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Photooxidation of some nickel(II) macrocyclic complexes in non-aqueous solvents

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Abstract

The complexes [Ni(tet-a)](ClO_4)$_2$, **1**, [Ni(htcd)](ClO_4)$_2$, **2** and [Ni(AT)]ClO_4, **3** (where tet-a = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, htcd = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene and AT = 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienato) were photolysed in the charge transfer to solvent band in non-aqueous solvents using 254 nm radiation. The complex [Ni(BG-opdn)], **4** (where BG-opdn = 4,9-dihydroxy-3,4,9,10-tetraphenyl-6,7-benzo-1,2,5,8,11,12-hexaazacyclotetradeca-2,6,10,12,14-pentaene) was photolysed using sunlight in dichloromethane and the solid product was isolated and characterised. Flash photolysis of the complex **1** or **2** in pure acetonitrile produces transients which could be assigned to the nickel(III)-carbon bonded species whereas continuous photolysis in presence of oxygen produces stable five coordinated nickel(III) complexes. Formation of nickel(III) complex is seen as a growth in absorbance at 370 nm in the case of complexes **1** and **2** on flash photolysis in oxygenated acetonitrile containing dichloromethane. Rate constants for the formation of nickel(III) by the reaction of alkylperoxyl radical with nickel(II) complex were determined as a function of the concentration of the complex. Formation of stable nickel(III)-complex was confirmed in the case of complexes **1** and **2** by absorption and ESR spectra on continuous photolysis of complexes in acetonitrile solutions containing 1 M dichloromethane. In the case of complex **3** which contains a negatively charged macrocyclic ligand the oxidation of the metal centre is followed presumably by another intramolecular electron transfer to produce a nickel(II) radical centred on nitrogen which decays subsequently. In the case of complex **4** continuous photolysis using sunlight in air-equilibrated dichloromethane shows absorption spectral change and the photoproduct was isolated and characterised as nickel(II) stabilised ligand radical. Flash photolysis of **4** does not show any transient species in the microsecond time scale. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Photooxidation; Nickel(II) complexes; Macrocycles; Non-aqueous solvents

1. Introduction

Nickel in the +3 oxidation state has attracted many studies with reference to the oxidation of the stable nickel(II) complexes by electrochemical [1,2] and pulse radiolytic methods [3–5] and the subject has been extensively reviewed [6,7]. The reported photochemical methods for preparing the nickel(III) tetraaza macrocylic complexes involve the use of benzophenone triplet as sensitizer [8] and oxidising radicals like $Cl_2^{\bullet -}$, produced by photolysing chloropentamminecobalt(III) in the presence of excess chloride [9]. Photooxidation of some nickel(II) complexes containing dithiolato ligands in chloroform solutions were reported [10] and the oxidation of the metal centre could not be established in these cases with certainty [11]. Recently [12] we have established the direct photooxidation of nickel(II) tetraaza macrocyclic complexes in aqueous solutions using ultraviolet irradiation. In the present study alkyl radicals are produced by the reaction of the solvents with the charge transfer to solvent excited state of the nickel(II) macrocyclic complexes. The alkyl radicals give rise to reactive alkylperoxyl radical in presence of dissolved molecular oxygen which in turn oxidises the metal centre. Metal-carbon bonded species are important and occur as key intermediates in industrial and biological processes with application potential in the synthesis of organic compounds. Most of the metal alkyl bonded species studied so for [14,15] are limited to cobalt (III) and chromium III as these complexes are Robust. A recent study [16] of the reaction of some alkyl radicals with nickel(II) complexes showed that the nickel(III)-carbon bonded complexes occur as transient intermediates. The oxidation of metal complexes by alkylperoxyl radicals is also important and has been studied in the recent past

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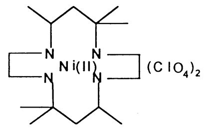
[17,18]. In all the previous studies the methyl radical is generated either by pulse radiolysis of dimethylsulfoxide [19] or by photolysis of another complex like $[CoLR]^{2+}$ (L = macrocyclic ligand and R = alkyl group) whereas in the present study for the first time we have attempted to investigate the photochemistry of the complexes directly in non-aqueous solvents. The structures of the starting complexes, **1** to **4** are shown below.



