J. Phys. Chem. A **1997,** *101,* 8115−8118

$Cu(NH_3)_{1-3}$ Complexes: A Matrix Isolation ESR Study

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Received: May 7, 1997[⊗]

The interaction between Cu atoms and ammonia molecules cocondensed in argon matrices was examined by ESR. The observed spectra revealed the formation of $Cu(NH_3)_{1-3}$ complexes. The **g** tensors and the hyperfine coupling tensors for the Cu and N nuclei of the complexes were determined. All three complexes showed large, essentially isotropic Cu hyperfine coupling interaction corresponding to 50−60% of that observed for isolated Cu atoms. No hyperfine structures due to protons were discerned. It is thus concluded that these complexes are formed merely by the dative interaction of the NH_3 lone pair electrons with vacant Cu 4s/4p valence orbitals. The unpaired electron resides in a Cu 4s/4p-hybridized orbital projected away from the ligand(s). The ESR spectrum of the monoligand complex $Cu(NH_3)$ showed reversible photoconversion to the second spectrum in accord with the photoisomerization process $Cu(NH_3) \leftrightarrow HCuNH_2$ reported in an earlier IR study. The second spectrum, though partially obscured by other signals, revealed a pattern consistent with the ionic character $H^-Cu^{2+}(NH_2)^-$ where the unpaired electron resides in the Cu $3d_{z^2}$ orbital.

Introduction

The interaction between Cu atoms and ammonia molecules cocondensed in argon matrices had been investigated earlier by Ball, Hauge, and Margrave using IR spectroscopy.[1] They established the formation of a mononuclear complex $Cu(NH_3)$ and the occurrence of a remarkable reversible isomerization process, $Cu(NH_3) \leftrightarrow HCuNH_2$, which takes place under UV−visible light. We report here the result of our ESR study of the interaction between Cu atoms and ammonia molecules similarly cocondensed in argon matrices. The study revealed the formation of not only the monoligand complex, $Cu(NH_3)$, reported in the IR study, but also the formation of bis- and tris-ligand complexes, $Cu(NH_3)_2$ and $Cu(NH_3)_3$. All three complexes showed large, essentially isotropic Cu hfs (hyperfine structures) corresponding to 50−60% of that shown by isolated Cu atoms. They also showed small but distinct hfs due to nitrogen nuclei but no resolvable hfs due to protons. The complexes are thus formed merely by the dative interaction of the NH_3 lone pair electrons with vacant Cu 4s/4p valence orbitals. The ESR spectrum of the monoligand complex, $Cu(NH_3)$, showed reversible photoconversion to the second pattern, consistent with the photoisomerization process mentioned above. The bis- and tris-ligand complexes were found to be photostable.

Experimental Section

A liquid helium cryostat that would enable trapping of vaporized metal atoms in an argon matrix and examination of the resulting matrix by ESR has already been described.[2] In a present series of experiments, copper atoms were vaporized from a resistively heated (∼1400 °C) tantalum cell and were trapped in argon matrices containing a controlled amount (0.5−4%) of ammonia. All the ESR spectra reported here were obtained while the matrix was maintained at ∼4 K. The spectrometer frequency locked to the sample cavity was 9.425 GHz. For photoirradiation of the matrix, a high-pressure Xe−Hg lamp (Oriel, 1 kW unit) was used. The light beam was passed through a water filter and a broad-band (±50 nm) interference filter of choice and was focused on the cold finger ∼40 cm away. An argon matrix containing ammonia alone appeared light blue, while an argon matrix containing Cu atoms appeared white. An argon matrix in which Cu atoms and ammonia molecules had been cocondensed appeared reddish yellow. Research grade argon (Matheson), CP grade ammonia (Matheson), and "doubly enriched" ammonia, $^{15}ND_3$ (Cambridge Isotope, enrichment of 98%), were used without further purification.

