

Photochemistry of Copper(II) Macrocyclic Complexes Bound to Poly(acrylic acid): Time-Resolved Observations in a Picosecond-Millisecond Time Domain and Sequential Biphotonic Excitations

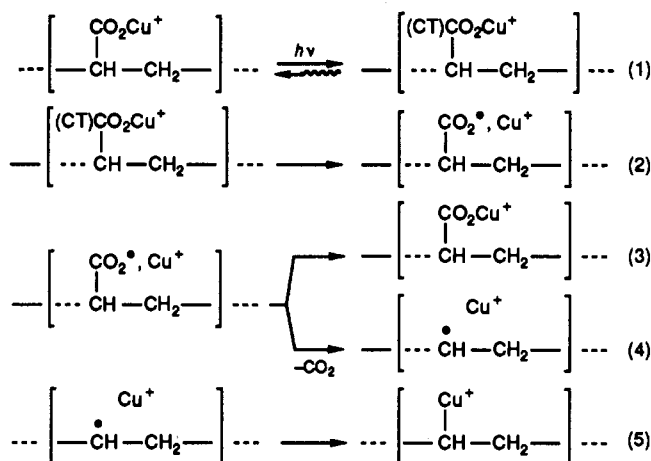
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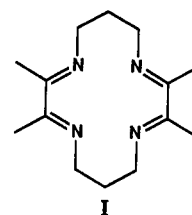
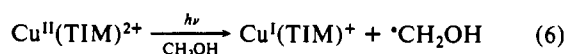
Flash photolysis of $\text{Cu}(2,3,9,10\text{-Me}_4\text{-[14]-1,3,8,10\text{-tetraeneN}_4\text{)}^{2+}$ -poly(acrylate) generates an intermediate, $\text{Cu}^{\text{III}}(2,3,9,10\text{-Me}_4\text{-[14]-1,3,8,10\text{-tetraeneN}_4\text{-alkyl})$, in less than 20 ps. This intermediate decomposes into $\text{Cu}^{\text{I}}(2,3,9,10\text{-Me}_4\text{-[14]-1,3,8,10\text{-tetraeneN}_4)$ with a 20- μs lifetime. We have followed, in a millisecond time scale, the disappearance of $\text{Cu}(2,3,9,10\text{-Me}_4\text{-[14]-1,3,8,10\text{-tetraeneN}_4)^+$, a process that exhibits a kinetics expected for consecutive first- and second-order reactions. The reactions rates are dependent on the number of photochemically generated Cu(I) species per molecule of poly(acrylic acid) but are independent of the solutions' bulk viscosity. Flash irradiations of $\text{Cu}^{\text{I}}(2,3,9,10\text{-Me}_4\text{-[14]-1,3,8,10\text{-tetraeneN}_4)$ -poly(acrylate) complexes in aqueous solutions form metastable $\text{Cu}^{\text{II}}(\text{ligand radical})$ -poly(acrylate) complexes. By contrast, $\text{Cu}^{\text{I}}(2,3,9,10\text{-Me}_4\text{-[14]-1,3,8,10\text{-tetraeneN}_4)^+$ in methanol exhibits no photoreactivity.

Introduction

Previous studies on the photochemistry of copper(II)-poly(acrylic acid) complexes were carried out with species having $\text{Cu}^{2+}(\text{aq})$ attached to a polyelectrolyte backbone.¹ Reactions of the metastable products follow the photodecarboxylation (eqs 1-5).



Such reactions, i.e. the formation of a copper-alkyl intermediate shown in eq 5, are similar to those observed in the photochemistry of copper(II) complexes with monomeric carboxylic acids.²⁻⁴ However, in complexes with poly(acrylate), they take place in the vicinity of the polyelectrolyte backbone and the ionic reactants have little tendency to escape to the bulk of the solution.¹ In these regards, the mechanism of a photochemical reaction in bulk can be affected, at least partially, by electrostatic interactions that influence the motion of ions and by concentration effects when photoreactants are bound to a polyelectrolyte. We have investigated some of these effects with $\text{Cu}(2,3,9,10\text{-Me}_4\text{-[14]-1,3,8,10\text{-tetraeneN}_4\text{)}^{2+}$ (I),⁵ whose photochemistry in methanolic solutions at wavelengths of the charge-transfer bands has been described (eq 6) as a photooxidation of weakly coordinated MeOH.⁶



