

Equilibria, Spectra, and Photochemistry of Copper(I)-Ammonia Complexes in Aqueous Solution

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The ultraviolet spectra of solutions of CuClO_4 in which ammonia concentration was varied from 0.4 to 14.2 M were obtained at 25 °C. An analysis of the variation of the molar extinction coefficient as a function of ligand concentration strongly suggests that there are at these ligand concentrations only two complexes, $\text{Cu}(\text{NH}_3)_2^+$ and $\text{Cu}(\text{NH}_3)_3^+$. The spectral information indicates that for the reaction $\text{Cu}(\text{NH}_3)_2^+ + \text{NH}_3 = \text{Cu}(\text{NH}_3)_3^+$ the value of the equilibrium constant, K_3 , is less than about 2×10^{-3} at unit ionic strength. Because of the uncertainty in the value of the equilibrium constant it is possible to obtain the extinction coefficient spectrum of only the diammine species, but a qualitative spectrum of relative absorbance values for the triammine complex can be obtained from the data, and the results reveal that both complexes possess absorption shoulders or bands at about 235 nm. The triammine complex has an additional strong shoulder at 290 nm. Photolysis of a mixture of these complexes into the 275–300-nm region in the presence of such electron scavengers as N_2O and NH_4^+ yields products (H_2 in the latter case) that are consistent with photoredox processes in which the hydrated electron is produced.

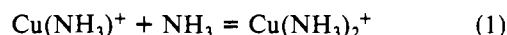
Introduction

Our work on copper(I) photochemistry has thus far focused on simple anionic complexes in aqueous solution that undergo charge-transfer-to-solvent (CTTS) transitions in the ultraviolet region.³⁻⁷ Detailed studies on the chloro complexes CuCl_2^- and CuCl_3^{2-} ⁵⁻⁷ and qualitative studies with the bromo⁸ and iodo complexes⁹ reveal that when these anions are irradiated into their CTTS bands at about 275 nm, an electron-transfer process occurs in which a geminate pair consisting of Cu(II) complex and hydrated electron is formed. In acid solution the subsequent processes lead to the production of hydrogen gas via hydride intermediates.^{5,6,10}

It was our desire to extend our photochemical studies to cationic Cu(I) complexes in order to see if such species, which are not normally considered to exhibit CTTS absorption bands,¹¹ do show behavior similar to that of the anionic complexes. We wanted to choose a ligand that, like the halo ligand, has no π systems so that metal-ligand charge-transfer processes would not complicate the spectra and photochemistry. While the aquo complex may seem to be a likely choice, it is unfortunately unstable to disproportionation in aqueous solution. We therefore chose to study the ammonia complexes of copper(I).

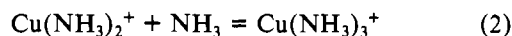
Surprisingly, unlike the case for the analogous silver(I) complexes, there is very little in the literature about the formation and equilibria of Cu(I)-ammonia complexes. Although they appear to be quite easy to make simply by dissolving a Cu(I) salt in aqueous ammonia, the fact that they are readily oxidized by air to the intensely blue and very stable Cu(II)-ammonia species has probably precluded their detailed study. Early work by Bodländer¹² established that the primary copper(I) species in aqueous ammonia solutions is $\text{Cu}(\text{NH}_3)_2^+$.

Subsequent electrochemical and polarographic studies indicated the presence at low ammonia concentrations of $\text{Cu}(\text{NH}_3)^+{}^{13,14}$ with a value for the stability constant for the reaction



of 0.86×10^5 at 2 M ionic strength. More recent polarographic work¹⁵ has indicated that a neutral complex, $\text{Cu}(\text{NH}_3)(\text{OH})$, may form at a pH greater than that of the natural pH of aqueous ammonia.

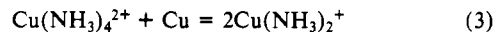
Apparently, there have been no ultraviolet absorption spectra published for any of these complexes in aqueous solution. In attempting to determine the spectrum of $\text{Cu}(\text{NH}_3)_2^+$, we observed that the molar extinction at all wavelengths in the 210–330-nm region increases as the concentration of ammonia increases, indicating that there may also be a triammine species formed at higher ligand concentrations as follows:



Our goal has been, then, to study this equilibrium spectrophotometrically in order to resolve the spectra of the individual species, as well as to study the electron-transfer photochemistry of the equilibrated systems.