Results

The ESR spectrum of Cu atoms ($3d^{10}4s^1$) isolated in rare gas matrices was analyzed some time ago.[3] There are two naturally abundant Cu isotopes, ^{63}Cu (natural abundance = 69%, $I = {}^3/_2$, $\mu = 2.2206\beta_n$) and ^{65}Cu (natural abundance = 31%, $I = {}^3/_2$, $\mu = 2.3790\beta_n$). Owing to the large hfc (hyperfine coupling) interactions with these nuclei, the ESR spectrum of Cu atoms observed with an X-band spectrometer shows only two resonance transitions; one corresponds to the "NMR" transition ($M_S = {}^1/_2$, $M_I = -{}^1/_2 \leftrightarrow -{}^3/_2$) and occurs at 1.5 and 2.0 KG for ^{63}Cu and ^{65}Cu, respectively, and the other corresponds to the ESR transition ($M_S = -{}^1/_2 \leftrightarrow +{}^1/_2$, $M_I = -{}^3/_2$) and occurs at 5.8 and 6.0 KG.

Figure 1a shows the ESR spectrum observed from the $Cu/NH_3(1\%)/Ar$ system. The signals due to isolated Cu atoms are indicated by letters A. In addition to these signals, three sets of quartets, labeled M, B, and T, were discerned as indicated. The quartet structures of extremely large spacing must be due to the hfc interaction with a Cu nucleus. For the quartet M, the minor set due to the ^{65}Cu isotope was also discerned; the minor sets for B and T species were masked by signals of the major ^{63}Cu patterns. A series of experiments (performed systematically changing the NH_3 concentration) revealed that the relative intensities [T]:[B]:[M] increased with increasing NH_3 concentration. Figure 1b shows the ESR spectrum observed from the $Cu/NH_3(4\%)/Ar$ system. The quartets M, B, and T were hence assigned (tentatively) to the mononuclear complexes $Cu(NH_3)_n$ where n = 1, 2, and 3, respectively.

The quartet splittings observed here for the $Cu(NH_3)_{1-3}$ complexes are so large that their spectral patterns cannot be analyzed based on the usual second-order solution of the spin Hamiltonian. The **g** tensors and the Cu hfc tensors of the complexes were analyzed based on the exact solution (Breit−Rabi equation)[4] of an isotropic spin Hamiltonian, eq 1:

$$H = g\beta\mathbf{H}\cdot\mathbf{S} + A\mathbf{I}\cdot\mathbf{S} \tag{1}$$

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1997.

S1089-5639(97)01533-8 CCC: $14.00

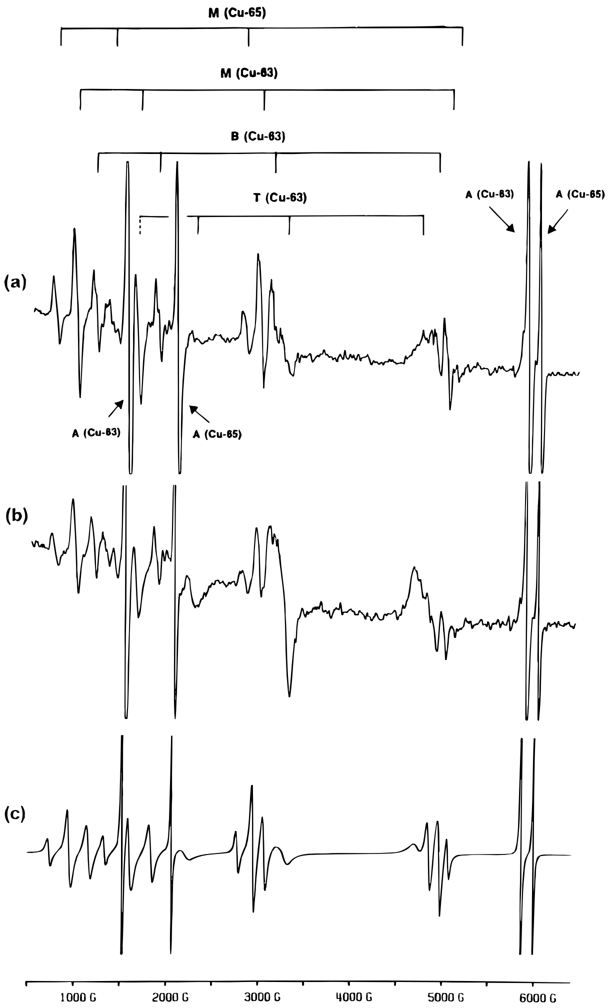

Figure 1. (a) ESR spectrum observed from the Cu/NH_3(1%)/Ar system. In addition to signals due to isolated Cu atoms (indicated by A's), three sets of quartets M, B, and T are recognized. (b) ESR spectrum observed from the Cu/NH_3(4%)/Ar system. (c) Simulated spectrum based on the parameters given in Table 1. See text for details.

