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Nitric Oxide Reduction of Copper(II) Complexes: Spectroscopic Evidence of Copper(II)−Nitrosyl Intermediate

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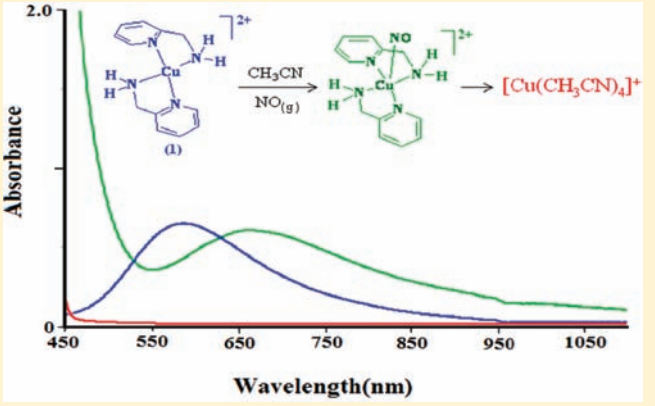
Supporting Information

ABSTRACT: Two copper(II) complexes, **1** and **2** with L_1 and L_2 [L_1 = 2- aminomethyl pyridine; L_2 = *bis*-(2-aminoethyl)-amine], respectively, in degassed acetonitrile solvent, on exposure to NO gas, were found to form a thermally unstable [Cu^{II}−NO] intermediate which then resulted in the reduction of the copper(II) centers. The formation of the [Cu^{II}−NO] intermediate was evidenced by UV−visible, FT-IR, and EPR spectroscopic studies. The reduction of the copper(II) centers by nitric oxide afforded ligand transformation through diazotization at the primary amine coordination site, in both cases. The modified ligands, in each case, were isolated and characterized.



INTRODUCTION

The coordination of nitric oxide to the transition metal ions and its activation have attracted the attention of chemists, as various biological and physiological reactivities of nitric oxide are attributed to the formation of nitrosyl complexes of metallo proteins, mostly iron or copper proteins.[1−3] For instance, it is believed that a [Cu^{I}−NO^{+} ↔ Cu^{II}−NO] intermediate is involved in the conversion of nitrite to NO or, in some cases, to N_2O by nitrite reductase, e.g., from *Achromobacter cycloclastes*.[4−6] Here, nitrite binding and dehydration to form the nitrosyl intermediate is believed to take place at a copper site in the protein, which is coordinated to three histidines and a water (or hydroxide) as a ligand in a pseudo-tetrahedral geometry.[7] On the other hand, metal−nitrosyl adducts presumably play important roles in nitrosation reactions of various thiols to give S-nitrosothiols which are proposed as important carriers of nitric oxide equivalents in cellular systems.[8−10] In this direction, the iron−nitrosyls, both in protein and synthetic model systems, have been studied extensively, and ferriheme proteins are known to undergo reduction in aqueous media in the presence of NO.[11−14] These reactions proceed through two distinct steps: (i) the formation of an iron(III)−nitrosyl adduct, (ii) followed by the pH dependent reduction of Fe^{III} to Fe^{II} with a simultaneous attack of the hydroxide ion to the activated nitrosonium group [Fe^{III}−NO ↔ Fe^{II}−NO^{+}], leading to the formation of nitrite.[15−17] NO reductions of copper(II) are also known, though they have not been studied as extensively as iron−nitrosyls, both in proteins and synthetic model systems.[18−21] The groups of Lippard and Ford have reported several examples of the reduction of copper(II) by nitric oxide and their use in NO detection.[22−28] The Ford group has reported on detailed studies of ligand nitrosation observed during reduction processes.[29] However, there are hardly any examples which show the distinct spectral evidence of the formation of a [Cu^{II}−NO] intermediate, except the very recent ones.[30]

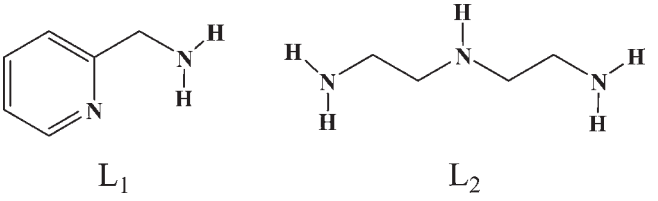


Figure 1. List of the ligands used for the present study.

