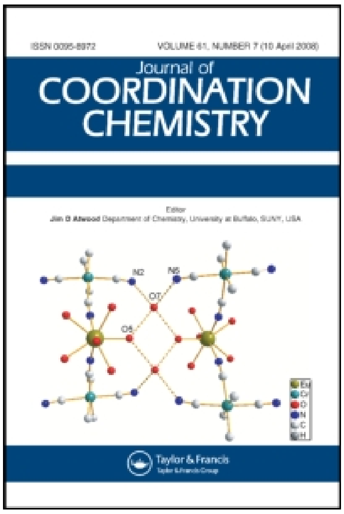

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Intermediates in the Ni^{II}(2,4,9,11-Tetramethyl-$Napho_2$[14]-2,4,6,9,11,13-$hexaeneN_4$)-catalyzed photoreduction of CO_2 to CO: A pulse-radiolytic and flash-photochemical study

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INTERMEDIATES IN THE Ni^{II}(2,4,9,11-tetramethyl-Napho$_2$[14]-2,4,6,9,11,13-hexaeneN$_4$)-CATALYZED PHOTOREDUCTION OF CO_2 TO CO: A PULSE-RADIOLYTIC AND FLASH-PHOTOCHEMICAL STUDY

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The photoreduction of CO_2 to CO was catalyzed by Ni(II) complexes of the 2,4,9,11-tetramethyl-Napho$_2$[14]-2,4,6,9,11,13-hexaeneN$_4$ and 2,4,9,11-tetra(1,1′-dimethylethyl)-Napho$_2$[14]-2,4,6,9,11,13-hexaeneN$_4$ ligands in methanol. In the experiments, the charge transfer excited state of Ru(bipy)$_3^{2+}$ was used as the reductant of the Ni(II) complexes and 2,2′,2″-nitrilotriethanol was used as a sacrificial reagent. Intermediates in these reactions were investigated by pulse-radiolytic and flash-photochemical procedures. Flash irradiations of the Ni(II) and Co(III) complexes in methanolic solutions at 350 nm resulted in oxidation of methanol. Transient species with a coordinated macrocyclic radical were observed in the photolysis and when radiolytically generated $^\bullet CH_2OH$ radicals reacted with the complexes. The pulse-radiolytically and flash-photochemically generated transients of the Ni(II) complex incorporated CO_2 and the resulting species could mediate in the formation of CO.

Keywords: Pulse radiolysis; Flash photolysis; Carbon dioxide; Azamacrocycle; Nickel

INTRODUCTION

In terms of the ligand's electronic saturation, the 2,4,9,11-tetramethyl-Napho$_2$[14]-2,4,6,9,11,13-hexaeneN$_4$ ligand, **I**, **II** in Scheme 1, its deprotonated relatives **III**, **IV** and the hexaazacyclophane **V** occupy an intermediate position between the [14]aneN$_4$ of one extreme and the porphyrin **VI** and phthalocyanine of the other.

It is expected that some photochemical/photophysical properties of the transition metal complexes of **I**–**V** will resemble those of the phthalocyanines or porphyrins [1, 2, 3]. The photophysical properties of the Ni(II) and Cu(II) complexes of 2,4,9,11-tetramethyl-Napho$_2$[14]-2,4,6,9,11,13-hexaeneN$_4$ have been investigated previously [4]. Scheme 2 presents photophysical processes associated with the population and relaxation of ligand-centered states, i.e., states localized in the naphthyl group.