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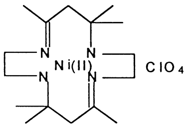

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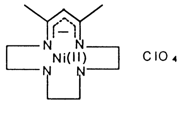

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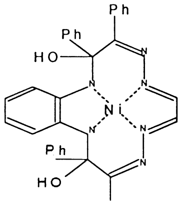

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2. Experimental details

$[Ni(tet\text{-}a)](ClO_4)_2$, **1**, $[Ni(htcd)]\ (ClO_4)_2$, **2**, $[Ni(AT)]\ ClO_4$, **3** and $[Ni(BG\text{-}odpn)]$, **4** were prepared and characterized as reported [20–22] in the literature. Continuous photolysis experiments for the complexes **1**, **2**, and **3** were carried out using a 254 nm low pressure mercury vapour lamp (Ultraviolet Products) as described earlier [13,15] and the complex **4** was irradiated using direct sunlight. In a typical experiment 0.2 mM solution of the complex in dichloromethane was irradiated using sunlight for 10 h and observing changes in the absorption spectrum in the range 800–350 nm monitored the progress of the reaction. The solid product isolated after removing solvent under reduced pressure at room temperature was purified by silica gel (100–200 mesh) column using dichloromethane-benzene/methanol mixture as eluents[1]. Magnetic susceptibility was measured in a Guoy balance and the ESR spectra were obtained in a Bruker X-band spectrometer. The electronic absorption spectra were recorded using a HP 8452A diode array and Shimadzu UV-160 spectrophotometers. Microsecond flash photolysis experiments were carried out using Applied Photophysics KN020 apparatus as described earlier [13]. Deaeration of the solution was carried out either by purging the solution with argon or by freeze-thaw method. The fast atom bombardment mass spectra was obtained from CDRI, Lucknow in a SX102/DA-6000 instrument. Quantum yield for the product formation in acetonitrile for the complex **1** was obtained by ferrioxalate actinometry.

3. Results

Flash photolysis of the complex **1** in oxygen saturated pure acetonitrile shows a transient which decays at 550 nm as shown in the Fig. 1 (inset). The transient species shows the absorption spectrum given in Fig. 1 which decays with a first order rate constant of $1.09 \pm 0.1\ s^{-1}$. The absorption maximum at 550 nm is not affected if the solution is completely deaerated. Continuous photolysis of an oxygen saturated acetonitrile solution of **1** using a 254 nm low-pressure mercury vapour lamp shows change in absorption spectra as given in Fig. 2. ESR spectra of the photoproduct obtained after evaporation of the extensively photolysed solution and the product dissolved in pyridine are shown in Fig. 2 (inset). However, if the photolysis is carried out under completely deaerated conditions the spectral changes are not appreciable and the photolysed solution is ESR silent. A similar behaviour is observed for the complex **2** also. When a solution of **1** or **2** in air-equilibrated acetonitrile containing 1 M dichloromethane is flash photolysed the transient decay observed at 550 nm in neat acetonitrile changes to an intense growth in absorbance at 370 nm as shown in Fig. 3. The growth follows pseudo first-order kinetics with the rate constant depending on the concentration of the nickel(II) complex as shown in Fig. 4. The second-order rate constants are evaluated from the slope of the plots and found to be $2.17 \pm 0.2 \times 10^6\ M^{-1}\ s^{-1}$ for the complex **1** and $1.75 \pm 0.2 \times 10^6\ M^{-1}\ s^{-1}$ for the complex **2**. The change in absorption spectrum of complex **1** on continous photolysis of an oxygen saturated acetonitrile solution containing 1 M in dichloromethane is shown in Fig. 5 and the inset is the ESR spectrum of the final solution at 77 K after photolysis.

In the case of complex **3** the behaviour is different from those of **1** and **2** as the complex contains a negatively charged macrocycle coordinated to nickel(II). Flash photolysis of the complex produces a transient which decays at 610 nm showing first-order kinetics (Fig. 6 inset). The absorption spectra of the transient is shown in Fig. 6 and the transient is found to be absent when acetone (300 nm cut off) filter is used. The transient is unaffected when the high energy radiation (<250 nm) is cut off by using dichloromethane filter which has maximum absorbance at <200 nm. The spectral changes observed on constant potential electrolysis of **3** in acetonitrile containing 1 M dichloromethane at +0.4 V versus Ag/AgCl are shown in Fig. 7a; the changes in absorption spectra on continuous photolysis of the complex using 254 nm light in acetonitrile-dichloromethane mixture are shown in Fig. 7b. The peaks at 260 nm and 320 nm are depleted and the final solution after photolysis is found to be ESR silent at room temperature as well as at 77 K.

Continuous photolysis of **4** in dichloromethane using direct sunlight shows changes in the absorption spectra in the

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[1] Initially 4 : 1 dichloromethane-Benzene mixture was used which gave a small fraction of uncharacterised product, after that 10 : 1 dichioromethane-methanol mixture gave purple coloured fraction of the product.

