data also indicate the presence of two clearly distinct metal release mechanisms for copper transferrin. The first, of dissociative type, is independent on both the nature and the concentration of the chelating agent whereas the second, "ligand-assisted", is strictly related to the type of chelating agent and exhibits saturation dependence on its concentration. The relative importance of the two coexistent mechanisms is also determined by the thermodynamic stability of the metal transferrin adduct; when the metal protein complex is weak, the dissociative mechanism is not negligible. Indeed, the thermodynamic stability of copper(II) transferrin can be estimated to be several orders of magnitude lower than that of iron(III) transferrin. Just to provide an estimate we can refer to a conditional stability constant for zinc(II) of $10^5$ versus $10^{20}$ for iron(III).[41] Metal displacement studies performed on ovotransferrin indicate that copper and zinc should have similar affinities for the protein.[42]

**Registry No.** $ClO_4^-$, 14797-73-0; $NCS^-$, 302-04-5; $Cl^-$, 16887-00-6; $CN^-$, 57-12-5; $P_2O_7^{4-}$, 14000-31-8.

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# Influence of Pentaamminechromium(III) on the Acidity of Coordinated Imidazoles and Pyrazole

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*Received September 1, 1987*

The p$K_a$'s at 298 K, $\mu$ = 0.08, and the temperature dependence (273-338 K) for the deprotonation of the pyrrole NH of imidazole, 2-methylimidazole, and pyrazole coordinated to $Cr(NH_3)_5^{3+}$ are reported. Complexes were isolated as $[Cr(NH_3)_5LH](tfms)_3$ salts. Data summarized for various systems are as follows (ligand, p$K_{298}$, $\Delta H_a°$ in kcal/mol, $\Delta S_a°$ in eu): imidazole = imH, 9.35, 13.9 ± 0.3, 3.9 ± 1.2; 2-methylimidazole = 2-$CH_3$imH, 10.20, 17.0 ± 0.4, 10.4 ± 1.4; pyrazole = pyzH, 6.71, 10.6 ± 0.3, 4.7 ± 0.9. The $(NH_3)_5Cr^{III}LH^{3+}$ p$K_a$, $\Delta H_a°$, and $\Delta S_a°$ values are found to follow very closely the values previously determined for the $(NH_3)_5Co^{III}LH^{3+}$ analogues. A very weak additional band is found on the low-energy side of the $^4T_{2g} \leftarrow {}^4A_{2g}$ d-d transition of the Cr(III) center. This additional band is assigned to the $t_{2g}^3(d\pi) \leftarrow (\pi_1)_L$ LMCT transition from the imH and 2-$CH_3$imH rings at ca. 525 and 550 nm, respectively. These bands are analogous to the LMCT bands observed between low-spin Fe(III) and Ru(III) $d^5$ centers and imidazoles.

## Introduction

The imidazole moiety of the amino acid histidine is an important functional group at the active site of a large number of metalloproteins.[1] The ability of this group to delocalize charge is important in its role to stabilize certain formal oxidation states such as Fe(III) and Fe(IV) in cytochromes or the oxygenated form of myoglobins and hemoglobins. Previous studies in these laboratories have probed the $\pi$ interactions between the imidazole chromophore and various metal centers in octahedral coordination.[2-7] The p$K_a$ of a coordinated imidazole pyrrole hydrogen is a useful measure of the extent that the charge of the central metal is transferred to the ligand by both $\sigma$ induction and $\pi$ donation from the ligand to the metal. Previous studies have been carried out on the low-spin $(CN)_5Fe^{2-}$ unit[2,3] and $(NH_3)_5M^{3+}$ units ($M^{III}$ = Co(III), Rh(III), Ir(III), and Ru(III)).[2-5] These systems revealed that $\pi$-donation into a partially filled $d^n$ set, $d^5$ in the case of $Ru^{III}$, is more important than the ionic potential of a metal center in raising the acidity of coordinated imidazoles. Most imidazoles are good $\sigma$ donors and moderate $\pi$ donors as ligands. Recently the 2-aldehyde-substituted imidazole, 2-CHOimH, was shown to be a strong $\pi$-acceptor group with a $\pi$-acceptor power comparable to that of pyrazine.[6,7] The 2-CHOimH ligand favors the lower oxidation states and forms stable complexes with low-spin $(NH_3)_5Ru^{2+}$ and $(CN)_5Fe^{3-}$ centers.[6,7] The $\pi$-acceptor power of 2-CHOimH stands apart from other substituted imidazoles that are only good $\pi$ donors. We became interested in the influence of the metal center to serve as a better $\pi$-acceptor toward d$\pi$-donating imidazole rings. If $d^3$ Cr(III) complexes of imidazoles and pyrazoles were prepared, one would have a good probe of the influence of imidazole $\pi$ donation for comparison with other M(III) systems because ionic potential influences would be held nearly constant. The influence of Cr(III) on the p$K_a$ of coordinated ligands can be rather large. For example, the p$K_a$ of HCN is lowered from 9.21 to 1.27 upon coordination of the terminal nitrogen to $(H_2O)_5Cr^{3+}$.[11] $(NH_3)_5Cr^{3+}$ raises the acidity of water by 10 orders of magnitude, changing the p$K_a$ from 15.0 to 5.0 upon coordination.[12] The synthetic routes to $(NH_3)_5CrL^{3+}$ species (L = imidazoles or pyrazole) have been accomplished by use of