Results

1. Time-Resolved Formation of the Cu(I) Intermediates. The 266-nm flash irradiations of $\text{Cu}^{\text{II}}(\text{TIM})^{2+}$ -poly(acrylate) complexes in deaerated aqueous solutions, pH 6, induce transient spectra in a time shorter than the resolution, ca. 15 ps, of the flash-photolysis apparatus (Figure 1). In a nanosecond time domain, transformations of the promptly generated spectra were kinetically of a first order with a rate constant $k = 2.0 \times 10^7 \text{ s}^{-1}$ (Figure 2). This process reduces the width of the 720-nm absorption band, and the spectrum recorded 100 ns after the flash is in agreement with the spectrum of $\text{Cu}^{\text{I}}(\text{TIM})^+$. These complex spectral changes stand in contrast with observations from the flash irradiation of $\text{Cu}^{\text{II}}(\text{TIM})^{2+}$ in deaerated methanol, where $\text{Cu}^{\text{I}}(\text{TIM})^+$ is generated within the flash, e.g. $t < 20 \text{ ps}$, and no further changes take place until several microseconds later.

We have also observed that 266-nm flash irradiations of $\text{Cu}^{\text{II}}(\text{aq})$ -poly(acrylate) in deaerated aqueous solutions, pH 6, generate the spectra of the previously observed intermediate,¹ $\dots\text{CH}(\text{Cu})^+-\text{CH}_2\dots$, within 15 ps (Figure 1).

2. Time-Resolved Decay of the Cu(I) Macrocycle. The mechanism of the $\text{Cu}^{\text{I}}(\text{TIM})^+$ -poly(acrylate) disappearance was investigated by measuring the rates of the optical density changes at 720 nm (Figure 3) as a function of the Cu(I) initial concentration. Least-squares curve fittings, based on the respective assumptions that spectral transformations are induced by either first- or second-order reactions, deviated from the experimental data and indicated that the mechanism of the Cu(I) disappearance was more complex. A similar least-squares treatment of the traces for the rate of consecutive first- and second-order reactions resulted in acceptable fittings (Figure 3). In addition, the dependence of the lifetime on the initial concentration (Figure 4) was the one predicted for two consecutive reactions (eqs 7 and 8) of first and second order, respectively.



Indeed, the 720-nm transient optical density, OD, can be expressed by using Beer's law (eq 9), where ϵ_i , $i = 1$ and 2, are the

$$\text{OD} = \epsilon_1[\text{Cu}^{\text{I}}(\text{TIM})^+] + \epsilon_2[\text{T}] \quad (9)$$

respective extinction coefficients of $\text{Cu}^{\text{I}}(\text{TIM})^+$ and T. An ex-

- (1) Das, S.; Ferraudi, G. *Inorg. Chem.* **1986**, *25*, 1066.
 (2) Ferraudi, G. *Inorg. Chem.* **1978**, *17*, 2506.
 (3) Natarajan, P.; Ferraudi, G. *Inorg. Chem.* **1981**, *20*, 3708.
 (4) Scaiano, J. C.; Leigh, W. J.; Ferraudi, G. *Can. J. Chem.* **1984**, *62*, 2355.
 (5) Abbreviation used in this work: TIM = 2,3,9,10-tetramethyl-[14]-1,3,8,10-tetraeneN₄.
 (6) Van Vlierberge, B.; Ferraudi, G. *Inorg. Chem.* **1987**, *26*, 337.

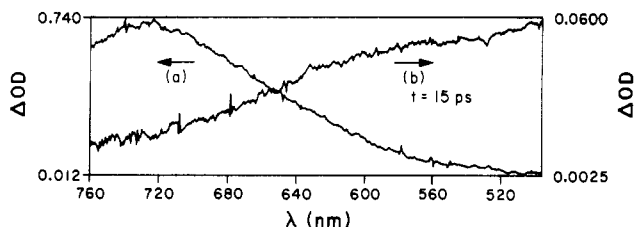


Figure 1. Spectra recorded 15 ps after the 266-nm irradiation of (a) 10^{-3} M $\text{Cu}^{\text{II}}(\text{TIM})^{2+}$ in 6.0×10^{-3} M poly(acrylate) and (b) 10^{-3} M $\text{Cu}^{\text{II}}(\text{aq})$ in 6.0×10^{-3} M poly(acrylate). The experiments were carried out with acidic solutions, pH 6.5, and a polyelectrolyte with 2.0×10^6 as an average formula weight.

