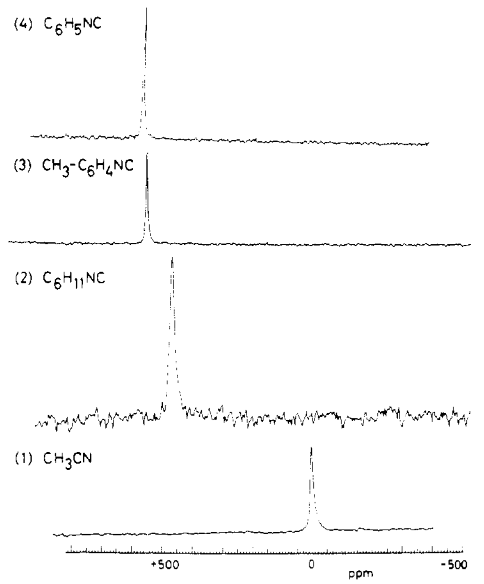

Figure 1. ^{63}Cu NMR spectra at 25 °C of $[Cu(CH_3CN)_4]ClO_4$ (1), $[Cu(C_6H_{11}NC)_4]ClO_4$ (2), $[Cu(CH_3C_6H_4NC)_4]ClO_4$ (3), and $[Cu(C_6H_5NC)_4]ClO_4$ (4).

The apparent increase antiparallels the increase of the ligand basicity:[13] 4-Me-py, $pK_a = 6.03$; 3-Me-py, $pK_a = 5.68$; py, $pK_a = 5.23$. We have demonstrated[3b,14] that ligands having good π-acceptor capability cause the metal to ligand charge-transfer (MLCT) band, L←Cu, to shift to longer wavelength. The copper(I) complexes of these pyridines give MLCT bands in the order 319 nm (4-Me-py) < 330 nm (3-Me-py and py). On this basis, the increasing order of π-acceptor capability is 4-Me-py < 3-Me-py $\approx$ py, indicative of good agreement with that in ^{63}Cu chemical shift. The dominant factor influencing the chemical shift of the ^{63}Cu NMR signal is linked to the π-acceptor properties of the pyridine nitrogen.

Second, the substituent effect on $\Delta\delta$ is estimated for copper(I) complexes of isocyanides as well as cyanide ion. The ^{63}Cu NMR spectra of $[Cu(RNC)_4]ClO_4$ are first observed here, and some of them are shown in Figure 1. A single sharp line is observed with quite a large downfield shift ranging 451-553 ppm. Table I exhibits that the downfield shift for the aryl isocyanide is greater than that for the alkyl isocyanide, which is also accounted for by the π-acceptor properties because the π-acceptor capability of aryl isocyanide is superior to that of alkyl isocyanide.[15] The IR stretching frequencies and ^{13}C NMR shift of the NC group of the aryl isocyanides have shown that there is minor electronic coupling[15,17] between the NC and the phenyl group. The ^{63}Cu NMR spectra, however, distinguish well between substituents attached to the 4-position of the phenyl isocyanide. With Me and Cl the observed shift varies ca. 6 ppm. The cyanide ion also shows a downfield shift[18] comparable with that of isocyanides. On the other hand, nitrile complexes of copper(I), $Cu(RCN)_4$ ($R = CH_3$ and C_2H_5), show a considerable upfield shift, attributable to the poor π-acceptor capability of RCN.[19] Table I reveals that propionitrile experiences a downfield shift 13 ppm more than that in the case of acetonitrile, indicative of the sensitiveness of the ^{36}Cu shift.

In conclusion, the ^{63}Cu resonances are deshielded with an increase in π-acceptor capability of the coordinated ligand. The substituent effect on the metal-ligand bonding in homologous series is reflected well by ^{63}Cu NMR spectra.

Acknowledgment. We appreciate the assistance of H. Konoike, K. Kameda, and Y. Ueda. This work is supported in part by grants from the Ministry of Education of Japan.

