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A single- and double-flash flash photolysis study of the sequential biphotonic photoprocesses of Cu(I) phenanthrolines. Comparison of the helicate complex, $[Cu_2(1,3\text{-bis}(9\text{-methyl-}1,10\text{-phenanthrolin-}2\text{-yl})\text{-propane})_2]^{2+}$, and $[Cu(2,9\text{-dimethyl-}1,10\text{-phenanthroline})_2]^{+}$ photoprocesses

L. Lemus,*[a] G. Ferraudi*[b] and A. Graham Lappin[c]

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Photochemical processes induced when two photons are sequentially absorbed by the helicate complex $[Cu_2(mphenpr)_2]^{2+}$, where mphenpr = 1,3-bis(9-methyl-1,10-phenanthrolin-2-yl)propane, and $[Cu(dmp)_2]^{+}$ were investigated in CH_2Cl_2 containing solvents. A strong resemblance was observed between the fs–ns photophysics of $[Cu_2(mphenpr)_2]^{2+}$ and Cu(I) phenanthroline complexes having a large steric hindrance. In the biphotonic regime, single-flash flash-photolyzed solutions were used for the determination of the product concentrations and quantum yields. The concentration of Cl^- produced by the photoinduced decomposition of CH_2Cl_2 increases linearly with flash intensity as expected for a monophotonic process. In contrast, the concentration of a decomposed Cu(I) complex exhibits the quadratic dependence on flash intensity of a biphotonic process. Results of a sequential double-flash flash photolysis experiment are consistent with the decomposition of CH_2Cl_2 ahead of the flattened excited state formation and with the absorption of the second photon by the flattened MLCT excited state.

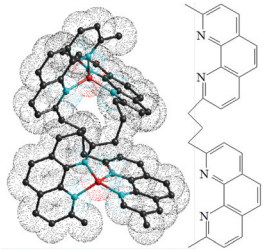
Introduction

Great effort has been directed to the preparation of novel Cu(I) complexes and to the study of their thermal and photochemical reactions.[1–8] In particular, attention has been paid to Cu(I) complexes containing the 1,10-phenanthroline, phen, group in the ligand and tetracoordinating ligands able to form supramolecular complexes. Besides the novel structure of these complexes,[4,9–13] the promise of practical applications to solar energy conversion and to information technologies has fueled the interest in these families of compounds. Starting with the pioneering work of McMillin *et al.*,[14–19] the photophysics of the tetrahedral $[Cu(NN)_2]^{+}$ complexes, where NN is a derivative of 1,10-phenanthroline with or without bulky substituents in the 2,9 positions, has been exhaustively investigated.[5–8,14,16–19] The experimentally established photophysical processes include the instantaneous formation of the Franck–Condon, FC, singlet metal-to-ligand charge transfer excited state, ^{1}MLCT, upon the absorption of light. The most accepted sequence of processes involves the following sequential processes.[20–24] The flattening of the initial tetrahedral or pseudo-tetrahedral structures of the FC ^{1}MLCT within a subpicosecond time scale, *e.g.* ~0.8 ps. Intersystem crossing from the flattened ^{1}MLCT to the lowest ^{3}MLCT is the second component occurring in tens of ps. Neither of these processes exhibits a solvent dependent kinetics, for example, on the donor strength of the solvent. Exciplex formation between the solvent and the ^{3}MLCT is the third step of the photonic energy degradation occurring in a time domain of nanoseconds.

Although these photophysical processes take place in a number of solvents, the biphotonic decomposition of $Cu(dmp)_2^{+}$, dmp = 2,9-dimethyl-1,10-phenanthroline, and the formation of Cl^- ions have been observed when solutions of the complex in CH_2Cl_2 are irradiated with high intensity monochromatic light in the UV-vis region.[16]

In contrast to $Cu(dmp)_2^{+}$ which is stable in $CH_{4-n}Cl_n$, n = 2–4, solutions, the helicate complex $[Cu_2(mphenpr)_2]^{2+}$, (I) in Scheme 1, where mphenpr = 1,3-bis(9-methyl-1,10-phenanthrolin-2-yl)propane, (II) in Scheme 1, slowly uncoils in $CH_{4-n}Cl_n$,