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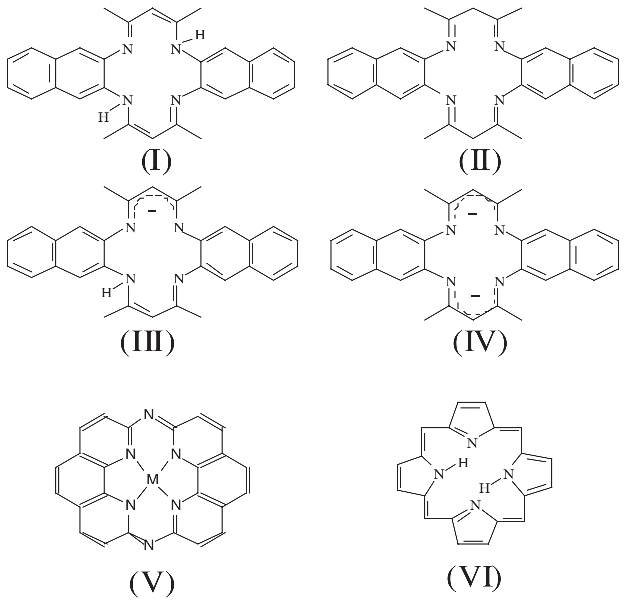
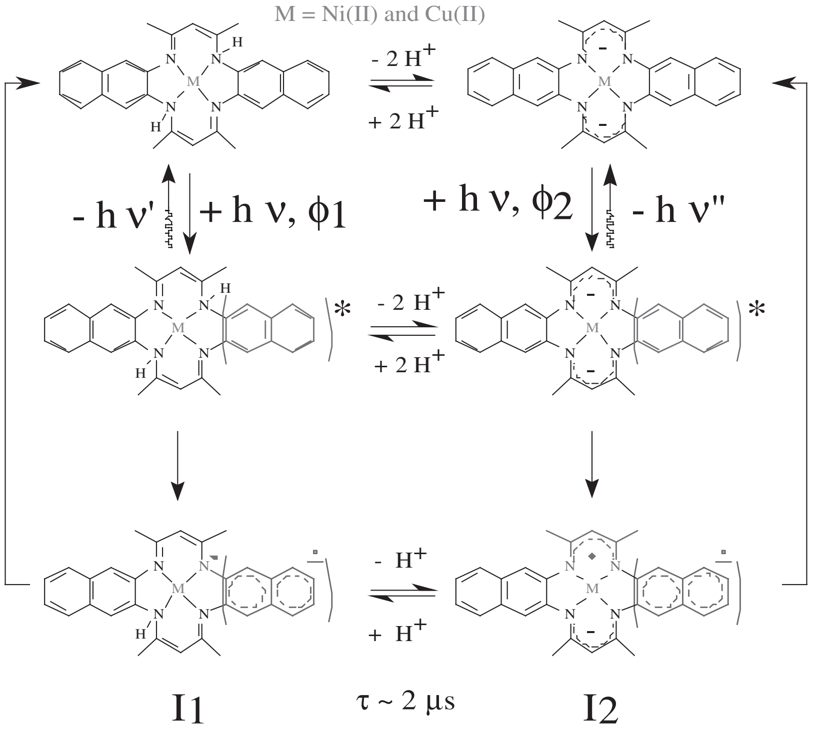


SCHEME 1.



SCHEME 2.

Medium-dependent luminescence and transient spectra have been accounted for by displacement of equilibria in the ground and excited states. Transient photochemical products were observed via flash photolysis and described as metal–ligand radical species. Transformations of the transient species to stable products have not been observed and the transients regenerate the ground state with lifetimes of several microseconds. Formation of adducts between $Cu(CH_3CN)_6^{2+}$ and excited states of the $Cu[2,4,9,11\text{-tetramethyl-Napho}_2[14]\text{-}2,4,6,9,11,13\text{-hexaene}N_4]^{2+}$ complex, not shown in Scheme 2, causes a displacement of the maximum in the emission spectrum and simultaneously quenches the luminescence.

In flash photolysis, the formation of these adducts caused changes in the shape of the transient absorption spectrum of the excited states. Since the 2,4,9,11-tetramethyl-$Napho_2$[14]-2,4,6,9,11,13-hexaeneN_4 complexes and their related hexaazacyclophane compounds catalyze the electrochemical reduction of CO_2 to CO [3, 4], we now report the possible use of the former complexes as catalysts of the photoinduced reduction of CO_2 to CO. An additional goal of the study was to establish the mechanism of the photocatalyzed CO_2 reduction and relate it to the electrochemical process. Therefore we investigated the intermediates involved in the reduction of CO_2 by flash-photochemical and pulse-radiolytic procedures, which provided different ways for their generation.

EXPERIMENTAL

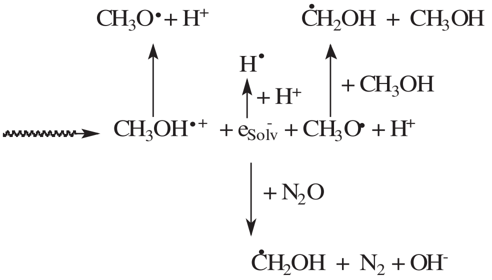
Photochemical Procedures

Optical density changes occurring on a time scale longer than 10 ns were investigated with a flash photolysis apparatus described elsewhere. In these experiments, 20-ns flashes of 351-nm light were generated with a Lambda Physik SLL -200 excimer laser [5, 6]. The concentrations of the complexes in solutions used for these experiments were adjusted by means of their UV-Vis spectra. Their concentrations insured homogeneous photogeneration of intermediates within the volume of irradiated solution, i.e., optical densities equal to or less than 0.1 in a 1-cm optical path at 351 nm. The liquids were deaerated with streams of ultrahigh-purity N_2 before and during the irradiations. A flow-stop system brought fresh solution to the reaction cell before each irradiation when the decomposition of the complexes and/or formation of products interfered with the optical measurements.