Experimental Section

Preparation of aqueous solutions of the Cu(I)-ammonia complexes was accomplished by adding a small volume of concentrated $\text{Cu}(\text{ClO}_4)_2$ solution to a flask containing a solution of aqueous ammonia of known concentration, sufficient NaClO_4 to fix the ionic strength at 1 M, a coil of copper wire, and a stirring bar. A septum was placed over the mouth of the flask, and the solution was stirred for at least 24 h. The copper wire reacted with the blue $\text{Cu}(\text{NH}_3)_4^{2+}$ by reverse disproportionation:



Since the value of E° for this reaction is about 0.12 V,¹³ the reaction goes to completion and the resulting solution is completely colorless. Any oxygen originally in the flask is removed by the oxidation of Cu(I) to Cu(II), which is then recycled to Cu(I) via reaction 3. The final concentration of copper was usually about 0.02 M and was determined by atomic absorption spectrophotometry. Some solutions were prepared by adding weighed samples of CuCl to deoxygenated solutions.

Spectra were taken in a Beckman ACTA M-VI UV-vis spectrometer interfaced with a Hewlett-Packard 85 or 86 microcomputer. Solutions were transferred from their reaction flasks to argon-filled quartz cuvettes with path lengths of 0.01, 0.05, 0.1, 1.0 or 5.0 cm by

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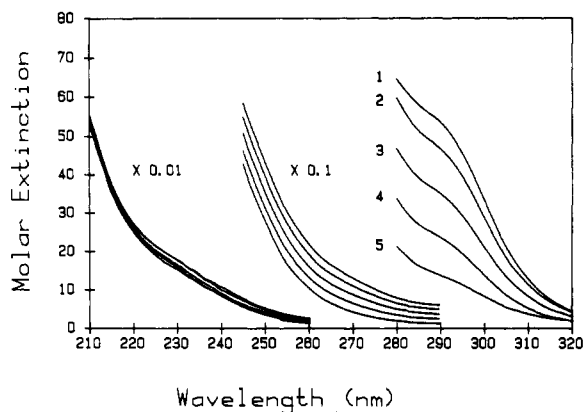


Figure 1. Molar extinction spectra of CuClO_4 , 1.0 M ionic strength, at five concentrations of ammonia: (1) 4.30 M; (2) 3.50 M; (3) 2.69 M; (4) 1.82 M; (5) 0.94 M.

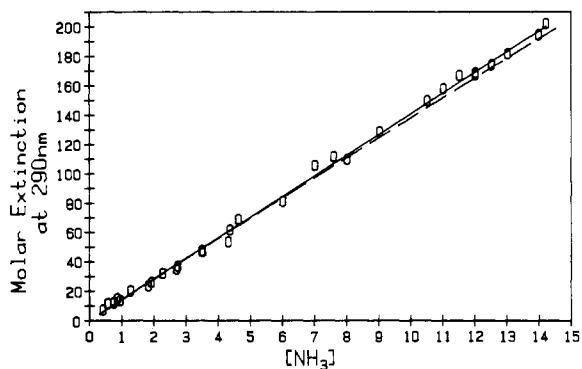


Figure 2. Plot of e at 290 nm vs. $[\text{NH}_3]$ at unit ionic strength, 25 °C: solid line, slope of linear regression analysis; dashed line, plot of e vs. $[\text{NH}_3]$ from eq 5 ($K_3 = 0.002$, $e_2 = 0.42$, $e_3 = 7035$).

using syringe techniques. At each ammonia concentration varying from 0.4 to 14.2 M, spectra were taken of two solutions identical in all respects except that only one contained copper. By the use of computer software we developed, differences between these two spectra were obtained and converted to extinction coefficient spectra.

Continuous-wave photolyses were carried out by using the 1000-W lamp and monochromator system described previously.⁵ The potassium tris(oxalato)ferrate(III) actinometer¹⁶ was used to determine light intensities. To determine the effect of N_2O concentration on quantum yield, two solutions of identical ammonia and copper concentrations were prepared and one of these was bubble degassed with $\text{N}_2\text{O}(\text{g})$ and the other with $\text{Ar}(\text{g})$. Mixing these two solutions in various ratios permitted the relative concentration of N_2O to be accurately adjusted. To determine the reaction rates, the absorbance of the irradiated solutions was measured periodically at 600 nm where the blue $\text{Cu}(\text{NH}_3)_4^{2+}$ absorbs strongly. Some reactions in which NH_4^+ was the electron scavenger could be followed by monitoring the output of $\text{H}_2(\text{g})$ with a recording microvolumeter.⁸

