on the basis of their polarizabilities.[53] Therefore, the Mn(III) and Mn(IV) ions are expected to be much harder acids because of their smaller size, their larger charges, and their lower polarizability. The hard nature of the vicinal oxo ions of catechol dianion should make the "hard–hard" interaction with the Mn(IV) ion exceptionally strong. The increased stability of the Mn(III) and Mn(IV) oxidation state in complexes with catechol anions reflect this hard acid–hard base interaction.

Interconversion of the Mn(II), -(III), and -(IV) complexes without the use of OH^- (base) (which competes for metal coordination sites) and in an aprotic medium that resembles the lipid layers of plant cells provides an interesting model system for photosystem II. The fact that this system requires the addition of four electrons to go from the Mn(II)–$(DTBQ)_3$ state to the $Mn^{IV}(DTBC)_3{}^{2-}$ complex is a unique feature. Because the $Mn^{IV}(DTBC)_3{}^{2-}$ complex also reversibly binds O_2 in aprotic media,[21] it may represent an effective activator for oxygenation reactions.

Acknowledgment. We thank Dr. William Schaefer of the California Institute of Technology for preliminary results from the X-ray structural characterization of the $Na_2[Mn^{IV}(DTBC)_3]\cdot 6CH_3CN$ molecule that is in progress in his laboratories. The work was supported by the National Institutes of Health—USPHS under Grant No. GM-22761 and by the U.S. Department of Agriculture Forest Service, Forest Products Laboratory, Madison, WI, under Agreement No. 12-167.

Registry No. $Na_2[Mn^{IV}(DTBC)_3]$, 72275-17-3; $Ba[Mn^{IV}(DTBC)_3]$, 79299-87-9; Mn, 7439965; DTBQ, 3383-21-9; $DTBSQ^{-\cdot}$, 18802-82-9.

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Photoinduced Dimerization of Macrocyclic Complexes Mediated by a Metal-Assisted Oxidation of the Macrocycle

G. FERRAUDI* and S. MURALIDHARAN

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The triplet state of benzophenone oxidizes $Ni([14]aneN_4)^{2+}$ to a Ni(III) intermediate which subsequently produces the dimer of the complex as a product. The nature of the product was confirmed by structural studies. $[Ni(13\text{-}At)]^+$ reacts with the triplet of fluorenone and ^2E state of $Cr(bpy)_3{}^{3+}$ forming also a dimer in a reaction that involves different intermediates. Intermediates in the photoinduced oxidations of the macrocycles have been investigated by flash photolysis. The mechanism of the photoinduced oxidation is discussed in terms of the reported properties of the macrocycles.

Introduction

A number of studies on the ligand oxidation of nickel(II) macrocyclic tetraaza complexes have postulated the involvement of nickel(III) intermediates in the reaction.[1-9] Such a participation of the tripositive oxidation state of nickel is in agreement with results obtained by electrochemical and reaction kinetic techniques.[1-5,10-13] Indeed, the study of the transformations of nickel(III) macrocycles by stop-flow, pulse radiolysis and flash photolysis has revealed several points of interest in their chemical reactivity. That the coordination of acido ligands, e.g., Cl^-, Br^-, and SCN^-, in the axial positions of the complex enhances the thermodynamic and kinetic stability of the nickel(III) species has been demonstrated in several studies.[10,12,14] Moreover, the hydrolysis of the coordinated acido ligands is a slow process. Rate constants $k \leq 20\ s^{-1}$ have been reported for such hydrolysis.[12,14,15] The dehydrogenation of the macrocycle, induced by nickel(III) intermediates, is a base-assisted process. Hence, the generation of nickel(II)–ligand radicals from nickel(III) intermediates seems to be controlled by the deprotonation of the macrocycle.[10,12,16] A mechanism for the oxidative dehydrogenation can be summarized by means of eq 1–4. The species [O], eq 1, represents the electrochemical or chemical oxidant, namely, Ce^{IV}, $Cl_2{}^-$, $Br_2{}^-$, $(SCN)_2{}^-$, and Br_2. The dehydrogenation process can be explained in terms of the oxidation of the Ni(II)–ligand radical by excess oxidant (eq 5), the disproportionation of the Ni(II)–ligand radical (eq 6), and reaction between Ni(II)–ligand radicals and excess Ni(III) species (eq 7). Ligand degradation products and Ni(II) can also be produced in reactions 5–7.

