spectrum indicated that the C-5 carbon atoms (Figure 1) of the pyrimidine rings were not equivalent, which suggested meridional geometry for the complex ion. The IR evidence based on C=O vibrations, however, indicated that the complex ion had facial geometry by comparison to other known tricarbonylrhenium(I) complexes. This ruled out the meridional possibility. By means of an X-ray diffraction study, the origin of the difference in the C-5 carbon atoms was traced to a twist of the pyrimidine rings of the bipyrimidine ligand.

A comparison of Re–N(bpm) and Re–N(MeQ) bond distances to those of rhenium(I) tricarbonyl complexes is of interest.[14-21] Ligands associated with these complexes are illustrated in Figure 1. The reported average Re–N bond distances vary from 2.13 Å for $[Re(CO)_3(CH_3CN)_3]^{2+}$ to 2.26 Å, for both Re(tmen)-$(CO)_3X$, where tmen is *N*,*N*,*N'*,*N'*-tetramethylene-1,2-diamine and X = F[14] and Br,[19] and $Re(NHR_2)_2(CO)_3Br$,[16] where NHR_2 is a dialkylamine and R = CH_3 and C_2H_5. The average bond distance in $Re(bpy)(CO)_3PO_2F_2)$,[17] where bpy is 2,2′-bipyridine, was 2.14 Å, while it was 2.22 Å for $Re(dmen)(CO)_3Br$,[12] where dmen is *N*,*N'*-dimethylethane-1,2-diamine. The diisopropylethanediamine analogue $Re((C_3H_7)_2en)(CO)_3Cl$[21] exhibited an average Re–N bond length of 2.24 Å. One other compound merits comment. The complex bromotricarbonyl(2,7-bis(2-pyridyl)-1,8-naphthyridine)rhenium(I)[15] contained a Re–N("py") bond length of 2.19 Å and a Re–N("naphthyridine") bond length of 2.21 Å. The tmen, dmen, $(C_3H_7)_2en$, and NHR_2 ligands are saturated amine systems which contain nitrogen donor atoms that can only form σ bonds. The other ligands bpy, bpm, CH_3CN, MeQ, and "naphthyridine" contain nitrogen donors that can both σ and π bond. On the basis of these arguments, it appears Re–N bond lengths fall into two categories. σ-bonded systems fall in the range 2.22–2.26 Å, whereas systems in which π bonding plays a role fall in the range 2.13–2.21 Å. The differences within each grouping may be due, in part, to steric factors. The order from the longest Re–N bond distance to the shortest for the systems discussed here is Re–N(en) > Re–N("py") > Re–N(bpm) > Re–N(bpy) > Re–$N(CH_3CN)$.

The bond distances between rhenium and coordinated nitrogen donors for $[Re(bpm)(CO)_3(MeQ)]^{2+}$ were different for the bpm and MeQ ligands. The average Re–N(bpm) bond distance was 2.17 Å; the Re–N(MeQ) bond distance was 2.21 Å. The difference in bond distances cannot be related to σ–donor strength. The pK_a of pyrimidinium is 1.3,[22] whereas the pK_a of pyridinium is 5.23,[23] indicating MeQ is the stronger σ donor. This difference in bond lengths could be related to steric factors. However, it is more likely due to more extensive π bonding between the dπ orbitals of rhenium with the empty π^* orbitals of bipyrimidine than with the empty π^* orbitals of MeQ.

The other structural feature of significance is the orientation of the two pyridine rings in the bipyrimidine ligand. The 38° angle has an important consequence for the design of donor/acceptor complexes. Meyer and co-workers[9] suggest charge separation can be achieved in $[Re(bpy)(CO)_3MeQ]^{2+}$ according to eq 1. According to eq 1, one pathway the excited electron may follow is to reside on the MeQ ligand but, in particular, to reside on the *N*-methyl-substituted pyridine, which has the more positive reduction potential. The 38° angle between the coordinated py component and the Me-py residue ensures that the direct communication between the π structure of the Me-py and py fragments of the MeQ ligand is broken, inhibiting back electron transfer between MeQ and rhenium. This break in communication, then, should allow one to generate these charge-separated intermediates on a detectable time scale.

$$[(bpy)Re^{I}(CO)_3(py\text{-}py\text{-}CH_3)]^{2+} \xrightarrow{h\nu} [(bpy)Re^{II}(CO)_3(py\text{-}py^{-}\text{-}CH_3)]^{2+*} \quad (1)$$

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Supplementary Material Available: Listings of bond lengths and bond angles, displacement parameters, and H atom positional and isotropic thermal parameters and a figure showing the unit cell packing (5 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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Notes

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Infrared Spectroscopic Studies of the Reactions of Copper and Ammonia in Cryogenic Argon Matrices

