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Photoinduced Redox Reactions of Macrocyclic Complexes with d^7 (Nickel(III)) Metal Ions. Photoredox Processes of Equatorial and Axial Ligands

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Utraviolet irradiations of Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ or Ni(tet a)(CH$_3$CN)$_2^{3+}$ induce a reduction of the metal center and oxidation of the coordinated acetonitrile. The photoprocesses of the tet a and [14]dieneN$_4$ complexes have the same threshold energy for photoreactivity, $E_{th} \approx 79.4$ kcal/mol. However, the limiting yield for Ni(tet a)(CH$_3$CN)$_2^{3+}$, $\phi = 0.03$, is smaller than the yield for Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$, $\phi = 0.15$. The photooxidation of the imino groups of the macrocycle has been observed in flash photolyses of Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ in the presence of sulfate ions. A Ni(II)–ligand radical ($\lambda_{max} \sim 535$ nm, $t_{1/2} \leq 600$ μs) was detected in these irradiations. The photochemistries of the Ni(III) complexes have been associated with the population of charge-transfer ligand to metal states, CT$_{\pi\text{-C}\equiv\text{N}\rightarrow\text{d-Ni}}$ and/or CT$_{\pi\text{-imino}\rightarrow\text{d-Ni}}$.

Introduction

The ability of macrocyclic ligands to stabilize a number of oxidation states of a coordinated metal ion has been amply demonstrated.[1-5] In this regard, macrocyclic complexes with Ni(III) metal centers are a clear example of such a stabilization. Indeed, it is generally recognized that the tripositive state of nickel participates in the introduction of new double bonds in macrocyclic ligands.[6-9] The mechanism for these oxidations in Ni(III) complexes has been investigated by several authors.[7,10-15] Results, obtained by oxidizing Ni([14]dieneN$_4$)$^{2+}$ or Ni(tet a)$^{2+}$ with radiolytically generated OH, Cl$_2^-$, Br$_2^-$, and (NCS)$_2^-$, show the formation of distorted Ni(III) complexes which are largely reactive in aqueous solutions.[11-13,16] However, Ni(III) macrocyclic complexes, Ni(tet a)(CH$_3$CN)$_2^{3+}$ and Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$, are very stable in acetonitrile. Such stability has permitted the investigation of the photochemistries of these species.

Experimental Section

The apparatus used for continuous-wave and flash photolyses have been described elsewhere.[17-19]

Continuous-wave irradiations were carried out for periods which yielded conversions to products smaller than 10%. Quantum efficiencies were obtained from the slopes of the product concentrations vs. irradiation time curves. Blanks, maintained in the dark, were used as a control for thermal reactions under the conditions of the photochemical experiments. Light intensities were measured with tris(oxalato)iron(III).

Solutions of the Ni(III) complexes were flash irradiated at wavelengths which were selected by means of appropriate cutoff filters. Concentrations of the intermediates were varied in a series of experiments by using different values of the stored electrical energy. Values of this energy were between 250 and 40 J/pulse.

The deaerations of the solutions used for continuous-wave or flash photolysis were carried out with solvent-saturated streams of Ar. The purity of the solvent was established by means of the stability of the Ni(III) species. Pure acetonitrile was able to sustain Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ or Ni(tet a)(CH$_3$CN)$_2^{3+}$ for more than 24 h.[21]

The electrochemical method of Olson and Vasilevskis was used for the preparation of [Ni([14]dieneN$_4$)(CH$_3$CN)]$_2$(ClO$_4$)$_3$ and [Ni(tet a)(CH$_3$CN)$_2$](ClO$_4$)$_3$.[4] The spectral properties of these compounds agreed with literature reports. Solid samples of the green complexes turned brown by standing under vacuum for large periods. However, the original green complexes were re-formed by exposing the brown solids to acetonitrile vapors; see ref 12.

Spectroquality chemicals, anhydrous acetonitrile and 98–100% sulfuric acid, were used in this work.

