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Ligand luminescence and photoinduced charge separation in bis(naphthalene) substituted fourteen-membered tetraazamacrocyclic complexes of Cu^{II} and Ni^{II}

Juan Costamagna,*[a] Guillermo Ferraudi,*[b] Manuel Villagran[a] and Ezequiel Wolcan[b]

[a] *Facultad de Química y Biología, Universidad de Santiago de Chile, Chile*
[b] *Radiation Laboratory, Notre Dame, IN 46556-0579, USA*

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Deaerated solutions of complexes of Ni^{II} and Cu^{II} of a bis(naphthalene) substituted fourteen-membered tetraazamacrocycle exhibited medium-dependent luminescence when they were irradiated at 351 or 337 nm. The addition of $Cu(CH_3CN)_6^{2+}$ in increasing concentrations resulted in the formation of a ground state adduct and led to displacements of the emission spectrum toward shorter wavelengths and to a progressive quenching of the luminescence. The rate of the luminescence decay was also dependent on the medium and on the monitoring wavelength and was fitted by single or multiple exponentials with lifetimes shorter than 30 ns. Steady state irradiations of the complexes at 370 nm induced a minor conversion among tautomeric forms. Transient photochemical products with lifetimes of several hundred ns were observed *via* flash photolysis and assigned as metal–ligand radical species. A mechanism for the formation of such intermediates and various ground and excited state species is proposed.

Introduction

Thermal and photochemical reactions of transition metal macrocyclic complexes have recently commanded considerable interest because of their potential applications to the reduction of CO_2 and to the removal of industrial pollutants, *e.g.* sulfite.[1–4] The recently studied charge transfer photochemistry of $Co^{III}L(SO_3)^+$, where L = macrocyclic ligand, may provide techniques for the photocatalysed oxidation of SO_3^{2-}.[4] Macrocyclic complexes with pendant arms have been proposed as probes and model molecules of biochemical processes. For example, complexes with a dansylamido-pendant cyclen (dansyl = 5-dimethylaminonaphthalene-1-sulfonyl, cyclen = 1,4,7,10-tetraazacyclododecane) were used as model compounds for the catalytic sites of zinc enzymes. Luminescence from the dansylamido-pendant is enhanced by Zn^{II} or Cd^{II} and quenched by Cu^{II}, Pb^{II} or Hg^{II}.[5] It has been proposed that an efficient conversion from the upper to the lower lying non-emissive charge transfer and/or metal-centred excited states influences the luminescence of the pendant arm. The effect of the pendant arm co-ordination to the metal on the energy of ligand-centred excited states, $\pi\pi^*$ and $n\pi^*$, has been considered as another factor that affects the luminescence of the compounds. In other macrocyclic complexes the emission from the excited states of highly unsaturated, largely planar ligands, *e.g.* phthalocyanines, is usually diminished and radiationless relaxation processes are greatly accelerated by co-ordination to Cu^{II} and Ni^{II}.[6] The luminescence is replaced by photoinduced redox processes when charge transfer excited states are placed at energies lower than those of the ligand-centred states. Phthalocyanines of Co^{III} with reducing ligands co-ordinated in axial positions provide examples of LMCT photochemistry.[6]

The example of the phthalocyanines and macrocyclic complexes with luminescent pendant arms suggests that similar photophysical properties should be found in compounds where aromatic groups are fused to the macrocycle. If luminescent ligand-centred excited states must be preserved, a necessary condition is to have a weak coupling of the metal and ligand electronic systems and a poor communication of the luminescent states with metal-centred and CT excited states. To establish the correctness of this proposition, the photochemical properties of the complexes of Cu^{II} and Ni^{II} of ligands **I**–**IV** were investigated in this work. The ligands **I** and **II** are tautomers, hence their complexes with Ni^{II} and Cu^{II} are tautomers. Deprotonation of **I** or **II** may occur with charge localization in the planar six membered chelate rings of the macrocycle to yield **III** and **IV**. A similar deprotonation was previously observed.[7–10] It must be noted that in one case the macrocycle has a saddle shaped structure and some metal ions are displaced from the N_4 plane.[9,10] On this basis, similar departures from a planar macrocycle are expected for **I**–**IV**.

Experimental

Materials

$CuLCl_2$, $NiLCl_2$ and the free macrocycles L = **I** or **II** were prepared by a variation of literature procedures previously used with related macrocycles.[9–11] In the preparation of $MLCl_2$ where M = Cu or Ni, 7.8 mmol of 2,3-diaminonaphthalene and 3.9 mmol of the corresponding chloride salt in MeOH were refluxed for 8 h and 7.8 mmol of 2,4-pentanedione were subsequently added. The resulting mixture was kept under reflux for 10 h more, chilled and the precipitate filtered off and washed with water. Pure materials were obtained by recrystallization from hot MeOH. The "free" ligand was obtained as the chlorohydrate by adding HCl to a methanolic solution of $NiLCl_2$. The characterization of the compounds was based on IR (Table 1), UV-Vis and ESR spectroscopy and the purity of each compound was ascertained by means of elemental analysis. Calc. for $N_4NiC_{30}H_{28}\cdot 2HCl$: C, 62.54; H, 5.25; Cl, 12.31; N, 9.72; Ni, 10.19. Found: C, 63.00; H, 5.32; Cl, 12.40; N, 9.67; Ni, 10.70. Calc. for $C_{30}H_{28}CuN_4\cdot 2HCl$: C, 62.01; H, 5.20; Cl, 12.20; Cu, 10.94; N, 9.64. Found: C, 61.71; H, 5.50; Cl, 12.00; Cu, 11.20; N, 9.84%.

