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Dinuclear excited-state complexes from UV laser excitation of aqueous ammonia, methylamine, and ethylamine copper(I) complexes

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Contents

Abstract

The temporal and spectral behavior of ammonia, methylamine, and ethylamine copper(I) complexes in aqueous solutions at 1 M ionic strength were probed using 266-nm laser flash photolysis on the nanosecond time-scale. Since stability constants and UV spectra for the ground state systems are needed to understand this behavior, these had to be determined for the methylamine and ethylamine complexes, and are reported here for the first time. The stepwise stability constants are 0.067 ± 0.007 and 0.040 ± 0.004 for the tris(methylamine) and tris(ethylamine) complexes, respectively. Moreover, in order to know the activities of the two amines in the unit ionic strength solutions, it was also necessary to measure their Henry's law constants, and these are 5.002 and 7.987 Torr M^{-1}, respectively. In each of the three systems an intermediate forms monophotonically, which absorbs in the 370–390-nm region, with a shoulder or weaker band at 420–430 nm, and a weaker, broad band at 550 nm. These species have been characterized as dinuclear triplet state complexes because their first-order decay lifetimes increase with copper(I) concentration, consistent with the quasi-equilibria, $^3CuA_2^+ + CuA_2^+ = {}^3Cu_2A_4^+$ (an *excimer*) or $^3CuA_3^+ + CuA_2^+ = {}^3Cu_2A_5^+$ (an *exciplex*) in concert with the decay of the monomeric triplet species, $^3CuA_2^+$ and $^3CuA_3^+$, via delayed electron ejection. Thermodynamic and kinetic stability of the dinuclear excited state complexes increase for the ligand series: ammonia < methylamine < ethylamine. One-electron copper–copper bonding is proposed for these dinuclear species. Parallel to the formation of the dinuclear species, the hydrated electron is ejected monophotonically from laser photolysis of all three ligand systems on a subnanosecond time-scale with quantum yields that range from 0.34 to 0.47. A complete mechanistic scheme is described which shows that the prompt electron ejection is from the excited singlet state of a photolyzed monomer, CuA_2^+ or CuA_3^+, in parallel with intersystem crossing to a triplet monomer, $^3CuA_2^+$ or $^3CuA_3^+$, whose longer lifetime allows the reaction with ground-state CuA_2^+ and equilibration with the dinuclear excited state.

Keywords: Ammonia; Methylamine; Ethylamine copper(I); Hydrated electron; Dinuclear exciplex; Excimer

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1. Introduction

Dinuclear inorganic exciplexes and excimers are relatively rare, and ones that unambiguously display metal–metal bonding are even rarer [1]. The first reports of such an exciplex, by Nagle et al. [1–3], described the reaction between photoexcited $Pt_2(P_2O_5H_2)_4^{4-}$ and Tl^+, forming a luminescent metal–metal-bonded exciplex in aqueous solution. Subsequently, Patterson and coworkers [4–8] have extensively described the luminescent, homoatomic, metal–metal exciplex formed in crystals doped with $Tl[Ag(CN)_2]$. Recently, we reported [9,10] that a dinuclear exciplex is formed upon UV irradiation of aqueous solutions containing $Cu(NH_3)_2^+$ and $Cu(NH_3)_3^+$. Because of the saturation and sp^3 configuration of the ammonia ligands, it is apparent that this exciplex must have a metal–metal bond.

The observation of exciplexes in the photolysis of inorganic systems is relatively recent [11]. Exciplex formation in copper(I) complexes was first demonstrated by McMillin and coworkers [12–15] in their studies of the quenching of metal-to-ligand charge transfer(MLCT)-induced photoluminescence of copper(I) diimine complexes in non-polar media. The quenchers, such as CH_3CN, acetone, and *p*-dioxane in methylene chloride solution, form five coordinate exciplexes by direct reaction with the MLCT excited states, which decay on the nanosecond or subnanosecond time-scale. In contrast, UV irradiation of aqueous solutions of chloro [16–19], bromo [19,20], iodo [21], dicyanochloro [16,22,23], dicyanobromo [22–24], and dicyanoiodocuprate(I) [22,23] complexes promoted the formation of triscoordinated excited state species that are more thermodynamically stable than their ground-state counterparts; hence, these were also termed exciplexes, although this usage assumes a broader and more controversial definition of *exciplex*.

The electronic transitions that promote such excited-state chemistry are charge-transfer in nature: either MLCT or what is generically referred to as charge-transfer-to-solvent (CTTS) which is the usual assignment if solvated electrons appear in solution, detected either by reaction with electron scavengers or by transient spectrometry. Thus, the overall reaction following the CTTS excitation of an anionic complex in aqueous solution is:

$$Cu(I)L_n^{1-n} + h\nu_{uv} \rightarrow Cu(II)L_n^{2-n} + e_{aq}^- \quad (1)$$

where L is an anionic ligand such as chloride [17,25], bromide [26], iodide [21,27], cyanide [28], or combinations of halide and cyanide [16], and *n* is usually 2 or 3. The primary process in the photolysis of these copper(I) complexes is assumed to be excitation to a singlet state, which is followed by an efficient intersystem crossing to two triplet species, $^3CuX_2^-$ and $^3CuX_2Y^{2-}$, where we let X be halo or cyano ligands, and Y a halo ligand only. Since these anionic complexes are weak emitters [17,24,25,27,29], we were able to carry out an exhaustive study [20,22–24] of the mechanism of the excited-state equilibrium,

$$^3CuX_2^- + Y^- \rightleftarrows {}^3CuX_2Y^{2-} \quad (2)$$

and the modes of decay of the two excited-state species. Two modes of electron ejection were observed in these complexes [18,19,30]: a *prompt* and a *delayed* ejection occurring on a subnanosecond and a nano- to microsecond time-scale, respectively. Our most recent results [31] indicate that the delayed ejection is correlated to the decay of the quasi-equilibrated excited state species, whereas the prompt ejection is a two-photon process resulting from the excitation of one or both of these two triplet species. Since the quantum yields of delayed electron ejection are much higher than for luminescence, it can be concluded that the primary mode of decay of these excited states is by the ejection of hydrated electrons [19].

The cationic complex, $Cu(NH_3)_3^+$, also photoejects electrons [32,33], but we have been unable to detect any room temperature photoluminescence in solution. Moreover, although there is a ground-state equilibrium with small equilibrium constant of about 0.04 [33,34],

$$Cu(NH_3)_2^- + NH_3 \rightleftarrows Cu(NH_3)_3^+ \quad (3)$$

time-resolved spectral studies do not confirm any ligand-dependent excited-state equilibrium reaction analogous to Eq. (2) or Eq. (3). Instead, we have observed [9,10] that an excited-state intermediate absorbing at 400 nm formed as copper(I) concentration is increased in the system, and that its decay lifetime increases with copper(I) concentration. We explained this behavior in terms of the establishment of an excited-state equilibrium involving a dinuclear exciplex following excitation of the triammine complex to an excited singlet state, which can either eject an electron, or undergo intersystem crossing to a triplet species, as follows:

$$Cu(NH_3)_3^+ + h\nu \text{ (266 nm)} \rightarrow {}^{*1}Cu(NH_3)_3^+ \quad (4a)$$

$$^{*1}Cu(NH_3)_3^+ \rightarrow Cu(NH_3)_3^{2+} + e_{aq}^- \quad (4b)$$

$$^{*1}Cu(NH_3)_3^+ \rightarrow {}^3Cu(NH_3)_3^+ \quad (4c)$$

$$^3Cu(NH_3)_3^+ + Cu(NH_3)_2^+ \rightleftarrows {}^3Cu_2(NH_3)_5^{2+} \quad (4d)$$

where the primary mode of decay of the dinuclear species is through back reaction of Eq. (4d) and delayed electron ejection from $^3Cu(NH_3)_3^+$.

This work reports more kinetic details of the excited-state chemistry of the copper(I)–ammonia system, and extends the analysis to methyl- and ethylamine complexes of copper(I).