Results

a. Continuous-Wave Photolysis. Solutions of Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ or Ni(tet a)(CH$_3$CN)$_2^{3+}$ in deaerated acetonitrile were irradiated at wavelengths of the intense charge-transfer bands ($250 \leq \lambda_{exc} \leq 400$ nm). These photolyses produced marked spectral changes (Figure 1). The increase of the absorbance at 230 nm and the isosbestic point at 250 nm (see Figure 1a) show the formation of Ni([14]dieneN$_4$)$^{2+}$. Moreover, the disappearance of the parent Ni(III) complex was followed by means of the decrease of the 315-nm absorbance (see Figure 1a). The spectra of the irradiated solutions compared well with those obtained with mixtures of the Ni(III) and Ni(II) complexes; [Ni([14]dieneN$_4$)(CH$_3$CN)$_2$]$^{3+}$ + [Ni([14]dieneN$_4$)]$^{2+}$ = 7.7×10^{-4} M (solvent CH$_3$CN).

The same quantum yields were obtained for both the formation of Ni([14]dieneN$_4$)$^{2+}$ and the disappearance of the parent Ni(III) complex (see Table I). Moreover, 320-nm irradiations of Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ in deaerated CH$_3$CN were carried out until 60–70% was converted into Ni([14]dieneN$_4$)$^{2+}$. The absorption spectra of the irradiated solutions failed to reveal the presence of any other Ni(II) product.[22] In addition, irradiations of Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ were carried out at wavelengths larger than 400 nm. The photochemical transformation indicated above was detected with very small yields, $\phi < 10^{-4}$.

Product yields were determined for photolyses of Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ in the presence of sulfate ions (see Table I). Although, species like sulfate had some influence on the shape of the charge-transfer spectra, they produce no modification of the photoreaction yields (see Table I and footnote 23).

A threshold energy for photochemical reactivity, $E_{phot}^{th} = 79.4$ kcal/mol, was obtained from the dependence of the quantum yield on excitation energy (see Figure 2a). Moreover, the quantum efficiency of the reaction reaches a limit: $\phi_{lim} = 0.15$ for photonic energies equal to or larger than 89.4 kcal/mol.

The photochemistry of the Ni(tet a)(CH$_3$CN)$_2^{3+}$ in deaerated solutions resembles that of the Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$. Transformations in the absorption spectrum, induced by irradiations at wavelengths of the charge-transfer bands, reveal the disappearance of the Ni(III) complex and the formation of Ni(tet a)$^{2+}$ in a 1:1 stoichiometry (see Figure 1b and Table I). Although the same thresholds for photochemical reactivity were obtained with Ni(tet a)(CH$_3$CN)$_2^{3+}$ and Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$, the limiting quantum yield for the tet a complex is almost 5 times smaller than for the [14]dieneN$_4$ complex (see above and Figure 2b).

b. Flash Photolysis. Flash irradiation ($\lambda_{exc} \geq 240$ nm) of Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ in deaerated acetonitrile failed to produce transient absorbances. However, the absorbance of the solution was bleached at wavelengths shorter than 430 nm (see Figure 3a). The bleach of the absorbance was in good agreement with spectral changes induced by continuous-wave photolysis (see Figure 1a).

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Table I. Quantum Yields for Photoreactions of Ni(III) Complexes with Macrocyclic Ligands (L)