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the $[(NH_3)_5M(tfms)](tfms)_2$ preparative chemistry.[10] (tfms = $CF_3SO_3^-$.) The effect of $(NH_3)_5Cr^{3+}$ on the acidity of coordinated imidazoles and pyrazoles are described in this report.

## Experimental Section

**Synthesis of Complexes via $(NH_3)_5CrO_3SCF_3^{2+}$.** $[(NH_3)_5CrO_3SCF_3](CF_3SO_3)_2$ was prepared by following literature procedures.[10] $[(NH_3)_5CrCl]Cl_2$ was obtained from Alfa, and $CF_3SO_3H$ was supplied by Aldrich. About 0.40-g samples of $(NH_3)_5Cr(tfms)_3$ were combined with a 20-fold molar excess of ligand in 30.0 mL of dry sulfolane that was freshly distilled. Several attempts to prepare the desired substituted complexes revealed that the commercial sulfolane solvent contains impurities that catalyze multiple ligand substitution, yielding $[(NH_3)_4CrL_2](tfms)_3$, $[(NH_3)_3CrL_3](tfms)_3$, and $[(NH_3)_5CrL](tfms)_3$ mixtures as shown by elemental analysis (Galbraith). Purification of sulfolane (Aldrich) by vacuum distillation (110 °C, 1 Torr) was essential to the production of a suitable $[(NH_3)_5CrL](tfms)_3$ product. The reactions were carried out in 100-mL round-bottom flasks, which were sealed by several layers of Parafilm covering a stopper to close the standard taper 14/20 openings. The contents of the flasks containing sulfolane, Cr(III), and one of the following ligands were stirred for a period of 3 days at room temperature: imidazole (Aldrich, recrystallized from benzene); 2-methylimidazole and pyrazole (used as supplied by Aldrich). The reaction progress was monitored by sampling of small aliquots for examination by UV–visible spectrophotometry. The reaction flasks were stirred continuously by means of a small internal magnetic bar; solutions were protected from room light by wrapping the flasks in aluminum foil. Room temperature was 21 ± 1 °C. Products were recovered from 20 mL of absolute ethanol with 300 mL of dry diethyl ether as described in the literature.[10] Recrystallization, usually three, were continued until dry pink to yellow solids that did not oil out in contact with ether were obtained. Maintenance of systems under low humidity is essential for product recoveries.

Analyses were performed by Galbraith Laboratories on the imidazole and pyrazole complexes. The analytical data fit the formulas $[(NH_3)_5Cr(pyzH)](CF_3SO_3)_3$ and $[(NH_3)_5Cr(imH)](CF_3SO_3)_3 \cdot {}^5/_8(C_2H_5)_2O$. For the pyrazole complex (found, calcd): C (11.15, 11.05), H (3.03, 2.48), N (14.66, 15.02), Cr (8.14, 7.97). For the imidazole complex (found, calcd): C (14.60, 15.11), H (3.38, 3.19), N (14.80, 14.03).