Anhydrous $Cu(OTF)_2$, OTF = trifluoromethanesulfonate, was prepared by removing water at 80 °C under a reduced

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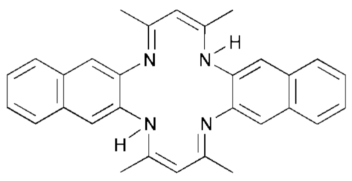
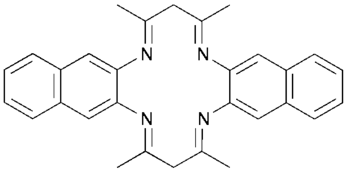
Table 1 Characteristic IR bands (cm^{-1}) of macrocyclic ligand **I** and its complexes of Ni and Cu

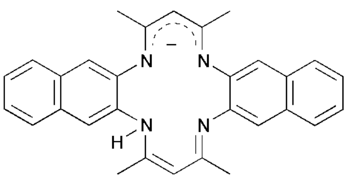
Compound	ν(N–H)	ν(C=N)	ν(C–C$_{arom}$)	ν(N–H)
I·2HCl	3334	1660	1588	753
Cu(**I**)Cl$_2$	3280	1630	1582	753
Ni(**I**)Cl$_2$	3400	1626	1580	750



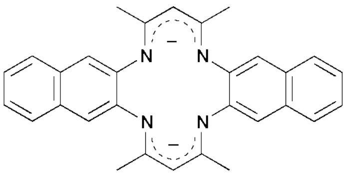
(I)



(II)



(III)



(IV)

pressure equal to or less than 1 Torr. Other materials were reagent grade and used as received.

Photochemical procedures

Continuous photolyses were carried out with light from a 500 W Oriel Xe-Hg lamp focused with appropriate fused-silica optics into a Bausch & Lomb monochromator for the isolation of 370 ± 10 nm light. An electrically activated shutter, placed before the reaction cell, allowed timing of the irradiations with errors smaller than ±0.1 s. Absolute values of the light intensity were determined with Parker's actinometer,[12] or Co(NH$_3$)$_5$-Br^{2+}.[13] The intensity of the light was monitored at various intervals with a photocell–millivoltmeter apparatus.

An apparatus used for 351 and 337 nm flash photolysis experiments in a ns to ms time domain has been described elsewhere.[4,14] An excimer laser, Lambda Physik LPX 200, was used for time-resolved spectroscopy and reaction kinetics longer than 10 ns. The flash intensity was measured by an actinometric procedure described elsewhere.[13–15] In this procedure, acid solutions of Co(NH$_3$)$_5$Br^{2+} in 10^{-2} M Br$^-$ were irradiated at wavelengths shorter than 380 nm and the photogenerated concentrations of Br$_2^-$ used for calculation of the light intensity. Time-resolved luminescence measurements were carried out with a PTI flash fluorescence instrument. The steady state luminescence was investigated with a SLM-Aminco-8100 spectrofluorometer interfaced to a DEL 333P microcomputer.

Solutions of complexes of Cu^{II} and Ni^{II} for photochemical experiments were prepared by adding appropriate weights of the solid salt to previously deaerated solutions of the solvent. Liquids were deaerated with streams of O$_2$-free N$_2$.

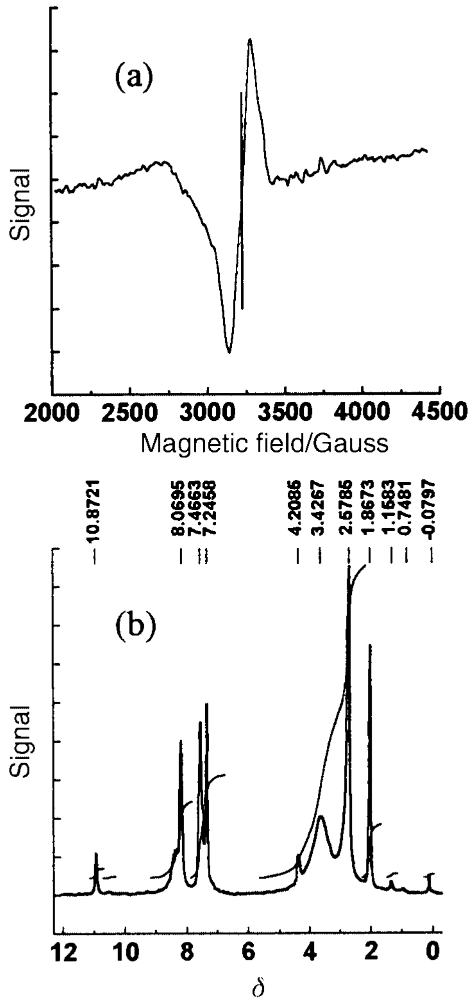


Fig. 1 ESR spectrum of 1.0 × 10^{-3} M Cu(**I**)$^{2+}$ in MeOH (a), with centre field at 3226 G. The NMR spectrum of Ni(**II**)$^{2+}$ in Me$_2$SO-d$_6$ with TMS as a standard is shown in (b).

