Photochemistry of nickel salen based complexes and relevance to catalysis

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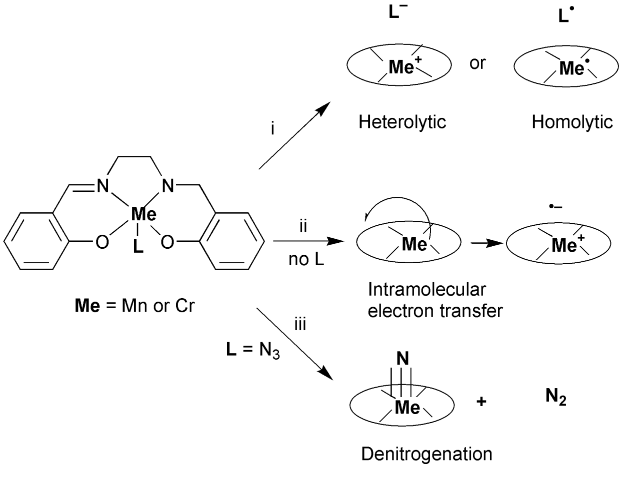
A series of four nickel salen complexes have been synthesised and their photochemical properties studied. These complexes emit in hexane at λ_{em} 580 nm with similar quantum efficiencies. Fluorescence decay occurs on the nanosecond time scale and its intensity is quenched by oxygen except for the complex with the shortest lifetime. For all complexes laser flash photolysis in CH_2Cl_2 or hexane generates a transient (lifetime on the μs time scale) that was assigned to a Ni-to-ligand electron transfer triplet excited state. In an attempt to show the relevance of photochemical data to catalysis, epoxidation of *β*-methylstyrene was carried out in the presence of the four complexes. It was found that the activity of the complexes correlates with the lifetime of the triplet charge-separated state. This relationship was interpreted as reflecting the intrinsic stability of the oxidised Ni ion in the different complexes, which is the common link between the photochemical and catalytic experiments.

Metal complexes with salen type ligands are important catalysts for oxidation, aziridine formation, epoxide opening and cycloaddition, both in the asymmetric and non-stereoselective versions.[1] It is obvious that the activity of these catalysts depends to a large extent on the characteristics and peculiarities of the metal-ligand interaction, which can be assessed with structural and spectroscopic techniques. Alternatively, photochemistry could serve as a complementary tool to probe the electronic configuration and electron density distribution of the complex. Since the photochemical pathways are governed by molecular orbitals and electronic configuration, valuable information about the complex can be gained that could be correlated with their catalytic activity. The major limitation of this approach is that most of the photochemistry of relevant metal complex catalysts, particularly those with Schiff bases, remains unexplored.

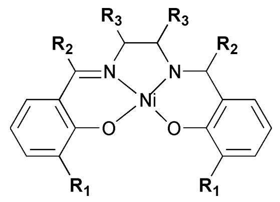
Recently, the photochemistry of a pentacoordinate Mn(III) salen complex has been studied by some of us[2] and it was found that the active species in the epoxidation reaction, the (salen)oxomanganese(V) complex, can be generated photochemically as a transient (Scheme 1, path i). This has provided kinetic data for the single step consisting in the reaction of the oxomanganese complex with the alkene, the crucial step in its asymmetric epoxidation.[2] The photochemical behaviour of Mn(III) salen complexes contrasts with that of tetracoordinate [Mn(II)(salen)][3] and [Mn(bpy)3]$^{2+}$ [4] encapsulated in zeolites.[5–7] In the latter cases, it has been found that the predominant photochemical pathway is an intramolecular metal-to-ligand electron transfer (ET) (Scheme 1, path ii), which initially generates an emissive transient that subsequently undergoes intersystem crossing.