**UV–Visible Spectra.** UV–visible spectra were obtained with the use of a Varian Cary 118C spectrophotometer with solutions in quartz cells.

**Infrared Spectra.** Infrared spectra of all complexes were obtained in KBr pellets pressed at 9 tons pressure. An IBM IR/32 FTIR instrument was scanned from 4000 to 400 $cm^{-1}$ with 64 averaged scans.

**p$K_a$ Determinations.** Aqueous solutions of $(NH_3)_5CrLH^{3+}$ (LH = imidazole, 2-methylimidazole, or pyrazole) were prepared to give 0.0200 M total Cr(III) by weighing samples of $[(NH_3)_5CrLH](tfms)_3$. These solutions were mixed with standard NaOH such that a $Cr^{III}$–complex buffer solution of 0.0100 M $(NH_3)_5CrL^{2+}$ and 0.0100 M $(NH_3)_5CrLH^{3+}$ was prepared. The solution was immediately stored in an ice slush at 0 °C to prevent side reactions including aquation or $NH_3$ loss, which occurs within 10 min above pH 7. Small aliquots of the solution at low temperature were taken and pipetted into one of two identical tubes containing rice-sized stirring bars. The second tube contained either phosphate or borate standard buffers at $\mu$ = 0.10. The tubes were surrounded by a 250-mL insulated beaker mounted on a Model SK12 Stir Kool device (Thermoelectronics Unlimited, Inc.). The Stir Kool Model SK12 device allowed for equilibration of the samples at sequentially higher temperatures at ±0.1 °C from 0 up to 45 °C; 2.00-mL samples of the 0 °C stock buffer of the $Cr^{III}$ complexes were used to measure the $Cr^{III}$ solution pH at several temperatures within a small range. The solution was then discarded, and fresh $Cr^{III}$ buffer was placed in the sample compartment. pH readings as a function of temperature were obtained by using an Accumet Model 810 Fisher Scientific pH meter. A miniature glass electrode combination (glass/SCE with saturated NaCl as the internal electrolyte) was used. The glass electrode was standardized at every temperature by placing the electrode in the standardizing buffer solution in the second compartment. Calibration was made from the data supplied by the manufacturer for pH vs temperature in 5 °C steps. Intermediate pH standard readings were obtained by constructing a smooth calibration curve for interpolation of intermediate temperatures. It is easily shown that the measured pH at each temperature is the p$K_a$ of the $(NH_3)_5CrLH^{3+}$ complex at the given temperature.[4] $\Delta H$ and $\Delta S$ parameters for the acid dissociation were obtained from plots of p$K$ = pH vs. $1/T$.[4]

**Data Reduction.** Linear least-squares procedures were used for plotting of p$K_a$ vs $1/T$; data were plotted and standard deviations were evaluated by programs on an Apple II computer. Graphics plotting was carried out with an IBM-AT.

**Table I.** UV–Visible Transitions for $Cr^{III}$ Complexes

| complex[d] | $\lambda_1$, mm ($\epsilon$) | $\lambda_i$, mm ($\epsilon$) |
|---|---|---|
| $A_5Cr^{III}OH_2^{3+}$ [a] | 476 (36) | 354 (32) |
| $A_5Cr^{III}(pyzH)^{3+}$ [a] | 462 (38) | 349 (36) |
| $A_5Cr^{III}(imH)^{3+}$ [a] | 469 (36) | 354 (36) |
| $A_5Cr^{III}(2\text{-}CH_3imH)^{3+}$ [b] | 469 (39) | 361 (50) |
| $A_5Cr^{III}(1\text{-}CH_3imH)^{3+}$ [b] | 463 (38) | 359 (52) |
| $Cr^{III}A_6^{3+}$ [c] | 465 (42) | 351 (37) |

[a] 1.00 M $HClO_4$. [b] 0.010 M $HClO_4$. [c] Reference 19. [d] A = $NH_3$.

