was followed spectrophotometrically. The synthetic reaction reaches completion when λ_{max} (d–d electronic transition) approaches 476 nm. For the examination of λ_{max}, 1 drop of the reaction mixture was diluted to about 4–5 mL with 0.5 M HCl and then scanned for visible spectra with a Varian-Cary 118C spectrophotometer. Typically, 20 g (4.2×10^{-2} mol) of $[(NH_3)_5CoOH_2](ClO_4)_3$ and 5 g (6.1×10^{-2} mol) of 4(5)-methylimidazole were heated in 90 mL of dimethyl sulfoxide at 70 °C for 90 min. The separation procedure of Harrowfield et al.[4] was followed except that Bio-Rad 200–400 mesh AG 50W-4X resin was used to carry out the ion exchange and 2 L of H_2O in 200-mL volumes removed unreacted ligand prior to elution with 1 M HCl. Final elution of the desired complex with 4–6 M HCl was followed by concentration under reduced pressure at 50° C nearly to dryness. The chloride salts of $(NH_3)_5CoL^{3+}$ were then purified by fractional crystallization from 3–6 M HCl, the main impurities, $[(NH_3)_5CoCl]Cl_2$, $[(NH_3)_5CoOH_2]Cl_3$, and $[(NH_3)_6Co]Cl_3$, being removed in the earlier fractions. The yields were over 70%.

Synthesis of Complexes via $(NH_3)_5MO_3SCF_3^{2+}$, M = Co, Rh, Ir. The triflate salts of $(NH_3)_5M^{III}O_3SCF_3^{2+}$, (M = Co, Rh, Ir) were prepared by following literature procedures[8] with some modifications. The chloride salts of $(NH_3)_5CoCl^{2+}$ (Alfa), $(NH_3)_5RhCl^{2+}$ (Strem Chemical), and $(NH_3)_5IrCl^{2+}$ (Johnson Matthey, Inc.) were dissolved in neat triflic acid, CF_3SO_3H (Aldrich), at room temperature. These respective solutions were heated over a paraffin bath until the d–d bands of the starting material disappeared. The formation of the triflato derivative was complete in 40–70 min at 100–110 °C. In the case of Ir(III), relatively higher temperatures (130–140 °C) were needed. The products, $[(NH_3)_5M^{III}O_3SCF_3](O_3SCF_3)_2$, were precipitated by adding the reaction mixture (cooled to room temperature) to ice-cold ether and then separated by filtration.

$(NH_3)_5Rh^{III}$ and $(NH_3)_5Ir^{III}$ complexes of imidazole (Aldrich) were synthesized as triflate salts by the reaction of $[(NH_3)_5M^{III}O_3SCF_3](O_3SCF_3)_2$ with an excess of the corresponding ligand in anhydrous sulfolane solvent at 85–95 °C. The progress of the reaction was followed spectrophotometrically as described for Co(III). The imidazole complexes of $(NH_3)_5Rh^{III}$ and $(NH_3)_5Ir^{III}$ were precipitated as chloride salts by adding acetone, followed by concentrated HCl, to the reaction mixture. The white precipitates separated by filtration contain $[(NH_3)_5MCl]Cl_2$ and $[(NH_3)_5M^{III}OH_2]Cl_3$. The product was dissolved in a minimum amount of 4 M HCl at 40–45 °C and allowed to stand at 10–15 °C overnight. Chloro complexes were separated as fine crystals and filtered out. The highly soluble imidazole complexes were precipitated along with aqua complexes by adding acetone. The white products were binary mixtures of the imidazole complex and the aqua complex as indicated by the following elemental analyses,[11] which correspond to a mixture of 83% $[(NH_3)_5Rh(imH)]Cl_3 \cdot H_2O$ and 17% $[(NH_3)_5RhOH_2]Cl_3 \cdot H_2O$. Anal. Calcd (found): C, 8.04 (8.03); H, 5.56 (5.61); N, 25.09 (24.79); Cl, 28.62 (28.62); Rh, 27.69 (29.22). Formation of any bis(imidazole) complex is precluded by the C/N analytical ratio. Presence of the ligand was confirmed by an IR spectrum of a KBr pellet and by ^1H NMR. For the Ir(III) sample 65% of the product is $[(NH_3)_5Ir(imH)]Cl_3$ and 35% $[(NH_3)_5IrOH_2]Cl_3$. Anal. Calcd (found) C, 5.39 (5.44); H, 4.22 (4.39); N, 20.32 (19.27); Cl, 24.50 (24.40); Ir, 44.28 (44.39). Characterization by IR and NMR confirmed the imidazole presence.

Synthesis of $(NH_3)_5RuL^{3+}$, L = Imidazole and 2,4(5)-Dimethylimidazole. $(NH_3)_5Ru^{III}$ complexes of imidazole and 2,4(5)-dimethylimidazole were prepared by the general method of combining aquapentaammineruthenium(II) with the ligand in aqueous solution, in analogy to the method of Taube et al.,[12] with some modifications. In a typical preparation, 0.50 g (1.65 mmol) of $[(NH_3)_5RuCl]Cl_2 \cdot {}^2/_3H_2O$ was suspended in 30 mL of deaerated, argon-saturated H_2O containing 20 g of amalgamated zinc. Subsequently 0.65 g (6.77 mmol) of 2,4(5)-Me_2imH was dissolved in 20 mL of H_2O; the pH of this solution was adjusted to 6.8 by adding 1 M HCl, followed by deaeration with an argon purge. The ligand solution was added after about 40 min for reduction of the Ru(III). A color change from yellow to orange indicated the formation of the imidazole complex (reaction time ~30 min). The solution was filtered through a medium-porosity frit, followed by bubbling with O_2 for 1 h to oxidize the $(NH_3)_5Ru^{II}(2,5\text{-}Me_2imH)^{2+}$ complex. The color turned to deep red, indicating oxidation to $(NH_3)_5Ru^{III}(2,5\text{-}Me_2imH)^{3+}$. The chloride salt of the Ru(III) complex was isolated from the reaction mixture by absorbing products on cation-exchange resin followed by washing with H_2O and 1 M HCl. The complex was then eluted with 3–5 M HCl. The impurities, $[(NH_3)_6Ru^{III}]Cl_3$ and $[(NH_3)_5Ru^{III}Cl]Cl_2$, were removed as yellow precipitates by cooling a saturated solution of the product in 4 M HCl at 50 °C to 10–15 °C overnight. Highly soluble $[(NH_3)_5Ru^{III}(2,5\text{-}Me_2imH)]Cl_3$ was precipitated by adding 95% ethanol to the mother liquor.

Linkage Isomers of 4-Methylimidazole and 2,4(5)-Dimethylimidazole. Each of these ligands have two nonequivalent coordination sites and are, therefore, expected to give two isomers, provided only one site is not preferentially coordinated. After isolation, these complexes were subjected to fractional crystallization. Except for (4(5)-methylimidazole)pentaamminecobalt(III),[13,14] other complexes gave fractions having identical NMR and UV–visible spectra, indicating only one isomer species. The Ru(III) complex was assigned by the NMR spectrum of the Ru(II) complex, prior to oxidation, as described in the text.