TABLE 1: *g* Values and the ^{63}Cu and ^{14}N Hyperfine Coupling Constants (in MHz) of $Cu(NH_3)_{1-3}$ Generated in the Cu/NH_3/Ar System[a]

	g	$A_{iso}(^{63}Cu)$	$A_{iso}(^{14}N)$
Cu atom	1.9994	6151	
$Cu(NH_3)$	2.014(4)	3632(15)	59(3)
$Cu(NH_3)_2$	2.019(4)	3365(15)	56(3)
$Cu(NH_3)_3$	2.000(5)	2920(20)	53(3)

[a] The *g* value and the hfc constant of Cu atoms isolated in argon matrices (from ref 3) are included for comparison.

The *g* values and the ^{63}Cu hfc constnats of the complexes thus determined are shown in Table 1 together with those of isolated Cu atoms determined earlier.[3] Figure 1c shows the theoretical spectrum based on these values, the assumed relative population of 1:1.5:2 and the line width (fwhm) of 20, 30, and 70 G for the mono-, bis-, and tris-ligand complexes, respectively. The signals due to isolated Cu atoms are superimposed for reference.

The large line width of the spectra discussed above must be ascribed to the (unresolved) hfs due to the nitrogen and/or proton nuclei. In fact, the spectra of higher resolution were obtained when the matrices were prepared with a larger slit width, which would allow a larger flux of incandescent light from the Cu cell to reach the target and thus better anneal the matrix during deposition. Figure 2 shows the ESR spectra observed from the Cu/NH_3(1%)/Ar and Cu/$^{15}ND_3$(1%)/Ar matrices thus prepared.

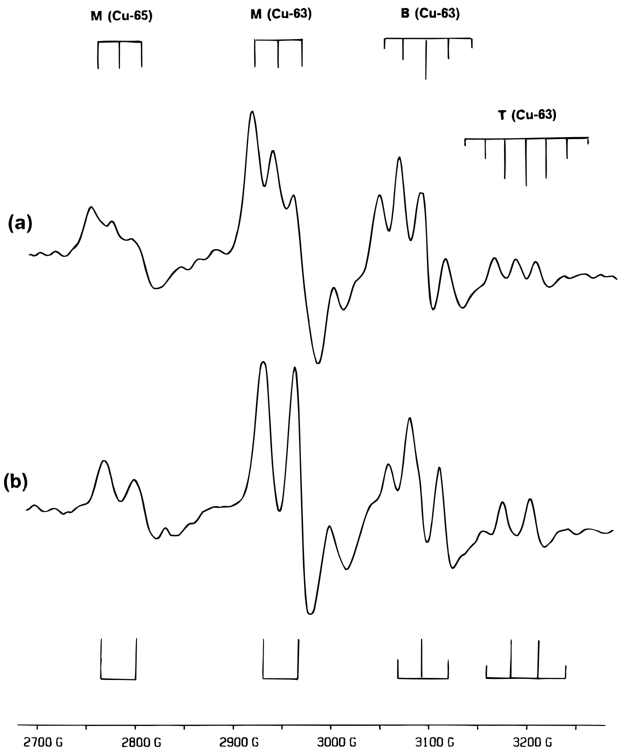

Figure 2. ESR spectra observed from (a) a Cu/NH_3(1%)/Ar matrix and (b) a Cu/$^{15}ND_3$(1%)/Ar matrix. The sections encompassing the second highest field components of quartets M, B, and T are shown. The hyperfine patterns expected from the nitrogen nuclei are indicated for each component.

