8 and 9) does indeed show a shift. At 15 °C the predominant Co(II) species at [SCN$^-$] = 0.1 M are the mono complex, the bis complex, and a small concentration of tris complexes. An increase in temperature to 25 °C increases the amount of the $CoSCN^+$ complex relative to that of the bis and tris forms. At 15 °C approximately 20% of the Co(II) exists as the aquo ion, and this increases to about 30% at 25 °C. There will be no measurable concentration of the tetrakis complex. Thus, the major change in complexed Co(II) species does not involve a geometry change, as would be expected for the formation of the tetrakis complex. Since the absorption peak corresponding to the various complexes extends through 580 nm, the wavelength in the temperature-jump study, we believe that the first absorption change corresponds to a rapid interchange of Co(II) complexes (<20 μs). However, the NMR and spectroscopic investigations of $Co(ClO_4)_2$ complexation in water and mixed solvents, which were not available for the temperature-jump study, indicate that the predominant solvated Co(II) species is octahedral in nature. This spectroscopic investigation cannot give any structural information about the nature of the aqeuous Co(II) solvated ion but does suggest that if significant concentrations of a tetrahedral species, $Co(H_2O)_4^{2+}$, were present, an observable color change should occur. However, it should be noted that the optical absorbance measured in a temperature-jump experiment is highly sensitive and might be able to detect a small concentration of $Co(H_2O)_4^{2+}$. Although this investigation does not eliminate the possibility that the earlier observations are correct, it does suggest that a temperature-jump relaxation reinvestigation of the Co(II)–SCN$^-$ system is in order. The reaction conditions should be modified to ensure for some of the experiments that only the mono complex is present and for others that the tetrakis complex is formed. Examination of Figures 8–10 reveals that as methanol is added to the solvent system, the range of stability of the tetrakis complex increases, suggesting that it may be possible to study the kinetics of the known octahedral–tetrahedral change for the Co(II)–SCN$^-$ system. With the more sensitive electronics presently available, the existence of the tetrahedral solvated Co(II) species should either be confirmed or eliminated.

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Photochemistry of Nickel(II) Azido Complexes: Singlet Nitrene

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The near-ultraviolet irradiation of $Ni(tet\text{-}a)(N_3)_2$ directly excites the $n \rightarrow \pi^*$ transition of the azido group, which yields a singlet nitrene intermediate. This intermediate scavenges ammonia to yield hydrazine. Because the primary quantum yield for nitrene formation is 0.042 and the quantum yield for azido group photodecomposition is 0.15, it is suggested that the remainder of the photodecomposition occurs via a triplet nitrene intermediate. It is shown that the formation of triplet nitrene is spin-allowed and energetically accessible.

Introduction

The photodecomposition of azido complexes has drawn a great deal of attention in recent years.[1-17] Among the reasons for this interest is the variety of modes of photodecomposition thus far demonstrated for azido complexes. Among those observed thus far are azide aquation, trans ligand aquation, azide radical formation, and coordinated nitrene formation. The quantum efficiencies for these reactions are wavelength-dependent, and often more than one mode is observed for the same complex. Much attention has been focused on the kinetic and thermodynamic factors that determine the patterns of reactivity with the hope of understanding the behavior of these complexes.

Much of the impetus for the more recent interest in azido group photochemistry results from the discovery by Basolo and coworkers of the nitrene photodecomposition pathway.[2-4] In contrast to organic azides, prior to these reports, azido group photodecomposition occurred exclusively via azide radical formation. In their original report Basolo and co-workers proposed that nitrene formation is favored for metals not having a stable one lower oxidation state and for metals having filled d orbitals that can back-donate into the vacant nitrogen orbitals of the nitrene and thus stabilize the metal nitrene. The importance of the former has been developed by Endicott and co-workers[21] in their quasi-thermodynamic treatment of redox photoreactivity. The importance of the latter has been demonstrated by Mansuy and co-workers,[10] who were able to isolate a stable iron porphyrin nitrene.

The first reported occurrence of metal nitrene intermediacy, both thermal[22,23] and photochemical,[2-4] employed metals of the

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second and third transition series. These has been one report of a photochemically generated nitrene involving a first-row transition metal.[9] This chromium(III) nitrene strictly speaking does not meet either of these criteria, and even after a long history its photochemistry has yet to be satisfactorily worked out. The conclusions drawn from this work will, however, have important implications for $Cr(NH_3)_5N_3^{2+}$ photochemistry. Nickel(II) is a first-transition-series metal that meets both of the criteria set forth by Basolo and co-workers. The complex under study is diazido(*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II), Ni(tet-a)$(N_3)_2$. Although Ni(tet-a)$^{2+}$ can be reduced to the univalent state, which is not stable under normal conditions, this complex is d^8 and therefore has filled π orbitals, which are available to stabilize a nitrene intermediate. Thus Ni(tet-a)$(N_3)_2$ should be an excellent candidate for coordinated nitrene intermediacy during photolysis.