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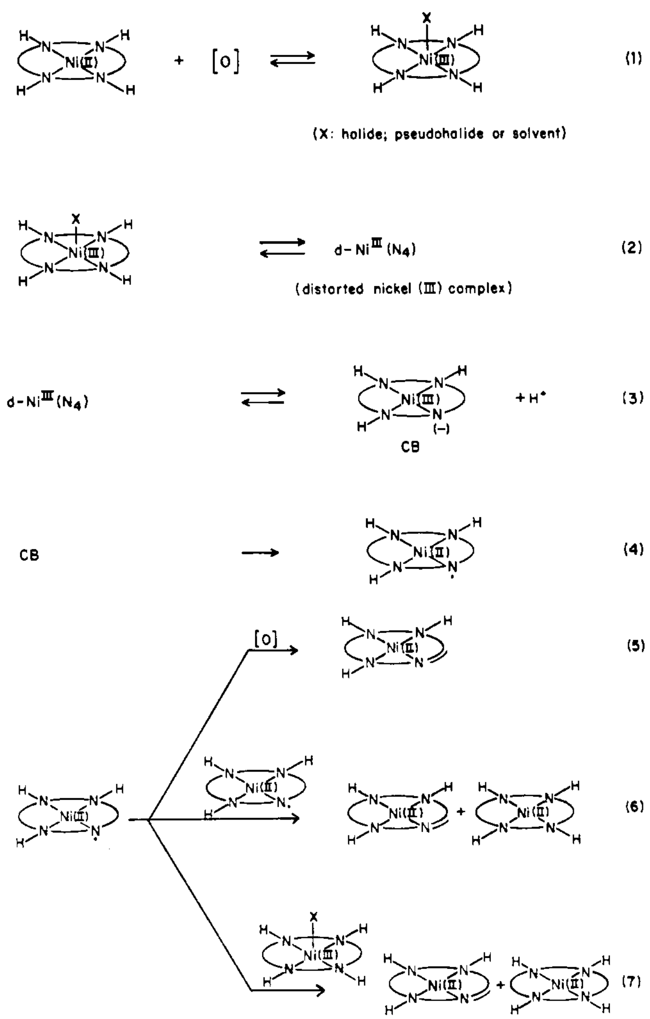


The existence of several reaction paths is suggested by the diversity of the reaction products already reported. Several studies demonstrated that the degradation of the macrocyclic ligand, the introduction of new imino groups in the ligand, and the formation of dimeric products are possible reaction paths. The presence of distinct reaction paths can be attributed to specific driving forces, associated with the structure of the nickel(II)–ligand radical species, under given medium conditions.[17]

The oxidation of Ni(II) and Cu(II) macrocycles by excited states has been investigated in this work. Dimerization seems to be related with intermediates generated in a migration of the oxidation from the metal center to the macrocyclic ligand.

Experimental Section

Photochemical Procedures and Apparatus. A high-pressure xenon lamp, a Vix-300 Eimac illuminator coupled with collimating lenses and a monochromator, was used for continuous wave irradiations. Relative values of the light intensity were determined with a photocell microvoltmeter. Preparative photolyses were carried out with a medium-pressure mercury lamp. The 360-nm line was isolated with appropriate filters. Tris(oxalato)ferrate(III) was used for the measurement of the light intensities.[19] Solutions of the photolyte were deaerated by using three freeze–thaw cycles.

Conventional flash irradiations were carried out in an apparatus described elsewhere.[20] Some details of the instrumental arrangement are indicated below. Two xenon flash lamps were fired in series. Light pulses with a length of 30 μs were generated for stored energies smaller than 250 *J*/pulse. The phototube output was digitized in a Biomation 805 wave recorder. A hundred data points were used for the calculations. Moreover, the results were analyzed in a Digital PDP-8L processor. Laser flash irradiations were carried out with a UV400 nitrogen Molectron laser.[21] The instrumental arrangements were previously described. Solutions, used for conventional and laser flash photolyses, were deaerated with streams of argon and discarded after a single irradiation.

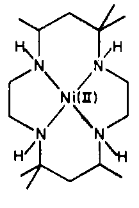
Emission spectra were recorded in an Aminco Bowman spectrofluorimeter. Solutions were deaerated with streams of argon in cells provided with Teflon stopcocks.

Conductometric Procedures. Determinations of the resistance of the solutions were carried out with an AC Wayne Kerr bridge. A cell with platinized electrodes was used for these measurements. The cell constant was obtained by using standard solutions of KCl. Molar conductances of the complexes at infinite dilution were obtained from conductance vs. concentration plots by extrapolating to zero concentration.

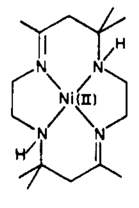
Analytical Determinations. The inorganic complexes in irradiated solutions were separated from the sensitizers, benzophenone or fluorenone, and other organic products that interfere in the determination of the spectral changes. The solvent, CH_3CN, of the irradiated solutions and blanks was slowly vacuum evaporated, and the solid material was dissolved in water. Organic products were extracted with either benzene or cyclohexane where the solubility of the inorganic complexes is negligible. The final aqueous solutions of the complexes were analyzed in cells with 0.2- or 1.0-cm optical path.

Nuclear magnetic resonance spectra, ^{1}H and ^{13}C, were obtained with a Varian XL-100 spectrometer with a Nicolet FT system. The molecular weight was determined in Schwarzkopf Laboratory.

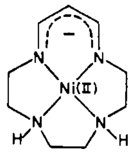
Materials. The copper(II) macrocycles were available from a previous work.[22] The complexes $[Ni([14]aneN_4)](ClO_4)_2$ (I), $[Ni([14]dieneN_4)](ClO_4)_2$ (II), and $[Ni(13\text{-}At)]NO_3$ (III) were synthesized and purified according to reported procedures. Benzophenone, purchased from Aldrich, was recrystallized three times from ethanolic solutions.



