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Photooxidation of nickel(II) macrocyclic complexes on excitation in the charge-transfer-to-solvent band in aqueous solution and in the presence of oxygen

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Abstract

Photooxidation of the well known nickel(II)-macrocyclic complexes [Ni(tet-a)] $(ClO_4)_2$, **1**, and [Ni(AT)] ClO_4, **2**, (where tet-a = -*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and AT = 11,13-dimethyl-1,4,7,10-tetraazacyclotetradeca-10,12-dienato) has been observed for the first time on excitation in the charge transfer to solvent band. The adduct formed in the primary photochemical process with the complex 1 is efficiently scavenged in presence of H^+ and O_2 to produce $HO_2^{\bullet}$ radical. This radical further oxidizes the nickel(II) macrocyclic complex to produce nickel(III) complex in the secondary thermal reaction as seen by the growth in absorbance at 370 nm in the conventional flash photolysis setup. Rate constants for the formation of nickel(III) by the reaction of $HO_2^{\bullet}$ radical with **1** was determined as a function of the concentration of the complex and hydrogen ion. Conventional flash photolysis of the complex **2** in presence of N_2O produces a transient which shows maximum at 610 nm. Stable nickel(III) complex is isolated on continuous photolysis of the complex **1** and characterized by electronic, IR, ESR spectroscopy and CHN analysis. In deaerated acidic aqueous solution containing alcohols, photolysis of **1** produced hydrogen gas as evidenced by gas chromatographic analysis. Quantum yield for the photooxidation of **1** to give the nickel(III) complex is found to be 0.03 ± 0.005. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photooxidation; Ni(II) macrocyclic complexes; Charge transfer processes; Ni(III) macrocyclic complexes

1. Introduction

Nickel is known to be involved in many biological reactions as cofactor and metalloenzymes [1–3]. More recently, there has been a large number of detailed studies on the biological role of nickel [4–6]. Crystal structure of none of the nickel containing enzymes has been solved in detail and the function and coordination environment of the nickel in natural systems are mostly investigated using synthetic nickel complexes as mimics of biological processes [1]. The common oxidation states of nickel which are suggested to be involved in the biological reactions are +1, +2 and +3. Tetraazamacrocyclic complexes of nickel(II) are known to be very stable and the metal ion in these systems could be reduced or oxidized by electrochemical, chemical and radiolytic methods [7–9]. The electrochemical properties of nickel(II) macrocyclic complexes have been extensively investigated [8,10]. The cofactor containing nickel(II) complexes in biological systems is proposed to have macrocyclic coordination geometry containing porphyrin derivatives [11]. Redox reactions of nickel(I) macrocyclic complexes with CO, CO_2 and the reactions of nickel(III) with H_2O_2 and other free radicals serve as models to understand the transformations occurring in biological and industrial catalytic reactions [12–15]. While the structure and reactivity of nickel(II) complexes have been extensively studied [16,17], photochemical reactions reported are only a few [18–20]. The present investigation describes in detail the photochemistry of well characterized tetraazamacrocyclic nickel(II) complexes **1** and **2** in aqueous solutions and the subsequent reactions of the primary photoproduct produced by photochemical method with hydrogen ion, molecular oxygen and free radicals.

2. Experimental

The complex **1** was prepared by the method of Curtis [21] and **2** by the procedure of Cummings and Sievers [22]. Water used in this investigation was triply distilled and other

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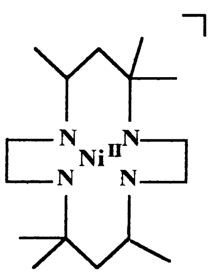

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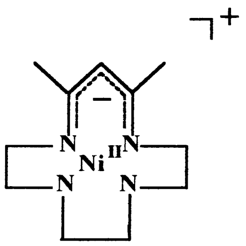

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reagents were of analytical grade. The purity of the complexes were checked by IR spectra, elemental analysis, NMR spectra, UV–VIS absorption spectra and electrochemical redox potential data, which were found to be identical or within ±2% with those reported.

Electronic absorption spectral measurements were carried out using a HP 8452A diode array spectrophotometer and the ESR spectra were recorded in a BRUKER ER-200D-SRC spectrometer. Continuous photolysis experiments were carried out using a low pressure mercury vapor lamp (Ultraviolet products Inc.), whose output is predominantly (>99.1%) with wavelength of 254 nm. Continuous photolysis of the complexes were monitored by observing the changes in absorbance with time of exposure and also by isolating the product of photolysis for **1**. Potassium ferric oxalate chemical actinometery method was used for the determination of the quantum yield for product formation. The quantum yield for the formation of Ni(III)complex was estimated knowing the spectrum of the Ni(III) complex [19]. Deaeration of the solutions for continuous photolysis was carried out by freeze-pump-thaw procedure in a vacuum line and the solutions for flash photolysis experiments were deaerated by bubbling argon gas through the solution for at least 30 min. Analysis of the gases evolved in the steady photolysis experiments was performed using a Shimadzu gas chromatograph. Conventional microsecond flash photolysis experiments were carried out using an applied photophysics model KN-020 spectrometer described earlier [23,24]. Electrochemical measurements were carried out using a standard three electrode configuration with Pt as working and counter electrodes and Ag/AgCl as reference electrode in a EG&G PAR system. IR spectra were recorded using a Nicolet IR spectrometer.

