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Photooxidation of nickel(II) azamacrocyclic complexes to trivalent nickel complexes on excitation in the charge-transfer-to-solvent band

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Abstract

The nickel(II) azamacroyclic complexes $[Ni(II)L_1](ClO_4)_2$ (**1**), $[Ni(II)L_2](ClO_4)_2$ (**2**) and $[Ni(II)L_3](ClO_4)_2$ (**3**) produce solvated electron on excitation using 248 nm laser in deaerated aqueous solutions where $L_1 = 1,4,8,11$-tetraazacyclotetradecane, $L_2 = 1,8$-diethylhydroxy-1,3,6,8,10,13-hexaazacyclotetradecane and $L_3 = 1,3,6,9,11,14$-hexaazatricyclo[12.2.1.16.9]octadecane. Formation of stable nickel(III) complexes occurs as a result of the scavenging of the solvated electron in the presence of acids and oxygen and as a result of the thermal reaction between the hydroperoxyl radical and the nickel(II) complexes. Continuous photolysis of the complexes using 254 nm radiation results in the photooxidation of the divalent nickel complexes to trivalent nickel complexes which are identified by ESR spectra. The mechanistic details of the formation of the photoproducts have been investigated in detail. The assignment of CTTS formalism for the reactive excited state was confirmed. Photooxidation of the nickel(II) macrocyclic complexes dissolved in acetonitrile and in a mixture of acetonitrile and dichloromethane has been investigated by flash photolysis of the complexes. Continuous photolysis of the complexes in non-aqueous solutions shows the formation of nickel(III) complexes as stable products, which was confirmed by ESR and optical spectral studies.
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Keywords: Nickel(II) azamacrocyclic complexes; Photolysis; ESR spectra; Nickel(I); Nickel(III); Photooxidation

1. Introduction

The role of nickel in many catalytic reactions and hydrogenation is well known for a long time [1,2]. The recent identification of nickel as an essential metal ion in enzymatic reactions has intensified investigations to examine the nature of oxidation states and precise nature of reaction centres [1–7]. Nickel in many biological and catalytic reactions is present as functional motif in +1 or +3 oxidation states while nickel(II) being more stable thermodynamically is commonly present in most of these systems [7]. Nickel(II) complexes with a variety of macrocyclic ligands and other common chelates are known to exist in the diamagnetic square planar form or paramagnetic octahedral form. Nickel(II) complexes in paramagnetic or diamagnetic forms could be reduced to +1 or oxidised to +3 oxidation states [8–11]. By changing the oxidation state of nickel, nickel complexes with one-dimensional structural network are obtained which

show non-linear optical behaviour [12,13]. In situ oxidation of nickel(II) azamacrocyclic complexes to trivalent nickel complexes has been employed for the oxidative cleavage of DNA molecules [14]. Several nickel(II) azamacrocyclic complexes were used as model for the enzyme, carbon monoxide dehydrogenase [15]. The electrocatalytic reduction of carbon dioxide by these complexes were reported [15,16]. Photochemical systems with the nickel(II) azamacrocyclic complex as active site were reported to bring about the reduction of carbon dioxide [17,18]. Electrochemical, pulse radiolysis and flash photolysis studies support that nickel(I) is the active state in the reduction of carbon dioxide [17]. The equilibrium reaction between the diamagnetic square planar and paramagnetic octahedral nickel(II) azamacrocyclic complexes has been utilised to develop nickel(II) azamacrocyclic complexes as novel sensor materials [19–21].

We have examined the charge-transfer-to-solvent (CTTS) excitation processes exhibited by the cationic nickel(II) azamacrocyclic complexes [22–24] by observing the hydrated electron and the nickel(III) complex in aqueous solution [25]. Photochemical synthesis of nickel(III) complexes by

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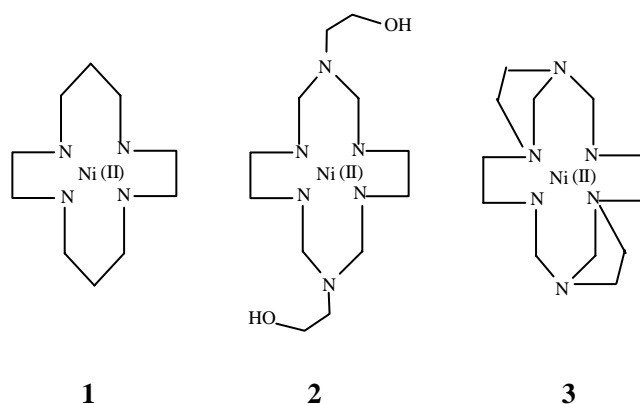
Scheme 1.

CTTS excitation of the complexes $[Ni(II)L_1](ClO_4)_2$ (**1**) and $[Ni(II)L_2](ClO_4)_2$ (**2**) has been reported recently [25].

The metal centre of the complex could be reduced by excitation in the ligand to metal charge transfer band (LMCT) or photochemically oxidised to higher oxidation states by excitation in the metal-to-ligand charge-transfer transition (MLCT) [26]. Study of charge transfer excited states in co-ordination compounds by laser flash photolysis and continuous photolysis has been of interest for a long time. The photoredox reactions of the co-ordination complexes by the LMCT or MLCT excitation are well documented but the charge-transfer-to-solvent transitions of the co-ordination compounds have been observed only in a few cases [26–28]. Photodetachement of electron from the CTTS excited states has been reported for several organic and inorganic anions [29]. Anionic $[Fe(CN)_6]^{4-}$ complex is a classical example for the production of solvated electron on photolysis in aqueous solution [30]. Time-resolved laser flash photolysis studies of anions have shown that electron transfer proceeds within 200 fs from the CTTS excited anions into a nearby cavity site in the surrounding solvent to form a solvated electron [29–32]. In this paper, we report the production of hydrated electron on exciting the CTTS band and observe the formation of nickel(III) complexes from the nickel(II) azamacrocyclic complexes $[Ni(II)L_1](ClO_4)_2$ (**1**), $[Ni(II)L_2](ClO_4)_2$ (**2**) and $[Ni(II)L_3](ClO_4)_2$ (**3**) (where L_1 = 1,4,8,11-tetraazacyclotetradecane, L_2 = 1,8-diethyl-hydroxy-1,3,6,8,10,13-hexaazacyclotetradecane, L_3 = 1,3,6,9,11,14-hexaazatricyclo[12.2.1.16.9]octadecane; Scheme 1) in detail by flash and continuous photolysis techniques under various conditions. The characteristics of stable trivalent nickel complexes were elucidated by ESR and absorption spectral techniques.

2. Experimental

The complexes **1**–**3** were synthesised following the procedures reported in the literature and were characterised by elemental analysis and spectral techniques as reported earlier (*Caution*: perchlorate complexes are explosive) [33–35].

Nickel chloride, nickel acetate and nickel carbonate were obtained from Merck, Sigma–Aldrich and SRL Chemicals, respectively. Methanol, acetonitrile and dichloromethane used were of HPLC and spectroscopy grade obtained from Merck, Qualigens and SRL Chemicals. Hydrochloric acid and perchloric acid used were from Qualigens and Merck, respectively. HPLC grade water obtained from Qualigens was used for the laser flash photolysis and other experiments. Water, triply distilled over alkaline permanganate was also used. The ligand cyclam was obtained from Sigma–Aldrich.

Electronic absorption spectral measurements were carried out using a Hitachi-320 double beam spectrophotometer or a computer controlled Hewlett-Packard 8452A UV-Vis diode array spectrophotometer.

The equilibrium composition of nickel(II) macrocyclic complexes in the square planar form compared to the paramagnetic octahedral form were determined spectrophotometrically as reported earlier [36,37].