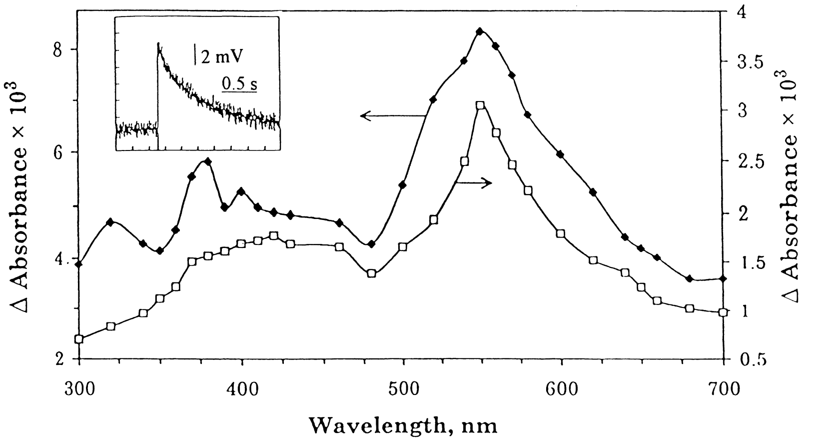


Fig. 1. Transient absorption spectrum of $[Ni(tet\text{-}a)]^{2+}$ in oxygen saturated (■—■—■) neat acetonitrile and in deaerated condition (□—□—□) recorded 5 min after flash. Inset- Trace obtained on flash photolysis in pure acetonitrile; monitoring wavelength 550 nm.

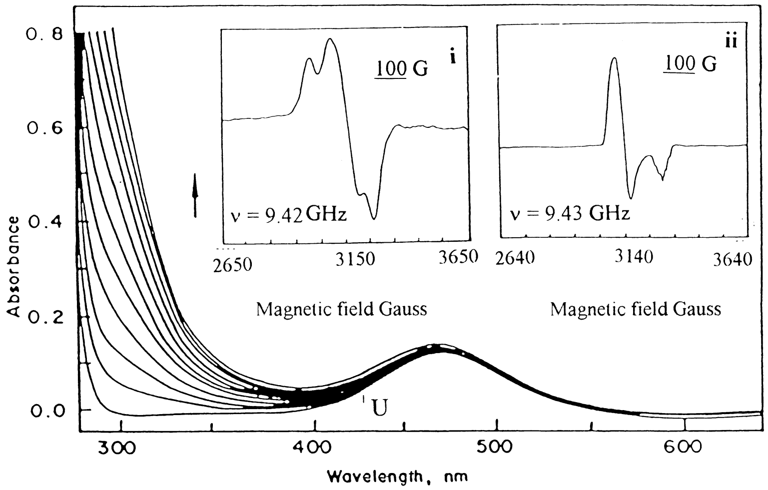


Fig. 2. Continuous photolysis of $[Ni(tet\text{-}a)]^{2+}$ in oxygen saturated neat acetonitrile using 254 nm pen-ray lamp. U-unphotolysed and successive increase in absorbance due to photolysis each for 5 min. Inset-i, ESR spectrum of the final solution after continuous photolysis of $[Ni(tet\text{-}a)]^{2+}$ in oxygen saturated neat acetonitrile recorded at 77 K. Inset-ii, ESR spectrum of the pyridine solution of the evaporated product obtained on continuous photolysis of $[Ni(tet\text{-}a)]^{2+}$ in oxygen saturated neat acetonitrile recorded at 77 K.

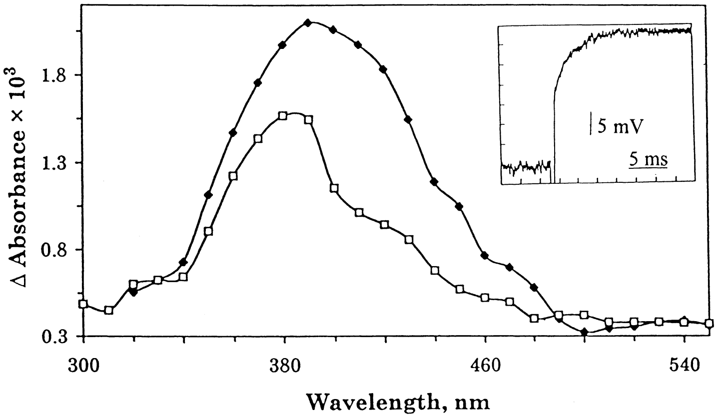


Fig. 3. Transient absorption spectra recorded in air-equilibrated acetonitrile containing 1 M dichloromethane of ■-$[Ni(tet\text{-}a)]^{2+}$ and □-$[Ni(htcd)]^{2+}$ 10 ms after flash. Inset- Trace obtained in flash photolysis of $[Ni(tet\text{-}a)]^{2+}$ under the above conditions; monitoring wavelength 370 nm.