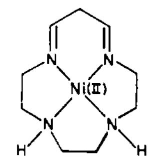
(I); $Ni([14]aneN_4)^{2+}$



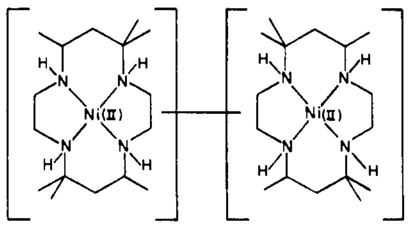
(II); $Ni([14]dieneN_4)^{2+}$



(III); Ni (13-At)$^+$



(IV); $Ni([13]dieneN_4)^{2+}$



(V); $Ni_2(dehydro\text{-}bis([14]aneN_4))^{4+}$

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(17) An example of this behavior can be found in the reactivity of the hydroxyalkyl radicals.[18] Indeed, the $\dot{C}H_2OH$ exhibit the tendency to dimerize and disproportionate while $CH_3\dot{C}OHCH_3$ only disproportionates.

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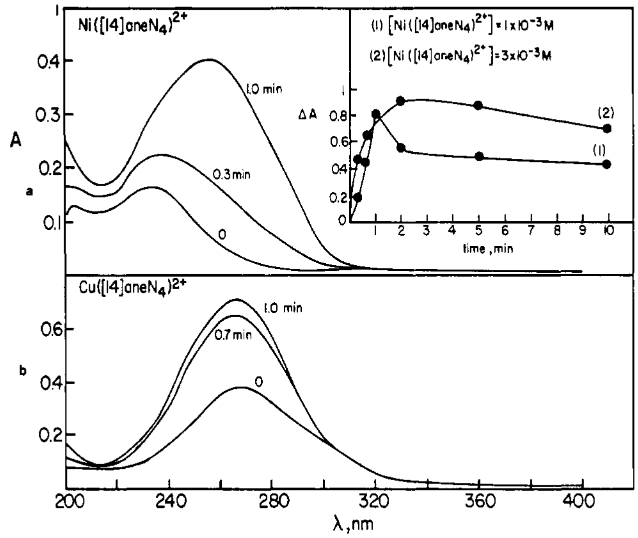

Figure 1. Changes in the spectrum of Ni([14]aneN$_4$)$^{2+}$ (a) and Cu([14]aneN$_4$)$^{2+}$ (b) sensitized by 360-nm irradiations of 5×10^{-3} M benzophenone in deaerated acetonitrile. Inset to a shows deviations from linearity for larger conversions to products. Conditions: [Ni^{II}] = 3.0×10^{-3} M; [Cu^{II}] = 3.0×10^{-3} M; $I_0 = 2.9 \times 10^{-4}$ einstein/L min. Absorbance measured in cells with 2-mm optical paths.

The product of the sensitized oxidation of Ni([14]aneN$_4$)$^{2+}$ by benzophenone triplets, [Ni$_2$(dehydrobis([14]aneN$_4$))](ClO$_4$)$_4$ (V), was obtained by a procedure based on our results on continuous photolysis (see below). Solutions, 3×10^{-3} M Ni([14]aneN$_4$)$^{2+}$ and 5×10^{-3} M benzophenone in CH$_3$CN, were irradiated at 360 nm for short periods, with conversions smaller than 3%. The irradiated solution was evaporated under vacuum until a solid residue was formed. Benzophenone was partly extracted with cyclohexane, and the solid was then dissolved in water. Two further extractions with cyclohexane were required in order to remove the residual benzophenone from the aqueous solution. The photolysis product was precipitated by a slow vacuum evaporation and addition of anhydrous NaClO$_4$. The crude material was recrystallized three times from aqueous solutions. The chloride salt of Ni$_2$(dehydrobis([14]aneN$_4$))$^{4+}$ was obtained by replacing the perchlorate anion. Such exchange was accomplished by passing a solution of the perchlorate salt through a Dowex-2, moderately basic, 50–100 mesh, anion exchanger. The liquids of the elution were vacuum evaporated until the formation of crystals.

Spectroquality acetonitrile and methanol were used as solvents. Other materials were reagent grade, and they were used without further purification.

Results

Continuous-Wave Photolysis. The 360-nm photolysis of benzophenone, in the solvent acetonitrile, in the presence of Cu([14]aneN$_4$)$^{2+}$ or Ni([14]aneN$_4$)$^{2+}$ produced new absorptions in the spectra of the macrocyclic complexes (Figure 1). The 240-nm absorbance increases linearly with irradiation time for conversion to products smaller than 2%. However, strong deviations from linearity were observed for conversions larger than 2%; see inset to Figure 1. These new absorbances were not observed when photolyses were carried out in aqueous solutions or mixed-solvent solutions, e.g., CH$_3$CN–H$_2$O. These conditions induce the disappearance of the Ni(II) or Cu(II) macrocycles and formation of the corresponding aqueous ions.