The photochemistry of [Mn(III)(salen)]$^+$ and [Cr(III)(salen)]$^+$ having azide as the apical ligand has also been investigated. These azide complexes undergo photochemical denitrogenation leading to the formation of metal (salen) nitrides with high preparative yields (Scheme 1, path iii).[8,9]

In spite of the importance of [Ni(salen)] complexes as catalysts, as far as we know the photochemistry of these complexes has ever been reported. Herein, we have studied the photochemistry of four nickel(II) complexes with salen type ligands (**1**–**4**, Scheme 2). Analogously to what has been reported for related [Mn(salen)] complexes encapsulated within zeolites,[3] we have found that the predominant photochemical process involves intramolecular metal-to-ligand ET. Furthermore, a change in the structure of the ligand is reflected in the lifetimes of the photogenerated transients. In addition, the catalytic epoxidation activity of these complexes towards *trans*-*β*-methylstyrene was determined and the results correlated with the photochemistry data.



Scheme 1



	R1	R2	R3
1	H	H	H
2	H	H	–(CH3)4–
3	H	CH3	H
4	OCH3	H	H

Scheme 2

Results and discussion

Photochemical studies

The UV-Visible absorption spectra of complexes **1**–**4** in dichloromethane show common features. There are three distinct absorptions that could correspond to ligand-centered bands as well as electronic transitions involving metal/ligand exchange. The spectra are depicted in Fig. 1, while the λ_{max} of the bands and their corresponding extinction coefficients (ε) are collected in Table 1.

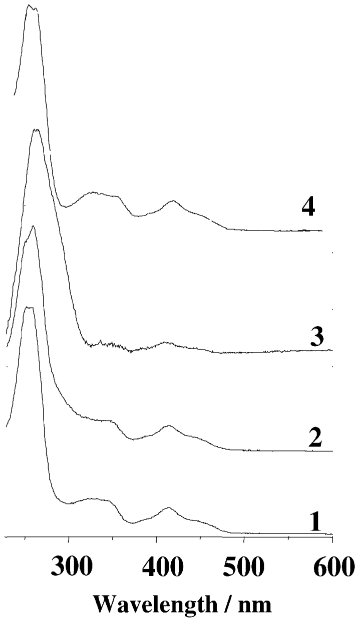


Fig. 1 Absorption UV-Vis spectra of nickel salen complexes **1**–**4** in dichloromethane (10^{-3} M).

Complexes **1**–**4** are much less soluble in hexane than in dichloromethane, but nevertheless, their solubility is high enough to exhibit a measurable absorption of the MLCT band, thus allowing a photochemical study in hexane. The influence of the solvent will become relevant later when commenting on the photophysics and photochemistry of the complexes. In hexane, a solvatochromic red shift of all the absorption bands was observed, as well as a remarkable decrease in the corresponding ε, when compared with the values in dichloromethane.

Interestingly, while complexes **1**–**4** do not emit in dichloromethane, room temperature emission was recorded for all complexes in hexane upon excitation at the MLCT band (λ_{ex} 425 nm). The emission spectra correspond to the mirror images of the absorption bands at longest wavelengths, although with a large Stokes shift and a lack of fine structure. In Fig. 2 are depicted the emission spectra, together with the corresponding excitation spectra for complexes **1**–**4**. A list of the maximum emission wavelengths (λ_{em}), as well as the absolute quantum yields are given in Table 1.

The lack of emission in dichloromethane can be explained by solvent quenching. Support for this explanation can be gained by noting that in recent studies on the photoluminescence of azo compounds the same influence of dichloromethane has been observed. In the case of azo compounds quantum chemical calculations have suggested the operation of a so-called *aborted hydrogen transfer* mechanism from dichloromethane to the singlet excited state, which would be responsible for the quenching.[10] A reduced emissive efficiency in dichloromethane compared to hexane has also been recently observed for titanolsilsesquioxanes.[11]

Molecular oxygen quenching of the emission of complex **1** in hexane cannot be accurately measured with our spectrofluorimeter. In contrast, we have been able to measure the influence of oxygen on the photoluminescence of complexes **2**–**4**. From the relative emission intensity decrease after nitrogen and oxygen purging, and assuming that the solubility of molecular oxygen in hexane is about 10^{-5} mol dm^{-3}, an estimate of the quenching rate constant can be obtained by applying the Stern–Volmer[12] equation; the calculated values are also presented in Table 1.