The section encompassing the second highest field components of the quartets is shown in an expanded scale. The triplet and the doublet features expected from the hfs due to a ^{14}N nucleus ($I = 1$) and ^{15}N nucleus ($I = {}^1/_2$), respectively, are readily recognized for the components assigned to the monoligand complex as indicated. The quintet and triplet patterns of binomial relative intensities expected for the hfs due to two equivalent nitrogen nuclei are also readily recognized for the bis-ligand complexes as shown. The complete patterns expected for the hfs due to three equivalent nitrogen nuclei are not discernible from the signals assigned to the tris-ligand complex. The observed signals, nonetheless, accord well with the strongest components of the indicated binomial patterns. The nitrogen hfc constants thus determined are included in Table 1. The line widths of individual hfc components seen in Figure 2 are ~15 G ($\Delta H_{peak-to-peak}$) for both the $^{14}NH_3$ and $^{15}ND_3$ species. The hfc interactions with protons must be substantially smaller than those with the nitrogen nuclei; we estimate that *A*(proton) $\leq$ 5 G for all three complexes.

Theoretical Excursion. As stated earlier, Ball et al. discovered, in their matrix IR study of the Cu/NH_3/Ar system, a reversible photoinduced isomerization process of $Cu(NH_3)$ as shown below:[1]

$$Cu(NH_3) \underset{\text{vis } (\lambda > 400 \text{ nm})}{\overset{\text{UV } (\lambda < 380 \text{ nm})}{\rightleftarrows}} H-Cu-NH_2$$

It would be elucidative if the corresponding photoinduced changes are observed for the ESR spectra presented above. Examination of the complexes $Cu(NH_3)_{1-3}$ by a semiempirical SCF molecular orbital method (ZINDO)[5] indicated that these complexes are formed by dative interaction of the NH_3 lone pair electrons with vacant Cu 4s/4p orbitals, and the unpaired electron resides in a Cu 4s/4p hybridized orbital projected away from the ligands. The large, essentially isotropic Cu hfc constants observed for these complexes are thus accounted for. For $HCuNH_2$ a similar examination indicated that it is characterized by the ionic form $H^-Cu^{2+}(NH_2)^-$ and SOMO (the semioccupied molecular orbital) is dominated by the Cu $3d_{z^2}$ orbital defined along the H−Cu−N internuclear axis. It is immediately predicted that the Cu hfc constant in $HCuNH_2$ would be very small. It is well-known that, for a radical with a nondegenerate SOMO given by $|0\rangle$, deviation of the **g** tensor from the spin-only value g_e is given by eq 2.[6]

$$g_i - g_e = -2\lambda \sum_n \frac{\langle 0|L_i|n\rangle\langle n|L_i|0\rangle}{E_n - E_0} \qquad (2)$$

Here, i (= x, y, z) represents a principal axis of the **g** tensor, L_i the orbital angular momentum operator, and λ the one-electron spin−orbit coupling constant. The summation is performed for all the excited states $|n\rangle$. In evaluating eq 2 in terms of LCAO-MO's, only one-centered integrals may be retained, and for each atomic orbital the spin−orbit coupling constant of the particular atom is used. For $HCuNH_2$ only the Cu atom has the spin−orbit coupling constant of consequence. It then follows from eq 2 that $g_{\parallel} = g_e$ and $g_{\perp} > g_e$, the parallel direction being that of the H−Cu−N internuclear axis. In the powder pattern of an ESR spectrum dominated by the anisotropy of such a **g** tensor, signals of characteristic shapes are observed at the positions corresponding to $g_{\parallel}$ and $g_{\perp}$, respectively.[7] Here, both the parallel and perpendicular signals may be split further by a small but distinct hfc interaction with the Cu nucleus.

Photoinduced Spectral Change. No spectral change was observed when $Cu/NH_3/Ar$ matrices showing the ESR spectrum shown in Figure 1 or Figure 2 were irradiated with light of $\lambda > 380$ nm. When these matrices were irradiated with UV ($\lambda = 325 \pm 50$ nm), the ESR signals due to the monoligand complex decreased conspicuously and strong signals due to H atoms and NH_2 radicals appeared. No significant change was observed for the signals due to the bis- and tris-ligand complexes.