Experimental Section

Materials. 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate was prepared by the published method.[24]

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane dihydrate, tet-a, was prepared by the reduction of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate and resolved by the published method.[25]

Ni(tet-a)$(ClO_4)_2$ was prepared by reacting equimolar amounts of nickel acetate and tet-a in dimethylformamide at 90 °C for 0.5 h. The product was isolated by precipitation with sodium perchlorate. It was purified by recrystallization from methanol.

Ni(tet-a)$_2$$(N_3)$ was prepared by treating Ni(tet-a)$(ClO_4)_2$ (1.0 g, 1.8 mmol) with NaN_3 (0.30 g, 4.6 mmol) in 10 mL of methanol to which 10 mL of NaN_3-saturated methanol was added. This mixture was stirred with heating for 30 min, cooled, and then filtered. The lavender product was purified by stirring with methanol followed by the addition of NaN_3-saturated methanol. The solid was filtered and then air-dried. Anal. Calcd for $Ni(C_{16}H_{36}N_4)(N_3)_2$: C, 45.40; H, 7.62; N, 33.10. Found: C, 44.59; H, 8.14; N, 32.39.

All other materials were reagent grade unless otherwise specified. Methanol was freshly distilled from magnesium turnings prior to use. Methanolic ammonia solutions were prepared by bubbling ammonia through freshly distilled methanol followed by standardization against standard hydrochloric acid.

Photolysis Procedures. Unless otherwise specified an optical train was employed in the irradiations. The light from a 1000-W Oriel Optics high-pressure xenon-mercury lamp was focused by means of two quartz lenses through a 14-cm quartz water filter onto the entrance slit of a Bausch and Lomb Model 33-86-08 grating monochromator. The entrance and exit slits were adjusted to yield 90% of the radiation with a 10-nm band-pass. The light from the exist slit of the monochromator passed into a Varian Model 01-44-4200-00 thermostated cell jacket. The cell jacket was modified to place the cell holder as close to the exit slit of the monochromator as possible. The jacket was thermostated to 25.0 ± 0.1 °C with a Haake Model FS constant temperature circulator. Light intensities were measured by using ferrioxalate actinometry.[26,27]

Quantum yield determinations were made from plots of concentration vs. time of irradiation. These plots were linear, and at no time was the reaction carried beyond 5% conversion to products. There was no evidence of secondary photolysis or an inner filter effect. Corrections were made for the fraction of incident radiation absorbed.

Preparative scale photolysis were carried out with a Rayonet chamber photochemical reactor. The 300- or 350-nm lamps were used, and solutions were contained in Pyrex vessels.

In studies in which the infrared spectrum was monitored in the 2200–2000-cm^{-1} region during photolysis, chloroform, methylene chloride, and tetrahydrofuran were used as solvents. In some cases specified amounts of cyclohexene were added. The reference cell contained the solvent or solvent mixture used in the irradiation. The solution under study was irradiated in a standard infrared cell with a nominal path length of 1 mm. After each irradiation the infrared spectrum was recorded over the 2200–2000-cm^{-1} region.

Table I. Visible and Ultraviolet Spectral Data for Ni(tet-a)$(N_3)_2$ and Ni(tet-a)$^{2+}$

assignt	abs max,[a] 10^3 cm^{-1} (M^{-1} cm^{-1}, 10^3 cm^{-1})
	Ni(tet-a)$(N_3)_2$
$^3E_g \leftarrow {}^3B_{1g}$	9.90 (11.86, 3.53)[b]
	9.49[c]
$^3B_{2g} \leftarrow {}^3B_{1g}$	13.89 (2.57, 2.68)[b]
	14.32[c]
$^3A_{2g} \leftarrow {}^3B_{1g}$	15.87 (1.15, 1.27)[b]
	15.60[c]
$^3E_g \leftarrow {}^3B_{1g}$	18.52 (8.26, 3.51)[b]
	19.50[c]
$\pi^* \leftarrow n$	31.65 (1669)[b]
	39.94 (3347)[b]
	45.04 (9025)[b]
	Ni(tet-a)$^{2+}$
	42.37 (9661)[d]
	47.17 (14110)[d]

[a] Reported as wavenumber (extinction coefficient, half-width). [b] This work. $CHCl_3$ as solvent. [c] Reference 30. Solid state. [d] This work. CH_3OH as solvent.

Analytical Procedures. Hydrazine was determined by the method of Watt and Chrisp.[28] Three milliliters of photolyte and 4.0 mL of hydrazine reagent were pipetted into a 10-mL volumetric flask and diluted to the mark with ca. 2 M hydrochloric acid. The optical density was then measured at 460 nm. The hydrochloric acid was prepared by diluting 10.0 mL of concentrated hydrochloric acid to 60.0 mL with methanol. A calibration curve was prepared by using reagent grade hydrazine dihydrochloride.

Azide was determined spectrophotometrically as its ferric complex. Fisher ferric nitrate (20.2% w/v) was diluted 1:5, and 2 mL of this solution was pipetted into a 10-mL volumetric flask. The solution was diluted to the mark with water and the optical density measured at 460 nm. A calibration curve was prepared by using reagent grade sodium azide.