λ_{exc}, nm	I_0, einstein/(L min)	$\phi_{\text{Ni(III)}}$[a]	$\phi_{\text{Ni(II)}}$[b]	$[H_2SO_4]$,[c] M
		L = [14]dieneN$_4$		
390	3.8×10^{-4}	$(3.2 \pm 0.2) \times 10^{-3}$	*d*	
370	3.0×10^{-4}	$(5.2 \pm 0.4) \times 10^{-3}$	*d*	
350	1.3×10^{-4}	$(2.5 \pm 0.3) \times 10^{-2}$	$(2.4 \pm 0.2) \times 10^{-2}$	
320	2.0×10^{-5}	$(1.5 \pm 0.2) \times 10^{-1}$	$(1.4 \pm 0.2) \times 10^{-2}$	
320	2.0×10^{-5}	$(1.4 \pm 0.2) \times 10^{-1}$	$(1.4 \pm 0.1) \times 10^{-1}$	1.8×10^{-3}
320	2.0×10^{-5}	$(1.7 \pm 0.2) \times 10^{-1}$	$(1.5 \pm 0.2) \times 10^{-1}$	7.3×10^{-3}
320	2.0×10^{-5}	$(1.8 \pm 0.3) \times 10^{-1}$	*d*	10.9×10^{-3}
300	2.2×10^{-4}	$(1.4 \pm 0.3) \times 10^{-1}$	*d*	
254	2.0×10^{-4}	$(1.5 \pm 0.2) \times 10^{-1}$	*d*	
		L = tet a		
400	4.2×10^{-4}	$(2.4 \pm 0.3) \times 10^{-3}$	*d, e*	
350	1.3×10^{-4}	$(2.6 \pm 0.3) \times 10^{-3}$	*d, e*	
320	2.0×10^{-5}	$(3.0 \pm 0.2) \times 10^{-2}$	$(2.4 \pm 0.3) \times 10^{-2}$	
320	2.0×10^{-5}	$(3.2 \pm 0.3) \times 10^{-2}$	*d*	1.8×10^{-3}
300	2.2×10^{-4}	$(3.3 \pm 0.3) \times 10^{-2}$	$(3.0 \pm 0.2) \times 10^{-2}$	
254	2.0×10^{-4}	$(2.8 \pm 0.2) \times 10^{-2}$	*d*	

[a] Quantum yields determined for the disappearance of the Ni(III) complexes (average of three to five determinations). [b] Quantum yields determined for the appearance of the Ni(II) products (average of three to five determinations). [c] Solutions in deaerated CH_3CN. Concentrations of the Ni(III) complexes were between 10^{-3} and 10^{-4} M. [d] Not determined. [e] The yield of succinonitrile, determined by GC, was almost half of $\phi_{\text{Ni(III)}}$ and $\phi_{\text{Ni(II)}}$. Indeed, $\phi = (0.48 \pm 0.05)\phi_{\text{Ni(II)}}$ for excitations at 300 and 254 nm.

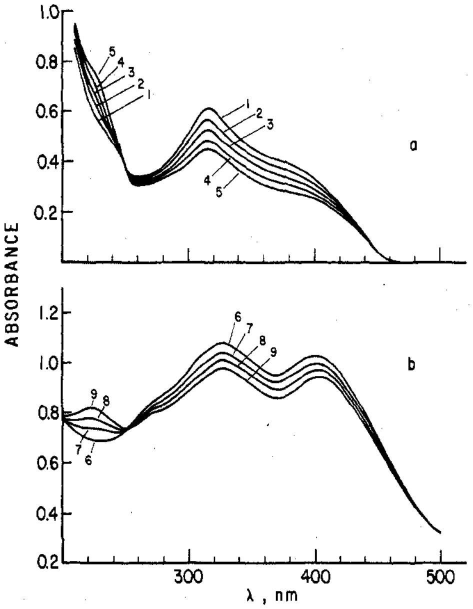


Figure 1. Spectral changes observed upon irradiation of (a) Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ for (1) 0 min, (2) 10.0 min, (3) 20.8 min, (4) 30.5 min, and (5) 40.6 min (λ_{exc} 320 nm, $I_0 = 2.0 \times 10^{-5}$ einstein/(L min), and (b) Ni(tet a)(CH$_3$CN)$_2^{3+}$ for (6) 0 min, (7) 2 min, (8) 4 min, and (9) 6 min (λ_{exc} 254 nm, $I_0 = 2.0 \times 10^{-4}$ einstein/(L min)). Absorbance was determined with a 2-mm optical path.