Isolation of the photoproduct, $[Ni(III)tet\text{-}aCl_2]ClO_4$ was achieved by extensively photolysing a solution of **1** in 1 M HCl solution at 4–5°C for 5–6 h using a low pressure mercury vapor lamp ($\lambda \sim 254$ nm), when the yellowish brown photoproduct precipitated. During the photolysis of the solution oxygen was bubbled through the solution. The photoproduct was separated by filtration and washed with ice cold water. The photoproduct was characterized by comparing the UV–VIS, IR, and ESR spectra at 77 K reported earlier [16]; CHN analysis was also carried out on the photoproduct.

3. Results and discussion

Tetraazamacrocycles which exert strong ligand fields when coordinated to nickel(II), form low spin complexes with square planar geometry [1]. The single absorption band in the visible region for the complexes investigated, is assigned to the transition $^1A_{1g} \rightarrow {}^1B_{1g}$ in the tetragonal formalism [4]. The intense charge transfer bands observed with maximum at 236 nm and 265 nm for the complexes **1** and **2**, respectively, are assigned primarily as charge transfer to solvent (CTTS) transitions, which is supported by the photolysis results discussed (vide infra). Complexes **1** and **2** show solvent sensitivity for these transitions and the charge transfer photochemistry in different non-aqueous solvents reported elsewhere [25] also supports the assignment of the excited state as CTTS in nature. The complexes investigated at present undergo photochemical reactions essentially on excitation in the CTTS band and irradiation at longer wavelengths does not lead to any appreciable decomposition with quantum yields for the net redox reactions found to be less than 10^{-3}.

3.1. Continuous photolysis of $[Ni(tet\text{-}a)]^{2+}$ ion in aqueous solutions and investigation of stable photoproduct

Continuous photolysis of **1** using 254 nm light from a low pressure mercury vapor lamp in air-equilibrated aqueous solution, deaerated 0.1 M $HClO_4$ solution and N_2O saturated aqueous solution, respectively, leads to changes in the absorption spectra of the complexes as shown in Fig. 1 for typical experiments. Continuous photolysis of $[Ni(tet\text{-}a)]^{2+}$ ion dissolved in aqueous solution (pH = 6.7) using a low pressure mercury vapor lamp under deaerated conditions does not lead to any appreciable changes in the absorption spectrum and also no transient was observed on conventional flash photolysis in millisecond time scale. However, laser flash photolysis experiments indicate formation of solvated electron by mono and biphotonic processes [26]. This observation is consistent with the interpretation that the photoproducts recombine rapidly to give back the parent complex.

Continuous photolysis of **1** in oxygen saturated 0.1 M HCl shows increase in absorbance at 320 nm, which decays thermally in minutes and the corresponding spectra are shown in Fig. 2 (see 2a-inset). Photolyzed solutions of **1** in 1 M HCl show an increase in absorbance at 320 nm as shown in Fig. 3, which does not change even after several minutes and the ESR spectrum of the solution is shown in the inset of Fig. 3. From the ESR spectrum, it is clearly understood that *trans*-$[Ni(III)tet\text{-}aCl_2]^+$ is the photoproduct formed. The ESR spectrum is characteristic

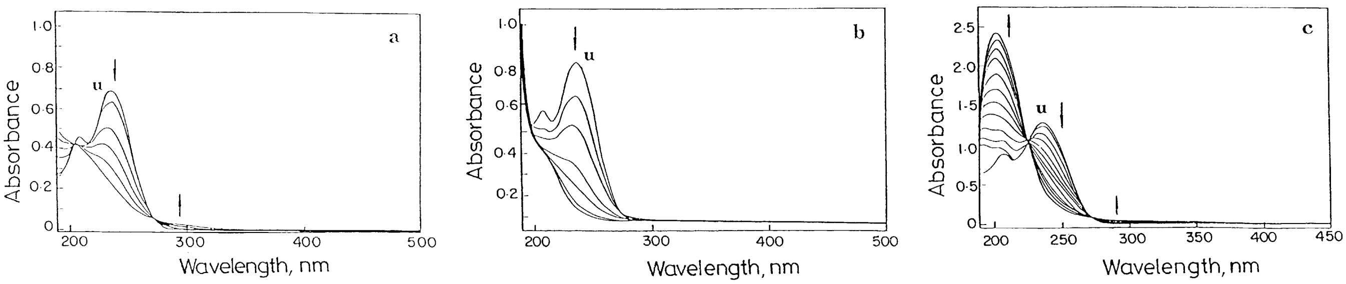

Fig. 1. Continuous photolysis of $[Ni(tet\text{-}a)]^{2+}$ ion using a 254 nm low pressure mercury vapor Pen-ray lamp at 25°C; (u) unphotolyzed and subsequent spectra recorded after photolysis each for 3 min; (a) photolysis in deaerated aqueous solution containing 0.1 M $HClO_4$; (b) photolysis in air-equilibrated aqueous solution at pH = 6.7; (c) photolysis in N_2O saturated aqueous solution at pH = 6.7.