The optical spectra were resolved into Gaussian components by entering the digitized spectra into a Digital PDP 11/34 minicomputer. Analyses were carried out by the least-squares procedure of Beecher.[29] The program has been modified to prevent distrotion by the intense unresolved ultraviolet absorptions.

Physical Measurements. All infrared spectra were recorded on a Beckman Model 4240 or Acculab infrared spectrometer. Ultraviolet and visible spectra were recorded on a Varian Cary Model 17 UV-vis-near-IR spectrophotometer. In some cases spectra were recorded on a Hitachi Model 100-60 spectrophotometer interfaced to an Apple II microcomputer. The digitized spectra were stored on disks. The spectra used in this work were unfiltered and unsmoothed. Single-wavelength ultraviolet and visible spectral measurements were made on a Sargent-Welch SM spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed by the Galbraith Laboratories.

Results

Under ultraviolet irradiation Ni(tet-a)$(N_3)_2$ undergoes photodecomposition in a number of solvents. In halocarbon solvents, such as chloroform and dichloromethane, the optical spectrum of Ni(tet-a)$(N_3)_2$ agrees with the solid-state spectrum reported by Busch and co-workers.[30] Deconvolution of the solution spectra into a series of Gaussian components and computation of the ligand field parameters yielded results that agreed very well with those of Busch et al. (Table I). In addition, the optical spectrum of several intense absorptions in the ultraviolet region were recorded. No curve fitting was attempted, however, since it is likely that such absorption bands arise from more than a single electronic transition (Table I). For comparison the spectrum of Ni(tet-a)$^{2+}$ in methanol was recorded in the same spectral region. Ni(tet-a)$^{2+}$ contains two of the three absorption bands found in Ni(tet-a)$(N_3)_2$, both of which were shifted to somewhat higher energies. Most of the results reported here are for photolyses performed in

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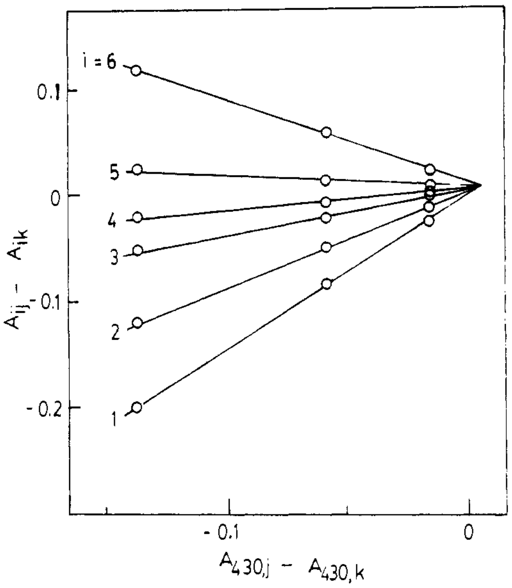

Figure 1. Plot of the difference in absorbance at wavelength *i* for solutions j and k, where k = 0.0020 M LiN_3, j = 0.0040, 0.00080, and 0.016 M LiN_3, and *i* = 450, 430, 390, 550, and 370 nm.

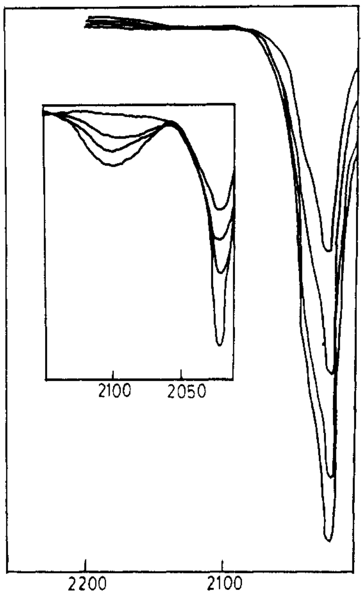

Figure 2. Infrared monitoring of the near-ultraviolet photolysis of Ni(tet-a)$(N_3)_2$ in tetrahydrofuran containing 5% cyclohexene. Insert: Infrared monitoring of the near-ultraviolet photolysis of $Co(CH_3COCH_2COCH_3)_2N_3NH_3$ under the same conditions as above.

Table II. Quantum Yield for the Formation of Hydrazine in the Photolysis of 0.0020 M Methanolic Ni(tet-a)$^{2+}$ in the Presence of Added Ammonia and Azide Ion

$\phi_{N_2H_4}$	$[NH_3]$	$\phi_{N_2H_4}$	$[NH_3]$
0.00003	0.000[a]	0.0016	0.240[b]
0.0015	0.295[a]	0.0019	0.300[b]
0.0029	0.590[a]	0.0029	0.350[b]
0.0039	0.857[a]	0.0036	0.600[b]
0.0071	1.47[a]	0.0064	1.08[b]
0.013	3.69[a]	0.0082	1.50[b]
0.0012	0.170[b]		

[a] $[NaN_3]$ = 0.0040 M, $[NH_4BF_4]$ = 0.0012 M, $[NaClO_4]$ = 0.0304 M, exciting wavelength = 320 nm. [b] $[LiN_3]$ = 0.0020 M, $[NH_4BF_4]$ = 0.00020 M, exciting wavelength = 310 nm.