In this context, here, we report the interaction of nitric oxide with copper(II) complexes of two N-donor ligands (Figure 1) in an acetonitrile solvent.

EXPERIMENTAL SECTION

Materials and Methods. All reagents and solvents were purchased from commercial sources and were of reagent grade. Acetonitrile was distilled from calcium hydride. Deoxygenation of the solvent and solutions was effected by repeated vacuum/purge cycles or bubbling with nitrogen for 30 min. NO gas was purified by passing it through a KOH and P_2O_5 column. UV−visible spectra were recorded on an HP/Agilent 8453 UV−visible spectrophotometer. FT-IR spectra of the solid

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samples were taken on a Perkin-Elmer spectrophotometer with samples prepared as KBr pellets, and for solutions, a Varian 660-IR FT-IR spectrometer and a NaCl cell of a 2 mm path length were used, and the spectra shown are the solvent subtracted ones. Solution electrical conductivity was checked using a Systronic 305 conductivity bridge. ^{1}H NMR spectra were obtained with a 400 MHz Varian FT spectrometer. Chemical shifts (ppm) were referenced either to an internal standard (Me_4Si) or to the residual solvent peaks. The X-band electron paramagnetic resonance (EPR) spectra were recorded on a JES-FA200 ESR spectrometer, at room temperature. Elemental analyses were obtained from a Perkin-Elmer Series II Analyzer. The magnetic moment of complexes is measured on a Cambridge magnetic balance.

Single crystals were grown by slow diffusion followed by a slow evaporation technique. The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine-focus 1.75 kW sealed tube with Mo K_α radiation (λ = 0.71073 Å) at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP software.[31] Multiscan empirical absorption corrections were applied to the data using the program SADABS.[32] Structures were solved by direct methods using SHELXS-97 and refined with full-matrix least-squares on F^2 using SHELXL-97.[33] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 for Windows.[34]

Synthesis of Complex 1, $[Cu(L_1)_2](ClO_4)_2$. Copper(II)perchlorate hexahydrate, $[Cu(H_2O)_6](ClO_4)_2$ (370 mg, 1.0 mmol), was dissolved in 10 mL of freshly distilled acetonitrile, and to this blue solution, the ligand $\mathbf{L_1}$, 2-aminomethyl pyridine (216 mg, 2.0 mmol), was added dropwise. The color of the solution changed to violet. The resulting mixture was stirred for 1 h. Then, the volume of the solution was reduced to ~2 mL and layered with benzene. Storage of this at ~−20 °C overnight resulted in the precipitation of a blue crystalline compound. Yield: 410 mg (~ 85%). Elemental Analyses Calcd (%) for $C_{12}H_{16}N_4O_8Cl_2Cu$: C, 30.09; H, 3.34; N, 11.70. Found (%): C, 30.03; H, 3.34; N, 11.66. UV−vis (acetonitrile), λ_{max}: 582 nm (ε = 130 M^{-1} cm^{-1}) and 302 nm (ε = 4120 M^{-1} cm^{-1}). FT-IR (KBr pellet), υ_{ClO4}^-: 1081 cm^{-1}, 625 cm^{-1}. X-band EPR data: g_{av} = 2.07. Molar conductance, Λ_M ($\Omega^{-1}cm^2$ mol^{-1}): 247 in acetonitrile. μ_{eff}: 1.77 μ_B

Synthesis of Complex 2, $[Cu(L_2)(CH_3CN)](ClO_4)_2$. $[Cu^{II}(H_2O)_6](ClO_4)_2$ (370 mg, 1.0 mmol) was dissolved in 10 mL of freshly distilled acetonitrile. To this solution, 103 mg (1.0 mmol) of the ligand $\mathbf{L_2}$, *bis*-(2-aminoethyl)amine, was added slowly with constant stirring. The color of the solution turned to a deep blue from light blue. The stirring was continued for 1 h at room temperature. The volume of the solution was then reduced to ~2 mL. Benzene (5 mL) was layered onto this solution, and storage at ~−20 °C overnight resulted in the precipitation of blue microcrystals of complex **2**. Yield: 350 mg (85%). Elemental Analyses Calcd (%) for $C_6H_{16}N_4O_8Cl_2Cu$: C, 17.71; H, 3.93; N, 13.78. Found (%): C, 17.66; H, 3.94; N, 13.73. UV−vis (acetonitrile), λ_{max}: 575 nm (ε = 140 M^{-1} cm^{-1}). FT-IR (KBr pellet), υ_{ClO4}^-: 1095 cm^{-1}, 627 cm^{-1}. The X-band EPR data: g_{av} = 2.14. Molar conductance, Λ_M ($\Omega^{-1}cm^2$ mol^{-1}): 259 in acetonitrile. μ_{eff}: 1.56 μ_B