The product of the sensitized reaction of Ni([14]aneN$_4$)$^{2+}$ by benzophenone triplets was assigned as a dimeric Ni(II) macrocycle. The apparent molecular weight of the perchlorate salt, determined from osmotic pressure changes in methanolic solutions, is 343. Moreover, relative measurements of the ionic conductivity of the perchlorate and chloride salts reveal that the dimeric nickel(II) complexes is a tetrapositive cation; see the Appendix. Correction of the apparent molecular weight for the dissociation in ions gave a molecular weight, M_r = 1354, which is in agreement with the proposed dimeric structure. The infrared spectra of the [Ni([14]aneN$_4$)](ClO$_4$)$_2$ and the dimeric product show virtually the same features. However, appreciable differences were observed between the NMR spectra, ^{13}C and ^{1}H, of the two complexes (Figure 2). Figure 3 shows the differences in the ultraviolet spectra of the dimeric product [Ni(dehydrobis([14]aneN$_4$))](ClO$_4$)$_4$ and [Ni([14]aneN$_4$](ClO$_4$)$_2$. Such spectra gave a quantitative justification of the spectral transformations observed in continuous-wave irradiations; e.g., see Figure 1.

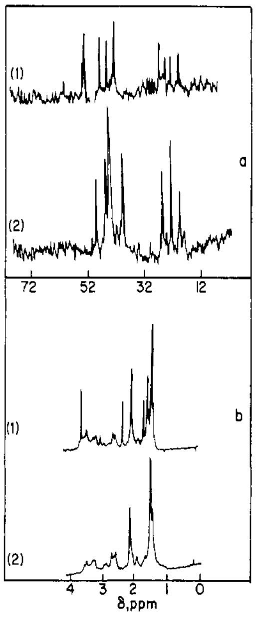

Figure 2. NMR spectra: (a) ^{13}C and (b) ^{1}H of Ni([14]aneN$_4$)$^{2+}$ (1) and [Ni$_2$(dehydro bis([14]aneN$_4$)](ClO$_4$)$_4$ (2).

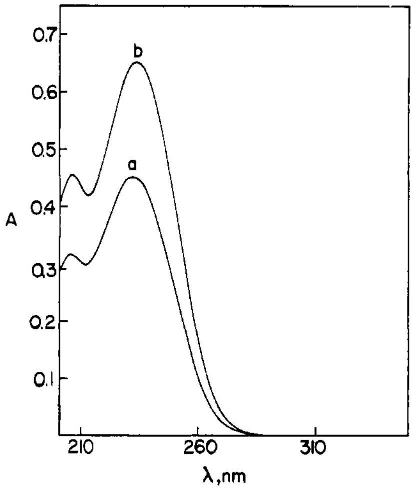

Figure 3. Ultraviolet spectra of Ni([14]aneN$_4$)$^{2+}$ (a) and Ni$_2$(dehydrobis([14]aneN$_4$))$^{4+}$ (b) in aqueous solutions.

Transformations in the spectrum of Ni(13-At)$^+$ were sensitized by benzophenone or fluorenone (λ_{excit} = 360 nm excit = excitation; solvent acetonitrile). Such spectral transformations are similar to those observed with complexes of [14]aneN$_4$; see above and Figure 4.

Laser and Conventional Flash Photolysis. The chemical and spectral transformations induced by the sensitizers were attributed to reactions between the excited states of the sensitizers and macrocyclic complexes. Laser flash photolysis of deaerated solutions of benzophenone produce a transient spectrum which corresponds to the benzophenone triplet. The value of the lifetime of the excited state in acetonitrile, $t_{1/2}$ = 1.2×10^{-4} s, has been found to be between those reported for benzene and cyclohexane solutions.[23] Moreover, the

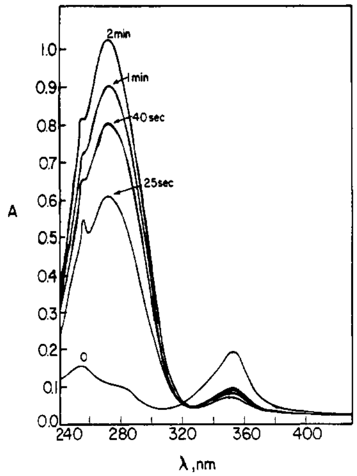

Figure 4. Changes in the spectrum of $Ni(13\text{-}At)^+$ induced by oxidation with fluorenone triplets. Conditions: $[Ni^{II}] = 5.0 \times 10^{-4}$ M; [fluorenone] $= 5.0 \times 10^{-3}$ M; $I_0 = 2.9 \times 10^{-4}$ einstein/L min.