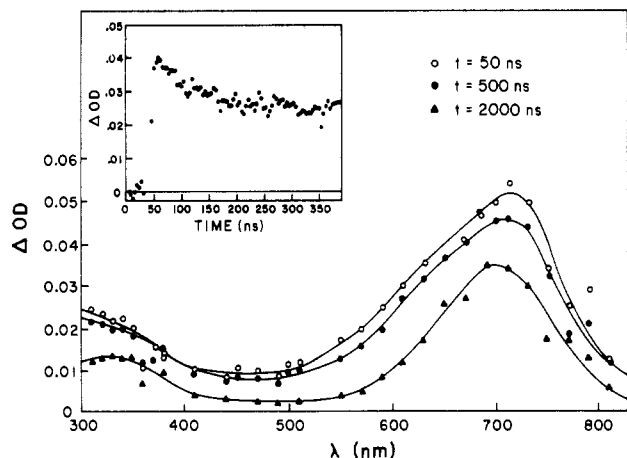


Figure 2. Transient spectra recorded in flash irradiations of 10^{-3} M $\text{Cu}^{\text{II}}(\text{TIM})^{2+}$ in 6.0×10^{-3} M poly(acrylate) solutions and a typical trace (insert) for the 650-nm optical transformations following the conversion of a copper-alkyl intermediate into $\text{Cu}^{\text{I}}(\text{TIM})^+$. For other experimental conditions, see Figure 1.

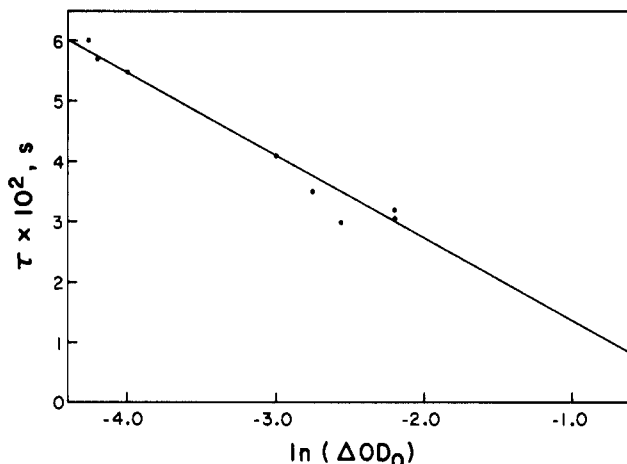


Figure 3. Dependence of the half-lifetime for the disappearance of $\text{Cu}^{\text{I}}(\text{TIM})^+$ -poly(acrylate) on the logarithm of the optical density change, ΔOD_0 . Changes in the 720-nm optical density, measured 50 μs after the flash irradiation, are proportional to the total concentration of $\text{Cu}^{\text{I}}(\text{TIM})^+$.

pression for the lifetime of the OD decay can be derived by assuming that the concentration of T is fixed under a steady-state regime (eq 10) and by replacing $[\text{Cu}^{\text{I}}(\text{TIM})^+]$ in eq 9 with its

$$[\text{T}] = ((k_7/2k_8)[\text{Cu}(\text{TIM})^+])^{1/2} \quad (10)$$

$$[\text{Cu}(\text{TIM})^+] = [\text{Cu}(\text{TIM})^+]_0 \exp(-k_7t) \quad (11)$$

integrated rate law (eq 11). In eq 12, the dependence of the $\frac{1}{2} \ln [\text{Cu}(\text{TIM})^+]_0 \sim \ln [(\epsilon_2/\epsilon_1)(k_7/2k_8)^{1/2}] - (k_7/2)\tau$ (12)

lifetime, τ , for the decay of OD, on the logarithm of the $\text{Cu}^{\text{I}}(\text{TIM})^+$ initial concentration is in accord with our results (Figure

