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Formation and Photoinduced Electron Ejection of Amminedicyanocuprate(I) and Cyano-Bridged Trinuclear Copper(I) Complexes in Aqueous Ammonia Solution

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UV absorption spectral evidence confirms that a mixed-ligand complex, $Cu(CN)_2(NH_3)^-$, is formed in an aqueous solution of $KCu(CN)_2$ and ammonia. The stepwise stability constant for the reaction, $Cu(CN)_2^- + NH_3 = Cu(CN)_2(NH_3)^-$, is 2.80 ± 0.40 in 1 M ionic strength, $NaClO_4$ medium at 25 °C. This amminedicyanocuprate(I) ion readily combines in aqueous solution in a 1:2 and 2:1 molar ratios with $Cu(NH_3)_2^+$ to form two trinuclear ionic species, presumably with cyano bridges, with the suggested formulas of $Cu_3(CN)_2(NH_3)_5^+$ and $Cu_3(CN)_4(NH_3)_3^-$. The resolved UV absorption spectra of the monomer and two trimers have been determined and exhibit strong bands, presumably metal–ligand charge transfer in nature, in the 200–250-nm region. When solutions of all three complexes absorb a pulse of 266-nm laser light, they photoeject hydrated electrons monophotonically, with quantum yields of 0.41 ± 0.02, 0.53 ± 0.02, and 0.50 ± 0.01 for the monomer, cationic trimer, and anionic trimer, respectively, suggesting that absorption in the charge-transfer-to-solvent bands of these complexes results in an efficient electron ejection process that is enhanced by the existence of a polynuclear structure with cyano bridges. No room-temperature luminescence is observed for these complexes.

Introduction

Monomeric copper(I) complexes, CuL_n, where $n = 2$ or 3 and $L = Cl^-, Br^-, I^-, NH_3, CH_3NH_2, C_2H_5NH_2$, and CN^- and mixtures thereof, have been shown[1−22] to undergo very efficient photoinduced electron ejection, when irradiated into their charge-transfer-to-solvent (CTTS) bands,

$$Cu^{I}L_n + UV\ (\lambda < 310\ nm) \rightarrow Cu^{II}L_n + e_{aq}^- \qquad (1)$$

with quantum yields on the order of 0.2−0.3. Interestingly, room-temperature luminescence is observed along with the electron ejection only when halo ligands are present in the complex, and this has been ascribed to the formation of exciplexes in an excited-state equilibrium.[1−20] Because of their very large stability constants,[23,24] the cyano complexes

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† Undergraduate students.

(1) Davis, D. D.; Stevenson, K. L.; Davis, C. R. *J. Am. Chem. Soc.* **1978**, *100*, 5344−9.
(2) Stevenson, K. L.; Kaehr, D. M.; Davis, D. D. Davis,C. R *Inorg. Chem.* **1980**, *19*, 781−3.
(3) Davis, C. R.; Stevenson, K. L. *Inorg. Chem.* **1982**, *21*, 2514−6.
(4) Braish, T. F.; Duncan, R. E.; Harber, J. J.; Steffen, R. L.; Stevenson, K. L. *Inorg. Chem.* **1984**, *23*, 4072−5.
(5) Horváth, A.; Papp, S.; Decsy, Z. *J. Photochem.* **1984**, *24*, 331−9.
(6) Stevenson, K. L.;.Braun, J. L.; Davis, D. D.; Kurtz, K. S.; Sparks, R. I. *Inorg. Chem.* **1988**, *27*, 3472−6.
(7) Horváth, A.; Zsilák, Z.; Papp, S. *J. Photochem. Photobiol., A* **1989**, *50*, 129−39.
(8) Horváth, O.; Stevenson, K. L. *Inorg. Chem.* **1989**, *28*, 2548−51.
(9) Horváth, A.; Stevenson, K. L. *Inorg. Chim. Acta* **1991**, *186*, 61−6.
(10) Horváth, A.; Horváth, O.; Stevenson, K. L. *J. Photochem. Photobiol., A* **1992**, *68*, 155−63.
(11) Horváth, A.; Stevenson, K. L. *Inorg. Chem.* **1993**, *32*, 2225−7.
(12) Horváth, O.; Fendler, J. H. *J. Photochem. Photobiol., A* **1993**, *71*, 33−7.
(13) Horváth, A.; Wood, C. E.; Stevenson, K. L. *J. Phys. Chem.* **1994**, *98*, 6490−5.
(14) Horváth, A.; Wood, C. E.; Stevenson, K. L *Inorg. Chem.* **1994**, *33*, 5351−4.
(15) Stevenson, K. L.; Knorr, D. W.; Horváth, A. *Inorg. Chem.* **1996**, *35*, 835−9.
(16) Stevenson, K. L.; Horváth, A. *J. Am. Chem. Soc.* **1996**, *118*, 6088−9.
(17) Stevenson, K. L.; Dhawale, R. S.; Horváth, A.; Horváth, O. *J. Phys. Chem. A* **1997**, *101*, 3670−6.
(18) Stevenson, K. L.; Bell, P. B.; Horváth, O.; Horváth, A. *J. Am Chem. Soc.* **1998**, *120*, 4234−5.
(19) Stevenson, K. L.; Bell, P. B.; Dhawale, Ravi, S.; Horváth, O.; Horváth, A. *Radiat. Phys. Chem.* **1999**, *55*, 489−496.
(20) Horváth, A.; Stevenson, K. L. *Coord. Chem. Rev.* **2000**, *208*, 139−151.
(21) Stevenson, K. L.; Bell, P. B.; Watson, R. E. *Coord. Chem. Rev.* **2002**, *229*, 133−146.
(22) Stevenson, K. L.; Jarboe, J. H. *J. Photochem. Photobiol., A* **2002**, *150/1−3*, 49−57.