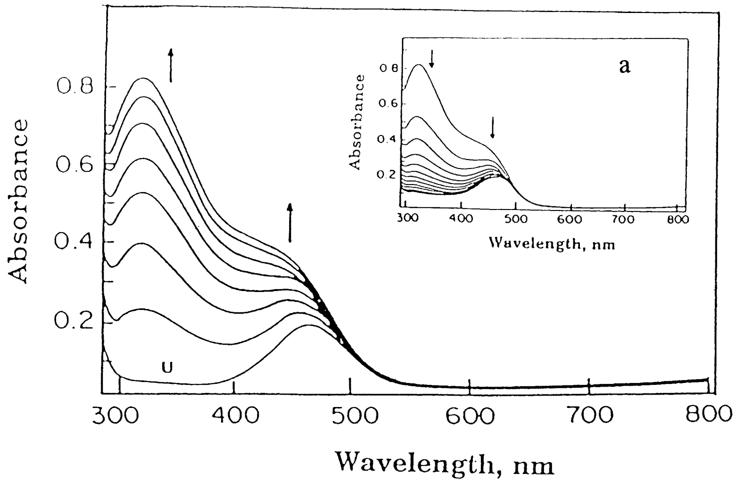

Fig. 2. Continuous photolysis of $[Ni(tet\text{-}a)]^{2+}$ ion in oxygen saturated aqueous solution containing 0.1 M HCl using the 254 nm lamp at 25°C; (u) unphotolyzed and subsequent spectra recorded after photolysis each for 3 min; (inset) change in the absorbance of the photolyzed solution at 23°C monitored after an interval of 5 min each in a UV–VIS spectrophotometer.

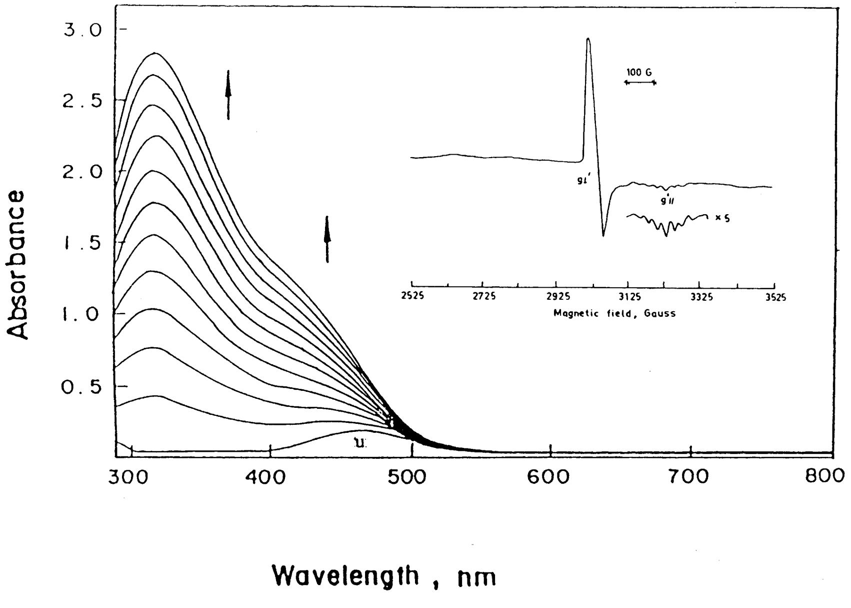

Fig. 3. Continuous photolysis of $[Ni(tet\text{-}a)]^{2+}$ ion in oxygen saturated aqueous solution containing 1 M HCl using the 254 nm lamp at 25°C; (u) unphotolyzed and subsequent spectra recorded after photolysis each for 1 min; (inset) EPR spectra of the photolyzed solution at 77 K.

of Ni(III) complexes and seven lines of the g_{11} feature confirms the axial coordination of two chloride ions to the Ni(III) [27]. This photoproduct is isolated as yellowish brown solid, when the photolysis of saturated solution is carried out at low temperatures. The photoproduct is characterized by elemental analysis (calculated: C 35.45%, H 6.69%, N 10.33%; experiment: C 36.07%, H 6.64%, N 10.19%) and the results agree well with the structure proposed. The photoproduct shows a band with λ_{max} at 320 nm as observed during the continuous photolysis of the complex in 1 M HCl. The IR spectra of complex **1** and the photoproduct does not vary much as the macrocyclic ligand remains unchanged during the photoreaction.