A closer inspection of the post-UV-irradiation spectrum revealed an appearance of additional signals in the 3000−3500 G range. Figure 3a shows the pertinent section of the ESR spectrum of a $Cu/NH_3(1\%)/Ar$ matrix observed immediately after deposition. Figure 3b is the spectrum of the same matrix (the same section) observed after irradiation with UV ($\lambda = 325 \pm 50$ nm) for 20 min. A decrease of signals due to the monoligand complex is apparent. The strong, photoinduced signals due to H atoms and NH_2 radicals[8] are indicated. Additionally, the UV radiation induced two broad signals of "the perpendicular shape" and one broad signal of "the parallel shape" indicated by the solid arrows. The presence of another perpendicular signal is suggested at the region indicated by the open arrow by the raised baseline of the bis-complex signals. These signals are in accord with the signal pattern predicted above for $HCuNH_2$ if we postulate that (1) the two clearly resolved perpendicular signals are the inner components of the perpendicular quartet, (2) the only parallel signal observed is the highest field component of the parallel quartet, and (3) $g_{\parallel} = g_e$. The spin Hamiltonian parameters of $HCuNH_2$ were thus assessed as follows:

$$g_{\parallel} = 2.002 \quad g_{\perp} = 2.108$$

$$A(^{63}\mathrm{Cu})_{\parallel} = 72\ \mathrm{G} \quad A(^{63}\mathrm{Cu})_{\perp} = 96\ \mathrm{G}$$

Figure 3c is the theoretical pattern based on these parameters; the hydrogen atom signals based on the known parameters are superimposed for reference.

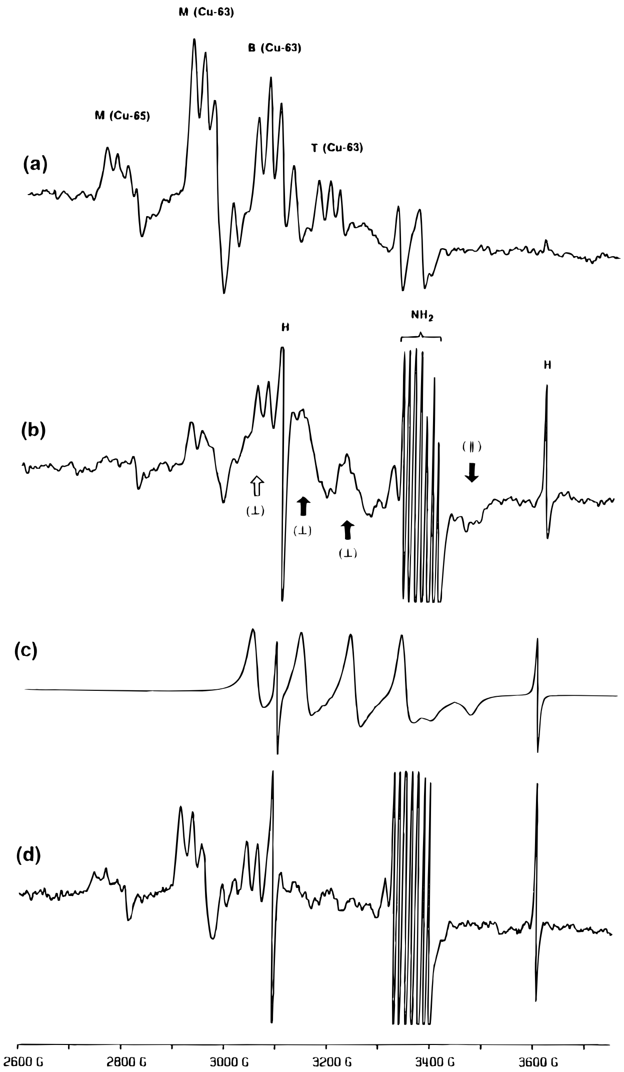

Figure 3. ESR spectra (the 3000−3500 G range) of the $Cu/NH_3(1\%)/Ar$ system observed (a) as prepared and (b) after irradiation with UV ($\lambda = 325 \pm 50$ nm) for 20 min. Photoinduced signals due to H atoms and NH_2 radicals are indicated. The solid and open arrows indicate additional photoinduced signals. (c) The theoretical pattern based on the parameters ascertained for $HCuNH_2$ (see text). Signals due to H atoms are superposed for reference. (d) ESR spectrum of the same matrix observed after subsequent irradiation with blue light ($\lambda = 450 \pm 50$ nm) for 20 min.