ESR spectra were recorded using a Bruker ER-200D-SRC model spectrometer. The spectrometer operates in the X-band of the microwave frequency at 10 GHz. The ESR spectrum at liquid nitrogen temperature, was measured by freezing the sample in liquid nitrogen in a Dewar flask which was then placed into probe cavity of the instrument. The magnetic field was calibrated using Bruker standard samples and by independently recording the standard signal of DPPH.

Continuous photolysis experiments were carried out using a low pressure mercury vapour 254 nm pen-ray lamp (Ultraviolet Products, USA). The quartz cuvette was kept near pen-ray lamp during photolysis and the absorbance was noted at regular intervals.

Nanosecond laser flash photolysis experiments were carried out as reported earlier [38]. KrF laser source used for excitation produces nanosecond pulses (20 ns) of 248 nm radiation and the energy of the laser pulse could be varied from 10 to 110 mJ.

The microsecond conventional flash photolysis experiments were carried out using an Applied Photophysics KN020 model flash kinetic spectrometer as reported earlier [23,24,38]. Two (LR-16) xenon flash lamps were used for excitation. A 12 V, 100 W quartz tungsten iodine lamp (Phillips, Holland) operated by a power supply unit (model 415/01) was used as the source for the monitoring beam.

3. Results and discussion

3.1. Absorption spectra of the complexes

Absorption spectra of the nickel(II) azamacrocyclic complexes in the visible region in aqueous and non-aqueous solutions shown in Fig. 1 reveal the presence of both square planar low spin and the solvent co-ordinated octahedral high
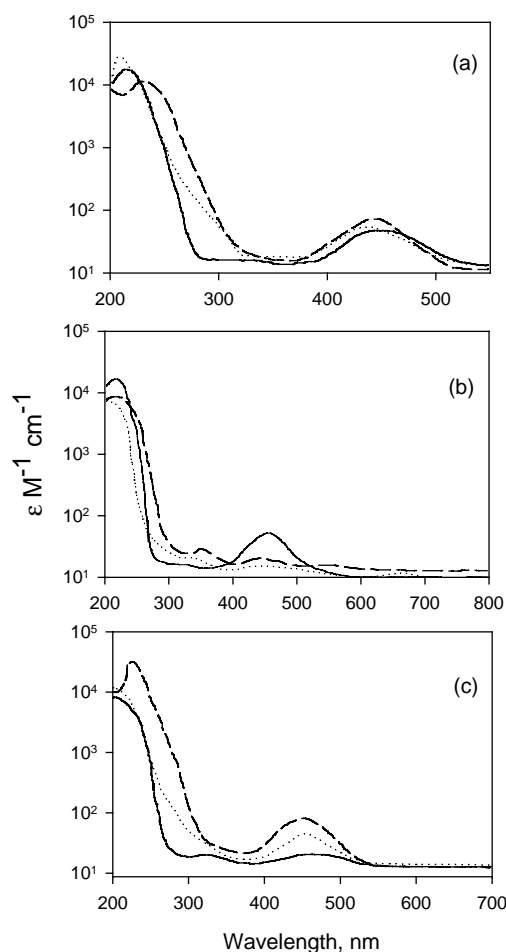
Fig. 1. Absorption spectra of the complexes in: (a) water; (b) 1 M HCl; (c) acetonitrile. (—) Complex **1**; (···) complex **2**; (– – –) complex **3**.

Fig. 2. Transient absorption spectra of hydrated electron obtained on 248 nm flash photolysis: (a) complex **1**; (b) complex **2**; (c) complex **3**. Insets: transient decay at 680 nm. Transient absorption spectra were obtained after 150 ns for the complexes **1** and **2**, and 200 ns for complex **3**.

spin forms as reported earlier [39]. When the low spin form is the predominant species, a single absorption band assigned to $^1A_{1g}$–$^1B_{1g}$ transition is observed and when the high spin form is the predominant species, three absorption features assigned to $^3A_{2g}$–$^3T_{2g}$, $^3A_{2g}$–$^3T_{1g}$ (F), $^3A_{2g}$–$^3T_{1g}$ (P) transitions [39,40] in the ligand field formalism are observed. It is clearly seen that all the nickel(II) azamacrocyclic complexes show one intense absorption band in the UV region as shown in Fig. 1 which is solvent sensitive suggesting that the band is due to charge-transfer transition. UV absorption band for the complexes are assigned to charge-transfer-to-solvent transitions from the flash photolysis results of the complexes as presented further.

3.2. Laser flash photolysis of the complexes in aqueous medium

Nanosecond laser flash photolysis of deaerated aqueous solution of the complexes **1**–**3** using 248 nm radiation shows transient absorption due to hydrated electron in microsecond time scale as shown in Fig. 2. We reported earlier the production of solvated electron and the photoionisation
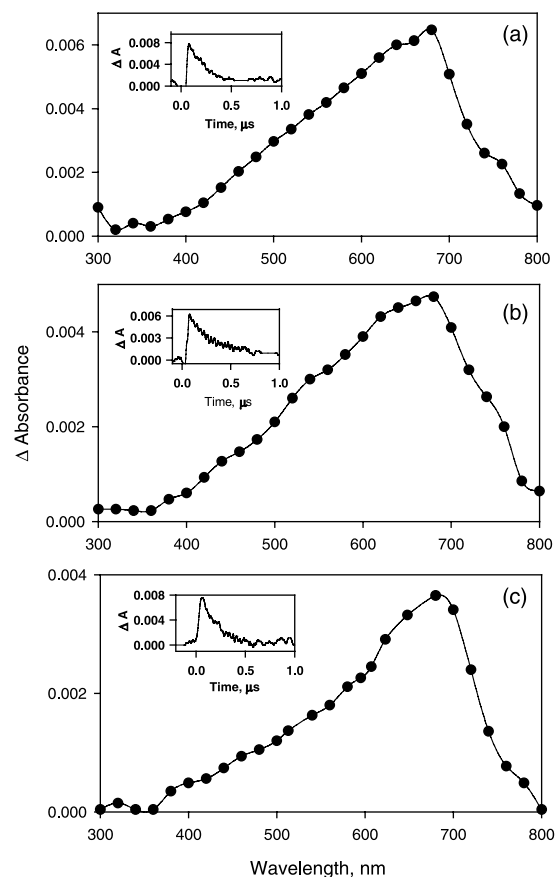
processes due to the CTTS excitation for the complexes [Ni(II)tet-a]$^{2+}$, [Ni(II)HTMe]$^{2+}$ and Ni(II)AT]$^+$ (tet-a = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane, HTMe = 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane, AT = 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienato) and the hydrated electron transient spectra reported is similar to that obtained in the present investigation [22]. In the presence of electron scavengers such as protonic acids or molecular oxygen, hydrated electron produced on photolysis is scavenged and the transient spectra of hydrated electron are not observed [22–24]. Identification of hydrated electron as a transient reveals that the UV absorption band of the complexes **1**–**3** indeed possesses CTTS character. The primary reaction on CTTS excitation is given as

$$[\text{Ni(II)L}]^{2+} \xrightarrow{h\nu} [\text{Ni(III)L}]^{3+} + e_{aq}^-, \quad L = \text{ligand} \quad (1)$$
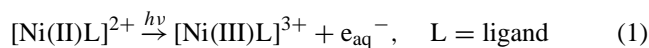
The rate constants for the decay of the hydrated electron transient monitored at 680 nm in aqueous solution vary with the concentration of the nickel(II) azamacrocyclic complexes obeying pseudo-first-order kinetics [22,41]. The second-order rate constants obtained (Table 1) are similar

Table 1
Rate constant for the decay of hydrated electron obtained on photolysis of aqueous solution of nickel(II) macrocyclic complexes