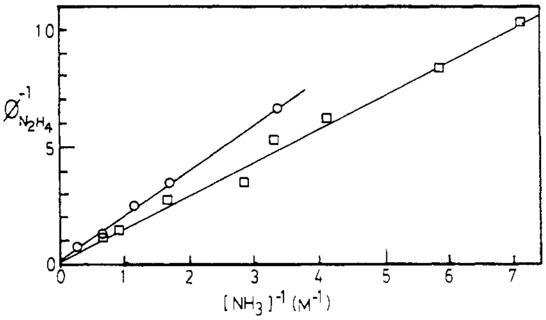

Figure 3. Plot of $\phi_{N_2H_2}^{-1}$ vs. $[NH_3]^{-1}$ for the photolysis of methanolic 0.0020 M Ni(tet-a)$^{2+}$: (□) 0.0020 M LiN_3 with 310 nm radiation; (○) 0.0040 M NaN_3 and 0.0304 M $NaClO_4$ with 320 nm radiation.

methanolic solutions. The behavior of Ni(tet-a)$(N_3)_2$ in methanol was studied by optically monitoring a series of solutions made 0.0080 M in Ni(tet-a)$^{2+}$ to which various amounts of LiN_3 (yielding 0.0–0.020 M solutions) had been added. Isosbestic points were maintained at 395 and 525 nm. Furthermore, the matrix rank analysis procedure of Coleman and co-workers[31] indicates the presence of only two absorbing species in this concentration range (Figure 1). Solutions of this complex in methanol and tetrahydrofuran exhibit an intense absorption at 317 nm, whereas $CHCl_3$ and CH_2Cl_2 solutions exhibit the same absorption at 315 nm. As evidenced by changes in the optical spectra, Ni(tet-a)$(N_3)_2$ in all of these solvents undergoes photodecomposition when irradiated into the 315-nm absorption. In addition, monitoring the infrared absorption spectra of Ni(tet-a)$(N_3)_2$ in CH_2Cl_2 and $CHCl_3$ during irradiation into this band revealed a steady decrease in the 2029-cm^{-1} absorption of the azido group. No new absorption appeared in this region. In a series of similar experiments, solutions of Ni(tet-a)$(N_3)_2$ in methylene chloride and tetrahydrofuran, which were respectively made 20% and 10% in cyclohexene, were irradiated. The infrared absorbance of the metal azide decreased in intensity with increasing time of irradiation. There was not concomitant increase in absorption near 2109 cm^{-1} (Figure 2). As a parallel experiment $Co(acac)_2N_3NH_3$ was irradiated, and along with a decrease in intensity at 2024 cm^{-1} there was a growth in intensity at 2100 cm^{-1} (Figure 2).

Quantum Yields. Quantum yields for the formation of hydrazine and the decomposition of azide were determined in methanolic media at 25.0 °C. In all cases NH_4BF_4 was added to supply the hydrogen ion required by the stoichiometry of the reaction. Conditions were such that Ni(tet-a)$(N_3)_2$ was the only absorbing species. Two series of experiments were run. In both cases azide ion was added to Ni(tet-a)$^{2+}$ solutions in the form of an alkali-metal azide salt. In the first series, irradiations were carried out at 320 nm, and $NaClO_4$ was added to maintain the ionic strength at 0.061 M. The ratio of N_3^- to N(tet-a)$^{2+}$ in the solutions was 2.0. The ammonia concentration was varied from 0.0 to 3.69 M. The quantum yield for the decomposition of azide was determined for solutions containing no added ammonia. It was found to be 0.15. Yields for hydrazine formation were determined at various ammonia concentrations, and these may be found in Table II. The quantum yields for the formation of hydrazine increase toward a limiting value as the ammonia concentration is increased. In a second series of similar experiments no provision was made for maintaining constant ionic strength. The N_3^-/Ni(teta)$^{2+}$ ratio was decreased to 1.0, and irradiations were carried out at 310 nm, (Table II), which was still in the same intense ultraviolet absorption band. In spite of these differences in conditions there were no significant differences in the kinetic behavior. A plot of $\phi_{N_2H_4}^{-1}$ vs. $[NH_3]^{-1}$ is linear in both cases (Figure 3), and this dependence is consistent with an experimental rate law of the form

$$\phi_{N_2H_4} = \frac{[NH_3]}{a + b[NH_3]} \qquad (1)$$

The first series of experiments yielded 190 M and 23 for *a* and *b*, respectively, and the second series yielded 140 M and 24.