Steady state irradiations were carried out with light from a 350-nm Rayonet lamp. Light intensities, $5 \times 10^{-4} \geq I_0 \geq 1 \times 10^{-4}$ Einstein $dm^{-3}\,min^{-1}$, were measured with Parker's actinometer [7]. Irradiations at 440 ± 2.5 nm were carried out with a 500-W Hg-Xe lamp whose output was collimated with appropriate optics and filtered with a Bausch and Lomb monochromator. Photolytes were irradiated in a 50-cm^3 gas-tight cell for the determination of gaseous products. Photolyzed solutions were frozen at $-180°C$ and the noncondensable gaseous products were pumped off with a Toepler pump. A Shimadzu GC-17A chromatograph provided with an RT-,MSIEVES 13X (fused silica) column and a TC detector was used for product analysis. The chromatogram were calibrated with known amounts of CO.

Pulse-radiolytic Procedures

Pulse radiolysis experiments were carried out with a model TB-8/16-1S electron linear accelerator. The instrument and computerized data collection for time-resolved UV-Vis spectroscopy and reaction kinetics have been described [8, 9]. Thiocyanate dosimetry was carried out at the beginning of each experimental session. The details of the dosimetry have been reported elsewhere [8–10]. The procedure is based on the concentration of $(SCN)_2^-$ radicals generated by the electron pulse in an N_2O-saturated 10^{-2} M SCN^- solution. In the procedure, the calculations were made with $G = 6.13$ and an extinction coefficient, $\varepsilon = 7.58 \times 10^3\,M^{-1}\,cm^{-1}$ at 472 nm, for the $(SCN)_2^-$ radicals [8, 10]. In general, the experiments were carried out with doses that in N_2-saturated aqueous solutions resulted in $(2.0 \pm 0.1) \times 10^{-6}$ M to $(6.0 \pm 0.3) \times 10^{-6}$ M concentrations of e_{aq}^-. In these experiments, solutions were prepared by the procedure indicated above for the photochemical experiments. The liquids were deaerated with streams of the O_2-free gases N_2, N_2O or the appropriate mixture of these gases with CO_2 that was required for the experiment. In order to radiolyze a fresh sample with each pulse, an appropriate flow of the solution through the reaction cell was maintained during the experiment. Other conditions used for the time-resolved spectroscopy of the reaction intermediates or in the investigation of the reaction kinetics are given in the Results section. Radiolyses with ionizing radiation of CH_3OH and CH_3OH/H_2O mixtures have been reported elsewhere in the literature [11–13]. These studies have shown that pulse radiolysis can be used as a convenient source of e_{Solv}^- and $^\bullet CH_2OH$ radicals according to Eq. (1).



(1)

Since e_{Solv}^- and $^\bullet CH_2OH$ have large reduction potentials, i.e., −2.8 V *vs.* NHE for e_{Solv}^- and −0.92 V *vs.* NHE for $^\bullet CH_2OH$, they have been used for reduction of coordination complexes and to study electron transfer reactions. The yield of e_{Solv}^- in CH_3OH ($G \approx 1.1$) is about a third of the *G*-value in the radiolysis of H_2O ($G \approx 2.8$) [11]. In solutions where e_{Solv}^- was scavenged with N_2O [13], the $^\bullet CH_2OH$ radical appears to be the predominant product (yield > 90%) of the reaction between CH_3OH and $O^{\bullet -}$.

Materials

The Ni(II) and Co(III) complexes of 2,4,9,11-tetramethyl-Napho$_2$[14]-2,4,6,9,11,13-hexaeneN_4^{2-} were synthesized by modification of a literature procedure [4]. In the modified procedure, the reactants are refluxed in butanol instead of methanol. Any residual solid was filtered off after 8 h and the solution was rotoevaporated. The solid materials were recrystallized from methanol. The modified protocol produced compounds with the basic form of the ligand, **IV**, instead of the protonated form previously communicated. Characterizations of the compounds were made on the basis of metal content; Calcd. for Ni^{II}(2,4,9,11-tetramethyl-Napho$_2$[14]-2,4,6,9,11, 13-hexaeneN_4): Ni, 11.58%. Found: Ni 11.80%. Calcd. for Ni^{II}(2,4,9,11-tetra(1,1′-dimethylethyl)-$Napho_2$[14]-2,4,6,9,11,13-hexaeneN_4): Ni, 8.67%. Found: Ni 8.80%. IR and UV-Vis spectra were used for the characterization of the compounds. Bands at 1569 cm^{-1} in the methyl derivative and 1586 cm^{-1} in the 1,1′-dimethyl ethyl derivative were assigned to the C=N stretching frequencies in the deprotonated ligand. The UV-Vis spectrum of Ni^{II}(2,4,9,11-tetramethyl-$Napho_2$[14]-2,4,6,9,11,13-hexaeneN_4) in methanol exhibited absorption bands at 400 nm ($\varepsilon = 1400\,M^{-1}\,cm^{-1}$), 450 nm ($\varepsilon = 800\,M^{-1}\,cm^{-1}$) and 590 nm ($\varepsilon = 200\,M^{-1}\,cm^{-1}$). The spectrum of Ni^{II}(2,4,9,11-tetra(1,1′-dimethylethyl)-$Napho_2$[14]-2,4,6,9,11,13-hexaeneN_4) in methanol exhibited absorption bands at 395 nm ($\varepsilon = 700\,M^{-1}\,cm^{-1}$) and 590 nm ($\varepsilon = 100\,M^{-1}\,cm^{-1}$) [14]. Aldrich spectroquality solvents, MeOH, CH_3CN and CH_2Cl_2 and 2,2′,2″-nitrilotriethanol (TEOA) were used as received.