Quantum yield for the formation of the photoproduct obtained on continuous photolysis of the complex **1** in oxygen saturated solution is 0.03 ± 0.005. Change in absorbance with respect to time at 320 nm on photolysis of the solution of **1** in air-equilibrated aqueous solution is found to be linear for more than 10% of decomposition of the complex. When 0.1 M hydrochloric acid is used instead of perchloric acid, the photoproduct is better stabilized due to the coordination of chloride ion to give *trans*-[Ni(tet-a)Cl$_2$]$^+$ ion which is well characterized by UV–VIS absorption and ESR methods [19,27]. At low concentrations of the acid, nickel(III) complex formed in the photochemical reaction decays fast to produce the nickel(II) complex as shown in the inset of Fig. 2. The forward reaction driven by light and the reverse process occurring in the dark could be observed for a number of cycles. The thermal reaction is attributed to the reaction between hydrogen peroxide and nickel(III) complex [19].

$$[\mathrm{LNi^{III}\text{–}(Cl_2)}]^+ + \mathrm{H_2O_2} \rightarrow [\mathrm{Ni^{II}L}] + \mathrm{HO_2}^\bullet \quad (1)$$

The reaction between [Ni(III)tet-aCl$_2$]$^+$ ion in 0.1 M HCl solution and hydrogen peroxide was followed after photolysis of the solution and the results are shown in Fig. 4. The decay of [Ni(tet-a)Cl$_2$]$^+$ ion monitored at absorption maximum (320 nm) shows a second order rate constant of 9.8×10^{-3} M^{-1} s^{-1} in 0.1 M HCl; the rate constant decreases with increasing concentration of HCl (inset-ii of Fig. 4).

Continuous photolysis of **2** in air-equilibrated and N$_2$O saturated aqueous solution (pH = 6.7) shows spectral changes indicated in Fig. 5. We reported earlier [25], the same absorbance change upon photolysis of the complex **2**

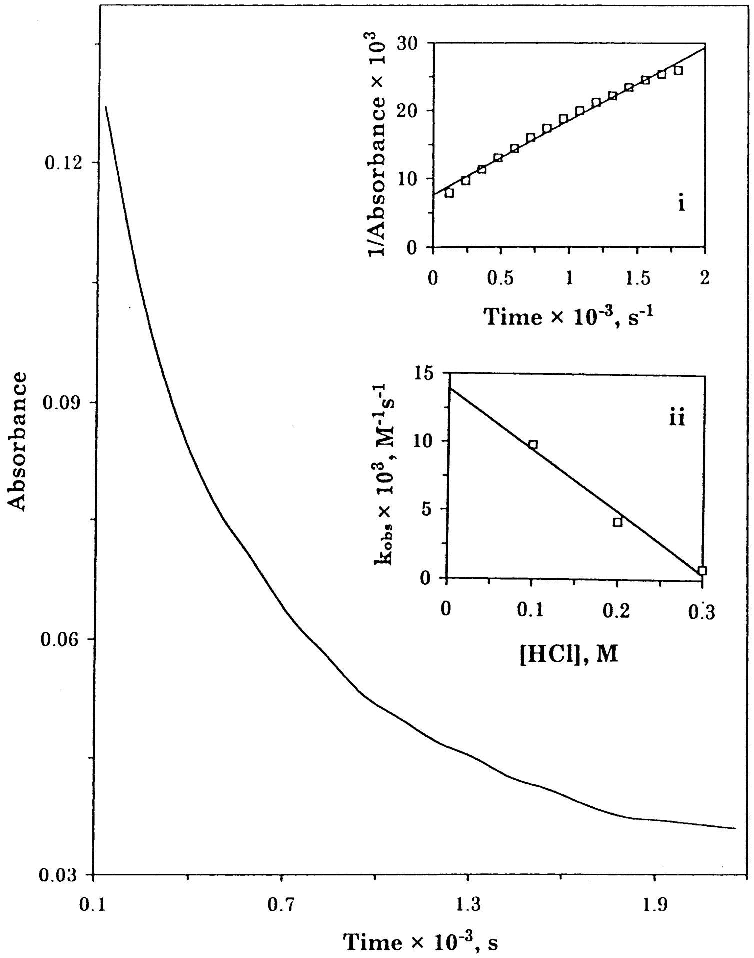

Fig. 4. Decay of the absorbance observed at 320 nm for the photolysed solution of the [Ni(tet-a)]$^{2+}$ complex in oxygen saturated 0.1 M HCl solution; (inset-i) second order plot (1/*A* vs. time) for the decay; (inset-ii) plot of k_{obs} vs. [HCl] for the decay at 320 nm.