Registry No. $[Cu(CH_3CN)_4]ClO_4$, 14057-91-1; $[Cu(C_2H_5CN)_4]ClO_4$, 15170-21-5; $[Cu(4\text{-}CH_3py)_4]ClO_4$, 35232-25-8; $[Cu(3\text{-}CH_3py)_4]ClO_4$, 93110-83-9; $[Cu(py)_4]ClO_4$, 21465-66-7; $[Cu(CN)_4]^{3-}$, 19441-11-3; $[Cu(C_4H_9NC)_4]ClO_4$, 93110-85-1; $[Cu(C_6H_{11}NC)_4]ClO_4$, 93110-87-3; $[Cu(4\text{-}MeC_6H_4NC)_4]ClO_4$, 77744-79-7; $[Cu(C_6H_5NC)_4]ClO_4$, 93110-88-4; $[Cu(4\text{-}ClC_6H_4NC)_4]ClO_4$, 93110-89-5; ^{63}Cu, 14191-84-5.

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Detailed Correlations between the Ligand-to-Metal Charge-Transfer (LMCT) Spectra of Copper(II) and Ruthenium(III) Imidazoles and Imidazolates. Electronic Structures of Carbon-Bound Ruthenium(III) Imidazoles and Imidazolates

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The common occurrence of histidine imidazole donors in numerous copper (and iron) proteins has prompted many studies of metal ion-imidazole interactions. We have been studying the imidazole → Cu(II) ligand-to-metal charge-transfer (LMCT) absorptions of model Cu(II) complexes in order to identify and better understand corresponding absorptions in the spectra of Cu(II) proteins.[1,2] Our previous studies have employed Cu(II)-tetrakis (imidazole) systems, and we have been searching for simpler model complexes that possess only one imidazole in order to bypass possible electronic and steric interactions among the imidazole units. We are concerned that such interactions may be partly responsible for the currently inexplicable differences in intensities between the LMCT absorptions of solid-state and solution $Cu(imidazole)_4^{2+}$ chromophores.[1,2] The possible motion of the imidazole ligands around the Cu-N axes makes it difficult to correlate the geometric as well as electronic structures of these complexes in the solid-state and solution phases. Moreover, the LMCT absorptions of Cu(II)-imidazolate chromophores are poorly characterized. Little is known aside from the observation that Cu(II)-imidazolate chromophores exhibit a LMCT absorption in the near-UV region that is not present in the spectra of reference Cu(II)-imidazole complexes.[2] Furthermore, the systems studied were polynuclear imidazolate-bridged Cu(II) complexes, and their suitability as spectroscopic models for the imidazolate-bridged Cu(II)/Zn(II) unit of superoxide dismutase must be suspect.

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Table I. Calculated Effects of Ring Methylation on the Orbital and Excited-State Energies of Imidazole and Imidazolium[a, b]

	Im-*N*	Im-*C*	4-MeIm-*N*	4,5-Me_2Im-*N*	4,5-Me_2Im-*C*
π_2*	1.30	1.31	1.39	1.45	1.44
π_1*	0.18	0.84	0.24	0.33	1.04
π_1	−8.71	−8.67	−8.46	−8.08	−8.00
n	−10.17	−9.66	−10.06	−9.90	−9.44
π_2	−10.61	−11.21	−10.40	−10.34	−10.98
n → π*	4.37, 0.01[c]	3.86, 0.04[c]	4.37, 0.01[c]	4.34, 0.01[c]	3.84, 0.04[c]
π → π*	5.48, 0.18	5.79, 0.14	5.27, 0.17	5.07, 0.20	5.79, 0.14
n → π*	5.82, 0.003	6.06, 0.00	5.82, 0.003	5.76, 0.003	6.09, 0.00
π → π*	6.23, 0.09	6.44, 0.24	6.19, 0.09	6.00, 0.11	6.07, 0.30

[a] Calculated by the INDO/S method of ref 15. The values for imidazoles have been reproduced from ref 1a. The molecular geometry used for imidazolium (Im-*C*) was that reported in ref 10. [b] Energies are given in eV. [c] Oscillator strength.

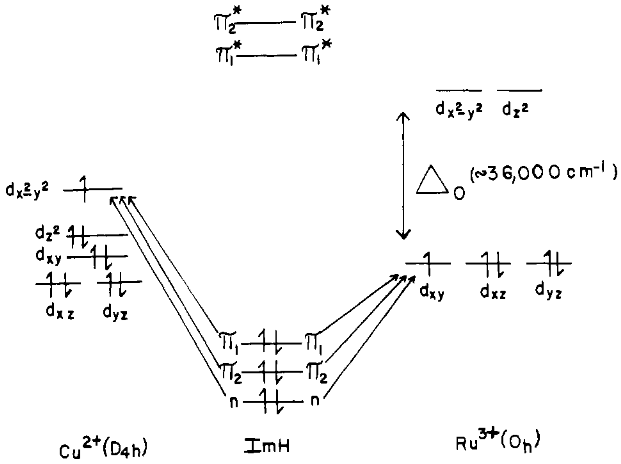

Figure 1. Schematic illustration of the LMCT transitions possible between a ligated imidazole unit and Cu^{2+} (D_{4h}) or Ru^{3+} (O_h).