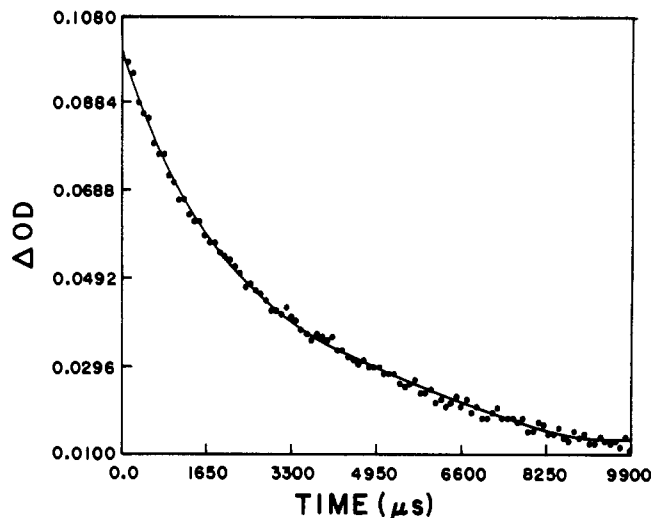


Figure 4. Typical trace for the disappearance of $\text{Cu}^{\text{I}}(\text{TIM})^+$ in poly(acrylate) solutions. The solid line shows a least-squares polynomial fitting of the experimental data for two consecutive reactions that are respectively of first and second order. $\text{Cu}^{\text{I}}(\text{TIM})^+$ was photogenerated in flash photolysis of 10^{-3} M $\text{Cu}^{\text{II}}(\text{TIM})^{2+}$ in 6.0×10^{-3} M poly(acrylate) solutions, and the optical changes were followed at 720 nm.

Table I. Rate Constants for the Consecutive First- and Second-Order Reactions in the Disappearance of $\text{Cu}^{\text{I}}(\text{TIM})^+$ -Poly(acrylate)^a

$k_7/10^1, \text{s}^{-1}$	$k_8/10^3, \text{M}^{-1} \text{s}^{-2}$	$10^6[\text{Cu}^{\text{I}}(\text{TIM})]_0, \text{M}$
3.5 ± 0.3	4.6 ± 0.6	13.8
2.9 ± 0.3	3.5 ± 0.5	7.4
3.3 ± 0.3	4.3 ± 0.7	2.2

^aThese reactions were investigated in flash photolysis of 10^{-3} M $\text{Cu}^{\text{II}}(\text{TIM})^{2+}$ in 6×10^{-3} M poly(acrylate) solutions with pH 6.5. A poly(acrylic acid) with fw 2×10^6 was used for the preparation of the solns. ^bConcentrations of the Cu^{I} complex generated with flashes of a given intensity.

Table II. Typical Effects of the Poly(acrylic acids) on the Lifetimes of Macrocylic Complexes in Unusual Oxidation States^a

fw of poly(acrylate)/ 10^3	lifetime, s		
	$\text{Cu}^{\text{I}}(\text{TIM})^+$	$\text{Cu}^{\text{I}}([\text{14}] \text{dieneN}_4)^+$	$\text{Ni}^{\text{I}}([\text{14}] \text{dieneN}_4)^+$
2.00	2.00	1.57	4.8×10^{-2}
2	9.8×10^{-2}	0.97	0.51
6		0.96	
25		2.2×10^{-6}	
2.5×10^2			1.7×10^{-5}
2×10^3	2.5×10^{-2}	2.2×10^{-6}	2.9×10^{-5}

^aAll in deaerated aqueous solutions with pH 6.5. In solutions of poly(acrylate) the concentrations were adjusted to $[\text{macrocylic complex}] = 2.0 \times 10^{-4}$ and $[-\text{CO}_2] = 1 \times 10^{-3}$ M. For other experimental conditions, see elsewhere in the text.

4). A rate constant, $k_7 \sim 10^2 \text{ s}^{-1}$, has been calculated from the slope of the line in Figure 4, a value in agreement with those calculated from curve fitting (Table I).

Different rates for the decay of the $\text{Cu}(\text{I})$ complex were measured in $\text{Cu}^{\text{II}}(\text{TIM})^{2+}$ -poly(acrylate) solutions with poly(acrylates) of different molecular weights (Table II) despite that the $\text{Cu}^{\text{II}}(\text{TIM})^{2+}/-\text{COOH}$ ratio, the concentration of $\text{Cu}(\text{II})$ complex, and the initial concentration of $\text{Cu}(\text{I})$ complex were kept the same in these experiments. It must also be noted that similar effects on the rate of disappearance were detected with other macrocylic complexes in unstable oxidation states (Table II).