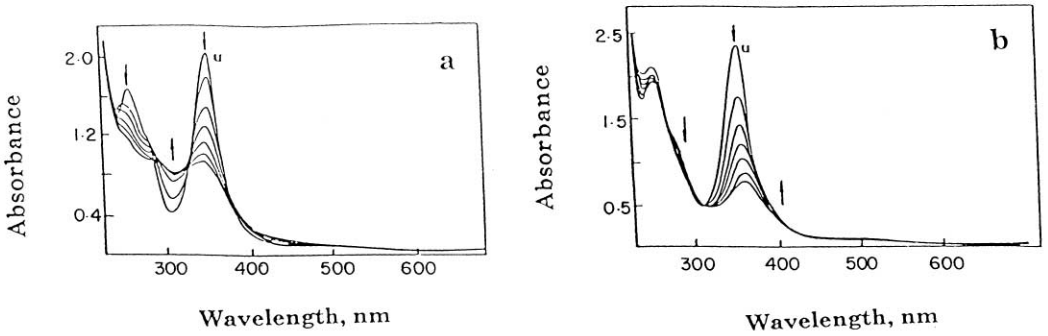

Fig. 5. Continuous photolysis of $[\text{Ni(AT)}]^{+}$ ion using the 254 nm lamp at 25°C; (u) unphotolyzed and subsequent spectra recorded after photolysis each for 5 min; (a) oxygen saturated aqueous solution; (b) N_2O saturated aqueous solution at pH = 6.7.

in non-aqueous solution and established the photooxidation of the metal center by comparing the results obtained from the spectroelectrochemical technique. It is understood that the primary photooxidation of the metal center is followed by the electron transfer from the negative site of the ligand, which leads to the decompositon of the complex, shown as the change in absorbance Fig. 5.

3.2. *Reactions of nickel(II) macrocyclic complexes with hydroperoxy radicals*

Conventional flash photolysis studies show that the product of primary photolysis reacts with solvated electron scavengers like molecular oxygen, hydrogen ion and nitrous oxide. In acidic solutions, the absorption spectrum of the transient observed on flash photolysis of **1** indicates a maximum at 370 nm. The transient observed on flash photolysis of **1** in 0.1 M perchloric acid in deaerated solutions shown in Fig. 6 is attributed to the formation of the nickel(III) complex according to the reactions shown below.

$$[(\text{tet-a})\text{Ni}^{\text{II}}] \overset{h\nu,\text{CTTS}}{\rightleftarrows} [(\text{tet-a})\text{Ni}^{\text{III}} \ldots e_{\text{aq}}^{-}] \qquad (2)$$

$$[(\text{tet-a})\text{Ni}^{\text{III}} \ldots e_{\text{aq}}^{-}] + \text{H}^{+} \rightarrow [(\text{tet-a})\text{Ni}^{\text{III}}] + \text{H}^{\bullet} \qquad (3)$$

Nickel(III) macrocyclic complexes are known to have intense absorption in the region 300–500 nm as shown in Fig. 7 [8,9]. In deaerated aqueous acidic solutions (0.1 M $HClO_4$), formation of nickel(III) is not observed on continuous photolysis, since the hydrogen atom and nickel(III) complex formed recombine to give back the nickel(II) complex as the second order rate constant for the recombination reaction is known to be diffusion controlled [19]. However in oxygen saturated acidic solutions, the hydrogen atom formed in reaction **2** reacts with molecular oxygen ($k = 2.1 \times 10^{10}\,\text{M}^{-1}\,\text{s}^{-1}$) [28,29] to give the hydroperoxy radical.

$$\text{H}^{\bullet} + \text{O}_2 \rightarrow \text{HO}_2^{\bullet} \qquad (4)$$

which is known to oxidize nickel(II) macrocyclic complexes [30].

In the conventional flash photolysis experiments, this thermal reaction is observed as the slower growth in absorbance at 370 nm as shown in Fig. 6b. The reaction of the nickel(II) complex occurring in presence of oxygen and hydrogen ion leads to the thermal oxidation process

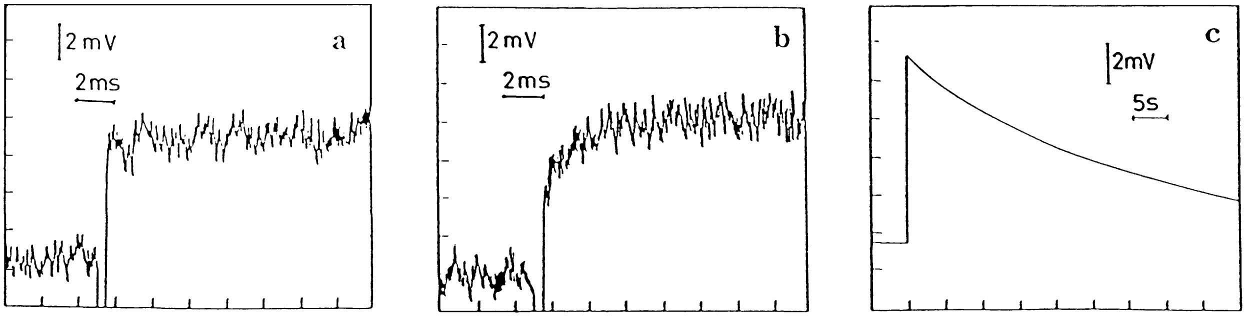

Fig. 6. Conventional flash photolysis of $[\text{Ni(tet-a)}]^{2+}$ ion in aqueous 0.1 M $HClO_4$ at 23°C monitored at 370 nm; (a) in freeze-pump-thaw deaerated solution; (b) in oxygen saturated solution; (c) in oxygen saturated solution observed at 50 s time scale.