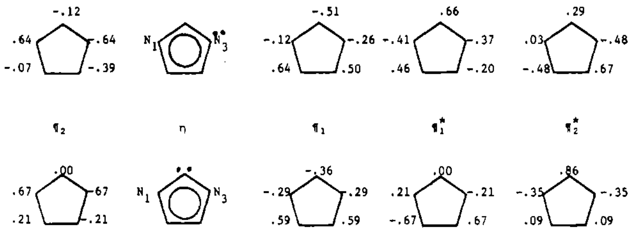

Figure 2. Coefficients of the π molecular orbitals in imidazole (top) and imidazolium (INDO/S). The imidazolate MO coefficients closely resemble the imidazole coefficients. Methylation does not appreciably change the calculated MO coefficients of either molecule.

Some of the above spectroscopic questions may be pursued profitably by examining the LMCT spectra reported for chromophores other than those containing Cu(II). This is primarily because the LMCT absorptions from the occupied ligand orbitals of highest energies into the single Cu(II) d vacancy essentially reflect the electronic structures of the *ligands*. Potentially complicated electron–electron interactions[3] are not possible within an excited-state configuration consisting of a d^{10} (closed shell) Cu(I) ion and an imidazole radical cation. A similar situation, illustrated schematically in Figure 1, pertains to complexes of Ru(III). LMCT absorptions into the sole *accessible* d vacancy of the Ru(III) t_{2g}^5 subshell should yield an analogous uncomplicated excited state consisting of the closed t_{2g}^6 subshell and a ligand radical cation. Owing to the large value of Δ_0 (>36 000 cm^{-1}) expected for approximately octahedral Ru(III) complexes of nitrogen donor ligands,[4] LMCT to the high-lying empty metal e_g* orbitals should occur at very short wavelengths, possibly beyond the quartz UV range. Furthermore, MCD studies[8] indicate that the LMCT absorptions originating from nitrogen donor ligands are not appreciably split by spin–orbit coupling with Ru(III) (ζ = 1180 cm^{-1}). Differences in band polarizations and intensities might be expected between the LMCT spectra of Cu(II)–imidazole and Ru(III)–imidazole complexes owing in part to the fact that the metal ion d vacancies have σ* and π* characters, respectively. These effects cannot be quantified from the currently available spectroscopic data. However, as will be demonstrated below, there are significant insights into the LMCT spectra of Cu(II) chromophores that can be gained from an analysis of the comprehensive solution spectra reported for Ru(III)–pentaammine systems containing as additional ligation either N-bound or C-bound imidazole or imidazolate.[9] We offer here a fuller interpretation of the LMCT absorption spectra reported for these Ru(III) species and rationalize on the basis of semiempirical molecular orbital (MO) calculations the intensity and energy changes resulting from (a) alkylation of the ligand rings, (b) linkage isomerism of the imidazole ligands from Ru(III)–N to Ru(III)–C bonding,[10] and (c) deprotonation of either the N- or C-bound ligands.

Results and Discussion

As indicated above, the electronic structures of nitrogen-bound (Im-*N*) and carbon-bound (Im-*C*) ligands will play a prominent role for the absorption spectra. In particular, the energies of the upper occupied ligand orbitals and the MO coefficients at the metal ion binding site will effect the positions and intensities of the observed LMCT absorptions. Calculated energies of the spectroscopically relevant Im-*N* and Im-*C* orbitals (occupied π_1 (HOMO), π_2, and n; unoccupied π_1* and π_2*) are presented in Table I, and the coefficients of the π MO's are shown in Figure 2. The remaining occupied ligand orbitals are well removed (>3 eV) toward lower energy and are consequently not of spectroscopic interest here. Considerable similarities exist in the compositions of the π_1 and π_2 orbitals of parent as well as methylated Im-*N* and Im-*C*, but the separation in orbital energy between π_1 and π_2 is about 0.7 eV greater for Im-*C* ligands. Larger differences are observed in the compositions of the unoccupied π orbitals. In