Complex	Rate constants ($\times 10^{-10}\,M^{-1}\,s^{-1}$)	[Complex] ($\times 10^4\,M$)
$[Ni(II)L_1]^{2+}$	3.8 ± 0.2	2.35
$[Ni(II)tet\text{-}a]^{2+a}$	6.0 ± 0.1	0.50
$[Ni(II)AT]^{2+a}$	2.1 ± 0.5	0.45
$[Ni(II)HTMe]^{2+a}$	4.5 ± 0.1	1.74
$[Ni(II)L_2]^{2+}$	4.0 ± 0.4	2.85
$[Ni(II)L_3]^{2+}$	5.1 ± 0.1	1.17

[a] From [22].

to the rate constants for the formation of nickel(I) aza-macrocyclic complexes observed for the reaction between hydrated electron and nickel(II) azamacrocyclic complexes which was earlier determined by the pulse radiolysis technique [41]. The pathways for decay of hydrated electron are given by the following reactions [41]

$$[Ni(II)L]^{2+} + e_{aq}^- \rightarrow [Ni(I)L]^+ \tag{2}$$

$$[Ni(III)L]^{3+} + e_{aq}^- \rightarrow [Ni(II)L]^{2+} \tag{3}$$
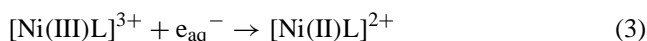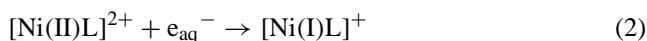
The first-order rate constants increase with increase in the concentration of the complexes (pseudo-first-order behaviour), reveals that reaction (2) is competitive with the reaction (3). However, in the present investigation the transient signal of nickel(I) complex was not observed as reported earlier [40,41] and also the spectral features due to nickel(III) of reaction (1) are not observed [41–44]. The absence of the spectral features of nickel(III) and nickel(I) transients in aqueous solution indicate that during the decay of hydrated electron, a synproportionation reaction (4) occurs between the nickel(I) and the nickel(III) transients [22]

$$[Ni(III)L]^{3+} + [Ni(I)L]^+ \rightarrow 2[Ni(II)L]^{2+} \tag{4}$$
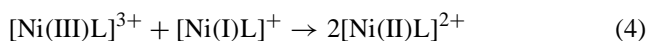
Use of hydrated electron scavenger reagents such as acids and oxygen results in the scavenging of hydrated electron and the transient spectra of the nickel(III) complex was observed at longer time scale by the microsecond conventional flash photolysis technique. The role of hydrated electron scavengers in the formation of stable trivalent nickel complexes was elucidated by microsecond conventional flash photolysis and continuous photolysis investigations discussed further.

3.3. Conventional flash photolysis of the complexes

It is well known that hydrated electron produced on pulse radiolysis of water under acidic conditions and in presence of oxygen results in the formation of hydroperoxyl radicals as the predominant species [41,44–48]
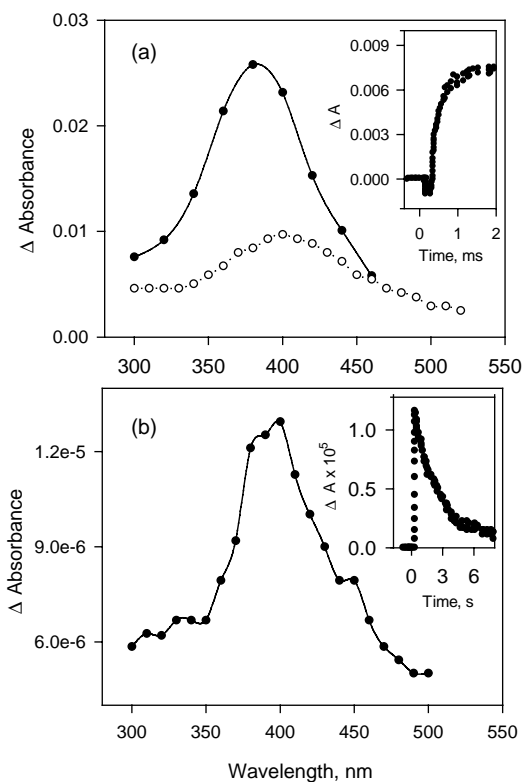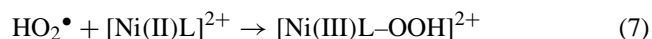
$$e_{aq}^- + H^+ \rightarrow H^\bullet \tag{5}$$

$$H^\bullet + O_2 \rightarrow HO_2^\bullet \tag{6}$$

Fig. 3. Transient spectra of the nickel(III) hydroperoxide co-ordinated complex obtained after 2 s and 3 ms on flash photolysis of complexes **1** and **2**, respectively: (a) complex **1** (●), complex **2** (○); (b) complex **3** (spectrum obtained immediately after the flash). Insets: transient signal monitored at 370 nm.

The reactions of hydrated electron with the acids, oxygen and formation of hydroperoxyl radicals are diffusion controlled processes with rate constants closer to $10^{10}\,M^{-1}\,s^{-1}$ [45], favouring the formation of hydroperoxyl radicals. Hydroperoxyl radicals produced on pulse radiolysis are known to oxidise nickel(II) azamacrocyclic complexes and the following reaction occurs [46]

$$HO_2^\bullet + [Ni(II)L]^{2+} \rightarrow [Ni(III)L\text{-}OOH]^{2+} \tag{7}$$

Formation of the nickel(III) hydroperoxide co-ordinated complex $[Ni(III)L\text{-}OOH]^{2+}$ occurs with rate constant of $3 \times 10^6\,M^{-1}\,s^{-1}$ [46] under acidic condition showing transient absorption in the region 300–450 nm with maximum at 370 nm. Flash photolysis of nickel(II) azamacrocyclic complexes in acidic solution and in presence of oxygen shows transient given in Fig. 3a. which is similar to that of the nickel(III) hydroperoxide co-ordinated complex [46] ($[Ni(III)L\text{-}OOH]^{2+}$) of the reaction (7). At the absorption maximum, the transient signal shows a growth in absorbance (Fig. 3a, inset) and the rate constants obtained from the transient signal for the complexes **1** and **2** are 1.3 $\times 10^6$ and $6.1 \times 10^6\,M^{-1}\,s^{-1}$, respectively. In the present investigation, the rate constants and the spectral features obtained under acidic conditions in presence of oxygen are similar to that observed for the formation of nickel(III)

hydroperoxide co-ordinated complex reported earlier [46]. The hydrated electron produced on CTTS excitation of the complexes in presence of acid and oxygen results in the formation of hydroperoxyl radical as the predominant species which oxidises nickel(II) azamacrocyclic complex as shown in the reaction (7) [46].

The hydroperoxyl radical is known to exist in equilibrium with the superoxide ion

$$HO_2{}^\bullet \leftrightarrows H^+ + O_2{}^{\bullet-} \tag{8}$$

with a pK_a value of 4.8 [45]. Effective scavenging of the hydrated electron and stabilisation of hydroperoxyl radical occur below pH 4 and the formation of nickel(III) hydroperoxide is favoured under highly acidic condition as indicated in Fig. 4a. It is inferred from Fig. 4a that flash photolysis of the nickel(II) azamacrocyclic complex in solution containing millimolar oxygen shows increase in absorption at 370 nm (absorption maximum) with increase in the concentration of the acid suggesting that the yield of nickel(III)

hydroperoxide complex increases due to the effective formation of hydroperoxyl radical under highly acid condition and stabilisation according to the equilibrium (8) [23]. In the absence of oxygen, growth in transient absorbance at 370 nm is not observed as the formation of hydroperoxyl radical and reaction (7) are not feasible. Earlier, pseudo-first-order behaviour for the reaction (7) was observed in the pulse radiolysis experiments and it was suggested that hydroperoxyl radicals are efficiently scavenged when the concentration of the nickel(II) complex is increased [46]. Similar behaviour was observed for the complexes in the present investigation as shown in the Fig. 4b, which shows that the rate constant increases with the concentration of the nickel(II) complexes suggesting that hydroperoxyl radicals are effectively scavenged when the concentration of the nickel(II) complexes are increased, favouring the reaction (7).