Analytical procedures

ESR spectra were recorded with a Bruker ER 080 spectrometer fitted with a TE102 wavebridge, UV-Vis spectra with a computer-interfaced Cary-219 spectrophotometer. The modified Kitson procedure was used for the investigation of Co(H$_2$O)$_6^{2+}$.[16] IR spectra were recorded with a Bio-Rad FTS 175 Spectrometer. Electrochemical measurements were carried out with a PAR 173 potentiostat coupled to a PAR 175 universal programmer. Deaerated solutions, 10^{-4} M complex and 10^{-2} M tetraethylammonium perchlorate in acetonitrile, were placed in a three electrode cell with a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel reference electrode. Solvents and supporting electrolyte for the electrochemical measurements were dried according to literature procedures.[17,18]

Results

Thermal stability in solution

The ESR spectra of the copper(II) complexes of ligands **I** and **II** in CHCl$_3$ or MeOH exhibited $g_\parallel$ and $g_\perp$ values close to 2 that were in accordance with the structure of an elongated octahedron, Fig. 1(a).[19] The NMR spectrum of the diamagnetic Ni(**II**)$^{2+}$ indicated no differences between the four methyl groups, Fig. 1(b). Also the two naphthyl groups were equiv-

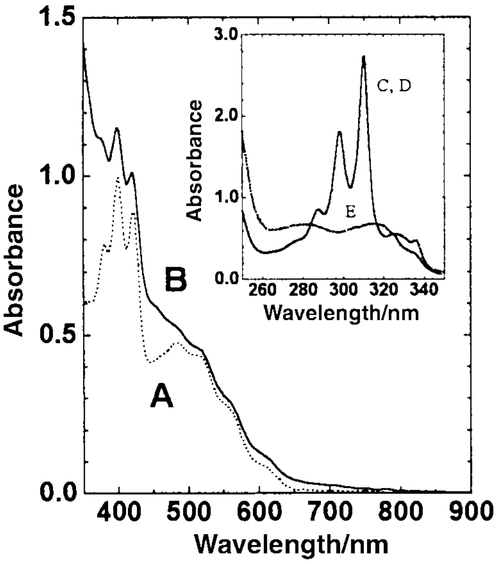


Fig. 2 Vis spectra of 4×10^{-4} M nickel(II) (A) and copper(II) (B) complexes of **I** in MeOH. The inset shows the effect of the medium on the spectrum of the 10^{-4} M nickel(II) complex in (C) MeOH, (D) 1×10^{-3} M NBu_4ClO_4 in MeOH and (E) 1×10^{-3} M NBu_4OH in MeOH.

alent. The nitrogen atoms of the ligand appear to be, therefore, in a square planar configuration.

Aerated and deaerated solutions of the complexes of Cu^{II} and Ni^{II} of **I** and **II** in various solvents, CH_3CN, MeOH or MeOH–water mixtures, were stable in the dark for more than 12 h. The UV-Vis spectra of the ligands and the complexes in methanolic solutions exhibited maxima at the same wavelengths. Strong absorptions of the macrocycle masked metal-centred transitions. Moreover, some spectral differences between the spectra of the nickel and copper complexes can be ascribed to the different positions of the charge transfer transitions.

The gradual addition of tetra-n-butylammonium hydroxide to methanolic solutions of the copper(II) or nickel(II) complex of **I** resulted in marked changes of the UV-Vis spectra, insert to Fig. 2. The disappearance of absorption bands between 400 and 800 nm with the addition of base resulted in a change of the solution from red to yellow. Titration of the base with methanolic $HClO_4$ reversed the spectral changes. The spectra of the solutions titrated to the end-point were the same as the complexes in neutral methanol. Similar spectral changes were observed when 10^{-4} M solutions of the ligand or its copper(II) and nickel(II) complexes in a 90% MeOH–10% water were titrated with 0.1 M NaOH. These spectral changes were related to the displacements of the acid–base equilibria (1),

$$\mathrm{M(H_2L)^{2+}} \underset{+\mathrm{H}^+}{\overset{-\mathrm{H}^+}{\rightleftharpoons}} \mathrm{M(HL)^{+}} \underset{+\mathrm{H}^+}{\overset{-\mathrm{H}^+}{\rightleftharpoons}} \mathrm{ML} \qquad (1)$$

where H_2L is **I** or **II**, HL is **III**, L is **IV** and M is Cu^{II} or Ni^{II}. The acid character of the complexes was also investigated by potentiometric titration of 10^{-3} M solutions with 10^{-3} M NaOH. Plots of pH *vs.* the volume of NaOH, Fig. 3, show inflections corresponding to $pK_{a_1} = 5.35$ and $pK_{a_2} = 8.08$ for the nickel(II) complex under an ionic strength, $I = 0.1$ M, adjusted with $NaClO_4$. A $pK_{a_1} = 5.40$ and a $pK_{a_2} = 7.40$ were calculated for the copper(II) complex. It is apparent that the effect of the metal is more pronounced on the second acid dissociation.

Electrochemistry

Two irreversible waves with peaks at −1.115 (reduction) and 1.33 V (oxidation) *vs.* SCE were recorded with solutions of the ligand **I** in N_2-saturated CH_3CN. The respective cyclic voltammograms of the copper(II) and nickel(II) complexes were characterized by irreversible waves. Irreversible cathodic peaks at −0.9, −1.25 and −1.40 V *vs.* SCE were observed with N_2-saturated solutions of $Cu^{II}(\mathbf{I})Cl_2$. Cathodic peaks at −0.93 and −1.28 V *vs.* SCE were observed in similar experiments with $Ni^{II}(\mathbf{I})Cl_2$. These peaks can be respectively assigned in the order of decreasing potential to the $M^{II/I}$ couple, the reduction of the ligand and to the $Cu^{I/0}$ couple, *i.e.* the demetallation of the copper complex.

