Structural Characterization of a Copper Nitrosyl Complex with a {CuNO}[10] Configuration

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Abstract: The synthesis and characterization of a {CuNO}[10] complex, namely, [Cu(CH$_3$NO$_2$)$_5$(NO)][PF$_6$]$_2$, has been achieved by the addition of [NO][PF$_6$] to copper metal powder in the presence of nitromethane. In the solid state, this complex exhibits a bent Cu$-$N$-$O moiety [Cu$-$N$-$O = 121.0(3)°] and a long Cu$-$N bond. This complex readily reacts with mesitylene to form [mesitylene, NO][PF$_6$] and [Cu(η^2-1,3,5-Me$_3$C$_6$H$_3$)$_2$][PF$_6$] by transfer of NO$^+$ to the mesitylene ring.

The reduction of NO$_2^-$ to nitric oxide (NO) by copper nitrite reductase (CuNIR) is an important component of the global nitrogen cycle.[1,2] It has been proposed that this transformation involves the formation of a Cu(II)$-$NO$^\bullet$ intermediate,[3] classified as a {CuNO}[10] complex in the Enemark$-$Feltham notation.[4] However, attempts to generate this intermediate in the enzyme have resulted only in the isolation of a Cu(I)$-$NO$^\bullet$ complex,[5,6] a molecule with a {CuNO}[11] configuration. Interestingly, X-ray crystallographic studies of this material revealed an unusual side-on interaction between the NO and the Cu center.[5,7,8] In addition to this material, several other {CuNO}[11] complexes have been reported, including Tp′Cu(NO) [Tp′ = tris(3-R-5-R′-pyrazolyl)hydroborate; R = ^{t}Bu, R′ = H, ^{i}Pr or R = R′ = Ph].[9] These complexes exhibit nearly linear nitrosyl ligands and are also considered to have a Cu(I)$-$NO$^\bullet$ electronic structure.[10,11] Only a few complexes with a {CuNO}[10] configuration are known, but to our knowledge, none have been structurally characterized. For example, alcohol solutions of CuX$_2$ (X = Cl, Br, F) have been reported to absorb NO, generating deeply colored solutions that exhibit strong ν_{NO} absorptions in their solution IR spectra, but the structures of these materials are not known.[12−14] The lack of structural data for these complexes highlights the need for new copper nitrosyls to be isolated and characterized. Herein, we report the synthesis and structural characterization of a new {CuNO}[10] complex and present a preliminary exploration of its reactivity.

We endeavored to reinvestigate the interaction of Cu(II) with NO gas. However, in place of CuX$_2$, we generated the required Cu^{2+} ions and NO gas in situ using weakly coordinating CH$_3$NO$_2$ as the solvent. Thus, addition of 2 equiv of [NO][BF$_4$] to copper powder in CH$_3$NO$_2$ results in gas evolution and production of a deep-purple solution, similar to that reported for CuX$_2$(NO) and [Cu(NO)(H$_2$SO$_4$)$_n$]$^{2+}$.[13−15] An IR spectrum of the solution reveals an intense ν_{NO} absorption at 1933 cm^{-1}. This vibration shifts to 1893 cm^{-1} when [^{15}NO][BF$_4$] is used in place of unlabeled [NO][BF$_4$]. Subsequent addition of Et$_2$O results in a rapid color change to green and loss of coordinated NO (according to IR spectroscopy). Storage of this solution at $-$25 °C leads to the isolation of pale-blue crystals of [Cu$_2$(μ-F)$_2$(μ-BF$_4$)$_2$(OEt$_2$)$_4$] (**1**).[16−18] Complex **1** has been fully characterized, including analysis by X-ray crystallography (see the Supporting Information). Its bridging fluoride ligands are likely derived from the well-established F$^-$ abstraction from BF$_4^-$.[16−18]

In an effort to hinder fluoride abstraction and stabilize the initially formed NO complex, [NO][PF$_6$] was used in place of [NO][BF$_4$].

Thus, addition of 2 equiv of [NO][PF$_6$] to copper metal powder at $-$25 °C in CH$_3$NO$_2$ produces a deep-purple solution exhibiting an IR vibration at 1933 cm^{-1}. An EPR spectrum of the solution reveals a weak signal consistent with the presence of an axial Cu^{2+} ion.[19] Application of a vacuum to this solution causes a color change to green and an increase in the intensity of the Cu^{2+} EPR signal. It also results in the disappearance of the ν_{NO} absorption feature in the IR spectrum, indicating loss of the nitrosyl ligand (Scheme 1). Layering of this solution onto CH$_2$Cl$_2$ provides pale-blue crystals of [Cu(CH$_3$NO$_2$)$_5$][PF$_6$]$_2$ (**2**) in 62% yield.