RESULTS

Photochemical Reactions

Solutions containing $Ni[N_4(CH_3)_4]$ or $Ni[N_4(terb)_4]$ (5.0×10^{-4} to 1.0×10^{-4} M, terb = *tert*-butyl) and $Ru(bipy)_3^{2+}$ (5.0×10^{-4} M) in 10% TEOA/90% DMF mixed solvent (v:v) were deaerated with streams of CO_2. Irradiation at 440 nm ($I_0 = 2 \times 10^{-4}$ $Einstein^{-1}\,dm^{-3}\,min^{-1}$) of the solutions saturated with CO_2 produced CO in amounts proportional to the irradiation time. No CO was detected when the experiment was repeated with a CO_2-saturated solution 5.0×10^{-4} M in $Ni[N_4(CH_3)_4]$ or $Ni[N_4(terb)_4]$ in a TEOA/DMF mixed solvent but having no $Ru(bipy)_3^{2+}$ complex. Little if any CO was detected after a 24-h irradiation of similar solutions at 350 nm, $I_0 = 3.5 \times 10^{-4}$ $Einstein^{-1}\,dm^{-3}\,min^{-1}$, or 300 nm, $I_0 = 4 \times 10^{-4}$ $Einstein^{-1}\,dm^{-3}\,min^{-1}$.

Although the $Ni[N_4(CH_3)_4]$ appears to be photoinert unless it is photosensitized by $Ru(bipy)_3^{2+}$, flash photolysis of the complex showed formation of transient species. The 351-nm flash irradiation of 1.0×10^{-4} M $Ni[N_4(CH_3)_4]$ and 1.0×10^{-4} M NaOH in MeOH deaerated with N_2 produced transient spectra communicated in the literature [4]. In flash photolysis experiments with solutions where NaOH was replaced by 1.5 M TEOA, differences between the photogenerated spectra suggest that the irradiated $Ni[N_4(CH_3)_4]$ is reduced by TEOA (Fig. 1). Further differences were observed between the transient spectra photogenerated with N_2-deaerated solutions of 1.0×10^{-4} M $Ni[N_4(CH_3)_4]$ and 1.5 M TEOA and similar solutions deaerated with CO_2. The spectral differences suggest reaction between CO_2 and the photoreduced $Ni[N_4(CH_3)_4]$. In terms of the transient spectra, these reactions were more evident in the flash photolysis of $Ni[N_4(terb)_4]$. Transient spectra obtained in flash irradiations of 1.0×10^{-4} M $Ni[N_4(terb)_4]$ and 1.5 M TEOA in MeOH deaerated with N_2 show the transformation of the flash-generated spectrum into the spectrum of long-lived products (Fig. 2(a)). In a solution of 1.0×10^{-4} M $Ni[N_4(terb)_4]$ and 1.5 M TEOA in MeOH deaerated and saturated with CO_2, the spectral transformations in Fig. 2(b) are in accordance with a reaction between the photoreduced $Ni[N_4(terb)_4]$ and CO_2.

Pulse Radiolysis

Pulse radiolysis was used for observation of the intermediates generated when the macrocyclic complexes are reduced by the e^-_{Solv} and/or $^{\bullet}CH_2OH$ radicals [15].

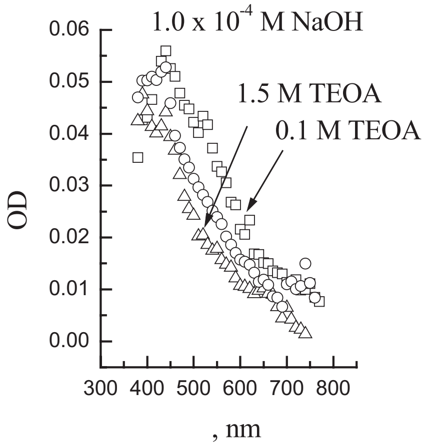


FIGURE 1 Transient spectra recorded in the 351-nm flash irradiation of 1.0×10^{-4} M Ni[$N_4(CH_3)_4$] solutions in MeOH containing 1.0×10^{-4} M NaOH, 0.1 M TEOA or 1.5 M TEOA.