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of copper(I), $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$, are quite robust and air-stable in aqueous solution and can be formed, especially in the case of the first two, essentially by the quantitative reaction of copper(I) salts, such as CuCl or CuCN, with aqueous solutions of KCN or NaCN. In contrast, the amminecopper(I) complexes, $Cu(NH_3)_2^+$ and $Cu(NH_3)_3^+$, are formed in aqueous solution only at high ammonia activity due to their small stability constants, and they are immediately oxidized to the deep blue amminecopper(II) upon exposure to air.[4,8,25] Yet these ammine complexes also efficiently undergo electron photoejection as in reaction 1, along with the formation of a metastable dinuclear complex in the excited state.[18,19,21] Mixed-ligand complexes of the type $Cu(CN)_2X^{2-}$, where X = Cl, Br, or I, readily form in solutions of high halide concentration, and these complexes also efficiently photoeject hydrated electrons and exhibit interesting luminescence properties.[9−11,13,14] One of the goals of this study, then, was to prepare a mixed-ligand species similar to the halodicyanocuprate(I) complexes, in which the halo ligand is replaced by the similarly weak donor ligand, NH_3, forming amminedicyanocuprate(I) anion, and to compare its photoredox behavior to that of the other complexes mentioned above.

In the exciting new field of nanotechnology it is becoming increasingly apparent that nanomachines will be developed from the "bottom up", i.e., from devices synthesized at the molecular level, and they will need to be powered by convenient energy sources such as light.[26,27] These molecular machines will be constructed of chains of atoms that can both serve as the structural framework and at the same time transfer energy from one part of the machine to the other. Thus, polynuclear complexes containing chromophoric metal centers and electron-conducting bridges, such as cyano ligands, may become important components of these systems.[28−30] Another goal of this study, then, was to see what effect the formation of cyano-bridged copper(I) trinuclear complexes has on the ability of the copper(I) chromophore to photoeject hydrated electrons into aqueous solution, as a potential building block for photodriven molecular devices.

Experimental Section

Aqueous solutions of the various complexes containing ammonia ligands were made at 25 °C by dissolving very pure CuCl, or $KCu(CN)_2$, both prepared as described previously,[1,5] or by adding Cu wire and aqueous standardized $Cu(ClO_4)_2$ in solutions of ammonia containing 1 M $NaClO_4$ to fix ionic strength at 1 M and bubble-degassed with Ar. (*Caution! Perchlorate salts may explode when heated*.) In most cases the ammonia concentration was targeted at 3 M and after bubbling with Ar solutions were standardized by titration of an aliquot with standard HCl. The activity of ammonia was determined from activity data published previously.[8] Syringe techniques were used to make mixtures of ammonia solutions containing CuCl or $KCu(CN)_2$ for spectral determinations of the stoichiometry of oligomer formation. UV absorption spectra were taken using a quartz, 0.1-mm cuvette (Hellma) in a Hewlett-Packard 8453 spectrophotometer and spectral calculations were made using Sigmaplot 5.0. A Beer's law study of $Cu(CN)_2^-$ in pure water was made with successive dilutions of the complex prepared by dissolving CuCN in a standardized solution of NaCN in a 1:1 molar ratio.

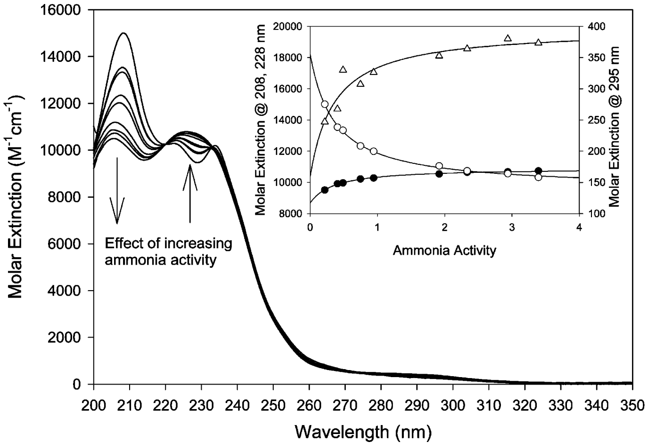

Figure 1. Molar extinction UV absorption spectra at 25 °C of aqueous solutions of 10 mM $KCu(CN)_2$, 1 M $NaClO_4$, and NH_3 in which the activity was varied from 0.223 to 3.39. Inset: molar extinction vs ammonia activity of the same solutions at (○) 208 nm, (●) 228 nm, and (△) 295 nm.