The effect of the medium viscosity on the rate of the $\text{Cu}(\text{I})$ disappearance was investigated in flash photolyses of the $\text{Cu}^{\text{II}}(\text{TIM})^{2+}$ -poly(acrylate) in either 50% glycerol-water or 50% methanol-water mixtures, respectively, and with the same concentration of complexes used in the experiments described above. The values of the rate constants determined under such conditions are extremely close to those measured in 100% H_2O (Table III)

Table III. Medium Effects on the Disappearance of Cu^I(TIM)-Poly(acrylate)^a

$k_7/10^2, \text{s}^{-1}$	$k_8/10^3, \text{M}^{-1} \text{s}^{-1}$	medium conditions
3.5 ± 0.4	4.6 ± 0.4	H ₂ O, pH 6.5
3.0 ± 0.3	2.1 ± 0.3	50% methanol, pH 6.5
3.2 ± 0.3	2.1 ± 0.3	50% glycerol, pH 6.5

^a The flash-photolysis-generated concentration of Cu(I) was ca. 10^{-5} M in all these experiments. For other experimental conditions, see Table.

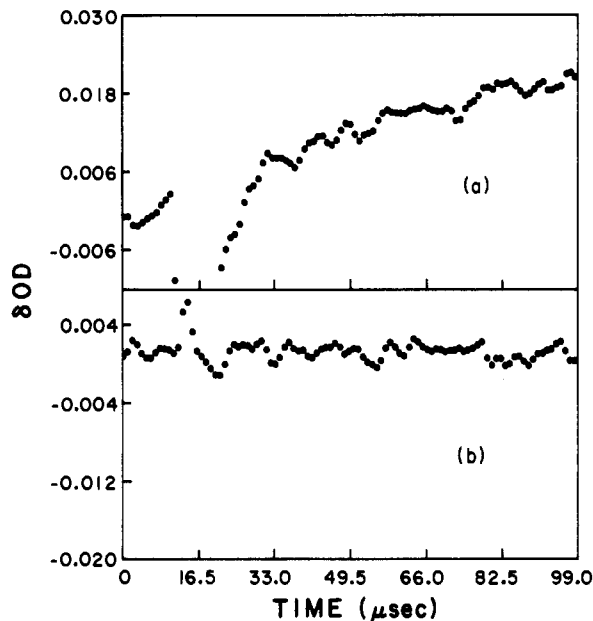


Figure 5. Transient optical changes generated by a 760-nm flash photolysis of Cu^I(TIM)⁺ in 6.0×10^{-3} M poly(acrylate) (a) aqueous solutions or (b) methanolic solutions. The Cu(I) complex was generated in 308-nm flash irradiations of 10^{-3} M Cu^{II}(TIM)²⁺ in 6×10^{-3} M poly(acrylate) aqueous solutions or methanolic solutions, respectively.

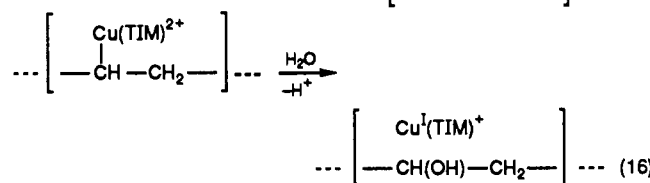
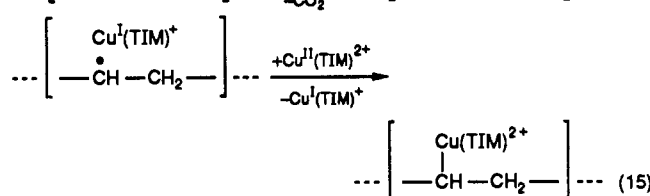
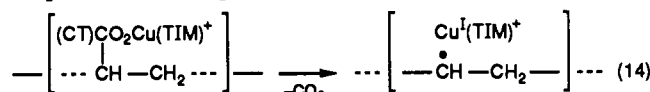
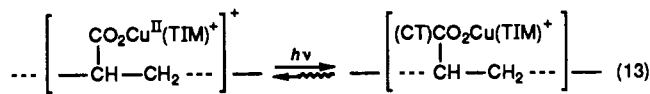
despite differences in the bulk viscosity and/or bulk dielectric constant of the solution.