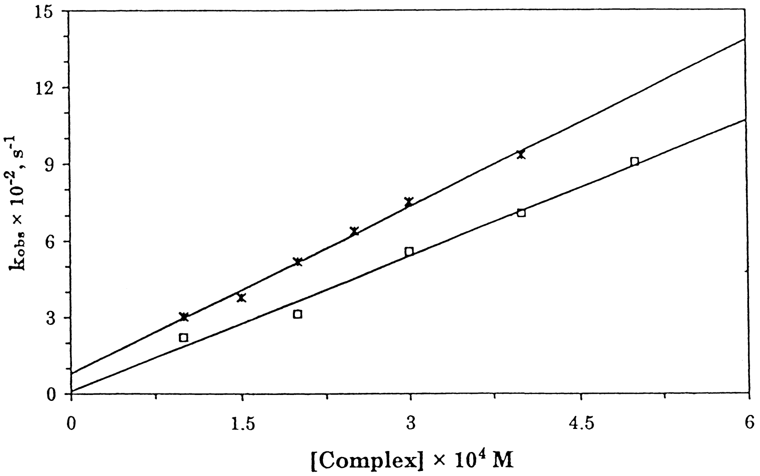


Fig. 4. Plots of k_{obs} vs. [complex] for the 370 nm growth in oxygen saturated acetonitrile containing 1 M dichloromethane ×-$[Ni(tet\text{-}a)]^{2+}$ and □-$[Ni(htcd)]^{2+}$.

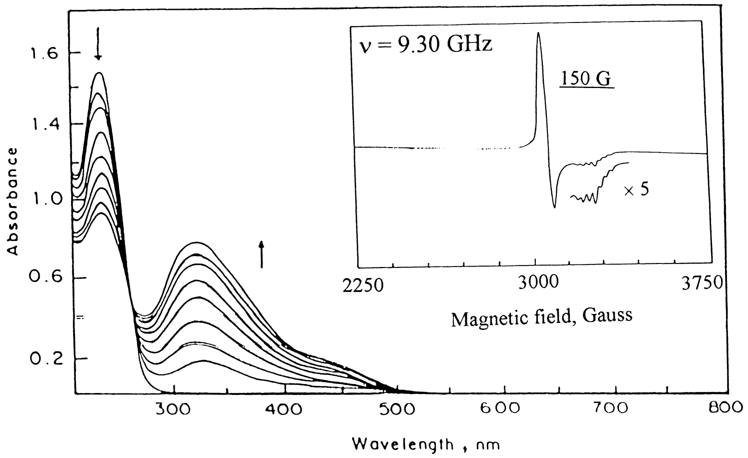


Fig. 5. Continuous photolysis of $[Ni(tet\text{-}a)]^{2+}$ in oxygen saturated acetonitrile containing 1 M dichloromethane using 254 nm low pressure mercury vapour lamp. in 0.1 cm cuvette; inset- ESR spectra of the final solution after photolysis at 77 K.

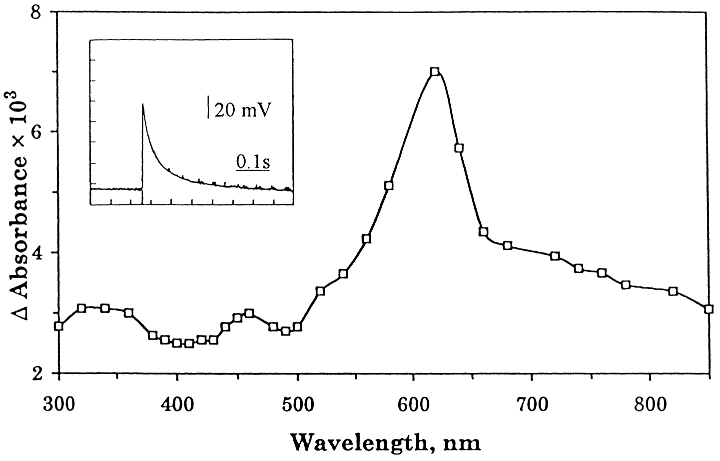


Fig. 6. Transient absorption spectra of $[Ni(AT)]^{+}$ in air-equilibrated acetonitrile containing 1 M dichloromethane recorded 10 ms after flash. inset- Trace obtained at 610 nm on flash photolysis under the above conditions.