Determination of pK_a's of Complexes at 25.0 °C. The pK_a's of imH, 2-MeimH, 4-MeimH, and 5-MeimH coordinated to $(NH_3)_5Co^{III}$ were determined by pH titration using an automatic titrator. The titrator was constructed with a Sage Instrument Model 341A syringe pump, a jacketed titration vessel, and a Fisher Recordall Series 5000 strip chart recorder. The titrant was delivered from a syringe mounted on the pump through a fine piece of Teflon tubing. Measurement of pH was made with a digital pH meter and directly recorded on the strip-chart recorder.

The pK_a's of $(NH_3)_5Co^{III}(2,5\text{-}Me_2imH)^{3+}$, $(NH_3)_5Ru^{III}(2,5\text{-}Me_2imH)^{3+}$, $(NH_3)_5Rh^{III}imH^{3+}$ and $(NH_3)_5Ir^{III}imH^{3+}$ were determined by spectrophotometric titration, absorbances being measured at 300, 700, 230, and 235 nm, respectively, with use of a flow cell connected to the titration vessel. pK_a's were evaluated from a plot of pH_{av} vs. $\Delta A/\Delta pH$, which approximates the derivative function. Values of pH_{av}, ΔpH, and ΔA are defined as $pH_{av} = (pH_1 + pH_2)/2$, $\Delta pH = pH_2 - pH_1$, and $\Delta A = A_2 - A_1$, where pH_1 and pH_2 are any two consecutive pH readings and A_1 and A_2 are the corresponding absorbances. The value of pH_{av} at the peak of the plot indicates the pK_a of the complex as shown for two examples in Figure 3 of the text.

^1H NMR and UV–Visible Spectra. UV–visible spectra of complexes were obtained with use of a Varian-Cary 118C spectrophotometer with solutions in quartz cells. ^1H NMR data were obtained with a Varian EM-360 NMR spectrometer with a probe temperature of 30 °C. TMPA[15] (δ(TMS) = 0.00) served as an internal standard. The

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(15) TMPA (3-(trimethylsilyl)propionic acid) sodium salt (δ(TMS) = 0.00) served as an internal standard for the D_2O-soluble complexes.

Table I. ^1H Chemical Shifts (ppm) for imH, imH_2^+, $(NH_3)_5M^{III}imH^{3+}$, and $(NH_3)_5M^{III}im^{2+}$ vs. TMPA (M = Co, Rh, Ir)

species	C-2	C-4	C-5
imH	7.67	7.03	7.03
imH_2^+	8.60	7.40	7.40
$A_5Co^{III}imH^{3+}$	8.03	7.03	7.33
$A_5Rh^{III}imH^{3+}$	7.93	6.97	7.30
$A_5Ir^{III}imH^{3+}$	7.95	7.02	7.25
$A_5Co^{III}(im)^{2+}$ [a]	7.33	6.83	7.17
$A_5Rh^{III}(im)^{2+}$ [a]	7.30	6.83	7.07
$A_5Ir^{III}(im)^{2+}$ [a]	6.28	6.83	7.00

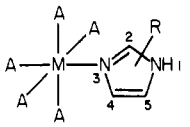
[a] Solution pD ~13.5.

^1H NMR spectra and ^{13}C NMR spectra of N-heterocyclic ligands are the subject of a detailed report.[16] The utility here of the ^1H NMR spectra is to show that coordination of the desired imidazole had occurred at Co(III), Rh(III), Ir(III), and Ru(II) centers and that the isolated samples were free of the uncoordinated ligand. The data are presented in Table I.

Results and Discussion

^1H NMR of Coordinated Imidazoles. All of the $(NH_3)_5M(imH)^{3+}$ complexes have a titratable pyrrole hydrogen; deprotonation forms the analogous imidazolate complex as shown in eq 1 (M = Co(III), Rh(III), Ir(III), Ru(III)). Coordination influences the positions of the ^1H NMR resonances of the ring hydrogens as reported in Table I. The numbering scheme for imidazole coordination for R = H or CH_3 is

$$(NH_3)_5M(imH)^{3+} + H_2O \overset{K_a}{\rightleftharpoons} H_3O^+ + (NH_3)_5M(im)^{2+} \quad (1)$$



The shift of equilibrium 1 to the right also alters the resonance position. The ^1H NMR spectra of N-heterocycles will be treated in a separate report in detail.[16] However, a number of spectral observations are notable. As anticipated for substitution-inert diamagnetic complexes of Co(III), Rh(III), and Ir(III), the ligands are not dissociated and coordination removes the symmetry at C-4 and C-5.

The chemical shifts of the low-spin d^6 $(NH_3)_5M^{n+}$ complexes of several nitrogen heterocycles reported in this paper are best rationalized by considering the competitive effects of σ donation, back-bonding on the charge densities of the heterocyclic ring, and paramagnetic anisotropic effect resulting from the temperature-independent paramagnetism (TIP) of the metal center. Several authors[17-19] have discussed how these factors change the chemical shifts of the ligand upon coordination to a metal center. (i) σ charge donation to the metal center removes electron density from the ligand, producing a deshielding effect. The σ effect changes inversely with distances so that the withdrawing effect will attenuate at positions remote from the metal center. (ii) π back-bonding into the ligand will cause an upfield shift. (iii) The temperature-independent paramagnetism (TIP) has very large shielding effects, i.e. upfield shifts. TIP of ruthenium(II) and rhodium(III) has been used to rationalize the very high field proton chemical shifts ($\tau \approx 17.0$–20.0) observed for rhodium and ruthenium hydride complexes, but the shielding effect of TIP falls off very rapidly with distance as a function of R^{-3}, where R is the distance from the metal atom.

Table II. ^1H Chemical Shifts for Free and Coordinated Ligands vs. TMPA (L = 4(5)-MeimH, 2,4(5)-Me_2imH)[c]

species	C-2	C-4	C-5
4(5)-MeimH,[a] 0.5 M	7.65	2.27 (6.77)	6.77 (2.27)
4(5)-$MeimH_2^+$, 0.5 M	8.53	2.45 (7.20)	7.20 (2.45)
A_5Co^{III}(5-MeimH)$^{3+}$ (R), 0.3 M	7.88	6.73	2.33
A_5Co^{III}(5-Meim)$^{2+}$ [b] (R_{-H}), 0.3 M	7.18	6.48	2.20
A_5Co^{III}(4-MeimH)$^{3+}$ (A), 0.3 M	7.80	2.22	7.08
A_5Co^{III}(4-Meim)$^{2+}$ [b] (A_{-H}), 0.3 M	7.10	2.13	6.83
2,4(5)-Me_2imH,[a] 0.5 M	2.35	2.19 (6.63)	6.63 (2.19)
2,4(5)-$Me_2imH_2^+$, 0.5 M	2.65	2.36 (7.06)	7.06 (2.36)
A_5Co^{III}(2,5-Me_2imH)$^{3+}$, 0.3 M	2.41	6.38	2.25
A_5Co^{III}(2,5-Me_2im)$^{2+}$ [b]	2.20	6.23	2.14
A_5Ru^{II}(2,5-Me_2imH)$^{2+}$	2.53	6.87	2.23