Emission lifetimes were measured by single photon counting from the best fit of the emission decay to a single exponential equation. τ values are listed in Table 1. As it can be seen, the estimated lifetimes vary significantly with the nature of the ligand. Complexes **1** and **3** have remarkable shorter emission lifetimes than those measured for complexes **2** and **4**. The latter have unusually long lifetimes (~25 ns). As expected, in view of the intensity decrease of the emission, molecular oxygen

Table 1 Absorption (in dichloromethane) and emission (in hexane) parameters and lifetime of the photogenerated transient (in dichloromethane) of Ni complexes

Complex	λ_{max}/nm	ε/M^{-1} cm^{-1}	λ_{em}/nm	$\Phi_{fluo}{}^{a}$	$\tau_{fluo}(N_2)$/ns	$\tau_{fluo}(O_2)^{b}$/ns	$k_q(O_2)$/s^{-1} M^{-1}	$\tau_{transient}{}^{c}$/μs
1	415	9750	580	0.05	4	–	–	66
	335	12 500						
	255	86 875						
2	415	3304	580	0.08	22	7	4×10^{9}	65
	350	3766						
	260	29 231						
3	415	3391	580	0.02	5	2	$>10^{10}$	31
	350	1810						
	260	29 000						
4	415	11 765	580	0.06	25	7	2×10^{9}	17
	350	15 294						
	260	87 647						

[a] Measured using Ru(bpy)$_3{}^{2+}$ as standard. [b] Obtained from the Stern–Volmer equation. [c] Obtained from the best fit of the transient to a single exponential kinetic rate law.

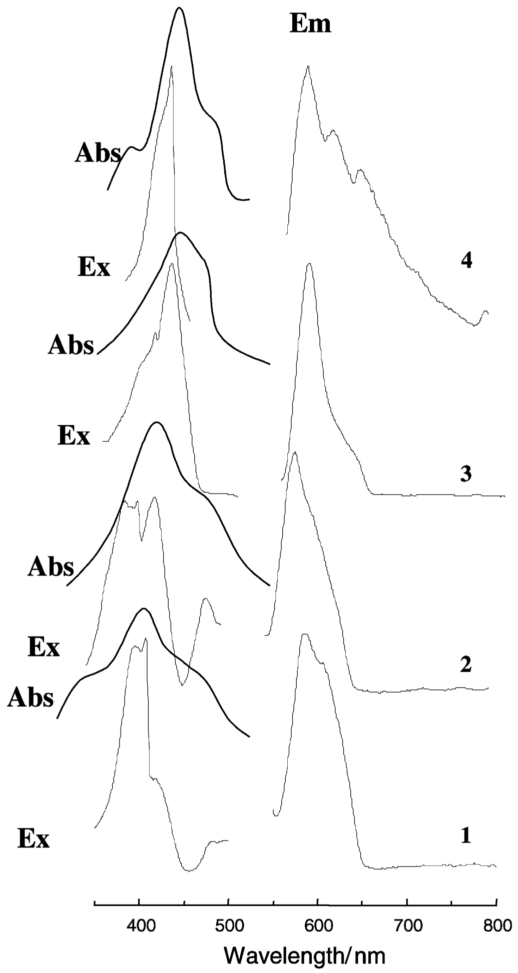


Fig. 2 Part of the absorption (Abs), emission (Em, λ_{ex} 425 nm) and excitation (Ex, λ_{em} 580 nm) spectra of complexes **1**–**4** in N_2-purged hexane solutions.