**Table II.** p$K_a$ Values and Enthalpy and Entropy Changes on Deprotonation of Selected Complexes

| species[b] | p$K_a$ (298 K) | $\Delta H_a$, kcal/mol | $\Delta S_a$, eu | $\mu$ | ref |
|---|---|---|---|---|---|
| $A_5Cr(imH)^{3+}$ | 9.35 | 13.9 ± 0.3 | 3.9 ± 1.2 | 0.08 | *a* |
| $A_5Cr(2\text{-}CH_3imH)^{3+}$ | 10.20 | 17.0 ± 0.4 | 10.4 ± 1.4 | 0.08 | *a* |
| $A_5Cr(pyzH)^{3+}$ | 6.71 | 10.6 ± 0.3 | 4.7 ± 0.9 | 0.08 | *a* |
| $A_5Co(imH)^{3+}$ | 9.99 | 14.0 ± 0.5 | 1.3 ± 1.6 | 0.10 | 4 |
| $A_5Co(2\text{-}CH_3imH)^{3+}$ | 10.67 | 17.8 ± 0.7 | 11.2 ± 2.4 | 0.10 | 4 |
| $A_5Rh(imH)^{3+}$ | 9.97 | 13.6 ± 0.3 | 0.1 ± 1.3 | 0.10 | 4 |
| $A_5Ru(imH)^{3+}$ | 8.9 | 10.0 ± 0.8 | 3.7 ± 1.2 | 0.003 | 15 |
| $A_5CrOH_2^{3+}$ | 5.00 | 8.3 ± 0.1 | 5.5 | 0.10 | 12 |
| $A_5RhOH_2^{3+}$ | 6.14 | 9.4 ± 0.1 | | 0.10 | 12 |
| $A_5CoOH_2^{3+}$ | 6.07 | 9.0 ± 0.1 | 2.9 | 0.10 | 12 |
| $A_5RuOH_2^{3+}$ | 4.2; 3.7 | | | 0.10 | 13, 14 |
| $A_5Co(pyzH)^{3+}$ | 6.07 | | | 1.00 | 3 |

[a] This work. [b] A = $NH_3$.

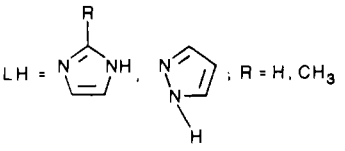
## Results

**Infrared Studies.** IR spectra of the isolated products $[(NH_3)_5CrLH](tfms)_3$ with imidazole, pyrazole, 2-methylimidazole, and 1-methylimidazole were essentially the same as the $[(NH_3)_5Cr(tfms)](tfms)_3$ starting material except that weak ligand bands appear at ca. 1560, 1509 and 1076 $cm^{-1}$ that are absent in the parent complex. IR spectra of the imidazole and pyrazole complexes are shown in Figure 1SM (supplementary material). Ring vibrational and fingerprint modes of imidazoles and pyrazoles are known to decrease significantly on coordination to $Co^{III}$,[3,4] and this effect is also observed for the Cr(III) complexes.

**UV–Visible Data.** The $(NH_3)_5CrLH^{3+}$ complexes were dissolved in 1.0 M and 0.01 M $HClO_4$ for recording the spectrum of the complex, which is fully protonated in solution. The anticipated spectrum with two visible bands was found as shown in Figure 1 for $A_5Cr(imH)^{3+}$ and $A_5Cr(pyzH)^{3+}$ (A = $NH_3$). In spite of nearly identical maxima positions for these complexes, the imidazole complex appears more reddish pink than the yellow pyrazole complex because the lower energy band is broader for the imidazole complexes. There is also a weak shoulder at 525 nm with $\epsilon \cong 15$ $M^{-1}$ $cm^{-1}$ above the base line set by the pyrazole complex for the imidazole complex and at 550 nm for the 2-methylimidazole complex, which we assign as a weak $d\pi \leftarrow (\pi_1)_L$ charge-transfer band. When the pH is adjusted to 10.2 for formation of the imidazolato complex, $A_5Cr(im)^{2+}$, the longer wavelength shoulder shifts to 550 nm while the d–d bands remains within 1 nm of their former values. Data for the maxima and extinctions for the ${}^4T_{2g} \leftarrow {}^4A_{2g}$ ($\lambda_1$) and ${}^4T_{1g} \leftarrow {}^4A_{2g}$ ($\lambda_2$) transitions are given in Table I. An $N_6$ donor set similar to $Cr(NH_3)_6^{3+}$ is observed for the isolated complexes.