Product Isolation. Solutions of Ni(tet-a)$(N_3)_2$ (ca. 0.008 M) in $CHCl_3$ were irradiated with the 300-nm lamps until 81% of

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the azide had decomposed. The solvent was removed and the residue dissolved in water. Upon the addition of $NaClO_4$ followed by chilling, a yellow solid formed. Typically the spectra of both filtrate and precipitate indicated the presence of Ni(tet-a)$^{2+}$ as well as other material absorbing in this region. In similar experiments the residue was absorbed on Bio-Rad AGW X2 cation-exchange resin (H^+ form). Development with various concentrations of HCl failed to elute a solution of pure Ni(tet-a)$^{2+}$.

Solutions of Ni(tet-a)$(N_3)_2$ (ca. 0.001 M) in CH_3OH were irradiated with the 350-nm lamps until 16–17% of the azide decomposed. The photolyte was passed onto a Bio-Rad AGW X2 cation-exchange resin (H^+ form). The resin was then treated with 0.1 M NaOH and then washed with water until neutral. The resin was then extracted with methanol for 15–17 h. The resin was then placed in a column and developed with HCl. The eluents contained pure Ni(tet-a)$^{2+}$ as evidenced by the optical spectra, and the amount of Ni(tet-a)$^{2+}$ recovered was determined spectrophotometrically. The amount of Ni(tet-a)$^{2+}$ not recoverable as the result of photolysis was between 35 and 100% of the azide ion decomposed during photolysis.

Discussion

Basolo and co-workers, in reporting the occurrence of coordinated nitrene formation in the photolysis of the azidopentaammineiridium(III), proposed two conditions that favor coordinated nitrene formation over the other modes of photodecomposition.[7] It was proposed that nitrene formation is favored when the metal does not possess a stable one lower oxidation state and when it can be stabilized by back-donation from filled d orbitals of π symmetry. The importance of these conditions is readily illustrated in the photolysis of the azido complexes of the cobalt triad. The generally harder metals of the first transition series are expected to favor nitrene formation to a lesser extent than the heavier transition metals, because of the diminished ability to stabilize the nitrene by π back-donation. The only reported case of coordinated nitrene formation via azido complex photolysis is that of the azido pentaammine complex of chromium(III),[12] which meets neither of the conditions set forth by Basolo and co-workers. The azido complexes of nickel(II), however, are first-transition-series complexes that meet both criteria.

Diacido complexes of the Ni(tet-a)XY type are kinetically labile with respect to the loss of the X and Y ligands. Careful analysis of halocarbon solutions of Ni(tet-a)$(N_3)_2$ shows that Ni(tet-a)$(N_3)_2$ is the only species present in detectable concentrations. Irradiation of purple solutions of this complex with near-ultraviolet radiation results in the formation of yellow solutions. Monitoring this reaction via infrared spectroscopy reveals that the photoreaction occurs via the destruction of the azido group. Similar experiments were carried out in tetrahydrofuran solutions containing added cyclohexene. As the photolysis proceeded, the intensity of the band assigned to coordinated azide (2035 cm^{-1}) decreased in intensity. There was, however, no new absorbance at higher frequency (ca. 2109 cm^{-1}) attributable to the formation of an organic azide. The conditions for this experiment were identical with those used to detect azide radical formation in the photolysis of *cis*-$Co(CH_3COCHCOCH_3)_2N_3NH_3$.[2] Thus photodecomposition occurs via destruction of the azido group, but no concomitant azide radical formation occurs. The formation of a metal nitrene is thus strongly indicated. Since the reactivity of metal and organic nitrenes toward the ROH function is known, methanol was chosen as the solvent for the remaining studies. Ni(tet-a)$(N_3)_2$ is highly dissociated in methanol. The maintenance of isobestic points in the titration of Ni(tet-a)$^{2+}$ with azide ion and the results of matrix rank analysis strongly support the simple equilibrium

$$\text{Ni(tet-a)}^{2+} + 2N_3^- \rightleftharpoons \text{Ni(tet-a)}(N_3)_2$$

There are no other nickel species present in significant concentration, and in the near-ultraviolet Ni(tet-a)$(N_3)_2$ is the only absorbing species.

The formation of hydrazine during photolysis is ideal, because hydrazine can be determined even at very low concentrations. Furthermore, Burak and Treinin have used the quantum yields for the formation of hydrazine in the presence of ammonia to elucidate the mechanism for the photolysis of azide ion and hydrazoic acid. Plots of $[N_2H_4]$ vs. irradiation time showed good linearity. Since, however, it has been shown that azide photodecomposes by the direct irradiation of azide ion, and because Ni(tet-a)$(N_3)_2$ is extensively dissociated in methanol, the possibility of photodecomposition as the result of direct azide excitation or by Ni(tet-a)$^{2+}$ sensitization of N_3^- must be considered.