Scheme 1
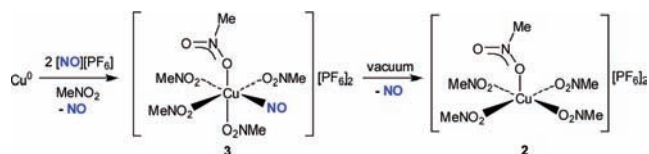
X-ray diffraction analysis of **2** reveals a square-pyramidal coordination environment about the copper center (Figure 1). The Cu$-$O$_{ax}$ bond length [Cu1$-$O5 = 2.261(4) Å] is elongated by 0.2 Å relative to the C$-$O$_{eq}$ bond lengths (av Cu$-$O$_{eq}$ = 1.98 Å). These metrical parameters are similar to those found in [Cu(H$_2$O)$_5$]$^{2+}$, which exhibits an average Cu$-$O$_{eq}$ bond length of 1.953 Å and a Cu$-$O$_{ax}$ bond length of 2.246(5) Å.[20] Complex **2** was also characterized by UV$-$vis (819 nm, ε = 43 L mol^{-1} cm^{-1}) and EPR (axial signal, $g_{||}$ = 2.38, $g_\perp$ = 2.065, $a_{||Cu}$ = 12.7 mT) spectroscopies.[19]
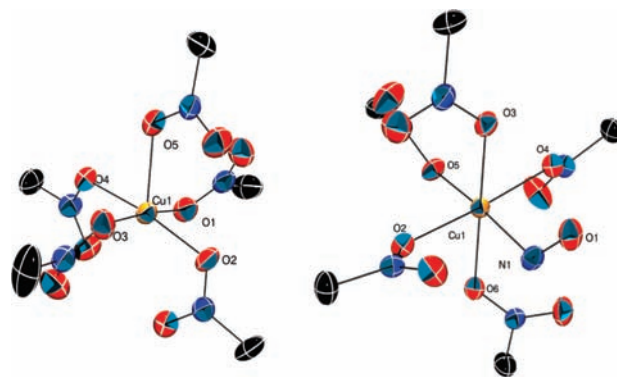
Figure 1. Solid-state molecular structures of (left) [Cu(CH$_3$NO$_2$)$_5$][PF$_6$]$_2$ (**2**) and (right) [Cu(CH$_3$NO$_2$)$_5$(NO)][PF$_6$]$_2$·CH$_3$NO$_2$ (**3**·CH$_3$NO$_2$), showing 50% thermal ellipsoids. Hydrogen atoms and PF$_6^-$ anions have been omitted for clarity.

When application of a vacuum during workup is avoided, deep-purple rods of [Cu(CH$_3$NO$_2$)$_5$(NO)][PF$_6$]$_2$ (**3**) can be isolated by crystallization from CH$_3$NO$_2$/CH$_2$Cl$_2$ in good yield (Scheme 1). Its IR spectrum in the solid state (Nujol mull) exhibits a strong ν_{NO} absorption feature at 1933 cm^{-1}, consistent with the solution-phase

IR spectrum. The UV−vis spectrum of complex **3** generated in situ from copper powder exhibits a broad absorbance at 480 nm. This absorbance is similar to that observed for $CuX_2(NO)$[13] and Tp^{tBu}-Cu(NO)[10] and is likely a charge transfer (CT) feature. It is not clear, however, whether this is a metal-to-ligand or ligand-to-metal CT feature, and further characterization is ongoing. The solid-state molecular structure of $3 \cdot CH_3NO_2$ reveals a Jahn−Teller-distorted octahedral geometry around copper (Figure 1). Surprisingly, the nitrosyl ligand is bound in a bent geometry [Cu1−N1−O1 = 121.0(3)°] at an *equatorial* site. The Cu−N bond length in **3** [Cu1−N1 = 1.955(4) Å] is significantly longer than previously reported terminal Cu−NO bond lengths (1.76−1.79 Å),[9,10] indicating a very weak copper−NO interaction. Additionally, the Cu−N bond length is comparable to the Cu−O_{eq} bond lengths in both **3** [2.008(3)−2.039(3) Å] and **2**. The Cu−O_{ax} bond lengths are 2.259(3) and 2.292(3) Å, which are similar to the Cu−O_{ax} bond length found in **2**.