Isolation of $[Cu^I(CH_3CN)_4]ClO_4$. In a 50 mL Schlenk flask, complex **1** (240 mg, 0.5 mmol) was dissolved in 10 mL of degassed acetonitrile. Nitric oxide gas was purged into this deep blue solution through a needle for 1 min and allowed to stand for 10 min. To the resulting colorless solution, 15 mL of degassed benzene was added through a syringe to make a layer. The layered solution was then kept overnight in a freezer. The white crystals of $[Cu(CH_3CN)_4]ClO_4$ were filtered out from the colorless solution under a nitrogen atmosphere using a Schlenk frit. Yield: 115 mg, ~70%.

The same procedure was followed to isolate the $[Cu(CH_3CN)_4]ClO_4$ from the reaction of complex **2** (204 mg, 0.5 mmol) and nitric oxide in acetonitrile solution. Yield: 100 mg, ~60%.

Isolation of $\mathbf{L_1}'$. In a 50 mL Schlenk flask, complex **1** (240 mg, 0.5 mmol) was dissolved in 15 mL of degassed acetonitrile. To this, nitric oxide gas was purged through a needle for 1 min, and the mixture was then allowed to stand for 10 min. To the colorless solution, thus obtained, 20 mL of degassed benzene was added through a syringe to make a layer. The layered solution was then kept overnight in a freezer. The white crystals of $[Cu(CH_3CN)_4]ClO_4$ were filtered out from the colorless solution under a nitrogen atmosphere using a Schlenk frit. The volume of the filtrate was then reduced to 5 mL and stirred for 1 h in the open air in order to allow the residual Cu^I center to oxidize to Cu^{II}. To this, 5 mL of a saturated aqueous solution of Na_2S was added and stirred for 1/2 h. The black precipitate thus obtained was filtered off, and the filtrate was diluted with 50 mL of distilled water. The organic part was then extracted from the mixture using $CHCl_3$ (3 portions × 25 mL). The collected organic layer was then dried under reduced pressure, and the residual oil was subjected to column chromatography using silica gel to yield $\mathbf{L_1}'$ (60 mg, ~60%). ^{1}H NMR (400 MHz, $CDCl_3$), δ_{ppm}: 1.54 (s, 4H), 7.00 (t, 2H), 7.41(t, 2H), 7.94(d, 2H), 8.36(d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$), δ_{ppm}: 158.92, 149.01, 136.32, 124.66, 120.51, 49.02. FT-IR in KBr pellet: 1035(m), 1069 (s), 1241(s), 1262(m), 1361(s), 1430(w), 1498(w), 1540(w), 1635(w) cm^{-1}. ESI-Mass: $(m + 1)/z$, 200.02.

Isolation of $\mathbf{L_2}'$. $\mathbf{L_2}'$ was isolated from the reaction of complex **2** with nitric oxide in acetonitrile following the same procedure for $\mathbf{L_1}'$. Yield: 30 mg, ~ 70%. ^{1}H NMR (400 MHz, $CDCl_3$), δ_{ppm}: 2.79 (CH_2), 1.90 (NH). ^{13}C NMR (100 MHz, $CDCl_3$), δ_{ppm}: 47.64. FT-IR in KBr pellet, 1551(s), 1434(s), 1274(s), 1129(w), 1000(m), 854(w) cm^{-1}. All data are found to be in agreement with those of piperazine.

RESULTS AND DISCUSSION

Complex **1** was reported earlier.[35] Complex **1** was prepared through the reaction of an acetonitrile solution of $[Cu(H_2O)_6](ClO_4)_2$ with 2 equiv of the ligand at room temperature for 1 h. After reducing the volume of the resulting deep blue solution, benzene was added to make a layer and the mixture was kept in a freezer overnight. The blue crystals of the complex were obtained from the mixture (Scheme 1).