[a] Two tautomeric forms in D_2O solution are not distinguishable by NMR. [b] Solution pD ~13.5. [c] A = adjacent isomer; R = remote isomer.[13,14]

Table III. ^1H Chemical Shifts for Coordinated Imidazoles vs. Free Ligand (L = imH, 4(5)-MeimH, 2-MeimH, 2,4(5)-Me_2imH)

species	$\Delta\delta(^1H)$[a] C-2	C-4	C-5
A_5Co(5-MeimH)$^{3+}$ (R)	0.23 (←)	0.04 (→)	0.06, CH_3 (←)
A_5Co(4-MeimH)$^{3+}$ (A)	0.15 (←)	0.05, CH_3 (→)	0.31 (←)
A_5Co(2-MeimH)$^{3+}$ [24]	0.12, CH_3 (←)	0.13 (→)	0.44 (←)
A_5Co(2,5-Me_2imH)$^{3+}$	0.06, CH_3 (←)	0.25 (→)	0.06, CH_3 (←)
$A_5Co^{III}imH^{3+}$	0.36 (←)	0.00	0.30 (←)
$A_5Rh^{III}imH^{3+}$	0.26 (←)	0.06 (→)	0.27 (←)
$A_5Ir^{III}imH^{3+}$	0.28 (←)	0.00	0.22 (←)

[a] $\Delta\delta(^1H)$ values are computed from Tables I and II: → = upfield vs. free ligand; ← = downfield vs. free ligand.

In order to establish whether a C-4 or C-5 resonance may be appropriately assigned, it is necessary to consider a labeling of positions by methyl substitution. The results for a number of Co(III) and Ru(II) complexes containing ring-methylated imidazoles are given in Table II. Assistance in the assignment of which ring resonance is C-4 or C-5 is given by the remote and adjacent isomers of (4-methylimidazole)pentaamminecobalt(III), which have been assigned in conjunction with separate X-ray studies of each isomer.[20] If the shifts of the various isomers and other ring-methylated imidazoles are considered, it becomes apparent that C-2 and C-5 positions exhibit downfield shifts on coordination to $(NH_3)_5Co^{3+}$ relative to the free-ligand resonance in each case (see Table III). Therefore, the C-5 position may then be assigned for the parent imidazole complex to the downfield-shifted resonance relative to the free ligand resonance as listed in Table III. This assignment forces the assignment for the C-4 and C-5 hydrogens as presented in Table I. Note that the shift differences at C-4 are generally smaller than at the other positions (Table III) and that the only likely factor causing an upfield shift, the TIP effect, comes to play most at C-4.

The downfield shift of the remote protons at C-5 sites of 4(5)-MeimH, 2-MeimH, and 2,4(5)-Me_2imH coordinated to $(NH_3)_5Co^{III}$ are attributed to charge withdrawal from the imidazole ring via σ donation, without much compensation by

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Table IV. ^{1}H Diamagnetic Shifts at Remote Sites for LH^+ and $(NH_3)_5Co^{III}L^{3+}$ vs. L

	$\Delta\delta(HL^+)$, $\Delta\delta(A_5Co^{III}L^{3+})$		
	imH	py, pyz	
L	C-5	C-3	C-4
4-MeimH	0.43, 0.31		
5-MeimH	0.18, 0.06		
2,5-Me_2imH	0.17, 0.06		
pyz[16]		0.49, 0.30	
4-Mepy[14,16]		0.72, 0.41	0.35, 0.20

[a] $\Delta\delta$ values computed from Table II and ref 16.

the TIP effect. The upfield shifts of the adjacent protons at C-4 sites of these complexes show that the TIP of the cobalt(III) center more than compensates the deshielding effect of σ withdrawal at the 4-position. The downfield shifts of the adjacent protons at C-2 sites of the imidazole complexes are in contrast to the upfield shifts of both adjacent (2 and 2') protons of pyridine and 4-picoline coordinated to $(NH_3)_5Co^{III}$ and $(NH_3)_5Rh^{III}$ observed by Lavallee et al.[19] and from other work in this laboratory.[16] Fleischer et al.[18] have also observed upfield shifts for both adjacent protons of pyrazine coordinated to $(NH_3)_5Ru^{II}$. However, the ^{1}H downfield shift for the C-2 position may be reconciled from the fact that coordination of imidazoles to a M(III) center polarizes the (C-2)–R bond much more than (C-4)–R. This is due to the location of C-2 adjacent to electronegative N-1 and N-3 in the imidazole ring. Greater polarization of the (C-2)–R bond results in greater depletion of charge density from the hydrogen at the C-2 position. The argument is equivalent for CH_3 as well as R = H. Also, it is shown by ^{13}C shift data[16] that the ring C-2 becomes more electron rich at the expense of its substituent, H or CH_3; thus the downfield $\Delta\delta(^{13}C)$ value for C-2 is about 50% of that for C-4. We should note that 1-methylimidazoles on coordination with $(NH_3)_5Co^{III}$ or $(NH_3)_5Ru^{II}$ exhibit diamagnetic ^{1}H shifts at all positions.[16,21] One possible reason might be the slightly higher basicities of the pyridine N in these N-1-methylated imidazoles, pK 7.39 vs. 7.25 for imidazole.[2] Therefore the 1-methylimidazole may be subject to greater changes in the σ framework, overshadowing the TIP effect on the adjacent positions, while weaker bases such as pyridines and pyrazines are not as easily withdrawn at adjacent carbons. These ligands have upfield shifts of adjacent C–H and downfield shifts at remote sites[16,18,19] consistent with this analysis. Thus the TIP influences adjacent H resonances as a function of σ donation, and the net effect is complicated. It can be seen from Table III that the downfield shifts at the remote C-5 site of the imidazole complexes of $(NH_3)_5M^{III}$ follow the order Co > Rh > Ir, suggesting that metal-center induction and σ charge withdrawal decreases with increasing metal size as suggested for a simple electrostatic model. This is also borne out by comparing Co(III) to H^+ as shown in Table IV. Remote positions of the ligands are taken as the purest measure of σ withdrawal at the coordination site. ^{1}H shifts at remote sites in Table IV suggest that electron density depletion by H^+ is significantly greater than that by the $(NH_3)_5Co^{3+}$ moiety. The reason is that although the metal center has higher charge, H^+ has much greater ionic potential, in harmony with the trend Co > Rh > Ir.

Remote Methyl Assignment for $(NH_3)_5Ru^{III}(2,4(5)\text{-}Me_2imH)^{3+}$. The Ru(III) complex was reduced to $(NH_3)_5Ru^{II}(2,4(5)\text{-}Me_2imH)^{2+}$ in D_2O solution by Zn/Hg, and its ^{1}H NMR spectrum was examined. All of the resonances are shifted downfield vs. those for the free ligand. So the shift in resonance position is not useful for the methyl assignment in the Ru(II) complex. However, the integration ratios for the resonances are

$$2\text{-}CH_3:CH_3:H = 2.2:3.0:0.7$$

(The corresponding ratios for $(NH_3)_5Co^{III}(2,5\text{-}Me_2imH)^{3+}$ are found to be 3.0:3.0:1.1). A Ru(II) center is known to reduce the intensity of the adjacent proton resonances by ruthenium–proton coupling for the ruthenium isotopes of $^5/_2$ nuclear spin. The decrease in the intensity of the 2-CH_3 resonance is expected because of its location adjacent to the ruthenium center. The loss of intensity in the ring proton (C–H) resonance establishes that the complex has a (C-4)–H bond which is adjacent to the metal center. The remaining methyl having its resonance unaffected must then be at the remote C-5 site of the coordinated imidazole. Similarly the $(NH_3)_5Co^{III}$-$(2,5\text{-}Me_2imH)^{3+}$ complex is found to have the CH_3 group remote and H adjacent, the strain-released remote methyl isomer. The adjacent methyl isomer was either not formed during synthesis or converted to the remote methyl form during manipulation for isolation. The basis of our remote assignment is as follows:

(i) The complex is stable toward isomerization. An adjacent isomer of these complexes is expected to be unstable because of significant strain energy (3 kcal/mol of adjacent methyl).