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(4) We adopt the plausible suggestions of Ballhausen[5] that the lowest energy LF absorption of $Ru(NH_3)_6^{3+}$ is the transition $^2T_{2g} \rightarrow {}^2A_{2g}$ of energy $\Delta_0 - 3F_2 - 20F_4$ with the estimates $F_2 = 10F_4 \simeq 1000$ cm^{-1}. The lowest energy electronic absorption of aqueous $[Ru(NH_3)_6]Cl_3$ was reported by Hartmann and Buschbeck[6] at 36 200 cm^{-1} (ϵ = 530); Meyer and Taube[7] reported absorptions at ~31 300 cm^{-1} (ϵ ~ 100) and 36 500 cm^{-1} (ϵ = 473). Consequently, the lower limit of Δ_0 may be estimated as 31 300 cm^{-1} + 5000 cm^{-1} ≃ 36 000 cm^{-1}.

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Table II. Spectral Assignments for $(NH_3)_5Ru^{III}L$ Complexes[a-c]

assignment	L = Im-*N*	L = *N*-MeIm-*N*	L = 4-MeIm-*N*	L = 4,5-Me_2Im-*N*
$\pi_2 \rightarrow$ Ru	33 400 (1800)	32 200 (2310)	33 000 (2020)	32 100 (2190)
$\pi_1 \rightarrow$ Ru	23 300 (259)	23 700 (186)	21 300 (267)	19 300 (168)
	L = Im-N^-		L = 4-MeIm-N^-	L = 4,5-Me_2Im-N^-
$\pi_2 \rightarrow$ Ru	27 700 (2990)		27 000 (3000)	25 500 (2830)
$\pi_1 \rightarrow$ Ru	18 000 (~350)		16 700 (472)	~13 300 (~750)
	L = Im-*C*		L = Hist-*C*	L = 4,5-Me_2Im-*C*
$\pi_1 \rightarrow$ Ru	20 700 (890)		19 400 (1450)[d]	16 600 (5100)[d]
	L = Im-C^-			
$\pi_1 \rightarrow$ Ru	17 000 (1300)			

[a] Spectroscopic data and ligand notation from ref 9. [b] Energies in cm^{-1}. [c] Molar extinction coefficient in parentheses. [d] Spectra of *trans*-L'$(NH_3)_4$RuL, where L' = H_2O.

particular, the C(2) ligand donor site in Im-*C* participates very little in the occupied orbitals and hence completely dominates one of the π^* orbitals (π_2^*). In view of the remarkable affinity of Ru(II) for π-acid ligands,[11] we suggest that the superior π-back-bonding possible with Im-*C* ligation supplies the major driving force in the heretofore unprecedented conversion of $(NH_3)_5Ru(Im\text{-}N)^{2+}$ to its linkage isomer $(NH_3)_5Ru(Im\text{-}C)^{2+}$.[10] Favorable interaction with the more accessible lone pair on C(2), which is about 0.5 eV destabilized relative to the lone pair on N(3) in Im-*N*, stabilizes the Ru–C σ-bonding.

Successive alkylation of imidazole at the carbon positions systematically raises the energy of π_1, which is mainly localized on the carbons. For tetrakis Cu(II) complexes, this results in a significant red shift of the lowest energy LMCT absorption, assigned as π_1(Im-*N*) $\rightarrow$ Cu(II).[1] A second LMCT absorption about 7000 cm^{-1} higher in energy and more intense in the solid-state spectra was assigned as π_2(Im-*N*) $\rightarrow$ Cu(II) on the basis of the π_1 and π_2 MO coefficients at the Cu(II) binding site [N(3)] and the anticipated larger stabilization of the n than of the π_2 orbital upon complexation with the metal. Associated with imidazolate- (Im-N^--) bridged Cu(II) units is the appearance of an additional LMCT absorption at lower energy, the details of which are not well understood.[1b]