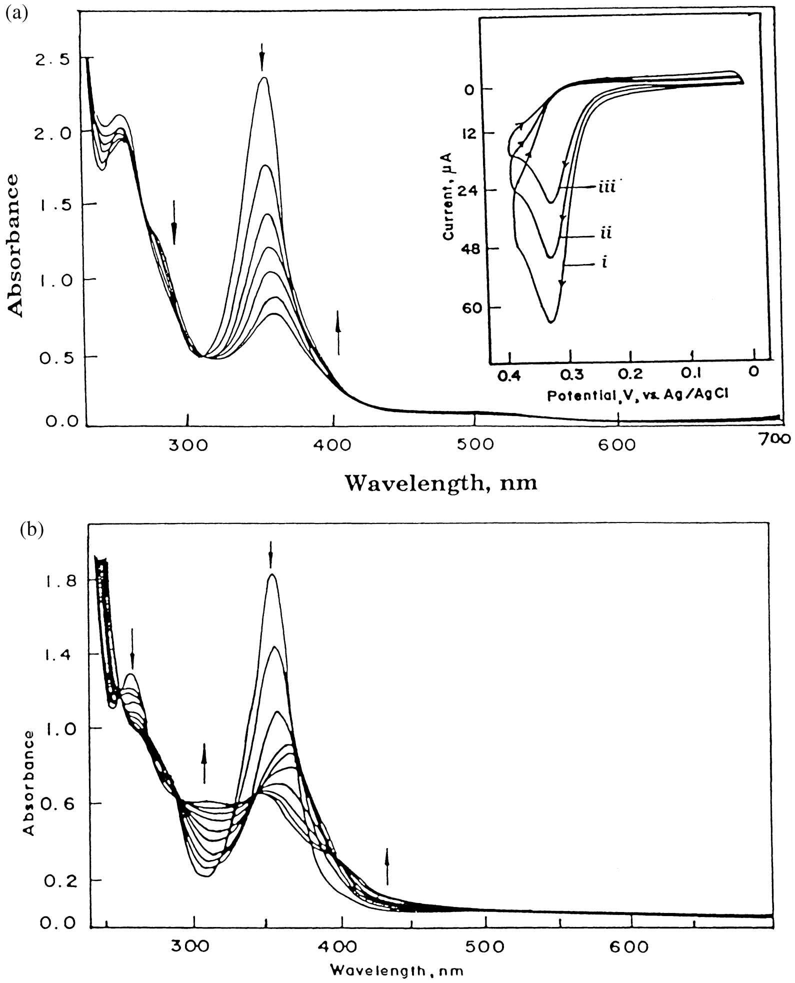


Fig. 7. (a) Spectral changes observed on constant potential electrolysis of $[Ni(AT)]^+$ in acetonitrile containing dichloromethane at +0.4 V vs. Ag/AgCl using a platinum plate as the working electrode. Spectra recorded after intervals of 5 min of electrolysis. inset-Cyclic voltammogram of the complex under the same conditions at different scan rates. (b) Spectral changes observed on continuous photolysis of $[Ni(AT)]^+$ in acetonitrile containing dichloromethane using a 254 nm low pressure mercury vapour penray lamp. Spectra recorded after photolysis each for 30 s.

range 800–350 nm as shown in Fig. 8. The absorbance of the 512 nm band increased whereas that of 389 nm band decreased showing an isosbestic point at 440 nm. The isolated photoproduct on evaporation of the solvent shows magnetic susceptibility corresponding to an unpaired electron and exhibits ESR signal at room temperature as well as at liquid nitrogen temperature (77 K) in chloroform as shown in Fig. 8 with a *g* value of 2.007 and peak width 9G and the molecular weight of the starting compound **4** is 635. When the photolysis of **4** was conducted in benzene under similar conditions then the observations were different. In the case of benzene initially the change in absorption was similar to that in dichloromethane and after 5 h the isosbestic point was disturbed as shown in Fig. 9.

Quantum yield for the formation of nickel(III) complex on photooxidation of **1** was obtained by irradiating a solution of the complex in acetonitrile containing 1 M dichloromethane and noting the absorption spectral changes observed at 340 nm which is a characteristic band for the nickel(III) complex. The molar absorption coefficient of 11,800 M^{-1} cm^{-1} for nickle(III) complex determined in acetonitrile solution was used [5] and the quantum yield was determined to be 0.025 ± 0.005.

4. Discussion

Continuous photolysis of **1** in oxygen saturated acetonitrile solution shows an increase in absorbance at 350 nm which is attributed to the formation of nickel(III) species in solution based on well documented spectral features for nickel(III) complexes [6,7]. The ESR spectrum of the final solution after photolysis recorded at 77 K shows that the complex is five coordinated since the spectrum does not show axial symmetry expected for an octahedral structure. The splitting of *g* values indicates that there is an unequal distribution of electronic charge in the $d_{X^2-Y^2}$ orbital and the symmetry is lowered. A similar ESR spectrum has been observed [23] for the five coordinated complex $[Ni^{III}LCl]^{2+}$ where L = cyclam. However, if the photolysed solution is

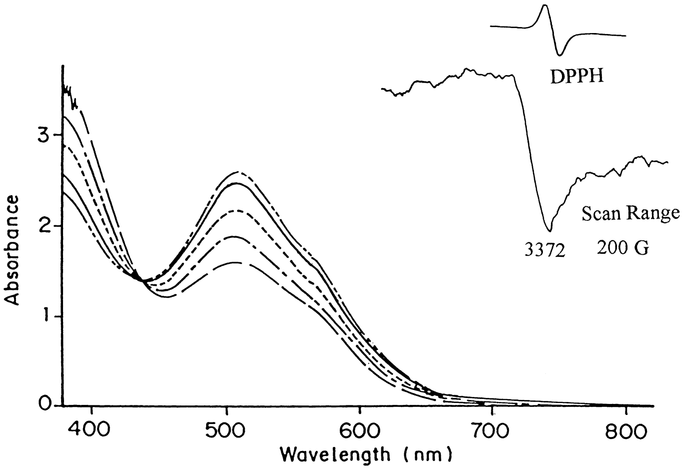


Fig. 8. Spectral Changes observed on continuous photolysis of [Ni-BG-(opdn)] in dichloromethane (0.2 M solution) using sunlight over a period of 10 h. inset-ESR spectrum of the photoproduct in chloroform at 77 K.