**p$K_a$ Determination.** The acid dissociation constants for reaction 1 with LH = imidazole, 2-methylimidazole, and pyrazole were

$$(NH_3)_5CrLH^{3+} \rightleftarrows (NH_3)_5CrL^{2+} + H_3O^+ \qquad (1)$$




determined as described in the Experimental Section. The p$K_a$'s at 298 K and the values for $\Delta H_a°$ and $\Delta S_a°$ are recorded in Table II. Plots of p$K_a$ vs $1/T$, which were obtained from the experimental pH vs temperature measurements, are given in Figure 2SM (supplementary material).

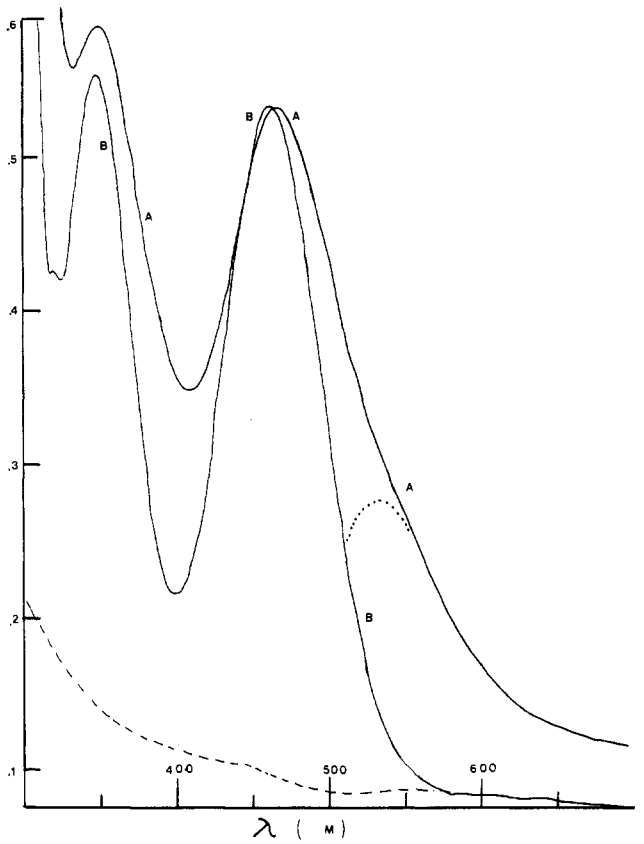



**Figure 1.** UV–visible electronic spectra of $(NH_3)_5CrLH^{3+}$ complexes: (A) imH complex, (B) pyzH complex. Both complexes are $1.15 \times 10^{-2}$ M in 1.00 M and $HClO_4$; 1.00-cm cell. The dotted curve shows the probable location of the LMCT band and was obtained by subtraction of B from A in the long wavelength region. The dashed curve is the solvent-cell blank.

## Discussion

The proton $pK_a$'s for HCN, $H_2O$, imidazole, and pyrazole are 9.21,[16] 15.0,[16] 14.2,[17] and 14.2,[17] respectively. Upon coordination there is a lowering of the $pK_a$ depending on the charge and identity of the coordinating metal. In the case of the $(NH_3)_5CoLH^{3+}$ series, the $pK_a$ decreases for $H_2O$, imH, and pyzH by 8.93, 4.21, and 8.13 units, respectively. Data in Table II for $(NH_3)_5CrLH^{3+}$ species show $pK_a$'s of 9.35 (imH), 6.71 (pyzH), and 5.00 ($H_2O$). The reductions in $pK_a$ for $Cr^{III}$ ($\Delta(pK_a)$ vs free ligand) are 10.0, 4.85, and 7.76 for $H_2O$, imH, and pyzH respectively. When the $Cr^{III}$ series is compared to the $Co^{III}$ series, the influences of $Cr^{III}$ ($\Delta\Delta(pK_a)$) are +1.07, +0.64, and −0.37 log units more active.