Figure 3d shows the spectrum observed when the matrix of Figure 3b was subsequently irradiated with blue light ($\lambda = 450 \pm 50$ nm) for 20 min. It is revealed, in total accord with the earlier IR study, that the $HCuNH_2$ signals are bleached and the signals due to the monoligand complex are (partially) restored by such irradiation. Figure 4 shows the corresponding section of the spectrum of a $Cu/^{15}ND_3(1\%)/Ar$ matrix observed (a) immediately after deposition and (b) after subsequent irradiation with UV ($\lambda = 325 \pm 50$ nm) for 20 min. Though of lesser intensity, the photoinduction of signals due to $DCuND_2$ is clearly noted. Signals due to H and D atoms and ND_2 radicals are also photoinduced. Figure 4c shows the theoretical pattern due to $DCuND_2$, H, and D atoms. Not unexpectedly, the isomerization process $Cu(NH_3) \rightarrow HCuNH_2$ is much impeded by the H → D isotope effect.

Discussion

The present study thus revealed that not only the monoligand complex but also the bis- and tris-ligand complexes are formed when Cu atoms and ammonia molecules are cocondensed in

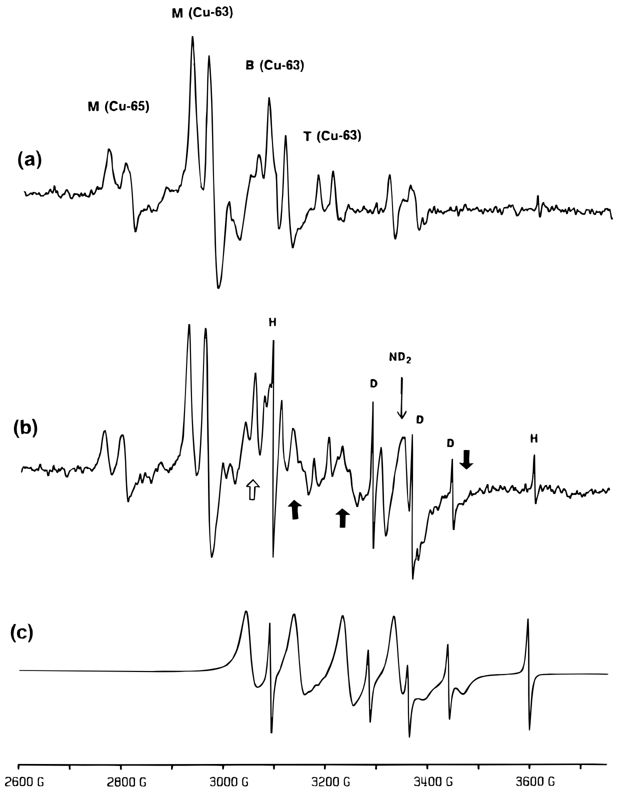

Figure 4. ESR spectra (the 3000−3500 G range) of the Cu/$^{15}ND_3$-(1%)/Ar system observed (a) as prepared and (b) after irradiation with UV (λ = 325 ± 50 nm) for 20 min. Signals due to H and D atoms, ND_2 radicals, and $DCuND_2$ are indicated. (c) Theoretical pattern based on the parameters ascertained for $HCuNH_2$ (see text). Signals due to H and D atoms are superposed for reference.

argon matrices. As stated earlier, we examined these complexes by a semiempirical SCF molecular orbital method with geometry optimization (ZINDO).[5] The theory predicted a bent, C_{2v} form for the bis-ligand complex with a N−Cu−N angle of 132°, and a pyramidal, C_{3v} form for the tris-ligand complex with a N−Cu−N angle of 109°. The Cu−N distances given by the theory are 1.88, 1.92, and 1.97 Å for the mono-, bis-, and tris-ligand complexes. The theory also predicted, for all the three complexes, that the SOMO was composed mostly of the Cu 4s, $4p_z$, and $3d_{z^2}$ orbitals and projected away from the ammonia ligand(s).