Complex **2** was synthesized following the same procedure, except only 1 equiv of the ligand, $\mathbf{L_2}$, was used. All of the complexes exhibited satisfactory elemental analyses (Experimental Section). The formulation of the complexes has been further supported by various spectroscopic analyses (Supporting Information). The single crystal X-ray structure of complex **1** was determined. Since the structure of the complex is already known, the ORTEP diagram is shown in the Supporting Information.[36] The room temperature magnetic moment measurement showed one electron paramagnetism for both of the complexes (1.77 and 1.56 μ_B for complexes **1** and **2**, respectively). Complexes **1** and **2** displayed axial spectra in X-band EPR at room temperature in an acetonitrile solvent which is characteristic of square planar Cu(II) complexes with $d_{x^2-y^2}$ ground state (g_{av} = 2.07 and 2.14 for complexes **1** and **2**, respectively).[37] Both of the complexes were found to behave as 1:2 electrolytes in acetonitrile solution [Λ_M (Ω^{-1} cm^2 mol^{-1}), 247 and 259 for complexes **1** and **2**, respectively].[38]

Reactivity with NO. The nitric oxide (NO) reactivity of both of the complexes was studied in acetonitrile solution, and the spectral changes were monitored by UV−visible spectrophotometry. The d−d transition for complex **1** was found to appear at 582 nm. On purging NO gas into a degassed acetonitrile solution of complex **1**, the position of the d−d transition shifted to 660 nm (Figure 2a). Recently, $[Cu^{II}-NO]$ intermediates observed in the reaction of $[Cu(tiaea)(CH_3CN)]^{2+}$ and $[Cu(teaea)(CH_3CN)]^{2+}$ [tiaea = *tris*(2-isopropylaminoethyl)amine and teaea =

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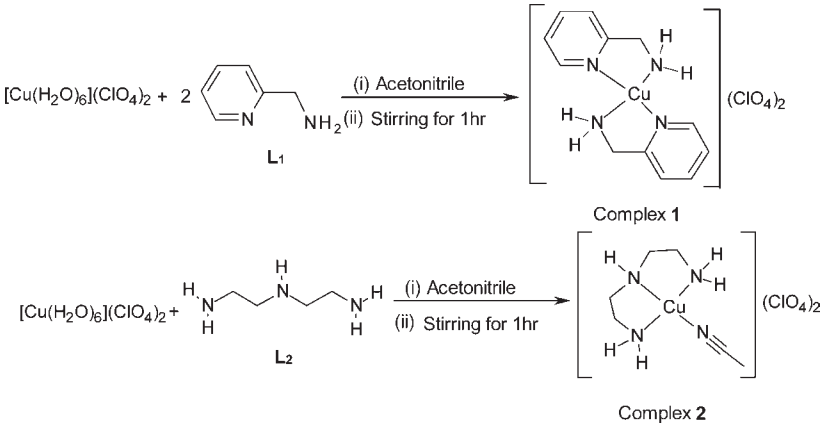
Scheme 1. Synthesis of Complexes 1 and 2



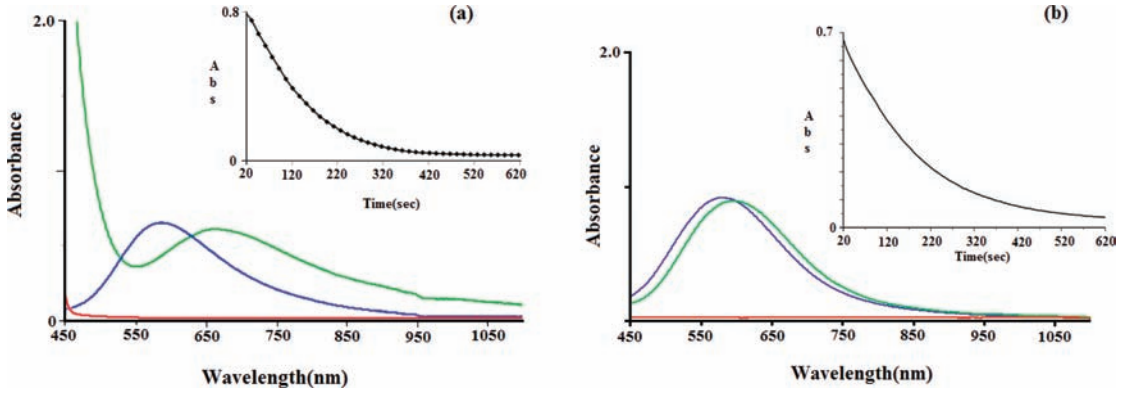


Figure 2. UV−visible spectra of the reaction of complexes **1** (a) and **2** (b) with nitric oxide in an acetonitrile solvent at room temperature. The blue trace represents the Cu^{II} species, green represents that of the $[Cu^{II}-NO]$ intermediate, and the red trace represents the spectrum of fully reduced Cu^{I}-species. The insets show the corresponding time scan plots at 660 and 595 nm, for complexes **1** and **2**, respectively.