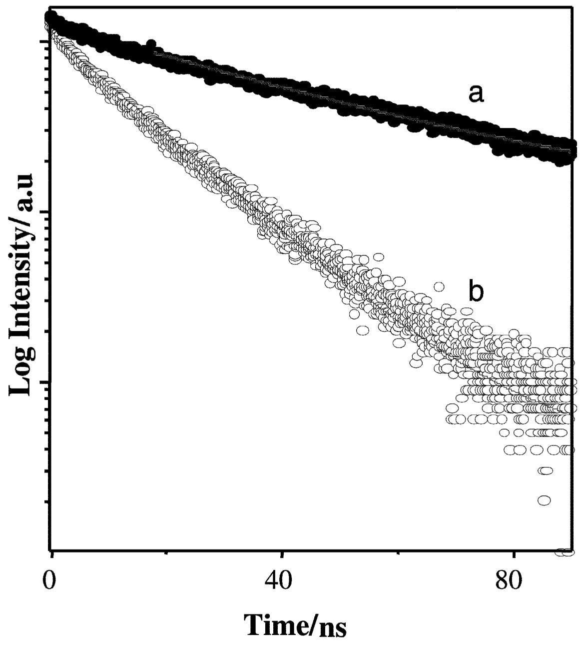


Fig. 3 Emission decay monitored at 580 nm upon 425 nm excitation of complex **1** after N_2 (a) and oxygen (b) purging. The solid lines correspond to the theoretical equation from which the lifetimes were calculated.

shortens the lifetime compared to molecular nitrogen. The corresponding quenching constants obtained from the decay profiles agree reasonably well with those obtained by the decrease in emission intensity presented in Table 1. Fig. 3 shows representative emission decays in hexane after nitrogen and oxygen purge.

Complexes **1**–**4** have transient absorption spectra upon 266 nm laser excitation. Laser flash photolysis experiments were conducted in a dynamic flow regime to ensure exposure of fresh complex to each laser shot, avoiding interference from any photochemical byproducts. The spectra recorded in dichloromethane and hexane solvents are very similar. This indicates that the transient species formed upon laser excitation of the salen complexes in dichloromethane or hexane are the same. The transient spectra show in general two absorption bands, the first around 450 nm and a second, much broader one, extending from 600 to 800 nm, the longest wavelength available with our monochromator. For complexes **1**–**4** the decay of the two bands, monitored at the wavelength of their absorption maxima, are very similar, which indicates that most likely they correspond to the same transient. A representative transient spectrum is shown in Fig. 4, in which normalized signal decays at 450 and 750 nm have been included.

The transient decays are not monoexponential and contain at least fast and slow components. Reasonably good fits to monoexponential kinetics could be obtained for the decays after neglecting the first 5 µs of the signal. The values obtained are collected in Table 1.

For a given complex, the lifetime in dichloromethane is remarkably shorter than in hexane; in Fig. 5 are shown some representative decays to illustrate this point. This observation suggests quenching of the transient by dichloromethane and agrees with the interpretation about the lack of emission in CH_2Cl_2 due to quenching by an aborted hydrogen transfer mechanism.[10] Comparison of the lifetime of the transient species observed by laser flash photolysis (that is on the time scale) with that monitored by emission spectroscopy for the emissive excited state (lifetimes in the ns range) clearly indicates that we are dealing with different species. In other words, the excited state responsible for emission has completely disappeared long before 1 µs after the laser pulse and, therefore, cannot be responsible for the transient spectra shown in Fig. 4.

Based on the electronic diagram of nickel complexes and on the similarity of the observed photochemistry of nickel(salen)

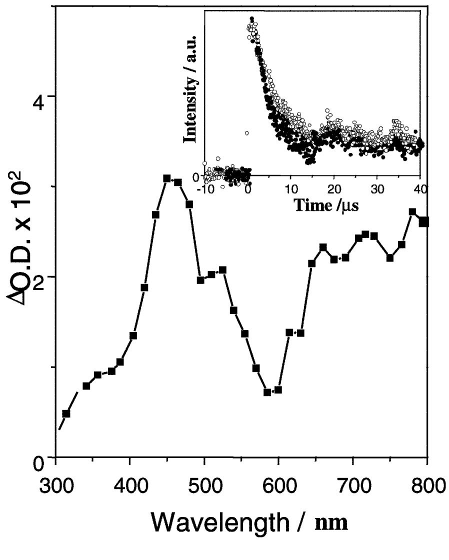


Fig. 4 Transient spectrum recorded 5 µs after 266 nm laser excitation of N_2 complex **1** in hexane (10^{-4} M). The insert shows normalised decays monitored at 450 (●) and 750 (○) nm, indicating that the transient spectrum most likely corresponds to a single species.