(ii) Methyl resonances in ^{1}H NMR spectra of the complex appear downfield vs. those of the free ligand. This indicates that one methyl substituent is remote from the metal center.

Table V. Electronic Transitions (d–d) for Low-Spin d^6 $(NH_3)_5M^{III}L^{n+}$ Imidazole Complexes

		λ_{max}, nm (ϵ, M^{-1} cm^{-1})[b]	
species	conditions	λ_1 (ϵ_1)	λ_2 (ϵ_2)
$A_5Co(5\text{-}MeimH)^{3+}$ (R)	pH 6.86 (phosphate)	472 (60)	330 (96)
$A_5Co(4\text{-}MeimH)^{3+}$ (A)	pH 6.86 (phosphate)	477 (68)	330 (109) sh
$A_5Co(2,5\text{-}Me_2imH)^{3+}$	pH 6.86 (phosphate)	478.5 (65)	337 (116)
$A_5Co(5\text{-}Meim)^{2+}$ (R_{-H})	0.5 M NaOH	478 (65)	348 (99)
$A_5Co(4\text{-}Meim)^{2+}$ (A_{-H})	0.5 M NaOH	483 (67)	352.5 (102)
$A_5Co(2,5\text{-}Me_2im)^{2+}$	0.5 M NaOH	485 (78)	347.5 (113)
$A_5Co(imH)^{3+}$ [23]	pH 6.86 (phosphate)	473 (60)	333 (71)
$A_5Rh(imH)^{3+}$ [a]	pH 6.86 (phosphate)	304 (146)	250 (153) sh
$A_5Ir(imH)^{3+}$	pH 6.86	≤240 (end abs)	
$A_5Co(im)^{2+}$ [23]	1 M NaOH	478 (70)	342 (114)
$A_5Rh(im)^{2+}$ [a]	0.1 M NaOH	307 (166)	252.5 (216)
$A_5Ir(im)^{2+}$	0.1 M NaOH	≤240 (end abs)	

[a] Spectrum was corrected for the presence of 17% $(A_5RhOH_2)Cl_3\cdot H_2O$ by using ϵ's from ref 36. [b] sh = shoulder.

Electronic d–d Transitions for Low-Spin d^6 $(NH_3)_5M^{III}L^{n+}$ Complexes. The d–d electronic transitions for low-spin d^6 $(NH_3)_5M^{III}L$, (L = imidazoles, imidazolates) prepared for our studies are given in Table V. With their C_{4v} symmetry, the lower energy transition (λ_1) is assigned to $^1A_1 \rightarrow (^1E^a, {}^1A_2)$ and higher energy transition (λ_2) to $^1A \rightarrow (^1E^b, {}^1B_2)$. Deprotonation of the pyrrole hydrogen in imidazole series complexes for Co(III) lowers energies of λ_1 and λ_2 peaks by 5–6 and 9–22 nm, respectively. The corresponding shifts for $(NH_3)_5Rh^{III}imH^{3+}$ are only 3 and 2.5 nm. Although imidazolate serves as a better σ donor than imidazole by about 7 kcal/mol toward transition-metal complexes,[2] lowering of d–d energy indicates that imidazolates have lower effective ligand field strengths compared to those of the corresponding imidazoles. This may be due to delocalization of the anion while the neutral imidazole has a nonresonant structure.

The λ_{max} values shown for $(NH_3)_5Co^{III}L^{3+}$ in Table V are typical for the N_6Co^{III} environment; the transitions for Co-

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Table VI. LMCT Spectral Data for $(NH_3)_5Ru^{III}L^{n+}$ (L = Imidazoles and Imidazolates)

LH	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	
	$A_5Ru^{III}LH^{3+}$	$A_5Ru^{III}L^{2+}$
2,5-Me_2imH[a]		272 (1448)
	311 (1318)	377 (1760)
	517 (198)	655 (310)
imH[25]	299 (1880)	362 (2990)
	430 (250)	555 (350)
1-MeimH[25]	312 (2310)	
	425 (186)	
5-MeimH[25]	303 (2020)	370 (3000)
	470 (267)	600 (472)
4,5-Me_2imH[25]	312 (2190)	392 (2830)
	520 (168)	750 (?)

[a] Conditions: 5×10^{-4} M complex in H_2O; $A_5Ru^{III}LH^{3+}$ solution pH ~6.0; $A_5Ru^{III}L^{2+}$ solution pH ~13.0.

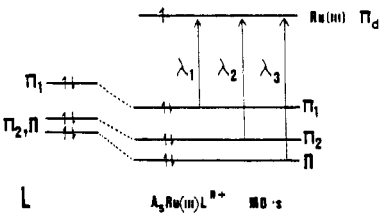

Figure 1. Qualitative MO picture of the LMCT absorption expected for A_5Ru^{III} complexes of imidazoles and imidazolates.

$(NH_3)_6^{3+}$ occur at 473 and 337 nm for comparison.[24] Similarly $Rh(NH_3)_6^{3+}$ has maxima at 306 and 256 nm,[35,36] comparable to those for its imidazole complex. $Ir(NH_3)_6^{3+}$ has transitions at 250 and 212 nm.[37] The extinction coefficients for these $(NH_3)_5M^{III}L^{n+}$ species are characteristic of the d–d transitions of pentaammine complexes. The shift toward higher energy for the d–d transition, Co < Rh < Ir, is consistent with $10Dq$ for these metal centers.

LMCT Spectra of $(NH_3)_5Ru^{III}(2,5\text{-}Me_2imH)^{3+}$ and $(NH_3)_5Ru^{III}(2,5\text{-}Me_2im)^{2+}$. The spectra of the 2,5-dimethylimidazole complex and the imidazolato complex of $(NH_3)_5Ru^{3+}$ were taken with use of 5.00×10^{-4} M complex in aqueous solution (pH ~6) and aqueous NaOH solution (pH ~13.0), respectively. The chloride salt appears reddish pink and produces a pink solution at pH ~6.0 and a blue-green solution at pH ~13.0. The data for λ_{max} in nm (ϵ, M^{-1} cm^{-1}) are recorded in Table VI along with those of analogous complexes for comparison. The extinction coefficients are too high for d–d transitions; thus, these are buried under the observed LMCT bands.