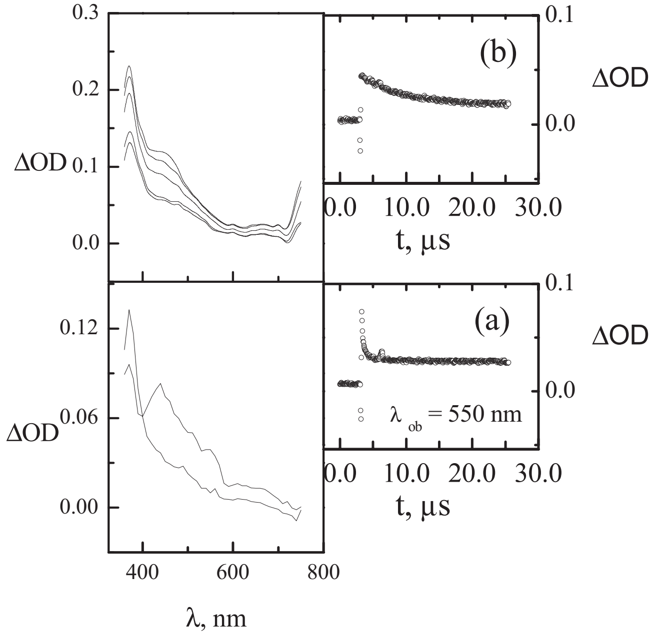


FIGURE 2 Traces (right of the figure) show the OD changes at 550 nm when two methanolic solutions containing 1.0×10^{-4} M Ni[N_4(terb)$_4$] in 1.5 M TEOA, one deaerated with N_2, (a), and another with CO_2, (b), were flash irradiated at 351 nm. The corresponding transient spectra (left of the figure) were recorded with a 150-ms delay from the 351-nm irradiation.

N_2O-saturated solutions of 1.0×10^{-4} M Ni[$N_4(CH_3)_4$] were pulse radiolyzed and the spectrum, recorded after e^-_{Solv} reacted with N_2O, exhibited a band with $\lambda_{max} = 520$ nm and a large increase of optical density (OD) below 420 nm (Fig. 3). Pulse radiolysis of an N_2O-saturated solution of 1.0×10^{-4} M Co[$N_4(CH_3)_4$]$^+$

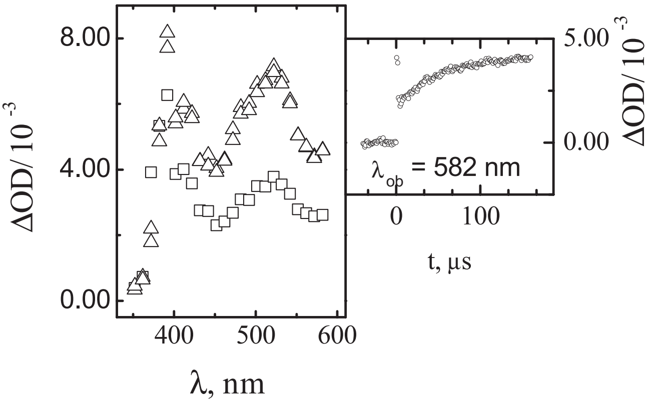


FIGURE 3 Spectral changes observed in pulse radiolysis of an N_2-saturated solution of 1.0×10^{-4} M $Ni[N_4(CH_3)_4]$. The spectra were recorded with 3- and 100-μs delays from the radiolysis pulse. The trace to the left of the figure shows the growth of the OD at 582 nm.

also produced a transient spectrum with an absorption band at ~520 nm. Similar positions of the absorption bands in the spectra generated when $^{\bullet}CH_2OH$ radicals respectively reduced $Ni[N_4(CH_3)_4]$ and $Co[N_4(CH_3)_4]^+$ are in accordance with the reduction of the common ligand rather than the two different metal centers. In these experiments with Ni(II) or Co(III) complexes, the radical–radical reaction competes with the reaction of the radical with the transition metal complex. Although competition between reactions prevented accurate evaluation of the later reaction rate constant, an estimate gives $k \sim 10^8\,M^{-1}\,s^{-1}$. It must also be noted that the flash-induced spectral changes are blue-shifted with respect to the transients observed in pulse radiolysis, i.e., their spectra are more intense below 450 nm. The spectral differences are probably due to the formation of different Ni(II)–ligand radical species in the more basic photochemical medium and not to Ni(I) transients.

In N_2-deaerated acidic solutions 0.1 M in H^+, the radiolytically produced solvated electron, e^-_{Solv}, is trapped by H^+ and only the radicals $^{\bullet}CH_2OH$ and $H^{\bullet}$ are present in a timescale $t > 1$ μs. Because of the small rate constant for reaction of $H^{\bullet}$ with MeOH to give $^{\bullet}CH_2OH$, an appreciable fraction of the $H^{\bullet}$ radicals reacts with $Ni[N_4(CH_3)_4]$. The transient spectra recorded when 1.0×10^{-4} M $Ni[N_4(CH_3)_4H_2]^{2+}$ in MeOH, N_2- and N_2O-saturated solutions were pulse radiolized are shown in Fig. 4. Since the most noticeable differences occur below 450 nm, i.e., where the spectrum of $N_4(CH_3)_4^{2-}$ exhibits intense absorption bands, these differences suggest the addition of $H^{\bullet}$ radicals to the ligand. Moreover, the spectral changes exhibited some common features with those observed in flash photolysis experiments (Fig. 1).