[a]*Facultad de Química y Biología, Universidad de Santiago de Chile, Av. Libertador Bernardo O'Higgins 3363, Estación Central, Santiago, Chile*
[b]*Radiation Research Building, Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA. E-mail: ferraudi.1@nd.edu*
[c]*Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA*



$[Cu_2(mphenpr)_2]^{2+}$ mphenpr

(I) (II)

Scheme 1

n = 2, 3, to form the monometallic $[Cu(mphenpr)]^+$ complex and it undergoes an oxidative decomposition, eqn (1), in CCl_4.[25]

$$[Cu_2(mphenpr)_2]^{2+} + CCl_4 \rightarrow [Cu^{II}Cu^{I}(mphenpr)_2]^{3+} + Cl^- + CCl_3^{\cdot} \quad (1)$$

We have investigated in this work whether the differences in the thermal reactivity of $Cu(dmp)_2^+$ and $[Cu_2(mphenpr)_2]^{2+}$ were reflected also in their photophysical and photochemical properties. In doing so, it was established that Cl^- from the photoreduction of CH_2Cl_2 took place *via* a monophotonic process while a parallel photodecomposition of the complexes was a biphotonic process.

Experimental

Materials

$[Cu(dmp)_2]PF_6$ and $[Cu(mphenpr)](ClO_4)_2$ were available from a previous work and used without further purification.[25] Other chemicals were of reagent grade and used without further purification.

Solution preparation

Intense transient spectra were observed in flash photolysis of the complexes in deaerated Fisher Scientific stabilized HPLC grade CH_2Cl_2. Because of the proximity of the boiling points of the stabilizer and CH_2Cl_2, cumbersome separation and purification procedures are required to eliminate the stabilizer from CH_2Cl_2. However, transient spectra were not observed when Fisher Scientific HPLC grade CH_2Cl_2 non-stabilized was used for the preparation of the solutions. Therefore, the solutions for photochemical work were made with freshly opened bottles of non-stabilized CH_2Cl_2. They were deaerated 30 min before the irradiation and all through the experiment with streams of Ultra-High Purity N_2.

It has been previously shown that $[Cu_2(mphenpr)_2]^{2+}$ is converted to the mononuclear species $[Cu(mphenpr)]^+$ with solvent dependent rates.[25] In a 10% (v/v) CH_2Cl_2–MeOH mixed solvent, the uncoiling occurs for a period longer than 24 h. Therefore all the photochemical work was done with freshly prepared deaerated solutions of $[Cu_2(mphenpr)_2]^{2+}$ in the CH_2Cl_2–MeOH mixed solvent.

Single-flash flash photolysis

Absorbance changes, ΔA, occurring in a time scale longer than 10 ns were investigated with a flash photolysis apparatus described elsewhere.[26,27] In these experiments, 10 ns flashes of 351 nm light were generated with a Lambda Physik SLL-200 excimer laser or 1 ns flashes of 532 nm were generated with an Nd YAG laser, Continuum's Powerlite. The energy of the laser flash was attenuated to values equal to or less than 20 mJ per pulse by absorbing some of the laser light in a filter solution of $Ni(ClO_4)_2$ with the appropriate optical transmittance, $T = I_t/I_0$. I_0 and I_t are respectively the intensities of the light arriving at and transmitted from the filter solution. The transmittance, $T = 10^{-A}$, was routinely calculated from the recorded absorbance, A, of the filter solution. A right angle configuration was used for the pump and the probe beams. Concentrations of the Cu(I) compounds were adjusted to provide homogeneous concentrations of photogenerated intermediates over the optical path, l = 1 cm, of the probe beam. To satisfy this optical condition, solutions were made with an absorbance equal to or less than 0.8 over the 0.2 cm optical path of the pump.

A CPA-2010 1 kHz Amplified Ti:Sapphire Laser System from Clark MXR and software from Ultrafast Systems were used for the observation of transient absorption spectra and the study of reaction kinetics in a 1.6 ns time domain. The flash photolysis apparatus provides 775, 387 or 258 nm laser pulses for excitation having a 150 fs bandwidth. Data points can be collected at intervals equal to or longer than 10 fs. A slow but constant flow of the solutions through a 2 mm cuvette was maintained during the photochemical experiments.