Laser flash photolysis of the solutions yielding transient absorbance signals for kinetic analysis and time-resolved spectra was carried out in the nanosecond Nd:YAG system described previously.[31]

Results and Discussion

Spectra. The molar extinction spectra of a series of solutions of $Cu(CN)_2^-$ in varying ammonia concentrations at constant ionic strength of 1.0 are shown in Figure 1, along with corresponding plots of extinction vs ammonia activity (inset) at the three, key wavelengths where there is the greatest variation in absorbance with ammonia activity. Assuming that these absorbance changes are due to the shift in the equilibrium

$$Cu(CN)_2^- + NH_3 = Cu(CN)_2(NH_3)^- \qquad (2)$$

the dependence of observed extinction, ϵ, on the individual extinction coefficients, ϵ_2 and ϵ_3 of $Cu(CN)_2^-$ and $Cu(CN)_2(NH_3)^-$, respectively, on the activity of ammonia, a, and on the equilibrium constant, K, is

$$\epsilon = \epsilon_3 + (\epsilon_2 - \epsilon_3)/(1 + Ka) \qquad (3)$$

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(23) Baxendale, J. H.; Westcott, D. T. *J. Chem. Soc.* **1959**, 2347−51.

(24) Izatt, R. M.; Johnston, H. D.; Watt, G. D.; Christensen, J. J. *Inorg. Chem.* **1967**, *6*, 132−5.

(25) Bjerrum, J. *Acta Chem. Scand.* **1986**, *A40*, 233−235.

(26) Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Venturi, M. *Acc. Chem. Res.* **2001**, *34*, 445−455.

(27) Balzani, V.; Gómez-López, M.; Stoddart, J. F. *Acc. Chem. Res.* **1998**, *31*, 405−414.

(28) Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. *Top. Curr. Chem.* **1990**, *158*, 73−149.

(29) Scandola, F.; Argazzi, R.; Bignozzi, C. A.; Chiorboli, C.; Indelli, M. T.; Rampi, M. A. *Coord. Chem. Rev.* **1993**, *125*, 283−92.

(30) Bignozzi, C. A.; Argazzi, R.; Bortoline, O.; Scancola, F.; Harriman, A. *New. J. Chem.* **1996**, *20*, 731−8.

(31) Stevenson, K. L.; Papadantonakis, G. A.; LeBreton, P. R. *J. Photochem. Photobiol., A* **2000**, *133*, 159−167.

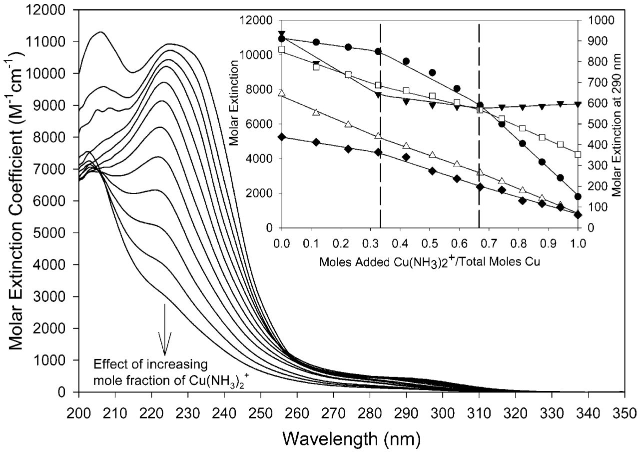

Figure 2. Molar extinction UV absorption spectra at 25 °C of mixtures of aqueous solutions containing 1 M $NaClO_4$, 2.89 M NH_3, and either 10 mM $KCu(CN)_2$ or 10 mM $Cu(NH_3)_2^+$ in varying molar ratios. Inset: molar extinction vs (moles added of $Cu(NH_3)_2^+$)/(total moles of Cu) at (▼) 202 nm, (□) 212 nm, (●) 225 nm, (△) 240 nm, and (♦) 290 nm.