The two distinct transitions generally observed for the imidazole and imidazolate ligands coordinated to $(NH_3)_5Ru^{III}$ are attributable to transitions from filled ligand π orbitals to a metal π_d vacant orbital.[21,25] A qualitative MO diagram showing possible LMCT transitions in $(NH_3)_5Ru^{III}L^{n+}$ (L = imidazoles and imidazolates) is in Figure 1. It has been observed that methyl substitution on a ring carbon shifts the λ_1 band toward lower energy.[21] The same substitution on the pyrrole-type N-1 shifts the λ_2 band also toward lower energy. Note that π_1 has larger MO coefficients on carbons and π_2 has larger coefficients on nitrogens.[26] However, for coordinated 4,5-Me_2imH, 2,5-Me_2imH, and corresponding imidazolates, the λ_2 band is shifted as much as for 1-methylimidazole, although neither 4,5-Me_2imH nor 2,5-Me_2imH has a methyl substituent on N-1. Still of relevance, the λ_1 shifts in these complexes are about double the shift observed for 5-MeimH vs. imH.

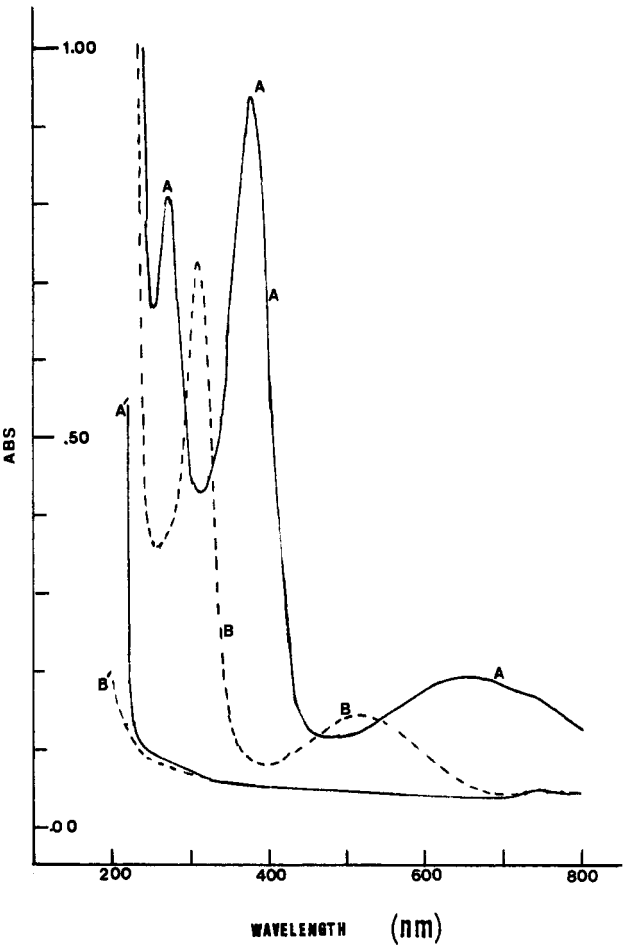

Figure 2. LMCT spectra of $(NH_3)_5RuL^{n+}$: (L) 2,5-Me_2imH and 2,5-Me_2im^-; (A) 5.0×10^{-4} M $A_5Ru(2,5\text{-}Me_2im)^{2+}$; (A′) 0.10 M NaOH base line; (B) 5.0×10^{-4} M $A_5Ru(2,5\text{-}Me_2imH)^{3+}$; (B′) H_2O base line.

Interestingly, we have observed three bands (Figure 2) for the imidazolato complex $(NH_3)_5Ru^{III}(2,5\text{-}Me_2im)^{2+}$, in contrast to two bands for analogous complexes in the literature. The bands at 655 and 377 nm are assigned to λ_1 and λ_2, respectively (Figure 1). The imidazole ring itself does not have absorption bands above 260 nm.[27,28] Hence the band at 272 nm might be attributed to an $n \rightarrow \pi_d$ transition.

pK_a's for Deprotonation at Pyrrole Nitrogen of Coordinated Imidazoles. The pK_a's of a series of $(NH_3)_5M^{3+}$ complexes of imidazoles, determined at 25.0 °C by the methods described in the Experimental Section, are given in Table VII. The pK_a of $(NH_3)_5Co(imH)^{3+}$ has been reported by Harrowfield et al. as 10.0,[4] which is found to be in excellent agreement with our results. The inclusion of methyl substituents increases basicity of the pyrrole nitrogen, as reflected by the higher pK_a values of coordinated 4(5)-MeimH, 2-MeimH, and 2,5-Me_2imH. When the methyl group is adjacent to the site of deprotonation in the case of the 2-MeimH or R complex (remote isomer of the 4-MeimH complex), the pK_a's are essentially the same, 10.69 ± 0.02 at 25.0 °C.[21] The pK_a of the A complex (adjacent isomer of the 4-MeimH complex) is about 0.25 log unit lower than that of R. The methyl group in A is remote from the pyrrole position. One would anticipate that the basicity of A would have to be less than that of R on the basis that the donation of methyl through the σ bond system decreases

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(26) Del Bene, J.; Jaffe, H. H. *J. Chem. Phys.* **1968**, *48*, 4050–4055.
(27) Walbe, H.; Isensee, R. W. *J. Org. Chem.* **1956**, *21*, 702–704.
(28) Shepherd, R. E.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392–1401.

Table VII. pK_a Values and Enthalpy and Entropy Changes on Deprotonation of Imidazole Complexes

species	pK_a(298 K)[a]	ΔH_a, kcal/mol	ΔS_a, eu	μ
$A_5Co^{III}imH^{3+}$	9.99	14.0 ± 0.5	1.3 ± 1.6	0.1
$A_5Rh^{III}imH^{3+}$	9.97[b]	13.6 ± 0.3	0.1 ± 1.3	0.1
$A_5Ir^{III}imH^{3+}$	10.05[c]	13.4 ± 0.3	1.2 ± 1.0	0.1
$A_5Ru^{III}imH^{3+}$	8.9[d]	10.0 ± 0.8	3.7 ± 1.2	3×10^{-3}
A_5Co^{III}(4-MeimH)$^{3+}$	10.46	17.6 ± 0.5[e]	11.2 ± 1.6[e]	0.1
A_5Co^{III}(5-MeimH)$^{3+}$	10.70	15.4 ± 0.6[e]	2.5 ± 1.8[e]	0.1
A_5Co^{III}(2-MeimH)$^{3+}$	10.67	17.8 ± 0.7	11.2 ± 2.4	0.1
A_5Ru^{III}(5-MeimH)$^{3+}$	9.0[d]			3×10^{-3}
A_5Co^{III}(2,5-MeimH)$^{3+}$	11.04	13.4 ± 0.5	5.3 ± 1.6	0.1
A_5Ru^{III}(2,5-Me_2imH)$^{3+}$	10.20	13.2 ± 0.6	−2.1 ± 2.2	0.1
$(CN)_5Fe^{III}imH^{2-}$	10.93	8.8 ± 0.8[f]	−21 ± 3[f]	0.1
free imH	14.2[g]	17.6 ± 1.6[g]	−7 ± 5[g]	

[a] Our pK_a's are accurate within ±0.08, the limiting accumulated errors from the procedure. The individual pH readings are good to ±0.03. [b] Determined in the presence of 17% A_5RhOH^{2+}. [c] Determined in the presence of 35% A_5IrOH^{2+}. [d] Reference 25. [e] Reference 13. [f] Reference 2. [g] Reference 3.