Chemical oxidation of the complex **3** to nickel(III) complex was reported to be unsuccessful as the oxidation potential (1.4 V) is higher as compared to the complexes **1** and **2** (1.0 ± 0.1 V) [47]. Conventional flash photolysis of the complex **3** shows absorption spectrum (Fig. 3b) similar to those of the complexes **1** and **2** but at absorption maximum the transient signal is very weak. The weak absorption is attributed to the low yield of nickel(III) hydroperoxide co-ordinated complex and this observation is due to the higher oxidation potential of complex **3**, when the extent of photooxidation is reduced with increase in the oxidation potential. The rate constant for the decay of the nickel(III) hydroperoxide co-ordinated complex (Fig. 3b, inset) obtained from the complex **3** is found to be higher (0.30 ± 0.1 s^{-1}) than the decay of the nickel(III) hydroperoxide co-ordinated complex observed on flash photolysis of the complexes **1** and **2** ((1.8 ± 0.2) × 10^{-3} s^{-1}) (Fig. 4c) revealing that the nickel(III) form of the complex **3** decomposes more rapidly as compared to the complexes **1** and **2** which have lower oxidation potential. The reaction of the peroxyl radical with the nickel(II) complexes to give peroxide co-ordinated nickel(III) complexes is further confirmed by the conventional flash photolysis of the complexes in acetonitrile and dichloromethane.

Conventional flash photolysis of the complexes in acetonitrile containing dichloromethane leads to the transient absorption spectrum as shown in Fig. 5a which is similar to the nickel(III) chloromethylperoxide co-ordinated complex reported earlier [24,28,49–52]. At the absorption maximum, the transient signal shows growth in absorbance and the rate constant obtained (3.3 × 10^6 M^{-1} s^{-1}) is similar to that for the reaction between chloromethylperoxyl radical and [Ni(II)cyclam]$^{2+}$ (3 × 10^6 M^{-1} s^{-1}) reported earlier [24] suggesting that chloromethylperoxyl radicals are formed on CTTS excitation of the complexes and the following reactions occur
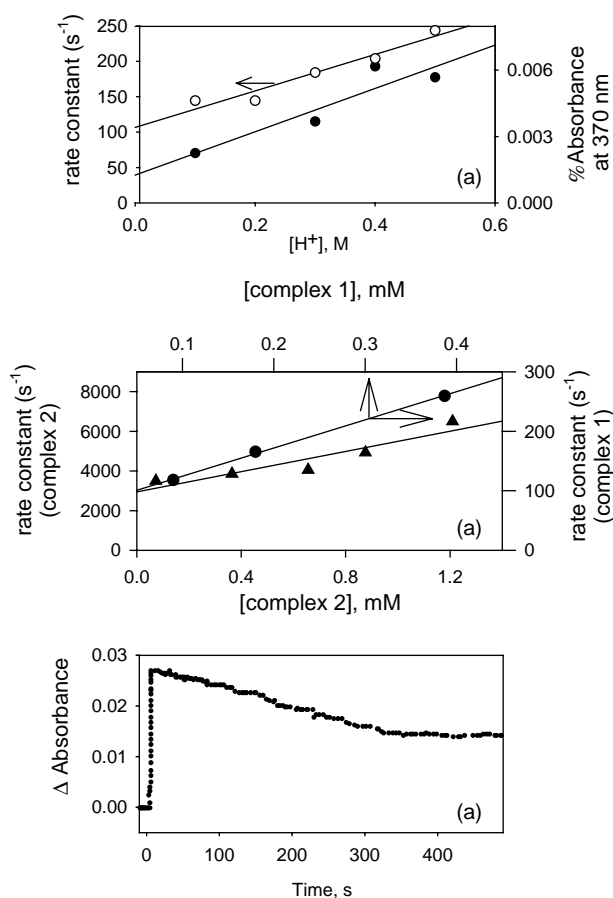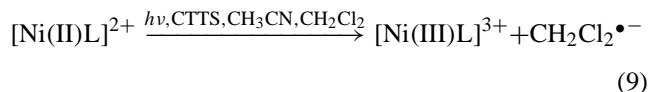

Fig. 4. Conventional flash photolysis of the complexes: (a) rate constant and absorption at 370 nm as a function of the concentration of the acid for complex **1**, at [complex] = 10^{-3} M and millimolar oxygen; (b) rate constant as a function of the concentration of the complexes **1** and **2** under [H$^+$] = 1 M and millimolar oxygen condition; (c) decay profile of nickel(III) transient for the complex **1** monitored at 370 nm in 1 M HCl at [complex] = 10^{-3} M.

$$[Ni(II)L]^{2+} \xrightarrow{h\nu, CTTS, CH_3CN, CH_2Cl_2} [Ni(III)L]^{3+} + CH_2Cl_2{}^{\bullet-} \tag{9}$$
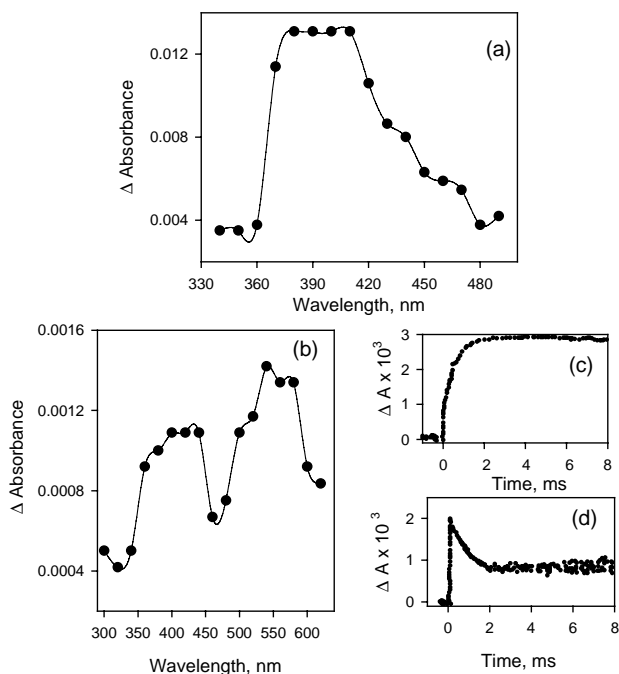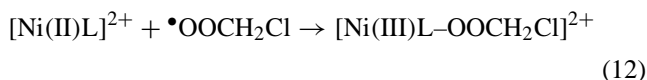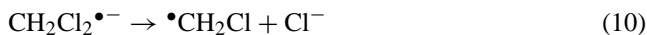
Fig. 5. (a) Transient absorption spectra of the complex **2** in acetonitrile containing 1 M dichloromethane obtained after 5 ms of the xenon lamp flash. (b) Transient absorption spectra of the complex **2** in acetonitrile obtained after 5 ms of the xenon flash lamp along with the transient signal monitored at 370 nm (c) and the decay signal monitored at 550 nm (d).

$$CH_2Cl_2{}^{\bullet -} \rightarrow {}^{\bullet}CH_2Cl + Cl^- \tag{10}$$

$$^{\bullet}CH_2Cl + O_2 \rightarrow {}^{\bullet}OOCH_2Cl \tag{11}$$

$$[Ni(II)L]^{2+} + {}^{\bullet}OOCH_2Cl \rightarrow [Ni(III)L-OOCH_2Cl]^{2+} \tag{12}$$

The reduction of dichloromethane by the electron to give chloromethyl radical is known to occur with diffusion controlled rate constants [53]. Insertion of molecular oxygen to chloromethyl radicals (11) is reported earlier and the rate constant for this reaction (11) is found to be higher than that for the reaction (12) [24,53]. In the absence of oxygen this absorption feature diminishes as these reactions do not take place.