The Ru(Im-*N*) complexes exhibit two low-energy CT absorptions (Table II) that are not masked by the weak ligand field absorptions[4] and are well removed from the intense ligand $\pi \rightarrow \pi^*$ absorptions at higher energies.[1] Successive methylation of ring carbons 4 and 5 (Table II) causes the lowest energy CT band to red shift from 23 300 through 21 300 to 19 300 cm^{-1}. The Ru(III) ion actually becomes *less* oxidizing[9] upon alkylation of the ligand. For example, $(NH_3)_5Ru(4,5\text{-}Me_2Im\text{-}N)^{3+/2+}$ is 0.025 V (200 cm^{-1}) less oxidizing than $(NH_3)_5Ru(Im\text{-}N)^{3+/2+}$. The red shift of this CT absorption can thus be attributed almost exclusively to the pronounced destabilization of π_1 (HOMO) by ring methylation (Table I)[1a] and strongly supports the assignment of this absorption as π_1(Im-*N*) $\rightarrow$ Ru LMCT. The alternative assignment to Ru $\rightarrow$ π_1^*(Im-*N*) MLCT would lead to the prediction of a blue shift, since π_1^* becomes destabilized by ca. 1200 cm^{-1} upon dimethylation of the imidazole. The second CT absorption at about 33 000 cm^{-1} (ϵ = 1880–2310) dwarfs the neighboring ligand field absorptions[4] and is a factor of 7–13 times more intense than the lowest energy CT absorption (ϵ = 168–267). This CT band also undergoes a small *red shift* ($\sim$1300 cm^{-1}) upon ring alkylation, and hence assignment as a π_2(Im-*N*) $\rightarrow$ Ru(III) LMCT is far preferable to the alternative Ru(III) $\rightarrow$ π_1^*(Im-*N*) MLCT; π_2 is calculated (Table I) to be destabilized by ca. 2200 cm^{-1} in the dimethylated species. Furthermore, the band intensity ratios quoted above best agree with that qualitatively predicted for LMCT by the π_2 and π_1 MO coefficients at the N(3) ligand donor site; i.e., $(-0.64)^2/0.26^2 = 6.0$. Assignment of the second CT absorption as MLCT Ru $\rightarrow$ π_1^*(Im-*N*) would yield a predicted intensity ratio from the π_1^* and π_1 coefficients of $(-0.37)^2/0.26^2 = 2.0$.

Finally, our assignment scheme as LMCT only is supported by detailed analysis of the ligand deprotonation studies, which reveal, most importantly, that two bands are still observed in the region for CT absorptions (Table II).[9] Relative to the π_1- and π_2(Im-*N*) $\rightarrow$ Ru LMCT absorptions, these absorptions of the Ru(Im-N^-) species consistently are red shifted by 5000–6000 cm^{-1}. Ring methylation causes the lowest energy absorption to shift from 18 000 to 13 300 cm^{-1}. Also, the band intensity ratios (3.8–8.5) are similar to those observed for π_1- and π_2(Im-*N*) $\rightarrow$ Ru LMCT. This striking correlation of CT bands for Ru^{III}(Im-*N*) and Ru^{III}(Im-N^-) species indicates that the electronic structures of these ligands are closely related, in particular as pertains to their π systems.[2] Deprotonation destabilizes the occupied (π_1, π_2) and unoccupied (π_1^*, π_2^*) orbitals with the predicted result that LMCT absorptions should red shift relative to those of the neutral parent species, whereas MLCT absorptions should blue shift. Consequently, the above considerations lead us to assign these two red-shifted CT absorptions of Ru^{III}(Im-N^-) species as π_1- and π_2(Im-N^-) $\rightarrow$ Ru LMCT, respectively. Interestingly, the conversion of Ru(Im-N^-) monomers to imidazolate-bridged Ru(III) dimers does not result in profound spectral changes. A Ru(III) dimeric species bridged by a (histidine) imidazolate ligand[12] (electronically very similar to 4-MeIm-N^-) exhibits absorptions at 19 000 ($\epsilon \sim 850$) and 27 700 cm^{-1} ($\epsilon \sim 2500$), which we logically assign as π_1- and π_2(Hist-N^-) $\rightarrow$ Ru LMCT, respectively.