tris(2-ethylaminoethyl)amine] with NO were reported to display the d−d transition at 640 and 605 nm, respectively.[39] The intensity of the transition at 660 nm was found to diminish gradually with time, indicating the reduction of the Cu(II) center to Cu(I) (Figure 2a). It is presumably because of the formation of the thermally unstable $[Cu^{II}-NO]$ intermediate prior to reduction of the Cu(II) center. The same reduction was observed with complex **2**, also. The d−d transition for complex **2** at 575 nm was found to shift to 595 nm immediately after purging NO gas and was found to disappear with time (Figure 2b), following a pseudo-first-order rate law with respect to the complex concentration. The calculated rate constants at 298 K are 1.3×10^{-3} s^{-1} and 2.2×10^{-3} s^{-1} for complexes **1** and **2**, respectively.

On NO purging into the degassed solution of complexes **1** and **2**, the solutions became EPR silent. This can be attributed to the formation of $[Cu^{II}-NO]$ intermediates in both cases (Figure 3).[30] With $[Cu(tiaea)(CH_3CN)]^{2+}$ and $[Cu(teaea)(CH_3CN)]^{2+}$ complexes, the $[Cu^{II}-NO]$ species are observed to be EPR silent.[39] The appearance of EPR silent signals in both cases might be because of the complete reduction of Cu(II) to Cu(I) by nitric oxide.

The FT-IR spectra of the acetonitrile solutions of complexes **1** and **2** after purging NO were recorded. A new intense and sharp band was found to appear at ∼1642 cm^{-1} and 1635 cm^{-1} for complexes **1** and **2**, respectively, corresponding to the vibration of NO coordinated to the Cu(II) center (Figure 4 and Supporting Information).[40] It would be worth mentioning here that the addition of nitrosyl perchlorate to an acetonitrile solution of the free ligands does not give rise to these vibrations (Supporting Information), which, in turn, supports their assignment. These ν_{NO}'s of $[Cu^{II}-NO]$ were found to disappear with time, indicating the unstable nature of the intermediate (Figure 4 and Supporting Information). Hence, the appearance of the band at ∼1642 cm^{-1} and 1635 cm^{-1} for complexes **1** and **2**, respectively, supports the formation of $[Cu^{II}-NO]$ prior to the reduction of Cu(II) centers in both cases. In the case of the $[Cu(tren)(CH_3CN)]^{2+}$ [tren = N,N-*bis*(2-aminoethyl)ethane-1,2-diamine] complex, the ν_{NO} of $[Cu^{II}-NO]$ was found to appear at 1650 cm^{-1}.[40] It would be worth mentioning here that, for the air-stable solid copper−nitrosyl of copper(II)−dithiocarbamate, the ν_{NO} for the NO coordinated to copper appears at 1682 cm^{-1}.[30] Recently, Hayton et al. reported the appearance of a ν_{NO} band at 1933 cm^{-1} for copper(II)−nitrosyl.[30]

The reduction of the copper(II) center has been further authenticated in the case of complex **2** by the single crystal structure determination of the reduced complex, $[Cu(CH_3CN)_4]ClO_4$ (Supporting Information). Since the crystal structure of $[Cu(CH_3CN)_4]ClO_4$ has already been reported by Soregh et al., attempts were not made to grow better quality crystals of $[Cu(CH_3CN)_4](ClO_4)$.[41]