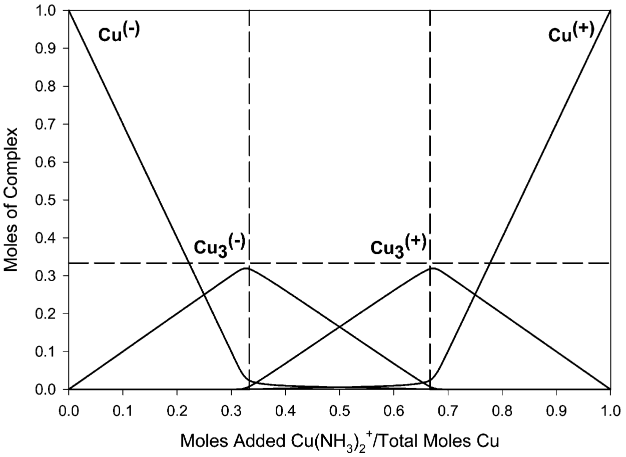

Figure 3. Distribution diagram at 25 °C for the solutions in Figure 2, showing moles of complex vs (moles added of $Cu(NH_3)_2^+$)/(total moles of Cu).

The best fit of the data in the inset at the three wavelengths yielded values of K that were averaged to give a value of $K = 2.80 \pm 0.40$, which was then used to plot the curves fitting the data in the inset. Using a linear regression of eq 3, all the spectra of Figure 1 could then be used to calculate the resolved spectra of $Cu(CN)_2^-$ and $Cu(CN)_2(NH_3)^-$, and these are shown in Figure 4. The fact that the resolved spectrum of $Cu(CN)_2^-$ is virtually identical to published spectra[6,32,33] is taken as verification that eq 2 represents the principle reaction of dicyanocuprate(I) ions with ammonia ligands, at least at ammonia concentrations up to about 4 M. The formation of polynuclear species at 0 and 2.98 M ammonia was ruled out by the observation that such systems strictly obey Beer's law (not shown) as copper concentration is varied up to 20 mM. We then conclude that in these concentration ranges of copper and ammonia, there are only the two monomers as described by eq 2.

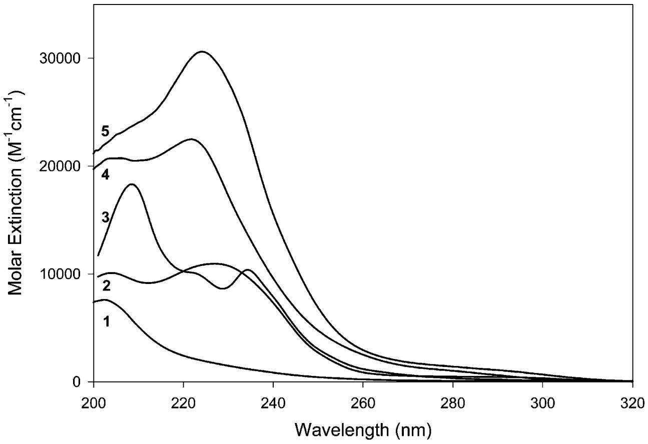

Figure 4. Resolved molar extinction spectra at 25 °C for (1) $Cu(NH_3)_2^+$, (2) $Cu(CN)_2(NH_3)^-$, (3) $Cu(CN)_2^-$, (4) $Cu_3^{(+)}$, and (5) $Cu_3^{(-)}$.

The spectral evidence for the formation of trinuclear species is contained in Figure 2, which shows the molar extinction spectra of a series of solutions in which the mole fraction of the added cationic species, $Cu(NH_3)_2^+$ (based on total moles of copper), is varied from 0 to 1 in mixtures of $Cu(NH_3)_2^+$ and $Cu(CN)_2^-$, at 2.93 M NH_3 and 1 M $NaClO_4$ concentration. The top spectrum is essentially that of $Cu(CN)_2(NH_3)^-$, and the bottom spectrum is that of $Cu(NH_3)_2^+$ in equilibrium with a small amount of $Cu(NH_3)_3^+$ ($K_{eq} = 0.050$).[8] As the mole fraction changes, it is clear that the spectrum changes significantly from that of either of the two monomeric species to spectra exhibiting primarily what appears to be a single absorption band between 220 and 230 nm for intermediate values of mole fraction. Spectophotometric titration plots of molar extinction coefficients from these spectra, at a variety of wavelengths, vs mole fraction of added $Cu(NH_3)_2^+$ are shown in the inset to Figure 2 and confirm the formation of two trinuclear oligomers: a cationic species of formula $Cu_3(CN)_2(NH_3)_n^+$ and an anionic species, $Cu_3(CN)_4(NH_3)_m^-$, where n and m are unspecified numbers of ammonia ligands. The linearity of these plots, the slopes of which change at mole fractions of 1/3 and 2/3, confirm that the system can be characterized as mixtures of the two starting monomers and the two trinuclear species.