Reaction of the reduced $Ni[N_4(CH_3)_4H_2]^{2+}$ with CO_2 was investigated by a literature procedure. Solutions of 1.0×10^{-4} M $Ni[N_4(CH_3)_4H_2]^{2+}$ in MeOH, deaerated and saturated with a gas mixture of 0.1 atm of CO_2 and 0.9 atm of N_2O were used for the pulse radiolysis experiments. Spectral changes detected under these conditions were markedly different from those observed when 0.1 atm of N_2 instead of CO_2 was used in the gas mixture, and indicated the formation of different reaction intermediates (Fig. 5). The formation of different reaction intermediates was also evident from the differences in

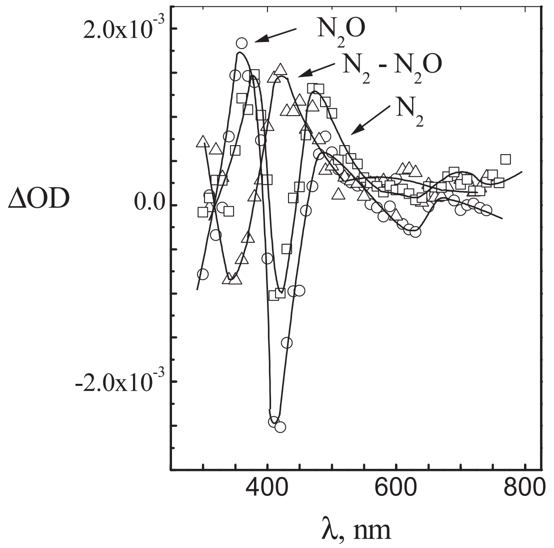


FIGURE 4 Difference between the spectra recorded when 1.0×10^{-4} M $Ni[N_4(CH_3)_4H_2]^{2+}$ is pulse radiolyzed in MeOH saturated with N_2 or N_2O. The difference, $N_2 - N_2O$, between the spectra recorded under N_2 and the spectra recorded under N_2O is attributed to the product of the addition of $H^\bullet$ radicals to $Ni[N_4(CH_3)_4H_2]^{2+}$.

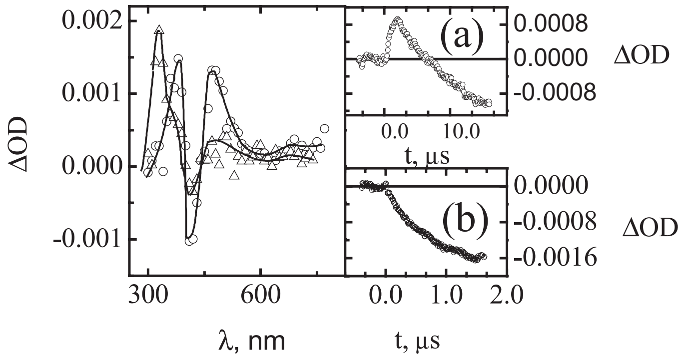


FIGURE 5 Solutions of 1.0×10^{-4} M $Ni[N_4(CH_3)_4H_2]^{2+}$ in MeOH, deaerated and saturated with a gas mixture of 0.1 atm of CO_2 and 0.9 atm of N_2O, ○, or 0.1 atm of N_2 and 0.9 atm of N_2O, Δ, were pulse radiolyzed and the spectral changes recorded with a 150-µs delay from the irradiating pulse. Differences in the kinetics of the spectral changes in solutions deaerated with gases containing CO_2, (a), and N_2, (b), provide evidence of the addition of CO_2 to the reduced macrocycle.

the kinetics of the spectral changes at given wavelengths (inset to Fig. 5). Addition of CO_2 to the reduced $Ni[N_4(CH_3)_4H_2]^{2+}$ accounts for the new absorptions and the kinetics of the spectral changes.