In the absence of dichloromethane, another absorption feature in the 450–600 nm region (Fig. 5b) with maximum near 550 nm appears which is similar to the absorption feature of $[Ni(III)L-CH_3]^{2+}$; the organonickel transient was observed earlier in the pulse radiolysis experiments [49–52]. The rate constants obtained for the decay of the transient signal at 550 nm ($0.8 \pm 0.2\,s^{-1}$) are close to the reported value for the decay of $[Ni(III)L-CH_3]^{2+}$ complex (reversible reaction (15)), revealing that methyl radicals are formed on CTTS excitation of the nickel(II) azamacrocyclic complexes which oxidise the nickel(II) azamacrocyclic complexes to the organonickel(III) complex $[Ni(III)L-CH_3]^{2+}$ as shown in the following reactions [49–52]
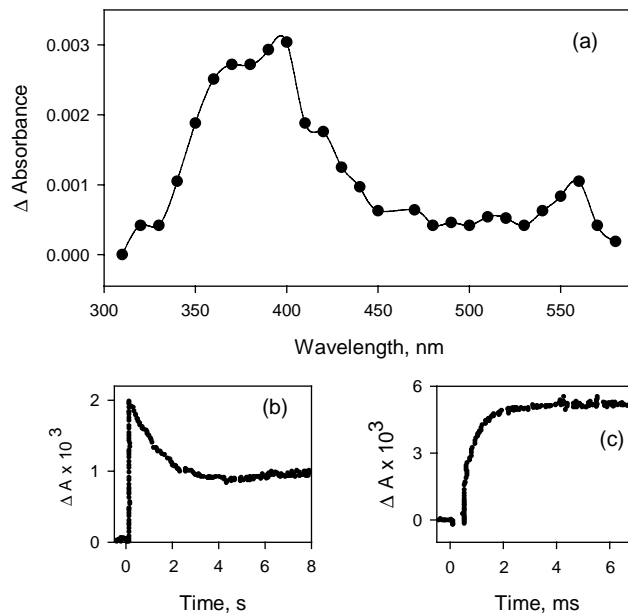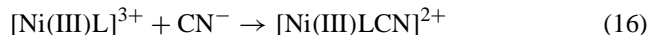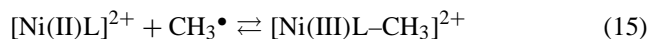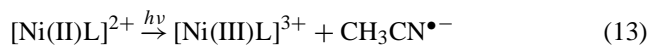

Fig. 6. (a) Transient absorption spectra of the complex **1** in acetonitrile obtained after 5 ms along with the decay (b) and growth (c) in absorbance monitored at 550 and 370 nm, respectively.

$$[Ni(II)L]^{2+} \overset{h\nu}{\rightarrow} [Ni(III)L]^{3+} + CH_3CN^{\bullet -} \tag{13}$$

$$CH_3CN^{\bullet -} \rightarrow CH_3{}^{\bullet} + CN^- \tag{14}$$

$$[Ni(II)L]^{2+} + CH_3{}^{\bullet} \rightleftarrows [Ni(III)L-CH_3]^{2+} \tag{15}$$

$$[Ni(III)L]^{3+} + CN^- \rightarrow [Ni(III)LCN]^{2+} \tag{16}$$

The formation of the acetonitrile anion radical and its dissociation to give methyl radicals were reported earlier [54–57]. It is presumed that the source of methyl radical is from the dissociation of the acetonitrile anion radical which is known to be formed in the presence of electron [54–57,24].

Oxidation of $[Ni(II)cyclam]^{2+}$ by alkylperoxyl radicals to $[Ni(III)(cyclam)OOCH_3]^{2+}$ peroxide complex shows transient absorption in the 300–500 nm region with maximum near 370 nm [49–52]. The absorption in the 300–500 nm region with maximum near 370 nm observed in the present flash photolysis investigation of the complexes (Figs. 5 and 6) reveals that $[Ni(III)LOOCH_3]^{2+}$ complexes are also formed on CTTS excitation due to the following reactions

$$CH_3{}^{\bullet} + O_2 \rightarrow CH_3OO^{\bullet} \tag{17}$$

$$[Ni(II)L]^{2+} + CH_3OO^{\bullet} \rightarrow [Ni(III)LOOCH_3]^{2+} \tag{18}$$

In the absence of oxygen, $[Ni(III)LOOCH_3]^{2+}$ transient absorption feature diminishes as these reactions do not take place. The intense absorption bands in the 300–500 nm region with maximum near 380 nm are also similar to the absorption spectra of the trivalent complexes ($[Ni(III)LOOH]^{2+}$) observed in acidic solution suggesting the formation of nickel(III) peroxide complexes.

The rate constant for the reaction (17), (1.6–$4.9 \times 10^9\,M^{-1}\,s^{-1}$) is higher than that for the reaction (15) (6.5

$\times\ 10^8\,\mathrm{M^{-1}\,s^{-1}}$) as reported earlier suggesting that in the presence of oxygen, reaction (17) is competitive with the reaction (15) to give methyl peroxide co-ordinated complex [49–52].

It is reported that the pulse radiolytically generated (Ni(III)–LCH$_2$Cl) species undergoes homolysis 80 times faster than that of the (Ni(III)–LCH$_3$) methyl co-ordinated species (reversible reaction (15)) and therefore conventional flash photolysis studies in acetonitrile containing dichloromethane, does not show transient due to (Ni(III)–LCH$_2$Cl) species with absorption maximum around 550 nm, even in absence of oxygen [49–52].

The transient absorption for the complex **3** in acetonitrile is very weak and could not be detected clearly in the conventional flash photolysis as it is known that the ligand is not favouring the formation of nickel(III) state [47].

3.4. Continuous photolysis of the complexes

The transient decay signal monitored at 370 nm on conventional flash photolysis of the complexes **1** and **2** in hydrochloric acid shows no change in absorption after 300 s from the flash which indicates that the peroxide co-ordinated trivalent nickel complex is converted to a stable product which shows no change in absorption with time (Fig. 4c). The stable photoproduct obtained on photolysis is identified by the continuous photolysis and ESR spectra of the continuous photolysed solution as discussed further.

Continuous photolysis of the complexes using 254 nm radiation leads to the formation of an absorption feature in the 280–400 nm region as shown in Fig. 7 [23] and this band is stable for more than 24 h. The ESR spectra (Fig. 7) of the photolysed solution is similar to that reported earlier [8] and confirms that the stable photoproduct is [Ni(III)LCl$_2$]$^+$ complex and it is understood that in presence of hydrochloric acid the following reaction occurs [23,46]

$$[\mathrm{Ni(III)L\text{–}OOH}]^{2+} + 2\mathrm{HCl}$$
$$\rightarrow [\mathrm{Ni(III)L\,Cl_2}]^+ + \mathrm{H_2O_2} + \mathrm{H^+} \qquad (19)$$
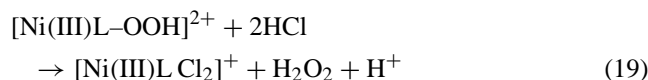
We have observed the reaction between nickel(III) complex and hydrogen peroxide under mild acidic condition and recently we have reported the isolation of trivalent nickel complexes [Ni(III)LCl$_2$]$^+$ with L = L$_1$ and L$_2$ from the photolysed solution of the divalent complexes dissolved in hydrochloric acid [25,11,48].