Using the shortened notation: $Cu^{(+)}$ = equilibrated $Cu(NH_3)_2^+$ and $Cu(NH_3)_3^+$, $Cu^{(-)} = Cu(CN)_2(NH_3)^-$, $Cu_3^{(+)} = Cu_3(CN)_2(NH_3)_n^+$, and $Cu_3^{(-)} = Cu_3(CN)_4(NH_3)_m^-$, the reactions would be (without showing ammonia molecules that might be needed to balance the equations depending on the values of n or m)

$$\mathrm{Cu}^{(+)} + 2\mathrm{Cu}^{(-)} \rightarrow \mathrm{Cu}_3^{(-)} \quad \text{mole fraction} < 1/3 \qquad (4)$$

$$2\mathrm{Cu}^{(+)} + \mathrm{Cu}^{(-)} \rightarrow \mathrm{Cu}_3^{(+)} \quad \text{mole fraction} > 2/3 \qquad (5)$$

and

$$\mathrm{Cu}^{(+)} + \mathrm{Cu}_3^{(-)} \rightleftarrows \mathrm{Cu}^{(-)} + \mathrm{Cu}_3^{(+)} \quad 1/3 < \text{mole fraction} < 2/3 \qquad (6)$$

Only two stability constants, designated K_{3-} and K_{3+}, for eqs 4 and 5, respectively, are needed at a given ammonia activity to describe the equilibria in such a system. These

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(32) Pierrard, J.-C.; Kappenstein, C.; Hugel, R. *Rev. Chim. Miner.* **1971**, *8*, 11−19.

(33) Kappenstein, C.; Hugel, R. *Inorg. Chem.* **1976**, *16*, 250−4.

are given by

$$K_{3-} = [\mathrm{Cu_3}^{(-)}]/[\mathrm{Cu}^{(+)}][\mathrm{Cu}^{(-)}]^2 \tag{7}$$

and

$$K_{3+} = [\mathrm{Cu_3}^{(+)}]/[\mathrm{Cu}^{(+)}]^2[\mathrm{Cu}^{(-)}] \tag{8}$$

Since solutions of all of these complexes can be prepared by mixing the two monomers, $\mathrm{Cu}^{(+)}$ and $\mathrm{Cu}^{(-)}$, in various ratios, we can relate the initial concentrations of these monomers to the equilibrium concentrations of all species as

$$\text{initial concentration of } \mathrm{Cu}^{(+)} = c_{0+} = [\mathrm{Cu}^{(+)}] + 2[\mathrm{Cu_3}^{(+)}] + [\mathrm{Cu_3}^{(-)}] \tag{9}$$

$$\text{initial concentration of } \mathrm{Cu}^{(-)} = c_{0-} = [\mathrm{Cu}^{(-)}] + [\mathrm{Cu_3}^{(+)}] + 2[\mathrm{Cu_3}^{(-)}] \tag{10}$$

Replacement of $[\mathrm{Cu_3}^{(+)}]$ and $[\mathrm{Cu_3}^{(-)}]$ follows from eqs 7 and 8 resulting in two simultaneous quadratic equations,

$$2K_{3+}[\mathrm{Cu}^{(-)}][\mathrm{Cu}^{(+)}]^2 + (1 + K_{3-}[\mathrm{Cu}^{(-)}]^2)[\mathrm{Cu}^{(+)}] - c_{0+} = 0 \tag{11}$$

$$2K_{3-}[\mathrm{Cu}^{(+)}][\mathrm{Cu}^{(-)}]^2 + (1 + K_{3+}[\mathrm{Cu}^{(+)}]^2)[\mathrm{Cu}^{(-)}] - c_{0-} = 0 \tag{12}$$

which can be solved iteratively for $[\mathrm{Cu}^{(+)}]$ and $[\mathrm{Cu}^{(-)}]$ if the two stability constants are known, leading to values for $[\mathrm{Cu_3}^{(+)}]$ and $[\mathrm{Cu_3}^{(-)}]$ at any concentration ratio of the two initial monomers. Since the observed molar extinction coefficient is, in terms of the individual extinction coefficients,

$$\epsilon = ([\mathrm{Cu}^{(+)}]\epsilon_+ + [\mathrm{Cu}^{(-)}]\epsilon_- + [\mathrm{Cu_3}^{(+)}]\epsilon_{3+} + [\mathrm{Cu_3}^{(-)}]\epsilon_{3-})/(c_{0+} + c_{0-}) \tag{13}$$

the plots of Figure 2 can be simulated if the extinction coefficients of all four complexes are known at the various wavelengths. For this we need the resolved spectra of all four complexes, which we already have for the monomers (Figures 1 and 2) but which must be calculated for the trinuclear complexes. This is done by assuming that if the reactions between monomers are quantitative, i.e., the trinuclear complexes have very large stability constants, then in the region where mole fraction of added $\mathrm{Cu}^{(+)}$ is less than 1/3 there is essentially only $\mathrm{Cu_3}^{(-)}$ and excess $\mathrm{Cu}^{(-)}$ after mixing, such that, from eqs 9 and 10,