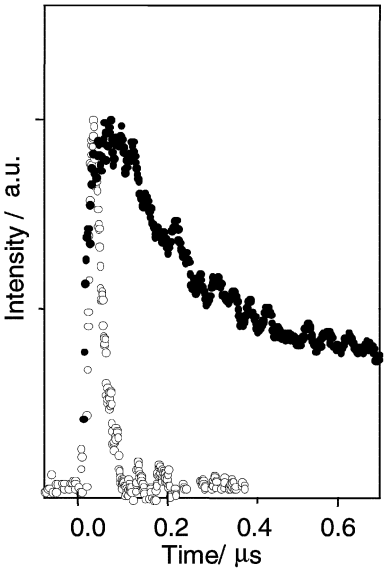


Fig. 5 Transient absorption for complex **1** in N_2-purged solutions ($\sim 10^{-4}$ M) monitored at 450 nm after 266 nm laser excitation in hexane (•) and in dichloromethane (○).

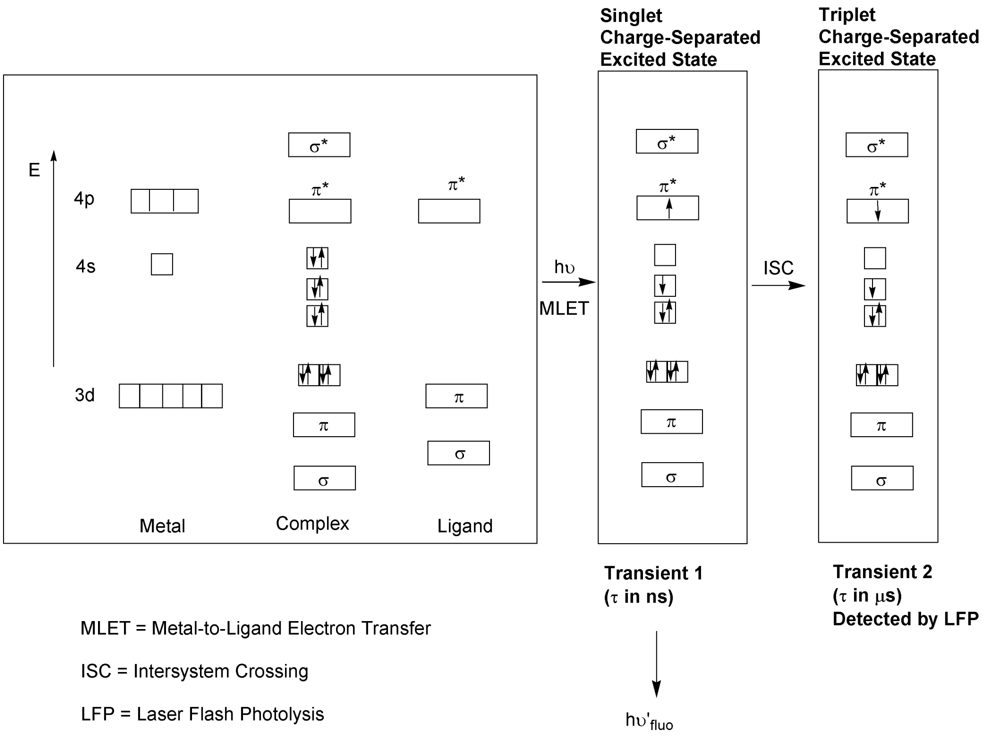
complexes with that reported for manganese(II)(salen) complexes,[3] a diagram that would be compatible with the experimental data is proposed in Scheme 3. Thus, upon light excitation one electron from the Ni degenerate d orbitals is promoted to the π anti-bonding orbital of the salen ligand without spin inversion. This primary metal-to-ligand ET excited state could deactivate back to the ground state in an emissive way and would be responsible for the observed photoluminescence. The lifetime of this primary excited state would lie in the nanosecond time scale since its deactivation would not violate the spin conservation rule. Alternatively, this excited state could undergo intersystem crossing to the corresponding triplet charge-separated state by spin flipping, a process favoured by the Hund rule. This secondary species would be the one that is detected by laser flash photolysis and its lifetime would be in the microsecond time scale, as its deactivation to the ground state is forbidden by the spin conservation rule. We notice, however, that the decay is not influenced by typical triplet quenchers, such as molecular oxygen ($E_T = 7.9$ kcal mol^{-1}) and 1,3-cyclohexadiene ($E_T = 52.4$ kcal mol^{-1}). In particular, the lack of influence of oxygen contrasts with the above-commented behavior for the emissive excited state. It could be that the energy of this triplet excited state is lower than that of the triplet state of the quenchers and, thus, no quenching should be observed.