Linkage isomerism results in a slight red shift ($\sim$2500 cm^{-1}) of the $\pi_1 \rightarrow$ Ru LMCT absorptions, and additional red shifts are caused by successive methylation of the ligand. The threefold increase in intensity of the $\pi_1 \rightarrow$ Ru LMCT band for Ru(Im-*C*) (ϵ = 890) relative to that of Ru(Im-*N*) (ϵ = 250) is qualitatively predicted by the respective π_1 MO coefficients at the ligand donor sites, C(2) in Im-*C* and N(3) in Im-*N*, respectively. This ratio of electron densities is $(-0.36)^2/0.26^2 = 1.9$. The surprisingly large intensity of this $\pi_1 \rightarrow$ Ru absorption for the trans complexes L'$(NH_3)_4$RuL (L' = H_2O; L = Hist-*C*, 4,5-Me_2Im-*C*), Table II, additionally may have been increased by similar MO effects as suggested for *trans*-$(NH_3)_4RuX_2^+$ (X = Cl^-, Br^-, I^-).[13] As might be expected from the behavior of the Ru(Im-*N*) complexes, ligand deprotonation of the Ru(Im-*C*) species results in a 4000-cm^{-1} red shift of the $\pi_1 \rightarrow$ Ru LMCT. However, LMCT absorption associated with π_2 appears absent in the spectra of the Ru^{III}(Im-*C*) and Ru^{III}(Im-C^-) species. A combination of two effects may be responsible for this. First, the symmetry-imposed node for the π_2 orbital at the C(2) position in the free ligand implies that the transitions π_2(Im-*C*) $\rightarrow$ Ru and π_2-

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(Im-C^-) $\rightarrow$ Ru should carry small oscillator strengths even in the reduced symmetry present in the complex. Second, the greater π_1–π_2 separations calculated for Im-*C* (Table I) and expected for Im-C^- should cause this second CT absorption to be shifted toward higher energy (about 6000 cm^{-1}) relative to the corresponding LMCT of the Ru(Im-*N*) and Ru(Im-N^-) linkage isomers. Due to their expected weakness, they would probably be obscured by the tail of the intense ligand $\pi \rightarrow \pi^*$ absorptions.[14]

Concluding Remarks

The above results illuminate several aspects of corresponding LMCT absorptions in Cu(II) systems. First, the lowest energy near-UV absorption of the Cu^{II}(Hist-N^-)Zn^{II} unit in superoxide dismutase logically corresponds to the expected π_1-(Hist-N^-) $\rightarrow$ Cu(II) LMCT.[16] It also would appear that Cu^{II}(Im-N^-)Cu^{II} dimers[17] are suitable spectroscopic models for this aspect of the protein chromophore. On the basis of the results of the Ru(III) model systems, the heretofore unknown Cu^{II}(Im-N^-) unit and Cu^{II}(Im-N^-)Cu^{II} models ought to exhibit comparable π(Im-N^-) $\rightarrow$ Cu(II) LMCT absorptions. Conversion of either species to a Cu^{II}(Im-N^-)Zn^{II} unit is not expected to profoundly affect the LMCT spectra.

Second, the characterization[18] of the related Ru(III) thiolate complex $[(NH_3)_5RuSEt]^{2+}$ allows the energies of S(thiolate) $\rightarrow$ metal and π_1(Im-*N*) $\rightarrow$ metal transitions to be compared directly. The actual proximity of S(thiolate) $\rightarrow$ Ru(III) LMCT (19 700 cm^{-1}, $\epsilon = 1900$) and the π_1(Hist-*N*) $\rightarrow$ Ru(III) LMCT (22 400 cm^{-1}, $\epsilon = 300$) indicates that, as suggested elsewhere,[1b] the corresponding LMCT absorptions in the spectra of blue Cu(II) protein chromophores have comparable energies. It appears likely that additional useful spectroscopic information can be obtained from these varied Ru(III) systems. We are currently in the process of better defining some of the above chromophores by crystallographic and comprehensive spectroscopic studies.

Finally, considerations similar to those presented above should prove useful in interpreting the LMCT spectra reported for pentaamine Ru(III) complexes of various nucleotide and nucleoside bases.[19] Work in that direction is also in progress.

Acknowledgment. This work was supported by the National Institutes of Health (Grant AM-16412 to H.J.S.), the Rutgers Research Council, and a Biomedical Research Support Grant (PHS RR 07058-18 to K.K.-J), as well as the Rutgers Center for Computer and Information Services. We thank Professors Stephan Isied and Edward Solomon for a number of useful discussions.

Note Added in Proof. Some of the ideas discussed here have also been presented in a recent paper in this journal (see ref 20).

Registry No. $(NH_3)_5$Ru^{III}(Im-*N*), 80593-52-8; $(NH_3)_5$Ru^{III}(Im-*C*), 93110-90-8; $(NH_3)_5$Ru^{III}(4-MeIm-*N*), 91209-01-7; $(NH_3)_5$Ru^{III}(4,5-Me$_2$Im-*N*), 91209-05-1; $(NH_3)_5$Ru^{III}(4,5-Me$_2$Im-*C*), 81802-38-2.

