(Im-C^-) → 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^-) → 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^-) → 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$_3$)$_5$RuSEt]$^{2+}$ allows the energies of S(thiolate) → metal and π_1(Im-N) → metal transitions to be compared directly. The actual proximity of S(thiolate) → Ru(III) LMCT (19 700 cm^{-1}, ϵ = 1900) and the π_1(Hist-N) → Ru(III) LMCT (22 400 cm^{-1}, ϵ = 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.

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.

(14) The INDO/S method used here[15] yields calculated values of Im-N π → π^* absorptions that are too low by about 0.5 eV;[1] the lowest π → π^* transition of Im-C species is, however, calculated about 0.7 eV higher than the lowest Im-N π → π^* 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-

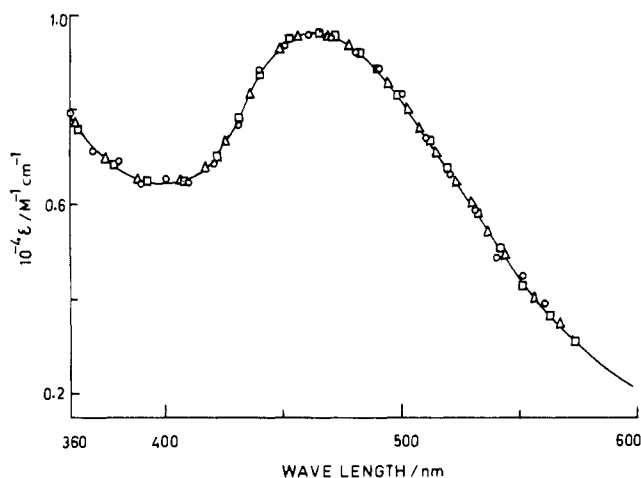†Present address: Department of Chemistry, Kent State University, Kent, OH 44242.

Figure 1. Visible spectra of the Ni(IV) complex in the absence and the presence of nucleophiles (X): line, Ni(IV) complex $(1 \times 10^{-4}$ M); point, mixture containing $[\text{Ni(IV)}]_0 = 1 \times 10^{-4}$ M, and $[X] = 1 \times 10^{-3}$ M; circle, azide; triangle, thiocyanate; square, cyanide; spectra were run in aqueous media with $\mu = 0.25$ M, $T = 35$ °C, pH 7, and the time scale in a 50-ms mode.

monia (each in concentration range $(1-50) \times 10^{-3}$ M), pyridine, glycine, imidazole, L-histidine, nitrilotriacetate, ethylenediaminetetraacetate, 2,2'-bipyridine, and 1,10-phenanthroline (each in the range $(1-10) \times 10^{-3}$ M). Kinetic data are available as supplementary material. The k_{obsd} values were also independent of the concentration and nature of the buffer used.[2] These observations suggested that under the conditions employed, the Ni(IV) disappearance rates were independent of the extent and the nature of the nucleophile present and that they depended only on [H$^+$] of the medium. The acid decomposition rates of Ni(IV), in the pH range 1.4–12.3, follow eq 7 in ref 2.

This decomposition process may involve either (a) a rate-determining intramolecular ligand oxidation followed by a rapid dissociation of the oxidized ligand[4,5] or (b) a rate-determining axial ring opening or dissociation preceding a rapid oxidation of the ring-opened or dissociated ligand. The latter mechanism can easily be ruled out by the spectral observations reported previously.[2]

The present observations also establish that the Ni(IV) species, $[\text{Ni(dmg)}_3]^{2-}$ and $[\text{Ni(dmg)}_3(\text{H})]^-$ (which are the predominant species in the pH range employed), do *not* have a labile site available for substitution in the presence of strong nucleophiles or intermolecular electron transfer by a substitution-controlled route in the presence of oxidizable substrates such as L-ascorbic acid,[6a] NH$_2$OH,[6b] N$_2$H$_5^+$,[6c] 1-*tert*-butylhydrazinium ion,[6c] and 1-phenylhydrazinium ion.[6d] The nucleophilic substrates (X), some of which also possess good reducing properties, are not oxidized, perhaps because of low redox potential of Ni(IV) (e.g., $E([\text{Ni}^{IV}(\text{dmg})_3(\text{H})]^-/[\text{Ni}^{III}\text{-}(\text{dmg})_3(\text{H})]^{2-}) \approx 0.4$ V).[6a,7]

Whether the two electrons involved in the intramolecular ligand oxidation are transferred concurrently or transferred

in a stepwise manner[5] cannot easily be inferred. Although evidence from ESR data at low temperatures has been obtained[1,6a] for a paramagnetic Ni(III) species in the ascorbic acid reduction of Ni(IV), the moderately high substitution lability[8] and redox reactivities of most Ni(III) complexes[8,9] discount the kinetic importance of a Ni(III) species in this system. The rate-determining step of intramolecular ligand oxidation, therefore, most probably involves a concurrent two-electron transfer.

The above arguments may not, however, apply to the diprotonated "kinetic intermediate" species $[\text{Ni(dmg)}_3(\text{H})\text{H}]$ (in which the second protonation is most probably a direct proton addition to a ligand nitrogen[2]) as sufficient data are not yet available to make an unambiguous judgment.

Registry No. $[\text{Ni(dmg)}_3]^{2-}$, 25973-84-6.

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Formation and Structure of an Unusual Complex from the Reaction of Formaldehyde with Alkali Halide Salt Molecules in Argon Matrices

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The chemistry of formaldehyde is of interest[1,2] due to its ability to coordinate to acids through the oxygen or to undergo nucleophilic attack at the carbon. In the latter case, weak complex formation is envisioned initially,[3] although theoretical calculations suggest that strong nucleophiles such as F$^-$ should bind very tightly.[4,5] The salt/molecule[6–9] was developed in conjunction with matrix isolation for the synthesis and characterization of anions formed through halide ion transfer; for example, the reaction[10] of CsF with CF$_2$O was shown to give the CF$_3$O$^-$ anion paired with Cs$^+$ in good yield. On the basis of analogy to CF$_2$O, as well as on theoretical calculations, the reaction of CsF with CH$_2$O might well give rise to the intermediate CH$_2$FO$^-$ anion. At the same time, previous studies have shown that the cesium salts of the heavier halogens do not readily form such intermediate anions.[10,11] With this

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