2. Experimental

Two techniques were used for the preparation of the ammonia and amine complexes of copper(I). In the first method, copper filings and a copper(II) salt such as $Cu(ClO_4)_2$ were sealed in an oxygen-free bottle containing the desired ammonia or amine and ionic medium, and stirred together until the blue color disappeared, according to the reverse disproportionation reaction,

$$Cu + CuA_4^{2+} \rightarrow 2CuA_2^+ \qquad (5)$$

where A represents ammonia, methyl-, or ethylamine. Alternatively, very pure CuCl, prepared as described previously [25], was dissolved in deoxygenated solutions of ammonia or the amines,

$$CuCl(s) + 2A \rightarrow CuA_2^+ + Cl^- \qquad (6)$$

The latter method was used for precisely fixing the concentration of copper(I) complex, but it has the drawback of requiring completely oxygen-free solutions, which are prepared by bubble degassing with Ar. On the other hand, the former method self-scavenges oxygen through the reaction,

$$4A + 2CuA_2^+ + H_2O + 1/2O_2 \rightarrow 2CuA_4^{2+} + 2OH^- \qquad (7)$$

and the copper(II) is then recycled back to copper(I) through reaction (5). In this case, copper concentrations were determined by removing the spent solutions from the copper filings, exposing them to air, and measuring the absorbance of the resulting blue copper(II) ammine or amine at λ_{max} of 600 nm, using as absorbance standards solutions containing precisely weighed copper(I) chloride at the same ligand and sodium perchlorate concentrations as the samples, and oxidized by air. Concentrated ammonium hydroxide from Fisher Scientific was used as the source of ammonia. Methylamine and ethylamine were used as obtained from Aldrich Chemicals in aqueous solutions that were 40 and 70% amine by weight, respectively.

Since there are no known equilibrium studies on the formation of methyl- and ethylamine complexes of copper(I), the equilibrium constants for the reaction,

$$CuA_2^+ + A \rightleftarrows CuA_3^+ \qquad (8)$$

had to be determined for the two amines. This was done using a method similar to that used for the study of the equilibria of the ammonia copper(I) complexes [32,33]. Initially, the activities, a, of the amines at 1 M ionic strength (sodium perchlorate medium) were determined from the dependence of the vapor pressure, p, on concentration, obtained by titration against standard HCl, using the expression,

$$a = p/K_H \qquad (9)$$

where K_H is Henry's law constant determined from the limiting slope of pressure versus molar concentration. This yields Henry's law constants of 5.002 and 7.987 Torr M^{-1}, for methylamine and ethylamine, respectively. From the cubic fits to such data, one obtains expressions relating the activity of the amine to its molar concentration, M. For methylamine,

$$a = M + 0.108M^2 + 0.016M^3 \qquad (10)$$

and for ethylamine,

$$a = M + 0.0970M^2 + 0.011M^3 \qquad (11)$$

These compare to the equation for ammonia obtained earlier [33]:

$$a = M - 0.027M^2 + 0.0095M^3 \qquad (12)$$

Spectra of CuCl in solutions of varying amine concentration were obtained using an HP8451 or HP8453 spectrometer. Pure CuCl was dissolved anaerobically in solutions containing the amine and 1 M sodium perchlorate, and placed in a 1-cm or 2-mm cuvette filled with argon. The reference used for each spectrum had the identical concentration of amine and sodium perchlorate, but no CuCl.

The equilibrium constant for reaction (8) for ammonia was previously determined [33] using the dependence of the molar extinction of copper(I) in the 290-nm region of the spectrum on ammonia activity, a, according to the expression,

$$\varepsilon = \varepsilon_3 + (\varepsilon_2 - \varepsilon_3)/(1 + Ka) \qquad (13)$$

where ε, ε_2, and ε_3 are the molar extinction coefficients of total copper(I), pure $Cu(NH_3)_2^+$, and pure $Cu(NH_3)_3^+$, respectively, and K is the equilibrium constant for reaction (8). Fits of Eq. (13) of ε versus a yield the three unknowns, ε_2, ε_3, and K. This same procedure was employed to determine the equilibrium constants for the methylamine and ethylamine complexes, which were assumed to conform to reaction (8). Moreover, from the average value of K determined in this way, the molar extinction spectra of each of the complexes, CuA_2^+ and CuA_3^+, for methylamine and ethylamine could be calculated from a linear regression analysis of the spectral data, according to Eq. (13).

The Nd-YAG laser kinetic spectrometer system and the techniques for determining quantum yields have been described previously [19,35].

3. Results and discussion

3.1. Equilibrium constants and spectra of the complexes

From the plots of the molar extinction coefficient versus activity of amine complex, values of K were obtained according to the method described above. Fig. 1 shows such plots for methyl- and ethylamine copper(I) complexes, at a wavelength of 290 nm, along with the

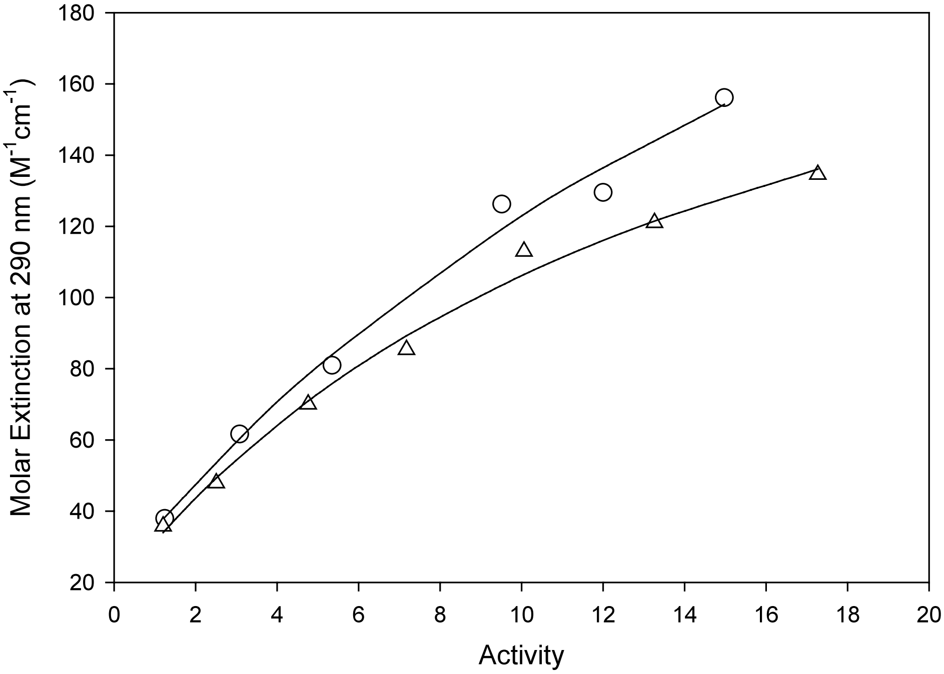


Fig. 1. Molar extinction (M^{-1} cm^{-1}) at 290 nm and 25 °C of solutions of CuCl (0.01 M or less) in (△) methylamine or (○) ethylamine at varying activity, at 1 M ionic strength (NaClO$_4$ medium). Curves are fits of Eq. (12), using average values of $K = 0.067$ for methylamine and 0.040 for ethylamine.

Table 1
Values of K at 25 °C, 1 M ionic strength for the equilibrium $Cu(A)_2^+ + A = Cu(A)_3^+$ and ε_2, ε_3 at 266 nm

Ligand, A	K	ε_2	ε_3 (M^{-1} cm^{-1})
NH_3 [a]	0.050 ± 0.005	45	718
CH_3NH_2	0.067 ± 0.007	227	732
$C_2H_5NH_2$	0.040 ± 0.004	163	1340

[a] From Ref. [33].

fits using the average value of K determined over the wavelength range of 280–296 nm. These average values, along with the value of K determined previously for the ammonia complex [33] are given in Table 1, indicating that the stabilities of the three triscoordinated complexes are rather similar. From the resolved UV spectra for the complexes, shown in Fig. 2, it can be seen that for all three ligands the triscoordinated complex is a stronger absorber in the near UV than the biscoordinated complex, as was noted earlier for the ammonia system [33]. However, the very obvious shoulder seen in the $Cu(NH_3)_3^+$ at 295 nm is less pronounced in $Cu(CH_3NH_2)_3^+$ and almost completely missing in $Cu(C_2H_5NH_2)_3^+$, although the latter has a stronger molar extinction throughout the UV than the other two tris complexes. While the molar extinctions of $Cu(CH_3NH_2)_2^+$ and $Cu(C_2H_5NH_2)_2^+$ are not significantly different from each other, they are considerably greater than that for $Cu(NH_3)_2^+$. From these spectra for all three ligand systems we can conclude that in an equilibrated mixture of the bis and tris complexes both will absorb light at the laser wavelength of 266 nm although the bis complex is far more ubiquitous than the tris complex.