The observed isotropic Cu hfc constants of the complexes and that of the isolated atoms (given in Table 1) yield the spin densities in the Cu 4s orbital of 0.59, 0.55, and 0.47 for the mono-, bis-, and tris-ligand complexes, respectively. The ZINDO calculations predicted, at variance with the experimental result, the same spin densities in an increasing order of 0.28, 0.41, and 0.58. However, the theory also predicted spin densities in the Cu 3d orbital in a decreasing order of 0.52, 0.24, and 0.03 for the mono-, bis- and tris-ligand complexes, respectively. It appears that the theory overemphasizes the 4s/$3d_{z^2}$ hybridization for the mono- and bis-ligand complexes. A series of complexes completely analogous to $Cu(NH_3)_{1-3}$ observed here had been detected in the Na/dialkyl ether/Ar system.[9] For the $Na(ether)_{1-3}$ complexes, the observed Na hfc constants yielded, respectively, the Na 3s orbital spin densities of 0.75, 0.56, and 0.41. No d orbitals are involved in these complexes. The ZINDO method yielded, for these complexes, the respective Na 3s spin densities of 0.78, 0.61, and 0.53 in a reasonable agreement with the experimental result.

The formation of the mono-, bis-, and tris-ligand complexes had also been observed in the Cu/CO/Ar system.[10,11] The ESR spectrum of CuCO is very much like that of $Cu(NH_3)$, though the Cu hfc constant of CuCO is decisively larger than that of $Cu(NH_3)$ (4142 vs 3632 MHz). The IR study revealed that the bis-ligand complex $Cu(CO)_2$ is linear; the unpaired electron is in the Cu $4p_\pi$ orbitals mixed with the CO antibonding π orbitals. The ESR spectrum of $Cu(CO)_2$ was not observed because of the degeneracy of the π orbital system. Both the IR and ESR studies showed that the tris-ligand complex $Cu(CO)_3$ is trigonal planar; the unpaired electron is in the Cu 4p orbital (perpendicular to the molecular plane) delocalizing into the CO antibonding π orbitals. The determinate role played by the CO π orbitals for the structure of Cu carbonyls is evident.

The reversible photoinduced change observed in the present ESR study (Figure 3) is in total accord with the reversible photoisomerization scheme, $Cu(NH_3) \leftrightarrow HCuNH_2$, concluded in the earlier IR study.[1] The UV excitation (λ = 325 ± 50 nm) required for the forward process must be that which would excite the unpaired electron into a vacant Cu 4p orbital; an intramolecular hydrogen abstraction then follows. The 4s → 4p transition of Cu atoms occurs at λ = 300 nm. The observed, large H → D isotope effect is readily rationalized. It is also insightful that a similar isomerization process does not occur for the bis-ligand system. That the reverse reaction is induced by radiation of lesser energy (λ = 450 ± 50 nm) indicates that the insertion product $HCuNH_2$ is a metastable species. ZINDO calculations predicted the ground state of $HCuNH_2$ at 140 kcal above that of $Cu(NH_3)$. The formation of H atoms and NH_2 radicals is attributed to photodecomposition of $HCuNH_2$ by the ensuing UV radiation: $HCuNH_2 \rightarrow H^\bullet + CuNH_2$ and $HCuNH_2 \rightarrow HCu + {}^\bullet NH_2$. The photoproduction of D atoms and ND_2 radicals in the Cu/ND_3/Ar system should thus be proportionately small (as seen in Figure 4). Formation of both $CuNH_2$ and CuH as a consequence of UV irradiation had been observed in the IR study.[1]

Acknowledgment. This research was supported in part by NSF Grant 9300131 and Dreyfus Foundation Grant SG94-120 to San Jose State University for undergraduate research.

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