The relevance to catalysis of an understanding of the photochemistry arises from the fact that the latter technique shows the influence of the substituents on the salen ligand on the interaction with Ni atoms. The electron acceptor ability of the ligand would influence the lifetime of the charge-separated excited state. Thus, complexes **1** and **2** that only differ by the presence of *ortho* methyl groups in the imine C atom have very similar transient spectra and lifetimes. At the other extreme the presence of two methyl groups on the imine C atom and *ortho* methoxy groups in the aldehyde moieties strongly influences both the transient spectra and the corresponding lifetimes, by increasing significantly the electron density on the aromatic rings of the ligands. Compared to the photochemistry of metal(salen) complexes in water, wherein the solvent donates an electron to the metal ion, the photochemistry of complexes **1**–**4** is governed by the poor electron-solvating capacity of hexane and by the existence of accessible LUMO orbitals in the ligand.

While one could argue that these effects could have been readily anticipated without the need for any photochemical study, we have provided quantitative data on the influence of ligand substituents (see Table 1) that could not be easily obtained by other means.

Catalytic epoxidation

[Ni(salen)] is known to act as a homogeneous catalyst in the epoxidation of alkenes.[13–15] In this work, nickel complexes **1**–**4** were tested in the epoxidation of *trans*-*β*-methylstyrene in CH_2Cl_2, at room temperature and under phase-transfer



Scheme 3

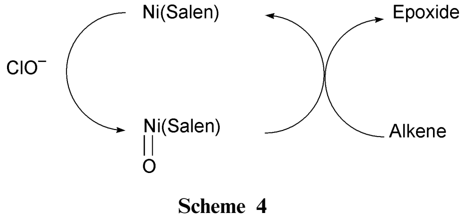
Table 2 Epoxidation of *trans*-β-methylstyrene using [Ni(salen)]-based complexes and NaOCl[a]

Complex	Conversion[b] (%)	Epoxide yield[c] (%)
1	100	55
2	94	51
3	84	50
4	61	32

[a] Reaction conditions: 1 mmol of *trans*-β-methylstyrene, 2.5 mol% nickel catalyst, 3 mol% of benzyltributylammonium bromide, 5 ml of NaOCl (2.8 mol dm^{-3}, adjusted to pH = 11 with 2.5 ml of a Na_2HPO_4 buffer solution) in 5 ml of CH_2Cl_2, room temperature and 9–12 h reaction time. [b] Based on disappearance of *trans*-β-methylstyrene. [c] Based on alkene conversion.

conditions using NaOCl as the terminal oxidant. The results of the epoxidation reaction are summarised in Table 2. All nickel complexes show catalytic activity with complex **1** being the most active catalyst, reaching 100% conversion in the experimental conditions used. Going from an ethane to a cyclohexane imine bridge in the salen ligand, as in complex **2**, only decreases the conversion of the substrate to 94%, but introduction of substituents on the imine carbon or aromatic ring (complexes **3** and **4**) decreases the conversion to 84 and 61%, respectively. Although the introduction of substituents in the salen ligand decreases markedly the reaction conversion, the epoxide selectivity is quite similar (53–59%) for all the complexes. The similar selectivities for this group of complexes suggest that the oxygen transfer from the active form of the nickel catalyst (the oxidised form) to alkene proceeds irrespective of the substituents on the ligand. Therefore, the different alkene conversions observed for the group of complexes studied would indicate that the formation of the intermediate oxidised nickel species is the key step in the overall epoxidation reaction (Scheme 4). As a consequence we could be tempted to correlate the epoxide yields with the oxidation potentials for the complexes in the same solvent, as has been done for epoxidation reactions with other nickel complexes.[16,17] However, these complexes show, in this solvent and in other low donor capacity solvents such as acetonitrile, irreversible ligand-based oxidation processes that result in the formation of conducting polymeric films at the electrode surface,[18–21] which prevents any tentative correlation between catalytic activity and oxidation potentials.