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Recent work from our laboratory[1,2] has focused on the study of new oxidative-addition products from metal atoms and 2p hydrides in cryogenic matrices via FTIR spectroscopy. These products have the general formula HMX, where M is a first-row transition-metal atom and X is a member of the isoelectronic series $CH_3/NH_2/OH/F$. Our goal is to study the vibrational spectra of the entire array of these oxidative-addition products in order to elucidate what trends might exist in the H–M and M–X bond characteristics. To this end, we have recently studied the vibrational spectra of $HNiCH_3$,[1] $HNiNH_2$,[2] and HNiOH.[3]

Recent experiments on the reaction of Cu and diazomethane[4] have turned our interest to Cu as a reactant. This interest was bolstered by the reports by Ozin et al.[5,6] on the reactivity of Cu

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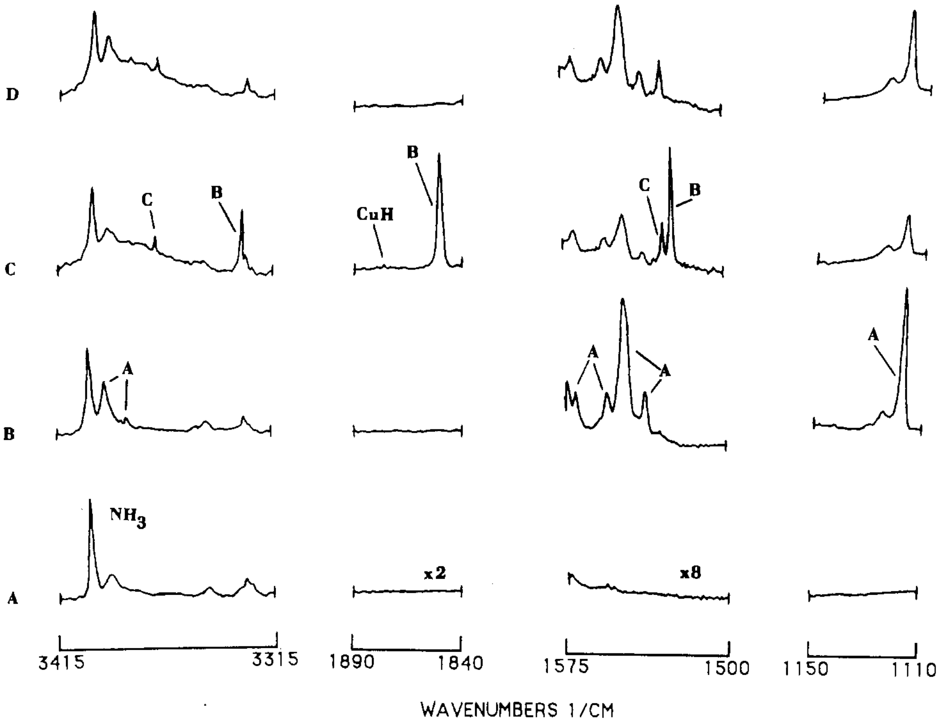

Figure 1. Cocondensation and photolyses of Cu and NH_3 in cryogenic argon matrices: (A) NH_3:Ar = 9.5:1000; (B) NH_3:Cu:Ar = 9.5:4.3:1000; (C) same as (B), photolyzed with UV-band-filtered light for 160 min (note the appearance of new absorptions, labeled "B" and "C", with concurrent decrease of Cu–NH_3 absorptions, labeled "A"); (D) rephotolysis of the same sample with 400-nm-cutoff light for 15 min (all of species B absorptions are totally bleached; the absorptions of species C are unaffected).

atoms in neat methane matrices. They reported that $^2P \leftarrow {}^2S$ excitation of Cu atoms promotes insertion into the C–H bonds of methane to form $HCuCH_3$; a competing photodimerization reaction known to occur via the ^2D state of Cu in undoped Ar and Kr matrices[7] appears to be effectively quenched. Continued photolysis of the Cu/neat CH_4 samples showed a photofragmentation of $HCuCH_3$ into H + $CuCH_3$, as detected by ESR. CH_3 and CuH were simultaneously observed, indicating scission of the Cu–C bond. Ozin's infrared data are for reactions in Kr matrices;[8] our recent work in Ar[4] indicates that the Cu–H stretch for CuH is blue-shifted somewhat from the frequency in methane or Kr. A similar blue-shifted frequency for CuH in Ar has been reported by Gruen et al.[9]

With this experimental background, we have studied the cocondensation and photolytic interactions of Cu and NH_3 in Ar matrices. This work follows a report[2] of the reaction of Ni with NH_3 to form $HNiNH_2$.