3.2. *Time-resolved spectra produced by 266-nm laser excitation*

Most of the temporal behavior of the ammonia and amine complexes of copper(I) at low and high concentrations can be inferred from the time-resolved spectra of Fig. 3, taken at delay times of 10, 20, 50 and 850 ns after exposure to the 266-nm laser pulse for pairs of solutions that are about 3 M in ammonia or amine but have copper concentrations of about 7 or 11–13 mM. On the short (10–50 ns) time-scale, all the spectra are dominated by the wide absorption band centered at 680–700 nm, which is clearly that of the hydrated electron [36], along with another sharp but less intense band centered at 400–420 nm. At longer times, the 700-nm absorbance disappears as the electron decays, whereas the band at 400–420 nm decays and transforms into a slower-decaying and more complex spectrum with a maximum at 390 nm and shoulders or bands at 440 and 550 nm.

Copper concentration has a marked effect on all the bands. All the 700-nm electron absorbance bands are decreased by higher copper concentration because of electron scavenging by univalent copper ions, with the order of effectiveness of scavenging occurring for

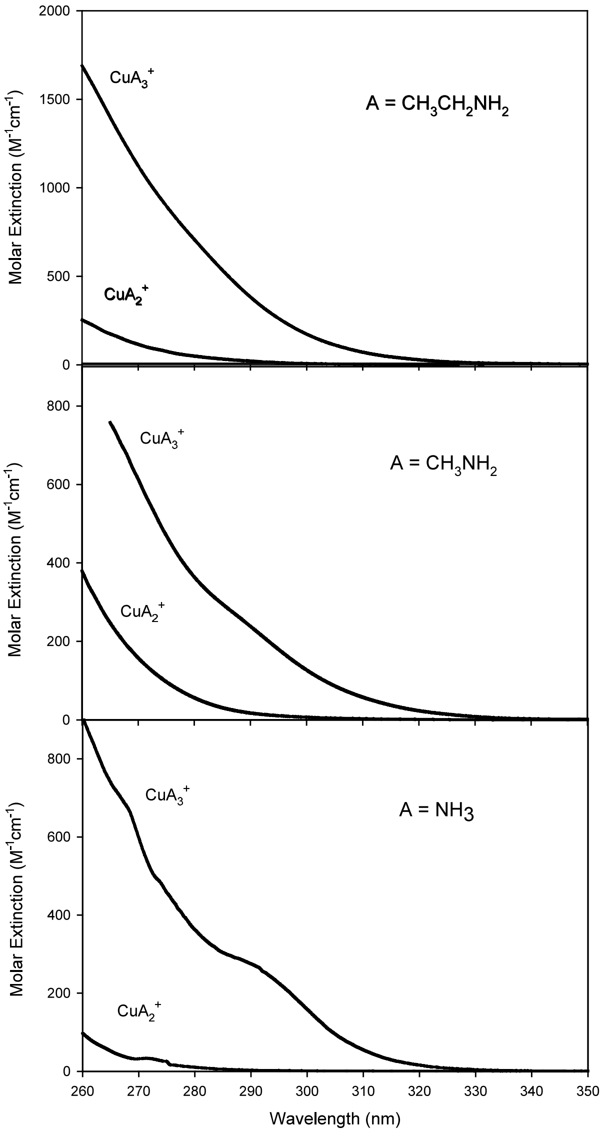


Fig. 2. Resolved absorption spectra at 25 °C of the bis- and triscoordinated copper(I) complexes with ammonia (from Ref. [33]), methylamine, and ethylamine at 1 M ionic strength ($NaClO_4$ medium). See legend on graph.

CuA_2^+–CuA_3^+ complexes with ligands $NH_3 > CH_3NH_2 > CH_3CH_2NH_2$. On the other hand, the 400–420-nm band, and the longer-lived complex absorption at 390, 440, and 550 are all enhanced by the addition of copper(I), suggesting they correspond to species that are formed by reaction of an excited-state intermediate with univalent copper.

3.3. Hydrated electron quantum yield, number of photons involved in formation, and the decay kinetics

Hydrated electrons are formed according to the reactions,

$$CuA_2^+ + h\nu \rightarrow CuA_2^{2+} + e_{aq}^- \qquad (14)$$

or

$$CuA_3^+ + h\nu \rightarrow CuA_3^{2+} + e_{aq}^- \qquad (15)$$

A typical absorbance decay curve at 670 nm, near the maximum of the hydrated electron absorbance spectrum, is shown in Fig. 4, along with an exponential fit to the data, for a solution that is 0.0081 M CuCl in 2.74 M ammonia, 1 M ionic strength. Comparison of the absorbance maximum at $t = 0$ in such a curve to that obtained in a similarly flashed solution of 0.001 M sodium ferrocyanide in an identical cuvette was used to determine quantum yields and number of photons involved in electron production, since it is well known that aqueous ferrocyanide ejects hydrated electrons with a quantum yield of 0.52 [37]. The inset to Fig. 4 is a double logarithmic plot of the initial absorbance at 670 nm in the flashed copper(I)–ammonia solution, above, versus initial absorbance at 670 nm in the ferrocyanide solution, at varying laser pulse energies, resulting in a slope of 1.07 which confirms that hydrated-electron production is a one-photon process in the copper(I)–ammonia system. Similar results were obtained in the other two amine systems. The quantum yields for electron production for various amine and ammonia solutions are given in Table 2, indicating that the efficiency of this process is very high, increasing somewhat with the molecular weight of the ligand.

The electron decay is almost always first order, with a pseudo first-order decay constant that varies linearly with the copper concentration (not shown); therefore the primary scavenger of the electron must be the copper(I)–ammine or amine complexes themselves, according to

$$e_{aq}^- + CuA_2^+ \rightarrow CuA_2 \qquad (16)$$

or

$$e_{aq}^- + CuA_3^+ \rightarrow CuA_3 \qquad (17)$$

From the slopes of these plots, we confirm the qualitative result, above, that the copper(I) ammonia complexes ($k = 1.9 \times 10^9$ M^{-1} $s^{-1} \pm 10\%$) scavenge electrons better than the methylamine complexes ($k = 1.2 \times 10^9$ M^{-1} $s^{-1} \pm 17\%$), that are, in turn, better than the ethylamine complexes ($k = 0.8 \times 10^9$ M^{-1} $s^{-1} \pm 25\%$). This trend is probably the result of the greater steric effects in the bulkier amine ligands.

3.4. Transient absorbance behavior at 400 nm

At 400 nm, near the absorbance maxima of the longer-lived intermediates, the decay has several components. A typical transient absorbance decay in a copper(I)–ammonia solution following excitation by the 266-nm laser pulse (Fig. 5) shows that there are at least three processes occurring over three time regimes:

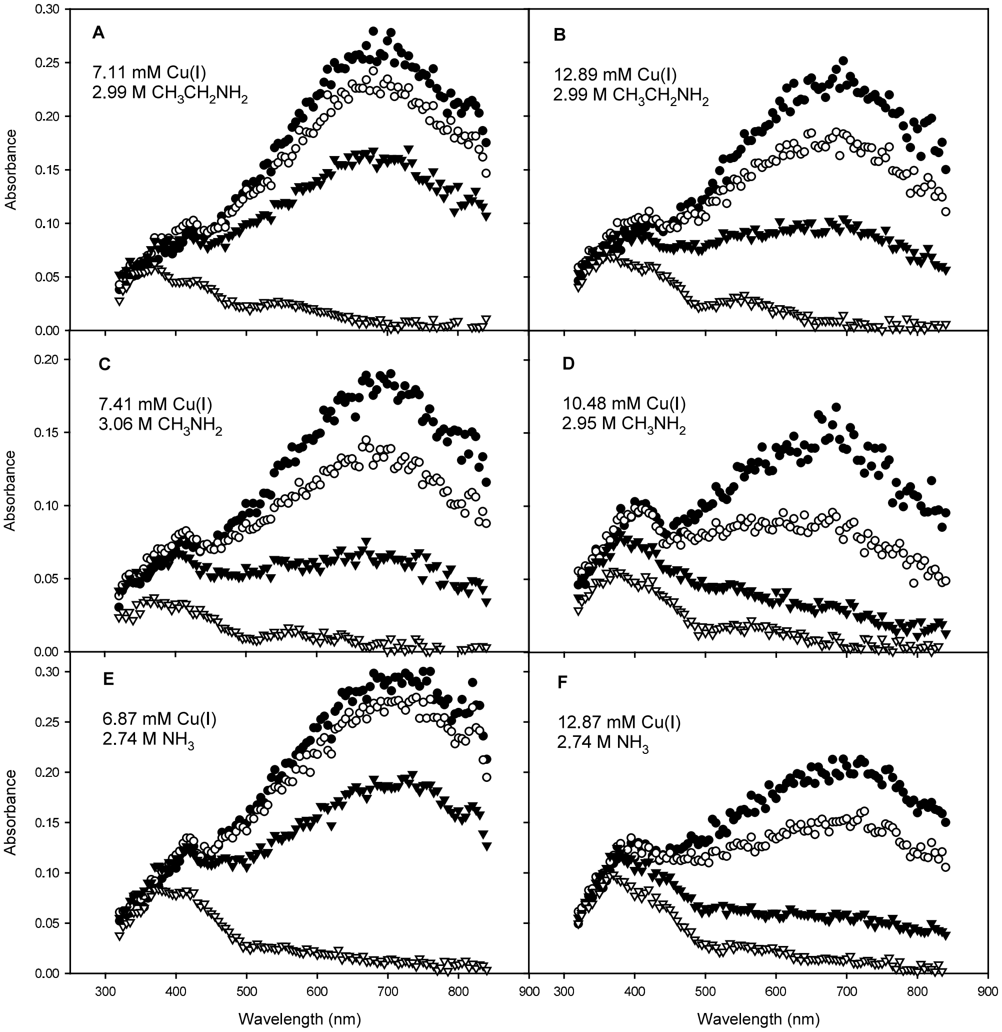


Fig. 3. Time-resolved spectra taken at 25 °C and at delay times after 266-nm laser pulse of (●) 10, (○) 20, (▼) 50, (▽) 850 ns for solutions containing 1 M $NaClO_4$ and the copper(I) complexes at the Cu(I) and ligand concentrations, respectively, of (A) 7.11 mM and 2.99 M ethylamine, (B) 12 mM and 2.99 M ethylamine, (C) 7.41 mM and 3.06 M methylamine, (D) 10.48 mM and 2.95 M methylamine, (E) 6.87 mM and 2.74 M ammonia, and (F) 12.87 mM and 2.74 M ammonia.

Region (1), a fast growing-in of about 17-ns lifetime (see inset) immediately after the pulse; Region (2), a precursor short exponential decay of about 90-ns lifetime; and Region (3), a long decay of about 7000-ns lifetime, which may be a mixture of first and second-order processes. The fast growing-in can also be seen on all of the transient spectra of Fig. 3, especially at the lower copper concentrations. This behavior suggests that there are at least three different processes.

It is difficult to measure the very short growing-in (Region 1) rate constant with much precision because its lifetime is not much longer than the laser pulse width. This fast reaction may be the rapid ligand association of nascent Cu(II) from reactions (14) and (15), such as

$$CuA_2^+ + A \rightarrow CuA_3^+ \qquad (18)$$

The rate constants for the short-decaying process (Region 2) can be obtained from biexponential fits to data like that in the inset of Fig. 5, and these turn out to be proportional to copper concentration, as indicated in Fig. 6 for all three ligand systems. It is apparent from the spectra of Fig. 3 that there are species formed within 10–20 ns after the laser pulse with absorption peaks at about 400 nm, for all three ligand systems, but during the course of the short decay, the 400-nm peaks disappear and are replaced by the spectra of the long-decaying species. Because the pseudo first-order rate constant depends on copper(I) concentration, this short decay may be the reaction of the ground-state copper(I) with excited mononuclear triplets, absorbing at 400 nm, in proceeding towards equilibrium with a long-lived dinuclear species, i.e.

$$\underset{\mathbf{I}}{3CuA_n^+} + CuA_2^+ \rightarrow \underset{\mathbf{II}}{{}^3Cu_2A_{n+2}^{2+}} \qquad (19)$$

where n is 2 or 3. As such, these measured pseudo first-order rate constants would be the true forward rate

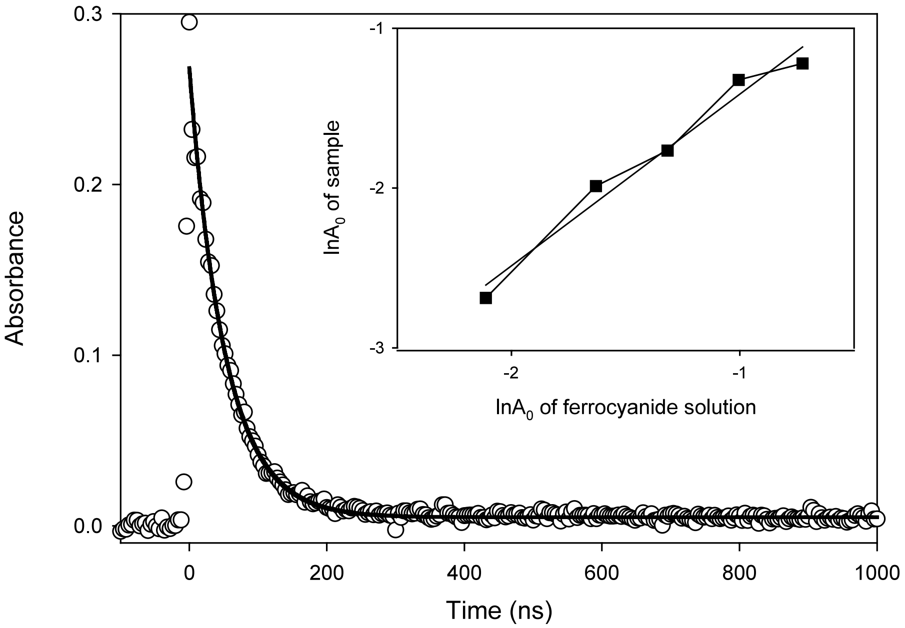


Fig. 4. Absorbance at 670 nm vs. time after 266-nm laser excitation of 0.0081 M CuCl in 2.74 M NH_3, 1 M $NaClO_4$. (○): measured absorbance; (—) monoexponential fit. Inset: ln(absorbance) at $t = 0$ and 670 nm for this copper solution vs. ln(absorbance) at $t = 0$ and 670 nm for 0.001 M sodium ferrocyanide solution.

constant times the ratio of the initial concentration of **I** to the equilibrium concentration of **II**. Nevertheless, these measured values give a qualitative indication of how fast the dinuclear species forms. The decrease in rate constants (2.1×10^9, 1.8×10^9, and 1.2×10^9 M^{-1} s^{-1}) for the ligand systems, NH_3, CH_2NH_2, and $CH_3CH_2NH_2$, shows how steric effects influence this process.

We showed previously [9,10] that the decay lifetime of the long-decaying band for the ammonia system increases with copper(I) concentration, leading to the conclusion that the long-decaying species must be a dinuclear exciplex or excimer in quasi equilibrium with ground-state copper(I)–ammonia complexes. Our initial report assumed that the dinuclear species decays exponentially, but a closer examination of behavior like the long decay as shown in Fig. 7 suggests that the decay is a combination of first and second-order processes. One piece of evidence for this is the fact that the apparent decay lifetime seems to increase with lower laser energies, as shown in Fig. 8. If the natural logarithm of the initial rate of such decays is plotted versus ln A_0 (see inset to Fig. 9) the result is a nearly straight line with slope 1.43, confirming that the decay law is a mixture of first and second order.