Dependence of the product concentration on laser flash intensity

Concentrations of a decomposed Cu(I) complex and Cl^- produced in the photolysis were determined as a function of the flash intensity. A fixed volume, V = 4 cm^3, of a deaerated solution of the Cu(I) complex was irradiated with a number, $n_{h\nu}$, of 532 nm flashes from the Nd YAG laser. The intensity of the flashes was attenuated to the desired value interposing a cell with H_2O or an $Ni(ClO_4)_2$ filter solution between the laser and the photolyte's cell. The total Cl^- concentration produced at the end of the photolysis, $[Cl^-]_{total}$, was determined with an ion specific electrode and it was normalized to the concentration per flash, $[Cl^-] = [Cl^-]_{total}/n_{h\nu}$. To estimate the concentration of the complex decomposed in each flash irradiation, the induced optical changes were monitored at λ_{ob} = 445 nm where the maximum bleach of the solution is observed. The absorbance change, ΔA_{445}, was calculated from an average of $n_{h\nu}$ traces collected using the same solution that will be used for the Cl^- analysis.

Double-flash–flash photolysis

The basic procedure and an early apparatus used for double-flash irradiations have been described elsewhere.[28,29] In the experiments, two lasers, a Lambda Physik SLL-200 and an Nd YAG Continuum Powerlite, were sequentially fired. The delay of the second laser with respect to the first could be set to a constant value between 0 and 1 μs with a jitter, $\delta t \leq \pm 0.2$ ns. While the excimer laser, Lambda Physik's SLL-200, was used as a source of the first pulse, an Nd YAG laser, Continuum Powerlite, was used for the generation of the second 532 nm pulse of light. The amounts of chemical products of the secondary photolysis were calculated in terms of the optical changes caused by two laser pulses fired sequentially and by each individual laser pulse. Delays used in the sequential firing of the lasers and specific details of the absorbance change calculation are described in the Results section. Solutions of the photolyte were refreshed after each irradiation. Laser energies were measured during each set of irradiations with a Scientech energy meter and values of the laser pulse energy divided by the frequency of the laser light were regarded proportional to the number of photons delivered by the flash.

Time-resolved fluorescence measurements

Time-resolved fluorescence experiments were carried out with a previously described PTI flash fluorescence instrument. The excitation light was provided by an N_2 laser (λ_{ex} = 337 nm, *ca.* 2 mJ per pulse and 200 ps bandwidth at half height).

Results

Photoprocesses of $[Cu_2(mphenpr)_2]^{2+}$ in the fs to 10^2 ns time domain

Transient spectra were recorded in a fs to ns time domain flash irradiating a deaerated 3.0×10^{-4} M $[Cu_2(mphenpr)_2]^{2+}$ solution in the CH_2Cl_2–MeOH mixed solvent at 387 nm. The observed changes in the shape of the spectra in this time period closely resemble those observed with other Cu(I)–phenanthrolines having cumbersome groups attached to the ligand, $Cu(phenR_2)_2^+$ where R = *n*-hexyl and 4-*n*-butylphenyl, Fig. 1.[8] Based on the previous work, the transient spectra are assigned to an excited state with a flattened structure. The decay of the luminescence occurs with lifetime comparable to those communicated for the $Cu(phenR_2)_2^+$, R = *n*-hexyl and 4-*n*-butylphenyl, in CH_2Cl_2. To investigate the luminescence of the $[Cu_2(mphenpr)_2]^{2+}$, a deaerated 5.0×10^{-4} M solution of the complex in the CH_2Cl_2–MeOH mixed solvent was flash irradiated at 337 nm with 1 mJ pulses of the N_2 laser. The decay of the emission, followed at 700 nm, was fitted to a single exponential, exp $(-t/\tau_{ems})$ with a lifetime $\tau_{ems} = (56 \pm 3)$ ns, Fig. 2. The rate constant $k = (1.78 \pm 0.01) \times 10^7$ s^{-1} was calculated as the inverse of τ_{ems}. Some differences were observed between the decays of the luminescence and the transient absorption spectrum. Irradiation of a similar solution at 351 nm with 10 mJ flashes of the excimer laser produces a transient