$$c_{0+} = [\mathrm{Cu_3}^{(-)}] \tag{14}$$

and

$$c_{0-} = [\mathrm{Cu}^{(-)}] + 2[\mathrm{Cu_3}^{(-)}] \tag{15}$$

This results in the relation

$$(c_{0+} + c_{0-})\epsilon/c_{0-} = \epsilon_- + c_{0+}(\epsilon_{3-} - 2\epsilon_-)/c_{0-} \tag{16}$$

suggesting that a linear regression plot of the left side vs c_{0+}/c_{0-} yields values of ϵ_{3-} from the slope and intercept. Similarly, linear regression analysis of the molar extinction coefficients in solutions for which the mole fraction of added $\mathrm{Cu}^{(+)}$ is greater than 2/3 yields values of ϵ_{3+}. This was done at all wavelengths, and the molar extinction spectra, Figure 4, of the two complexes, $\mathrm{Cu_3}^{(+)}$ and $\mathrm{Cu_3}^{(-)}$, were obtained. Subsequently, eqs 11−13 were used to simulate the plots of Figure 2 (solid lines) using very large values ($K = 10^6$ in both cases) of the stability constants of the two trinuclear complexes. It should be noted that only such large values of the stability constants result in linear plots. Figure 3 shows a distribution diagram for the four complexes involved in terms of mole fraction of added $\mathrm{Cu}^{(+)}$.

The spectra of $\mathrm{Cu}^{(+)}$ and $\mathrm{Cu(CN)_2}^-$ are shown in Figure 4 (labeled 1 and 3, respectively) for comparison to those of the monomer, $\mathrm{Cu(CN)_2(NH_3)}^-$, and the two trinuclear complexes, $\mathrm{Cu_3}^{(+)}$ and $\mathrm{Cu_3}^{(-)}$ (labeled 2, 4, and 5, respectively). The three main UV bands in $\mathrm{Cu(CN)_2}^-$, at about 234, 223, and 208 nm, have all previously been assigned[7] as metal−ligand charge-transfer (MLCT) bands that are notably missing in that of $\mathrm{Cu}^{(+)}$ (which is primarily $\mathrm{Cu(NH_3)_2}^+$) since the latter has no ligand π-orbitals into which the electrons may be excited.[8] The addition of the ammine ligand to form $\mathrm{Cu(CN)_2(NH_3)}^-$ (spectrum 2) appears to shift at least two of these MLCT bands to higher energy suggesting that there may be a small increase in the crystal-field splitting of the copper(I) d-orbitals, from which the MLCT transitions originate, consistent with the ammonia's middle position in the spectrochemical series. In the case of the trinuclear species, it is difficult to sort out the fine structure of the various transitions that contribute to the broad absorptions that peak at 222 and 224 nm respectively for $\mathrm{Cu_3}^{(+)}$ and $\mathrm{Cu_3}^{(-)}$, but it is clear that the MLCT bands have oscillator strengths that are 2−3 times stronger than in the monomers due to the tripling of the number of chromophoric copper atoms. Moreover, the monomer, $\mathrm{Cu(CN)_2(NH_3)}^-$, and the two trinuclear complexes all exhibit a very weak absorption band at 290−295 nm, which does not appear in $\mathrm{Cu(CN)_2}^-$ nor $\mathrm{Cu(NH_3)_2}^+$ but was reported earlier to be in the spectrum of $\mathrm{Cu(NH_3)_3}^+$. [8] Although the assignment of this band has not been made, it would appear to be associated with trigonal planar structures containing ammine ligands, as discussed below.

Structure. It is generally recognized[34] that, in aqueous solution, copper(I) complexes such as di- and tricyanocuprate do not have water in the inner coordination sphere, and therefore, their structures are consistent with their simple coordination numbers, i.e., *linear* for biscoordinated and *planar* for triscoordinated complexes. Since copper(I) is a d^{10} system, the bonding involves the empty 4s and 4p orbitals, resulting in sp or sp^2 bonding. We should expect therefore that the monomeric, mixed-ligand complex, $\mathrm{Cu(CN)_2(NH_3)}^-$, is also planar. While strong donor ligands such as CN^- can force the formation of tetracoordinated copper(I) species that are tetrahedral, weaker ligands such

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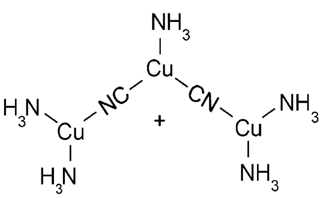
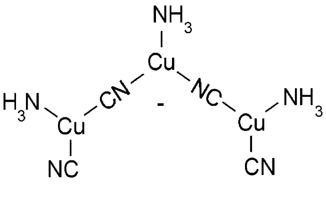
(34) Kappenstein, C.; Hugel, R. P.; Alix, A. J. P.; Beaudoin, J. L. *J. Chim. Phys.* **1978**, *75*, 427−43.

as NH_3, Cl^-, and Br^- tend to saturate the copper(I) ion when the coordination number is 3.[1,8,35] Therefore, it is quite reasonable to suggest that the two trinuclear species would have the following structures:



$Cu_3^{(+)}$



$Cu_3^{(-)}$

Although these structures seem to be the most likely on the basis of their monomeric parentage, it should be noted that other possibilities may exist, such as linkage isomers in which the configuration of the CN-bridging ligands are reversed. Future studies of these systems using Raman spectroscopy may provide definitive structural information.