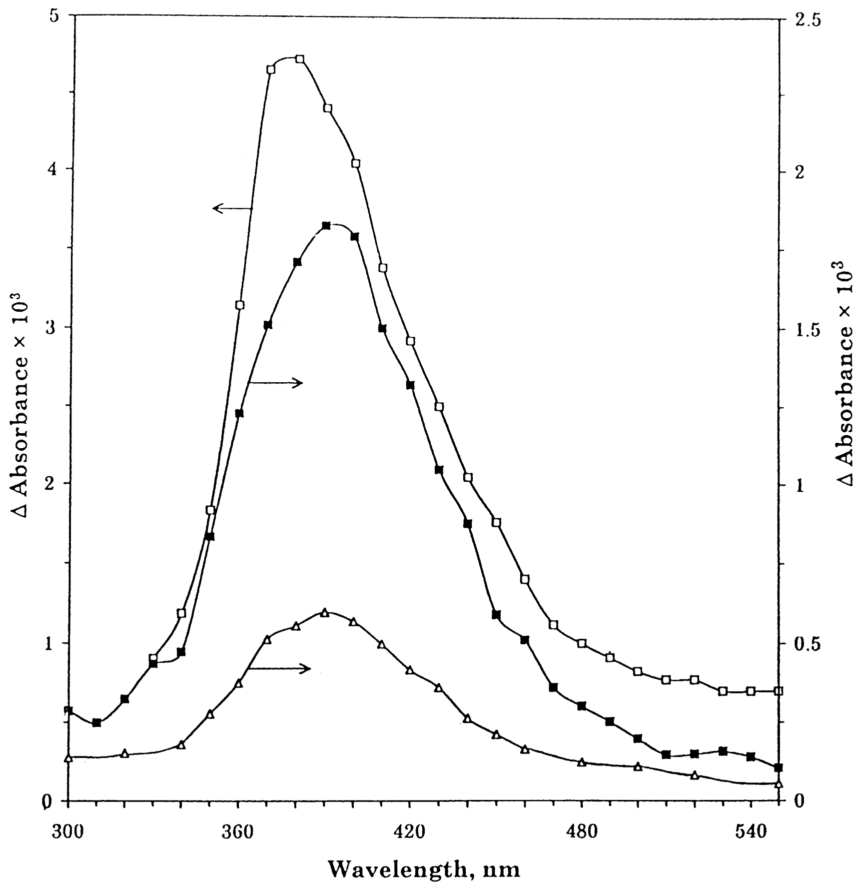

Fig. 7. Absorption spectra of the transient recorded 10 ms after the flash photolysis of $[Ni(tet\text{-}a)]^{2+}$ ion in (Δ–Δ–Δ) freeze-pump-thaw deaerated aqueous 0.1 M $HClO_4$, (■–■–■) in oxygen saturated aqueous 0.1 M $HClO_4$ solution and (□–□–□) in oxygen saturated aqueous 0.1 M HCl solution.

given as

$$[(tet\text{-}a)Ni^{II}] + HO_2^{\bullet} \xrightarrow{H^+} [(tet\text{-}a)Ni^{III}] + H_2O_2 \qquad (5)$$

The concentration of the dissolved oxygen is in millimolar quantities and hence the nickel(III) complex ($<10^{-4}$ M) is not able to effectively compete in the reaction with hydrogen atom. The rate constants for the formation of the nickel(III) complex depend upon the concentration of hydrogen ion and the nickel(II) macrocyclic complex as shown in Fig. 8. The increase in the rate constant with increasing concentration of hydrogen ion is due to the stabilization of hydroperoxy radical according to the equilibrium.

$$HO_2^{\bullet} \rightleftarrows H^+ + O_2^{\bullet -} \qquad (6)$$

which has a pK_a value [28] of 4.8. The nickel(III) complex formed in air-equilibrated perchloric acid medium decomposes at 50 s time scale as there are no coordinating ligands present in the medium to stabilize the nickel(III) macrocyclic complex. However, when flash photolysis is carried out in 0.1 M HCl, the transient observed with absorption spectrum showing maximum at 370 nm is found to be stable for longer periods; in continuous photolysis reaction, the formation of