A rigorous analysis of kinetic data for the copper(I)–ammonia system further substantiates the mixed-order decay scheme. If a single species decays through two parallel pathways, one of which is first order and the other second order, the rate of decay of absorbance of that species is given by,

$$dA/dt = -k_1A - k_2A^2/\varepsilon \qquad (20)$$

where k_1 and k_2 are the first and second-order rate constants, and ε is the molar extinction coefficient, assuming a 1-cm pathlength. If the first term is small compared to the second, then the integrated rate law would be that of a simple second-order reaction,

$$1/A = k_2t/\varepsilon + 1/A_0 \qquad (21)$$

whereas, if the two terms are comparable, then the integrated rate law would be [35]

$$\ln[(k_1 + Ak_2/\varepsilon)/A] = k_1t + \ln[(k_1 + A_0k_2/\varepsilon)/A_0] \qquad (22)$$

It can be seen that if the value of k_1 can be made to decrease, the second term in Eq. (20) will begin to dominate and eventually the kinetics should ‘level off’ to

Table 2
Quantum yield of hydrated electron production in 1 M ionic strength solutions flashed with 266-nm laser pulse

Ligand	Ligand concentration (mol l^{-1})	Copper(I) concentration (mol l^{-1})	ϕ_e
NH_3	2.74	0.0081	0.34 ± 0.03
CH_3NH_2	2.95	0.0116	0.37 ± 0.04
$C_2H_5NH_2$	3.00	0.0088	0.47 ± 0.04

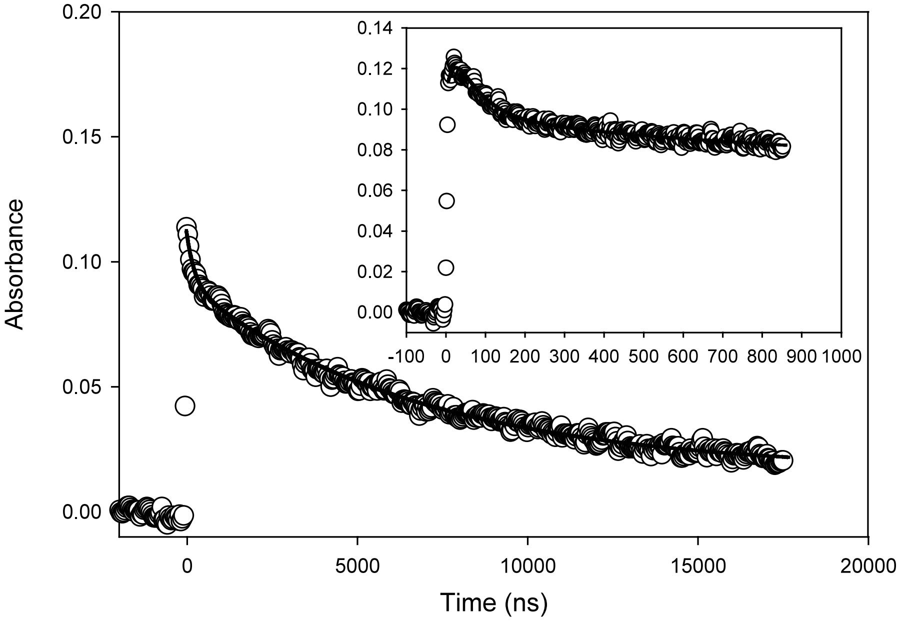


Fig. 5. Absorbance at 400 nm vs. time after 266-nm laser excitation of 0.00687 M CuCl in 2.74 M NH_3, 1 M $NaClO_4$ on long time-scale (20 μs), and, inset, on short time-scale (1 μs). (○): measured absorbance; (—) tri- or biexponential fit.

that of the simple second-order decay of Eq. (21). Our original reports [9,10] on this system suggested that the formation of the dinuclear species was corroborated by the increasing first-order decay lifetime with copper(I) concentration in the ground state. If we now accept that this applies to the pseudo first-order rate constant, k_1, only, then its value should decrease as copper(I) concentration is increased, and thus, the rate law for decay of the dinuclear species should approach the simple second-order decay of Eq. (21) at higher copper(I) concentrations. Evidence that this is so is presented in Fig. 9, which shows that the second-order rate constant, as calculated from data fits using Eq. (21), approaches a constant value at higher copper concentration. If the constant value of the second-order rate constant (actually k_2/ε) is taken as the true value and used to find k_1 by plotting the function on the left side of Eq. (22) versus t (as shown for a typical example in the inset to Fig. 9) then the first-order lifetimes can be found as a function of copper concentration. These are indeed

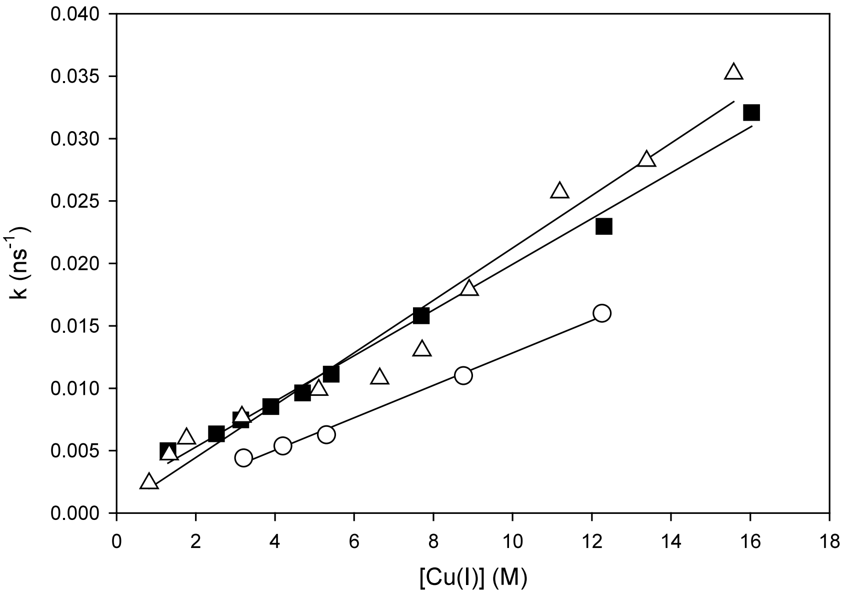


Fig. 6. Short (see text) first order decay constant at 400 nm as a function of Cu(I) concentration for solutions of the Cu(I)–ammonia or amine complexes, excited by a 266-nm laser pulse. The ligands and slopes are (△): 2.83 M NH_3, 2.1×10^9 M^{-1} s^{-1}; (■): 2.80 M CH_2NH_2, 1.8×10^9 M^{-1} s^{-1}; (○) 2.83 M $CH_3CH_2NH_2$, 1.2×10^9 M^{-1} s^{-1}.

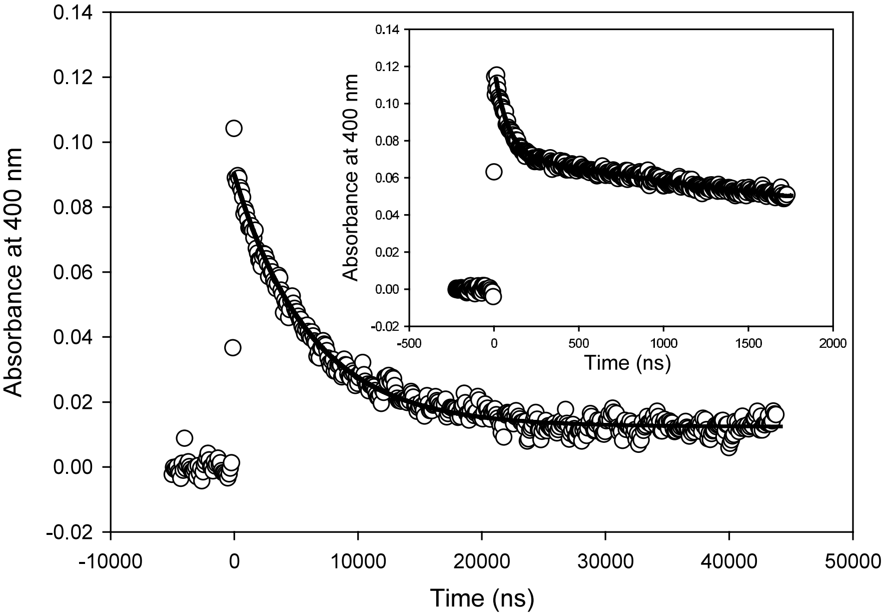


Fig. 7. Absorbance at 400 nm vs. time after 266-nm laser excitation of 0.0081 M CuCl in 2.74 M NH_3, 1 M $NaClO_4$, on 50 000-ns time-scale, and 2000-ns time-scale (inset). (○): measured absorbance; (—) monoexponential fit (long time-scale), or biexponential fit (short time-scale), yielding rate constants of 1.26×10^7 and 1.64×10^5 s^{-1}, for the long and short decays, respectively.