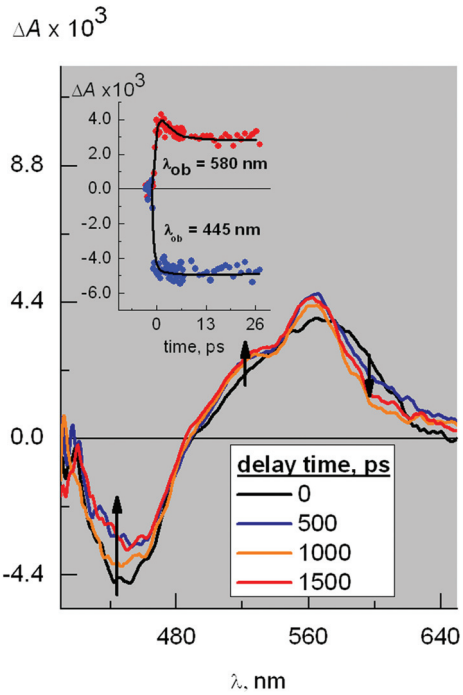


Fig. 1 Transient spectra recorded in a ps to ns time domain when a deaerated solution of 5.0×10^{-4} M $[Cu_2(mphenpr)_2]^{2+}$ in CH_2Cl_2 was irradiated at 387 nm. Two oscillographic traces showing the absorbance changes recorded at λ_{ob} = 580 nm (top) and 445 (bottom) are presented in the inset.

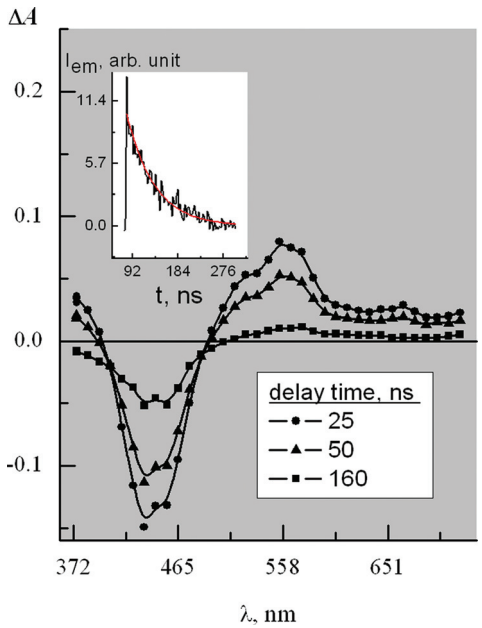


Fig. 2 Transient absorption spectra generated when a deaerated solution of 1.0×10^{-4} M $[Cu_2(mphenpr)_2]^{2+}$ in CH_2Cl_2 is irradiated at 351 nm. Delays from the laser flash irradiation are shown in the figure. A trace in the inset shows the decay of the luminescence at λ_{ob} = 700 nm. The trace in the figure was calculated as the average of 50 oscillographic traces, each one recorded irradiating the $[Cu_2(mphenpr)_2]^{2+}$ solution at 337 nm. A least squares fit of the trace to an exponential, $I_{em} = I_{em,\ t=0} \times \exp(-t/\tau_{ems})$, is superimposed with the trace.

spectrum with the features of the excited state, Fig. 2. The lifetime of the monoexponential disappearance of the transient spectrum was calculated with traces collected at λ_{ob} = 445 nm for the recovery of the bleach and 560 nm for the decay of the absorbance. The decay lifetime $\tau = (74 \pm 4)$ ns $(1/\tau = k = (1.35 \pm 0.07) \times 10^7\ s^{-1})$ is slightly longer than the one calculated for the luminescence decay. Moreover, the initial spectrum of the solution was not recovered after the disappearance of the transient spectrum. A noticeable bleach of the 445 nm absorption band of the $[Cu_2(mphenpr)_2]^{2+}$, ΔA_{445}, remained after the decay of the transient spectrum. Previous work by McMillin *et al*. has shown that a similar spectroscopic change and the production of Cl^- when $Cu(dmp)_2^+$ is photolyzed in CH_2Cl_2 are caused by the sequential absorption of two photons by the complex.[16]

The lifetimes obtained from oscillographic traces corresponding to the absorbance and emission decays showed no dependence on the laser flash intensity and for this reason on the concentration of excited state. Bimolecular processes such as the excited state–excited state annihilation reaction do not account therefore for the mentioned experimental observations. The latter reaction, being kinetically of a second order, has a concentration dependent half life period.