3. Sequential Biphotonic Reactivity. The irradiation of Cu^{II}(TIM)²⁺-poly(acrylate) complexes in deaerated aqueous solutions, pH 6, with two sequential laser pulses of 308 and 690 nm separated by a 30- μ s interval resulted in the formation and photolysis of the Cu^I(TIM)⁺, respectively. These observations are shown in Figure 5, where the ordinate, $\delta\Delta\text{OD}$, is the result of subtracting optical density changes induced respectively with 760- and 308-nm irradiations from those induced with a sequential irradiation in the manner described elsewhere.⁶ The photolysis of the Cu(I) species leads to the formation and disappearance of a new intermediate (Figure 5a) whose absorptions overlap those of Cu^I(TIM)⁺ and which shows no reactivity toward Cl₃CCO₂⁻. No such photochemical intermediate could be observed in the similar sequential irradiation of Cu^{II}(TIM)²⁺ in deaerated methanol (Figure 5b).

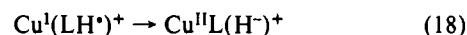
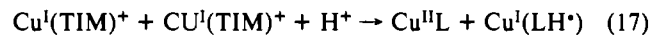
Discussion

The photogeneration of a short-lived intermediate in flash photolysis of Cu^{II}(TIM)²⁺-poly(acrylate) complexes contrasts with a prompt formation of the Cu(I) product in similar irradiations of Cu^{II}(aq)-poly(acrylate). Such an intermediate can be assigned as a Cu^{III}(TIM)-alkyl complex on the basis of its spectral properties.⁷ This assignment is also in accord with the stability of the species, i.e. with regard to the formation of the Cu^I(TIM)⁺ product in a nanosecond to microsecond time domain. Since Cu^I(TIM)⁺, the product of the photolyses of Cu^{II}(TIM)²⁺ in methanol, and ...CH(Cu^I)-CH₂..., the product of the photolyses of Cu^{II}(aq)-poly(acrylate), are photogenerated in less than 15

ps, the formation of the Cu(III)-alkyl intermediate must be a result of combined effects from large local concentrations of Cu(II) ions in the poly(acrylate) backbone and the relative reactivities of the Cu(I) and Cu(II) species with free radicals formed by decarboxylation of the polyelectrolyte. In these regards, it is possible to describe the time-resolved spectral observations from a picosecond to a microsecond time domain in terms of a mechanism (eqs 13–16) that includes a reaction between poly(acrylate) radicals and excess Cu^{II}(TIM)²⁺ (eq 15) for the formation of ...[CH(Cu^{III}(TIM)²⁺)-CH₂]... in less than 15 ps.



Since the stability of Cu^I(TIM)⁺ in the poly(acrylate) is much shorter than in bulk methanol, dependent on the molecular weight of the poly(acrylate) and independent of the bulk viscosity of the solvent, the transformation of Cu^I(TIM)⁺ into stable products must occur within the close vicinity of the polyelectrolyte, i.e. within its double layer. Indeed, with those concentrations of Cu(I) complex generated in our flash-photolysis experiments there must be several molecules of Cu^I(TIM)⁺ in one of polyelectrolyte. It is possible, therefore, that the process with a first-order kinetics (eq 7) can be described as consisting of leapfrog displacements having an overall rate that kinetically have a first-order dependence on the Cu(I) concentration. Such a process must be followed by a slower formation of the copper(I)-ligand radical (eq 17) and a copper(II) hydride (eq 18).⁷⁻⁹



This mechanism (eqs 17 and 18) for the decay of Cu^I(TIM)⁺ will exhibit a rate with a second-order dependence on Cu(I) concentration if eq 18, for the transformation of a Cu(I)-ligand radical complex into a copper(II) hydride, is fast.