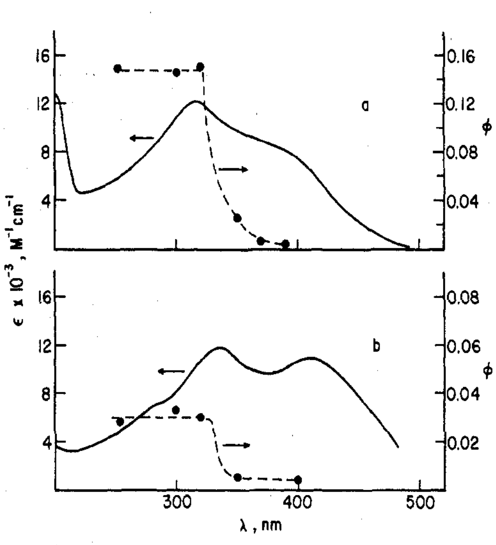


Figure 2. Absorption spectra and quantum yields obtained for the photoreduction of (a) Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ and (b) Ni(tet a)(CH$_3$CN)$_2^{3+}$. See Table I for experimental conditions.

The photochemical generation of radicals was investigated with Ni([14]dieneN$_4$)$^{2+}$. Flash irradiation ($\lambda_{\text{exc}} \geq 240$ nm) of Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ in solutions which contain 10^{-4}–10^{-6} M Ni(II) complex produce a long-lived intermediate with $\lambda_{\text{max}} \sim 535$ nm. The decay of this species, characterized as a distorted Ni$^{\text{III}}$–[14]dieneN$_4$ complex,[11] exhibited a first-order dependence in transient concentration. A rate constant, $k = 3.6\ 10^{-1}\ s^{-1}$, was obtained from these measurements.

The photochemical behavior of Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ was investigated in solutions which were 10^{-2}–10^{-4} M in H_2SO_4 or Et$_4$N(H)SO$_4$. A transient species (λ_{max} 540 nm) was detected for irradiations of the Ni(III) complex at wavelengths larger than 240 nm (see Figure 3b,c). This reaction intermediate, assigned as a Ni(II)–ligand radical species, is formed with an efficiency that increases with acid concentrations (see Figure 4a). In addition, the decay of the Ni(II)–ligand radical exhibited a first-order dependence in the initial concentration of the transient species. However, the decay half-life changed in a complex form with H_2SO_4 concentration (see Figure 4b). The bleach of the Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ absorbance was observed at wavelengths shorter than 450 nm (see Figure 3c). The bleached absorbance was partially recovered with the same half-lifetime that was obtained for the decay of the 540-nm transient absorbance (Figure 3b). Moreover, the amount of the absorbance that remains bleached at an infinite reaction time is the same determined for flash irradiations of Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ in the absence of H_2SO_4 (see Figure 3a,b$_1$). Irradiations at wavelengths longer than 400 nm produce a transient bleach of the absorbance. However, the permanent bleach of the absorbance was not observed at an infinite reaction time.

The effect of Et$_4$N(H)SO$_4$ on the photochemical reactivity of Ni([14]dieneN$_4$)(CH$_3$CN)$_2^{3+}$ is nearly the same as that of H_2SO_4.

Flash irradiations of the Ni(tet a)(CH$_3$CN)$_2^{3+}$ either in acetonitrile or in 10^{-2}–10^{-4} M H_2SO_4 in acetonitrile failed to produce transient absorbances. However, the interception of