In this context, laser flash photolysis appears as a very good alternative and some correlations to catalytic data can be observed, although we must recognise that the set of complexes that have been used in this study is limited and further studies are desirable. Thus, complexes **1** and **2** exhibit the longest lifetime for the triplet charge-separated transient in which the Ni atom is in a higher oxidation state and they are the two catalysts with the highest alkene conversion/epoxide yield (easier formation of the catalytically active oxidised Ni species, Scheme 4). The transient from complex **3** has an intermediate lifetime and the catalytic activity for methylstyrene conversion and epoxide yield are likewise intermediate in the series. Finally, complex **4**, with methoxy groups in the aldehyde moiety and which exhibits the lowest alkene conversion/epoxide yield, shows in laser flash photolysis a photogenerated transient in which oxidised Ni atoms exhibit the shortest lifetime. It is obvious that the nickel species involved in the photochemistry and epoxidation reactions are not the same, but they have in common that starting from the same compound a central Ni ion in a higher oxidation state is generated. Thus, on the basis of this study, we can propose that the structural factors favouring a long lifetime of the transient generated upon light excitation will also favour formation of the oxo nickel that is supposedly the active species in epoxidation.



Scheme 4

Concluding remarks

The photochemistry of nickel(II)(salen) complexes follows a pattern common with that found for manganese(II)(salen) complexes. The predominant photochemical process is the intramolecular metal-to-ligand ET that produces an emissive charge-separated excited state. This transient intersystem crosses to the corresponding triplet. Substitution on the aromatic rings of the salen ligand does not substantially alter the photochemical pathway, but influences the lifetimes of the excited states, reflecting the electron-donating or -withdrawing ability of the substituents. Substitution on the diiminocentral bridge has much less influence. The values of the lifetimes obtained reflect the relative stability of the complexed nickel atom in a higher oxidation state and, therefore, it is proposed that they parallel the relative catalytic activity of oxidised species of the Ni(salen) complex. The observed trend between the catalytic activity of these complexes in the epoxidation reaction of *trans*-β-methylstyrene and the lifetime of the photogenerated transient supports this idea.

Experimental

Materials

The solvents used in the preparation of the complexes were of reagent grade and used without further purification: salicylaldehyde, acetophenone, ethylenediamine and cyclohexanediamine were from Merck, 2-hydroxy-3-methoxy-benzaldehyde from Aldrich, and nickel acetate from Riedel de Haën. *trans*-β-Methylstyrene and benzaldehyde were purchased from Aldrich and dichloromethane from Merck (Lichrosolv); the epoxide was prepared as described in the literature.[22] GC was used to check the purity of all chemicals used in catalytic reactions.

Preparation of nickel complexes 1–4. The ligands were prepared by a standard procedure: to an ethanolic solution of the corresponding aldehyde was added the corresponding diamine in a 2 : 1 molar ratio (ethylenediamine or cyclohexanediamine), and the mixture refluxed for 2 h (typically 0.5 mmol of the aldehyde, and 0.25 mmol of the diamine in 100 ml of ethanol). Upon crystallisation the yellow solids were filtered off, recrystallised from ethanol and dried under vacuum for several hours (yields in the range 70–80%). The complexes were synthesised by refluxing ethanolic solutions of the Schiff base and $Ni(CH_3COO)_2{\cdot}4H_2O$ in equimolar quantities (typically 2.5 mmol of the ligand and complex in 100 ml of ethanol).[23] After refluxing for 2 h reddish-brown compounds were filtered, washed with ethanol and dried (yields in the range 65–70%). The complexes were recrystallised from ethanol or dichloromethane and dried at 120 °C for several hours.