$\Delta(pK_a)$'s for $H_2O$ in other systems have followed the trend

$$\underset{10.8}{Ru(III)} > \underset{10.0}{Cr(III)} > \underset{8.93}{Co(III)} \sim \underset{8.86}{Rh(III)}$$

for the increasing acidity of a coordinated ligand.[12,13] With imidazole as the ligand,[4,15] the order in $\Delta(pK_a)$ vs the free ligand is much closer together:

$$\underset{5.3}{Ru(III)} > \underset{4.85}{Cr(III)} \simeq \underset{4.21}{Co(III)} \sim \underset{4.23}{Rh(III)}$$

With pyrazole as the ligand[3] the order in $\Delta(pK_a)$ vs free energy is nearly the same for all three centers:

$$\underset{8.22}{Ru(III)} > \underset{8.13}{Co(III)} > \underset{7.69}{Cr(III)}$$

Comparison of the $H_2O$, pyzH, and imH complexes' data show that the influence of metal 3+ centers attenuates rapidly with distance between the metal ion and the titratable hydrogen. Thus the sensitivity of the $pK_a$ to the metal center follows the order $H_2O$ > pyrazole > imidazole. This trend has been noted before;[3] the Cr(III) complexes not only obey this rule but also generally fall into the position of lessening influence between Ru(III) and Co(III) as identified for $H_2O$.[12,13]

Some interesting comparisons in the trends in $\Delta H_a$ and $\Delta S_a$ for acid dissociation may be made between $(NH_3)_5CrLH^{3+}$ and $(NH_3)_5CoLH^{3+}$ complexes. $\Delta H_a$ ($Cr^{III}$:$Co^{III}$) values are seen to be 13.9 ± 0.3 and 14.0 ± 0.5 kcal/mol for imH and 17.0 ± 0.4 and 17.8 ± 0.7 kcal/mol for $2CH_3$imH. $\Delta S_a$ values are all positive small numbers as anticipated for reaction 1: 3.9 ± 1.2 and 1.3 ± 1.6 eu for imH $Cr^{III}$:$Co^{III}$ complexes and 10.4 ± 1.4 and 11.2 ± 2.4 eu for $2CH_3$imH complexes. The close agreement between the values of $\Delta H_a$ and $\Delta S_a$ for both pairs is rather striking. This suggests that there is not much difference in the bond energies of the pyrrole hydrogens for each pair of complexes. That $\Delta H_a$ is larger for $2CH_3$imH vs imH complexes by virtually the same 3.4 kcal/mol for the $(NH_3)_5M(2CH_3imH)^{3+}$ species ($M^{III} = Co^{III}$ and $Cr^{III}$) and that the $\Delta S_a$ values are also separated by 8.2 eu are significant. First, 2-$CH_3$ substitution raises the basicity of the pyrrole nitrogen by the same amount; second, solvation values for all four species are similar and the imidazolato form of the $2CH_3$imH complex is solvated less by about one water molecule's rotational entropy of 10 eu compared to the solvation of the $(NH_3)_5Cr(im)^{2+}$ species. Perhaps one less $H_2O$ molecule is contained in the solvation sphere of $(NH_3)_5Cr(2CH_3im)^{2+}$; the molar volumes of $CH_3$ and $H_2O$ are quite similar: ca. 22 vs 18 $cm^3/mol$.[18]

The $t_{2g}^3$ configuration for Cr(III) offers a spacially empty orbital toward a $\pi$-donor ligand twice as available as for the low-spin $d^5$ complexes in octahedral coordination. The advantage of a more empty $t_{2g}$ set is not manifest in a greater change in acidity for coordinated $\pi$-donating, titratable ligands ($H_2O$, imH, pyzH, etc.). This can be interpreted as the failure of Cr(III) to utilize its symmetry advantage and electron count due to the smaller effective nuclear charge of early transition-metal centers compared to later first-row-series members or to second-row-metal centers. As a consequence the polarizing ability of Cr(III) toward ligand $\pi$ electrons is not particularly strong. The intensity of the $d\pi \leftarrow (\pi_1)_L$ charge-transfer band of $(NH_3)_5CrLH^{3+}$ (L = imH or $2CH_3$imH) is very weak at 525 nm, $\epsilon \sim 15$ $M^{-1}$ $cm^{-1}$ compared to $\epsilon$ ca. 200 $M^{-1}$ $cm^{-1}$ for $(NH_3)_5RuLH^{3+}$ and ca. 400 $M^{-1}$ $cm^{-1}$ for $(CN)_5FeLH^{2-}$ with analogous $d\pi \leftarrow (\pi_1)_L$ bands.[3,5] The assignment of the lowest energy band to an LMCT transition is supported by the sensitivity of the position of the band to ring substituents. Intense absorptions of charge-transfer character have been observed previously with Cr(III) complexes of catecholato and acetylacetonato ligands;[8,9] these delocalized organic anions are stronger $\pi$ donors than the imidazoles. The primary d–d transition for both $(NH_3)_5Cr(imH)^{3+}$ and $(NH_3)_5Cr(2\text{-}CH_3imH)^{3+}$ occurs at 469 nm while the shoulder band shifts to 550 nm (2-$CH_3$imH complex) from the 525-nm position of the parent $(NH_3)_5Cr(imH)^{3+}$ species. The sensitivity of the imidazole-to-metal LMCT transition to ring methylation has been noted previously for $d^5$ acceptor metal centers.[3-5]