Light Intensity dependence of the photoprocesses

To investigate the dependence of the photoprocess on the laser light intensity, a deaerated 5.0×10^{-4} M solution of the complex in CH_2Cl_2 was flash irradiated at 532 nm with different laser powers. Both the concentration of Cl^- formed in the photoprocess, $[Cl^-]$, and ΔA_{445} were determined in the same photolyzed solution. The concentration of $[Cu_2(mphenpr)_2]^{2+}$ decomposed in the photolysis, $\Delta[[Cu_2(mphenpr)_2]^{2+}] = -\Delta A_{445}/\Delta\varepsilon \times 0.5$ where $\Delta\varepsilon = \varepsilon_{[Cu_2(mphenpr)_2]^{2+}} - \varepsilon_{mon}$, was calculated subtracting the extinction coefficient ε_{mon} of the monomeric product, $[Cu(mphenpr)]^+$, from the extinction coefficient of $[Cu_2(mphenpr)_2]^{2+}$, $\varepsilon_{[Cu_2(mphenpr)_2]^{2+}}$. This estimate of $\Delta[[Cu_2(mphenpr)_2]^{2+}]$ is made under the assumption that the photoprocess that decomposes $[Cu_2(mphenpr)_2]^{2+}$ can be represented by eqn (2) and that no products other than $Cu(mphenpr)^+$ with intense absorptions at 445 nm are formed.

$$[Cu_2(mphenpr)_2]^{2+} \xrightarrow{+h\nu} [Cu(mphenpr)]^+ + \text{products} \quad (2)$$

Different functional dependencies of $[Cl^-]$ and $\Delta[[Cu_2(mphenpr)_2]^{2+}]$ on the laser flash intensity can be observed in Fig. 3. The quadratic dependency of $\Delta[[Cu_2(mphenpr)_2]^{2+}]$ on the light intensity is expected for a photoprocess induced when two photons are sequentially absorbed by the complex. In contrast to $\Delta[[Cu_2(mphenpr)_2]^{2+}]$, the linear dependency of $[Cl^-]$ on the light intensity shows that the Cl^- formation requires the absorption of only one photon, Fig. 3. Based on the laser flash energy, a quantum yield of Cl^- formation $\phi \sim 4 \times 10^{-3}$ was estimated.

The photochemical formation of Cl^- and the decomposition of $[Cu(dmp)_2]^+$ in CH_2Cl_2 were investigated in order to have a basis of comparison with the biphotonic process of $[Cu_2(mphenpr)_2]^{2+}$. To this aim, a deaerated 5.0×10^{-4} M solution of the complex in neat CH_2Cl_2 was flash irradiated at 532 nm with different laser powers, Fig. 3. The depletion of the $[Cu(dmp)_2]^+$ concentration, $\Delta[[Cu(dmp)_2]^+] = -\Delta A_{445}/\varepsilon_{[Cu(dmp)_2]^+} \times 0.5$, was calculated using the extinction coefficient, $\varepsilon_{Cu(dmp)_2^+}$, of the complex at 445 nm. A χ^2 fitting of $\Delta[[Cu(dmp)_2]^+]$ to a 2nd degree polynomial is best when a linear term on the relative laser intensity is included. The linear dependence of $[Cl^-]$ on laser intensity is (as in the case of $[Cu_2(mphenpr)_2]^{2+}$) distinctive of a monophotonic process. This monophotonic decomposition of $[Cu(dmp)_2]^+$ is ascribed to the photogeneration of Cl^-. The quantum yield of Cl^- formation, $\phi \sim 1 \times 10^{-2}$, was calculated in one order of magnitude larger than in the $[Cu_2(mphenpr)_2]^{2+}$ complex.