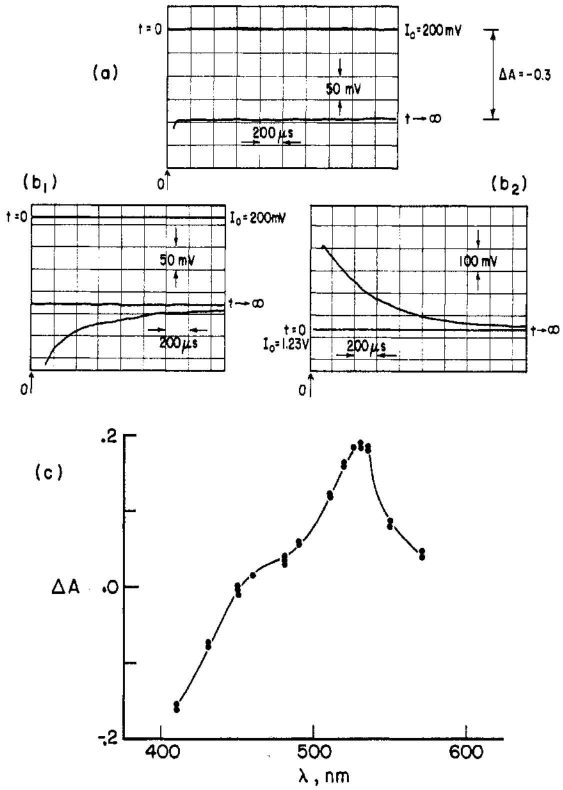


Figure 3. Flash photolyses of $Ni([14]dieneN_4)(CH_3CN)_2^{3+}$: (a) absorbance bleach, ΔA, observed at 360 nm for irradiations of $Ni([14]dieneN_4)(CH_3CN)_2^{3+}$ in deaerated CH_3CN; (b) transient bleach of the 360-nm absorbance (b_1) and transient absorbances (b_2) determined for flash irradiations of the Ni(III) complex in 2.0×10^{-3} M H_2SO_4; (c) spectrum of the transient Ni(II)–ligand radical generated in flash photolyses of the Ni(III) complex in 2.0×10^{-3} M H_2SO_4. Solutions were irradiated at $\lambda_{exc} \geq 240$ nm with 250 J/pulse.

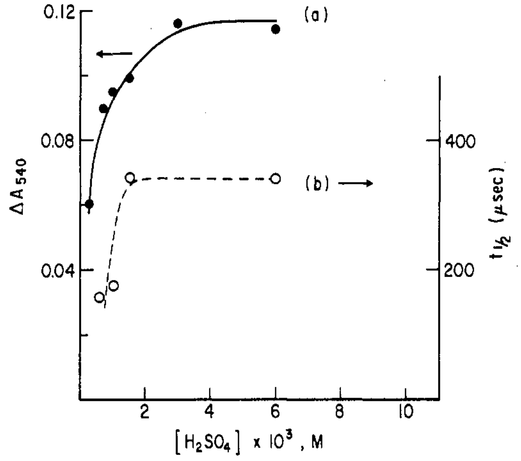


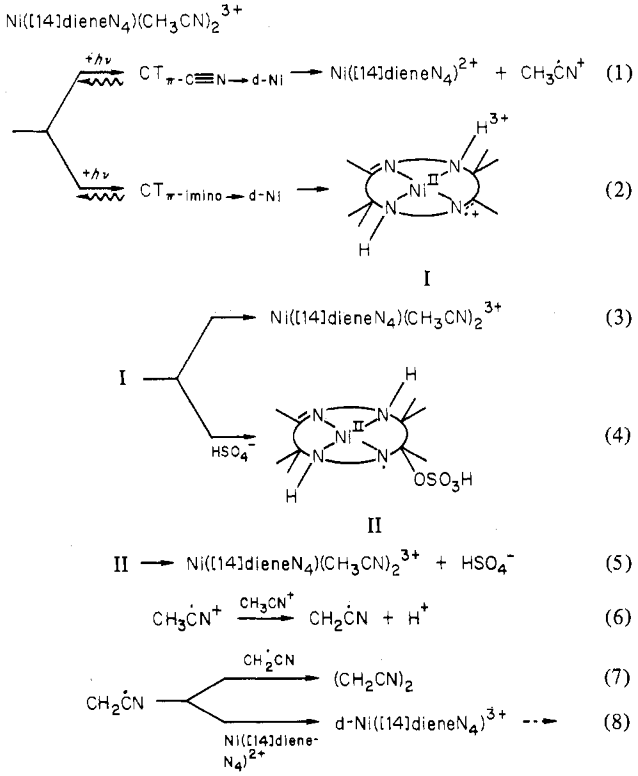
Figure 4. Dependence of the Ni(II)–ligand radical yield (a) and half-lifetime (b) on H_2SO_4 concentration. Flash irradiations of the $Ni([14]dieneN_4)(CH_3CN)_2^{3+}$ in deaerated solutions were carried out at $\lambda_{exc} \geq 240$ nm with 250 J/pulse.

the photogenerated radicals with $Ni([14]dieneN_4)^{2+}$ produces the distorted Ni^{III}–$[14]dieneN_4$ species that has been described above.