Studies of copper in matrices are well represented in the matrix-isolation literature.[10] Of interest are reports of the interactions of Cu with O_2,[11-13] H_2O,[14] and N_2,[15] as well as a multitude of Cu_x (x = 1–5) UV–visible spectral studies.[16] Also reported are studies on heteronuclear copper dimers, such as CuFe,[17,18] CuHg,[19] CuCd,[19] CuMg,[19] and CuZn.[19] Ammonia was among the first species studied in cryogenic matrices[20] and has since been studied extensively.[10]

Experimental Section

The experimental apparatus used in these experiments has been recently described in detail.[21] Copper metal (Fisher, 99.97%) was placed in an alumina crucible and vaporized from a resistively heated tantalum tube furnace. The temperature of the furnace ranged from 1105–1180 °C, as measured with a microoptical pyrometer (Pyrometer Instrument Co.); no emissivity corrections were made. Three isotopic forms of ammonia, NH_3 (anhydrous, Big Three Industries), $^{15}NH_3$ (99%, Cambridge Isotopes Laboratories), and ND_3 (99.9% US Services, Inc.), were used without further purification.

A typical experiment consisted of cocondensing copper vapors, ammonia, and excess argon onto a rhodium-plated copper block cooled to 12–14 K with a closed-cycle helium refrigerator (Air Products, Displex Model CSW-202). The molar ratios of reactants to matrix gas were measured previous to deposition with a quartz-crystal microbalance attached to the block. In general, the concentrations of reactants were kept to <10 parts per thousand of argon to minimize dimerization or self-association. The depositions lasted 30 min. After deposition, the block was rotated 180° and the infrared spectrum in the range 4000–500 cm^{-1} was measured by reflection with an IBM IR-98 Fourier-transform infrared spectrophotometer. Resolution was 1 cm^{-1}.

The photolysis studies were performed by using a 100-W medium-pressure Hg arc lamp (Schoeffel Instrument Co.) in conjunction with the following filters: 500-nm cutoff (Corning 3384), 400-nm cutoff (Corning 3060), and UV band (240 nm < λ < 380 nm; Corning 9863). When the 400-nm- and 500-nm-cutoff filters were used, a water-filled quartz cylinder was placed in the beam path to absorb infrared radiation. Photolysis times ranged from 5 to 160 min.

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Table I. Infrared Absorptions of the Isotopomers of Cu–NH_3 Adducts (Species A) in Cryogenic Argon Matrices (cm^{-1})

Cu–NH_3	Cu–$^{15}NH_3$	Cu–ND_3
897.6	1038.6	809.6
1116.9	1110.8	866.3
1124.7	1117.5	895.2
1153.0	1147.0	946.4
1537.3	1531.3	1163.9
1547.0	1540.4	2294.0
3142.2	1549.4	2384.3
3382.5	3136 br	2532.5
3392.8	3290.4	
	3374.1	
	3383.7	

Results and Discussion

Complexes. When copper vapors were cocondensed with NH_3 in excess Ar, new infrared absorptions appeared, as listed in Table I and illustrated in Figure 1B. Since these new absorptions were detectable at relatively low concentrations of reactants (<4 ppth), they are assigned to the Cu–NH_3 adduct. Some of the absorptions are very close in frequency, which we attribute to differences in the matrix-site structure around the Cu–NH_3 adduct. In all of the concentration studies examined for this report, no complex was conclusively identified as having a stoichiometry other than Cu–NH_3, despite reports of the aggregation of Cu in cryogenic matrices.[7] It appears that only a small amount of doping is sufficient to retard photoaggregation of Cu.[22]

Qualitatively, the Cu–NH_3 absorptions resemble the absorptions reported for the Ni–NH_3 complex.[2] The variation in frequency is generally ± 15 cm^{-1}, with no apparent trend in shifts (i.e. some of the Cu–NH_3 absorptions are red-shifted relative to Ni–NH_3, while some are blue-shifted). Use of isotopically labeled ammonia (^{15}N, D) yielded adducts assigned as Cu–$^{15}NH_3$ and Cu–ND_3; the absorptions for these proposed species are also listed in Table I.

Photoproducts. Photolysis of the cocondensed samples using 500-nm- and 400-nm-cutoff filters caused no change in the infrared spectra. Photolysis using a UV-band filter caused the adduct absorptions to decrease and new absorptions to appear (see Figure 1C). This photorearrangement is probably due to the $^2P \leftarrow {}^2S$ transition of Cu, located at about 300 nm, which has been previously identified as the reactive state.[5,6]

Two distinct sets of new absorptions were observed. The first set of absorptions, labeled "B" in Figure 1C, appeared rapidly upon photolysis, reaching maximum intensities after about 15 min of photolysis and then showing a very slight decrease at longer photolysis times (ca. 7% after 160 min). The second set of absorptions, labeled "C" in Figure 1C, appeared after prolonged photolysis times (>30 min) and showed a uniform monotonic increase in strength versus photolysis time.