The spectroscopy of azide ion has been studied by a number of investigators.[32,33] Excitation by 254-nm radiation results in photodecomposition yielding nitrene formation, but the 254-nm radiation excites an n → π^* transition, which is not itself dissociative.[34] Its band maximum is at 230 nm; consequently one can not unequivocally rule out the possibility that direct 310-nm excitation of azide ion might yield photodecomposition. The quantum yield for azide ion decomposition in Ni(tet-a)$(N_3)_2$ photolysis is 0.15, which puts a lower limit on the fraction of incident radiation directly absorbed by azide ion. At the concentrations used, the absorption of N_3^- is not measurable at 310 nm; thus it is evident that far less than 15% of the incident radiation is absorbed by azide ion at 310 nm. Therefore no significant direct excitation of N_3^- exists. The quantum yield for azide decomposition also places a lower limit on the fraction of incident radiation absorbed by Ni(tet-a)$^{2+}$ as well as the efficiency of energy transfer. Virtually all of the incident radiation is absorbed by Ni(tet-a)$(N_3)_2$; thus Ni(tet-a)$^{2+}$-sensitized photolysis does not contribute significantly to the observed photodeomposition.

We propose the following mechanism for the photodecomposition of Ni(tet-a)$(N_3)_2$ by direct excitation:

$$\text{Ni(tet-a)}(N_3)_2 + h\nu \xrightarrow{I_a} \text{Ni(tet-a)}(N_3)_2^* \tag{2}$$

$$\text{Ni(tet-a)}(N_3)_2^* \xrightarrow{k_3} \text{Ni(tet-a)}(N_3)_2 + \Delta \tag{3}$$

$$\text{Ni(tet-a)}(N_3)_2^* \xrightarrow{k_4} \text{Ni(tet-a)}(N_3^+) + N_3^- \tag{4}$$

$$\text{Ni(tet-a)}(N_3)_2^* \xrightarrow{k_5} \text{Ni(tet-a)}(N_3)(N) + N_2 \tag{5}$$

$$\text{Ni(tet-a)}(N_3)_2^* \xrightarrow{k_6} X \tag{6}$$

$$\text{Ni(tet-a)}(N_3^+) + N_3^- \xrightarrow{k_7} \text{Ni(tet-a)}(N_3)_2 \tag{7}$$

$$\text{Ni(tet-a)}(N_3)(N) + H^+ \xrightarrow{k_8} \text{Ni(tet-a)}(N_3)(NH)^+ \tag{8}$$

$$\text{Ni(tet-a)}(N_3)(NH)^+ + NH_3 \xrightarrow{k_9} \text{Ni(tet-a)}(N_3)(N_2H_4)^+ \tag{9}$$

$$\text{Ni(tet-a)}(N_3)(NH)^+ + S \xrightarrow{k_{10}} Y \tag{10}$$

$$\text{Ni(tet-a)}(N_3)(N_2H_4)^+ + N_3^- \xrightarrow{k_{11}} \text{Ni(tet-a)}(N_3)_2 + N_2H_4 \tag{11}$$

If a steady state is assumed for Ni(tet-a)$(N_3)_2^*$, Ni(tet-a)$(N_3)(N)$, and Ni(tet-a)$(N_3)(NH)^+$ the following theoretical rate laws are derived:

$$\begin{aligned} \phi_{N_2H_4} &= \frac{k_2k_9[NH_3]}{(k_3+k_4+k_5+k_6)(k_9[NH_3]+k_{10}[S])} \\ -\phi_{N_3} &= \frac{k_5+k_6}{k_3+k_4+k_5+k_6} \end{aligned} \tag{12}$$

In this case, S is any other nitrene scavenger(s) and Y is the product of such a reaction(s).

Letting Φ_N, $k_5/(k_3+k_4+k_5+k_6)$, be the primary yield for nitrene formation gives

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$$\phi_{N_2H_4}{}^{-1} = \Phi_N{}^{-1} + \Phi_N{}^{-1}\frac{k_{10}[S]}{k_7[NH_3]}$$
$$-\phi_{N_3} = \Phi_N + \frac{k_6}{k_3 + k_4 + k_5 + k_6} \qquad (13)$$

This rate law agrees with the experimental rate law, eq 1. The intercept yields values for the primary quantum yield of 0.043 and 0.042 for the two runs. The equality of the yields for such different conditions indicates several things. It further rules out the possibility of nitrene formation by a Ni(tet-a)$^{2+}$-sensitized decomposition of N_3^-. In such a case the decreased N_3^- concentration in the second run would have significantly decreased Φ_N, eq 21.

$$\mathrm{Ni(tet\text{-}a)^{2+}} \xrightarrow{I_a} \mathrm{Ni(tet\text{-}a)^{2+*}} \qquad (14)$$

$$\mathrm{Ni(tet\text{-}a)^{2+*}} \xrightarrow{k_{15}} \mathrm{Ni(tet\text{-}a)^{2+}} + \Delta \qquad (15)$$

$$\mathrm{Ni(tet\text{-}a)^{2+*}} + N_3^- \xrightarrow{k_{16}} \mathrm{Ni(tet\text{-}a)^{2+}} + N_3^{-*} \qquad (16)$$

$$N_3^{-*} \xrightarrow{k_{17}} N_3^- + \Delta \qquad (17)$$

$$N_3^{-*} \xrightarrow{k_{18}} X \qquad (18)$$

$$N_3^{-*} \xrightarrow{k_{19}} N_2 + N^- \qquad (19)$$

$$H^+ + N^- \xrightarrow{k_{20}} NH \qquad (20)$$

yields

$$\Phi_N = \frac{k_{16}k_{19}[N_3^-]}{(k_{10} - k_{16}[N_3^-])(k_{17} + k_{18} + k_{19})} \qquad (21)$$

These results point to the same photoactive species being formed in both runs even though different N_3^-/Ni(tet-a)$^{2+}$ ratios were used. This confirms the conclusions drawn earlier from the spectral analysis of azide-containing Ni(tet-a)$^{2+}$ solutions. Finally, the efficiency of nitrene formation is independent of the ionic strength of the medium, which is consistent with the proposed mechanism.