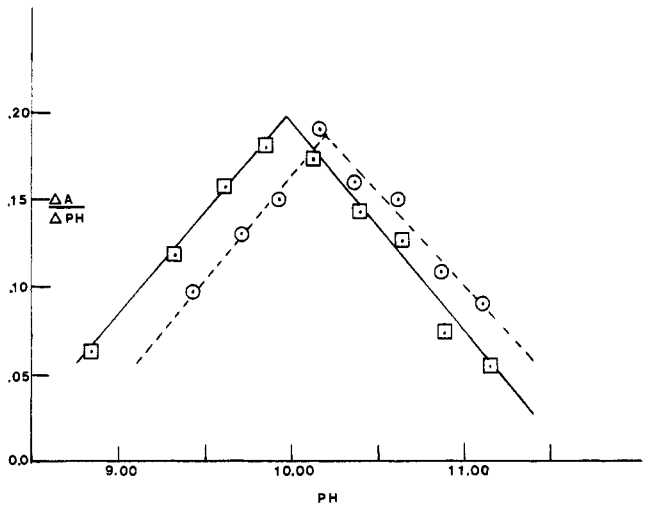

Figure 3. Spectrophotometric determination of pK_a's from a plot of $\Delta A/\Delta$pH vs. pH: (○, ---) $(NH_3)_5Ru$(2,5-Me_2imH)$^{3+}$, λ = 700 nm, μ = 0.10, T = 25.0 °C (pK_a = 10.20); (□, —) $(NH_3)_5Rh(imH)^{3+}$, λ = 230 nm, μ = 0.10, T = 25.0 °C (pK_a = 9.97).

with distance. The derivative method described in the Experimental Section was used for obtaining the pK_a's of the $(NH_3)_5Co$(2,5-Me_2imH)$^{3+}$, $(NH_3)_5Ru$(2,5-Me_2imH)$^{3+}$, $(NH_3)_5Rh(imH)^{3+}$, and $(NH_3)_5Ir(imH)^{3+}$ complexes. Representative cases are shown for $(NH_3)_5Rh(imH)^{3+}$ and $(NH_3)_5Ru$(2,5-Me_2imH)$^{3+}$ complexes in Figure 3. The change in the LMCT band of the Ru(III) complex was monitored; the Rh(III) complex was titrated in the UV region.

The pK_a's of $(NH_3)_5Ru^{III}$-coordinated imH and 2,5-Me_2imH are about 1 pH unit lower than those of Co(III) analogues. The reason for higher acidity in the case of Ru(III) is apparently the presence of an electron hole in the t_{2g} set. This is described more completely in comparison to Rh(III) below. Imidazoles are only σ donors to $(NH_3)_5M^{III}$, M = Co, Rh, Ir, compared to $\sigma + \pi$ toward Ru(III).

The pK_a's of imH coordinated to $(NH_3)_5Co^{III}$, $(NH_3)_5Rh^{III}$, and $(NH_3)_5Ir^{III}$ have been found in this present work to be nearly the same, 10.01 ± 0.04. In agreement with this observation, the literature pK_a's of the corresponding aqua complexes are also close, 6.50 ± 0.28: $(NH_3)_5CoOH_2^{3+}$ (6.6, μ = 1.0;[29] 6.22, μ = 0.3[30]); $(NH_3)_5RhOH_2^{3+}$ (6.78, μ = 0.5[31]); $(NH_3)_5IrOH_2^{3+}$ (6.70, μ = 0.5[31]). Since the σ charge withdrawal decreases with the increase of size, one would apparently predict higher pK_a's for Rh(III) and Ir(III) complexes.

Table VIII. Temperature Dependence of pK_a's for $(NH_3)_5M^{III}imH^{3+}$ [a] (M = Co, Rh, Ir)

	pK_a		
T, °C	$A_5Co(imH)^{3+}$	$A_5Rh(imH)^{3+}$ [b]	$A_5Ir(imH)^{3+}$ [c]
0		10.88	10.94
25	9.99	9.97	10.05
30		9.79	9.84
35	9.64		
40	9.40	9.57	9.64
50	9.17	9.28	9.33
60	8.92	8.92	8.99
70	8.61	8.62	8.75

[a] Ionic strength = 0.1; $[complex]_{tot} = 0.020$ M. [b] $[complex]_{tot} = 1.66 \times 10^{-2}$ M; A_5RhOH^{2+} (3.4×10^{-3} M) was present.[38] [c] $[complex]_{tot} = 1.3 \times 10^{-2}$ M; A_5IrOH^{2+} (7.0×10^{-3} M) was present.[38] T is ±0.1 °C below 35 °C and ±0.5 °C above 40 °C.

To examine whether or not the pK_a's are equal by a fortuitous compensation of $\Delta H_a°$ and $\Delta S_a°$ or perhaps by a solvation dependence of these ions, the pK_a values of these imidazole complexes were measured as a function of temperature as given in Table VIII.

Because the value of K_a is very small for the Co(III), Rh(III), and Ir(III) imidazole complexes (ca. 10^{-10}), the change in temperature that produces a change in K_a of equilibrium 1 does not produce a significant change in concentration of the imidazole and imidazolate complexes if these are present at greater than 10^{-6} M. In the situation of this study the buffer species of eq 1 were present at about 0.01 M each. The equilibrium could then be conveniently studied at a glass electrode, appropriately calibrated at each temperature with borate or sodium carbonate buffers. The activity of hydrogen ion yields K_a directly when the imidazole and imidazolato forms are made analytically equal.

This was readily achieved for each complex by adjusting a solution of the complex at 25.0 °C to the pK_a value of the complex, which was determined carefully in each case as mentioned above. Samples were maintained at 0 °C and aliquots taken to adjust and measure at higher temperatures. With this approach a potentially long waiting time which might allow for base-catalyzed loss of ammonia or imidazole was avoided. A plot of $1/T$ vs. pK_a is a good straight line. Enthalpy and entropy changes evaluated from the slope and intercept of the line according to eq 2 are recorded in Table VII.

$$pK_a = \frac{\Delta H°}{2.303R}\frac{1}{T} - \frac{\Delta S°}{2.303R} \qquad (2)$$

The data show that $\Delta S_a°$ is nearly zero within experimental error for all three complexes and that only a very small, if real, difference occurs for $\Delta H_a°$ down the series Co(III), Rh(III), Ir(III). The direction for the change is, in fact, opposed to

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(30) Splinter, R. C.; Harris, S. J.; Tobias, R. S. *Inorg. Chem.* **1968**, *7*, 897–902.
(31) Palmer, D. A.; Harris, G. M. *Inorg. Chem.* **1974**, *13*, 965–969.