shown in Fig. 10 to increase with copper concentration (in both Eqs. (21) and (22), A and A_0 were taken as measured absorbance and absorbance at infinite time). The slope of this plot, 1840 ns mM^{-1}, is about twice what we originally reported [9] for a solution of about the same ammonia concentration, but with no added $NaClO_4$ and in which the less rigorous kinetic analysis assumed first-order decay only. We showed earlier [10] that this slope is roughly the ratio of the equilibrium constant for reaction (19) to the first-order rate constant, k_{de}, for the decay of the triplet mononuclear species, **I**, which we suggested was a delayed electron ejection process. Since the intercept of such a plot should be roughly the reciprocal of k_{de} we can estimate the equilibrium constant by equating k_{de} to the 400-nm decay constant in the most dilute copper(I) solutions, because at very low copper(I) concentration there seems to be little spectral evidence for the formation of

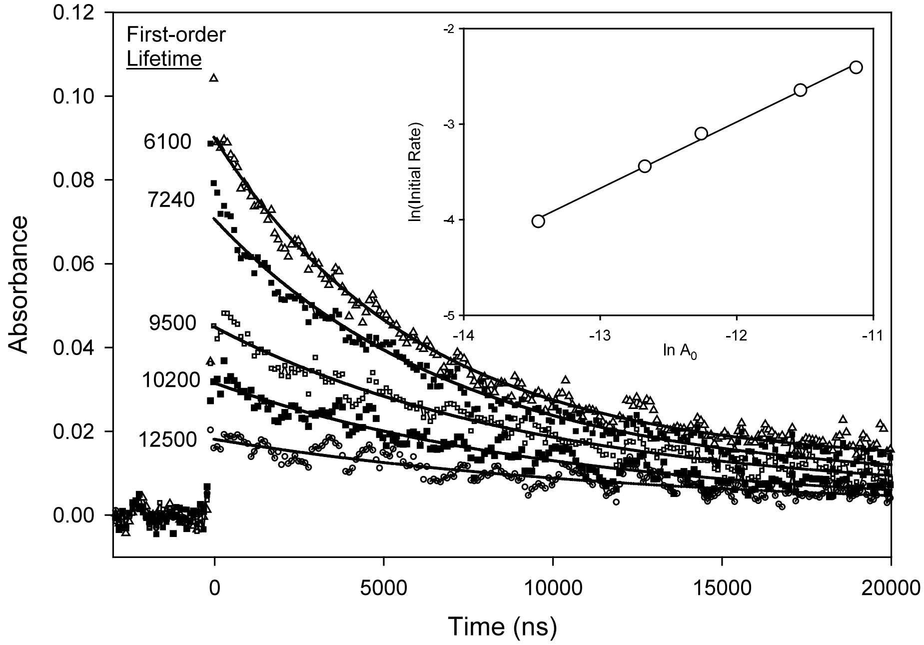


Fig. 8. Comparison of 400-nm first-order decay lifetimes at varying laser pulse energies, for the system, 8.1 mM $CuClO_4$ in 2.74 M NH_3 (aq) and 1 M $NaClO_4$.

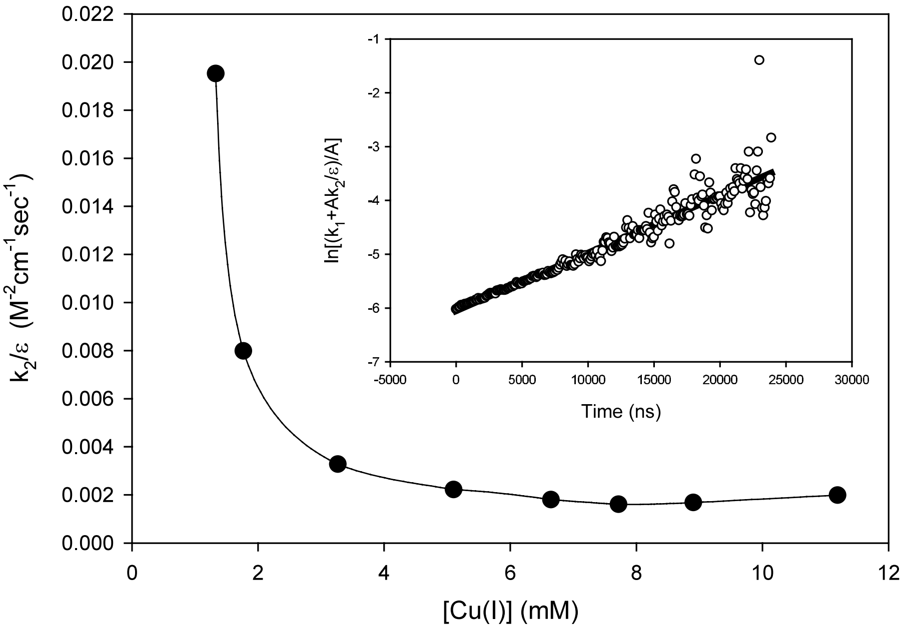


Fig. 9. Graphically determined second-order rate constant (k_2/ε) for long decay of 400-nm signal vs. copper(I) concentration for solutions of copper(I) in 2.83 M NH_3 and 1 M $NaClO_4$, flashed by 266-nm laser pulse. Inset: mixed-order decay plot, according to Eq. (21), for a typical solution containing 5.1 mM copper(I) in 2.83 M NH_3 and 1 M $NaClO_4$. The value of k_2 used in the mixed-order plot was the constant value from the second-order plot, i.e. 1.7×10^{-3} M^{-2} cm^{-1} s^{-1}, and the value of k_1 was iterated until it agreed with the slope.

dinuclear species. We get a lifetime of about 400 ns for a large number of trials, allowing us to estimate a value for K of about 4600 M^{-1}, suggesting that the dinuclear species is quite stable in solution.

The number of photons involved in the formation of the intermediates can be obtained from a double logarithmic plot of the initial absorbance at 400 nm for both the short- and long-decaying species in a flashed sample versus the initial absorbance at 670 nm of the actinometric ferrocyanide solution, and this is shown in Fig. 11 for a solution that contains 8.1 mM Cu(I) and 2.7 M NH_3 at 1 M ionic strength. The slopes for the two lines are 1.16 and 1.18, respectively, suggesting that the formation of short- and long-decaying species are essentially one-photon processes, although some two-photon processes probably also occur to a small extent. The fact that electron-production is a one-photon process in the same solution (see

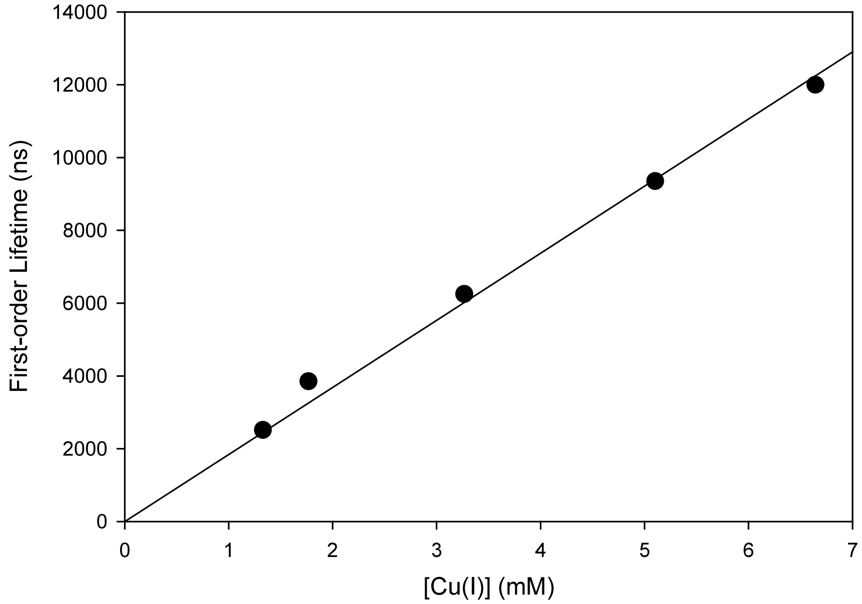


Fig. 10. First-order lifetimes as a function of copper(I) concentration, from the values of k_1 obtained from mixed-order plots such as the inset to Fig. 10, in laser-flashed solutions of copper(I) in 2.83 M NH_3 and 1 M $NaClO_4$.