Similar pulse radiolysis experiments were conducted with solutions containing $Ni[N_4(terb)_4]$ instead of $Ni[N_4(CH_3)_4]$ but having otherwise the same composition. Figure 6 shows the different spectral features of a pulse-radiolyzed solution deaerated and saturated with a gas mixture 0.1 atm of CO_2/0.9 atm of N_2O and a pulse-radiolyzed solution where CO_2 was replaced with 0.1 atm of N_2. A transient increase of the OD at

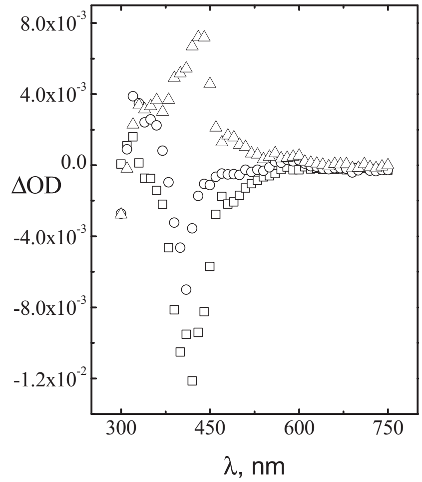


FIGURE 6 Solutions of 1.0×10^{-4} M $Ni[N_4(terb)_4H_2]^{2+}$ in MeOH, deaerated and saturated with a gas mixture of 0.1 atm of CO_2 and 0.9 atm of N_2O, □, or 0.1 atm of N_2 and 0.9 atm of N_2O, ○, were pulse radiolyzed and the spectral changes recorded with a 150-μs delay from the irradiation. For comparison, the difference, Δ, between the former and the latter transient spectrum is also shown.

~430 nm was observed in the pulse radiolysis of the former solution and assigned to formation of an adduct of CO_2 with the reduced $Ni[N_4(terb)_4]$.

DISCUSSION

The reduction of $M[N_4(CH_3)_4]^z$ ($M = Ni^{II}$, $z = 0$; $M = Co^{III}$, $z = 1+$) or $Ni[N_4(terb)_4]$ by $^{\bullet}CH_2OH$ radicals appears to occur at the ligand rather than the metal center, a reaction represented in Eq. (2) for $M[N_4(CH_3)_4]^z$ ($M = Ni^{II}$, $z = 0$ $M = Co^{III}$, $z = 1+$).

$$M[N_4(CH_3)_4]^z + {}^{\bullet}CH_2OH + CH_3O \rightarrow M\left[N_4(CH_3)_4^{\bullet}\right]^{z-1} + CH_3OH + CH_2O \quad (\lambda_{max} \approx 520 \text{ nm}). \tag{2}$$

Since cyclic voltammetry shows that the metal reduction in complexes of the $N_4(CH_3)_4$ ligand occurs at potentials more positive than those of the $N_4(CH_3)_4/N_4(CH_3)_4^{\bullet-}$ couple, the preferential reduction of the ligand in Eq. (2) suggests that the reorganization energy for electron transfer in the $N_4(CH_3)_4/N_4(CH_3)_4^{\bullet-}$ couple is smaller than in the metal couples. This retardation of the rate of the metal-center reduction allows the competing reduction of the ligand within the lifetime of the $^{\bullet}CH_2OH$ radical. A similar kinetic condition for reduction of the ligand instead of the metal center has been previously seen in the redox reactions of transition metal phthalocyanines [1], and was also attributed to the disparity between the reorganization energies of the metal center and the phthalocyanine ligand. The kinetics for formation of the reduced products show that in the competition between Eq. (2) and disproportionation of $^{\bullet}CH_2OH$ radicals, Eq. (3), the latter is slower than a diffusion-controlled process with a rate constant, $k \leq 10^8\ M^{-1}\ s^{-1}$.

$$^{\bullet}CH_2OH + {}^{\bullet}CH_2OH \rightarrow CH_3OH + CH_2O \quad 2k = 2.0 \times 10^9\ M^{-1}\ s^{-1}. \tag{3}$$

Transient spectra collected in pulse radiolysis with solutions containing CO_2 indicate formation of transient species formed when $Ni[N_4(CH_3)_4^{\bullet}]^-$ or $Ni[N_4(terb)_4]^-$ react with CO_2, Eq. (4).

$$Ni[L^{\bullet}]^- + CO_2 \leftrightarrows Ni[L^{\bullet}]CO_2^- \tag{4}$$

where ($L = N_4(CH_3)_4, N_4(terb)_4$).

It is not evident from the spectra whether CO_2 is forming an adduct with the ligand or is coordinated to the metal center. Because $Ni[N_4(CH_3)_4^{\bullet}]^-$ and $Ni[N_4(terb)_4^{\bullet}]^-$ must be Ni(II) species with a ligand radical, coordination of CO_2 to the metal implies that charge must be transferred from the ligand to the metal in order to make the latter a stronger nucleophile.