That there are two separate species in the photolyzed matrices was confirmed by rephotolysis of the samples with 400-nm-cutoff light. After 15 min of visible photolysis, the absorptions of photoproduct "B" had bleached totally, while the absorptions of photoproduct "C" persisted with no change in intensity. Concurrent with the bleaching of photoproduct "B", the intensities of the absorptions of the Cu–NH_3 adduct increased. Such behavior was seen for all of the ammonia isotopomers.

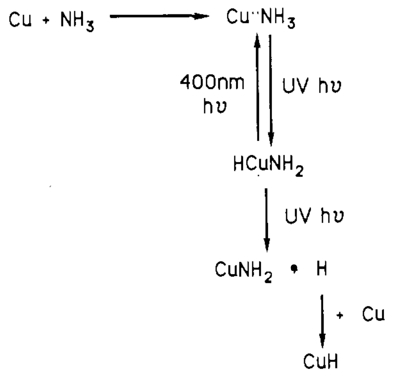
Table II. Infrared Frequencies of the Isotopomers of $HCuNH_2$ (Species B) in Cryogenic Argon Matrices (cm^{-1})

$HCuNH_2$	$HCu^{15}NH_2$	$DCuND_2$	assgnt
592.2	588.9		NH_2 wag
1524.1	1519.3	1133.4	NH_2 bend
1851.2	1851.8	1334.2	Cu–H str
3329.5	3325.3	2444.1	N–H str

Table III. Infrared Absorptions of the Isotopomers of the Photofragmented Products (Species C) after Prolonged Photolysis of $HCuNH_2$ (cm^{-1})

$CuNH_2$	$Cu^{15}NH_2$	$CuND_2$	assgnt
748.2	734.3		Cu–N str
1528.0	1522.9	1147.9	NH_2 bend
3369.3	3364.5	2471.7	N–H str
CuH	CuH	CuD	assgnt
1876.5	1876.5	1350.6	Cu–H str

Scheme I



We conclude that the absorptions of the bleachable photoproduct "B" belong to the species $HCuNH_2$. The absorptions of $HCuNH_2$ can be assigned to various vibrational modes of the molecule as listed in Table II. The absorption at 592.2 cm^{-1} for $HCuNH_2$ was assigned to the NH_2 wagging motion instead of the Cu–N stretch because of (a) its small ^{15}N shift (one would expect a shift on the order of 15 cm^{-1} for a substituted Cu–N stretch; here it is <4 cm^{-1}) and (b) its lack of appearance in the $DCuND_2$ spectra (indicating that this absorption shifted out of the range of the MCT detector (<500 cm^{-1}), as was expected for an ND_2 wagging mode). Disappointingly, no Cu–N stretch was identified for $DCuND_2$, as it would have corroborated this assignment. The Cu–H stretch for this species shifted upward very slightly in frequency (0.6 cm^{-1}) upon substitution with ^{15}N, which is similar in behavior to the Ni–H stretch in the case of isotopic substitution in $HNiNH_2$.[2]

We also conclude that the permanent photoproduct "C" is due to $CuNH_2$, infrared absorptions of which are listed in Table III. There are several arguments favoring this assignment. First, the product has absorptions in the N–H stretching and NH_2 scissors regions and so must contain an intact NH_2 moiety. We also identify a Cu–N stretch for this photoproduct that shows an appropriate ^{15}N shift. Second, the irreversibility of the absorptions of this species suggests that some sort of permanent fragmentation took place so that the Cu–NH_3 adduct could not be remade upon visible photolysis. Such a fragmentation is supported by the appearance of small amounts of diatomic CuH or CuD in the infrared spectra, whose identities are confirmed by our earlier work[4] and that of Gruen et al.[9] The absorptions of CuH and CuD show a dependence on photolysis time consistent with that of the second photoproduct, thereby ruling out the possibility that CuH or CuD was formed by some impurity. The fact that, after long-term photolysis, the absorptions of $HCuNH_2$ decreased slowly suggests that $HCuNH_2$ is a precursor to this final photoproduct.

The reaction between Cu and NH_3 proposed in this study is illustrated in Scheme I.

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Registry No. Cu, 7440-50-8; NH_3, 7664-41-7; Ar, 7440-37-1; Cu-NH_3, 100012-08-6; Cu-$^{15}NH_3$, 119638-08-3; Cu-ND_3, 119638-09-4; $HCu^{15}NH_2$, 119620-32-5; $DCuND_2$, 119620-33-6; $CuNH_2$, 77590-45-5; $Cu^{15}NH_2$, 119620-34-7; $CuND_2$, 119620-35-8; CuH, 13517-00-5; $HCuNH_2$, 119620-36-9; D_2, 7782-39-0; $^{15}N_2$, 14390-96-6.

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(22) In refs 5 and 6, it is mentioned that the photoaggregation of Cu is quenched in neat CH_4 matrices.