Results and Discussion

1. Spectra and Equilibria. As the concentration of NH_3 is increased from 0.4 to 14.2 M, there is an increase in the molar extinction coefficient in the 210–330-nm range, as Figure 1 demonstrates for five ammonia concentrations. Although there are no different absorption maxima in this range, there are obvious shoulders at 230 and 290 nm and a less obvious one at about 275 nm. The one at 290 nm is the most sensitive to ammonia concentration, and if the value of molar extinction is plotted vs. ammonia concentration for the complete set of spectra, one obtains the linear plot shown in Figure 2. Such linear behavior is observed at all wavelengths. In order to explain this behavior in a way that is consistent

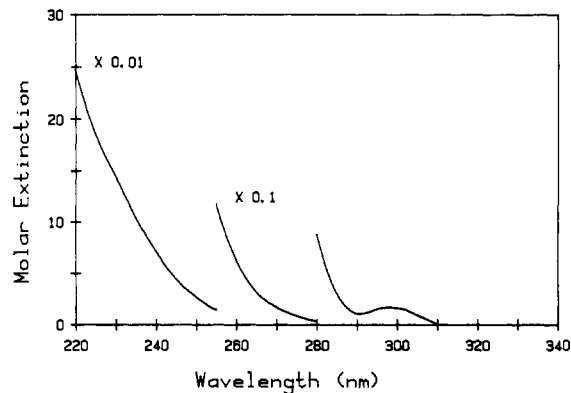


Figure 3. Ultraviolet absorption spectrum of $\text{Cu}(\text{NH}_3)_2^+$ at 1.0 M ionic strength, 25 °C.

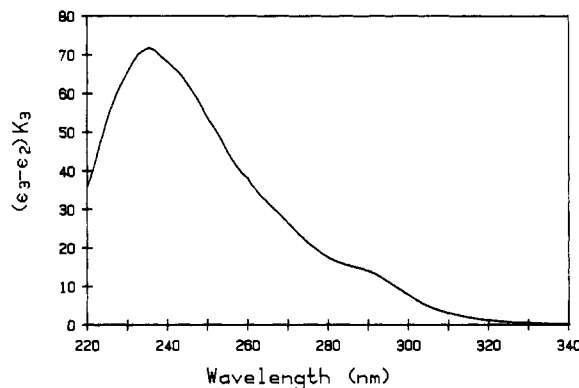


Figure 4. Plot of $(e_3 - e_2)K_3$ vs. wavelength at 1.0 M ionic strength, 25 °C.

with the previous work,^{12–15} one must conclude that these solutions consist largely of $\text{Cu}(\text{NH}_3)_2^+$ with very small amounts of $\text{Cu}(\text{NH}_3)_3^+$. Reaction 2 is then the only important one at these ligand concentrations since the equilibrium constant for reaction 1 rules out the existence of $\text{Cu}(\text{NH}_3)^+$ in any significant amount. Therefore, if the equilibrium constant for reaction 2 is given by

$$K_3 = c_3/c_2x \quad (4)$$

where c_2 , c_3 , and x are the molar concentrations of diammine complex, triammine complex, and ammonia, respectively, one can show that the molar extinction coefficient, e , of the solution is related to the individual extinction coefficients, e_2 and e_3 , of the di- and triammine complexes by the expression

$$e = e_2 + (e_3 - e_2)K_3x/(1 + K_3x) \quad (5)$$

As long as K_3x is small compared to 1, which is true if K_3 is about 2×10^{-3} or less, e will indeed be linear with respect to x . The dashed line in Figure 2 is obtained by plotting e vs. x in eq 5 and using the values of e_2 , 0.42, and $(e_3 - e_2)K_3$, 14.07, obtained from the linear regression analysis and the value of 0.002 for K_3 , considered to be the largest value that does not cause more than about 1.5 standard deviations of the y values from the straight line at the high- x end of the plot. We are forced to conclude that K_3 cannot be directly determined by this method; rather, we can only estimate its maximum value. By performing the linear regression of the e vs. x data at all wavelengths, we can reconstruct the spectrum of $\text{Cu}(\text{NH}_3)_2^+$ from the y intercepts, and we obtain from the slopes of the linear regression a kind of difference spectrum, $(e_3 - e_2)K_3$ vs. wavelength, for the $\text{Cu}(\text{NH}_3)_3^+$ ion.