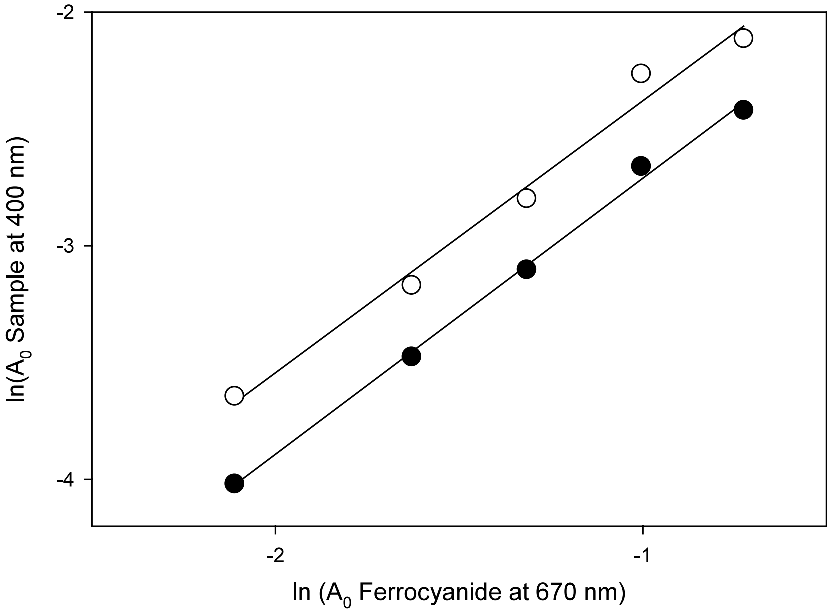
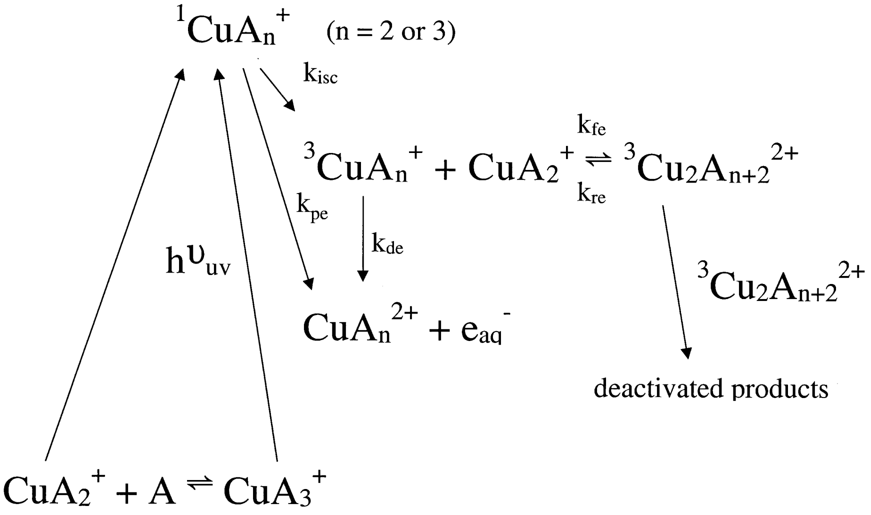


Fig. 11. Plots of ln(absorbance) at $t = 0$ and 400 nm for (○) the short-decay signal, and (●) for the long-decay signal in a solution containing 8.1 mM Cu(I), 2.74 M NH_3, and 1.0 M $NaClO_4$, vs. ln(absorbance) at $t = 0$ and 670 nm for 0.001 M sodium ferrocyanide solution as an actinometer. The slopes are 1.16 and 1.18, respectively.

Fig. 4) suggests that both the electron and the dinuclear species may arise from the same precursor.

The kinetic behavior of the amminecopper(I) system and the qualitative similarity of the behavior of the methyl- and ethylamine systems to the ammonia system leads to a general outline of the photochemical mechanism for all these systems, as shown in Scheme 1.

In the ground state, the ammonia and amine complexes of copper(I) exist as an equilibrated mixture of the bis and tris complexes, CuA_2^+ and CuA_3^+. The mole fraction of each will depend on ligand concentration; for the case of the ammonia system the dot–dashed line in Fig. 12 shows how the mole fraction of bis complex varies over a wide range of ammonia concentration, showing that this complex is the predominant one in all these systems. On the other hand, the much higher 266-nm extinction coefficients of the tris complexes means that they will absorb a major portion of the excitation laser pulse energy, particularly at the higher ligand concentrations. Fig. 12 also illustrates this for the ammonia system by showing that the mole fraction of light absorbed by the tris complex exceeds that of the bis complex when the activity of the ammonia becomes greater than about 1.5. Thus, both the bis and tris complexes may be excited by the laser pulse to singlet states (represented by $^1CuA_n^+$, where n is 2 or 3) each of which may undergo two very rapid, parallel decay pathways: (1) a prompt electron ejection, represented



Scheme 1.

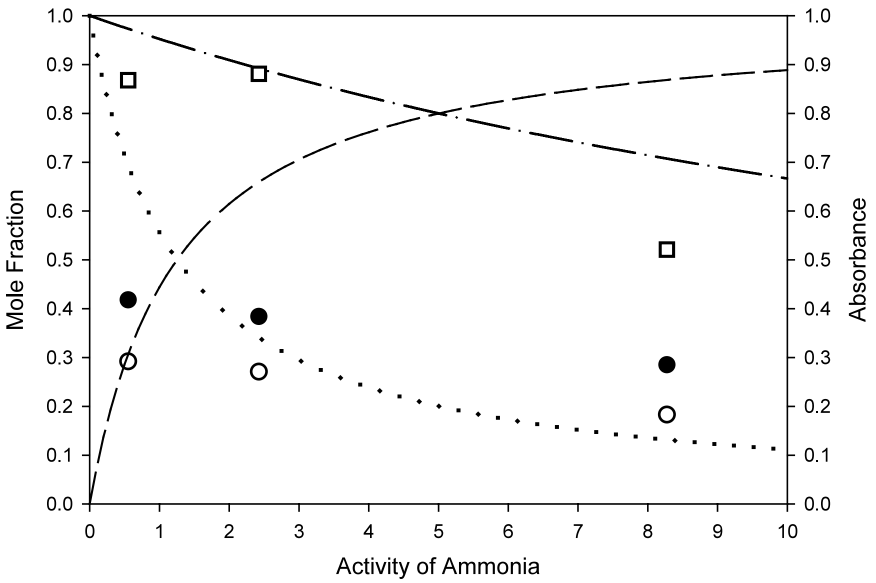


Fig. 12. (-·-) Mole fraction of $Cu(NH_3)_2^+$, (···) mole fraction of light absorbed at 266 nm by $Cu(NH_3)_2^+$, and (- - -) mole fraction of light absorbed at 266 nm by $Cu(NH_3)_3^+$ in an equilibrated mixture of $Cu(NH_3)_2^+$ and $Cu(NH_3)_3^+$ at 1 M ionic strength ($NaClO_4$ medium) as a function of ammonia activity. Initial absorbances in such solutions at (□) 670 nm, (●) 400 nm, fast-decaying species, and (○) 400 nm, slow-decaying species, that have been excited by 266-nm laser pulse, at three ammonia activities.