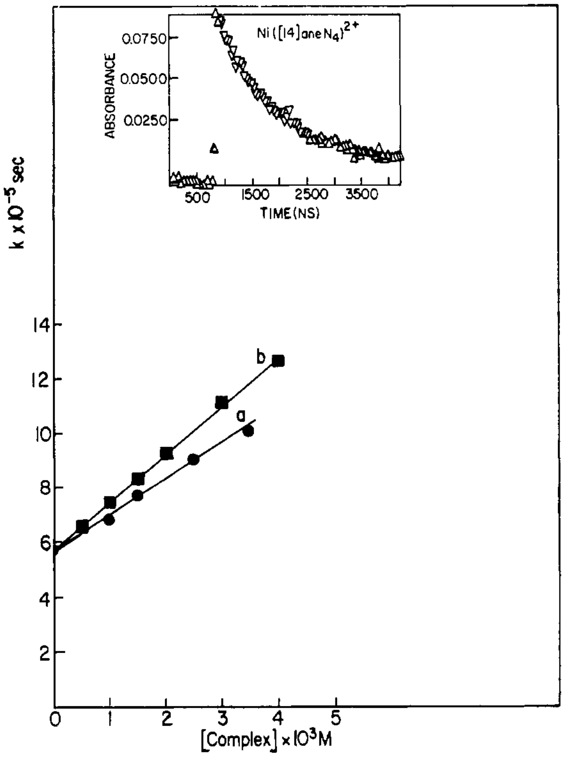

Figure 5. Dependence of the rate constant for the decay of the benzophenone triplet on quencher concentration: (a) $Ni([14]aneN_4)^{2+}$; (b) $Cu([14]aneN_4)^{2+}$. Inset shows a typical trace for the decay of the benzophenone triplet in deaerated acetonitrile.

first-order decay of the benzophenone triplet is accelerated by $Ni([14]aneN_4)^{2+}$ (Figure 5). A second-order rate constant, $k = 1.3 \times 10^8$ M^{-1} s^{-1}, was obtained for the reaction between $Ni([14]aneN_4)^{2+}$ and the benzophenone triplet. Also, the benzophenone triplet reacts with $Cu([14]aneN_4)^{2+}$, $k = 1.9 \times 10^8$ M^{-1} s^{-1}; see Figure 5.

Transients with half-lifes longer than 10 μs were investigated by conventional flash photolysis. Flash irradiations ($\lambda_{excit} \geq 320$ nm) of 5×10^{-3} M benzophenone and 10^{-3} M $Ni([14]aneN_4)^{2+}$ in deaerated acetonitrile produce a transient spectrum with $\lambda_{max} = 380$ nm and 520 nm (Figure 6a). This spectrum resembles the spectrum of the benzophenone ketyl radical. The decay of the 380-nm absorbance exhibited a first-order dependence on transient concentration, $k = 1.5 \times 10^4$ s^{-1}. Moreover, the decay of the 380-nm absorbance is faster than the disappearance of the 520-nm absorbance. A second-order dependence on transient concentration was observed for the decay rate of the 520-nm absorbance at reaction times longer than 1 ms. The ratio of the second-order rate constant to the extinction coefficient, $k/\epsilon = 2.4 \times 10^5$ cm s^{-1}, was determined at 520 nm. A value of the rate constant, $k = 10^9$ M^{-1} s^{-1}, was obtained by using the reported extinction coefficient of the benzophenone ketyl radical.[24] Such a value is in good agreement with one reported for the dimerization–disproportionation of the benzophenone ketyl radical.

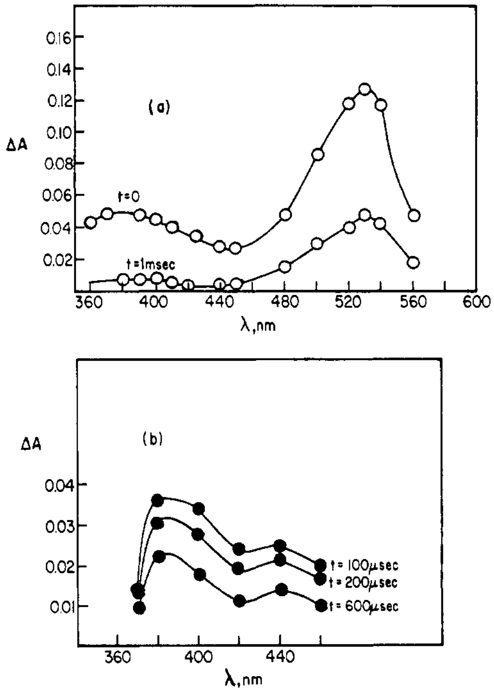

Figure 6. Transient spectra observed in flash photolysis of (a) 5×10^{-3} M benzophenone and 10^{-3} M $Ni([14]aneN_4)^{2+}$ in deaerated acetonitrile and (b) 5×10^{-3} M benzophenone and 10^{-3} M $Cu([14]aneN_4)^{2+}$ in deaerated acetonitrile.

Appropriate concentrations of methanol were used in order to intercept the benzophenone triplets in acetonitrile solutions, namely, $[CH_3OH] \geq 2.5$ M. The decay of the benzophenone ketyl radical exhibited a second-order dependence in radical concentration, $k = 1.3 \times 10^9$ M^{-1} s^{-1}, and it was independent of the nickel(II) concentration, namely, for $[Ni([14]aneN_4)^{2+}] \leq 2.5 \times 10^{-4}$ M.

Also the interception of the benzophenone triplet by $Cu([14]aneN_4)^{2+}$ produces transient absorbance with $\lambda_{max} = 380$ and 440 nm (Figure 6b). The rate of decay of the absorbances exhibited a first-order dependence in transient concentration: $k = 1.2 \times 10^3$ s^{-1}.