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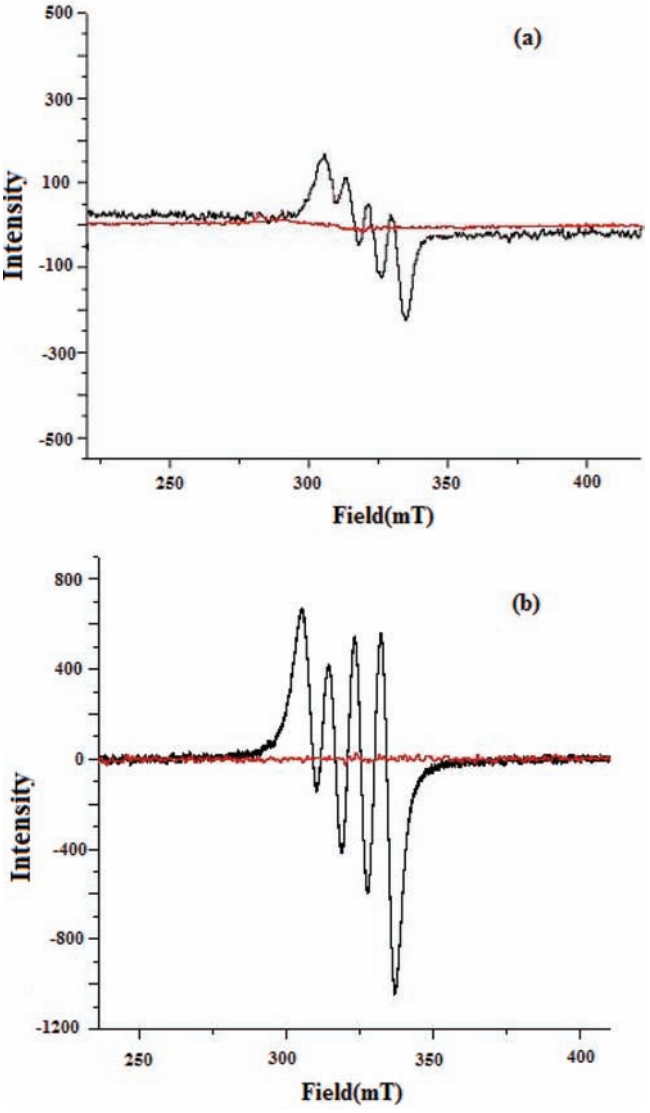

Figure 3. X-band EPR spectra of the reaction of complexes **1** (a) and **2** (b) with nitric oxide in an acetonitrile solvent at room temperature. Black traces correspond to the respective complexes, and red traces represent the spectra of [Cu−NO] intermediates.

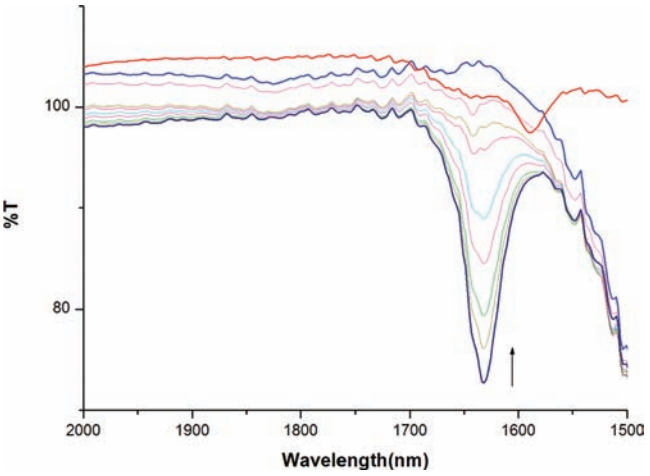

Figure 4. The solvent subtracted FT-IR spectra obtained from the reaction of complex **2** with NO in acetonitrile at room temperature. The top blue trace represents the spectrum of complex **2** in acetonitrile. The bottom dark trace represents the spectrum of the $[Cu^{II}—NO]$ intermediate after the reaction of complex **2** with NO, and the red one represents the spectrum of the colorless species obtained after complete reduction. The gradual decrease of the intensity of the band is represented by the arrow. The spectra were recorded from 1500 cm^{-1} to 2000 cm^{-1} to see the υ_{NO} band clearly.

There are not many reports on the detailed studies of the Cu(II)/NO reactions. Tran et al. studied the NO reduction of the copper(II) complex, $[Cu(dmp)_2(H_2O)]^{2+}$ (dmp = 2,9-dimethyl-1,10-phenanthroline), in aqueous solution and in various mixed solvents.[42] In methanol, the product of the $[Cu(dmp)_2(H_2O)]^{2+}$ oxidation of NO is CH_3ONO; in water, it is NO_2^-. They observed that the reaction did not occur in pure acetonitrile or CH_2Cl_2 unless a protic reactant such as methanol or water was added, and in such solutions, the reaction rate was linearly dependent on the concentration of the alcohol/water added.[42] In comparison, complexes **1** and **2** exhibited facile reduction of the Cu(II) center in neat acetonitrile without the presence of any protic solvent.