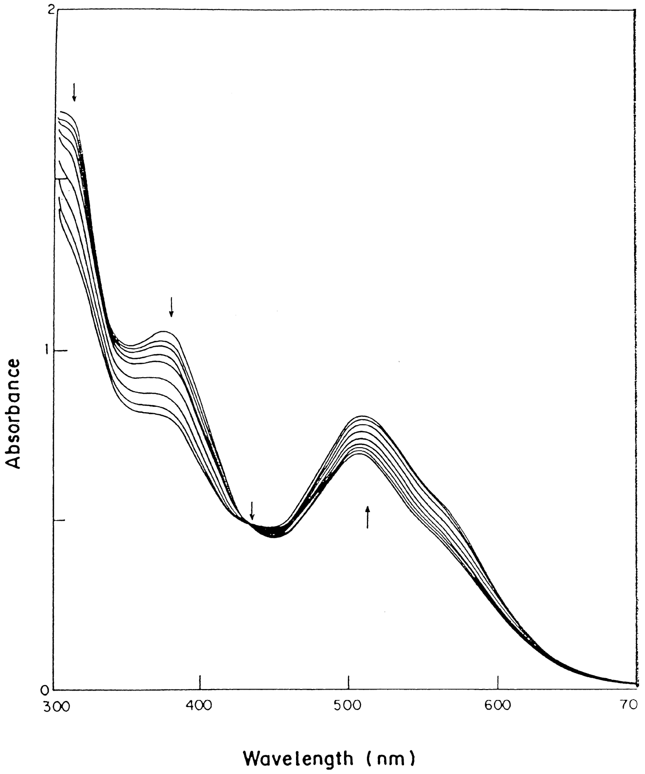


Fig. 9. Spectral changes observed on continuous photolysis of **4** in benzene (0.2 M solution) using sunlight over a period of 5 h.

evaporated and the residue dissolved in pyridine, the ESR spectrum obtained at 77 K retains the axial symmetry due to the axially coordinated pyridine. The five lines splitting of the ESR spectral line is a further confirmation of the pyridine coordination [24]. The photolysed solution containing the nickel(III) complex is found to be stable for days as there is little decrease in ESR signal. The following reactions are suggested to explain the observations on photolysis of **1** in pure acetonitrile in air-equilibrated solution. Flash photolysis studies of the complex in next acetonitrite lend additional support to this mechanism. The continuous photolysis behaviour of **2** is very similar to that of Ni(tet-a)$^{2+}$ in acetonitrile

$$\left[\mathrm{LNi^{II}}\right] \xrightarrow[\mathrm{CH_3CN}]{h\nu,\mathrm{CTTS}} \left[\mathrm{LNi^{II}}\right] + \mathrm{CH_3}^{\bullet} + \mathrm{CN}^- \tag{1}$$

$$\mathrm{CH_3}^{\bullet} + \left[\mathrm{LNi^{II}}\right] \rightarrow \left[\mathrm{LNi^{II}\text{–}CH_3}\right] \tag{2}$$

$$\mathrm{CH_3}^{\bullet} + \mathrm{O_2} \rightarrow \mathrm{CH_3O_2}^{\bullet} \tag{3}$$

$$\mathrm{CH_3O_2}^{\bullet} + \left[\mathrm{LNi^{II}}\right] \rightarrow \left[\mathrm{LNi^{III}\text{–}O_2\text{–}CH_3}\right] \tag{4}$$