A comparison of the photobehavior of Cu^I(TIM)⁺ in poly(acrylate) aqueous solutions and in bulk methanol suggests that association with such a polyelectrolyte changes the photoreactivity of the Cu(I) complex. The intermediate observed in flash photolysis has neither the spectrum nor the reactivity of the solvated electron, a reported product in the photolysis of other Cu(I) complexes.^{10,11} In these regards, a better reason for our experimental observations is the formation and disappearance of a Cu(I)-alkyl intermediate (eqs 19 and 20).

The photodecarboxylation in eq 19 can be induced in either an ion-pair charge-transfer state or a ligand to metal charge-transfer state. These assignments depend on how the association

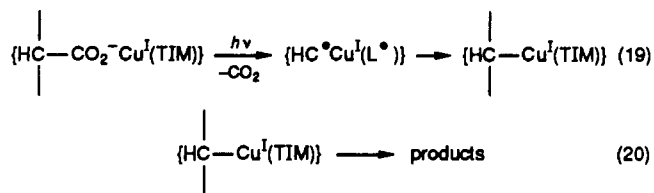
(8) An alkyl-Cu^{III}(TIM) species, generated by a fast reaction between an alkyl radical and Cu^I(TIM)⁺, is expected to have absorptions at higher energies than those in the spectrum of the transient.^{2,6,8}

(9) Ferraudi, G.; Muralidharan, S. *Coord. Chem. Rev.* **1981**, *36*, 45.

(10) Horváth, O.; Stevenson, K. L. *Inorg. Chem.* **1989**, *28*, 2548.

(11) Ferraudi, G. *Inorg. Chem.* **1978**, *17*, 1370.

(7) Ferraudi, G.; Barrera, P.; Granifo, J.; Ham, J. H., IV; Rillema, D. P.; Nowak, R. *Inorg. Chem.* **1985**, *24*, 281.



between a poly(acrylate)'s carboxylate and $\text{Cu}^{\text{I}}(\text{TIM})^+$ is regarded.⁹⁻¹² It is improbable, however, that an ion-pair charge-transfer transition can be placed at energies as low as those in a charge transfer involving the electronic density of the TIM ligand. In terms of Jørgensen's optical electronegativities (eq 21),

$$\Delta\epsilon_{\text{CT}} = 35.8(\chi_{\text{L}} - \chi_{\text{M}}) + \Delta + \delta\text{SPE} + \dots \quad (21)$$

reported values for the ligands, TIM and $-\text{CO}_2^-$, and Cu(I) suggest that the $-\text{CO}_2^-$ to Cu(I) transition is at a similar or lower energy than the energy of the Cu(I) to TIM transition.^{9,13,14}

Experimental Section

Photochemical Procedures. Flash irradiations were carried out in experimental setups described elsewhere.^{1,15} For flash-photolysis experiments with nanosecond time resolution, a Quanta Ray Nd Yag pumped dye laser was used as a source of 266-nm flashes with ca. 10-ns duration and 20-mJ energy. A mode-locked Yag laser was used as a source of 266-nm light pulses with ca. 18-ps width for measurements of

spectra and reaction kinetics in a picosecond time domain. The apparatus used for the photogeneration and photolysis of transients has been described elsewhere and is based on the synchronous triggering of two lasers; it consists of a Questek excimer laser and a Candela flash-pumped dye laser for the respective photogeneration and photolysis of the Cu(I) complex.⁶ In these flash-photolysis experiments, solutions of the complexes were deaerated with streams of ultrapure N_2 .

Pulse Radiolysis. The apparatus and procedures used for the generation of the reduced macrocyclic complexes have been described elsewhere.¹⁶ In these experiments, the solutions, ca. 10^{-4} M in a given complex, 6.0×10^{-4} M in poly(acrylate), and 0.1 M in 1,1-dimethylethanol, were deaerated with streams of ultrapure N_2 . The alcohol scavenged the OH radicals, and carbon-centered secondary radicals exhibited no reactivity toward the macrocycle-poly(acrylate) complexes.