Discussion

The overall photochemical processes of $Ni([14]dieneN_4)(CH_3CN_2)^{3+}$ and $Ni(teta)(CH_3CN)_2^{3+}$ can be described as a photoreduction of Ni(III) to Ni(II). Moreover, the nature of the photoproducts shows that the photoreactions must involve the oxidation of the coordinated acetonitrile (eq 1). In this regard, the photogeneration of radicals is demonstrated by interception of these species with $Ni([14]dieneN_4)^{2+}$. The formation of a distorted Ni^{III}–$[14]dieneN_4$, d-$Ni([14]dieneN_4)^{3+}$, with a 1.5-s half-lifetime agrees with that reported for oxidations of $Ni([14]dieneN_4)^{2+}$ with various oxidant radicals in aqueous solutions.[11,12]

A second photoreaction, in addition to the photooxidation of the coordinated acetonitrile, is observed for flash photolyses of the $Ni([14]dieneN_4)(CH_3CN)_2^{3+}$ in solutions which contain given concentrations of H_2SO_4. Indeed, the transient Ni(II)–ligand radical is photogenerated for excitation energies smaller than the threshold energy for photooxidation of acetonitrile. The absence of a similar intermediate in photochemical reactions of the $Ni(teta)(CH_3CN)_2^{3+}$ suggests that the Ni(II)–radical species is originated in a charge-transfer process which involves imino groups of the $[14]dieneN_4$ ligand (eq 2). In this regard, the photoreactivity discussed above can be described by eq 1–8.



Reactions 1–4 must be too fast for detection in flash photolysis. However, the Ni(II)–ligand radical, formed in eq 4, must have a life which allows its observation in similar experiments. A mechanism for the photoredox reactions of $Ni(teta)(CH_3CN)_2^{3+}$ will have those features that remain after the exclusion of the pathway originated in eq 2.

The absorption spectra of the Ni(III) complexes of the teta and $[14]dieneN_4$ ligands present several absorptions within the 450–200-nm region. These absorptions have been assigned to charge-transfer transitions which must have origins in various groups (acetonitrile, imino, and/or amino) coordinated to Ni(III).[4,24] In this regard, the photochemistry of the Ni(III) complexes seems to be related to the population of charge-transfer ligand to metal states. The values of the threshold energies for photochemistry in teta and $[14]dieneN_4$ complexes of Ni(III) suggest that the photoprocesses can be induced in excited states with similar characters. Indeed, one can associate the photooxidation of the coordinated acetonitrile with a charge-transfer state, $CT_{\pi\text{-C}\equiv N\rightarrow d\text{-Ni}}$, that involves the π-electronic density of the acetonitrile. Moreover, the limiting yields suggest that the excited state of the teta complex might have a lifetime which is 5 times smaller than the state of the $[14]dieneN_4$ complex.[25] The other photochemical mode, photooxidation of the imino groups—eq 2, can be related to the reactivity of an excited state with charge-transfer character, $\mathrm{CT}_{\pi\text{-imino}\rightarrow\text{d-Ni}}$.

The photochemistries of the Ni(III) complexes contrast with that of the isoelectronic Co(II) species.[26] Indeed, the primary photochemical process of $\mathrm{Co([14]dieneN_4)^{2+}}$ is determined by population of a metal to ligand, $\mathrm{CT}_{\text{d-Co}\rightarrow{}^{*}\pi\text{-imino}}$, charge-transfer state. The differences that exist between the photochemistries of these isoelectronic systems might be related to the distinct accessibility of the oxidation states, a tripositive cobalt and a dipositive nickel.[2] A large unfavorable energy must be associated with the generation of a metal to ligand charge-transfer state, $\mathrm{CT}_{\text{d-Ni(III)}\rightarrow{}^{*}\pi\text{-imino}}$, in the Ni(III) complex.[27] Therefore, either such a state might be out of the range of the excitation energies used here or it can be efficiently depopulated toward underlying charge-transfer states.