L = tet-a or htcd

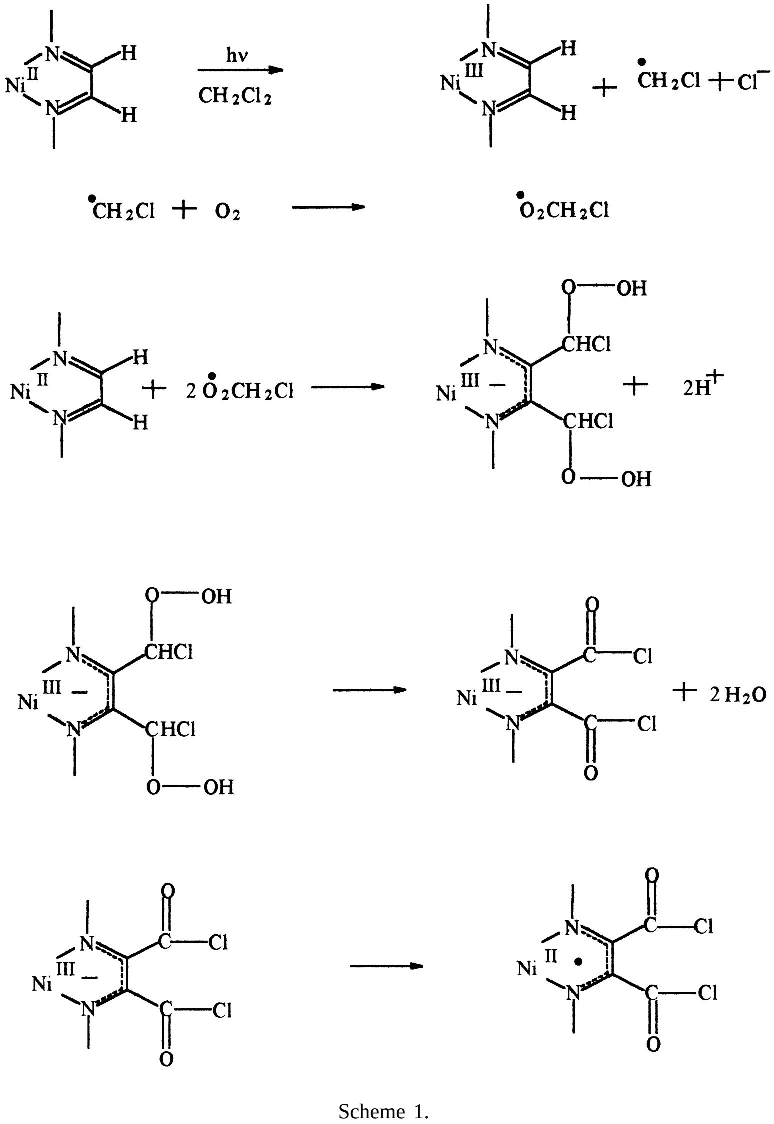
Earlier studies on [Ni(tet-a)]$^{2+}$ revealed that methyl radicals generated by pulse radiolysis [19] of aqueous solutions containing dimethyl sulfoxide reacted with [Ni(tet-a)]$^{2+}$ complex to give [(tet-a)Ni^{III}-CH$_3$]. In the pulse radiolysis experiment the transient species which showed maximum at 550 nm is attributed to this nickel(III) complex. In the presence of molecular oxygen homolysis of the nickel(III)-carbon bond occurred and the methyl radicals reacted with oxygen to produce alkylperoxyl radicals which oxidised the metal centre of another molecule of the complex. Based on the above information, the transient formed in this study could be assigned to the formation of nickel(III)-carbon bond, since the absorption spectrum of the transient observed matches with that characterised in the earlier work [19]. The rate constant for the formation of nickel(III)-carbon bond could not be measured as the rate of the reaction is faster and also the signal at 550 nm is very weak.

We have suggested that the band irradiated is due to charge transfer to solvent (CTTS) excited state of the complex on the basis of the results obtained on photolysis of the complexes **1** and **2** in aqueous solutions [12] and in this case nickel(III) complexes are isolated and confirmed by electronic and ESR spectra. The flash photolysis studies confirmed the observation and detailed kinetic analysis indicated the formation of nickel(III) species. Similarly in non-aqueous systems the first step is proposed to be the formation of nickel(III) as a result of the reaction of the CTTS excited state with acetonitrile. The above conclusion is supported by earlier reports [25–28] on the irradiation of nickel(II) complexes in acetonitrile. Acteronitrile dimer anion radical is known to be produced when electron react with acetonitrile which might decay at a faster rate to produce the carbon centred radical. The alkyl radicals thus produced are extremely reactive towards molecular oxygen [17] ($k = 4.7 \times 10^9\, m^{-1}\, s^{-1}$) and towards nickel(II)-cyclam complex ($k = 1.09 \times 10^9\, m^{-1}\, s^{-1}$). The former produces highly reactive alkyperoxyl radical whereas the latter produces the nickel(III)-carbon bonded species. The formation of nickel(III)-carbon bond has been extensively studied [16] recently by Epsenson et al. The complex studied $[Ni(cyclam)]^{2+}$, is very similar to the complexes **1** and **2** investigated and hence the rate constants could be compared.

In the presence of small amounts of dicholoromethane in acetonitrile continuous photolysis of **1** and **2** indicates the formation of stable nickel(III)- complex coordinated to chloride ion in solution as seen by an increase in the absorption at 320 nm (Fig. 5) and well known ESR spectrum [23,24] of nickel(III) which is shown in Fig. 5 (inset). The $g_{||}$ line is split into seven lines due to the coordination to two chloride ions in the axial positions. The direct photolysis of dichloromethane by 254 nm light is ruled out in this case since the absorbance of the complex at 254 nm is very large compared to that of dichloromethane and >99% of the light is absorbed by the complex.