what one predicts on the pyrrole hydrogen bond strength on the basis of a simple electrostatic model for repulsion of H^+ by M^{3+}, since the ion size increases in the series Co(III) through Ir(III). The important observation, however, is that within this d^6 series the pK_a, $\Delta H_a°$, and $\Delta S_a°$ values are nearly the same in contrast to a large change in pK_a and $\Delta H_a°$ for the Ru(III) and Rh(III) ions (d^5 and d^6, respectively), where the ion size is virtually constant, but the d^5 ion is a much better π acceptor due to the hole in the t_{2g}^5 configuration. This feature favors π bonding from either imidazole or imidazolate, but only the imidazolate form is a really good π donor. Thus the net effect for Ru(III) will favor the imidazolato complex in stability, shifting the acid dissociation to the right (lowering pK_a). Rh(III) has the filled d^6 configuration, which cannot participate in the π influence and is at a disadvantage to Ru(III) in this regard. That the $\Delta S_a°$ is still near 0 for the Ru(III) system, as for the Rh(III) complex, shows that the solvation changes on deprotonation are comparable for all of the $(NH_3)_5M(imH)^{3+}$ complexes, M = Co, Rh, Ir, Ru. The influence of π donation from imidazolate to Ru(III) is therefore manifest in a lowering of $\Delta H_a°$ for the reaction (eg. 10.0 kcal/mol for Ru(III) vs. 13.6 kcal/mol for Rh(III). Somewhat surprisingly then, $(CN)_5Fe(imH)^{2-}$ gives a larger effect on $\Delta H_a°$ [2], suggesting an order of Fe(III) > Ru(III) > Os(III) for d^5 low-spin ions.

The same argument has been made for hydroxide ion participating in ligand-to-metal π bonding[32] to account for the more acidic character of $(NH_3)_5RuH_2O^{3+}$ (pK_a = 4.2)[33] compared to $(NH_3)_5RhH_2O^{3+}$ (pK_a = 6.78). A parallel, but smaller, influence is observed for anionic complexes M(edta)$(H_2O)^-$: M = Ru(III), pK_a = 7.63; Rh(III), pK_a = 9.1.[34]

An absence of data for deprotonation of free ligands other than imidazole itself makes comparisons among the substituted ring systems in Table VII more difficult. However, several trends are discernible. The entropy change on dissociation of the pyrrole NH remains a small positive value for the ring-methylated systems (Table VII). The value of $\Delta S_a°$ appears to be near zero for $(NH_3)_5Ru(2,5\text{-}Me_2imH)^{3+}$ and becomes as great as 11 eu for the 2-MeimH and 4-MeimH complexes of $(NH_3)_5Co^{3+}$. Overall, the influence on the free energy change is not much different from that for the imidazole complexes, $\Delta S_a° \approx 1$ eu. The differentiation between d^6 and d^5 ions appears to be largely removed when one considers the close values of $\Delta H_a°$ for the 2,5-Me_2imH complexes of $(NH_3)_5Co^{3+}$ (13.4 ± 0.5 kcal/mol) vs. $(NH_3)_5Ru^{3+}$ (13.2 ± 0.6 kcal/mol). One possible explanation is that ring methylation alters the ability of the neutral ligand to serve as a π donor toward Ru(III), thus reducing the net difference in energy between the coordinated 2,5-Me_2imH vs 2,5-Me_2im^- species in equilibrium 1. Therefore, the effect of Co(III) and Ru(III) are more equivalent for this pair.

It appears that substitution of CH_3 at C-2 or C-4, adjacent to Co(III), raises $\Delta H_a°$ while substitution at C-5 is less efficient as a σ donor or even lowers $\Delta H_a°$. The influence at C-2 or C-4 follows the inductive effect, which should reduce the charge influence of M(III) at N-1. However, the σ donation of CH_3 at C-5 should be even stronger. Yet the observed influence at C-5 is the reverse. The best explanation is a local effect of a hydrophobic group that changes the local solvation near the NH. The solvation change must operate in opposition to the σ induction of CH_3 at this position. Thus the local solvation influence must be great in spite of the fact that the net change for $\Delta S_a°$, which is sensitive to the overall solvation of the complex, remains small. At least for the Co(III) complexes the combined effect of C-2 and C-5 substitution with 2,5-Me_2imH shows that the local solvation influence overshadows σ induction by CH_3 groups. Although these effects are complicated to sort out, it is clear that the acidity of the pyrrole NH is sensitive to local solvation and/or hydrophobicity of the region. This fact is clearly an important consequence for the imidazole unit in biochemical systems where a more hydrophobic region enhances the acidity. The site of ring attachment of the histidine side chain should operate in the σ sense as a CH_3 at C-5 in these studies, providing for less strained coordination to metal centers at N-3. Some enzymes adopt coordination in the strained mode, such as Zn^{2+} in carbonic anhydrase and carboxypeptidose A.[39]

Conclusions

The influence of σ withdrawal in $(NH_3)_5M(imH)^{3+}$ complexes or substituted imidazole analogues follows the anticipated behavior based on ionic potential ($H^+ >> Co^{3+} > Rh^{3+} > Ir^{3+}$) for the downfield contribution to the ^1H ring resonance of coordinated imidazoles. However, when one considers the deprotonation of a coordinated ligand, the influence is attenuated to the point that $Co^{3+} \approx Rh^{3+} \approx Ir^{3+}$ for the low-spin d^6 configuration as shown by nearly constant pK_a, $\Delta H_a°$, and $\Delta S_a°$ values for the acid dissociation of the pyrrole NH. This suggests that solvation factors compensate for electrostatics in this series. By contrast, if ions of similar size and solvation are considered (e.g. Ru(III) vs. Rh(III)) and one is a π acceptor (d^5), the influence on the pK_a is much larger than for a filled t_{2g}^6 set (d^6). Among d^5 ions with a limited set of data for Fe(III) and Ru(III), it appears that much larger differences exist based on ion size than for the series Co(III), Rh(III), Ir(III). Methyl substitution at ring carbons of the imidazoles influences the pK_a as anticipated for an electron-releasing group, unless substitution perturbs the local solvation at NH. C-5 substitution appears more important in this regard. The σ induction by a methyl substituent on imidazole coordinated to $(NH_3)_5Co^{3+}$ raises $\Delta H_a°$ ca. 3.7 kcal/mol if R is located at C-2 or C-4 of the ring; the increase in $\Delta H_a°$ over the parent imidazole complex is less if R is located at C-5 in spite of its closer distance to the NH group. C-5 substitution raises $\Delta H_a°$ by ca. 1.4 kcal/mol. Furthermore, the influence of two methyl groups adjacent to NH shows a *lowering* of $\Delta H_a°$ by ca. 0.6 kcal/mol. These influences are opposed to the ability of a σ donor at positions C-2 and C-5 to increase the basicity of the pyrrole NH. The σ effect of CH_3 in raising of the enthalpy for dissociation is overcome if both C-2 and C-5 positions are methylated; if both C-2 and C-5 are methylated, the pyrrole NH is in a more hydrophobic region. The advantage of the imidazolate to π donate to an ion of the low-spin d^5 configuration relative to d^6 is lost when methyl substitution is present at C-2 and C-5. For the 2,5-dimethylimidazole complexes of $(NH_3)_5Co^{3+}$ and $(NH_3)_5Ru^{3+}$ $\Delta H_a°$ values are nearly equal (13.3 ± 0.7 kcal/mol). This suggests that the 2,5-dimethylimidazole ligand can π donate to $(NH_3)_5Ru^{3+}$ nearly as well as its imidazolato form; therefore, other factors such as net charge and solvation operate to make the influence of Co(III) and Ru(III) more comparable than in the parent imidazole complexes.