Deprotonation of the $(NH_3)_5Cr(imH)^{3+}$ complex promotes a shift of this band by about 25 nm to lower energy while the Ru(III) and Fe(III) analogues shift between 95 and 150 nm upon deprotonation, which suggests greater overall mixing of the metal and ligand wave functions in the latter complexes as compared to Cr(III) complexes.

The $(NH_3)_5CrLH^{3+}$ series (LH = imH, 2-$CH_3$imH, pyzH and 1-$CH_3$imH) proved more difficult to handle experimentally than their Co(III) and Ru(III) analogues because the complexes are prone to aquation, hydrolysis, and polymerization reactions. Blue precipitates form in under ~15–30 min near room temperature and physiological pH. The absence of tuning of the properties of the Cr(III) center by $\pi$ donors and even more so presumably by $\pi$ acceptors, as well as the inherent instability of the Cr(III)–imidazole bond toward aquation, would be a major factor

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(17) Yagil, G. *Tetrahedron* **1967**, *23*, 2855.
(18) Calculated from the molar volumes of $H_2O$ and $CH_3OH$.
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in rejecting $Cr^{III}$ as an important biologically active metal center during evolution. The natural abundance of chromium would also oppose its evolutionary selection.

**Acknowledgment.** We gratefully acknowledge support for this work through the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE8417751). Early synthetic efforts on this project were also carried out by L. W. Warner.

**Registry No.** 2-$CH_3$imH, 693-98-1; imH, 288-32-4; pyzH, 288-13-1; $[A_5Cr(pyzH)](tfms)_3$, 112793-26-7; $[A_5Cr(imH)](tfms)_3$, 112793-27-8; $[A_5Cr(2\text{-}CH_3imH)](tfms)_3$, 112793-29-0; $A_5Cr^{III}(1\text{-}CH_3imH)^{3+}$, 112793-30-3; $A_5Cr^{III}OH_2^{3+}$, 15975-47-0; $[A_5Cr(tfms)](tfms)_2$, 84254-61-5.

**Supplementary Material Available:** IR spectra of the imidazole and pyrazole complexes (Figure 1SM) and plots of $pK_a$ versus $1/T$ (Figure 2SM) (2 pages). Ordering information is given on any current masthead page.

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# Spin-Trapping Studies of the Reduction of $O_2$ and $H_2O_2$ by Titanium(III), Iron(II), and Ruthenium(II) Complexes

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*Received September 25, 1987*