The following mechanism is proposed for the observed results in the presence of dichloromethane:

$$\left[LNi^{II}\right] \underset{CH_2Cl_2}{\overset{h\nu,CTTS}{\rightarrow}} \left[LNi^{III}\right] + CH_2Cl^{\bullet} + Cl^{-} \quad (5)$$



Scheme 1.

$$^{\bullet}\mathrm{CH_2Cl} + \mathrm{O_2} \rightarrow {}^{\bullet}\mathrm{OOCH_2Cl} \tag{6}$$

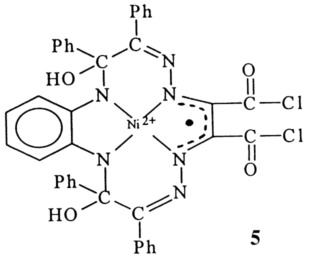
$$^{\bullet}\mathrm{OOCH_2Cl} + \left[\mathrm{LNi^{II}}\right] \rightarrow \left[\mathrm{LNi^{III}\text{–}O_2\text{–}CH_2Cl}\right] \tag{7}$$

$$\left[\mathrm{LNi^{III}\text{–}O_2\text{–}CH_2Cl}\right] \xrightarrow{\mathrm{Cl^-}} \left[\mathrm{LNi^{III}Cl}\right] + \text{Products} \tag{8}$$

L = tet-a or htcd.

Excitation of nickel(II) complex in the charge transfer to the solvent band in presence of good electron accepting solvent like dichloromethane leads to reduction of the dichloromethane which dissociates in solution to form the chloroalkyl radical and $\mathrm{Cl^-}$ ion. The chloroalkyl radical is scavenged effectively by molecular oxygen ($k = 1.9\times10^9\,\mathrm{M^{-1}\,s^{-1}}$) [17,18] to produce the highly reactive chloroalkylperoxyl radical. This alkylperoxyl radical reacts with the nickel(II)-complex oxidising it to the +3 oxidation state which is seen as a growth in absorbance at 370 nm. The 370 nm peak is observed for the alkylperoxide coordinated nickel(III) complex studied earlier [17,18]. The growth at 370 nm follows pseudo first-order kinetics with the rate constant depending up on the concentration of the nickle(II) complexes. The second-order rate constant determined for the reaction of chloroalkylperoxyl radical with complex **1** is found to be $2.2 \pm 0.2 \times 10^6\,\mathrm{M^{-1}\,s^{-1}}$ whereas for the complex **2** the same is determined as $1.7 \pm 0.1 \times 10^6\,\mathrm{M^{-1}\,s^{-1}}$.

In the case of **3** the transient is found to disappear if acetone filter is used indicating clearly that the transient observed is not produced on excitation of the complex in the intense 350 nm band. The signal is unaffected when dichloromethane filter is used, indicating that the transient produced is due to the charge-transfer absorption peak at 260 nm. The electrochemical oxidation of the complex studied earlier [1] shows an irreversible cyclic voltammetric pattern. The changes observed in the absorption spectra on electrochemical oxidation of the complex are very similar to the changes observed on photolysis as shown in Fig. 7a and b indicating that the oxidation of the metal centre is followed by a chemical reaction where the nickel(III) is reduced presumably by intramolecular electron transfer to produce a nickel(II) coordinated to a ligad radical which is observed as a decay at 610 nm with a rate constant of $11.8\,\mathrm{s^{-1}}$. The assumption is based on the intense transient absorption at a longer wavelength (610 nm) which is not due to the nickel(III) complex.



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In the case of **4** the ESR parameters of the photoproduct indicate the formation of ligand radical coordinated to the metal centre [29]. The FAB mass spectral data ($\mathrm{M^+} = 760$) strongly supports the proposed structure [2]. Satisfactory elemental analysis was also obtained considering the structure **5** as the photoproduct. In the IR spectra a strong band at $1730\,\mathrm{cm^{-1}}$, a region expected for $\gamma_{(C=0)}$ of acid chloride [30], also supports the structure. Based on the spectral data of the photoproduct formation of a metal stabilised ligand radical as depicted in **5** is proposed. Since the photoproduct does not crystallise out further confirmation of the structure could not be attempted. The following mechanism shown in the Scheme 1 is suggested for the observed reaction. The first step is similar to that of complex **1** in dichloromethane. The trivalent nickel with dianionic ligand thus formed is not stable and generates proton from CH centres and the carbanion reacts with chloroalkylperoxyl radicals. The intermediate thus formed after dehydration [31] transfers an electron to trivalent nickel to form nickel(II) π-radical compound as end product. There are examples of macrocyclic compound with unusual oxidation states of metal, specially nickel(II) [32–35], which undergo deprotonation leading to ligand oxidation. The present study shows a new example of a nickel(II) π-radical system which is generated by continuous photolysis of **4** using direct sunlight leading to a redox reaction.

Acknowledgements

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[2] Molecular weight of the starting complex excluding two-OH protons is 633, addition of two COCl units results in a molecular weight of 760.

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