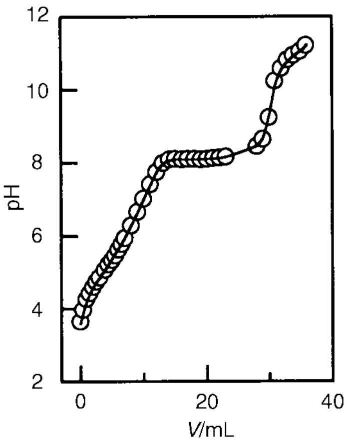


Fig. 3 Acid behaviour of $Ni(\mathbf{I})^{2+}$. Changes of pH with the volume of 10^{-3} M NaOH added to a 10^{-3} M solution of the complex in MeOH–10% v/v water.

The reduction wave of CO_2 was observed at near −2.6 V *vs.* SCE in CO_2 saturated solutions of the copper(II) complex. While the catalysed wave is near that of the uncatalysed CO_2 reduction in a blank without complex, the absence of any detectable demetallation and a much higher efficiency for the CO_2 reduction were characteristics of the catalysed reduction. This behaviour correlates well with the electrochemical behaviour of other complexes.[20–22] It is possible that demetallation is prevented by the formation of adducts either or both between CO_2 and the copper(I) product and the parent copper(II) macrocycle. Such adducts were previously observed with related macrocyclic complexes.[23]

The cyclic voltammetry of the nickel complex in CO_2 saturated solutions showed no increase in the efficiency of the CO_2 reduction.

Luminescence of the complexes

The effect of the ground state, eqn. (1), and excited state, eqn. (2), equilibria on the luminescence of the complexes was

$$\mathrm{M(H_2L)^{2+}}\,{*} \underset{+\mathrm{H}^+}{\overset{-\mathrm{H}^+}{\rightleftharpoons}} \mathrm{M(HL)^{+}}\,{*} \underset{+\mathrm{H}^+}{\overset{-\mathrm{H}^+}{\rightleftharpoons}} \mathrm{ML}{*} \qquad (2)$$

investigated as a function of the medium and excitation wavelength. Irradiation of $Cu^{II}(\mathbf{I})^{2+}$ at 400 nm in deaerated CH_3CN or MeOH leads to a broad emission centred at 600 nm. A weakly structured emission centred at 400 nm is observed upon irradiation at 300 nm, Fig. 4(a). The emission spectrum of the nickel(II) complex was the same in CH_3CN and MeOH and exhibited the dependence on base and excitation wavelength shown in Fig. 4(b). It must be noted that similar features were observed in the emission spectra respectively recorded in 300 nm irradiations of the protonated ligand, the copper(II) and the nickel(II) complexes. The dependence of the emission spectra on medium conditions and excitation wavelength suggests that light is absorbed by several species in eqn. (1). Moreover the relaxation of equilibria (2) appears to occur with a rate comparable to the rate of decay of the excited species. Luminescence lifetimes shorter than 30 ns were measured at λ_{em} 400 and 600 nm with deaerated solutions under various medium conditions, Table 2. In most of the cases traces had to be fitted by a double exponential decay, $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$.

Table 2 Emission lifetimes of the macrocyclic ligand **I** and its complexes of Ni and Cu measured upon irradiation at 337 nm

		τ/ns	
Compound	Solvent	λ_{em} = 400 nm	λ_{em} = 600 nm
Cu(**I**)Cl$_2$	CH$_3$CN	2.7 ± 0.3 8.0 ± 0.3	3.7 ± 0.1 14.6 ± 0.6
	MeOH	1.3 ± 0.4 5.2 ± 0.08	1.8 ± 0.1^a 21.3 ± 0.3
Ni(**I**)Cl$_2$	CH$_3$CN	5.22 ± 0.01 11.95 ± 0.01	12.9 ± 0.1^b
	MeOH	5.4 ± 0.2 19 ± 2	6 ± 1 20.3 ± 0.5
I·2HCl	CH$_3$CN	7.35 ± 0.04^b	3.8 ± 0.6 14.4 ± 0.4
	MeOH	5.42 ± 0.01^b	3.2 ± 0.2 17.1 ± 0.7

^{a} The data were better fitted by a three exponential decay with lifetimes τ_1 = 0.33 ± 0.008, τ_2 = 4.5 ± 0.5 and τ_3 = 24.5 ± 0.9 ns. ^{b} The data were better fitted by a single or double exponential decay.