The results of such a deconvolution are shown in Figure 3 for the diammine complex and in Figure 4 for the triammine complex. Even though the latter is a difference spectrum, in the wavelength range shown e_3 must be much larger than e_2

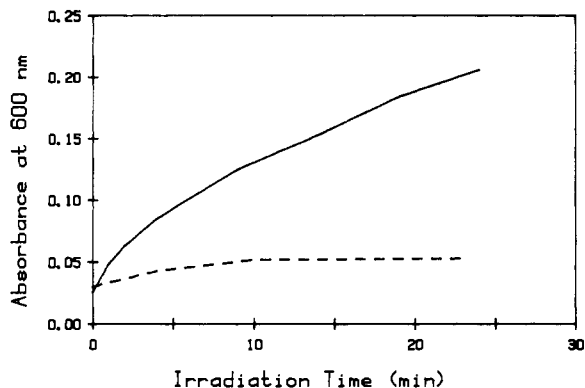


Figure 5. Absorption at 600 nm for a 2.0-mL solution of 0.016 M CuClO_4 in 1 M NH_3 vs. time of photolysis at 274 nm in a 1-cm cuvette: (—) solution bubbled with N_2O ; (---) solution bubbled with Ar.

because $K_3 \leq 0.002$. Thus, for example, at 290 nm, $(e_3 - e_2)K_3 = 14.07$ and $e_3 \geq 7035$, compared to $e_2 = 0.4$. Similarly, at the maximum in Figure 4 occurring at 236 nm, one obtains a value of $e_3 \geq 35400$, compared to $e_2 = 955$. Therefore, one can interpret the spectrum in Figure 4 as essentially that of $\text{Cu}(\text{NH}_3)_3^+$, although the actual values of the extinction coefficients remain unknown.

This treatment, of course, assumes ideal behavior for the ammonia solutions over the entire concentration range shown in Figure 2, probably not a realistic expectation. Our original intent was to observe the change in the spectrum for concentrations up to 5 M in ammonia, where deviation from ideality is not so great. However, we decided to push for high ammonia concentrations because we wanted to see if there were any significant changes in the spectrum that might indicate formation of a tetrammine complex. That there were no detectable new bands or shoulders or marked deviations from the linear behavior of Figure 2 at such a high ammonia concentration as 14.7 M has led us to conclude that the only species present in addition to the diammine complex is the triammine complex. Because activity coefficients for ammonia in such high concentrations are unknown, we do not claim that Figure 4 is anything more than a qualitative spectrum of the triammine complex.

2. Photochemical Behavior. When the Cu(I) species is oxidized, the solution changes from colorless to blue because of the formation of $\text{Cu}(\text{NH}_3)_4^{2+}$,¹⁷ which has an absorbance maximum at 600 nm. Since the Cu(I) complexes are transparent at this wavelength, it was convenient to monitor the photooxidation by following this absorbance at 600 nm. N_2O was used as an oxidant since it is known¹⁸ to scavenge hydrated electrons by the reaction

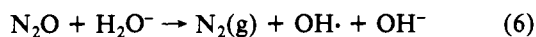


Figure 5 shows the photooxidation of Cu(I) in an aqueous ammonia solution containing N_2O compared to that of one without N_2O , when irradiated at 274 nm. Both solutions were bubble degassed prior to irradiation for about 10 min with either N_2O or Ar gas, which was first bubbled through a CrCl_2 solution to remove traces of O_2 . It is evident that N_2O promotes photooxidation of Cu(I) whereas the Ar-saturated solution exhibits almost no photooxidation. The small amount of copper oxidized in the first 5 min of the reaction of the latter solution may be attributed to a residual (about 10^{-4} M) amount of O_2 , which probably enters the solution during the syringe transfer from stock solution to cuvette.

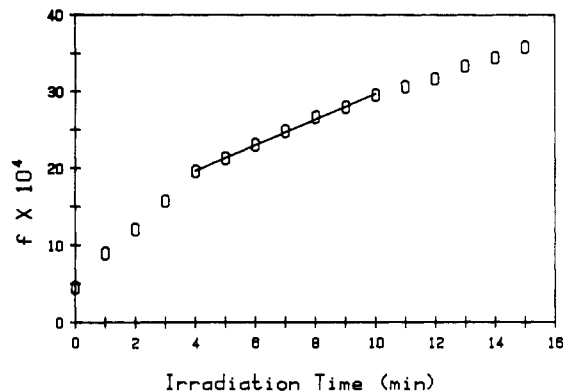


Figure 6. Plot of f vs. t for 0.035 M CuCl in 0.944 M NH_3 bubbled with N_2O and photolyzed at 274 nm.