In these systems there appears to be a charge stabilization of the trinuclear species in water, since the spectral titration data, Figure 2, indicated no formation of a soluble or insoluble 1:1 neutral species at these concentrations. Thus, the self-assembly of copper(I) oligomers in water may be enhanced by the formation of charged species and perhaps by the presence of donor ligands such as ammonia that can easily form and break bonds to the metal center as needed to accommodate the preferred trigonal planar geometry.

Photoinduced Electron Ejection. Figure 5 shows the time-resolved absorption spectra obtained after exposure to a 7-ns pulse of 266-nm laser light in oxygen-free solutions at 1 M ionic strength and approximately the same concentration of ammonia (3 M), in which the ratios of moles of CuCl to $KCu(CN)_2$ were adjusted to yield solutions of nearly pure $Cu^{(-)}$ (bottom), $Cu_3^{(-)}$ (middle), or $Cu_3^{(+)}$ (top) at a constant total copper concentration of 6 mM. Since the spectra are all dominated by the well-known absorption band of the hydrated electron,[36] with $\lambda_{max} = 700$ nm, we can conclude that hydrated electron is produced very efficiently. The electron decays are exponential in all three systems, suggesting that the copper(I) species is the primary scavenger of electrons. Moreover, all three systems produce electrons monophotonically, as revealed by linear plots (not shown) of initial electron absorbance at 670 nm vs pulse energy, measured by initial electron absorbance produced in ferrocyanide solution.[37] Such plots can be used to calculate the quantum yield of electron production, and these results are listed along with earlier ones for comparison in Table 1.

Earlier work[17] has shown that, for anionic complexes of copper(I), particularly the halocuprates, an increase in coordination number from 2 to 3 has a detrimental effect on the quantum yield of photochemical hydrated electron production. The recent results obtained for the cyanocuprates,[22] given in Table 1, are consistent with this idea. However, when the third ligand is ammonia rather than halo or cyano, the quantum yield seems to stay the same or increase slightly (from 0.37 to 0.41), as demonstrated by comparison of the quantum yields for $Cu(CN)_2^-$ and for $Cu(CN)_2(NH_3)^-$, reported in this work. This suggests that it may be the increase in the number of negatively charged ligands in the inner coordination sphere that causes a loss in