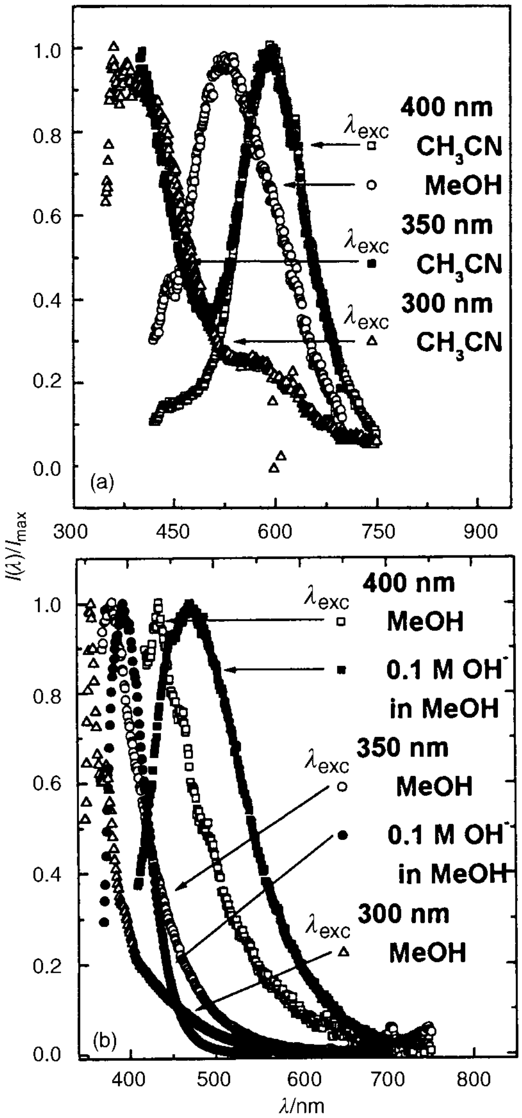


Fig. 4 Room temperature emission spectra of copper(II) (a) and nickel(II) (b) complexes of **I** in various deaerated solutions recorded by irradiation at various wavelengths and medium conditions.

Luminescence quenching

Attempts to ascertain the role of the excited species in eqn. (2) by quenching the luminescence with Cu(CH$_3$CN)$_6^{2+}$ resulted in a more complex photophysical process. A shift of the Cu^{II}(**I**)$^{2+}$ emission spectrum and quenching of the emission were recorded with deaerated solutions of the complex containing Cu(CH$_3$CN)$_6^{2+}$ in various concentrations, Fig. 5. Since the UV-Vis absorption spectrum of solutions containing Cu(CH$_3$CN)$_6^{2+}$ and Cu^{II}(**I**)$^{2+}$ was different from that resulting from adding the spectra of the individual species, it must be concluded that there is some ground state association between these species. Also the dependence of the rate of luminescence decay on Cu(CH$_3$CN)$_6^{2+}$ concentration, *i.e.* faster than diffusion control at low Cu(CH$_3$CN)$_6^{2+}$ concentrations, suggested a static mechanism of quenching. This proposition was also confirmed by the results of flash photolysis experiments described below. Moreover, different rates of decay of the electronically excited species in eqn. (2) and the Cu(CH$_3$CN)$_6^{2+}$ adduct(s) account for the displacement of the maximum in the emission spectrum and the progressive quenching of the emission.

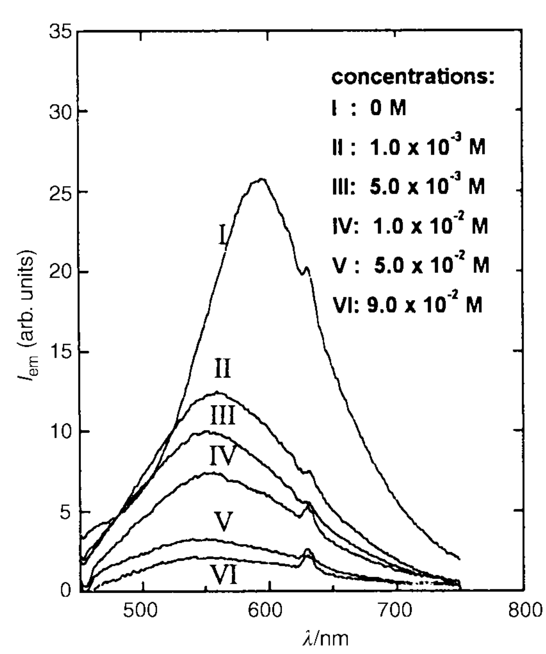


Fig. 5 Quenching of the Cu(**I**)$^{2+}$ emission by Cu(CH$_3$CN)$_6^{2+}$. Spectra recorded by irradiating deaerated solutions in CH$_3$CN at 400 nm. The key gives the concentrations of Cu(CH$_3$CN)$_6^{2+}$.

Flash photochemical observations

Transient absorption spectra were recorded in 351 nm flash irradiations of M^{II}(**I**)$^{2+}$, M = Ni or Cu, in deaerated CH$_3$CN or MeOH with delays of several hundred ns relative to the laser irradiation, Figs. 6, 7. It must be noted that the lifetimes of the transients observed with these complexes are much larger than those recorded for the luminescence, Table 3. The species associated with these absorption spectra are not, therefore, the luminescent species in eqn. (2) and must be assigned as reaction intermediates. A comparison of the observed transient spectra and literature spectra of naphthyl radicals suggests that they are related species.[24–26]

The spectra recorded in CH$_3$CN exhibited a maximum at 525 nm. In methanolic solutions, the band maximum shifted below 400 nm. A less defined maximum in Pr^{i}OH appears to be a convolution of the 400 and 525 nm maxima. Oscillographic traces recorded at various wavelengths were well fitted by a single exponential and the rate of decay exhibited no dependence on the concentration of the flash-generated species. Also, the rate constant calculated in these experiments exhibited little if any dependence on medium conditions, Table 3. The presence of 5.0 × 10^{-3} M Cu(CH$_3$CN)$_6^{2+}$ makes the transient spectra, Fig. 6(b), resemble the one in Pr^{i}OH and leads to longer lived species. The spectral features and formation of long-lived products are consistent with the formation of an adduct that in the excited state undergoes electron transfer reactions.