The measurement of quantum yields of photooxidation is complicated not only because this residual oxygen is present at the start of the reaction but also because the Cu(II) that is formed has a higher molar absorbance at the irradiating wavelength than does the Cu(I) complex of interest. Hence there is a distribution of absorbed light between the photoactive Cu(I) species and the Cu(II) product, causing a constantly diminishing photochemical rate. The rate of formation of Cu(II) is

$$dC_p/dt = I_0\phi e_r C_r / (e_r C_r + e_p C_p) \quad (7)$$

where e and C represent molar extinction coefficient and concentration, respectively, r and p indicate reactant Cu(I) and product Cu(II), respectively, I_0 is the average incident light intensity per unit volume, and ϕ is the quantum yield. In the situation where not all the light is absorbed, the right side must be multiplied by $(1 - 10^{-A})$ where A is the optical density. Equation 7 can be modified by observing that $C_0 = \text{total copper concentration} = C_r + C_p$ and by integrating. The result, after substituting A_x/le_x for C_p , is

$$A_x/le_x - (e_p/e_r)[A_x/le_x + C_0 \ln(1 - A_x/le_x C_0)] = I_0\phi t = f \quad (8)$$

where A_x is the absorbance of the solution and e_x is the molar extinction coefficient of Cu(II) at the analyzing wavelength of 600 nm and l is the path length of the cuvette in centimeters. This allows for the determination of quantum yields at any stage in the course of the reaction by plotting the function f vs. t .

Such a plot is shown in Figure 6 for a typical reaction run in a solution with N_2O as scavenger. The fact that the plot is not a straight line means that the quantum yield, ϕ , changes during the irradiation. The higher, initial slope may be attributed to the photooxidation by residual O_2 , or it may be the result of some initial side reaction that builds up the concentration of some inhibiting intermediate, as was observed in the case of the chloro complexes.⁶ After this sudden change to a smaller slope after about 5 min, there is a more gradual diminution in the slope with time. This continual diminishing of ϕ can probably be explained by the scavenging of the photoactive primary species by product Cu(II), which increases in concentration during the photolysis. We used the slope of the plot immediately following the initial rise because this gave much more reproducible results.

The dependence of quantum yield on N_2O concentration is shown in Figure 7. Although the absolute concentration of N_2O was not determined, the relative concentrations were known from dilution factors, and the plot clearly shows that ϕ is proportional to $[\text{electron scavenger}]^{1/2}$. This kind of dependence on scavenger concentration is usually observed in hydrated electron scavenging reactions involving geminate-pair primary products.^{5,19,20}

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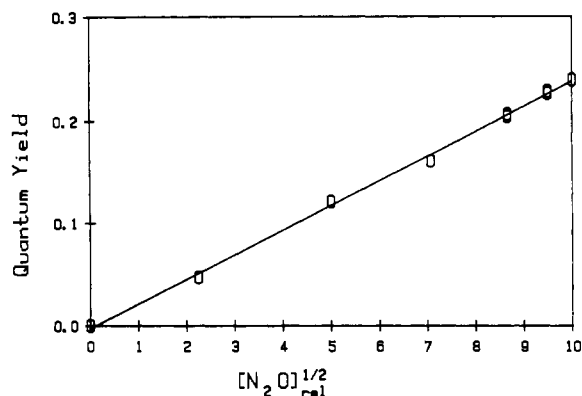


Figure 7. Quantum yield of photooxidation of 0.035 M CuCl in 0.944 M NH₃ at 274 nm vs. (relative concentration of N₂O)^{1/2} at 25 °C.

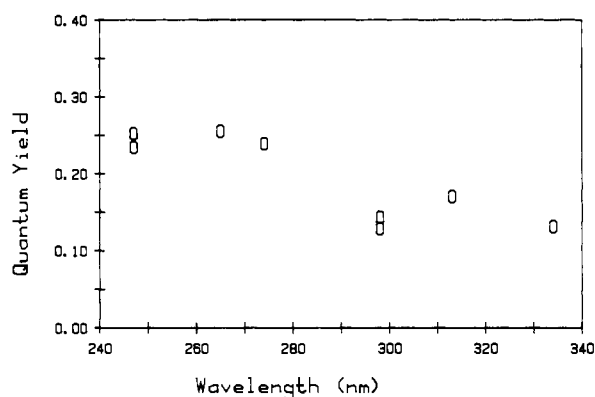


Figure 8. Quantum yield for photooxidation of 0.035 M CuCl in 0.944 M NH₃ bubbled with N₂O, as a function of wavelength of irradiation at 25 °C.