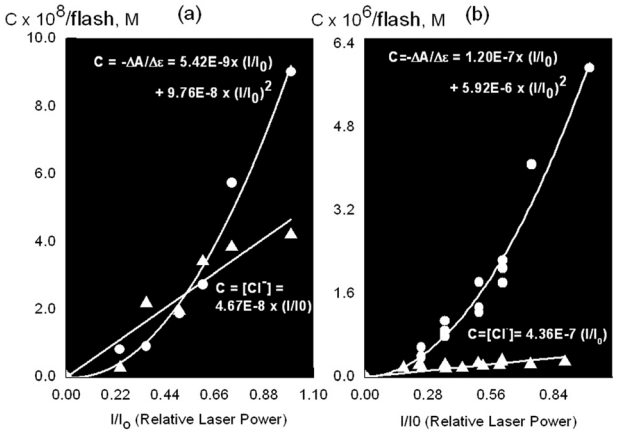


Fig. 3 Dependencies of the product concentrations, *C*, on the relative laser power I/I_0 where I_0 is the maximum laser power used in the experiments, *i.e.*, I_0 = 20 mJ per pulse. The dependencies of $[Cl^-]$ and $\Delta[[Cu_2(mphenpr)_2]^{2+}]$ are shown in (a). The dependencies of $[Cl^-]$ and $\Delta[Cu(dmp)_2^+]$ are shown in (b). The solid lines are the respective least squares fits of the data to a first and a second degree polynomial whose equations are shown in the figure.

Photoresponse in double-pulse flash photolysis

A deaerated solution 2.0×10^{-4} M of $Cu(dmp)_2^+$ in CH_2Cl_2 was irradiated with flashes of the excimer laser at 351 nm. The solution was also irradiated with 532 nm flashes from the YAG laser, each one of them delayed 1.5 ns with respect to a given flash of the excimer. The absorbance change, $\delta(\Delta A)$, caused by the double flash irradiation was calculated with eqn (3), Fig. 4.

$$\delta(\Delta A) = \Delta A_{XMR+YAG} - (\Delta A_{XMR} + \Delta A_{YAG}) \quad (3)$$

In eqn (3), $\Delta A_{XMR+YAG}$ is the absorbance change observed when the solution is irradiated with both lasers and ΔA_{XMR} and ΔA_{YAG} are the absorbance changes caused when the solution is irradiated by each laser alone. Absorption of the 532 nm light in the second flash by the MLCT excited state causes a prompt bleach of the absorbance at 580 nm. A growth of the solution's absorbance is observed after the prompt bleach. The absorbance growth was fitted to an exponential, $\delta(\Delta A_{XMR+YAG}) = (\delta\Delta A_{XMR+YAG,\ \infty}) + \delta(\Delta A_{XMR+YAG,\ 0}) - \delta(\Delta A_{XMR+YAG,\ \infty}) \times \exp(-t/\tau)$ where $(\delta\Delta A_{XMR+YAG,\ \infty})$ and

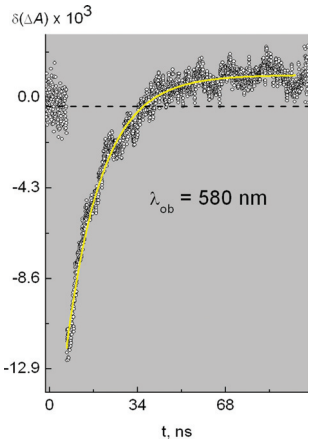
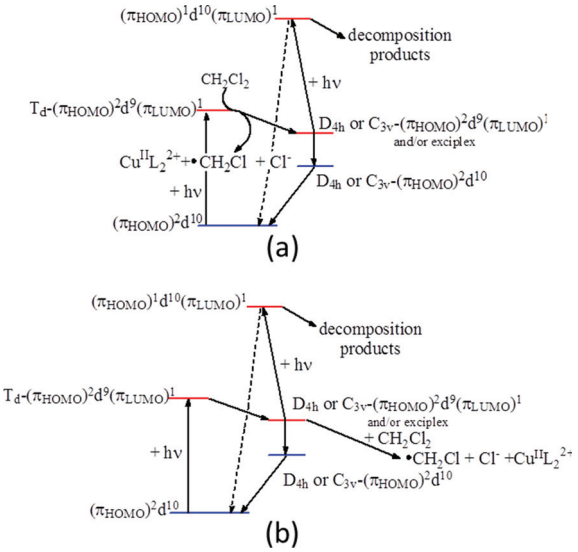


Fig. 4 Trace showing changes of $\delta(\Delta A)$ with time at λ_{ob} = 580 nm when a deaerated solution of 1.0 × 10^{-4} M $[Cu_2(mphenpr)_2]^{2+}$ in CH_2Cl_2 was irradiated at 351 nm (excimer laser) and 532 nm (Nd YAG laser). The excimer laser was triggered with a 7 ns delay relative to the oscilloscope and the YAG laser was triggered 1.5 ns after the extinction of 351 nm flash. The curve superimposed with the trace is least squares fitting of the data to the exponential growth.