Continuous photolysis of the complex **3** does not show the absorption band due to nickel(III) complex indicating that stable trivalent nickel complex is not favoured (Fig. 7c). The oxidation potential of the complex **3** is 0.4 V higher compared to the complexes **1** and **2** as reported earlier [47] and the higher oxidation potential for the complex **3** suggests that the feasibility for the photooxidation is reduced compared to complexes **1** and **2**.

Seven lines are observed in the parallel feature of the ESR spectrum due to the co-ordination of two chlorides along the
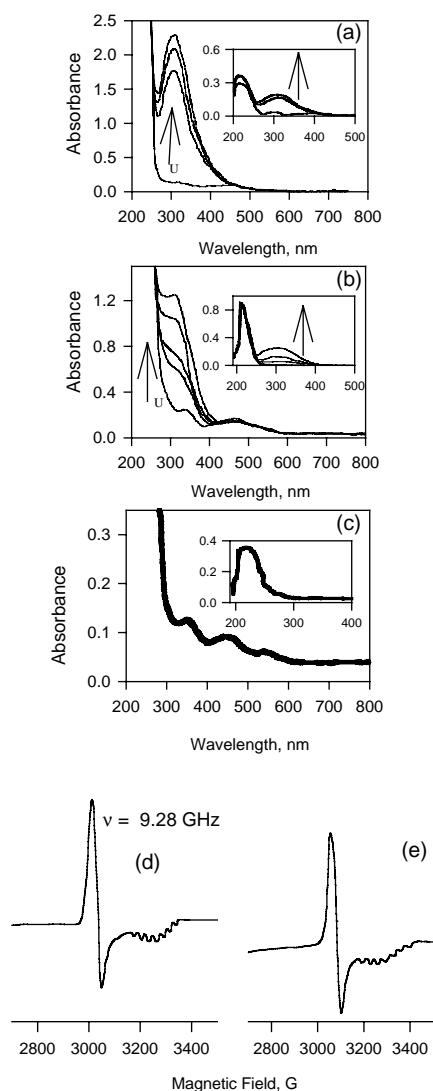

Fig. 7. (a) Change in absorption on photolysis (recorded every 2 min) of the complex **1** in 1 M HCl (U: unphotolysed solution). (b) Change in absorption on photolysis (recorded every 2 min) of the complex **2** in 1 M HCl. (c) Continuous photolysis of the complex **3** (no change in absorption). (d and e) ESR spectra of the photolysed solution of the complexes **1** and **2**, respectively, obtained at 77 K. Insets: change in absorbance observed in the UV region.

z-axis [8] when nickel(II) complexes in hydrochloric acid are photolysed. When continuous and conventional photolysis of the complexes are performed in perchloric acid, stable nickel(III) complexes were not formed suggesting that perchlorate is not stabilising the nickel(III) complex as reported earlier in the chemical oxidation [23].

In the absence of oxygen, there is no change in the absorption spectrum of the acidic solution of the complexes on photolysis indicating that stable nickel(III) complexes are indeed obtained only in presence of molecular oxygen [25]. In the absence of oxygen, the primary photolysis products recombine to give back the parent nickel(II) complexes. The rate constant for the reduction of nickel(II) azamacrocyclic
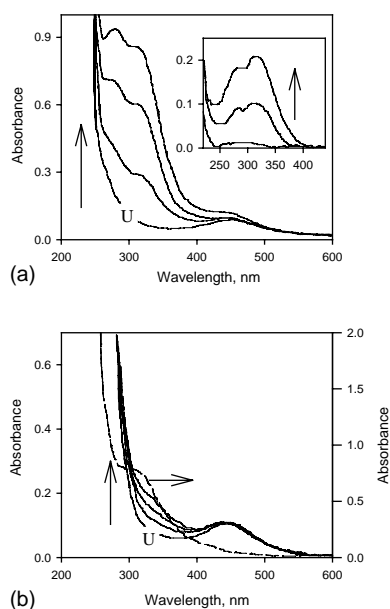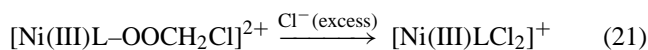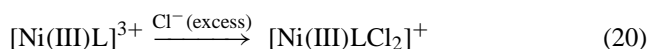
Fig. 8. Continuous photolysis of the complexes **2** and **3** in acetonitrile containing 0.1 M dichloromethane, at 254 nm: (a) complex **2**, absorbance recorded every 1 min; (b) complex **3**, (—) recorded every 1 min and (– – –) recorded after 30 min (U: unphotolysed solution).

complexes to nickel(I) complex by $H^\bullet$ was reported to be $(5 \pm 2) \times 10^9 \, M^{-1} \, s^{-1}$ and therefore it is clear that in the absence of oxygen formation of nickel(III) complex is not favoured even under acidic conditions.

The complex $[Ni(II)tet\text{-}a]^{2+}$ was observed to yield $[Ni(III) tet\text{-}aCl_2]^+$ complex when the divalent complex is photolysed in acetonitrile and dichloromethane mixture [24]. Continuous photolysis of the complexes **1**–**3** in dichloromethane and acetonitrile mixture (Fig. 8) shows spectral changes similar to those observed for $[Ni(II)tet\text{-}a]^{2+}$ in hydrochloric acid and in dichloromethane and acetonitrile mixture [24]. Presumably reaction (10) is the source of chloride ions, which co-ordinates to the nickel(III) complex formed during photolysis as shown in the following reactions

$$[Ni(III)L]^{3+} \xrightarrow{Cl^- (excess)} [Ni(III)LCl_2]^+ \quad (20)$$

$$[Ni(III)L\text{–}OOCH_2Cl]^{2+} \xrightarrow{Cl^- (excess)} [Ni(III)LCl_2]^+ \quad (21)$$

The complex $[Ni(III)LCl_2]^+$ exhibits the characteristic intense absorption band with maximum near 320 nm and this band is readily observed during the photolysis of the complexes **1** and **2** (Fig. 8a). However, in the case of complex **3**, the change in absorbance at 320 nm shown in Fig. 8b could be observed clearly only after 30 min of photolysis [23,24] suggesting the low yield of nickel(III) complex due to the higher oxidation potential of the complex **3** [23,24,47].

Photolysis of **1** and **2** in neat acetonitrile leads to change in absorbance as shown in Fig. 9a and b. ESR spectrum of the photolysed solution is an axial spectrum confirming the pres-
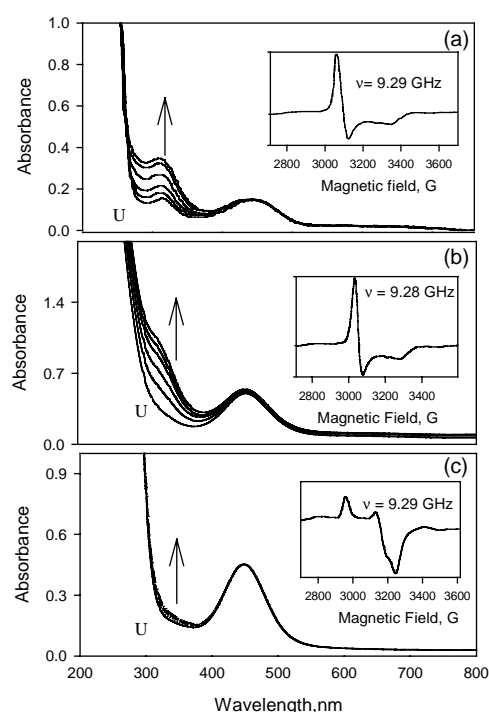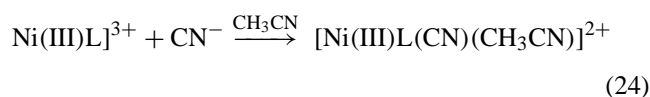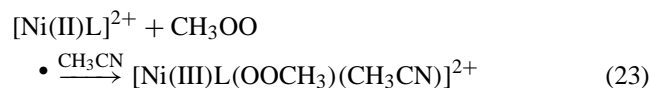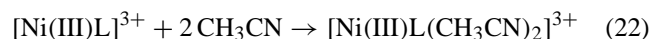