Complex **3** can also be formed by addition of NO gas to cold CH_3NO_2 solutions of **2**. Following this reaction by EPR spectroscopy reveals a dramatic reduction in the intensity of the EPR signal of **2** upon addition of NO.[15,21] Additionally, no new signals were observed in the spectrum, suggesting the presence of antiferromagnetic coupling between the Cu^{2+} ion and the NO ligand.[22] As with other copper−NO complexes,[10] it is likely that only a portion of the Cu^{2+} in solution is coordinated by NO, explaining the presence of a residual Cu^{2+} EPR signal in these samples. Application of vacuum to these solutions causes the loss of the purple color and a return in the intensity of the Cu^{2+} EPR signal (see the Supporting Information).

Complex **3** has proven to be incredibly thermally sensitive. At room temperature in the solid state, a pale-green patina forms on crystals of **3** over a period of 10 min, indicating loss of NO. The application of vacuum accelerates this loss and converts the solid to a pale-green powder. Solutions of **3** in CH_3NO_2 also decomposes upon standing, resulting in the formation of complex **2**. However, it appears that the decomposition of **3** is slower in more concentrated solutions.

In view of the redox activity of the NO ligand, the copper−NO interaction in **3** can be formally described in three ways: (a) Cu(III)−NO^-, (b) Cu(II)−NO•, or (c) Cu(I)−NO^+. The Cu−N−O bond angle of 121.0(3)° is suggestive of sp^2 hybridization at N and the presence of a Cu(III)−NO^- electronic structure, although the ν_{NO} value (1933 cm^{-1}) is considerably higher than expected for a NO^- ligand.[23] In addition, the N−O bond length in complex **3** [1.109(5) Å] is shorter than that expected for an NO^- complex (1.15−1.18 Å)[23] but identical to the N−O bond length in $Tp^{tBu}Cu(NO)$,[10] a complex containing the Cu(I)−NO• electronic configuration. The Cu(I)−NO^+ formalism is also unlikely, given the bent Cu−N−O bond angle. Furthermore, octahedral Cu(I) complexes are extremely rare.[24] As a result, we prefer the Cu(II)−NO• formalism, as this electronic configuration best explains the observed Jahn−Teller distortion in **3** and the metrical parameters of the nitrosyl moiety. Additionally, theoretical studies of the intermediates of the CuNIR enzyme support a Cu(II)−NO• formalism with a bent Cu−N−O angle.[22]

We have also started to probe the reactivity of complex **3**. Surprisingly, addition of 10 equiv of mesitylene to **3** suspended in CH_2Cl_2 results in the formation of a donor−acceptor complex, [1,3,5-$Me_3C_6H_3$,NO][PF_6], and a Cu(I)−arene π complex, namely, [Cu(η^2-1,3,5-$Me_3C_6H_3$)$_2$][PF_6] (**4**) (eq 1):
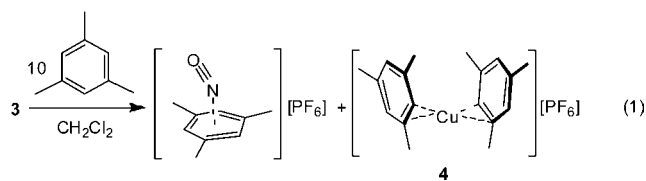
The presence of the former was confirmed by IR spectroscopy,[25] but separating the latter material from the nitrosonium−arene complex proved to be challenging. Thus, it was synthesized independently to facilitate its complete characterization (see the Supporting Information). In generating [1,3,5-$Me_3C_6H_3$,NO][PF_6], complex **3** formally transfers the nitrosonium cation to the arene. This reactivity is consistent with the reductive nitrosylation reported previously for the Cu(II) ion upon reaction with NO gas in the presence of secondary amines.[21,26−28] Complex **3** also transfers NO^+ to hexamethylbenzene, pentamethylbenzene, and durene, forming the corresponding donor−acceptor complexes (see the Supporting Information).

In summary, we report the synthesis and structural characterization of [Cu(CH_3NO_2)$_5$(NO)][PF_6]$_2$, a rare example of a {CuNO}^{10} complex. This complex contains a significantly bent Cu−N−O moiety with a long Cu−N bond length and may provide a model of how nitric oxide coordinates to Cu(II) during the CuNIR catalytic cycle. The metrical parameters of this material suggest that it is best described as a Cu(II)−NO• complex, although it acts as a strong NO^+ donor with arene substrates. In view of the potent reactivity of [Cu(CH_3NO_2)$_5$(NO)][PF_6]$_2$ as a nitrosylating agent, we will continue to explore the reactivity of this complex with other NO^+ acceptors.

Supporting Information Available: Experimental procedures, crystallographic details (CIF), and spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA105930B