Values of 8.26 and 5.83 are obtained, respectively, for $k_8[S]/k_7$ for the first and second run. This result cannot be unambiguously interpreted, but among the possible known nitrene scavengers in the medium is N_3^- ion.[22,23,32] The reduced value of $k_8[S]/k_7$ in the second run can be attributed to the decreased N_3^- ion concentration in this run. The difference may also be attributed to an ionic strength effect. Although the primary quantum yield for nitrene formation is 0.043, the quantum yield for azide decomposition is 0.15. This suggests that reaction 6 is the dominant mode of azido group photodecomposition.

It is obvious from the proposed mechanism and the fact that Ni(tet-a)$^{2+}$ is labile with respect to axial ligands that it should be possible to quantitatively recover Ni(tet-a)$^{2+}$ from the photolytes. This appears not to be the case. Whether small or large amounts of azide are decomposed, a cationic material is formed that absorbs in the 350–380-nm region. This material becomes electroneutral in basic media and is thus extracted from the resin with CH_3OH. This type of behavior is suggestive of fragmentation of the macrocyclic ligand during photolysis, which is accounted for in reaction 6. The identity of this material is currently under investigation.

For both quantitative and preparative photolyses, the irradiations were restricted to the 310–390-nm region. This region is dominated by a single absorption feature at 316 nm (ϵ = 1669 M^{-1} cm^{-1}), which is not present in the spectrum of Ni(tet-a)$^{2+}$. This band is assigned to an internal transition of the azido group. This assignment is justified on several grounds. The large intensity of this band speaks against its assignment as a ligand field transition. Jørgensen's optical eleectronegativities[35,36] for nickel(II) and N_3^- are 2.1 and 2.8, respectively. These values and the ligand field parameters predict the charge-transfer transition involving the azido group should occur at a wavelength that is consistant with the band at 251 nm (ϵ = 3347 M^{-1} cm^{-1}). In addition the internal azide bands for $Rh(CN)_5N_3^{3-}$ and $Ir(CN)_5N_3^{3-}$ have been identified near 312 nm.[16] These transitions appear at similar energies for organic azides.[34,37] Finally, this work has shown that excitation into this band results in nitrene formation, which is a reaction correlated with an internal azide excited state. The fact that the charge-transfer transition is at such high energy, similar to that of $Rh(NH_3)_5N_3^{2+}$, also explains why nitrene formation is favored over azide radical formation. The failure of Φ_N to equal the quantum yield for photodecomposition of the azido group points to the existence of an intermediate that is not scavenged by NH_3 and that is able to react with the nickel tetraammine ligand. The nature of this reaction is as yet undetermined, except that it appears to involve cleavage of the macrocyclic ring. We believe that the second mode for the photodecomposition of Ni(tet-a)$(N_3)_2$ involves the intermediacy of a triplet nitrene. Whereas the two nitrene intermediates are structurally identical, their chemical behavior is vastly different. The triplet nitrene is a diradical whereas the singlet is a strong Lewis acid. The ground state of nitrene is a triplet. As a diradical the triplet would be relatively unreactive toward Lewis bases such as NH_3, but would be effective in abstraction and insertion reactions, which might result in distruction of the macrocycle.

Table III. Estimation of the Relative Energies of the Spectroscopic States Available to Ni(tet-a)(N_3)(NH)$^+$

state	energy, 10^3 cm^{-1}	state	energy, 10^3 cm^{-1}
	Ni(tet-a)$(N_3)_2$[a]		
$^3A_1$	0	$^3T_1(P)$	30.91
$^3T_2$	12.46	^1E	14.76
$^3T_1(F)$	20.30	$^1A_1$	24.08
	NH[b]		
$X^3\Sigma$	0	$b^1\Sigma$	24.519
$a^1\Delta$	14.704		
	Ni(tet-a)(N_3)(NH)$^{+}$[c]		
$^3A_{1g}$, $X^3\Sigma$	0	^1E_g, $X^3\Sigma$	14.76
$^3A_{1g}$, $a^1\Delta$	14.70	$^1A_{1g}$, $X^3\Sigma$	24.08
$^3A_{1g}$, $b^1\Sigma$	24.52		

[a] Ligand field parameters taken from ref 30. States are based on an octahedral parent symmetry. [b] Data taken from ref 38. [c] The metal state is followed by the nitrene state.