Fig. 9. Continuous photolysis of the complexes in acetonitrile at 254 nm and the ESR spectrum of the photolysed solution: (a) complex **1**; (b) complex **2**; (c) complex **3** (U: unphotolysed solution).

ence of octahedral nickel(III) complexes. It is well known that acetonitrile co-ordinates to nickel(II) azamacrocyclic complex leading to the high spin octahedral form [24,40,49]. Axial ESR spectra of the photolysed solution suggests that acetonitrile co-ordinates to the nickel(III) metal centre and a mixture of octahedral trivalent nickel complexes are formed as given in the following reactions

$$[Ni(III)L]^{3+} + 2\,CH_3CN \rightarrow [Ni(III)L(CH_3CN)_2]^{3+} \quad (22)$$

$$[Ni(II)L]^{2+} + CH_3OO$$
$$\bullet \xrightarrow{CH_3CN} [Ni(III)L(OOCH_3)(CH_3CN)]^{2+} \quad (23)$$

$$Ni(III)L]^{3+} + CN^- \xrightarrow{CH_3CN} [Ni(III)L(CN)(CH_3CN)]^{2+}$$
$$(24)$$

The ESR spectra (Fig. 9c) of the photolysed solution of complex **3** in acetonitrile correspond to a rhombic structure which is typical of the nickel(III) complexes with square pyramidal geometry given as $[Ni(III)LX]^{2+}$ [24]. From reactions (16) and (18), it is inferred that photolysis of the complex **3** in acetonitrile leads to a mixture of square pyramidal trivalent nickel complexes $[Ni(III)LX]^{2+}$ where X $= CH_3OO^-$ or CN^-. The rhombic ESR spectra suggests that square pyramidal $[Ni(III)LX]^{2+}$ is the predominant trivalent complex and co-ordination of acetonitrile is not favoured to give octahedral nickel(III) complexes. The absorption spectrum of divalent nickel complex **3** in acetonitrile also reveals

that the nickel divalent complex predominantly exists in the low spin form (around 90%) indicating that co-ordination of acetonitrile to the nickel(II) complex **3** is not favoured compared to the divalent nickel complexes **1** and **2** [49]. Earlier, rhombic ESR spectra was observed on continuous photolysis of the complex $[Ni(II)tet-a]^{2+}$ in acetonitrile which is known to exist in the low spin form (above 90%) [24]. ESR spectra of the square pyramidal complexes observed in the present investigation [23,24] are similar to the square pyramidal complex $[Ni(III)LCl]^{2+}$ (L = tet-a) observed earlier [23,24].

3.5. Comparison of the theoretical and experimental values of charge-transfer-to-solvent energy maximum of nickel(II) azamacrocyclic complexes

The absorption maximum of the charge-transfer-to-solvent transition could be determined approximately from the following expression [26]

$$h\nu_{max} = \Delta G^{\circ} + (390 \pm 16 \, kJ/mol)$$

where $h\nu_{max}$ is the energy maximum of the CTTS band and ΔG° the free energy change for the one electron oxidation process obtained from the redox potential of the complexes, E° (versus NHE).

The calculated CTTS absorption maximum for the complexes **1**–**3** are 231, 229 and 219 nm, respectively, and the ultraviolet absorption bands of the complexes in water show absorption maximum at 210, 206 and 228 nm for the complexes **1**–**3**, respectively. The calculated and experimental values are close for complex **3** suggesting the presence CTTS character in the UV absorption band. The values for the complexes **1** and **2** are not agreeable. However, experimentally hydrated electron is observed for all the complexes on excitation of the complexes in the UV absorption band. The above relation was found to agree well for the complexes $[Ni(II)tet-a]^{2+}$ and $[Ni(II)AT]^{+}$ which was reported earlier [22]. In this investigation, a plot of CTTS energy maximum (obtained from absorption spectrum) versus standard free energy of various nickel(II) azamacrocyclic complexes is shown in Fig. 10.

The complexes $[Ni(II)tet-a]^{2+}$, $[Ni(II)AT]^{+}$ and complex **3** are obeying the expression $h\nu_{max} = \Delta G^{\circ} + (390 \pm 16 \, kJ/mol)$ indicating that the ultraviolet absorption
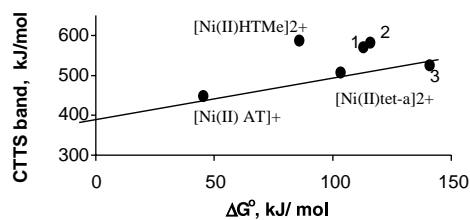
band of nickel(II) azamacrocyclic complexes possesses charge-transfer-to-solvent character.

The oscillator strengths of these bands for these complexes are surprisingly strong: the absorption coefficient of $10^4 \, mol^{-1} \, cm^{-1}$ observed for the CTTS band of these nickel(II) complex is quite high. A theoretical treatment for CT interaction predicts that the intensity of CT band is proportional to the magnitude of interaction between the donor and acceptor molecular orbitals and inversely proportional to the energy gap between them [58]. This theoretical consideration is consistent with the trend that the probabilities of the CTTS transitions with anions having higher oscillator strengths than cations [59]. The energy gap of the former is generally smaller than the latter. Thus, CTTS bands observed in these nickel(II) complexes seems to be usually strong irrespective of their higher oxidation potentials, i.e. larger energy gap for CTTS transition.

4. Summary

The absorption spectra of the nickel(II) azamacrocyclic complexes show an intense absorption band in the UV region. Excitation of the nickel(II) azamacrocyclic complexes using 248 nm radiation produces hydrated electron confirming the charge transfer band with CTTS character. The decay of hydrated electron on flash photolysis of the complexes and the absence of spectral features characteristic of the nickel(III) and nickel(I) transients suggest the occurrence of synproportionation reaction between nickel(III) and nickel(I) complexes. In presence of molecular oxygen and protonic acids, scavenging of hydrated electron occurs to give hydroperoxyl radicals which reacts with nickel(II) complexes. Conventional flash photolysis of the complexes in acetonitrile and acetonitrile–dichloromethane mixture reveals the formation of alkyl peroxyl radicals and its reaction with the nickel(II) complex. Continuous photolysis of the complexes in presence of oxygen yields stable trivalent nickel complex in both aqueous and non-aqueous solution as confirmed by electron spin resonance spectra. In the absence of oxygen, nickel(III) complexes were not observed as suggested by the proposed mechanism. The oxidation potential of the complex **3** is higher as compared to other complexes and stable nickel(III) complexes were observed only for the complexes **1** and **2** which has lower oxidation potentials. The theoretical CTTS energy maximum of the complex **3** is comparable with the experimental value.

Fig. 10. Plot of experimental CTTS energy maximum vs. free energy for various nickel(II) azamacrocyclic complexes.

References

[1] R.A. Gossage, L.A. Van De Kuil, G. Van Koten, Acc. Chem. Res. 31 (1998) 423.

[2] M.A. Halcrow, G. Christou, Chem. Rev. 94 (1994) 2421.