by the rate constant, k_{pe}, and (2) an intersystem crossing, with k_{isc}, to triplet states $^3CuA_n^+$. Fig. 12 shows how the maximum photoejected electron absorbance (□) at 670 nm obtained at constant laser pulse energy in solutions containing ammonia and copper(I) at high enough concentrations to absorb all the 266-nm laser pulse changes with ligand concentration, strongly suggesting that both CuA_2^+ and CuA_3^+ photoeject electrons efficiently. In fact, it appears that CuA_2^+ somewhat more efficiently photoejects electrons than does CuA_3^+, which stands in contrast to the older CW results [33] obtained for the photo-oxidation of Cu(I) in aqueous solutions containing ammonia and ammonium ion. The triplet monomers, $^3CuA_n^+$, formed in competition with the prompt electron ejection may decay through a delayed electron ejection process, k_{de}, or they may react with the ubiquitous CuA_2^+ to equilibrate with a dinuclear species, $^3Cu_2A_{n+2}^{2+}$, via the forward reaction, k_{fe}, which is related to the measured second-order decay constant for the short decay. Fig. 12 also shows the maximum absorbance at 400 nm for both the triplet monomer, $^3CuA_n^+$ (●) and the dinuclear species, $^3Cu_2A_{n+2}^{2+}$ (○), depending on ligand concentration, again demonstrating that excitation of the bis complex is somewhat more efficient in generating these triplet species than the tris complex. The dinuclear species, $^3Cu_2A_{n+2}^{2+}$, which may or may not be a single species, would be referred to as an exciplex, if $n = 3$, or an excimer, if $n = 2$[1], and has two pathways for decay: (1) through the equilibrium back-reaction, k_{re}, and the delayed ejection, k_{de}, of electron from the monomeric triplet, $^3CuA_n^+$, a process that predominates at low copper(I) concentration, or (2) at high copper(I) concentration, through a second-order collision with itself, forming unspecified deactivated products.

The 400-nm decay lifetimes (determined from a simple first-order analysis) for methylamine and ethylamine copper(I) systems are shown in Fig. 13 as a function of copper(I) concentration. In both cases the lifetimes increase with copper concentration as in the ammonia system, confirming that these systems also form dinuclear species. The initial slopes of the plots are about 2000 and 3600 for the methylamine and ethylamine systems, respectively, and these values, along with that obtained for the ammonia system, above, suggest that the stability constant increases with the series: ammonia, methylamine, ethylamine. Moreover, both lifetimes approach a limiting value that may represent the lifetime of the self-deactivation step of the dinuclear species. Thus, the ethylamine dinuclear species is not only thermodynamically more stable than the methylamine species, but it is also kinetically more stable.

3.5. *Spectral features of the individual species*

If we now revisit the transient spectra in Fig. 3, we can gain some insight into the spectra of the individual species in Scheme 1. The spectra of the dinuclear species most likely corresponds to the one in each set with the longest (850 ns) delay time. All three ligand systems produce strikingly similar dinuclear spectra, with a strong band in the 370–390-nm region, a shoulder or

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[1] A second excimer, $^3Cu_2A_6^{2+}$, might also form in small quantities through the reaction of $^3CuA_3^+$ with CuA_3^+.

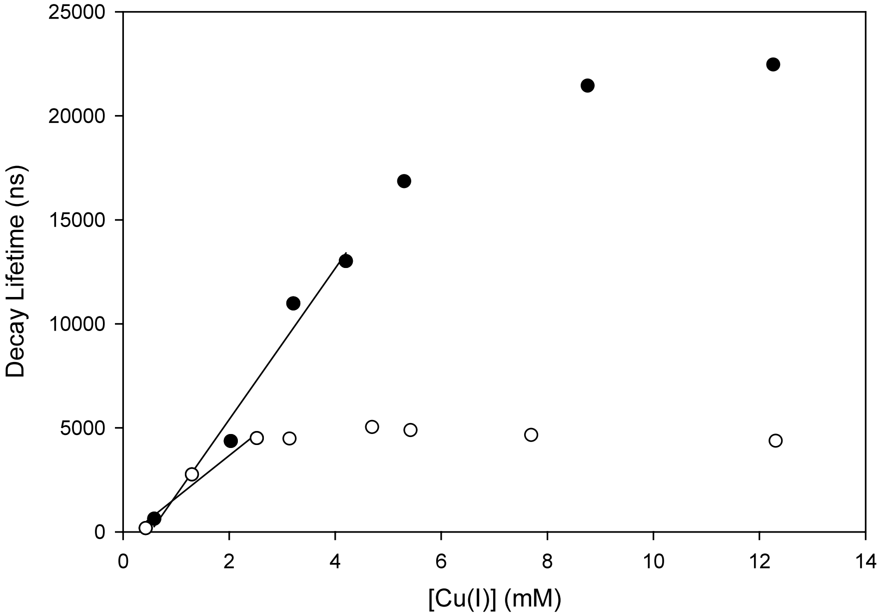

Fig. 13. First-order decay lifetime for 400-nm absorbing transient in (○) 2.8 M methylamine, or (●) 3.0 M ethylamine, both at unit ionic strength ($NaClO_4$ medium), as a function of copper(I) concentration. Straight lines are linear regressions of first three points for methylamine, and first four points for ethylamine.

weaker band at 420–430 nm, and a weaker, broad band at 550 nm. The triplet mononuclear precursor in each ligand system has a sharp, strong band at 400–410 nm, that appears on the shortest delay spectrum as a shoulder to the very broad and intense hydrated electron band with maximum at 700 nm.

3.6. Bonding in the dinuclear species

Because the ammonia or amine ligands are highly saturated with only a lone pair of sp^3 electrons on the nitrogen atom of each molecule, they would not be expected to bridge to two copper atoms in $^3Cu_2A_4^{2+}$ or $^3Cu_2A_5^{2+}$. Instead, it is likely that there is a copper–copper bond of some sort holding the species together. This can be justified if we consider that in the triplet state of monomeric copper(I), such as in $^3CuA_2^+$ or $^3CuA_3^+$, an electron has been promoted from the d^{10} ground state to an s or p orbital, so that its electron configuration is d^9p^1 or d^9s^1. These species might then form one-electron bonds with the empty p or s orbitals of the ground state species, CuA_2^+. The possibility of a stable bond between two ground-state copper(I) atoms was first proposed by Mehrotra and Hoffmann [38], who used extended Hückel calculations involving 3d, 4s, and 4p orbitals to show there can be a weak, attractive Cu(I)–Cu(I) interaction. A copper–copper bond was later confirmed [39–41] in a mixed-valence dinuclear copper complex coordinated to a macrobicyclic octaaza ligand which forces the copper(I) ions to be within bonding proximity and form a one-electron bond, presumably between a singly occupied d orbital on one copper atom to the empty s or p orbitals of the other copper atom. In the copper–copper system we describe here there could be a stronger interaction between the ground-state copper(I) and triplet copper(I) because the latter has two singly occupied orbitals, a 3d and a 4s or 4p, that can interact with the empty 4s and 4p orbitals of the former, forming two one-electron bonds and resulting in a bond order of unity.

4. Conclusions

1) Henry's law constants were obtained for methylamine and ethylamine in aqueous solution at 1 M ionic strength, and these are 5.002 and 7.987 Torr M^{-1}, respectively.
2) Copper(I) readily forms bis- and triscoordinated complexes with methyl- and ethylamine ligands in aqueous solution, with spectral and photochemical properties very similar to those of the amminecopper(I) complexes. The stepwise stability constants are 0.067 ± 0.007 and 0.040 ± 0.004 for the tris(methylamine) and tris(ethylamine) complexes, respectively.
3) One-photon excitation at 266 nm of the ammine, methyl-, and ethylamine copper(I) complexes produces hydrated electrons with a high quantum yield (0.37–0.47), along with several short-lived species that undergo reactions dependent on copper concentration.

4) The rate constants for electron scavenging by the parent copper(I) ammine or amine follow the ligand order ammonia > methylamine > ethylamine.
5) Kinetic analysis strongly supports the hypothesis that dinuclear exciplexes and excimers containing copper–copper bonds are formed after photoexcitation of the ammine and amine complexes. Prompt electron ejection occurs from the excited singlet state of a photolyzed monomer, CuA_2^+ or CuA_3^+, in parallel with intersystem crossing to a triplet monomer, $^3CuA_2^+$ or $^3CuA_3^+$, whose longer lifetime allows the reaction with ground-state CuA_2^+ and equilibration with the dinuclear excited state.
6) Thermodynamic and kinetic stability of the dinuclear excited state complexes increase for the ligand series: ammonia < methylamine < ethylamine.

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