[Ni(salen)] (**1**): $NiC_{16}H_{14}N_2O_2$, anal. found C, 59.2; H, 4.3; N, 7.4; calc. C, 59.1; H, 4.1; N, 8.6%. [Ni(salhd)] (**2**): $NiC_{20}H_{20}N_2O_2$, anal. found C, 63.4; H, 5.1; N, 7.3; calc. C, 63.4; H, 5.3; N, 7.4%. [Ni(α,α'-Me_2salen)] (**3**): $NiC_{18}H_{20}N_2O_2{\cdot}0.5\,H_2O$, anal. found C, 59.9; H, 5.2; N, 7.7; calc. C, 59.7; H, 5.3; N, 7.7%. [Ni(3-MeOsalen)] (**4**): $NiC_{18}H_{22}N_2O_5 \cdot H_2O$, anal. found C, 53.2; H, 5.0; N, 6.9; calc. C, 53.6; H, 5.0; N, 6.9%.

Photochemistry

UV-Vis spectra. Optical spectra were recorded in dichloromethane or hexane solutions ($\sim 1 \times 10^{-3}$ mol dm^{-3}) using quartz cuvettes in a Shimadzu PC spectrophotometer. Extinction coefficients were obtained from Beer–Lambert plots of the variation of the absorption at different concentrations in the range between 0.2 and 1 optical density units.

Luminescence measurements. Emission spectra were recorded on an Edinburgh FS900 spectrofluorimeter, equipped with a Czerny–Turner monochromator in the wavelength range 200–800 nm. A sample of the Ni complex was dissolved in dichloromethane or hexane ($\sim 1 \times 10^{-3}$ mol dm^{-3}) and placed into a 7×7 mm^2 Suprasil quartz cell sealed with a septum cap. The solutions were purged with nitrogen or dry air for at least 15 min before the measurements. Excitation and emission slits were maintained unchanged during the emission experiments. The fluorescence spectra were obtained by using the absorption maximum of the MLCT band as the excitation wavelength. Absolute luminescence quantum yields were measured using a hexane solution of $Ru(bpy)_3^{2+}$ optically matched (ϕ_{hexane} 0.2) at 425 nm.

Laser flash photolysis experiments. Laser flash photolysis experiments were performed at concentrations in the 10^{-4} mol dm^{-3} range with the fourth harmonic of a pulsed Nd–YAG laser (pulse width: 10 ns, energy per pulse: ~ 14 mJ, repetition rate: ~ 0.2 Hz). The data were captured with a Tektronics TDS 640A oscilloscope and the data transferred to a PC for analysis. Stock solutions were placed in a reservoir (150 ml) capped with a septum and the solution flushed by gravity through a 3×7 mm^2 Suprasil quartz cell during data acquisition. The volume of the reservoir and the solution flow ensures that fresh solution was exposed to each laser shot. In all measurements the reservoir was continuously purged with nitrogen or air and the stream started at least 15 min prior to the laser flash.

Epoxidation reaction

In a typical experiment 1 mmol of *trans*-β-methylstyrene, 2.5 mol% nickel catalyst, 3 mol% of benzyltributylammonium bromide (phase transfer catalyst) and 5 ml of NaOCl (2.8 mol dm^{-3}, adjusted to pH = 11 with 2.5 ml of a Na_2HPO_4 buffer solution) were stirred in 5 ml of CH_2Cl_2 at room temperature for 9–12 h. A 0.05 mL aliquot of the organic phase was taken out periodically and directly analysed by GC. Independent reactions under the same conditions showed reproducible epoxide yields.

GC analysis. Analyses of organic compounds were conducted on a Varian 3400 CX gas chromatograph that was fitted with a 30 m $\times$ 0.53 mm fused silica Chrompack CP-Sil 8CB capillary column and equipped with a TCD detector. The column temperature was programmed from 60 °C (3 min) to 170 °C (5° min^{-1}). *trans*-β-Methylstyrene, epoxide and benzaldehyde were identified by GC-MS and by comparison of their retention times to those of pure compounds. *n*-Decane was used as an internal standard for the quantitative analysis of the products.

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