The oxidations of $Ni([13]dieneN_4)^{2+}$ and $Ni(13\text{-}At)^+$ by the fluorenone triplet and (^{2}E) $Cr(bpy)_3{}^{3+}$ were studied by conventional flash photolysis. Figure 7 shows the transient spectra generated in these photolyses. Flash irradiations of deaerated acidic solutions of $Cr(bpy)_3{}^{3+}$ in acetonitrile produce (^{2}E) $Cr(bpy)_3{}^{3+}$. However, $Cr(bpy)_3{}^{2+}$ is generated in flash photolysis of $Cr(bpy)_3{}^{3+}$ in the presence of $Ni(13\text{-}At)^+$ (Figure 7). The disappearance of $Cr(bpy)_3{}^{2+}$ exhibited a second-order dependence on the concentration of Cr(II). A second-order rate constant, $k = 2.5 \times 10^8$ M^{-1} s^{-1}, was obtained from the ratio of the rate constant to the extinction coefficient, $k/\epsilon = 5.3 \times 10^4$ cm s^{-1}, determined at 560 nm. The formation of

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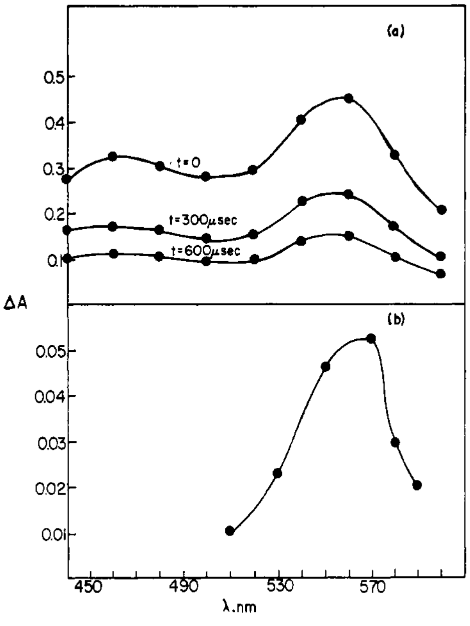


Figure 7. Transient spectra generated in oxidations of Ni(13-At)$^+$ by (a) (^{2}E) Cr(bpy)$_3$$^{3+}$ (medium: 10^{-5} M HClO$_4$ in CH$_3$CN) and (b) fluorenone triplets (medium: CH$_3$CN).

Table I. Quenching Rate Constants

sensitizer[a]	quencher	λ_{excit}, nm	λ_{em}, nm	k_Q,[b] $M^{-1}\,s^{-1}$
fluorenone	[Ni(13-At)]$^+$	430	580	2.0×10^9
fluorenone	[Ni([14]aneN$_4$)]$^{2+}$	360	500	5.1×10^8
fluorenone	Ni([14]aneN$_4$)$^{2+}$	390	500	5.9×10^8
fluorenone	Ni([14]aneN$_4$)$^{2+}$	430	500	6.8×10^8
Cr(bpy)$_3$$^{3+}$	[Ni(13-At)]$^+$	425	730	2.6×10^8
Cr(bpy)$_3$$^{3+}$	Ni([14]aneN$_4$)$^{2+}$	425	730	1.2×10^6

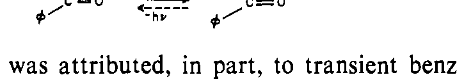
[a] Deaerated solutions with CH$_3$CN as solvent of 10^{-3} M fluorenone or 3.3×10^{-4} M Cr(bpy)$_3$$^{3+}$ were used. [b] Quenching rate constants were obtained from Stern–Volmer plots by using the excited-state decay constants $k = 1.8 \times 10^6$ s^{-1} for fluorenone and 8.6×10^3 s^{-1} for Cr(bpy)$_3$$^{3+}$.

Cr(bpy)$_3$$^{2+}$ was also induced in the reaction of (^{2}E) Cr(bpy)$_3$$^{3+}$ with Ni([13]dieneN$_4$)$^{2+}$. The back-electron-transfer reaction between Cr(II) and the oxidation product of Ni([13]dieneN$_4$)$^{2+}$ ($k = 2.5 \times 10^9$ M^{-1} s^{-1}) is faster than the reaction of Cr(II) with the oxidation product of Ni(13-At)$^+$. The oxidation of Ni(13-At)$^+$ by the fluorenone triplet in neutral solutions produce a transient spectrum with $\lambda_{max} \approx 570$ nm (Figure 7). Such absorbances decay by a first-order process with $t_{1/2} \approx 0.2$ s.

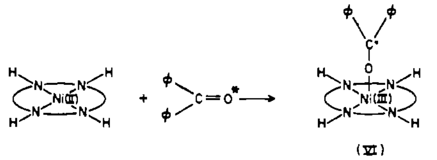
Emission Studies. Table I shows some of the results obtained on the quenching of the emission of the fluorenone triplet and (^{2}E) Cr(bpy)$_3$$^{3+}$ by Ni(II) macrocycles. Linear Stern–Volmer plots were obtained for these systems in the range of quencher concentrations indicated in Table I. Quenching rate constants were determined from the slopes of the Stern–Volmer plots and the rate constants for the decay of the excited states.