Studies of the imidazole complexes of Co(III) reveal that predicting the influence of ^1H resonances is a complicated

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(38) The presence of $(NH_3)_5RhOH^{2+}$ and $(NH_3)_5IrOH^{2+}$ in the determination of the pK_a's of the respective imidazole complexes will not affect the result since neither of these species establishes a competitive equilibrium in the pH region 8.6–10.9.
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problem due to the influence of TIP in opposition to σ withdrawal. The net effect can be changed simply by methylation at N-1 for the C-4 resonance, whereas the C-2 resonance always is shifted downfield. This is not always true for pyridines and pyrazines at adjacent positions.

The 2,5-dimethylimidazole ligand coordinates with only the C-2 position in the hindered orientation as a matter of necessity for Co(III) and Ru(II). The Ru(III) complex, obtained an oxidation of the parent $(NH_3)_5RuL^{2+}$ species, displays LMCT spectra which may be related to the HOMO's of imidazole rings. The imidazolato form seems to have altered the energies of the n and π_2 orbitals sufficiently that three bands are detected for the n, π_2, and π_1 to π_d transitions. The near-equivalence of n and π_2 for less substituted imidazoles has not produced splitting of n and π_2 previously.

Acknowledgment. The authors gratefully acknowledge support for this work by the National Science Foundation (Grant No. CHE802183).

Registry No. $[(NH_3)_5CoOH_2](ClO_4)_3$, 13820-81-0; $(NH_3)_5Co(Me_2SO)^{3+}$, 44915-85-7; $[(NH_3)_5CoCl]Cl_2$, 13859-51-3; $[(NH_3)_5RhCl]Cl_2$, 13820-95-6; $[(NH_3)_5IrCl]Cl_2$, 15742-38-8; $[(NH_3)_5Co^{III}O_3SCF_3](O_3SCF_3)_2$, 75522-50-8; $[(NH_3)_5Rh^{III}O_3SCF_3](O_3SCF_3)_2$, 84254-57-9; $[(NH_3)_5Ir^{III}O_3SCF_3](O_3SCF_3)_2$, 84254-59-1; $(NH_3)_5Co^{III}(imH)^{3+}$, 38716-02-8; $(NH_3)_5Rh^{III}(imH)^{3+}$, 87571-37-7; $(NH_3)_5Ru^{III}(imH)^{3+}$, 80593-52-8; $(NH_3)_5Ir^{III}(imH)^{3+}$, 87571-40-2; $(NH_3)_5Co^{III}(2\text{-MeimH})^{3+}$, 89955-97-5; $(NH_3)_5Co^{III}(2,5\text{-Me}_2imH)^{3+}$, 89922-03-2; $(NH_3)_5Ru^{III}(2,5\text{-Me}_2imH)^{3+}$, 89922-04-3; $(NH_3)_5Co(5\text{-MeimH})^{3+}$, 89922-05-4; $(NH_3)_5Co(4\text{-MeimH})^{3+}$, 89955-98-6.

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Influence of Oxygen Insertion on the Electrochemistry of Chromium(III) Dithiocarbamate Complexes

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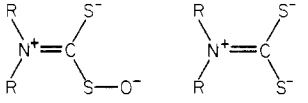
Received July 7, 1983

Dithiocarbamate (dtc) complexes of chromium(III) containing oxygen-expanded ligands, odtc, can be synthesized. With pyrrolidine-*N*-carbodithioate ([pdtc]$^-$) as the dithiocarbamate ligand, the electrochemistry of both $Cr(pdtc)_3$ and $Cr(pdtc)_2(opdtc)$ has been examined in detail. On the basis of studies employing cyclic and differential-pulse voltammetry at platinum, gold, and glassy-carbon electrodes in methanol, acetone, acetonitrile, and dichloromethane, it has been shown that the formally chromium(IV) complex, $[Cr(pdtc)_2(opdtc)]^+$, is kinetically more stable than $[Cr(pdtc)_3]^+$. Thermodynamically, the same stability order also applies in the sense that $Cr(pdtc)_2(opdtc)$ is easier to oxidize than $Cr(pdtc)_3$. The enhanced stability is attributed to the increased importance of the resonance form containing a partial positive charge on the nitrogen atom gained by oxygen insertion (i). The related structural form (ii) is frequently associated with stabilization



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of high-oxidation-state dithiocarbamate complexes. Polarographic reduction of the complexes at mercury electrodes demonstrates that [opdtc]$^-$ is a strongly coordinated ligand since [pdtc]$^-$ is preferentially lost in forming Cr(pdtc)(opdtc). The reduction processes are defined by the following equations: (i) $Cr(pdtc)_2(opdtc) + e^- \rightleftharpoons [Cr(pdtc)_2(opdtc)]^-$; (ii) $[Cr(pdtc)_2(opdtc)]^- \rightarrow Cr(pdtc)(opdtc) + [pdtc]^-$; (iii) $2Cr(pdtc)(opdtc) \rightarrow Cr(pdtc)_2 + Cr(opdtc)_2$; (iv) $Cr(pdtc)_2 + 2e^- \rightarrow Cr(0) + 2[pdtc]^-$; (v) $Cr(opdtc)_2 + 2e^- \rightarrow Cr(0) + 2[opdtc]^-$. Exchange reactions with mercury are also important at mercury electrodes. Other aspects of the redox behavior of $Cr(pdtc)_3$ and $Cr(pdtc)_2(opdtc)$ are also presented as well as a brief report on the redox behavior of the diethyldithiocarbamate analogues.

Introduction

Transition-metal dithiocarbamate complexes have been the subject of numerous electrochemical investigations[1-4] because of their ability to exist as stable entities in a wide variety of oxidation states. For example, the electrochemistry of a range of chromium(III) dithiocarbamate complexes $Cr(dtc)_3$ (Figure 1A) has been considered,[5-8] with both oxidation and reduction processes being noted. The products resulting from oxidation of chromium(III) dithiocarbamates have not been isolated, and even though the electrode process is chemically irreversible in most solvents, it has been assumed by simple analogy with other metal dithiocarbamates that a chromium(IV) species $[Cr(dtc)_3]^+$ is produced. Reduction processes also have not been adequately characterized in most studies, although there seems little doubt that a chromium(II) dithiocarbamate is the product of the first reduction step.

Recently a new type of chromium(III) dithiocarbamate (Figure 1B), $Cr(dtc)_2(odtc)$, incorporating chelate-ring expansion by oxygen insertion has been prepared and characterized.[9] In this complex, the chromium is still formally in oxidation state III and resembles other metal dithiolato complexes that have undergone ring expansion by insertion of a sulfur atom.[10,11] Comparison of the electrochemical oxidation of the normal and sulfur-rich complexes[11] was said to lead to more reversible oxidation for the sulfur-rich complexes. Although data presented in the original work actually do not support this conclusion, Fackler has more recently shown that at very fast scan rates, under conditions of cyclic voltammetry,

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0020-1669/84/1323-1858$01.50/0