The differences between the spectra of the products formed in reactions of Ni(II) complexes with $^{\bullet}CH_2OH$ and $H^{\bullet}$ radicals give some indication of the possible structural differences. Given the tendency of $H^{\bullet}$ radicals to add to double bonds, the shift of the intense absorptions to $\lambda < 450\,nm$ is consistent with disruption of the extended π electronic system in the $N_4(CH_3)_4^{2-}$ ligand. By comparison to Eq. (2), the addition of $H^{\bullet}$ radicals to the $N_4(CH_3)_4H_2$ ligand can be written,

$$Ni[N_4(CH_3)_4H_2]^{2+} + H^{\bullet} \rightarrow M[N_4(CH_3)_4H_3^{\bullet}]^{2+} \quad (\lambda_{max} \leq 450\,nm). \tag{5}$$

Similarities in the spectral changes due to formation of the adduct $Ni[N_4(CH_3)_4H_3^{\bullet}]^{2+}$, Eq. (5), and in the flash irradiations of $Ni[N_4(CH_3)_4]$, Figs. 1 and 4, suggest that the excited states of the macrocycles, $Ni[N_4(CH_3)_4^{*}]$, abstract hydrogen atoms from TEOA, Eq. (6).

$$Ni[N_4(CH_3)_4] \xrightarrow{h\nu,\phi} Ni[N_4(CH_3)_4^{*}] \xrightarrow{TEOA} Ni[N_4(CH_3)_4H] + (HOCH_2CH_2)_2NCH_2C^{\bullet}HOH. \tag{6}$$

Time-resolved spectra obtained in pulse radiolysis and flash photolysis experiments show that $Ni[N_4(terb)_4]$ undergoes addition of $H^{\bullet}$ radicals and abstracts hydrogen from TEOA in reactions similar to those of $Ni[N_4(CH_3)_4]$.

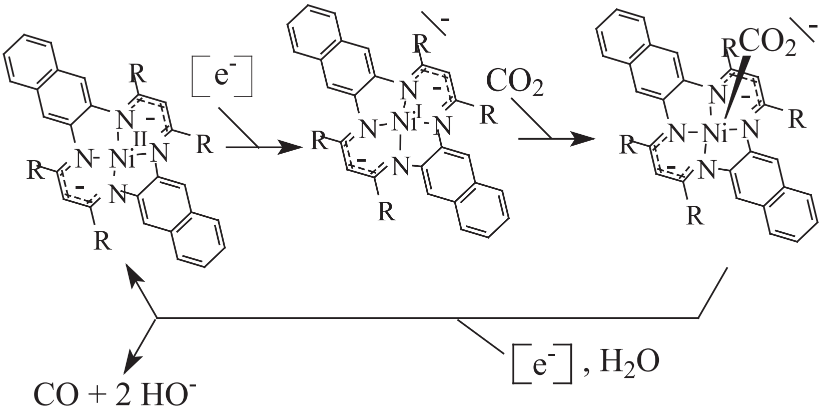
When the species $Ni[N_4(CH_3)_4H^{\bullet}]$ or $Ni[N_4(terb)_4H^{\bullet}]$ are flash-photochemically generated in solutions containing CO_2, the transient spectra show formation of new intermediates attributed to reactions of the hydrogen adducts with CO_2. The reaction with CO_2 suggests that $Ni[N_4(CH_3)_4H^{\bullet}]$ or $Ni[N_4(terb)_4H^{\bullet}]$ can convert to $Ni[N_4(CH_3)_4{}^{\bullet}]^-$ or $Ni[N_4(terb)_4^{\bullet}]^-$, respectively, and add CO_2 to the reduced ligand or to the metal, Eq. (7).

$$Ni[LH^{\bullet}] + CO_2 + Base \leftrightarrows Ni[L^{\bullet}]CO_2^{1-} + Base{:}\ H^+ \tag{7}$$

where ($L = N_4(CH_3)_4, N_4(terb)_4$; $Base = TEOA, CH_3O^-$).

The species $Ni[N_4(CH_3)_4^{\bullet}]CO_2$ and $Ni[N_4(terb)_4^{\bullet}]CO_2$ must also be produced in the steady-state photolysis of $Ni[N_4(CH_3)_4]$ or $Ni[N_4(terb)_4]$ solutions containing CO_2

and TEOA. However, their subsequent thermal reactions do not lead to formation of CO. It is possible that photolysis of the Ni(II) complexes does not provide an adequate path for further reduction of the adducts. By contrast to photolysis of the Ni(II) complexes, the $Ru(bipy)_3^{2+}$-sensitized reaction produces CO (Eq. (8)).



(8)

where [e⁻] = cathodic reduction in the electrochemical experiment or [e⁻] = $\{+(MLCT)Ru(bipy)_3^{2+}/-Ru(bipy)_3^{3+}\}$ in the photocatalyzed reduction.

The proposed mechanisms for formation of CO in Eq. (8) are based on the cyclic voltammogram of the complexes where the cathodic wave for reduction of CO_2 appears after addition of the first electron to Ni(II). The proposed adduct between CO_2 and the one-electron reduced complex is now supported by flash photolysis and pulse radiolysis observations.

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[14] Other structural and electrochemical properties of these Ni(II) complexes and those of related macrocycles will be communicated elsewhere. Work in preparation.

[15] In these medium conditions, literature values of the equilibrium constants show more than 99% of the ligand remains deprotonated [4].