Unlike the formation of nitrene intermediates observed to date, the formation of the triplet nitrene state is not a spin-forbidden or energetically unfavorable process for Ni(tet-a)$(N_3)_2$. Since octahedral nickel(II) is a ground-state triplet, the formation of a triplet nitrene does not involve a change in spin state as long as singlet nickel is formed in the process. The spectroscopy of nickel(II) and NH have been extensively studied. Table III contains the energies of the NH states and estimates of the Ni(tet-a)$(N_3)_2$ states in octahedral parent symmetry. The ligand field parameters Dq_z, Dq_{xy}, and B were taken from the work of Busch and co-workers,[30] and the state energies were estimated by using Tanabe–Sugano diagrams.[39] It is assumed that the ligand field strength of nitrene is similar to that of azide. Because the change in spin states should result in only minor changes in structure and bonding, the relative energies of the Ni(tet-a)(N_3)(NH)$^+$ states can be reasonably estimated from the ligand field energies and the isolated NH energies. On the basis of these considerations the ground state for Ni(tet-a)$(N_3)_2$(NH)$^+$ would be ($^3A_{1g}$, a^3 Δ). The formation of this state during photolysis is unlikely, because the process is spin-forbidden. The other states available to Ni(tet-a)(N_3)(NH)$^+$ are ($^3A_{1g}$, a^1 Δ), (^1E_g, X^3 Σ),

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($^1A_1$, $X^3\ \Sigma$) and ($^3A_1$, $^1b\ \Sigma$). All of these states are triplets and may be formed by spin-allowed processes. The ($^3A_1$, $a^1\ \Sigma$) and (^1E_g, $X^3\ \Sigma$) states are of similar energy, differing by only 0.06×10^3 cm^{-1}, and are respectively singlet and triplet nitrene intermediates. Thus, although this procedure yields a rough estimate of the relative energies of a singlet and triplet nickel nitrene, it does show that both states are energetically accessible.

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Luminescence Study of the Adsorption of Ammonia and Other Simple Molecules on an Activated Europium Ion Exchanged Mordenite

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The adsorption of ammonia and other simple molecules on an activated Eu(III) ion exchanged mordenite (Eu–M) has been studied by the measurement of the luminescence of the Eu^{2+} ion, which was produced by dehydration at 500 °C. The emission peak of the Eu^{2+} ion shifted to a shorter wavelength on exposure to ammonia and other simple molecules. The magnitude of the shift was correlated to the specific dielectric constant of the adsorbate. The quantum yield for the Eu^{2+} emission bands decreased after the adsorption of NH_3 and CH_3CN. Also, the lifetime in the Eu^{2+}–adsorbate system was shorter than that in an activated Eu–M sample. The rate constant for the radiationless transitions was more sensitive to the nature of the adsorbate, and the order of the quenching power was $CH_3CN > NH_3 > (CH_2NH_2)_2$.

Introduction

The rare earth ion exchanged zeolites have superior catalytic properties in isomerization and cracking reactions. Especially, within rare earth ion exchanged zeolites, europium ion exchanged zeolites have been attractive in recent years.[1,2] The coordination environment of Eu^{3+} ions in hydrated A and Y zeolites has been determined by luminescence lifetime and EXAFS measurements.[3] Also, the presence of Eu^{4+} in zeolite A has been postulated by X-ray analysis.[4,5] The postulated coexistence of europium in divalent and tetravalent states has been criticized in a Mössbauer spectroscopic study.[6]

The divalent europium ion, Eu^{2+}, $E°_{ox} = +0.35$ V, photolyzes in aqueous acidic solutions with reasonable efficiency in the near-UV range to produce the colorless trivalent europium ion, Eu^{3+}, and H_2.[7,8] Meanwhile, the luminescence of europium has been studied, and a number of europium ion containing phosphors emitting in the blue (Eu^{2+}) or the red region (Eu^{3+}) have been described.[9-11] Recently, Horrocks and co-workers have demonstrated that the luminescence method has been employed to probe the Ca^{2+} binding site in proteins as well as to monitor the ligand-exchange kinetic process in the chelate system since the Eu^{3+} ion possesses an ionic radius close to that of Ca^{2+}.[12-16] This method has the advantage of the study for gas on rare earth ion exchanged zeolite as described elsewhere.[17-19] In this paper, the unique features that have been observed only in activated Eu–M during the adsorption of ammonia and other simple molecules are presented.

Table I. Adsorption Measurement of Ammonia and Other Simple Molecules in Mordenites at 25 °C

	mordenites	
	Na–M	Eu–M (5.8%)
cation content, mmol/g	2.28 (Na^+)	0.044 (Eu^{3+}) 2.15 (Na^+)
NH_3 adsorption (5.32×10^4 Pa), mmol/g	7.37	7.54
CH_3CN adsorption (8.64×10^3 Pa), mmol/g	3.14	3.14
$(CH_2NH_2)_2$ adsorption (1.86×10^3 Pa), mmol/g	3.43	2.57

Experimental Section

Materials. Eu–M samples were prepared, starting from Na-mordenite, which was supplied by the Norton Co. The parent mordenite has

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