Scheme 2

$\delta(\Delta A_{XMR+YAG,\ 0})$ are respectively the final and initial values of $\delta(\Delta A_{XMR+YAG})$. A good curve fitting with $\chi^2 = 10^{-7}$ and R^2 = 0.98 yields a lifetime τ = (13.7 ± 0.1) ns. The final value of $\delta(\Delta A_{XMR+YAG})$, $\delta(\Delta A_{XMR+YAG,\ \infty})$ = (1.07 ± 0.02) × 10^{-5} was reached after the growth completion. This value corresponds to an absorbance larger than the one the solution had prior to the double flash irradiation. It shows that the second flash irradiation of the solution forms a new product. An essentially similar experimental observation showed the formation of a product in the double-pulse flash photolysis of $[Cu_2(mphenpr)_2]^{2+}$. These experiments were carried out with a deaerated solution containing 4 × 10^{-4} M of $[Cu_2(mphenpr)_2]^{2+}$ in 10% (v : v) CH_2Cl_2 in MeOH.

Discussion

The experimental observations show that UV-vis irradiations of CH_2Cl_2 solutions of $Cu(dmp)_2^+$ and $[Cu_2(mphenpr)_2]^{2+}$ complexes induce in each complex two distinct photochemical processes. One photoprocess causes the decomposition of CH_2Cl_2 with a concomitant production of Cl^-. The decomposition of the complexes occurs in another photoprocess which has been assessed by the permanent bleach of the UV-vis spectrum. This photoprocess exhibits the second order degree dependence on light intensity characteristic of the biphotonic photolysis.[28,29] In contrast to the biphotonic decomposition of the complex, the linear dependence of the Cl^- concentration on light intensity must be ascribed to a monophotonically induced photoreaction. A non-linear dependence of the Cl^- concentration on light intensity would be indicative of a significant biphotonic contribution to the formation of Cl^-. This process is caused by a sequential absorption of two photons. Given the concentration of the photolyte and the optical path of the cell, l = 0.5 cm, the light intensity of the flash in our experiments is orders of magnitude below the threshold for the coherent absorption of two photons.[30]

Mechanisms consistent with the experimental observations need to have two independent photochemical paths. One for the biphotonic formation of products and the other for the decomposition of CH_2Cl_2 with formation of Cl^-. One possible mechanism is shown in Scheme 2(a). The reaction with CH_2Cl_2 occurs before or during the thermalization process converting the Franck–Condon MLCT excited state, Td- $(HOMO)^2d^9(LUMO)^1$, to the triplet excited state with flattened (D_{4h}) or trigonal (C_{3v}) symmetry, D_{4h} or C_{3v} – $(HOMO)^2d^9(LUMO)^1$. The biphotonic decomposition of the complex takes place when the D_{4h} or C_{3v} – $(HOMO)^2d^9(LUMO)^1$ excited state and/or the exciplex are photolyzed. While the exciplex is included for completion in the mechanism, the observed luminescence of the complexes in CH_2Cl_2 suggests that its interaction with the metal center in the excited state is weak. In addition, the reaction with CH_2Cl_2 must occur with a frequency equal to or less than $\phi/\tau \leq 10^9\ s^{-1}$, since hundreds of fs are associated with the excited state thermalization, $\tau \sim 10^{-13}$ s, and the highest value of the quantum yield is $\phi \sim 1 \times 10^{-2}$. In another mechanism shown in Scheme 2(b), the flattened D_{4h} or C_{3v} – $(HOMO)^2d^9(LUMO)^1$ and/or the exciplex react with CH_2Cl_2 and are also photolyzed. In a plot of concentration of the complex decomposed by the photolysis *vs.* light intensity, an upward quadratic deviation from linearity will be caused by the photolysis. The photolysis will also diminish the concentrations of D_{4h} or C_{3v} – $(HOMO)^2d^9(LUMO)^1$ and/or the exciplex reacting with CH_2Cl_2. Therefore the concentration of Cl^- produced in the reaction will also show a quadratic downward dependence on the light intensity. This latter expectation does not agree with the experimental observations, Fig. 3. An improbable mechanism that must also be considered requires the parallel formation of two excited states. They can be the D_{4h} or C_{3v} –

$(HOMO)^2d^9(LUMO)^1$ and a metal- or ligand-centered excited state. Experimental observations in this and previous work have failed to detect the formation of such additional excited state in the 532 nm photolysis at room temperature. However a ligand-centered excited state whose luminescence was observed at low temperatures is populated irradiating the $Cu(dmp)_2^+$ complex at 365 nm.[15] It will be positioned therefore at an energy higher than the one required for the biphotonic process driven with 532 nm photons.