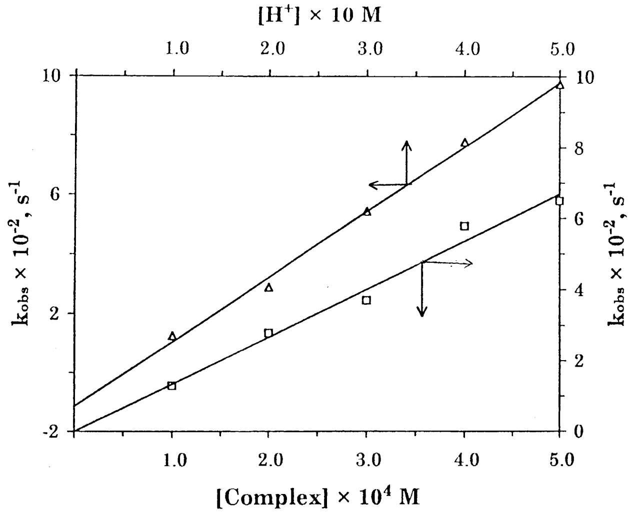

Fig. 8. Plot of k_{obs} vs. [complex] for the growth observed at 370 nm on conventional flash photolysis ion in oxygen saturated 0.1 M $HClO_4$ and plot of k_{obs} vs. $[H^+]$ (□–□–□) for the 370 nm growth in oxygen saturated solution with [complex] = 1.0×10^{-4} M; (Δ–Δ–Δ), $[Ni(tet\text{-}a)]^{2+}$; (□–□–□), AT.

the stable nickel(III) complex with axially coordinated chloride ligands is indicated with the characteristic ESR spectrum (see inset of Fig. 3).

$$[\mathrm{LNi^{III}}\text{–}(\mathrm{HO_2}^-)]^{2+} \xrightarrow{2\mathrm{HCl}} [\mathrm{LNi^{III}}\text{–}(\mathrm{Cl})_2]^{+}\mathrm{H_2O_2} + \mathrm{H}^+ \qquad (7)$$

Absorption spectra of the transients recorded 10 ms after photolysis of **1** under different conditions in solution are shown in Fig. 7 which confirms our interpretation. Oxidation of the nickel(II) complex **1**, by pulse radiolytically generated hydroperoxy radical in phosphate buffer in the pH range 4–7 has been reported earlier [30] which shows that the rate constant increases with decrease in pH and it was proposed that the hydroperoxide coordinates with nickel(III) in the axial position after the oxidation reaction. The large difference observed in the volume of activation from +1 to $-7\,\mathrm{cm^3\,mol^{-1}}$ is attributed to a mechanism, which is more favorable towards an associative bond formation [30]; the rate constant observed in the present study ($k = 2.0 \pm 0.1 \times 10^6\,\mathrm{M^{-1}\,s^{-1}}$) is close to the rate constant obtained in the pulse radiolysis investigation ($2.3 \times 10^6\,\mathrm{M^{-1}\,s^{-1}}$ at pH = 3.5).

The nickel(II) complex, **2**, is known to change its structure under acidic conditions [21,22] and hence the scavenging reaction of nickel(III) electron adduct I by $\mathrm{N_2O}$ alone was investigated in neutral aqueous solutions. The nickel(II) macrocyclic complex, **2**, with the unsaturated macrocycle on flash photolysis in neutral aqueous solution (pH = 6.7) saturated with $\mathrm{N_2O}$ shows a transient (inset of Fig. 9) with spectrum having maximum at 610 nm (Fig. 9), indicating that photolysis leads to some species other than nickel(III) complex. The transient observed at 610 nm in the case of **2** is suggested to be due to the formation of a free radical coordinated to nickel(II), which decays with a rate constant of $11.99\,\mathrm{s^{-1}}$. In this case, the charge transfer to excited state of the nickel(III) formed in the primary photochemical reaction, oxidizes the ligand to give a free radical. In the case of complex **2** cyclic voltammetric experiments also indicate an irreversible oxidative reaction indicating an intramolecular electron transfer from the ligand to the oxidized metal center [8].