In the present cases, on the basis of spectral evidence of the formation of the $[Cu^{II}—NO]$ intermediate, the NO reduction process can be rationalized in terms of an inner-sphere mechanism, as illustrated in Scheme 2. It is believed that, in the first step, NO coordinates to the Cu(II) center to form an inner-sphere complex, $[Cu^{II}—NO]$, which is susceptible to nucleophilic attack by the amine center of the ligands, owing to charge transfer from NO to the metal center $[Cu^{II}—NO \leftrightarrow Cu^{I}—NO^+]$. The presence of terminal primary amine groups in the ligand frameworks might provide a facile site for the attack of the generated NO^+, resulting in ligand modification through diazotization (Figure 5). The dissociation of the modified ligand from the metal center would be a rapid step, owing to the higher stability of $[Cu^{I}(CH_3CN)_4]^+$ and preferential tetrahedral coordination. It would be worth mentioning here that in the case of $[Cu(dmp)_2(H_2O)]^{2+}$, reported by Tran et al., though a putative inner-sphere complex $[Cu(dmp)_2(NO)]^{2+}$ was proposed to form, no spectral evidence of such was observed.[42] Even in the early stages of spectral changes when the reactive aqueous solutions were mixed in the stopped-flow kinetics spectrophotometer, there was no obvious indication of the formation of the $[Cu^{II}—NO]$ intermediate, in the case of $[Cu(dmp)_2(NO)]^{2+}$.[42]

To evaluate the viability of both of the potential mechanisms, Ford et al. studied the NO reduction of $[Cu(dpp)_2]^{2+}$ (dpp = 2,9-diphenyl-1,10-phenanthroline) in a methanol solution.[42] Since $[Cu(dpp)_2]^{2+}$ has a higher reduction potential compared to $[Cu(dmp)_2(H_2O)]^{2+}$ and 2,9 diphenyl groups in dpp are more bulky than methyl groups in the same site in dmp, it is expected that $[Cu(dpp)_2]^{2+}$ would be more reactive compared to $[Cu(dmp)_2(H_2O)]^{2+}$ *via* an outer-sphere mechanism but less so *via* an inner-sphere one. It has been found that the latter one appears to be the case. However, there was no direct spectral evidence of the formation of the $[Cu^{II}—NO]$ intermediate complex. This inner-sphere mechanism scheme involving NO coordination to the metal center before reduction is consistent with the reductive nitrosylation of various ferrihemes and ferrihemoproteins reported by Wayland et al. and Hoshino et al.[15a,43,44] It would be worth mentioning here that for the reduction of the Cu(II) center by NO in $[Cu(DAC)_2]^{2+}$ (DAC = 1,8-bis(9-anthracylmethyl) derivative of the macrocyclic tetraamine cyclam), a somewhat different mechanism has been proposed.[22b] The initial step is proposed to be the reversible

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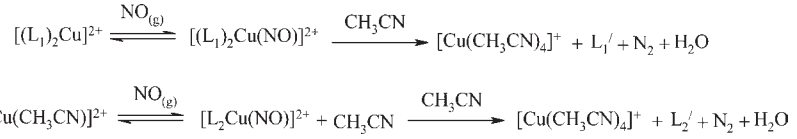
Scheme 2



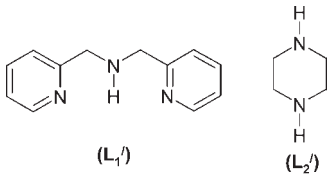
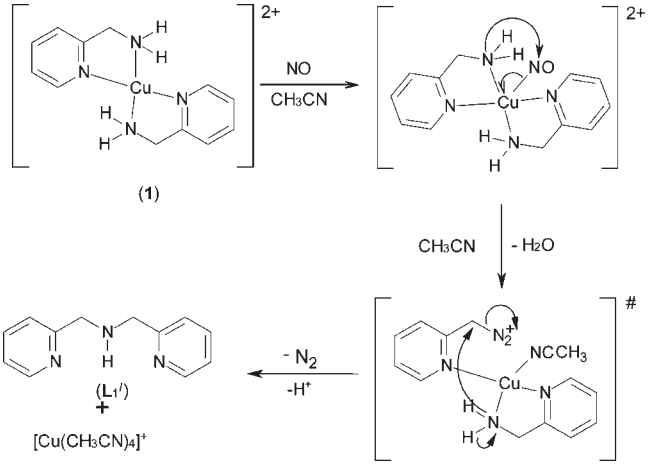


Figure 5. Modified ligands, L_1' and L_2'.