It is possible to associate now the biphotonic photochemistry with the excited state → excited state electronic transition that gives rise to the D_{4h} or C_{3v} – $(HOMO)^2d^9(LUMO)^1$ absorption band in the excited state spectrum. An absorption band centered at ~570 nm is observed in the spectrum of the excited state, Fig. 1. The chromophore responsible for this absorption band is also seen in the spectra of metallo complexes having the ligand-radical moiety···M($dmp^{\cdot -}$), where M = Cu(I),[25] Re(I)[31,32] among other metal ions, and the free radicals $dmpH_n^{\cdot -(1-n)}$ (n = 1 or 2).[33] An electronic transition centered mainly in the $phen^{\cdot -}$ group of these species explains that the position of the absorption band is almost the same in the spectra of all of them. On the basis of the energy diagram (a) in Scheme 2, the absorption of one photon by the ground state, $(\pi_{HOMO})^2d^{10}$, generates the D_{4h} or C_{3v} – $(HOMO)^2d^9(LUMO)^1$ excited state in eqn (4).

$$(HOMO)^2d^{10} \overset{h\nu,\phi}{\rightarrow} D_{4h} \text{ or } C_{3v} - (HOMO)^2d^9(LUMO)^1 \quad (4)$$

Two possible electronic transitions from the flattened MLCT generate ligand-centered excited states, eqn (5).

$$D_{4h} \text{ or } C_{3v} - (HOMO)^2d^9(LUMO)^1 \overset{h\nu}{\rightarrow} \begin{cases} (HOMO)^1d^9(LUMO)^2 \\ \text{or} \\ (HOMO)^1d^{10}(LUMO)^1 \end{cases} \quad (5)$$

In one electronic transitions, the electron is promoted from the highest occupied π orbital centered in the dmp ligand, HOMO, to the lowest unoccupied π* orbital also centered in the dmp, LUMO. In the other electronic transition, the transfer is from the HOMO to a singly occupied orbital with a large metal character. Possibly the d_{z^2} is the geometry of a flattened tetrahedron. Since electronic transitions at wavelengths shorter than 400 nm in the spectra of the Cu(I) complexes populate ligand-centered excited states, the electronic transition to the $(HOMO)^1d^{10}(LUMO)^1$ in eqn (5) is (in energy terms) most likely to occur for the two electronic transitions.

The formation of these ligand-centered excited states can be rationalized in terms of the photonic energy available for the photoprocess. Based on the luminescence of the $[Cu(dmp)_2]^+$ complex,[34] the D_{4h} or C_{3v} – $(HOMO)^2d^9(LUMO)^1$ must be ~14 kK above the ground state and the absorption of the 532 nm photon in eqn (5) rises the energy to ~33 kK. Inspection of the dmp spectrum[35,36] and the spectra of copper dmp complexes[37,38] shows that ligand-centered excited states are populated with 27–28 kK photonic energies. Therefore, the corresponding excited states can be easily populated when the D_{4h} or C_{3v} – $(HOMO)^2d^9(LUMO)^1$ excited state absorbs a 532 nm photon. Population of the ligand-centered excited state in the biphotonic process is also in agreement with a monotonic increase of the quantum yield with decreasing exciting wavelength communicated in the literature.[16]

In as much as the observed biphotonic decompositions of the $Cu(dmp)_2^+$ and $[Cu_2(mphenpr)_2]^{2+}$ complexes without Cl^- formation is related to the population of the $(HOMO)^1d^{10}(LUMO)^1$ excited state, the excited state reaction cannot lead to a homolytic or heterolytic dissociation of the C–Cl bond of CH_2Cl_2. An intramolecular decomposition of the phen ligand without the participation of CH_2Cl_2 is a possible reaction. Also the observed decomposition could be caused by a covalent insertion of CH_2Cl_2 into the ligand. Such a reaction will bear some resemblance with the formation of covalent hydrates of the phen ligand that has been reported in the literature.[37]

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