[3] J.R. Lancaster, The Bioinorganic Chemistry of Nickel, VCH Publishers, New York, 1988.

[4] C.A. Craig, Q.G. Mulazzani, E.L. Blinn, M.A.J. Rodgers, Inorg. Chem. 35 (1996) 5122.

[5] U. Ermler, W. Grabarse, S. Shima, M. Goubeand, K.R. Thaver, Science 278 (1997) 1457.

[6] J. Telser, in: R.J.P. Willams (Ed.), Structure and Bonding, vol. 91, Springer-Verlag, Heidelberg, 1998, p. 31.

[7] J. Telser, Y.C. Hong, D.F. Becker, B.M. Hoffman, S.W. Ragsdale, J. Am. Chem. Soc. 122 (2000) 182.

[8] V.F. Lovecchio, S.E. Gore, H.D. Busch, J. Am. Chem. Soc. 96 (1974) 3109.

[9] H.J. Espenson, A. Bakac, J. Am. Chem. Soc. 108 (1986) 713.

[10] D.J. Szalda, E. Fujita, R. Sanzenbacher, H. Paulus, H. Elias, Inorg. Chem. 33 (1994) 5855.

[11] R.I. Haines, A. McAuley, Coord. Chem. Rev. 39 (1981) 77.

[12] H. Kishida, H. Matsuzaki, H. Okamoto, T. Manabe, M. Yamashita, Y. Taguchi, Y. Tokura, Nature 405 (2000) 929.

[13] T. Manabe, K. Yokoyama, S. Furukawa, C.K. Terajima, K. Nakata, F. Iwahori, H. Miyasaka, K. Sugiura, M. Yamashita, H. Kishida, H. Okamoto, Inorg. Chem. 41 (20) (2002) 4993.

[14] C. Burrows, S.E. Rokita, Acc. Chem. Res. 27 (1994) 295.

[15] M. Beley, P.J. Collin, R.P.J. Sauvage, J. Am. Chem. Soc. 108 (1986) 7461.

[16] H. Prakash, P. Natarajan, Res. Chem. Intermed. 29 (4) (2003) 349.

[17] E. Kimura, S. Wada, M. Shionoyas, Y. Okasaki, Inorg. Chem. 33 (1994) 770.

[18] C.A. Craig, L.O. Spreer, J.W. Otvos, M. Calvin, J. Phys. Chem. 94 (1990) 7957.

[19] A.D. Blas, G.D. Santis, L. Fabbrizzi, M. Licchelli, A.M.M. Lanfredi, P. Pallavicini, A. Poggi, F. Ugozzoli, Inorg. Chem. 32 (1993) 106.

[20] E. Marianne, L. Fabbrizzi, M. Licchelli, D. Sacchi, Chem. Commun. (1999) 1191.

[21] L. Fabbrizzi, M. Licchelli, P. Pallavicini, Acc. Chem. Res. 32 (1999) 846.

[22] H. Prakash, P. Natarajan, Chem. Phys. Lett. 329 (2000) 357.

[23] T. Dhanasekaran, H. Prakash, P. Natarajan, J. Photochem. Photobiol. A: Chem. 141 (2001) 17.

[24] T. Dhanasekaran, P. Paul, P. Natarajan, J. Photochem. Photobiol. A: Chem. 131 (2000) 75.

[25] H. Prakash, P. Natarajan, Inorg. Chem. Commun. 6 (2003) 1017.

[26] O. Horvath, K.L. Stevenson, Charge Transfer Photochemistry of Coordination Compounds, VCH Publishers, New York, 1993.

[27] M.A. Fox, M.T. Duley, Chem. Rev. 93 (1993) 341.

[28] V. Balzani, Supramolecular Photochemistry, Reidel, Boston, 1987.

[29] M.A. El-Sayed, I. Tanaka, Y. Molin, Ultrafast Processes in Chemistry and Photobiology, Blackwell Science, 1995.

[30] J. Kloepfer, V. Vilchiz, S. Bradforth, Chem. Phys. Lett. 342 (2001) 277.

[31] P. Natarajan, R.W. Fessenden, J. Phys. Chem. 93 (1989) 6095.

[32] K. Phoil, K. Wieghardt, W. Kaim, S. Steenkeen, Inorg. Chem. 27 (1988) 440.

[33] B. Bosnich, M.L. Tobe, G.A. Webb, Inorg. Chem. 4 (1965) 1109.

[34] M.P. Suh, B.Y. Shim, T.S. Yoon, Inorg. Chem. 33 (1994) 5509.

[35] M.P. Suh, W. Shin, S.G. Kang, M.S. Lah, T.M. Chung, Inorg. Chem. 28 (1989) 1602.

[36] S.G. Kang, J.S. Choi, S.J. Kim, Bull. Korean Chem. Soc. 16 (1995) 518.

[37] S.J. Kim, J.S. Choi, S.G. kang, C.S. Kim, M.P. Shu, Bull. Korean Chem. Soc. 16 (1995) 217.

[38] E. Natarajan, P. Natarajan, Inorg. Chem. 31 (1992) 1215.

[39] L.G. Warner, D.H. Busch, J. Am. Chem. Soc. 91 (1969) 4092.

[40] D.J. Szalda, E. Fujita, R. Sanzenbacher, H. Paulus, H. Elias, Inorg. Chem. 33 (1994) 5855.

[41] A.M. Tait, M.Z. Hoffman, E. Hayon, Inorg. Chem. 15 (1976) 934.

[42] N. Jubran, G. Ginzburg, H. Cohen, Y. Koresh, D. Meyerstein, Inorg. Chem. 24 (1985) 251.

[43] C.A. Kelly, Q.G. Mulazzani, M. Venturi, E.L. Blinn, M.A.J. Rodgers, J. Am. Chem. Soc. 117 (1995) 4911.

[44] R.V. Eldik, D. Meyerstein, Acc. Chem. Res. 33 (2000) 207.

[45] A.K. Pikaev, Pulse Radiolysis of Water and Aqueous Solutions, Indiana University Press, London, 1967.

[46] A. Meshulam, H. Cohen, R.V. Eldik, D. Meyerstein, Inorg. Chem. 31 (1992) 2151.

[47] M.P. Suh, E.Y. Lee, B.Y. Shim, Inorg. Chim. Acta 269 (1998) 337.

[48] K.D. Whitburn, G.S. Laurence, J. Chem. Soc., Dalton Trans. (1979) 139.

[49] H. Prakash, Ph.D. thesis, University of Madras, 2002.

[50] A. Marchaj, D.G. Kelly, A. Bakac, J.H. Espenson, J. Phys. Chem. 95 (1991) 4440.

[51] D.G. Kelly, A. Marchaj, A. Bakac, J.H. Espenson, J. Am. Chem. Soc. 113 (1991) 7583.

[52] A. Sauer, H. Cohen, D. Meyerstein, Inorg. Chem. 27 (1988) 4578.

[53] E. Lindsay, A.Y.S. Malkhasian, C.H. Langford, Inorg. Chem. 33 (1994) 944.

[54] Y. Hirata, N. Mataga, Y. Sakata, S. Misumi, J. Phys. Chem. 87 (1983) 1493.

[55] D.E. Sprauge, F. Williams, J. Am. Chem. Soc. 92 (1970) 429.

[56] K. Takedo, F. Williams, J. Phys. Chem. 74 (1970) 4007.

[57] B.P. Ayscough, G.R. Collins, J.T. Kemp, J. Phys. Chem. 70 (1966) 2220.

[58] R.J. Cave, M.D. Newton, Chem. Phys. Lett. 249 (1996) 15.

[59] O. Horváth, K.L. Stevenson, Inorg. Chem. 28 (1989) 2548.