The dependence of quantum yield on wavelength for a solution in which ammonia concentration is about 1 M is shown in Figure 8. Since the quantum yield values extend all the way out to the long-wavelength onset of the absorption by the triammine complex at about 330 nm, where the diammine complex does not absorb at all, one can conclude that the triammine complex is photochemically active. The increase in ϕ with shorter wavelengths may indicate that the triammine complex becomes more photoactive as the wavelength of excitation shifts from one CTTS band to another. At this point it is not possible to conclude which of the shoulders or bands are more photoactive, nor can one determine the degree of photoactivity of the diammine complex without some very careful measurements of ϕ vs. [NH₃].

Because the photoactivity of these Cu(I)-ammonia complexes does extend to about 330 nm, which is about 15 nm further toward the visible region than what is observed for the chloro complexes,⁵ they should be a little more attractive as solar energy harvesters than the chloro complexes would be. Therefore, we undertook to investigate the possibility of using an electron scavenger, other than nitrous oxide, which would yield products capable of storing free energy. The scavenger

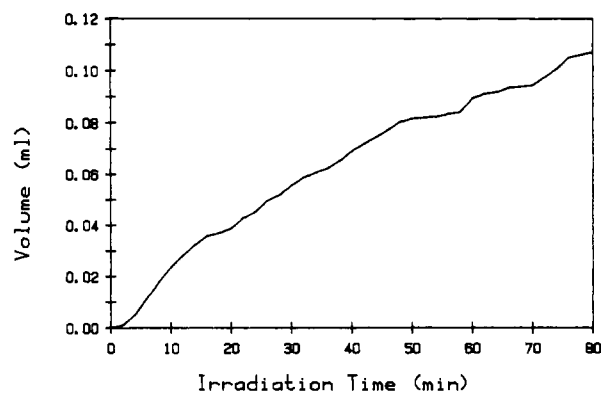
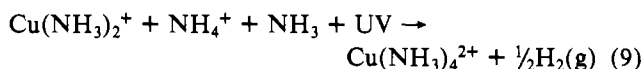


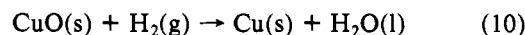
Figure 9. Gas evolution in 0.016 M CuCl in a solution containing 1 M NH₃ and 1 M NH₄ClO₄ photolyzed at 274 nm, 25 °C.

of choice is hydronium ion, which would yield hydrogen gas, but since these complexes can exist only in basic solutions of high ammonia concentration, the ammonium ion served as the hydronium analogue. Thus one might expect to observe the overall reaction



when light of wavelength shorter than 330 nm is used. From standard electrode potentials and equilibrium constants,¹² one obtains about 45 kJ mol⁻¹ and -0.47 V for the values of ΔG° and E° , respectively.

Figure 9 shows the gas evolution for the irradiation of 0.016 M CuCl in a solution containing 1 M NH₃ and 1 M NH₄ClO₄ at 274 nm. To prove that the gas was dihydrogen, it was cycled into a loop containing CuO powder, which was then heated to red heat for 15–20 min. The black CuO turned to a copper red color, and the reduction in volume of the gas after cooling was nearly equal to the volume of gas evolved in the photolysis, indicating that the reaction



had taken place. This test is specific for dihydrogen when compared to the gases NH₃, H₂O, N₂, and Ar. The quantum yield for the reaction was 0.03, which is considerably lower than the maximum value of about unity observed for hydronium ion scavenging of the electron in the chloro complexes,⁵ presumably because NH₄⁺ has a much smaller electron-scavenging rate constant than H₃O⁺ (3 × 10⁶ vs. 2.3 × 10¹⁰ M⁻¹ s⁻¹).²¹ Although these results are certainly not a breakthrough in terms of solar conversion, they do demonstrate that wavelength sensitivity for Cu(I) photoredox can be improved somewhat by substituting ammonia for halo ligands.

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Registry No. Cu(NH₃)₂⁺, 16089-31-9; Cu(NH₃)₃⁺, 92694-75-2; Cu(NH₃)₄, 16828-95-8; Cu(ClO₄)₂, 13770-18-8; CuCl, 7758-89-6; N₂O, 10024-97-2; NH₄⁺, 14798-03-9; NH₃, 7664-41-7.

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