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Registry No. $\mathrm{Ni([14]dieneN_4)(CH_3CN)_2^{3+}}$, 71435-49-9; $\mathrm{Ni(tet\,\alpha)(CH_3CN)_2^{3+}}$, 71484-74-7.

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(16) Ligand abbreviations: $\mathrm{[14]dieneN_4}$, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; tet a, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.
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(21) Notice that small amounts of either water or reducing impurities produce a rapid disappearance of the Ni(III) complexes.[4]
(22) The experimental error in these determinations and the yields for Ni(III) disappearance or Ni(II) formation give an upper limit for the yield of secondary photoreactions; $\phi \leq 2 \times 10^{-3}$.
(23) A significant anation of the $\mathrm{Ni([14]dieneN_4)(CH_3CN)_2^{3+}}$ by sulfate ions is expected for concentrations of these species larger than those used here. Modifications of the absorption spectrum of $\mathrm{Ni([14]dieneN_4)(CH_3CN)_2^{3+}}$, induced by sulfuric acid, reveal that the percentage of anated species must be equal to or smaller than 10%.
(24) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes", Addison-Wesley, Reading, Mass., 1962, pp 146–72.
(25) Notice that the disparity in the limiting yields can be attributed to differences between the efficiencies of interconversion to the reactive excited states, the lifetime of these states, and the rate constants of the redox processes in the excited state. However, some properties of the Ni(III) complexes[1-15] suggest that differences in the lifetimes of the charge-transfer states are more likely the reason for the distinct limiting yields.
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(27) The oxidation of Ni(III) to Ni(IV) has not been observed with nickel complexes of tet a and $\mathrm{[14]dieneN_4}$.[2-4] However, the oxidation potentials of Co(II)/Co(III) couples show that oxidation of Co(II) to Co(III) in the field of the macrocycle is a more favorable process.[2,3]

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Chemical and Electrochemical Properties of 2,2′-Bipyridyl Complexes of Ruthenium Covalently Bound to Platinum Oxide Electrodes

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The covalent attachment of 2,2′-bipyridyl complexes of ruthenium to silanized platinum oxide electrodes by two different surface synthetic procedures is demonstrated. The electrodes, once prepared, show an impressive stability toward cycling between the ruthenium(II) and -(III) oxidation states. The surface-attached complexes largely retain the chemical characteristics exhibited by their homogeneous solution analogues, but a quenching of photochemical behavior is observed. Although stable indefinitely in the Ru(II) state, once oxidized to Ru(III), the surfaces undergo a slow decay process which results ultimately in the complete loss of ruthenium from the surface. The surface decay processes have been found to follow first-order kinetics. Current–potential wave shapes for the surface-bound Ru(III)/Ru(II) couples are treated in the light of surface activity parameters.

Synthesis, structural and redox properties, and possible applications are all topics of current research on chemically modified electrodes.[1] Organosilane reagents form stable chemical bonds to the surfaces of metal oxide electrodes[2] including thin, anodically generated oxide films on platinum metal.[3] Other species can then be immobilized on the electrode surface by exploiting the chemical properties of the attached silane. We describe here the preparation and properties of platinum oxide surfaces bearing attached 2,2′-bipyridyl complexes of ruthenium.

One of the major themes of chemically modified electrode research is the transfer of chemical and electrochemical behavior of a reagent in homogeneous solution to the surface of an electrode. Catalytic reactions are of particular interest and attractiveness and, among homogeneous catalysts, many involve transition-metal complexes that exhibit a variety of stable oxidation states. Complexes of the type $\mathrm{[(bpy)_2Ru^{II}LL']}$ (bpy is 2,2′-bipyridyl), as a rule, undergo reversible metal-localized $\mathrm{Ru^{II}} \rightarrow \mathrm{Ru^{III}}$ oxidations and bipyridyl-localized reductions.[4] Further, the potential for the $\mathrm{Ru^{III,II}}$ couples can be systematically varied by ca. 1.5 V by an appropriate selection of the ligands L and L′.[4] In some cases, the excited states of the $\mathrm{Ru^{II}}$ complexes have been shown to have an extensive redox chemistry which could conceivably provide the

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