The reductions of $H_2O_2$ and $O_2$ by $Ti(edta)(H_2O)^-$, $Ti(H_2O)_6^{3+}$, $Fe(edta)^{2-}$, $Fe(H_2O)_6^{2+}$, and $Ru(NH_3)_6^{2+}$ have been studied by the spin-trapping technique using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) and *N*-*tert*-butyl-$\alpha$-phenylnitrone (PBN) radical traps. The resultant radical adducts RDMPO• and RPBN• have been characterized by ESR spectroscopy in agreement with literature values. $Ti(edta)(H_2O)^-$, $Fe(edta)^{2-}$, $Fe(H_2O)_6^{2+}$, and $Ru(NH_3)_6^{2+}$ reductions of $H_2O_2$ produce HO• identified by the HO–DMPO• and HO–PBN• spectra. HO• formed in these reductions may be intercepted by chemical mediators ($CH_3OH$, $C_2H_5OH$, $(CH_3)_2CO$, $(CH_3)_3COH$) to provide more long-lived secondary carbon-centered radicals, which are trapped by DMPO or PBN. Excellent spectral matches for RDMPO• and RPBN• species are obtained for the $Ti(edta)(H_2O)^-$, $Fe(edta)^{2-}$, $Fe(H_2O)_6^{2+}$, $Ti(H_2O)_6^{3+}$, and $Ru(NH_3)_6^{2+}$ reductants for $H_2O_2$ in the presence or absence of mediators. When $O_2$ is used as the oxidant for $Ru(NH_3)_6^{2+}$, this reaction known to proceed outer sphere via $O_2^-$, only the dismutation/reduction product (HO•) is trapped at pH 6.86. Both $HO_2$• and HO• are trapped at pH 2.57 in a 1.0:7.6 ratio. $Ti(edta)(H_2O)^-$ is known to be oxidized inner sphere by $O_2$ via coordinated $O_2^-$. No radical adducts for the $Ti(edta)(H_2O)^-/O_2$/radical trap system are observed with or without mediators in the solvent cage. The reduction of $O_2$ by either $Fe(edta)^{2-}$ or $Fe_2(tha)^{2-}$ proceeds by an inner-sphere pathway in which the coordinated $O_2^-$ survives long enough to attack an adjacent carboxylate moiety, forming a trappable ligand-based carbon-centered radical, or to attack sacrificial mediators in the solvent cage.

## Introduction

The reduction of $O_2$ and $H_2O_2$ is an important chemical problem. Its ramifications are the central issue in the energy-transducing apparatus and protective enzymes for aerobic biochemical cells, the rate-controlling factors of many electrochemical fuel cells, and the wide class of chemical autoxidations of inorganic and organic substrates. A crucial question for the reactivity of $O_2$ and $H_2O_2$ with transition-metal centers is whether the processes proceed by inner- or outer-sphere paths. Inner-sphere reduction of $H_2O_2$ by labile metal centers frequently proceeds about $10^4$ times faster than when $H_2O_2$ is restricted to an outer-sphere role.[1] Reduction of $H_2O_2$ by labile aqua transition-metal reductants such as $Fe(H_2O)_6^{2+}$, $Cr(H_2O)_6^{2+}$, or $Ti(H_2O)_6^{3+}$ proceeds predominantly by one-electron paths with formation of hydroxyl radical (HO•) as the initial product.[2-4] The reduction sequence for $O_2$ is typically more complicated in aqueous solution because any $O_2^-$ that is formed by a one-electron pathway carries out a self-dismutation into $O_2$ and $H_2O_2$. Since the latter product is also chemically reactive, it is often difficult to discern between a reaction of one-electron steps involving $O_2^-$ and a two-electron reduction forming $H_2O_2$ directly. This problem has been more frequently addressed by biophysical chemists in the study of biological redox reactions such as the electron transport chain in spinach chloroplasts[5] or in the characterization of bleomycin-type antitumor drugs and their chemical models.[6-9] The technique of spin trapping with DMPO or PBN has proven useful as a diagnostic tool in detection of intermediates that are produced in $O_2$ and $H_2O_2$ reductions from organic reagents. The technique has been reviewed previously by Janzen[9] and by Evans.[10] The use of spin-trapping reagents to study metal ion/peroxide redox reactions is less common in the literature,[11-13] but the tool was recently added to the mechanistic arsenal for inorganic chemists in the study of $H_2O_2$ reductions by $Fe(edta)^{2-}$, $Ti(edta)(H_2O)^-$, and $Ru(NH_3)_6^{2+}$.[14] Myser and Shepherd have used the DMPO spin trap in conjunction with parallel trapping agents to examine the mechanism of the $O_2$ oxidations of binuclear polyamino carboxylate complexes including $Fe_2(tha)^{2-}$[15] and $V_2O(tha)^{2-}$.[16] These binuclear complexes of triethylenetetraaminehexaacetate, $tha^{6-}$, have proven to be interesting comparison systems for the hemerythrin $O_2$-carrier enzyme[15] and for certain features of the

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