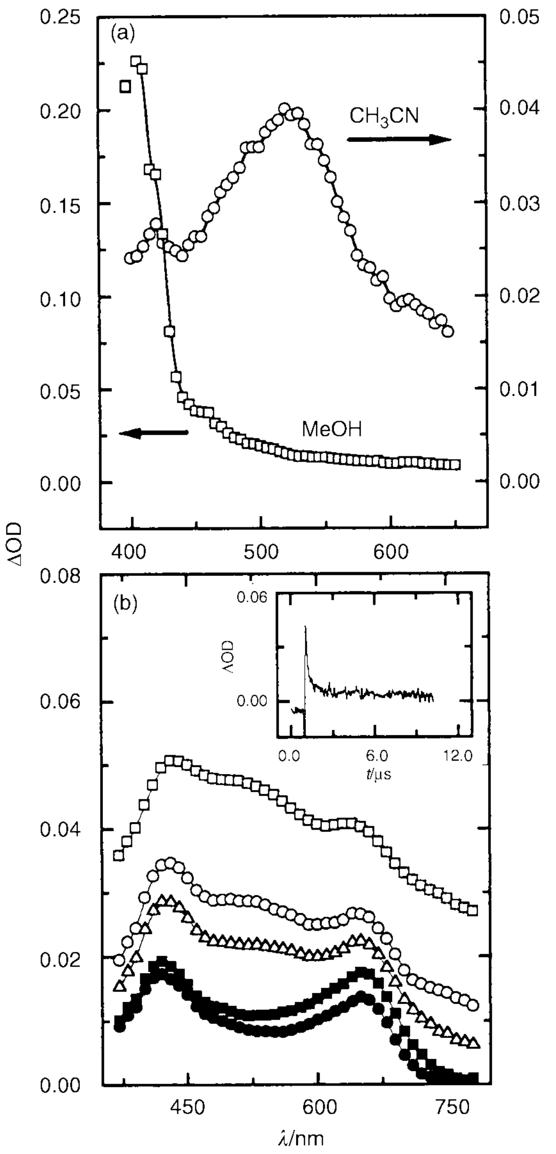


Fig. 6 Transient spectra generated after the 351 nm laser flash irradiation of 8×10^{-5} M $Cu(I)^{2+}$ in (a) deaerated MeOH, □, and CH_3CN, ○, with 100 ns delays after the laser irradiation. The spectra in (b) were recorded in CH_3CN in the presence of 5.0×10^{-3} M $Cu(CH_3CN)_6^{2+}$ and the trace in the inset showing the formation of long-lived products was recorded at λ_{mon} 480 nm. The delays used for the determination of the spectra were, from top curve to bottom curve, 0.29, 0.49, 0.69, 0.89 and 1.19 μs.

Table 3 Rate constants measured for the decay of flash-generated transient absorptions

Medium	λ_{obs}/nm	$k \times 10^{-6}$/s^{-1}
$Cu(I)^{2+}$		
CH_3CN	525	1.5
CH_3CN, CO_2 sat.	525	0.75
$(CH_3)_2CHOH$	425	7.8
	515	7.6
$(CH_3)_2CHOH$, 10^{-4} M AcOH	425	0.64
	500	2.2
$(CH_3)_2CHOH$, CO_2 sat.	525	0.35
CH_3OH	400	0.47
CH_3OH, CO_2 sat.	400	0.47
$Ni(I)^{2+}$		
CH_3CN	440	0.57
$(CH_3)_2CHOH$	440	0.59
CH_3OH	440	0.7
CH_3OH, 1×10^{-4} M NBu_4OH	440	0.87
CH_3OH, 1×10^{-1} M NBu_4OH	445	12
	630	0.077

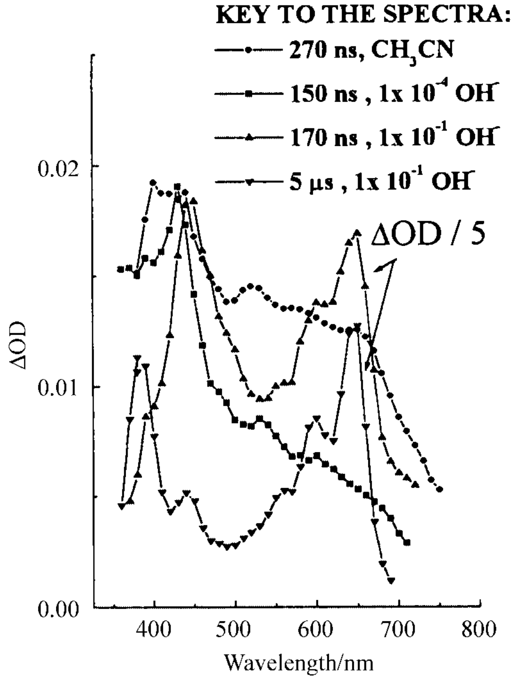


Fig. 7 Transient spectra recorded with given delays after the 351 nm laser flash irradiation of $Ni(I)^{2+}$ in deaerated solutions. The solvent is MeOH unless specially indicated.

By contrast to the copper complex, 351 nm flash irradiations of the $Ni^{II}(I)^{2+}$ complex in deaerated solutions produced transient spectra with a maximum at 440 nm, Fig. 7 and Table 3. In basic methanolic solutions, *i.e.* those containing NBu_4OH in concentration larger than 10^{-3} M, new absorptions at 550–680 nm were observed in addition to the 440 nm feature. The near IR absorptions decayed with a longer lifetime, $\tau \approx 22$ μs, than those at 440 nm, $\tau \approx 0.14$ μs.