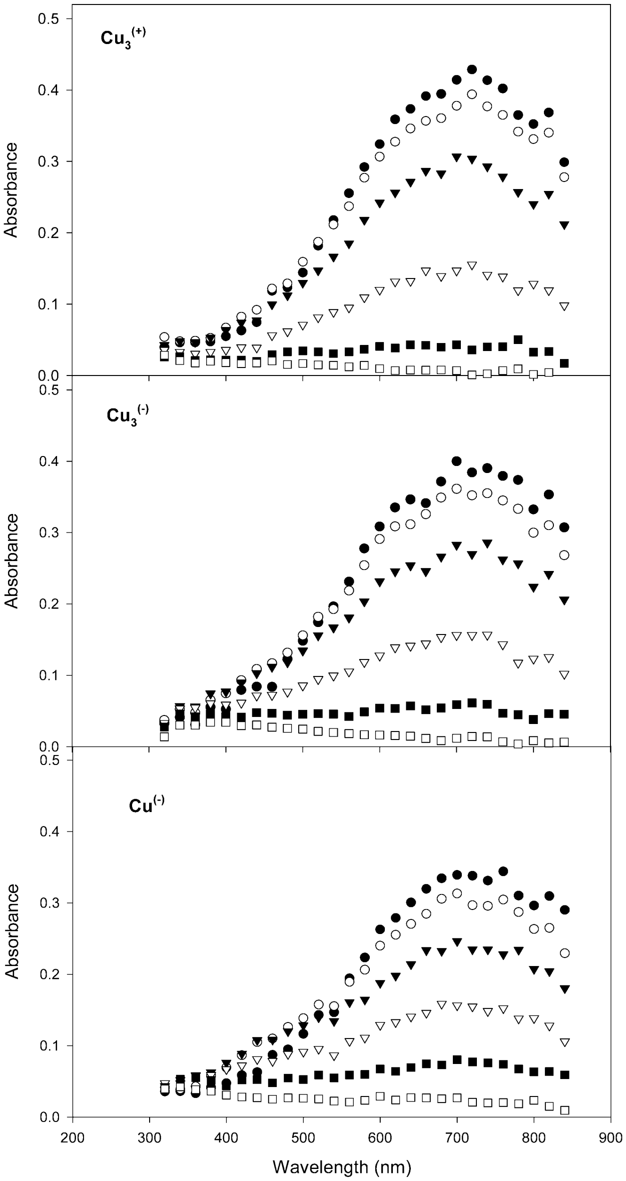


Figure 5. Time-resolved absorption spectra at 25 °C after absorption of a 7-ns pulse of 266-nm laser light at delay times of (●) 10 ns, (○) 20 ns, (▼) 40 ns, (▽) 100 ns, (■) 200 ns, and (□) 400 ns, for solutions that are ($Cu^{(-)}$) 6 mM $KCu(CN)_2$ in 3.30 M NH_3 and 1 M $NaClO_4$, ($Cu_3^{(-)}$) 4 mM $KCu(CN)_2$ and 2 mM CuCl in 2.71 M NH_3 and 1 M $NaClO_4$, and ($Cu_3^{(+)}$) 2 mM $KCu(CN)_2$ and 4 mM CuCl in 2.74 M NH_3 and 1 M $NaClO_4$.

Table 1. Quantum Yield at 25 °C of Hydrated Electron Formation following Irradiation at 266 nm of Cyano and Ammine Complexes of Copper(I) in 1 M Ionic Strength ($NaClO_4$) Aqueous Solution

complex	quantum yield	ref
$Cu(CN)_2^-$	0.37 ± 0.06	22
$Cu(CN)_3^{2-}$	0.224 ± 0.021	22
$Cu(NH_3)^{2+}/Cu(NH_3)^{3+}$	0.34 ± 0.03	21
$Cu(CN)_2(NH_3)^-$	0.41 ± 0.02	this work
$Cu_3^{(+)}$	0.53 ± 0.02	this work
$Cu_3^{(-)}$	0.50 ± 0.01	this work

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(35) Stevenson, K. L.; Grush, M. M.; Kurtz, K. S. *Inorg. Chem.* **1989**, *29*, 3150−3.

(36) Hart, E. J.; Boag, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 4090−5.

(37) Shirom, M.; Stein, G. *Nature* **1964**, *204*, 778−779.

efficiency of the hydrated electron production, which is consistent with the notion that an increased negative charge on the complex raises the energy barrier for ejection of the electron. Addition of a third ligand, NH_3, to dicyanocuprate(I) does not change the charge, but it does change the geometry from linear to trigonal planar, without causing much of a change in quantum yield. On the other hand, the two trinuclear species, also presumably trigonal planar with respect to each copper(I) chromophore (see structures I and II), both show marked increases in quantum efficiency (from 0.3 or 0.4 to 0.5) for hydrated electron production compared to the monomeric species from which they are formed, suggesting that cyano bridging ligands somehow promote electron ejection. This could be the result of the fact that the photoexcitation of copper(I) by the 266-nm laser pulse gives rise to a transition denoted as charge-transfer-to-solvent (CTTS) or $d^{10} \rightarrow d^9p^1$ or d^9s^1, creating a “hole” in the d-shell of the copper(I) chromophore, which, in turn, is rapidly filled by electron transfer via the cyano bridge from an adjacent copper(I) species. This could suppress the relaxation of the excited chromophore rendering electron ejection more likely. Another explanation for the enhanced electron ejection may be the formation of stable Cu(I)−Cu(II) species, which would present a barrier to the back electron transfer. At the present time, it is not possible to say which copper centers in either of the two trimeric species serve as chromophores; most likely, all of them do.

Conclusions

(1) In aqueous ammonia solutions at 25 °C, the complex $Cu(CN)_2(NH_3)^-$ readily forms from the reaction of $Cu(CN)_2^-$ with NH_3, with a stepwise stability constant of 2.80 ± 0.40 in 1 M ionic strength ($NaClO_4$ medium).

(2) Two trinuclear species, with probable formulas of $Cu_3(CN)_2(NH_3)_5^+$ and $Cu_3(CN)_4(NH_3)_3^-$, are easily formed in aqueous ammonia solutions by mixing proper stoichiometric amounts of $Cu(CN)_2(NH_3)^-$ and $Cu(NH_3)_2^+$.

(3) All three new complexes have strong absorption bands, presumably MLCT, in the UV.

(4) All three complexes undergo photoinduced electron ejection at 266 nm, presumably by excitation into a CTTS band, with the quantum efficiencies of the two trinuclear species somewhat higher than the monomeric complex (ca. 0.5 vs ca. 0.4) suggesting an enhancement in quantum efficiency promoted by cyano-bridged polynuclear copper(I) structures.

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