Discussion

The sensitized oxidation of the Ni([14]aneN$_4$)$^{2+}$ by the benzophenone triplet, (T) Ph$_2$CO in eq 8, produce a transient


$$\phi_2C{=}O \underset{-h\nu}{\overset{h\nu}{\rightleftarrows}} \phi_2C{=}O^* \qquad (8)$$

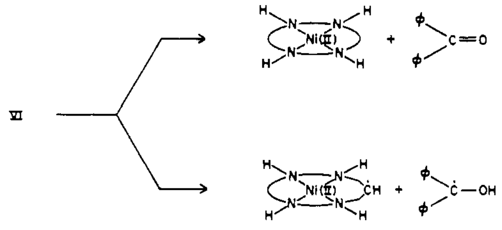
spectrum that was attributed, in part, to transient benzophenone ketyl radical, $\lambda_{max} \approx 520$ nm (Figure 6). Moreover, the fast first-order decay of the ultraviolet absorbances indicate that a precursor of the free benzophenone ketyl radical is formed in the oxidation process. The reported second-order disproportionation–dimerization of the radical was observed at reaction times longer than those required for the disappearance of the ultraviolet absorbances. Since a number of one-electron oxidants oxidize macrocyclic complexes of Ni(II) by an inner-sphere mechanism, the precursor can be regarded as a nickel(III)–benzophenone ketyl radical complex, namely, eq 8 and 9. Indeed, the formation of nickel(III) macrocycle


(9)

(VI)

with axially coordinated acido ligands, acido = Cl$^-$, Br$^-$, and SCN$^-$, has been reported in oxidations with Cl$_2$$^-$, Br$_2$$^-$, and (SCN)$_2$$^-$.[10,12] The nickel(III) is stabilized by coordination of the halides, and the hydrolysis of the acido ligand is a slow process. Such a behavior suggests that the benzophenone ketyl radical must remain coordinated to Ni(III) after the oxidation of the parent Ni(II) complex by the benzophenone triplet (eq 9).

The product of the photoinduced oxidation of Ni([14]aneN$_4$)$^{2+}$ has been characterized as a dimeric Ni(II) macrocycle. The structural evidence indicates that the dimer must contain a carbon–carbon bond between two Ni([14]aneN$_4$)$^{2+}$ units, namely, as in V. Such a dimerization in nonaqueous solvents, e.g., CH$_3$CN, contrasts with other processes, observed in aqueous solutions, namely, the degradation of the macrocycle and/or introduction of imino groups. It seems feasible that the observed dimerization is related to the nature of the precursor nickel(III)–benzophenone ketyl radical. Indeed, the radical nature of the coordinated benzophenone ketyl radical and the oxidation potential of the nickel(III) can be required for a transfer of the oxidation from the metal center to a carbon in the macrocycle ligand. The fast hydrolysis of the Ni(II) species, produced in the transfer of the oxidation from the Ni(III) to the macrocyclic ligand, will liberate the benzophenone ketyl radical, eq 10 and 11. Hence the dimerization must be the result of the generation of a Ni(II)–ligand radical which has little tendency to disproportionate, namely producing monomeric species with a two electron oxidized macrocycle, eq 12.

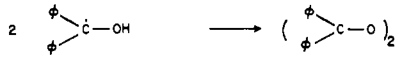

(10)

(11)

(VII)

$$2\ \text{VII} \longrightarrow \text{dimerization product} \qquad (12)$$

It is feasible that the mechanism for the photoinduced oxidation of Ni([14]aneN$_4$)$^{2+}$ (eq 8–13) can be extended to


$$2\ \phi_2\dot{C}{-}OH \longrightarrow (\phi_2C{-}O)_2 \qquad (13)$$

Cu([14]aneN$_4$)$^{2+}$. However, the photoinduced oxidations of Ni([13]dieneN$_4$)$^{2+}$ and Ni(13-At)$^+$ by the triplet of fluorenone and (^{2}E) Cr(bpy)$_3$$^{3+}$ can produce either a nickel(III) or a nickel(II)–ligand radical as precursors of the products or both. The last alternative, a nickel(II)–ligand radical intermediate, has been already postulated in the reaction mechanism for the oxidative dimerization of various macrocyclic complexes.[25]

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The rate constants for reactions with (^{2}E) $Cr(bpy)_3^{3+}$ show that $Ni(13\text{-}At)^+$ is a better redox quencher than $Ni([13]dieneN_4)^{2+}$. The back-electron-transfer reactions between the oxidation products and $Cr(bpy)_3^{2+}$ show the opposite tendency. Indeed, the oxidation product of $Ni([13]dieneN_4)^{2+}$ reacts faster than the one of $Ni(13\text{-}At)^+$ with $Cr(bpy)_3^{2+}$. This behavior can be related, in part, with the expected differences in the redox potentials of the two nickel complexes.