Materials. Aldrich poly(acrylic) acids with given formula weights were purified by dialysis according to a literature procedure.¹ The concentration of the poly(acrylic acids) was determined by titration with NaOH to neutral pH. Solutions of $\text{Cu}^{\text{II}}(2,3,9,10\text{-Me}_4\text{-[14]-1,3,8,10\text{-tetraeneN}_4})^{2+}$ -poly(acrylate) were prepared by adding appropriate amounts of the copper complex to solutions containing a known concentration of poly(acrylate) and adjusting the pH of the final solution to a value 6.5 with minute volumes of diluted NaOH or HClO_4 solutions as required. The compound $[\text{Cu}(2,3,9,10\text{-Me}_4\text{-[14]-1,3,8,10\text{-tetraeneN}_4)](\text{ClO}_4)_2$ was prepared by a literature procedure and its purity established from its UV-vis absorption spectrum.^{7,17} Other materials were reagent grade and used without further purification.

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(12) Berger, R. M.; McMillin, D. R.; Dallinger, R. F. *Inorg. Chem.* **1987**, *26*, 3802.

(13) Jørgensen, C. K. *Prog. Inorg. Chem.* **1962**, *4*, 73.

(14) Ferraudi, G. *Elements of Inorganic Photochemistry*; Wiley Interscience, John Wiley & Sons: New York, 1988; pp 127-132.

(15) Ebbesen, T. W. *Rev. Sci. Instrum.* **1988**, *59*, 1307.

(16) Ronco, S.; Van Vlierberge, B.; Ferraudi, G. *Inorg. Chem.* **1988**, *27*, 3543.

(17) Fabbri, L.; Lari, A.; Poggi, A. *Inorg. Chem.* **1982**, *21*, 2083.

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Luminescent and Redox-Reactive Building Blocks for the Design of Photochemical Molecular Devices: Mono-, Di-, Tri-, and Tetranuclear Ruthenium(II) Polypyridine Complexes

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The syntheses, characterization, absorption spectra, luminescence spectra, luminescence lifetimes, and electrochemical behavior of 16 mono-, di-, tri-, and tetrametallic ruthenium(II) polypyridine complexes have been investigated. The general formulas of the complexes studied are $\text{RuL}_2(\text{BL})^{2+}$, $\text{L}_2\text{Ru}(\mu\text{-BL})\text{RuL}_2^{4+}$, $\text{LRu}[(\mu\text{-BL})\text{RuL}_2]_2^{6+}$, and $\text{Ru}[(\mu\text{-BL})\text{RuL}_2]_3^{8+}$, where L = 2,2'-bipyridine (bpy) or 2,2'-biquinoline (biq) and BL = 2,3- or 2,5-bis(2-pyridyl)pyrazine (dpp). The absorption spectra of the complexes exhibit broad and intense (ϵ up to $\sim 50\,000\text{ M}^{-1}\text{ cm}^{-1}$) metal-to-ligand charge-transfer (MLCT) bands, which in the oligonuclear complexes extend all over the visible region. All the complexes exhibit luminescence in the 600-850-nm region in a rigid matrix at 77 K (lifetimes of the order of 1 μs) and in fluid solution at room temperature (lifetimes of the order of 100 ns). Emissions can be assigned to specific metal-ligand chromophoric units, and the trends in the emission energies on changing ligands and/or nuclearity can be rationalized in the light of the trends observed for the potentials of first oxidation and first reduction processes. Corrected excitation spectra show that the luminescent excited state is populated with the same efficiency regardless of the excitation wavelength throughout the MLCT bands. In electrochemical experiments, the complexes show metal-centered oxidation and ligand-centered reduction processes. Most of the redox waves are reversible and can be assigned to specific metal(s) or ligand(s). The interaction between equivalent redox centers of the same complex is more or less weak, depending on the nature of BL and L. Each one of the mono-, di-, tri-, and tetranuclear complexes studied can be used as a building block for the design of luminescent and redox-reactive species containing a higher number of metal centers. Because of their broad and strong absorption bands in the visible region, relatively long luminescence lifetimes, and rich redox behaviors, complexes of this type can prove useful as antenna components for photosensitization purposes (including electron or hole injection on semiconductors), luminescence probes, and multielectron photocatalysts.

Introduction

A major research area in photochemistry is currently that concerning supramolecular systems capable of performing pho-

toinduced energy migration and/or charge separation.²⁻¹³ Such systems can be designed from building blocks that contain the

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(2) Balzani, V., Ed. *Supramolecular Photochemistry*; Reidel: Dordrecht, The Netherlands, 1987.

(3) Carter, F. L., Ed. *Molecular Electron Devices II*; Dekker: New York, 1987.