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(14) The INDO/S method used here[15] yields calculated values of Im-*N* $\pi \rightarrow \pi^*$ absorptions that are too low by about 0.5 eV;[1] the lowest $\pi \rightarrow \pi^*$ transition of Im-*C* species is, however, calculated about 0.7 eV higher than the lowest Im-*N* $\pi \rightarrow \pi^*$ transition. Thus, the Im-*C* ligand should be optically transparent up to quite high energies ($\gtrsim$45 000 cm^{-1}), not obscuring possible LMCT bands at lower energies.

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Acid Decomposition of Tris(dimethylglyoximato)nickelate(IV) in the Presence of Nucleophiles. Evidence for Substitution Inertness of the Nickel(IV) Complex

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First-order disappearance in the dissociation of metal chelates, independent of the concentration of added nucleophiles, is generally indicative of substitution lability of the chelate and a rate-determining dissociative reaction mechanism. In this paper we present evidence, based on the acid decomposition of potassium tris(dimethylglyoximato)nickelate(IV)[1] in the presence of various nucleophiles, (i) that the above mechanistic inference is not general for reactions of chelates of metals in higher oxidation states and (ii) that limiting first-order disappearance kinetics is consistent with a mechanism in which the substitution-inert Ni(IV) undergoes a rate-determining intramolecular ligand oxidation with a subsequent and rapid dissociation of the oxidized ligand.

The products of acid decomposition of Ni(IV) were 3,4-dimethylfurazan (3,4-dimethyl-1,2,5-oxadiazole) and [Ni(dmgH)$_2$] at pH $\gtrsim$4.5 and 3,4-dimethylfurazan, Ni^{2+}(aq), and dmgH$_2$ at pH <3, in both the absence[2] and the presence of nucleophiles (X). In the acid decomposition of Ni(IV), X was not involved in any reaction (oxidation or displacement) with Ni(IV), as shown by the following representative examples.

(1) An aqueous solution containing Ni(IV) (2×10^{-2} M) and azide (0.1 M) was allowed to decompose at pH ca. 3 (acetate–acetic acid buffer). The solution was then treated with excess lead acetate, and the precipitate of $Pb(N_3)_2$ was filtered, washed well with water, vacuum-dried in the cold, and weighed. (A blank was run in the absence of Ni(IV).) The weight of lead azide corresponded to the amount of azide initially taken (±3%). The filtrate was then brought to pH ca. 9, and the red precipitate of [Ni(dmgH)$_2$] was identified after purification.[2]

(2) Similarly, a solution of Ni(IV) (2×10^{-2} M) and potassium thiocyanate (0.1 M) was allowed to completely decompose at pH ca. 7; [Ni(dmgH)$_2$] was filtered off, and the washings and filtrate (containing SCN$^-$) were quantitatively collected in a volumetric flask. Known aliquots of this solution were acidified (HCl, ca. 1 M) and estimated spectrophotometrically as $[Fe(SCN)_6]^{3-}$, with suitable blank corrections. The amount of SCN$^-$ estimated on recovery agreed well (±3%) with that initially taken.

Results of spectral scans of solution mixtures also led to the same conclusion. The point-by-point spectrum[3] of a solution mixture, containing equal volumes of freshly prepared aqueous solutions of Ni(IV) (1×10^{-4} M) and each X, at different pH values (5.0, 6.1, 7.5, or 9.2) corresponded to that of the original Ni(IV) at that particular pH. *No change* in the λ_{max} or ϵ was noticeable in the 380–600-nm range. A representative set of spectra is presented in Figure 1.

The disappearance kinetics of Ni(IV) were monitored at 460 nm as described earlier.[2] At [X] = 0, the average values of k_{obsd} (pH) were 2.0×10^{-3} (5.0), 5.2×10^{-4} (5.6), 1.6×10^{-4} (6.1), 1.0×10^{-4} (6.4), 3.0×10^{-5} (7.0), 1.3×10^{-5} (8.3), 1.1×10^{-5} (9.4), 9×10^{-6} (10.4), and 2.6×10^{-7} s^{-1} (12). These k_{obsd} values remained practically unchanged when the nucleophiles (X) present were azide, thiocyanate, cyanide, am-

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