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Appendix

The formula of the product of the sensitized oxidation of $Ni([14]aneN_4)^{2+}$ was investigated by combining the results of the apparent molecular weight, determined by measurements of osmotic pressure, and condutiometric determinations. A formula X_nD was assigned to the complex in the mathematical treatment described below. Such a compound will dissociate in n X^- anions, $X^- = Cl^-$ or ClO_4^-, and D^{n+} cations. The apparent molecular weight, $M^{ap}{}_{X_nD}$, can be expressed according to the molecular weight of the corresponding ions, namely, M_x and M_D in eq 14.

$$M^{ap}{}_{X_nD} = (n/(n+1))M_x + (1/(n+1))M_D \qquad (14)$$

The expression for the molar conductance of the chloride or perchlorate salts of the compound, eq 15, contains the molecular weight of the salt, $M^T{}_{X_nD}$, which can be replaced by the molecular weight of the ions. Combination of eq 14 and 15 for X = Cl^- and ClO_4^- gave eq 16 and 17 for the molar conductance of the chloride and perchlorate salts.

$$\Lambda_{X_nD} = K_{X_nD}\frac{1000}{w_{X_nD}}M^T{}_{X_nD} = K_{X_nD}\frac{1000}{w_{X_nD}}(nM_x + M_D) \qquad (15)$$

$$\Lambda_{(ClO_4)_nD} = K_{(ClO_4)_nD}\frac{1000}{w_{(ClO_4)_nD}}(n+1)M^{ap}{}_{(ClO_4)_nD} \qquad (16)$$

$$\Lambda_{Cl_nD} = K_{Cl_nD}\frac{1000}{w_{Cl_nD}}[(n+1)M^{ap}{}_{(ClO_4)_nD} - 64n] \qquad (17)$$

We used $w_{(ClO_4)_nD} = w_{Cl_nD} = w$ in our experiments. Moreover, conductance measurements were carried out with various concentrations of complexes, $[X_nD] \leq 2.7 \times 10^{-4}$ M, and extrapolated to infinite dilution. Such conditions allowed to express the molar conductance in terms of the independent conductances of the ions (eq 18). The combination of eq

$$\lambda^{\infty}{}_{X_nD} = \lambda^0{}_D + n\lambda^0{}_x \qquad (18)$$

16–18 gave an explicit expression for n (eq 19). An average

$$n = \frac{M^{ap}{}_{(ClO_4)_nD}(K_{(ClO_4)_nD} - K_{Cl_nD})}{(\lambda^0{}_{ClO_4^-}\text{-}\lambda^0{}_{Cl^-})\frac{w}{1000} - M^{ap}{}_{(ClO_4)_nD}(K_{(ClO_4)_nD} - K_{Cl_nD}) - 64K_{Cl_nD}} \qquad (19)$$

value $n = 3.9 \pm 0.1$ is consistent with a dimeric structure of the Ni(II) product. Substitution of the n value in eq 14 and use of the expression of $M^T{}_{X_nD}$, in terms of M_D and M_x, gave $M^T{}_{(ClO_4)_nD} = 1301$.

Registry No. $[Ni(13\text{-}At)]^+$, 79135-14-1; $[Ni([14]aneN_4)]^{2+}$, 18444-42-3; fluorenone, 486-25-9; $Cr(bpy)_3^{3+}$, 15276-15-0; $[Cu([14]aneN_4)]^{2+}$, 33727-14-9; benzophenone, 119-61-9.

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Optical Activity in Mixed-Ligand Terbium Complexes Containing Pyridine-2,6-dicarboxylic Acid and Chiral Hydroxycarboxylic Acids

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The optical activity associated with the f–f emission bands of Tb(III) complexes which contain chiral hydroxycarboxylic acids has been studied by means of circularly polarized luminescence (CPL) spectroscopy. Complexes having the general formulas Tb(DPA)(L) and $Tb(DPA)_2(L)$ were studied (where DPA signifies pyridine-2,6-dicarboxylate), with the chiral L ligand being L-lactic acid, L-α-hydroxyisocaproic acid, L-argininic acid, L-mandelic acid, L-phenyllactic acid, L-malic acid, L-hydroxyglutaric acid, and D-isocitric acid. The CPL spectra were found to be sensitive to the mode of bonding existing between the metal and the chiral ligand and therefore enabled predictions to be made regarding how the hydroxycarboxylic acid ligands attach to the Tb(III) ion. In addition, the degree of optical activity varied systematically with the concentration of chiral ligand, and we have used this dependence to calculate formation constants for the addition of a hydroxycarboxylic acid ligand to the Tb/DPA complexes. Finally, the line shapes and magnitudes of the CPL spectra provide information regarding the type of chirality experienced by the Tb(III) ion.

Introduction

The lanthanide complexes of α-hydroxycarboxylic acids have been of interest since the early observations that these ligands could be used in the ion-exchange separation of the rare-earth cations.[2,3] The formation constants of these complexes have been extensively studied by potentiometric means, although there has been some dispute regarding which particular hydroxycarboxylic acid ligand yields the most stable complex.[4] More recently, a variety of NMR techniques have been used to study the dynamics of aqueous solutions this class of lanthanide complexes.[5]

Much less is known about the mixed-ligand complexes of lanthanide ions with hydroxycarboxylic acids and about the influence of other ligands on the binding of the hydroxycarboxylic acid ligands by lanthanide ions. In one recent study, the potentiometric method has been used to study the complexation phenomena associated with mixed lanthanide com-

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