The experimental observations made in irradiations of Ni^{II} and Cu^{II} at 337 nm were similar to those reported above for irradiations at 351 nm.

Steady state photolysis

Steady state irradiations of deaerated solutions of the complexes of **I** at 370 nm were carried out for periods shorter than 1 h. The small spectral changes observed in these photolyses suggested a trace formation of the complexes of **II** with a rate not linearly dependent on the absorbed light intensity, $I_{ab} \approx 10^{-4}$ Einstein dm^{-3} s^{-1}. A rough estimate of the photoisomerization quantum yield gave an upper limit, $\varphi \leq 10^{-4}$. It is apparent that the decay of the transient species observed in flash photolysis mostly regenerates the starting material. Photolyses of the complexes of **II** induced negligible spectral changes under the experimental conditions indicated above.

Discussion

The acid nature of the complexes of Ni^{II} and Cu^{II} is reflected in their electrochemical, photophysical and photochemical properties. In basic media, the disappearance of the 300 nm features, Fig. 2, in the absorption spectra of the complexes of **I** and **II** are indicative of pronounced changes in the electronic structure of the naphthalene chromophores. Deprotonation of amino groups in **I** may occur with charge localization in the planar six-membered chelate rings of the macrocycle to yield **III** and **IV** in a manner similar to that seen previously.[7–10] Since tautomeric structures **I** and **II** have been isolated and remain stable in solution, there must be sufficient steric strain in the planar six-membered chelate ring to make the interconversion of **I** and **II** a slow process. Indeed, the irreversibility of the metal-centred electrochemical reactions could be caused by energetically demanding nuclear reorganizations which may include displacements of the metal centre from the plane of the nitrogens.[10]

The acid–base properties of the macrocyclic complexes are also observed in their excited states and will be considered in the following paragraphs.

(a) Acid–base properties of the excited state

In photochemical experiments with neutral solutions the species **I** is predominant but **III** or a mixture of **III** and **IV** could be present in basic solutions. A comparison of the luminescence of the Ni^{II} and Cu^{II}, Fig. 4, with related phenomena in naphthalene derivatives, *e.g.* naphthols and naphthylamines,[27,28] suggests that the complexes' luminescence is originated in naphthalene-centred excited states. This assignment is also supported by the lack of luminescence from ligand field or charge transfer excited states of Cu^{II} and Ni^{II}.

Changes in the absorption and emission spectra of these complexes with solvent, base concentration and excitation wavelength show that ground state equilibria allow more than one species to coexist under various medium conditions. Moreover, the disparity between the emission lifetimes measured respectively at 400 and 600 nm, Table 2, suggests that an equilibration or conversion between excited states is not completely achieved during the lifetime of these excited species under the various experimental conditions. The complex kinetics of the luminescence appears to indicate that the decay of such excited species with intrinsic lifetimes is kinetically coupled to the relaxation of equilibria (2). Under some other experimental conditions, a relaxation of the equilibria (2) achieves a rate comparable to the rates of decay of the various excited species. Such a kinetic coupling results then in a single exponential decay of the luminescence. In this context, the emission lifetimes in Table 2 reflect more the combined kinetics of equilibria relaxation and decay of electronically excited species to the ground state than acid–base properties in the excited state.

(b) Intramolecular redox reactions of the excited state

Long lived intermediates are formed within the lifetime of the excited species in eqn. (2). One rationale of this experimental observation is that the formation of the intermediates constitutes a form of decay of the excited species as is shown in eqn. (3). The top and bottom parentheses of eqn. (3) respectively represent the excited species in eqn. (2) and the ground state species in eqn. (1). Support to eqn. (3) is provided by transient spectra recorded in flash irradiations of copper(II) and nickel(II) complexes of **I** in neutral or acid media. Such spectra display intense absorptions below 425 nm that are similar to those seen in the literature spectra of naphthyl anion radicals.[19–21] The absence of such intermediates in the photolysis of complexes of **II** suggests that amino groups in the tautomer **I** or negatively charged six-membered rings in **III** or **IV** function as electron donors to a naphthyl group. An amino group of the six-membered ring of the diamino macrocycle functions as an electron donor to produce I_1. Electron transfer from the six-membered ring in the anionic macrocycle will form an intermediate I_2 in a basic medium where the concentrations of **III** and/or **IV** are chemically significant. A shift of the absorption spectrum of I_2 to longer wavelengths with respect to the spectrum of I_1 can be expected on the basis of their different electronic structures. Experimental observations, Fig. 7, with the nickel(II) complex indicate that the conversion of I_1 into I_2 may be too slow to compete with regeneration of the ground state species. Therefore, different lifetimes must be observed, in accordance with the results, at different probing wavelengths.

(c) Adduct formation and photophysics

The quenching of the excited state emission by $Cu(CH_3CN)_6^{2+}$ must be described by static and dynamic processes. The former can be related to the formation of the ground state adducts that were made evident by changes in the absorption spectrum of the complexes of **I**. Modifications to the emission spectrum and to the decay kinetics of excited species can be associated with displacements of ground and excited state equilibria similar to those in eqns. (1), (2). In addition, the photochemical processes of electronically excited adducts emphasize differences between experimental observations made in the presence and absence of $Cu(CH_3CN)_6^{2+}$. Some spectral features in time-resolved experiments and the formation of long-lived products in solutions containing $Cu(CH_3CN)_6^{2+}$ suggest that the electronically excited adducts undergo intramolecular electron transfer reactions. Although these can be intrinsic reactions of the excited adduct, it is possible that they are the same as those observed in the absence of quencher but are now favoured over the decay to the ground state.