Scheme 3. Putative Mechanism of the Formation of L_1' from the Reaction of Complex 1 with NO in Acetonitrile



deprotonation of the coordinated secondary amine followed by the addition of NO at the amide site with a simultaneous electron transfer to reduce the copper(II) center.

The reduction of the Cu(II) ion by nitric oxide in the present set of complexes was accompanied by a concomitant diazotization of the primary amine center of the ligands, which resulted in the modification of the respective ligand frameworks (Scheme 2), and a putative mechanism of the formation of L_1' is illustrated in Scheme 3. The diazotization of primary amines by copper–nitrosyls has been observed previously also.[40]

In the case of $[Cu(tren)(CH_3CN)]^{2+}$, in pure acetonitrile, the formation of 2-piperazin-1-ylethanamine was reported because of the diazotization of the primary amine center of tren by the in situ generated NO^+ from the reduction of the Cu(II) center by NO.[40] However, the same reaction in an acetonitrile/water (10:1) mixture was not found to result in the diazotization product. This is because of the higher reactivity of NO^+ toward water, affording NO_2^-.[40] On the other hand, $[Cu(tiaea)(CH_3CN)]^{2+}$ and $[Cu(teaea)(CH_3CN)]^{2+}$ are reported to afford tri-N-nitrosoamine concomitant with the reduction of the Cu(II) center.[39]

Ford et al. reported the reduction of the Cu(II) center by nitric oxide in the $[Cu^{II}(DAC)]^{2+}$ complex in a methanol solution.[22b] This was accompanied by N-nitrosation of the ligand.[22b] In the case of $[Cu^{II}(DAC)]^{2+}$, after reduction and nitrosation, the release of the modified ligand was attributed to the fact that Cu(I) favors a tetrahedral geometry, whereas the DAC ligand favors a square planar one. At the same time, the nitrosation also weakens the binding ability of the amine nitrogen.[22b] In the present case, the release of L_1' and L_2' can be attributed to the weakening of amine binding to the Cu(I) due to the planar structure of the modified ligand in the case of complex **1** and the ring structure in the case of complex **2**.

The modified ligand L_1' was characterized by ^1H NMR, ^{13}C NMR, FT-IR, and ESI-mass spectra (Supporting Information). The formation of L_2' was confirmed by comparing its spectral data with that of the authentic sample (Supporting Information). It is observed that the free ligands, in degassed acetonitrile, upon bubbling with nitric oxide do not result in the same ligand transformation.

Thus, the present set of examples evidently proves the formation of a $[Cu^{II}—NO]$ intermediate before the reduction of the Cu(II) center, as was observed in the case of the reductive nitrosylation of ferrihemes and ferrihemoproteins. In comparison, there are well-defined examples of nitrosation with a cyclam ligand and another with a nitrosylated ligand as a probable intermediate.[29,30]

CONCLUSION

The reduction of two copper(II) complexes, **1** and **2**, by nitric oxide have been studied in acetonitrile. Both of the complexes resulted in the formation of a thermally unstable $[Cu^{II}—NO]$ intermediate prior to reduction. The intermediate has been characterized by UV–visible, FT-IR, and EPR spectral analyses. The decomposition of the intermediate resulting in the completely reduced $[Cu^{I}(CH_3CN)_4]$ is found to follow pseudo-first-order kinetics. A detailed study of the NO reduction kinetics of $[Cu^{II}(dmp)_2(H_2O)]^{2+}$ and $[Cu(dpp)_2]^{2+}$ was reported earlier, where the involvement of the $[Cu^{II}—NO]$ intermediate was speculated without any spectral evidence. A completely different mechanism has been proposed for the similar reduction of the copper(II) center by NO in $[Cu(DAC)_2]^{2+}$. The present study demonstrates the formation of a well characterized $[Cu^{II}—NO]$ intermediate, as seen in case of the reductive nitrosylation of ferrihemoproteins.

The reduction of copper(II) centers in complexes **1** and **2** is observed to yield ligand modification. The modified ligands were isolated and completely characterized.

ASSOCIATED CONTENT

Supporting Information. FT-IR, X-band EPR, ^1H NMR, and ^{13}C NMR spectra of complexes **1** and **2**, L_1' and L_2' included. Crystallographic files in CIF format are also provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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