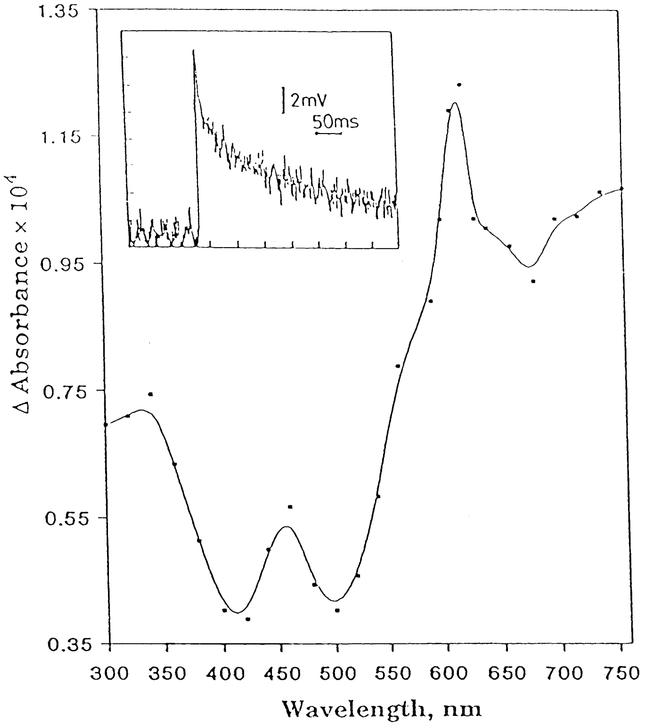

Fig. 9. Absorption spectrum of the transient recorded 10 ms after flash photolysis of the complex $[\mathrm{Ni(AT)}]^+$ ion in $\mathrm{N_2O}$ saturated aqueous solution (pH = 6.7); (inset) decay of the transient at 610 nm.

In the presence of methanol, the hydrogen atom produced on photolysis of nickel(II) macrocyclic complexes in acidic solutions, reacts with the alcohol ($k = 2.6 \times 10^6\,\mathrm{M^{-1}\,s^{-1}}$) [30], which is present in large excess to evolve hydrogen gas. The organic compound formed could not be identified with certainty as the concentration is low and part of the organic product undergoes thermal reactions in the photolysed solution.

Acknowledgements

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References

[1] M.A. Halcrow, G. Christou, Chem. Rev. 94 (1994) 2421.
[2] J.R. Lancaster, The Bioinorganic Chemistry of Nickel, VCH Publishers, New York, 1988.
[3] T.J. Collins, T.R. Nichols, E.S. Uffelman, J. Am. Chem. Soc. 113 (1991) 4708.
[4] J.A. Kovacs, Adv. Bioinorg. Chem. 9 (1994) 173.
[5] R.P. Hausinger, Bioinorganic Chemistry of Nickel, Plenum Press, New York, 1993.
[6] A.F. Kolodziecz, Prog. Inorg. Chem. 41 (1994) 493.
[7] E.K. Barefield, D.H. Busch, Inorg. Chem. 10 (1971) 108.
[8] F.V. Lovecchio, E.S. Gore, D.H. Busch, J. Am. Chem. Soc. 96 (1974) 3109.
[9] M. Jaacobi, D. Meyerstein, J. Lilie, Inorg. Chem. 18 (1979) 429.
[10] P.V. Bernhardt, G.A. Lawrance, D.F. Sangster, Inorg. Chem. 27 (1988) 4055.
[11] K.C. Bible, M. Buytendorp, P.D. Zierath, K.L. Rinehart, Proc. Natl. Acad. Sci. U.S.A. 85 (1988) 4582.
[12] A. Bakac, J.H. Espenson, J. Am. Chem. Soc. 108 (1986) 713.
[13] A. Bakac, J.H. Espenson, J. Am. Chem. Soc. 108 (1986) 719.
[14] A. Buttafava, L. Fabbrizzi, A. Perotti, A. Poggi, G. Poli, B. Seghi, Inorg. Chem. 25 (1986) 1456.
[15] M.G. Fairbank, A. McAuley, Inorg. Chem. 25 (1986) 1233.
[16] R.I. Haines, A. McAuley, Coord. Chem. Rev. 39 (1981) 77.
[17] K. Nag, A. Chakravorthy, Coord. Chem. Rev. 33 (1980) 87.
[18] O. Horvath, K.L. Stevenson, Charge Transfer Photochemistry of Coordination Compounds, VCH Publishers, New York, 1993.
[19] K.D. Whitburn, G.S. Laurence, J. Chem. Soc., Dalton Trans. (1979) 139.
[20] G. Ferraudi, S. Muralidharan, Inorg. Chem. 20 (1981) 4262.
[21] N.F. Curtis, J. Chem. Soc. (1964) 2644.
[22] S. Cummings, R.E. Seivers, J. Am. Chem. Soc. 92 (1970) 215.

[23] P. Ramamurthy, J. Chem. Educ. 9 (1993) 56.
[24] E. Natarajan, P. Natarajan, Inorg. Chem. 31 (1992) 1251.
[25] T. Dhanasekaran, P. Paul, P. Natarajan, J. Photochem. Photobiol. A: Chem. 131 (2000) 75.
[26] H. Prakash, P. Natarajan, Chem. Phys. Lett. 329 (2000) 357.
[27] A. Desideri, J.B. Raynor, J. Chem. Soc., Dalton Trans. (1977) 2051.
[28] G.V. Buxton, C.L. Greeenstock, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 513.
[29] B.H.J. Bielski, D.E. Cabelli, R.L. Arudi, A.B. Ross, J. Phys. Chem. Ref. Data 14 (1985) 1041.
[30] A. Meshulam, H. Cohen, R.V. Eldik, D. Meyerstein, Inorg. Chem. 31 (1992) 2151.