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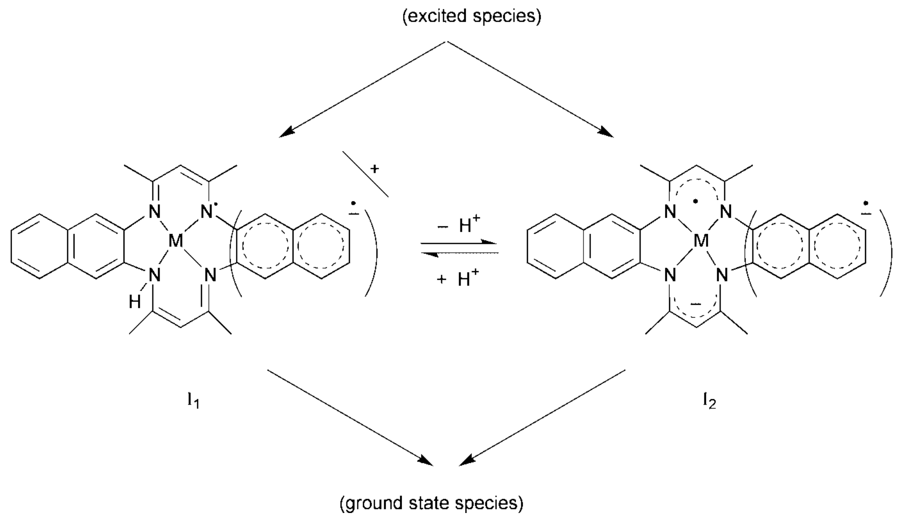

(3)

References

1 J. Costamagna, G. Ferraudi, J. Canales and J. Vargas, *Coord. Chem. Rev.*, 1996, **148**, 221.

2 J. Costamagna, G. Ferraudi, B. Matsuhiro, M. Campos, J. Canales, M. Villagrán, J. Vargas and M. J. Aguirre, *Coord. Chem. Rev.*, 1999, **196**, 125.

3 V. Lepentsiotis, J. Domagala, I. Grgic, R. van Eldik, J. G. Muller and C. J. Burrows, *Inorg. Chem.*, 1999, **38**, 3500.

4 S. C. Gibney, G. Ferraudi and M. Shang, *Inorg. Chem.*, 1999, **38**, 2898 and references therein.

5 T. Koike, T. Watanabe, S. Aoki, E. Kimura and M. Shiro, *J. Am. Chem. Soc.*, 1996, **118**, 12696.

6 G. Ferraudi, in *Phthalocyanines, Properties and Applications*, C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989, ch. 4.

7 J. G. Martin, R. M. C. Wei and S. C. Cummings, *Inorg. Chem.*, 1972, **11**, 475.

8 J. G. Martin and S. C. Cummings, *Inorg. Chem.*, 1972, **11**, 1477.

9 V. Goedken, J. Molin-Case and Y. A. Whang, *J. Chem. Soc.*, *Chem. Commun.*, 1973, 337.

10 F. A. Cotton and J. Czuchajowska, *Polyhedron*, 1990, **9**, 2553.

11 C. Bailey, R. Bereman, P. D. Rillema and R. Nowak, *Inorg. Chem.*, 1984, **23**, 39.

12 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London*, *Ser. A*, 1956, **235**, 518.

13 J. E. Endicott, G. Ferraudi and J. R. Barber, *J. Phys. Chem.*, 1975, **79**, 630.

14 M. Sarakha and G. Ferraudi, *Inorg. Chem.*, 1999, **38**, 4605.

15 M. Feliz and G. Ferraudi, *Inorg. Chem.*, 1998, **37**, 2806.

16 R. E. Kitson, *Anal. Chem.*, 1957, **22**, 664.

17 J. F. Coetzee, G. P. Cunningham, D. K. McGuire and G. R. Padmanabhan, *Anal. Chem.*, 1962, **31**, 1139.

18 I. M. Kolhoff and J. F. Coetzee, *J. Am. Chem. Soc.*, 1957, **79**, 870.

19 B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.

20 I. Bhugun, D. Lexa and J. M. Saveant, *J. Phys. Chem.*, 1996, **100**, 19981.

21 I. Bhugun, D. Lexa and J. M. Saveant, *J. Phys. Chem.*, 1996, **118**, 1769.

22 B. R. Eggins and J. McNeill, *J. Electroanal. Chem. Interfacial Electrochem.*, 1983, **148**, 17.

23 J. Vargas, G. Ferraudi, J. Canale and J. Costamagna, *Inorg. Chim. Acta*, 1994, **226**, 151.

24 E. L. Evers, G. G. Jayson, I. D. Robb and A. J. Swallow, *J. Chem. Soc.*, *Faraday Trans.*, 1980, 528.

25 J. H. Fendler, H. A. Gillis and N. V. Klasen, *J. Chem. Soc.*, *Faraday Trans.*, 1974, 145.

26 A. Treinin and E. Hayon, *J. Am. Chem. Soc.*, 1976, **98**, 3884.

27 G. Jackson and F. R. S. Porter, *Proc. R. Soc. London*, *Ser. A*, 1961, **260**, 30.

28 A. D. Head, A. Sigh, M. G. Cook and M. J. Quin, *Can. J. Chem.*, 1973, **51**, 1624.